EMPIRICAL APPROACH TO DESCRIPTION OF SOLVENT EFFECT ON PROCESSES IN SOLUTIONS: A REVIEW

Oldřich Pytela

Department of Organic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

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The review summarizes and evaluates the empirical models used for description of effects of solvents and solvent mixtures on processes in solutions. Analyzed are the principles of application of the empirical relations and their theoretical basis. A survey is given about empirical parameters of individual solvents with respect to the model process and also about the parameters derived by mathematical-statistical treatment. Also analyzed is the relation between the individual parameter scales, and their physical meaning is evaluated. Furthermore the review gives a survey of relations with empirical parameters used for description of effects of individual solvents on processes in solutions and presents results of tests of selected equations with a set of 368 experimental data series. The Kamlet & Taft equation in the basic version (only with the π^*, α, and β parameters), has been evaluated as the best one, the best parameter according to the STEPWISE procedure being the π^* parameter by Kamlet & Taft and the BASITY parameter by Swain et al. The best fit has been found for the processes involving electronic excitation of molecules in absorption and fluorescence spectroscopy. The section concerning mixed solvents presents a survey of empirical models used for description of effect of changes in composition of solvent mixtures on processes in solutions. The testing with 29 data series has shown the practically advantageous properties of the relations based on application of the additional Gibbs function expressed by empirical linear expansion (Margules).

1. INTRODUCTION

Since 1890, when Menshutkin[1] for the first time quantitatively described solvent effect on chemical reaction, much scientific effort has been spent on the problems of evaluation of solvent effect on the processes in solutions. Greater attention was paid to individual solvents, which is documented by a series of monographs dealing either directly with the solvent effects[2-6] or with the allied regions (e.g. refs[7-13]). Journals present both reviews[14-17] and series of original papers including several tens of communications at present (a survey of one of the most significant series is given in ref.[10]). Less attention was paid to mixed solvents, although they are more important practically. Except the monographs already quoted there exists no complete review dealing with mixed solvents, although interpretation of experimental results was several times successful in this area (see Chap. 5).

With increasing amount of experimental data the trend to quantitative interpretation of solvent effect on processes in solutions grew stronger (for a historical survey see e.g. refs[6,10,11]). A quantitative description of the respective process necessitates the choice of a suitable model – either mathematical or physical or chemical. Purely mathematical models, allowing to fit the experimental points found to a suitable curve, are almost useless for understanding of the essence and applications of solvent effects. The physical and chemical models can be divided into theoretical, semiempirical, and empirical ones. The theoretical models are based on exactly physico-chemically expressed ideas about solute–solvent interactions at the molecular level. The semiempirical models (see e.g. refs[18–25]) are based on a theoretical description involving some macroscopical characteristics of the solvent itself as e.g. relative permittivity or refractive index. Various functions of these experimental quantities are used for the quantitative description of the solvent effect. The empirical models describe a solvent by means of manifestations of a suitable process taking place in the solvent. In the model process the solvent can act as a solvating medium or – in addition to it – as a reactant, too. Hence, the direct measurement result represents the empirical parameter which quantitatively characterizes the solvent. In some cases the results from several measurements with one or several similar (from the point of view of the model) compounds are averaged. Both the semiempirical characteristics and empirical parameters are sometimes used side by side in the correlation equations which are denoted as empirical ones (see Part 3.7.). In terms of the above-mentioned classification, the present review deals with the empirical parameters, empirical correlation equations, and their applicability to quantitative description of solvent effects. Only those of semiempirical characteristics are mentioned which appear in the empirical correlation equations.

The application of individual models has its advantages as well as drawbacks. The theoretical and – more or less – also the semiempirical methods provide an unambiguous picture of the process described, but – due to the approximations inevitably introduced – they need not be sufficiently satisfactory in describing real practically occurring processes. In this respect, the empirical approach provides more acceptable results which, however, often depend on the model system used and are less understandable from the point of view of the solute–solvent interactions. Although the ETR (LFER) principle adopted here proved useful, the theoretical background is not sufficiently developed and the correlations are less close than those of e.g. the substituent effects. Statistical models represent a certain variant, their parameters being determined by a sort of extraction of the most significant common manifestations from a set of large amount of experimental data. In principle, they are more hopeful of success in close correlation between the model function and experimental data, but they have a drawback in that they still more obscure the nature of the interpreted processes in solutions.

2. BASIC PRINCIPLES OF APPLICATION OF EMPIRICAL RELATIONS TO DESCRIPTION OF EFFECTS OF INDIVIDUAL AND MIXED SOLVENTS ON PROCESSES IN SOLUTIONS

As it has already been mentioned the basis for application of empirical relations to interpretation of solvent effects is represented by the so-called extrathermodynamic relationships[26] (ETR) or, otherwise, linear free energy relationships (LFER). Although doubt has been thrown upon this concept as a general law[26], on the other hand broad validity and applicability of this approach has been shown in the case of interpretation of effects of individual solvents on processes in solutions[27]. Another evaluation can be found in some monographs (ref.[3], p. 271; ref.[6], p. 225) and periodicals[28–30]. The application of this principle to the solvent problem is denoted by the abbreviation LSER (linear solvation energy relationships, refs[9,16]).

The basic model is linear additive, i.e. it presumes more or less independent operation of several factors whose superposition causes the resulting effect observed. Therewith connected are two basic problems: the number and the physico-chemical meaning of the parameters used. Although it seems probable that the statistical analysis could contribute to the decision about the necessary number of parameters, the problem remains unsolved so far. The same or similar statistical methods were applied by various authors and led to two[31–34], three[35,36], or even four parameters[37]. Hence it can obviously be concluded that the number of parameters needed for description of solvent effects is small, most likely equal to three, and particular conclusions in literature are affected by the extent and selection of data.

The number of parameters is closely connected with their physical meaning. As the individual models differ in the extent and amount of the solvent-solute interactions involved (for a survey see e.g. refs[38,39]), there is so far no clear unity with respect to the views on physical meaning of the parameters which would express the predominant part of the manifestations of a solvent. In principle it is possible to extract three basic characteristics of solvent (irrespective of the terminology used in individual papers), viz. acidity, basicity, and interactions of electrostatic nature. Whereas there is no difference (in the consequences) between the term of basicity in the Lewis theory and that in the Brönsted theory, the term of acidity is distinctly different in the two theories. The term of electrostatic interactions involves inter alia first of all the polarity (dipolarity) and polarizability of the solvent. Some aspects of this problem are discussed e.g. in refs[4,5,9,30,34,40–42].

2.1. THEORETICAL BASIS OF APPLICATION OF EMPIRICAL RELATIONS

Any process in solution is connected with a change in the energy of the system which can be denoted generally as ΔG. A change in quality of solvent makes itself felt, as a consequence of changed solvation stabilization, in the energy of the system undergoing a transformation: either before the process, or in its course in some key moment, or after the process. The respective differences consist in different solvation of educts and activated complexes in chemical reactions, in different solvation of chemical species at an equilibrium, in electronic spectra of solvation of a ground and an excited states; in infrared spectra e.g. the formation of hydrogen bonds affects the potential and kinetic energy of a system; in NMR there can exist differences in chemical shielding of nuclei, etc. In spite of great diversity of processes in solutions the manifestations observed are due to few reasons (see above), and the situation can generally be described by Eq. (*1*)

$$\Delta G = f(T, P_1, P_2, \ldots, P_N)\,, \tag{1}$$

where ΔG represents the measured result of the process at the temperature T and under the conditions $P_1, P_2, \ldots, P_N$. According to Taylor's theorem the change in the ΔG quantity with the change in the condition P can be approximated by Eq. (*2*)

$$\begin{aligned}\Delta G(T, P_1^0 + \varDelta P_1, \ldots, P_N^0 + \varDelta P_N) &= \Delta G(T, P_1^0, \ldots, P_N^0) + \\ &+ \left[\frac{1}{1!}((\partial/\partial P_1)\,\varDelta P_1 + \ldots + (\partial/\partial P_N)\,\varDelta P_N)\,\Delta G + \ldots + \right. \\ &\left. + \frac{1}{n!}((\partial/\partial P_1)\,\varDelta P_1 + \ldots + (\partial/\partial P_N)\,\varDelta P_N)^{(n)}\,\Delta G\right]_{\Delta G = \Delta G^0}\,,\end{aligned} \tag{2}$$

where $\varDelta P$ means the change in the conditions of the process with respect to the standard, (n) denotes the n-th total differential, and the superscript 0 denotes the standard state. If only the first-order correction is considered, Eq. (*2*) can be wirtten in the form of Eq. (*3*)

$$\Delta G = \Delta G^0 + (\partial \Delta G/\partial P_1)\,\varDelta P_1 + \ldots + (\partial \Delta G/\partial P_N)\,\varDelta P_N\,, \tag{3}$$

the meaning of the symbols ΔG and ΔG^0 being clear from comparison of Eqs (*2*) and (*3*). The latter equation will approximate the reality the better the better the $\varDelta P$ parameters approximate the change in conditions, because the respective partial derivatives are considered constant within the whole extent of the change.

Under the presumption that in all the processes considered there takes place a change in a manifestation as a consequence of few identical internal reasons it is possible to expect an analogous character of the process response to the change of each of these reasons. The response intensity will then be a function of only the character of the process and the particular system. If the internal change is described by suitable parameters $\varDelta P$, then the application of Eq. (*3*) to real processes presents no difficulties. However, just the finding of suitable parameters represents the key problem in empirical description of solvent effects. Although the above-mentioned presumptions are undoubtedly valid, having been verified in many cases[27], the model parameters determined from model experiments do not seem to be those internal fundamental parameters but their linear combinations or even more complex functions. As an example we can mention the measure of solvation stabilization by hydrogen bond which is simultaneously affected by electrostatic properties of the solvent. Similar situation is encountered with the electron-donor-acceptor processes. Obviously it is more correct to consider at least a second-order approximation which reflects the corresponding interactions and to neglect the a priori insignificant members. Thereby the merely additive relation becomes an additive-multiplicative one which better reflects the reality. This fact is documented e.g. by the successful application of the product term in the region of semiempirical methods for interpretation of empirical parameters[25,43-46]. The model described by Eq. (4) could represent a possible model of this type for the individual solvent.

$$\Delta G = \Delta G^0 + [(\partial^2 \Delta G/\partial P_A \partial P_E)\, \Delta P_A + (\partial^2 \Delta G/\partial P_B \partial P_E)\, \Delta P_B + \\ + (\partial \Delta G/\partial P_E)]\, \Delta P_E\,, \qquad (4)$$

where ΔP_A, ΔP_B, and ΔP_E denote the acidic, basic, and electrostatic properties of the solvent, respectively. The ΔP_E parameter can also be taken as a product of two terms in the sense of a product term.

The above considerations apply to both individual and mixed solvents, with the latter ones, however, the situation being complicated by possible interactions between the solvent components: the final effect is not merely a sum of the effects of the components. Consequently it is necessary to introduce parameters as a function of the composition, which results in the loss of the simple character of the empirical approach.

2.2. TREATMENT OF EXPERIMENTAL RESULTS

As it was already mentioned the empirical relations most often have a form of combination of solvent parameters. The expansion coefficients are usually calculated by linear regression[47]. Obviously the result will be the more significant the larger number of solvents will be included (at least 3–4 for each regression parameter) and the more uniformly covered will be the region of possible manifestations of the solvent. Applications of selected solvent sets (e.g. SSS (ref.[9])) improve the fit, but, on the other hand, many pieces of information are thereby lost. Not always are the published equations accompanied by all necessary statistical data as the number of experimental points, standard deviation of regression coefficients, residual standard deviation, and multiple correlation coefficient. It should be a matter of course that the statistically insignificant regression coefficients were omitted. In the case of a bad fit it is useful to represent graphically the relation between found and calculated dependent variables, which can help to reveal the reasons of failure and, at the same time, provide further information about both the process taking place and the solvent.

3. EMPIRICAL MODELS AS A SOURCE OF PARAMETER SCALES FOR DESCRIPTION OF EFFECT OF INDIVIDUAL SOLVENTS ON PROCESSES IN SOLUTIONS

The basic prerequisite of any description of effects of individual (pure) solvents on a process in solution consists in the choice of a suitable model system for the construction of the solvent scale, because the mathematical form of the empirical model is – more or less – already given. At present there exist several tens of solvent scales. Not all of them, however, meet the requirements of practical applications. The most frequent drawback is a little solvent set for which the parameters are given. In this respect a positive example is the $E_T(30)$ (E_T^N) scale[48] containing data for 243 solvents. Another drawback consists in low generality of the model process. A suitable choice of model compounds leads to a broad applicability as it is seen in the above-mentioned $E_T(30)$ parameter and especially in the case of the π^*, α, β parameter set[9,16,27,49]. As far as the type of model process is concerned the most often applied are spectral methods particularly UV-VIS spectroscopy. This is quite understandable, since spectral characteristics can be determined easily and accurately, sometimes even the solubillity of the substance at the desired concentration being the only limiting factor.

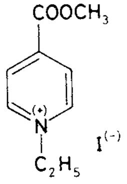
The problem of transferability of scales adjusted with one type of process to interpretation of another type, although quite essential, is often neglected. If a choice of model can ensure that the parameters obtained will reflect, almost exclusively, some fundamental property of solvent (see Part 2.1.), then applications to other areas usually present no difficulties. None of the parameter scales suggested, however, can fully meet this requirement. This is clearly seen in the case of the parameters obtained from fast processes[49] (the excitation processes in electronic spectra) and their application to other processes (e.g. equilibria, non-excitation spectral processes) as it is shown in refs[44,45,50] and criticized in ref.[51].

3.1. SPECTRAL PROCESSES

This area includes the parameters derived from the measurements of electronic absorption and fluorescence spectra, infrared spectra, NMR and EPR spectra. Other spectral processes were not used for definition of solvent parameters to any significant extent.

3.1.1. *Electronic Absorption and Fluorescence Spectroscopy*

Among the oldest parameters belongs the Z parameter defined by Kosower[52–57] and extended and evaluated by other authors[58,59] on the basis of spectral shift of CT band of 1-ethyl-4-methoxycarbonylpyridinium iodide (*I*). The model compound *I* initiated a serch for other solvatochromic indicators of zwitterionic type. The parameter suggested by Griffith et al.[60] on the basis of the CT transitions of complex compounds with iodide anion falls in the same historical period. In 1960 Brownstein[61] proposed a parameter derived from Kosower's Z parameter and characterizing the solvent in a simple equation similar to the Hammett equation for substituent effects. One of the most important parameters of this group is the $E_T(30)$ parameter suggested by Dimroth & Reichardt[62] in 1963 and extensively developed by these authors and coworkers[48,63-70] in the following years. The model compound is 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)-phenoxide (*II*) and its alkyl derivatives with enhanced solubility in non-polar solvents. The $\pi \rightarrow \pi^*$ transition of this compound exhibits the highest solvatochromic sensitivity known so far.



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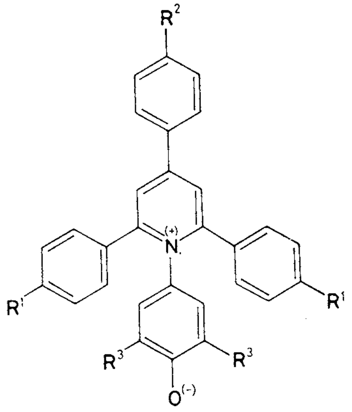
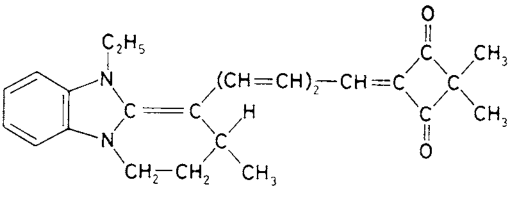


II

The effects of solvents on the $n \rightarrow \pi^*$ transitions in aliphatic ketones form the basis for the $\Phi(F)$ scale suggested by Dubois et al.[71,72]. Brooker et al.[73] used the



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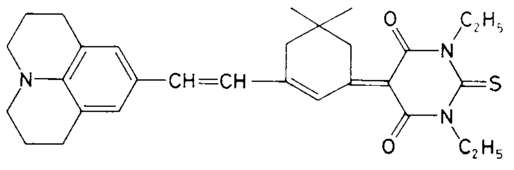
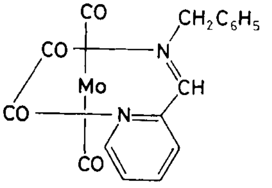


IV

merocyanine dyestuffs *III* and *IV* to define the χ_B and χ_R scale. Davis[74] based his scale on the solvent effects on the spectra of CT complexes with halogenide anions of quaternary salts and various electron acceptors. The complex compound diacetylacetonatooxovanadium was used by Selbin[75] for construction of the $D_{I,II}$ scale, and similarly, tetracarbonylpyridine-2-carbaldehydebenzyliminemolybdenum-(0) (*V*) was adopted by Walther[76] as the basis of his E_k scale. The RPM scale suggested by Dähne et al.[77] makes use of solvatochromic properties of 5-dimethylamino-2,4-pentadienal. Pyridinium iodide derivatives became the model compounds for the $E_T(SB)$ and $E_T(MPI)$ scales described by Štrop et al.[78]. Walter et al.[79] based their E_T^{SO} scale on the solvatochromic shifts of N,N-dimethylthiobenzamide-S-oxide.



V

From the practical point of view very important parameter scales were defined by Kamlet, Taft et al. on the basis of spectra properties of aromatic amines and phenols: these parameters include the β parameter reflecting the solvent basicity[9,49,80,81], the α parameter reflecting the solvent acidity[17,49,82,83], the π* parameter describing the solvent polarity/polarizability[9,49,81,84–86] or also the δ parameter denoted as a polarizability correction term[87]. The effect of solvents on spectral properties of selected models connected with theoretical presumptions was used by Bekárek et al.[50] for defining the W scale and the parameters derived therefrom. The fluorescence spectra were applied to proposing of solvent scales to a substantially smaller extent. In this field noteworthy are the works by Zelinskii et al.[88] making use of 4-amino-N-methylphthalimide, those by Davis[89] based on the solvent effects on fluorescence bands of CT complexes (the E_{CT} parameter), and those by Dong et al.[90] who, more recently, proposed a parameter called "Py-scale".

3.1.2. *Infrared Spectroscopy*

The studies of solvents in the field of infrared spectroscopy first of all make use of the excellent possibility of IR spectroscopy to study the hydrogen bonds. Allerhand & Schleyer[91,92] used the changes of the valence vibration frequence $\tilde{\nu}_{OH}$ of some alcohols and phenol to define a relative scale G. In an analogous way Koppel & Palm[40,93] based their parameter scale on the valence vibration $\tilde{\nu}_{OD}$ in O-deuteriomethanol. The same substrate was also used by Burden, Shorter et al.[94]. The greatest number of solvents whose parameters were derived from the valence vibration

$\tilde{\nu}_{OH}$ of phenol in carbon tetrachloride and the corresponding solvent were described by Koppel & Paju[95] (the B parameter). The series was complemented and evaluated by Aslam, Shorter et al.[96]. An analysis of results of measurements of OH and/or OD valence vibrations in several model compounds carried out by Kamlet, Taft et al.[9,97–99] enabled to correct the scale of the β basicity parameter and introduce the correction term ξ.

3.1.3. *Nuclear Magnetic Resonance and Electron Paramagnetic Resonance*

The solvent–induced chemical shifts in ^{19}F NMR spectra of 4-fluoronitrosobenzene were used by Taft et al.[100] for construction of a scale. A large amount of data were published by Gurka & Taft[101] about the results of ^{19}F NMR measurements of 4-fluorophenol in carbon tetrachloride in the presence of another solvent. Although this data set was not declared as a solvent parameter scale, it can be used for this purpose. The chemical shifts in ^{31}P NMR spectra of triethylphosphine oxide were suggested by Mayer, Gutmann et al.[4,102–105] to describe the electron-acceptor properties of solvents under the name AN (acceptor number). Later the scale was extended by Elias et al.[106].

Out of the results obtained by the electron paramagnetic resonance spectroscopy in the measurements of solvent effects only one paper is usually quoted, viz. that by Knauer & Napier[107] who defined the $\mathscr{A}_N$ (or also $a^{^{14}N}$) scale on the basis of the ^{14}N hyperfine splitting constants of model aminoxides.

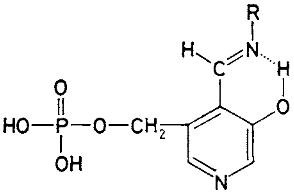
3.2. RATE PROCESSES

By the extent and importance of the models suggested for description of solvent effects, kinetic measurements assume the second place after the electronic absorption spectroscopy. Historically the oldest is the Y_{GW} scale suggested by Grunwald & Winstein[108] on the basis of logarithm of the solvolysis rate constant of 2-methyl-2-chloropropane (the S_N1 mechanism). The same substrate was used by Fainberg & Winstein[109] in the following communication of the same series. 2-Methyl-2-(4-methoxyphenyl)propyl toluenesulphonate proved to be a more suitable model (the E1 mechanism), since it allowed measurements to be carried out in a greater number of solvents[110]. Nevertheless, the importance of these solvolytic scales is limited only to some solvents and/or their mixtures. A quite different type of reaction was used by Berson et al.[111]: their Ω parameter was derived from the solvent effect on stereoselectivity of the Diels–Alder reaction of cyclopentadiene with maleic anhydride. The reaction of tetramethyltin (as an electrophile) with bromine served as a model for the X scale defined by Gielen & Nasielski[112,113]. One of the most significant reactions in solvents – the Menshutkin quaternization – was chosen by Lassau & Jungers[114] for characterization of solvation properties of solvents. The same type of reaction was used also by Drougard & Decroock[115] for definition of the $\mathscr{S}$ scale.

Solvolytic reactions served as a model for simultaneous action of the solvent as both the medium and the nucleophilic reagent. In this sense they were used in the works by Winstein et al.[116,117], Bentley et al.[118-121], and Peterson & Waller et al.[122].

3.3. EQUILIBRIUM PROCESSES

The equilibrium processes belong to less important models for parametrization of solvent effects. Out of the chemical equilibria we can quote the solvent effect on the NH-OH tautomeric equilibrium of the Schiff base *VI* described by Llor & Cortijo[123] and denoted as the $-\Delta G^0$ parameter. Eliel et al.[124-126] suggested the parameter $-\Delta G^0_{OCH_3} \equiv D_1$ based on the solvent effect on the conformational equilibrium of substituted 1,3-dioxanes.



VI

3.4. OTHER PROCESSES

In this group it is possible to include a number of processes of markedly different nature and significance. First of all this group includes the heats of formation for reactions of strong Lewis acceptors with solvents as donors in inert medium. One parameter of this type is denoted as DN (donor number) and was defined by Gutmann et al.[127-131] as the reaction heat of the interaction of antimony(V) chloride with the solvent in 1,2-dichloroethane medium. Earlier Olofson et al.[132-135] used carbon tetrachloride as the solvent.

The molar heat of evaporation was used by Hildebrand[136] as a basis for definition of the so-called solubility parameter δ_H reflecting the effect of non-specific interactions of the solvent on the process taking place therein. The δ solubility parameters were summarized by Barton[137]. The distribution coefficients between solvent and gas phase for several model solutes were used by Rohrschneider[138], who suggested the so-called P′ scale (as well as the parameter δ and V_m – molar volume), and by Snyder[139].

Snyder[140] also suggested the ε_0 scale (also denoted $\varepsilon_{Al_2O_3}$, eluant strength parameter) reflecting the adsorption energy of solvent per surface area unit of adsorbent. Kováts et al.[141,142] used chromatographical data for the definition of the so-called retention index I and $\Delta I^{Cl/Br}_{50}$.

The parameter $\hat{\eta}$ based on the activation energy of solvent viscosity[143] was suggested by Kupfer & Abraham[144].

3.5. THE PARAMETER SCLALES DERIVED FROM PRIMARY MODEL PROCESSES BY MATHEMATICAL-STATISTICAL TREATMENT

The possibility of applications of mathematical-statistical methods to construction of solvent parameter scales has already been mentioned in Introduction. The methods most frequently used for treatment of the primary sets of solvent characteristics are the method of principal components (PCA)[145] and the factor analysis (FA)[146,147]. In the cases of sufficiently homogeneous data (in the sense of description of the same or analogous properties) these methods enable to express the whole information involved by few vectors (principal components, score vectors). These vectors are orthogonal (mutually independent, non-correlated) and can be used as new parameter scales e.g. just for the description of solvent effects on processes in solutions. More appropriate for this purpose appear to be some of the variants of the factor analysis[147] or the PLS method[148,149]. Another significant result is the determination of the number of factors necessary for the description of properties of the given set, although this number is a function of quality of the applied set of primary parameters, which was discussed in Chap. 2.

Although the above-mentioned methods have been used for analysis of solvent parameters several times (sometimes together with physical properties of solvents) [31–37,150–157], there exist only few useful scales. Chastrette[152] analyzed a set of 22 solvents characterized by the empirical parameters $E_T(30)$, DN, AN and physical quantities or expressions derived therefrom – dipole moment, molar refraction, and the Kirkwood function[158] of relative permittivity $(\varepsilon - 1)/(2\varepsilon + 1)$. The first 5 principal components are given, out of which the first several principal components selected can serve as the solvent parameters. Cramer[155,156] used the principal component analysis for construction of the BC(DEF) scale based on physical properties of 114 solvents (aqueous solvation energy, partition coefficient, boiling point, molar refractivity, molar volume, and molar evaporation heat). This scale first of all characterizes well the physical properties of solvents, but also significant is the correlation with e.g. the $E_T(30)$ parameter. The same method (PCA) combined with the so-called "Cross-validation" procedure was used by Sjöström & Wold[32]. Their report gives the statistical parameters ϑ_1 and ϑ_2 for 80 solvents obtained from the spectral characteristics of the models by Kamlet & Taft (see Paragraph 3.1.1.). Elguero & Fruchier[35] in their work used a set of 51 solvents to show that the parameters $P(= (n^2 - 1)/(n^2 + 1))$, $Y(= (\varepsilon - 1)/(2\varepsilon + 1))$, E, and B suggested by Koppel & Palm[40] (see Paragraph 3·7·3·) can be expressed by a merely three-parameter scale without any loss of information. The factor analysis of 51 solvents characterized by 20 solvent parameters made it possible for Svoboda, Pytela & Večeřa[37] to suggest a four-

-parameter scale expressing the acidity (AP) and basicity (BP), electrostatic interactions (EP) and manifestations of polarizability (PP) of the solvents. The above-mentioned parameter scales were obtained as linear combinations of the original score vectors (by the VARIMAX method), which also made it possible to express the physical meaning of the new parameters.

Swain et al.[34] carried out an extensive analysis of 77 selected processes in solutions (kinetics, equilibria, spectra) with 55 individual and 6 mixed solvents. The two scales constructed were denoted as ACITY (AC, anion-solvating tendency) and BASITY (BA, cation-solvating tendency). The application of these parameters to the source data gave very good correlations, but the scale suggested does not sufficiently interpret the basic properties of the solvents, as it was shown in ref.[159]. Swain expressed his opinion to these objections in ref.[41]. For further analysis of this scale see Paragraph 3.7.2. and Chap. 4.

3.6. EVALUATION AND COMPARISON OF PARAMETER SCALES

Beside the choice of the model process and proper construction of the parameter scale it is obviously necessary to analyze the physico-chemical meaning and relation to other existing scales. A survey of these problems is given e.g. in refs[9,10,15,16,30,160,161]. In addition it is possible to find a number of reports dealing with interpretation of only one or few parameters. Perhaps the greatest attention was focused on the π^* parameter suggested by Kamlet & Taft[85] (see paragraph 3.1.1.). This parameter was theoretically and semiempirically interpreted[162-166], and several attempts were also made at its modifications[25,43-46]. The relation of this parameter to a number of other empirical parameters is disclosed in refs[50,51,85,87,159,167-170]. Less attention was focused on the other two basic parameters suggested by the same authors, viz. α and β. Beside their modification[43] also described were their correlations with other solvent parameters[49,159,167,169]. The relation between the α parameter and some spectral parameters can be found in ref.[82], that between α and the σ^* parameter by Taft in ref.[83]. The correlations concerning the β parameter are given in refs[15,98,99,157,171]. Also the $E_T(30)$ parameter by Reichardt & Dimroth was well evaluated by correlations[10,50,69,106,107,165,166,172], the same being true of the AN, DN parameters by Gutmann & Mayer[15,102,105,106,169,171]. Other correlations between various empirical parameters can be found e.g. in refs[45,107,111,117,173,174].

In order to evaluate the importance and relations of the individual parameters in a uniform way, a set of 51 solvents has been selected for which literature supplies a sufficient number of parameters of several most significant scales (Table I). This selection includes representatives of all kinds of solvents. Table II summarizes the correlation coefficients between the solvent parameters which form a part of basic empirical model equations (see Part 3.7.) or are especially important for interpretation. Table II indicates some basic bonds between the parameters, which reveals their physico-chemical meaning. First of all, a close interdependence exists among the parameters $E_T(30)$, AC, AN, α, and E, and partially W (through $E_T(30)$). This group can be denoted as parameters describing the solvent acidity. Another group is formed by the parameters BA, W, W . $f(n^2)$, Y, π^*, and partially $E_T(30)$ (through W). The parameters of this group express the solvent polarity. The group of the empirical parameters related to basic manifestations of solvents includes B and DN (and, very indistinctly, the β parameter). A special group is formed by the virtually identical semiempirical parameters P $(= (n^2 - 1)/(n^2 + 1))$ and $f(n^2)$ $(= (n^2 - 1)/ /(2n^2 + 1))$ which reflect the deformation polarizability of solvents. This group arrangement of the parameters confirms the ideas about the role of solvent played in a chemical or physical process in solution. A rather exceptional position is occupied by the $E_T(30)$ and W parameters each of which combines two properties, viz. acidity and polarity. This fact can be reason of good success of the $E_T(30)$ parameter in the correlation equations with a single solvent parameter. Rather surprising is the separate position of the β parameter and/or its little close relation to the B parameter.

TABLE I

The selected solvent set for evaluation of empirical parameter scales describing the effect of individual solvents on processes in solutions

No.	Solvent	No.	Solvent	No.	Solvent
1	Hexane	18	Diisopropyl ether	35	Water
2	Heptane	19	Methoxybenzene	36	Methanol
3	Cyclohexane	20	Ethoxybenzene	37	Ethanol
4	Benzene	21	Tetrahydrofurane	38	1-Butanol
5	Toluene	22	Dioxane	39	2-Propanol
6	*m*-Xylene	23	Acetone	40	2-Methyl-2-propanol
7	*p*-Xylene	24	Butanone	41	Benzyl alcohol
8	Mesitylene	25	Cyclohexanone	42	1,2-Ethandiol
9	Tetrachloromethane	26	Methyl acetate	43	2-Methoxyethanol
10	Chloroform	27	Ethyl acetate	44	Acetic acid
11	Dichloromethane	28	Acetanhydride	45	Triethylamine
12	1,2-Dichloroethane	29	Formamide	46	Pyridine
13	Chlorobenzene	30	N,N-Dimethylformamide	47	Nitromethane
14	Bromobenzene	31	N,N-Dimethylacetamide	48	Nitrobenzene
15	Fluorobenzene	32	HMPA[a]	49	Dimethyl sulphoxide
16	Diethyl ether	33	Acetonitrile	50	Sulpholane
17	Dibutyl ether	34	Benzonitrile	51	Carbon disulphide

[a] Hexamethylphosphoric triamide.

TABLE II

The matrix of statistically significant correlation coefficients between selected empirical parameters for the solvent set of Table I. The dash represents statistical insignificance of the respective correlation coefficient. The ACITY and BASITY parameters by Swain et al.[34] are denoted as AC and BA for simplicity. The parameter values were taken from literature: $E_T(30)$ ref.[48]; AC, BA ref.[34]; π^*, α, β ref.[49]; Y, P, E, B ref.[8]; W, $f(n^2)$, $W\,.\,f(n^2)$ ref.[50]; AN, DN refs[4,15,105]

	$E_T(30)$	AC	BA	π^*	β	α	Y	P	E	B	W	$f(n^2)$	$W\,.\,f(n^2)$	AN
AC	0·940													
BA	0·442	—												
π^*	0·592	0·459	0·912											
β	0·438	—	—	—										
α	0·840	0·930	—	—	0·351									
Y	0·767	0·625	0·743	0·778	0·584	0·414								
P	−0·336	−0·404	—	—	—	−0·419	—							
E	0·917	0·938	—	0·339	—	0·935	0·465	−0·392						
B	—	—	—	—	0·809	—	0·347	—	—					
W	0·947	0·821	0·906	0·863	0·499	0·374	0·933	—	0·640	—				
$f(n^2)$	—	—	—	—	—	—	—	0·991	−0·329	—	—			
$W\,.\,f(n^2)$	0·895	0·786	0·958	0·987	0·441	—	0·904	—	0·469	—	0·911	—		
AN	0·927	0·984	—	0·404	—	0·939	0·497	—	0·941	—	0·801	—	0·820	
DN	—	—	—	—	0·776	—	—	—	—	0·977	—	—	—	—

A detailed analysis indicates differences especially for alcohols (ethanol, 1-butanol, 2-propanol, tert.butyl alcohol), amines (triethylamine, pyridine), and nitrobenzene, the β parameter appearing (with regard to B and DN) underestimated for alcohols and nitrobenzene and overestimated for amines. The analysis also supports an idea of different physico-chemical meaning of the BASITY parameter[159] as compared with that declared in the original paper[34]. Surprisingly, no relation exists between the quantities describing the deformation polarizability (P, $f(n^2)$) and basicity (B, β, DN), although both phenomena have more or less the same basis – relatively mobile π and n electrons in the solvent molecules. Also noteworthy is the insignificant correlation between the π^* parameter and the semiempirical polarizability parameters P and $f(n^2)$.

Beside the correlation analysis, suitable tools for studies of relations between variables are further methods of multidimensional analysis as the principal component analysis, the factor analysis, PLS etc. An analysis carried out by Fawcet & Krygowski[31] for six parameters characterizing solvent (relative permittivity, refractive index, DN, B, $E_T(30)$, Z, and AN) and for 25 solvents showed a good linear dependence between the DN and B parameters as well as between $E_T(30)$, Z, and AN. The first two principal components included more than 90% of the original information, and the closest correlation ($r > 0.85$) was found for E_T and DN. Therefrom the authors denoted the solvent acidity and basicity as the dominant solvent properties. The papers by Chastrett et al.[152–154] are preferably focused on the relation between the parameters $E_T(30)$, AN, DN, Z, δ_H (Hildebrand[136]), and π^* and further semiempirical ($(\varepsilon - 1)/(2\varepsilon + 1)$) and physical (molar refraction, dipole moment, refractive index, boiling point) characteristics. Inter alia found was the proportion of polarity (expressed by the function $(\varepsilon - 1)/(2\varepsilon + 1)$), polarizability (assessed by means of the refractive index), and cohesion forces (Hildebrand's δ_H) in the two most significant empirical parameters, viz. $E_T(30)$ (the proportion 43%, 18%, and 39%, respectively) and π^* (53%, 18%, 29%). Another paper[36] deals with the analysis of physical and theoretical characteristics of solvents, Elguero & Fruchier[35] analyzed the parameter set suggested by Koppel & Palm[40] for 51 solvents. Three factors are sufficient for expressing the origin of information: the first one includes the E parameter (acidity) and corresponds to the first factor by Chastrett[152] (first of all AN and molar refraction); the second factor is formed by the B (basicity) and P (polarizability) parameters and corresponds to the second factor by Chastrett (especially DN and $E_T(30)$); the last factor includes the semiempirical parameters Y (polarity) and P (polarizability) and is related to the fourth factor by Chastrett (the Kirkwood function). The third factor by Chastrett (especially the dipole moment) is not markedly connected with the parameters by Koppel & Palm. The analysis carried out by Svoboda, Pytela, and Večeřa[37] for the 20 most frequent empirical, semiempirical, physical, and theoretical characteristics showed the existence of four groups of parameters. The first group includes (in the sequence of decreasing pertinence) the parameters AN, Z, S_1 (ref.[88]), S_2 (ref.[61]), E, $a^{14}N$, log P, δ, δ^2 (ref.[175]) and reflects the solvent acidity. The parameters χ_R, $E_T(3)$, relative permittivity ε, Y, π^*, and the connectivity of the *n*-th order χ^n (ref.[176]) form the second group reflecting the solvent polarity. The third group includes the B, DN, and β parameters which unambiguously describe the solvent basicity. The last group includes the quantities P and refractive index and relates to the solvent polarizability. Carlson et al.[33] applied the principal component analysis to a group of 82 solvents described by eight characteristics of predominantly physical nature. Out of the empirical parameters the analysis includes the $E_T(30)$ parameter. The set appears considerably non-homogeneous, because the first principal component includes only 29% and the second principal component only further 22% of the original variability. Nevertheless, the results allowed a suggestion of a selected set of solvents for the experiments planned in the field of organic synthesis. Maria et al.[157] published a paper predominantly focused on the analysis of basicity. Ten characteristics reflecting the electron-donor properties of 22 solvents form a relatively homogeneous set (in the first three factors totally included is 82·5%, 96·5%, and 99% of the original information). Most of the quantities used correlate well with the first three principal components, the only exception being the quantity denoted as pK_{HB} (log *K* of formation of the complex between the base and 4-fluorophenol in carbon tetrachloride[177,178]) and the β parameter which are in close mutual correlation. This indicates the existence of two types of basicity roughly corresponding to the Lewis and Brönsted theories of acid and bases, and the same is documented also by Table II.

The survey given shows that the results of the individual analyses are not unambiguously agreeing. This fact is first of all due to the amount, type, and quality of the solvent characteristics included and, to a substantially lesser extent, to the statistical method adopted. In spite of the differences in results, these studies are useful, sice they allow to obtain a clearer idea about the nature of the empirical parameters in connection with the semiempirical and physical characteristics of solvents. Irrespective of the extent of participation it is possible to suggest three to four basic solvent effects. This conclusion is supported by the following analysis, too.

The principal component analysis of a set of selected solvents from Table I characterized by 26 empirical parameters (Table III) with the highest number of the given values provided (after the VARIMAX rotation) a picture of distribution of the parameters in the factor space. If only the first two factors are involved (i.e. 79% of the original variability, Fig. 1), the corresponding principal components can be assigned the meanings of acidity (in connection with the AN, ACITY, E, α, Z, Φ, S_1, $a^{14}N$, $E_T(30)$, $\varepsilon_{Al_2O_3}$, S_2) and polarity (in connection with the π^*, BASITY, $\int_H^{p-NO}$, χ_R, Y parameters). From Fig. 1 it can be seen that the basicity parameters (B, DN, β) lie near the centre of gravity and do not make themselves felt as an independent factor. Hence the dominant variability of experimental values is in the fields of acidity and polarity, and application of only two principal components (or other characteristics of this type in the multidimensional analysis) leads (if sufficiently representative sets are treated) to omission of description of basicity. This

TABLE III

Selected empirical and semiempirical solvent characteristics used in the principal component analysis

No.	Parameter	Ref.	No.	Parameter	Ref.
1	$E_T(30)$	48	14	AN	4, 15, 105
2	ACITY (AC)[a]	34	15	DN	4, 15, 105
3	BASITY (BA)[a]	34	16	Z	52
4	π^*	49	17	S1[b]	88
5	β	49	18	S2[c]	61
6	α	49	19	Φ	71, 72
7	Y	8	20	$a^{^{14}N}$	107
8	P	8	21	δ_H	136
9	E	8	22	χ_R	73
10	B	8	23	δ^2	175
11	W	50	24	f_H^{p-NO}	87
12	$f(n^2)$	50	25	$\varepsilon_{Al_2O_3}$	140
13	$W \, . \, f(n^2)$	50	26	${}^n\chi$[d]	37, 176

[a] The abbreviations used in order to avoid confusion; [b] S1 — the S parameter defined by Zelinskii; [c] S2 — the S parameter defined by Brownstein; [d] index of molecular connectivity of the *n*-th order.

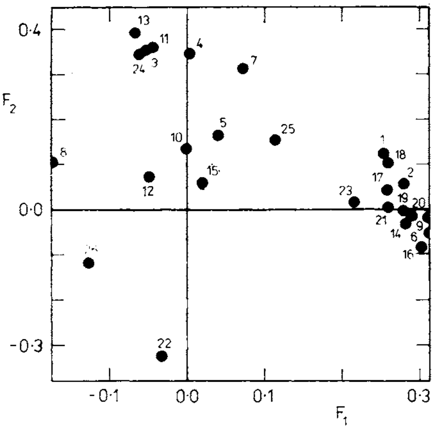


FIG. 1

Distribution of empirical solvent parameters in the space of the first two principal components after rotation. For the numbers see Table III statement can also be documented with the parameters by Swain et al.[34]. The application of the first three principal components (92%, Figs 2, 3) already provides a physically more realistic picture. The first principal component expresses the solvent acidity and is formed by roughly the same parameters as those in the previous case. The shift of the α parameter (point 6, Figs 2, 3) on the polarity axis is noteworthy: it indicates a certain contribution of this property. The second principal component can be considered identical with polarity and, partially, polarizability, and it is expressed e.g. by the π^* and BASITY parameters. Out of the other parameters it is possible to assign especially χ_R, Y, W . f(n^2). An interesting relation exists between the semiempirical parameters P and f(n^2): although they express the same, we intentionally used the f(n^2) parameter only for the aprotic solvents in accordance with ref.[50]. For these solvents the relation between polarity and polarizability seems closer. Figure 3 represents a sort of "side view" with regard to Fig. 2 and indicates the equality between the third principal component and the basicity expressed by the β, B, and DN parameters. The $\varepsilon_{Al_2O_3}$ parameter involves both acidity and basicity to roughly the same extent. If we use the first four principal components, the fourth one will markedly appear as a characteristics described by the semiempirical parameters P and f(n^2), the above-given meaning of the first three principal components being maintained. The fourth principal component is only slightly associated with the parameters of connectivity and W, i.e. a theoretical parameter and only one

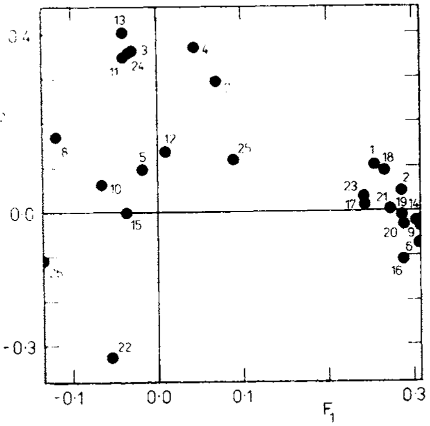


FIG. 2

Distribution of empirical solvent parameters in the space of the first three principal components after rotation — a projection in the direction of the third principal component. For the numbers see Table III

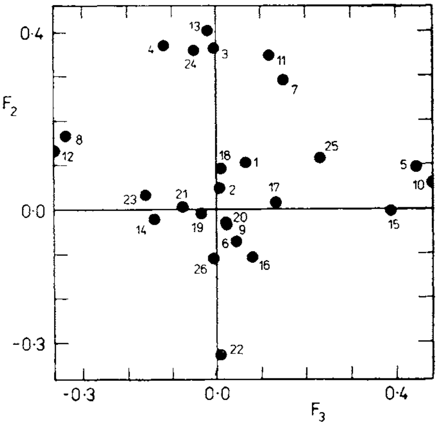


FIG. 3

Distribution of empirical solvent parameters in the space of the first three principal components after rotation — a projection in the direction of the first principal component. For the numbers see Table III more or less empirical parameter. Hence there arises a problem as to what is the contribution of the properties described by the functions $f(n^2)$ and/or P to the description of manifestations of real processes in solutions.

3.7. THE MODEL EQUATIONS BASED ON EMPIRICAL PARAMETER SCALES

As already mentioned in Chap. 2 the model equations used for interpretation of solvent effect of individual solvents have the linear additive form. According to number of the parameters describing the solvent properties, the model equations can be divided into one-, two-, three-, or multi-parameter ones. As the action of a solvent represents a complex interplay of several basic interactions which can only hardly be expressed by a single parameter (even though a complex one), we cannot expect the correlations to be successful with the one-parameter models applied to any possible processes. More promising are the multi-parameter models, nevertheless, with the limitations discussed in Chap. 2. Any multi-parameter model designed for practical purposes must contain the parameters reflecting the specific interactions (acidity, basicity) and polarity/polarizability. Further parameters usually only extend the region of validity of the model equation and improve the fit.

3.7.1. *One-Parameter Equations*

A great part of the parameters mentioned in the paragrahps 3.1. through 3.4. do not appear in the one-parameter equations of the type (*5*)

$$Q = q_0 + q_1 \bar{\mathrm{P}} \,, \qquad (5)$$

where Q means a result of some process in dependence on a solvent change characterized by the parameter $\bar{\mathrm{P}}$, and q_0, q_1 are the regression parameters involvig the other conditions of the process. The equation by Grunwald & Winstein[108] belongs to this type: it has limited applicability for individual solvents but is considerably significant from the historical point of view. The equation usually reads as follows (*6*)

$$\log k = \log k_0 + m \, \mathrm{Y_{GW}} \,. \qquad (6)$$

The validity of the equation was verified with solvolytic reactions, the m parameter representing the extent of solvation of the activated complex. For some reactions with participation of a nucleophile, Eq. (*6*) is usually extended by a term describing the effect of the nucleophile[116,117] (Eq. (*7*)):

$$\log k = \log k_0 + m \, \mathrm{Y_{GW}} + lN \,. \qquad (7)$$

Other applications of Eq. (*6*) can be found e.g. in refs[108–110,116,117,179–184].

An equation of the type (*5*) which continues to be important is Eq. (*8*) involving the $E_T(30)$ or E_T^N parameter by Reichardt & Dimroth (see paragraph 3.1.1.)

$$Q = q_0 + q_1 E_T . \qquad (8)$$

With regard to the fact that the $E_T(30)$ parameters reflect – in a ballanced ratio – the solvent polarity, polarizability, and acidity, Eq. (*8*) appears to be the most promising of the one-parameter equations for successful correlations. The other equations of the type (*5*) can be considered less significant for applications with empirical parameters.

3.7.2. *Two-Parameter Equations*

One of the first equations using two parameters for description of solvent effects is the equation by Swain, Mosely & Bown[185] which reads as follows (*9*)

$$\log k = \log k_0 + c_1 d_1 + c_2 d_2 . \qquad (9)$$

The parameters c_1 and c_2 describe the sensitivity of substrate to the nucleophilic and electrophilic properties of the solvent described by the parameters d_1 and d_2, respectively, 80% aqueous ethanol being used as the standard solvent. The equation is of little practical importance with respect to the insufficient number of solvents with known parameters.

In 1975 Krygowski & Fawcett[173,186] defined an equation in the following form (*10*)

$$Q = q_0 + \alpha E_T + \beta \, DN , \qquad (10)$$

which makes use of the parameters $E_T(30)$ by Reichardt & Dimroth and DN by Gutmann et al. (see Parts 3.1. and 3.4.). The authors suggest to use the regression coefficients α and β for calculation of the contributions of the behaviour of solvent as an acid and base, respectively. The basic form of the equation can be extended with a term S which reflects the arrangement of solvent and sensitivity to a change of structure (the entropical term). The original papers also present examples of interpretations of the solvent parameters known at that time.

A two-parameter model based on statistical treatment of a large amount (77) of kinetic and equilibrium and spectral measurements (mostly in individual solvents) was published by Swain et al.[34]. The equation can be expressed in the form (*11*)

$$Q = a \, \mathrm{ACITY} + b \, \mathrm{BASITY} + c , \qquad (11)$$

where ACITY and BASITY represent the solvent characteristics, and *a*, *b*, *c* are the regression parameters. The ACITY (AC) parameter is a measure of the tendence of the solvent to solvate anions, BASITY (BA) similarly refers to cations. The parameters are standardized in such way that AC = BA = 0 for heptane and AC = BA = = 1 for water, and AC = 0 for hexamethylphosphoric triamide (as the substance with the lowest ability to solvate anions) and BA = 0 for trifluoroacetic acid (as the substance with the lowest ability to solvate cations). The parameters are mutually non-intercorrelated (see also Table II), although acording to Fig. 1 of ref.[34] it is possible to find a number of solvents for which the relation between AC and BA can be described by one straight line, the same being also shown in ref.[159]. This co-linearity, however, can be found for a certain set of solvents in every empirical scale as well as in the scales obtained by the mathematical-statistical methods not ensuring a selection of orthogonal characteristics. The equation *(11)* was tested on the definition set of processes in solutions with excellent results, however, the insignificant regression coefficients are not excluded from the calculations, which somewhat distorts the evaluation. The equation *(11)* unsufficiently accepts the basic properties of solvents (ref.[159], Table II), hence a failure can be expected when describing the processes in which this property is significant.

3.7.3. *Three- and Multiparameter Equations*

A relatively old but still useful and practicable equation of this group is that by Koppel & Palm[40] *(12)* involving four solvent parameters.

$$\bar{A} = \bar{A}_0 + y\,\mathrm{Y} + p\,\mathrm{P} + e\,\mathrm{E} + b\,\mathrm{B} \qquad (12)$$

The semiempirical parameter Y expresses the solvent polarity and is identical with the Kirkwood function[158], i.e. $\mathrm{Y} = (\varepsilon - 1)/(2\varepsilon + 1)$. The semiempirical parameter P describes the solvent polarizability usually in the form $(n^2 - 1)/(n^2 + 1)$; in some cases the form $(n^2 - 1)/(2n^2 + 1)$ is used (see the monograph[8] by Palm, p. 107) and sometimes $(n^2 - 1)/(n^2 + 2)$ (see the same monograph, p. 108). The E parameter is expressed by means of the $E_T(30)$ parameter by Reichardt & Dimroth from which the contributions of non-specific solvation expressed by the former terms were subtracted. Koppel & Paju[187] extended the E parameter and made it more accurate by application of 26 selected solvents. The B parameter expresses the basic properties of the solvent (see Paragraph 3.1.2.). Although the description of solvent properties by Eq. *(12)* is redundant[35] and there exists intercorrelation of the parameters (Table II), which sometimes makes the regression calculations difficult, a good interpretation of broad region of processes in solutions can be expected.

With respect to the interesting interpretation of solvent effects, the equation by Dougherty[188] is well worth mentioning: this equation is based on the idea of HOMO/LUMO interactions between solvent and solute.

One of the most important equations for interpretation of solvent effects on processes in solutions is that by Kamlet & Taft (*13*) involving, in its basic version, the π^*, α, β parameters (see the Paragraph 3.1.1. and Part 3.6.) and usually presented in the form

$$XYZ = XYZ_0 + s\,\pi^* + a\,\alpha + b\,\beta\,. \qquad (13)$$

The equation can be extended by further terms according to the nature of the process in solution. The π^* parameter expressing, according to the authors, the solvent dipolarity/polarizability is sometimes corrected by addition of the δ parameter in the form $(\pi^* + d\delta)$; δ is the so-called polarizability correction term with the value $\delta = 0{\cdot}5$ for polychlorinated aliphatic hydrocarbons and $\delta = 1{\cdot}0$ for aromatic hydrocarbons. For the solvents whose molecules tend to association, the associates acting as "monomers" on the process in question, the α parameter is replaced[16] by α_m. The same meaning is ascribed also the analogous substitutions of β_m for β, and π_m^* for π^*. For amphiprotic solvents in aqueous solutions, the equation uses the so-called amphiprotic parameter of hydrogen bond (ω). In addition, Eq. (*13*) can be extended by the terms expressing the cavity contribution (δ_H^2, ref.[136]), the molar volume of the molecule dissolved, and the so-called coordination-covalent parameter allowing to correlate some basicity-dependent properties. A survey of these terms is given e.g. in ref.[27]. The additional terms and modifications of the basic parameters improve the fit of the correlation and enable a more detailed insight into the process taking place in solution, but, on the other hand, they can be little synoptical and impractical for a potential user. Kupfer et al.[144] modified Eq. (*13*) by including the term $\hat{\eta}$ derived from viscosity.

Mayer[190] suggested an equation based on the parameters AN and DN (see Paragraph 3.1.3. and Parts 3.4. and 3.6.) and extended by the standard Gibbs evaporation energy[189] in the form (*14*)

$$\varDelta\,\Delta G = a\varDelta\,\mathrm{DN} + b\varDelta\,\mathrm{AN} + c\,\Delta G^0_{\mathrm{vp}}\,. \qquad (14)$$

The symbol $\varDelta$ denotes the relation to the reference solvent according to the definition of the parameters. Some applications of Eq. (*14*) can be found in ref.[105]; in the cases given Eq. (*14*) proved successful.

The correlation equation suggested by Svoboda, Pytela & Večeřa[37] and based on statistical treatment of solvent parameter scales contains four solvent parameters (see Part 3.5.); the equation has the classical additive form (*15*)

$$\bar{A} = \bar{A}_0 + a\,\mathrm{AP} + b\,\mathrm{BP} + e\,\mathrm{EP} + p\,\mathrm{PP}\,. \qquad (15)$$

Results of application to 22 model processes are given in ref.[37], too. The EP term (electrostatic action) appears to be dominant, the PP term (polarizability) is of minor significance.

The equations suggested by Bekárek et al.[50] are two-parameter equations (the solvent parameters) and are designed for various types of processes in solution, but altogether they contain three parameters and can be expressed by one equation: the original set of Eqs (*16*) and (*17*) can be replaced by Eq. (*18*),

$$Y = A + B\,\mathrm{W}\,.\,\mathrm{f}(\mathrm{n}^2) + C\,\mathrm{f}(\mathrm{n}^2) \qquad (16)$$

$$Y = A + B\,\mathrm{W} + C\,\mathrm{W}\,.\,\mathrm{f}(\mathrm{n}^2) \qquad (17)$$

$$Y = A + B\,\mathrm{W} + C\,\mathrm{f}(\mathrm{n}^2) + D\,\mathrm{W}\,.\,\mathrm{f}(\mathrm{n}^2) \qquad (18)$$

which is not only formal, as it is seen from further analyses (Chap. 4). A drawback of this equation (or better – of the parameters involved therein) consists in its being restricted to a solvent set not involving the protic solvents.

3.8. EVALUATION AND COMPARISON OF MODEL EQUATIONS WITH EMPIRICAL PARAMETERS

The basic decisive factors for applicability of an empirical correlation equation include the number of parameters, their type composition and quality, and – last but not least – also a sufficiently representative scale of solvents for which all the parameters of the equation have been determined. From the above discussion it follows that the one-parameter equations have only a poor chance of universal applicability. From the principal component analysis of solvent parameters (Table III) (Part 3.6.) it follows that the contributions in the first principal component expressing the greatest non-correlated part of variability of the starting set are dislocated in the following way: 55·9% the first rotated principal component predominantly expressing the acidity, 17·8% the second rotated principal component predominantly expressing the polarity, 17·3% the third rotated principal component predominantly expressing the basicity, and 7·9% the fourth rotated pricipal component reflecting the polarizability. The one-parameter equations have the best chance of succeeding, if the solvent parameter expresses the properties roughly in the above-given proportions. The analogous values for the second principal component are 34·1%, 51·7%, 0·3%, 13·9%, and for the third principal component 7·8%, 0·7%, 76·0%, 15·5%. Hence the second and the third most significant properties determining the magnitude of differences between the solvent effects on processes in solutions are the polarity and the basicity, respectively. Therefrom it follows that two-parameter equations should preferably contain the parameters describing the solvent acidity and polarity, whereas the three-parameter ones should additionally contain that of basicity.

Also interesting is the interpretation of the solvent parameters by means of the correlation equations. Tables IV and V present these relations for selected correlation equations and the parameters involved therein. Table IV gives the statistically significant terms of the correlation equations in the sequence of their decreasing significance (according to the partial correlation coefficient) and with the respective sign; Table V gives the corresponding coefficients of multiple correlation. As it can be seen from the tables, a close fit can be found between the $E_T(30)$ parameter and E, Y, P (which could be expected from the definition of the E parameter), between the π^* parameter and $f(n^2)$, W, and W . $f(n^2)$, P and $f(n^2)$ (analogous quantities,) W . $f(n^2)$ and π^*, β and – according to expectation – also AN and α, π^*. The most frequent terms are AC(ACITY) in Eq. (*11*), π^* and α in Eq. (*13*), the Y parameter in Eq. (*12*), the W . $f(n^2)$ term in Eq. (*18*), and the AN term in the modified equation (*14*). This result also confirms the coclusions concerning the dominant effects of solvent acidity and polarity on processes in solutions. Further evaluation of selected equations for various types of processes can be found in the following chapter.

4. APPLICATION OF EMPIRICAL MODELS TO DESCRIPTION OF EFFECTS OF INDIVIDUAL SOLVENTS ON PROCESSES IN SOLUTIONS

Practicability of the individual empirical models can be evaluated first of all by the application to a great number of various experimental data. For the testing selected

TABLE IV

Statistically significant terms in the correlation equations (*11*), (*13*), (*12*), (*18*), and (*14*) (without the ΔG^0_{vp} term) interpreting the selected empirical solvent parameters

Parameter	Empirical correlation equation				
	(*11*)	(*13*)	(*12*)	(*18*)	(*14*)
$E_T(30)$	AC, BA	α, π^*, β	E, Y, P	$-f(n^2)$, W . $f(n^2)$	AN
AC	AC	α, π^*	E, Y	W	AN
BA	BA	π^*, β, $-\alpha$	Y, P	W . $f(n^2)$	—
π^*	BA, AC	π^*	Y, P	$f(n^2)$, W, W . $f(n^2)$	AN
β	—	β	B, Y	$-f(n^2)$, W . $f(n^2)$, $-$W	DN
α	AC, $-$BA	α	E	W, $-$W . $f(n^2)$, $f(n^2)$	AN
Y	BA, AC	π^*, β, α	Y	W . $f(n^2)$, $-f(n^2)$	AN
P	$-$AC	$-\alpha$, π^*	P	$f(n^2)$	—
E	AC	α, π^*	E	W, $-$W . $f(n^2)$	AN
B	—	β, $-\alpha$	B	$-f(n^2)$, W . $f(n^2)$, $-$W	DN
W	BA, AC	π^*, β, α	Y, E	W	AN
$f(n^2)$	—	π^*, $-\beta$, $-\alpha$	P	$f(n^2)$	—
W . $f(n^2)$	BA	π^*, β	Y, P, E	W . $f(n^2)$	AN, DN
AN	AC	α, π^*	E, Y, P	W, $f(n^2)$, $-$W . $f(n^2)$	AN
DN	—	β	B	—	DN

were the representative one-, two-, three-, and four-parameter equations for which the solvent parameter values are available in considerable amount (Table I). Out of the one-parameer equations we selected Eq. (*8*) with the $E_T(30)$ parameter by Reichardt & Dimroth and the data of ref.[48]. As a two-parameter relation we used Eq. (*11*) by Swain et al.[34] (it also represents a model with mathematical-statistical parameters). The three-parameter equations were represented by Eq. (*13*) by Kamlet & Taft (in the basic version without the correction terms, in the parametrization according to ref.[49]). The equation (*12*) by Koppel & Palm[40] with the parameters taken from the Palm's monograph[8] was tested as a four-parameter model. Beside these equations also included were Eq. (*18*) (a modification of Eqs (*16*) and (*17*) by Bekárek et al.[50]) which reflects a semiempirical approach in an empirical version, and a shortened version of Eq. (*14*) involving only the terms which describe the specific interactions in the form (*19*)

$$\Delta\,\Delta G = a\Delta\,\mathrm{DN} + b\Delta\,\mathrm{AN}\,. \tag{19}$$

The equation (*14*) and/or its variant (*19*) are related to Eq. (*10*) and, according to

TABLE V
The multiple correlation coefficients for equations of Table IV

Parameter	Equation				
	(*11*)	(*13*)	(*12*)	(*18*)	(*14*)[a]
E_T (30)	0·960	0·965	0·995	0·953	0·927
AC	1·000	0·975	0·963	0·821	0·984
BA	1·000	0·955	0·817	0·958	—
π^*	0·938	1·000	0·886	0·994	0·404
β	—	1·000	0·868	0·655	0·776
α	0·966	1·000	0·935	0·552	0·939
Y	0·863	0·902	1·000	0·952	0·497
P	0·404	0·578	1·000	0·991	—
E	0·938	0·950	1·000	0·719	0·941
B	—	0·841	1·000	0·469	0·977
W	0·930	0·919	0·983	1·000	0·801
$f(n^2)$	—	0·677	0·991	1·000	—
$W\,.\,f(n^2)$	0·958	0·991	0·986	1·000	0·913
AN	0·984	0·991	0·966	0·879	1·000
DN	—	0·776	0·977	—	1·000

[a] Without the term ΔG^0_{vp}.

the definition of parameters, it is possible to expect involvement of further variants of the basic solvent-solute interactions.

The evaluation of validity of the empirical correlation equations was carried out on the basis of residual variances, the statistically insignificant regression parameters being excluded by means of the Student test. Due to large diversity of the series tested (and hence also the magnitude and precision of the respective experimental quantities), the tables presented give only selected coefficients of multiple correlation. The conclusions about the significance of the individual correlation equations based on the coefficient of multiple correlation and residual variance stand in accordance in most cases. The statistical significance or insignificance of a correlation equation is determined by several reasons. First of all, the process need not be affected by the solvent. In such case the validity of the correlation equation can be evaluated. From the statistical point of view, all or at least most relations are insignificant. If the process is affected by the solvent, then the validity of a correlation equation can be evaluated by comparison with other correlation equations. In this case it is possible to find statistical significance with most relations tested. Hence the test not only provides information about validity of the given empirical correlation equation but also gives information abut the extent of solvent effects on various processes in solutions.

A set of the 368 processes tested was divided into spectral processes (which were further divided into electronic absorption and fluorescence spectroscopy, infrared spectroscopy, nuclear magnetic resonance and electron paramagnetic resonance spectroscopy), kinetic and equilibrium processes, and other processes. By means of multiple linear regression with the use of the above-mentioned equations we found the values of statistically significant regression coefficients inclusive of the standard deviations, the coefficients of multiple correlation, the partial correlation coefficients, and the residual standard deviations. For the selection of the most appropriate parameter set of Eqs (*8*), (*11*), (*12*), and (*13*) we used the multiple linear regression with the STEPWISE procedure in the usual version with inclusion and exclusion of variables on the basis of the Fisher–Snedecor test. The frequency of the parameters selected by this procedure for a sufficiently extensive and representative set indicates the significance of the often selected parameters for interpretation of experimental data of similar nature. The calculations were carried out with an EC 1033 computer according to our own programs.

4.1. APPLICATION OF SELECTED EMPIRICAL MODELS TO SPECTRAL PROCESSES

4.1.1. *Electronic Absorption and Fluorescence Spectroscopy*

Table VI gives description of the selected spectral data, Table VII summarizes the statistically significant solvent parameters for the individual models along with the

TABLE VI

Description of the test data (wavenumbers) – electronic absorption (Nos 1–114) and fluorescence (Nos 115–122) spectroscopy, n is number of solvents

No.	Substrate (indicator), characteristics of the process	n	Ref.
1	Kosower's Z, 1-ethyl-4-methoxycarbonylpyridinium iodide	16	52, 55
2	Revised and new Z values	34	59
3	$E_T(30)$ by Dimroth & Reichardt	35	6, p. 270
4	$E_T(26)$, formula *II*, $R^1 = R^2 = H$, R^3 = tert. butyl, 26°C	21	62
5	Betaine[a] *VII*	10	191
6	$E_T(SB)$, 1-((methacryloyl)-ethyl-4-(ethoxycarbonyl)pyridinium iodide	13	78
7	1-Methyl(4-cyanoformylpyridinium oximate), the lowest E_1 band	8	192
8	3-Methoxypyridinium-N-oxide, λ_1 (the longest-wave band)	14	34
9	3-Methoxypyridinium-N-oxide, λ_2	14	34
10	3-Methoxypyridinium-N-oxide, λ_3	6	34
11	5,5-Dimethyl-1-pyrroline-1-oxide	7	193
12	E_T^{SO}, N,N-dimethylthiobenzamide-S-oxide	23	79
13	A by Davis, tetrahexylammonium iodide–1,3,5-trinitrobenzene CT complex	20	74
14	B by Davis, tetrabutylammonium bromide–bromochloranil CT complex	15	74
15	*All-trans*-retinylidenemethylbutylammonium iodide	14	194
16	CT complex iodide anion–solvent	10	195
17	Phenol Blue	15	196
18	Phenol Blue	23	197
19	χ_R by Brooker, merocyanine *IV*	28	73
20	Merocyanine[b] *VIIIa*	18	198
21	Merocyanine[b] *VIIIb*	18	198
22	Lycopene, the 1st absorption band	22	196
23	Nile Blue A Oxazone	20	199
24	Pyrimidine, $n \rightarrow \pi^*$ transition	18	200
25	Pyridazine, $n \rightarrow \pi^*$ transition	20	200
26	Pyrazine, $n \rightarrow \pi^*$ transition	18	200
27	Acetone, $n \rightarrow \pi^*$ transition	17	201
28	Pinacolone, $n \rightarrow \pi^*$ transition	17	201
29	Hexamethylacetone, $n \rightarrow \pi^*$ transition	17	201
30	Bis[N-(2-pyridylmethylene)-3,4-dimethylaniline]bis(cyanoferrium)	12	202
31	Bis[α-(2-pyridyl)benzylidene-3,4-dimethylaniline]bis(cyanoferrium)	17	202
32	CT complex acenaphthene–tetrachlorophthalic anhydride	24	203
33	CT complex acenaphthene–3,5-dinitrophthalic anhydride	19	204
34	CT complex 2,6-dimethoxynaphthalene–tetrachlorophthalic anhydride	24	204
35	CT complex 9-methylanthracene–tetrachlorophthalic anhydride	19	204
36	CT complex anthracene–3,5-dinitrophthalic anhydride	19	204
37	Tetracarbonylchromiumbipyridyl	23	205
38	Tetracarbonylmolybdenumbipyridyl	23	205
39	Tetracarbonyltungstenbipyridyl	23	205
40	Tetracarbonyltungsten-1,10-phenanthrolinyl	23	205
41	Molybdenum complex *V*	31	76

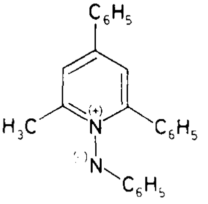
TABLE VI
(*Continued*)

No.	Substrate (indicator), characteristics of the process	n	Ref.
42	Benzene, transition $^1A_{1g} \rightarrow {}^1B_{2u}$	17	206
43	Chlorobenzene, $^1A_{1g} \rightarrow {}^1B_{2u}$	17	207
44	Nitrobenzene, $^1A_{1g} \rightarrow {}^1B_{2u}$	17	208
45	Bromobenzene, $^1A_{1g} \rightarrow {}^1B_{2u}$	17	209
46	Benzaldehyde, $^1A_{1g} \rightarrow {}^1B_{2u}$	16	210
47	Toluene, $^1A_{1g} \rightarrow {}^1B_{2u}$	17	211
48	Benzonitrile, $^1A_{1g} \rightarrow {}^1B_{2u}$	17	212
49	Nitrobenzene, $\pi \rightarrow \pi^*$ transition	6	213
50	4-Nitroaniline	31	80
51	4-Nitroaniline	9	214
52	4-Nitroaniline, S_1 band	15	215
53	2-Nitroaniline, aprotic solvents	8	216
54	2-Nitroaniline	20	217
55	4-(N,N-Dimethylamino)aniline	9	214
56	4-Aminobenzophenone	9	214
57	2-Aminoacetophenone, aprotic solvents	9	216
58	4-Aminobenzonitrile	9	214
59	4-Aminobenzonitrile, aprotic solvents	8	216
60	2-Aminobenzonitrile, aprotic solvents	9	216
61	Methyl 2-aminobenzoate, aprotic solvents	9	216
62	4-Methyl-2-nitroaniline, aprotic solvents	8	216
63	4-Methyl-2-nitroaniline	20	217
64	3-Methyl-4-nitroaniline	27	218
65	4-Methoxy-2-nitroaniline, aprotic solvents	8	216
66	4-Methoxy-2-nitroaniline	20	217
67	4-Amino-4′-nitrobiphenyl	10	219
68	4-Amino-4′-nitrostilbene	10	219
69	1-Aminoanthraquinone, the longest-wave band	20	220
70	1,2-Diaminoanthraquinone, $\pi \rightarrow \pi^*$ transition	13	221
71	1,4-Diaminoanthraquinone, $\pi \rightarrow \pi^*$ transition	15	221
72	1,5-Diaminoanthraquinone, $\pi \rightarrow \pi^*$ transition	14	221
73	4-Nitro-N-methylaniline, aprotic solvents	8	216
74	4-Nitro-N-methylaniline	21	222
75	4-Nitro-N-methylaniline	29	218
76	4-Nitro-N-ethylaniline	29	218
77	4-Nitro-N-isopropylaniline	29	218
78	2-(N-Methylamino)benzonitrile, aprotic solvents	8	216
79	4-(N-Methylamino)benzonitrile, aprotic solvents	8	216
80	Methyl 2-(N-methylamino)benzoate, aprotic solvents	8	216
81	Ethyl 4-(N-methylamino)benzoate, aprotic solvents	8	216
82	3-Methyl-4-nitro-N-ethylaniline	27	218
83	4-Nitro-N,N-diethylaniline	31	80

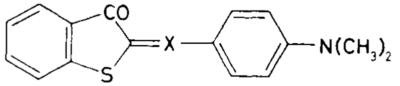
TABLE VI
(*Continued*)

No.	Substrate (indicator), characteristics of the process	n	Ref.
84	4-Nitro-N,N-dimethylaniline	9	214
85	4-Nitro-N,N-dimethylaniline	21	222
86	4-Nitro-N,N-dimethylaniline	13	223
87	2-Nitro-N,N-dimethylaniline	20	217
88	1,4-Bis(N,N-dimethylamino)benzene	9	214
89	4-(N,N-Dimethylamino)benzonitrile	9	214
90	4-(N,N-Dimethylamino)benzonitrile, aprotic solvents	8	216
91	2-(N,N-Dimethylamino)benzonitrile, aprotic solvents	8	216
92	4-(N,N-Dimethylamino)benzophenone	9	214
93	4-(N,N-Dimethylamino)benzaldehyde	13	223
94	4-(N,N-Dimethylamino)-4′-nitrobiphenyl	10	219
95	4-(N,N-Dimethylamino)-4′-nitrostilbene	10	219
96	N-(4-Nitrophenyl)aziridine	22	224
97	N-(4-Nitrophenyl)pyrrolidine	22	224
98	N-(4-Nitrophenyl)piperidine	22	224
99	4-Methyl-2-nitro-N,N-dimethylaniline	20	217
100	4-Methoxy-2-nitro-N,N-dimethylaniline	20	217
101	3-Methyl-4-nitro-N,N-diethylaniline	27	218
102	4-Nitrobenzylidene-4′-(N,N-dimethylamino)aniline	25	225
103	4-(N,N-Dimethylamino)benzylidene-4′-nitroaniline	26	225
104	*trans*-1-(4-(N,N-Dimethylamino)phenyl)-2-nitroethene	18	226
105	2,3-Dioxo-N-phenylbutanamide-2-(N-(4-(N,N-dimethylamino)phenyl)-monoimine)	22	227
106	4-Nitrophenol	25	80
107	8-Hydroxyquinoline, the longest-wave band	10	228
108	2-Hydroxyanthraquinone, the longest-wave band	17	220
109	4-Nitroanisole	26	80
110	4-Nitroanisole	13	223
111	2-Nitroanisole	13	223
112	1-Methoxynathraquinone, the longest-wave band	11	220
113	Benzophenone, $\pi \rightarrow \pi^*$ transition	10	229
114	Azobenzene	13	223
115	E_{CT} by Davis, CT complex tetrachlorophthalic anhydride–hexamethylbenzene	7	89
116	Py parameter, pyrene	33	90
117	1-Aminonaphthalene	9	230
118	2-Aminonaphthalene	9	230
119	1-Aminoanthracene	9	230
120	2-Aminoanthracene	9	230
121	4-(N,N-Dimethylamino)benzylidene-4′-nitroaniline	24	225
122	trans-1-(4-(N,N-Dimethylamino)phenyl)-2-nitroethene	13	226

[a] See formula *VII*; [b] see formula *VIII*.



VII



VIII a, X = CH
VIII b, X = N

results of the STEPWISE procedure[231], and Table VIII presents the multiple correlation coefficients. If only Eqs (*8*), (*11*), (*12*), and (*13*) (for which the calculations were carried out with roughly the same number of solvents) are compared, then according to Table VIII Eq. (*8*) exhibits the greatest number of failures followed gradually by Eqs (*11*), (*13*), and (*12*). By far the most successful equation – according to the criterion of the minimum residual standard deviation (which in most cases is identical with the maximum coefficient of multiple correlation in Table VIII) – is Eq. (*13*) followed gradually by Eqs (*12*), (*11*), and (*8*). Equation (*18*) gives comparable results with those of the former methods (with respect to the selection of aprotic solvents). Eq. (*19*) is less successful than most equations tested. On the whole, the interpretability of the spectral data measured by the methods of electron absorption and fluorescence spectroscopy can be denoted as very good. With regard to the choice of the best interpreting parameters (Table VII), the best measure of polarity is the π^* as well as BASITY parameter, the best measure of basicity is unambiguously the β parameter, the parameters of acidity having roughly the same frequence of occurrence. Of course, the results can, to a certain extent, be affected by the data set used, because almost one half of them are data for aniline derivatives which represent model indicators for the π^*, β, and α scales.

A more detailed analysis of the spectral data from Table VI leads to the following conclusions. The solvatochromism of derivatives of pyridinium salts (Nos 1–7) can very well be quantified, the most appropriate being Eq. (*12*) and the $E_T(30)$ parameter. Polarity and acidity represent the dominant effects. Obviously, the positive charge is partially stabilized by the inductive effect and – first of all – is little accessible for the solvating molecules for sterical reasons. Interesting differences are observed between the $E_T(30)$ scales taken from different sources[6,48]. Similarly, the dipolar N- and S-oxides (Nos 8–12) give very well correlated data, especially so with application of Eqs (*12*) and (*13*). The predominant solvent effect is the acidity (for the same reasons as with the previous indicators) and, partially, the polarity. The complexes used by Davis for suggestion of solvent scales (Nos 13, 14) exhibit spectral bands which depend predominantly on the solvent acidity, which is probably a consequence of interactions with iodide ion and oxygen atoms of nitro groups. The correlation can be denoted as good. In contrast to the previous ammo-

TABLE VII

Statistically significant empirical solvent parameters in Eqs (*11*)—(*13*), (*18*), (*19*) and results of the STEPWISE procedure — electronic absorption and fluorescence spectrosopy. For numbers see Table VI

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
1	AC, BA	π^*, β, α	Y, E	W, $f(n^2)$	AN	E_T, β
2	AC, BA	π^*, β, α	Y, E, B	$f(n^2)$, W . $f(n^2)$	AN	E_T, π^*
3	AC, BA	π^*, α	Y, E	W	AN	E_T
4	AC	π^*, α	Y, E	W, $f(n^2)$	AN	E_T, β, B, BA
5	AC	π^*	Y, E	$f(n^2)$, W . $f(n^2)$	AN	E_T
6	AC, BA	π^*, α	Y, E	W	AN	AC, BA
7	AC	π^*, α	E, B	[a]	AN	E_T, AC
8	AC	π^*, α	Y, E	W	AN	AC, B
9	AC, BA	π^*, α	E	$f(n^2)$, W . $f(n^2)$	AN, DN	E, AC, P
10	AC	α	Y, P, E, B	[a]	AN, DN	E, β
11	AC	π^*, α	Y, E	[a]	AN	AC, β
12	AC, BA	π^*, β, α	E	W	AN	AC, α, Y
13	AC, BA	π^*, α	E	W	AN	E, α, P
14	AC, BA	α	E	W	AN	α
15	—	π^*, β	Y, B	W, $f(n^2)$	DN	B, π^*
16	AC, BA	α	E	[a]	AN	α, P, BA
17	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	π^*, α, Y, AC
18	BA	π^*	Y, P, E	W, W . $f(n^2)$	AN, DN	π^*, E, E_T
19	AC, BA	π^*, β, α	Y, P, E	W . $f(n^2)$	AN	π^*, E_T, P
20	AC, BA	π^*, α	Y, P, E	$f(n^2)$, W . $f(n^2)$	AN	π^*, α, P
21	BA	π^*	Y, P	W, $f(n^2)$	AN	π^*, BA
22	—	π^*, α	P	$f(n^2)$	—	P
23	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	Y, P, AC
24	AC, BA	π^*, α	Y, E	W	AN	AC, α
25	AC	π^*, α	Y, E	W	AN	AC
26	AC, BA	β, α	P, E, B	—	AN, DN	α, β, P, π^*, E
27	AC	π^*	E	W, W . $f(n^2)$	AN	AC
28	AC	π^*, α	E	W	AN	E, BA
29	AC, BA	π^*, α	E	W	AN	E_T, β, B
30	AC	π^*, α	E	—	AN, DN	AC, BA, P, Y, B
31	AC	π^*, α	Y, E	W	AN	AC
32	—	π^*, β	P, B	$f(n^2)$	DN	β, π^*, B, E_T, E, AC
33	—	β	P	$f(n^2)$	DN	β, π^*
34	—	β	P, B	$f(n^2)$	DN	P, β, α, B
35	AC, BA	β	P, B	—	DN	B
36	—	β	P, B	$f(n^2)$	DN	β, P, AC, E_T
37	AC, BA	π^*, β	Y, P	W . $f(n^2)$	—	π^*, β, P, α, E
38	AC, BA	π^*, β	Y, P	$f(n^2)$, W . $f(n^2)$	—	Y, BA
39	AC, BA	π^*, β	Y, P	$f(n^2)$, W . $f(n^2)$	—	Y, BA
40	AC, BA	π^*, β	Y, P	$f(n^2)$, W . $f(n^2)$	—	π^*, Y, B, P
41	BA	π^*, β, α	Y	$f(n^2)$, W . $f(n^2)$	DN	BA, β

TABLE VII
(*Continued*)

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
42	–	–	P	$f(n^2)$	DN	P
43	–	–	P	$f(n^2)$	DN	P
44	AC, BA	π^*, α	Y	W, $W . f(n^2)$	AN	π^*, AC
45	AC	π^*, β	P	$f(n^2)$	DN	P, E_T
46	–	α	–	$f(n^2)$	–	α, E, P
47	–	–	P	$f(n^2)$	DN	P
48	BA	π^*	–	W, $W . f(n^2)$	AN, DN	BA
49	AC, BA	π^*	Y, B	[a]	–	π^*
50	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	Y, β, AC, BA
51	BA	π^*, β	Y, P, E, B	$W . f(n^2)$	AN, DN	BA, β, E_T
52	AC, BA	π^*, β, α	Y, P, E, B	W, $f(n^2)$, $W . f(n^2)$	DN	β, π^*
53	BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	BA, β, P
54	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	DN	β, π^*
55	BA	–	B	$W . f(n^2)$	–	B
56	AC, BA	π^*, β	Y, P, B	$W . f(n^2)$	AN, DN	BA, β, P, B, α
57	AC, BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	β, π^*, AC, Y
58	AC, BA	π^*, β	Y, P, B	$W . f(n^2)$	AN, DN	BA, β, P
59	AC, BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	BA, B
60	AC, BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	β, BA, Y, E_T
61	AC, BA	π^*, β	Y, B	$W . f(n^2)$	DN	β, BA, AC, Y, E_T, π^*
62	BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	[a]
63	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	DN	BA, β, α
64	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	Y, B, AC, BA, β
65	BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	BA, β
66	AC, BA	π^*, β	Y, P, E, B	$W . f(n^2)$	DN	BA, β, α, P
67	AC	π^*, β	Y, P, B	$W . f(n^2)$	AN, DN	β, P
68	AC	π^*, β	E, B	–	DN	E, β
69	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	β, π^*, E_T
70	AC	β	B	$W . f(n^2)$	DN	β
71	–	–	–	$W . f(n^2)$	DN	–
72	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	DN	β, π^*, E
73	AC, BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	Y, β, P, E_T
74	AC, BA	π^*, β	Y, P, E, B	$W . f(n^2)$	DN	π^*, β
75	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	π^*, β, AC, BA
76	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	π^*, β, AC, BA
77	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	π^*, β, AC, BA
78	BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	Y, B
79	BA	π^*, β	E, B	$W . f(n^2)$	AN, DN	BA, β, Y
80	BA	π^*	Y	$W . f(n^2)$	AN	BA, Y
81	BA	π^*, β	Y, B	$W . f(n^2)$	AN, DN	BA, β
82	AC, BA	π^*, β, α	Y, P, E, B	$W . f(n^2)$	AN, DN	π^*, β, α

TABLE VII
(*Continued*)

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
83	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	π^*, α, BA, AC
84	BA	π^*, β	Y, P, E	W . $f(n^2)$	AN, DN	BA
85	BA	π^*, β	Y, P	W, $f(n^2)$	—	π^*, β, P, Y
86	AC, BA	π^*, α	Y, P	W, W . $f(n^2)$	AN	π^*, E_T
87	AC, BA	π^*, α	Y, P, E	W, W . $f(n^2)$	AN	E_T, BA, P
88	BA	π^*	Y, P	W, W . $f(n^2)$	—	BA
89	BA	π^*	Y, P	W, $f(n^2)$	AN	π^*, P
90	BA	π^*	Y, P, E	W, W . $f(n^2)$	AN	π^*, E_T, P
91	AC	π^*	Y, E	W . $f(n^2)$	AN	E_T, BA
92	BA	π^*	Y, P, E	$f(n^2)$, W . $f(n^2)$	AN, DN	π^*, P, Y
93	AC, BA	π^*, α	Y, P, E	W, W . $f(n^2)$	AN	π^*, α
94	BA	π^*	Y, P	$f(n)$, W . $f(n^2)$	AN	BA
95	BA	π^*	Y, P	W, W . $f(n^2)$	AN	BA
96	AC, BA	π^*, β, α	Y, P	W, W . $f(n^2)$	—	E, π^*, B
97	AC, BA	π^*, α	Y, P, E	$f(n^2)$, W .$f(n^2)$	AN	AC, BA
98	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$, W . $f(n^2)$	AN	π^*, E
99	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	E_T, BA, B
100	AC, BA	π^*	Y, P	$f(n^2)$, W . $f(n^2)$	—	π^*
101	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	π^*, E_T
102	BA	π^*	Y, P	W, W . $f(n^2)$	—	π^*, P, Y
103	BA	π^*	Y, P	W, W . $f(n^2)$	—	π^*, P, Y
104	AC, BA	π^*, β, α	Y, P	W . $f(n^2)$	—	π^*, AC, B
105	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$	AN	E_T, BA, AC, P, π^*
106	AC, BA	π^*, β	Y, P, E, B	W . $f(n^2)$	DN	B, π^*, β, E
107	AC	π^*	Y	W	AN	AC, β, B
108	AC	π^*, β	Y, B	W	DN	β, π^*, Y
109	AC, BA	π^*, β	Y, P, E	$f(n^2)$, W . $f(n^2)$	AN	π^*, β
110	AC, BA	π^*, α	Y, P, E	W . $f(n^2)$	AN	π^*, E
111	BA	π^*	Y, P	W . $f(n^2)$	AN	BA, E_T
112	AC, BA	π^*, α	Y	W, $f(n^2)$	AN	π^*, AC
113	AC	π^*, α	Y, E	W	AN	AC, E_T
114	BA	π^*	P, E	$f(n^2)$	—	π^*
115	AC, BA	π^*, β	Y, E, B	W	[a]	π^*, B, P
116	AC, BA	π^*, β	Y	$f(n^2)$, W . $f(n^2)$	—	BA, P, β, Y
117	AC, BA	π^*, β, α	Y, E	W . $f(n^2)$	AN	Y, AC
118	BA	π^*, β	Y, B	W . $f(n^2)$	DN	Y, β, P, AC
119	BA	π^*, β	Y	$f(n^2)$, W . $f(n^2)$	DN	Y, BA
120	BA	π^*, β	Y, B	$f(n^2)$, W . $f(n^2)$	DN	Y, β, BA
121	BA	π^*	Y, E	W	—	BA
122	BA	π^*, β	Y	W . $f(n^2)$	AN, DN	Y, π^*

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[a] Insufficient number of data.

TABLE VIII

The multiple correlation coefficients (*R*) and numbers of solvents (n) in Eqs (*8*), (*11*)–(*13*), (*18*), (*19*) – electronic absorption and fluorescence spectroscopy. For numbers see Table VI

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
1	0·989 (15)	0·986 (15)	0·980 (14)	0·993 (15)	0·993 (8)	0·979 (9)
2	0·970 (34)	0·927 (29)	0·940 (28)	0·979 (33)	0·800 (22)	0·912 (23)
3	0·976 (35)	0·964 (35)	0·955 (31)	0·982 (33)	0·916 (27)	0·941 (23)
4	0·976 (21)	0·928 (19)	0·934 (20)	0·974 (21)	0·975 (13)	0·884 (14)
5	0·973 (10)	0·927 (10)	0·890 (10)	0·983 (10)	0·964 (8)	0·893 (8)
6	0·978 (13)	0·993 (12)	0·986 (12)	0·978 (13)	0·865 (6)	0·974 (9)
7	0·995 (8)	0·989 (8)	0·983 (8)	0·999 (8)	[a] [a]	0·977 (8)
8	0·970 (14)	0·989 (14)	0·991 (14)	0·978 (13)	0·880 (11)	0·996 (14)
9	0·953 (14)	0·990 (14)	0·981 (14)	0·985 (13)	0·953 (11)	0·974 (14)
10	0·971 (6)	0·984 (6)	0·982 (6)	1·000 (6)	[a] [a]	0·995 (6)
11	0·994 (7)	0·995 (7)	0·995 (7)	0·999 (7)	[a] [a]	0·986 (4)
12	0·899 (23)	0·991 (22)	0·992 (21)	0·922 (23)	0·921 (13)	0·979 (17)
13	0·929 (20)	0·980 (20)	0·981 (18)	0·978 (19)	0·704 (14)	0·973 (13)
14	0·912 (15)	0·986 (15)	0·978 (13)	0·951 (14)	0·695 (10)	0·984 (11)
15	— —	— —	0·882 (14)	0·870 (14)	0·698 (13)	0·752 (12)
16	— —	0·913 (9)	0·874 (9)	0·665 (10)	[a] [a]	0·802 (7)
17	0·821 (15)	0·946 (14)	0·988 (13)	0·965 (14)	0·979 (13)	0·835 (6)
18	0·861 (23)	0·966 (21)	0·981 (20)	0·984 (23)	0·989 (23)	0·890 (17)
19	0·831 (28)	0·971 (28)	0·985 (25)	0·981 (25)	0·987 (24)	0·710 (17)
20	0·855 (18)	0·946 (18)	0·962 (17)	0·980 (18)	0·987 (14)	0·857 (15)
21	0·524 (18)	0·578 (18)	0·650 (17)	0·725 (18)	0·710 (14)	0·852 (15)
22	— —	— —	0·837 (11)	0·971 (11)	0·977 (10)	— —
23	0·867 (20)	0·925 (20)	0·922 (17)	0·959 (20)	0·947 (16)	0·797 (18)
24	0·916 (18)	0·994 (18)	0·993 (18)	0·963 (18)	0·836 (14)	0·976 (15)
25	0·968 (20)	0·996 (20)	0·994 (20)	0·988 (19)	0·935 (15)	0·988 (17)
26	0·525 (18)	0·832 (18)	0·959 (18)	0·932 (18)	— —	0·893 (15)
27	0·852 (17)	0·909 (17)	0·840 (15)	0·895 (17)	0·800 (11)	0·895 (15)
28	0·924 (17)	0·961 (17)	0·940 (15)	0·956 (17)	0·983 (11)	0·952 (15)
29	0·890 (17)	0·931 (17)	0·929 (15)	0·878 (17)	0·954 (11)	0·888 (15)
30	0·979 (12)	0·993 (12)	0·998 (11)	0·989 (12)	— —	0·997 (9)
31	0·963 (17)	0·980 (16)	0·984 (16)	0·973 (17)	0·840 (9)	0·979 (12)
32	— —	— —	0·794 (22)	0·658 (23)	0·553 (24)	0·592 (17)
33	— —	— —	0·683 (17)	0·650 (18)	0·680 (19)	0·603 (12)
34	0·428 (24)	— —	0·775 (21)	0·869 (23)	0·708 (24)	0·799 (15)
35	— —	0·641 (17)	0·859 (17)	0·920 (18)	— —	0·913 (12)
36	— —	— —	0·896 (18)	0·914 (19)	0·504 (19)	0·904 (15)
37	0·535 (23)	0·915 (21)	0·932 (22)	0·866 (23)	0·940 (17)	— —
38	0·591 (23)	0·921 (21)	0·938 (22)	0·898 (23)	0·963 (17)	— —
39	0·610 (23)	0·919 (21)	0·930 (22)	0·905 (23)	0·966 (17)	— —
40	0·594 (23)	0·930 (21)	0·945 (22)	0·903 (23)	0·969 (17)	— —

TABLE VIII
(*Continued*)

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
41	0·425 (31)	0·788 (29)	0·860 (28)	0·678 (30)	0·936 (23)	0·561 (23)
42	— —	— —	— —	0·845 (17)	0·848 (12)	0·632 (14)
43	0·537 (17)	— —	—	0·857 (17)	0·870 (12)	0·582 (14)
44	0·722 (17)	0·985 (16)	0·983 (17)	0·801 (17)	0·991 (12)	0·704 (14)
45	0·656 (17)	0·624 (16)	0·569 (17)	0·846 (17)	0·841 (12)	0·664 (14)
46	— —	— —	0·535 (16)	— —	0·591 (12)	— —
47	0·520 (17)	— —		0·822 (17)	0·855 (12)	0·596 (14)
48	— —	0·715 (16)	0·691 (17)	— —	0·960 (12)	0·765 (14)
49	0·864 (6)	0·998 (6)	0·996 (6)	0·984 (6)	*a* *a*	— —
50	0·731 (31)	0·857 (30)	0·996 (31)	0·969 (31)	0·901 (23)	0·743 (20)
51	0·859 (9)	0·976 (9)	0·999 (9)	0·998 (9)	0·963 (9)	0·998 (7)
52	0·793 (15)	0·837 (13)	0·991 (15)	0·962 (15)	0·976 (11)	0·826 (12)
53	0·910 (8)	0·961 (8)	0·997 (8)	0·988 (8)	0·956 (8)	0·995 (6)
54	0·752 (20)	0·900 (19)	0·995 (20)	0·978 (20)	0·947 (12)	0·758 (14)
55	0·670 (9)	0·667 (9)	— —	0·697 (9)	0·699 (9)	— —
56	0·778 (9)	0·983 (9)	0·998 (9)	0·996 (9)	0·913 (9)	0·991 (7)
57	0·828 (9)	0·965 (9)	0·996 (9)	0·995 (9)	0·888 (9)	0·988 (7)
58	0·772 (9)	0·978 (9)	0·995 (9)	0·996 (9)	0·908 (9)	0·988 (7)
59	0·873 (8)	0·983 (8)	0·989 (8)	0·985 (8)	0·927 (8)	0·980 (6)
60	0·840 (9)	0·960 (9)	0·996 (9)	0·989 (9)	0·894 (9)	0·992 (7)
61	0·814 (9)	0·970 (9)	0·993 (9)	0·990 (9)	0·873 (9)	0·952 (7)
62	0·916 (8)	0·969 (8)	0·999 (8)	0·993 (8)	0·964 (8)	0·990 (6)
63	0·744 (20)	0·904 (19)	0·995 (20)	0·975 (20)	0·959 (12)	0·741 (14)
64	0·702 (27)	0·817 (26)	0·997 (27)	0·975 (27)	0·908 (19)	0·891 (18)
65	0·913 (8)	0·973 (8)	0·998 (8)	0·991 (8)	0·966 (8)	0·989 (6)
66	0·725 (20)	0·898 (18)	0·994 (20)	0·971 (20)	0·952 (12)	0·740 (14)
67	0·940 (10)	0·967 (8)	0·995 (10)	0·998 (10)	0·971 (10)	0·987 (7)
68	0·948 (10)	0·956 (8)	0·993 (10)	0·992 (10)	— —	0·945 (7)
69	0·818 (20)	0·882 (20)	0·991 (20)	0·973 (20)	0·882 (17)	0·913 (14)
70	0·736 (13)	0·701 (13)	0·835 (13)	0·826 (13)	0·788 (10)	0·952 (9)
71					0·940 (10)	0·922 (10)
72	0·786 (14)	0·946 (14)	0·988 (14)	0·969 (14)	0·946 (11)	0·864 (12)
73	0·934 (8)	0·994 (8)	0·999 (8)	0·995 (8)	0·982 (8)	0·986 (6)
74	0·748 (21)	0·905 (20)	0·991 (21)	0·978 (21)	0·980 (14)	0·741 (13)
75	0·760 (29)	0·941 (28)	0·994 (29)	0·965 (29)	0·975 (21)	0·814 (19)
76	0·764 (29)	0·947 (28)	0·996 (29)	0·965 (29)	0·977 (21)	0·817 (19)
77	0·776 (29)	0·950 (28)	0·995 (29)	0·965 (29)	0·977 (21)	0·825 (19)
78	0·840 (8)	0·927 (8)	0·992 (8)	0·994 (8)	0·919 (8)	0·980 (6)
79	0·930 (8)	0·973 (8)	0·994 (8)	0·980 (8)	0·968 (8)	0·995 (6)
80	0·944 (8)	0·962 (8)	0·951 (8)	0·926 (8)	0·956 (8)	0·923* (6)
81	0·884 (8)	0·938 (8)	0·993 (8)	0·977 (8)	0·930 (8)	0·995 (6)

TABLE VIII
(*Continued*)

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
82	0·781 (27)	0·935 (26)	0·997 (27)	0·971 (27)	0·977 (19)	0·801 (18)
83	0·773 (31)	0·995 (31)	0·995 (30)	0·936 (31)	0·998 (23)	0·694 (21)
84	0·917 (9)	0·994 (9)	0·996 (9)	0·981 (9)	0·998 (9)	0·990 (7)
85	0·640 (21)	0·928 (20)	0·973 (21)	0·932 (21)	0·997 (14)	— —
86	0·865 (13)	0·996 (11)	0·993 (13)	0·985 (13)	0·996 (12)	0·952 (9)
87	0·688 (20)	0·994 (19)	0·989 (20)	0·876 (20)	0·994 (12)	0·564 (14)
88	0·723 (9)	0·794 (9)	0·785 (9)	0·877 (9)	0·912 (9)	— —
89	0·845 (9)	0·955 (9)	0·959 (9)	0·955 (9)	0·982 (9)	0·802 (7)
90	0·987 (8)	0·990 (8)	0·990 (8)	0·997 (8)	0·997 (8)	0·988 (6)
91	0·988 (8)	0·986 (8)	0·985 (8)	0·985 (8)	0·988 (8)	0·991 (6)
92	0·902 (9)	0·985 (9)	0·990 (9)	0·993 (9)	0·997 (9)	0·981 (7)
93	0·885 (13)	0·986 (11)	0·974 (13)	0·992 (13)	0·977 (12)	0·946 (9)
94	0·885 (10)	0·991 (8)	0·985 (10)	0·979 (10)	0·994 (10)	0·939 (7)
95	0·843 (10)	0·991 (8)	0·976 (10)	0·991 (10)	0·993 (10)	0·967 (7)
96	— —	0·925 (19)	0·954 (20)	0·715 (22)	0·991 (14)	— —
97	0·765 (22)	0·994 (19)	0·991 (20)	0·869 (22)	0·996 (14)	0·662 (17)
98	0·705 (22)	0·974 (19)	0·975 (20)	0·826 (22)	0·999 (14)	0·540 (17)
99	0·677 (20)	0·989 (19)	0·989 (20)	0·876 (20)	0·993 (12)	0·548 (14)
100	0·611 (20)	0·991 (19)	0·990 (20)	0·832 (20)	0·992 (12)	— —
101	0·753 (27)	0·979 (26)	0·974 (27)	0·900 (27)	0·976 (19)	0·553 (18)
102	— —	0·686 (24)	0·763 (24)	0·922 (24)	0·936 (22)	— —
103	0·432 (26)	0·905 (25)	0·941 (25)	0·942 (25)	0·985 (23)	— —
104	0·693 (18)	0·970 (17)	0·979 (18)	0·933 (18)	0·984 (15)	— —
105	0·872 (22)	0·981 (21)	0·979 (19)	0·926 (22)	0·991 (16)	0·867 (18)
106	0·656 (25)	0·854 (25)	0·990 (25)	0·980 (25)	0·899 (18)	0·869 (18)
107	0·849 (10)	0·877 (10)	0·815 (10)	0·704 (10)	0·821 (6)	0·806 (8)
108	0·883 (17)	0·865 (17)	0·987 (17)	0·963 (17)	0·920 (13)	0·945 (11)
109	0·643 (26)	0·996 (26)	0·996 (25)	0·928 (25)	0·997 (18)	0·510 (18)
110	0·878 (13)	0·992 (11)	0·990 (13)	0·979 (13)	0·985 (12)	0·944 (9)
111	0·825 (13)	0·982 (11)	0·978 (13)	0·972 (13)	0·989 (12)	0·950 (9)
112	0·849 (11)	0·991 (11)	0·986 (11)	0·920 (11)	0·999 (7)	0·861 (9)
113	0·973 (10)	0·996 (10)	0·997 (10)	0·994 (10)	0·987 (7)	0·991 (8)
114	— —	0·707 (11)	0·675 (13)	0·800 (13)	0·721 (12)	— —
115	0·861 (7)	0·989 (7)	0·997 (6)	1·000 (6)	0·963 (7)	[a] [a]
116	0·538 (33)	0·890 (31)	0·864 (30)	0·735 (33)	0·948 (24)	— —
117	0·911 (9)	0·974 (9)	0·996 (8)	0·985 (9)	0·979 (7)	0·886 (8)
118	0·845 (9)	0·840 (9)	0·996 (8)	0·988 (9)	0·886 (7)	0·886 (8)
119	0·890 (9)	0·838 (9)	0·980 (8)	0·968 (9)	0·967 (7)	0·851 (8)
120	0·825 (9)	0·839 (9)	0·998 (8)	0·989 (9)	0·956 (7)	0·900 (8)
121	— —	0·752 (23)	0·686 (23)	0·743 (23)	0·885 (21)	— —
122	0·672 (13)	0·834 (12)	0·885 (13)	0·906 (13)	0·906 (11)	0·971 (6)

[a] Insufficient number of data.

nium salts, the spectra of the indicator No. 15 depend on the solvent basicity and polarity, due probably to better sterical accessibility of the solvent molecules to the indicator molecule. A poor correlation was found with the iodide ion (No. 16) and its spectral sensitivity to solvents, mainly the solvent acidity and partially polarity and polarizability being responsible for this fact. The dominant effect affecting the position of the longest-wave band in the spectrum of Phenol Blue (Nos 17 and 18) is the polarity followed by acidity, the situation with the merocyanines (Nos 19–21) being similar. Except compound *VIIIb* the correlations can be denoted as fairly close. The solvent sensitivity of the first band of lycopene (No. 22) could be interpreted by only two model equations, the dyestuff Nile Blue A Oxazone (No. 23) also being very little sensitive to solvent changes. In both last cases the spectral shifts are comparable with experimental error. The positions of bands corresponding to the $n \rightarrow \pi^*$ transitions of heterocyclic bases (Nos 24–26) and ketones (Nos 27–29) are – according to expectations – only affected by acidity, the effect being stronger with the nitrogen compounds than with the oxygen compounds. This consequence of different basicity is also manifested in the respective correlation coefficient. The spectra of complex compounds with charge transfer exhibit various degrees of sensitivity to solvent effects. Whereas the iron complexes (Nos 30 and 31) give well correlatable results showing the predominant effect of acidity, the solvent effect on the spectra of CT complexes of aromatic compounds (Nos 32–36) is almost negligible. The reason can lie in the small change of charge distribution in going from the ground to the excited states. Also the correlations of solvent effects for complex compounds with a central atom (Nos 37–41) can be denoted as being of only medium quality, the solvent polarity appearing dominant.

A significant part of the data set used is formed by simple aromatic derivatives. The solvent effects on the $\pi \rightarrow \pi^*$ transitions of benzene derivatives containing heteroatoms without hydrogens (Nos 42–49) are small and badly interpretable by empirical equations. Specific interactions do not make themselves felt to a decisive extent. The picture is markedly changed, if the molecule contains an amino group in combination with electron-acceptor groups. If this group is not further substituted (Nos 52–68; No. 55 does not contain any electron-acceptor group), then the spectral shifts are very well correlatable by Eq. (*13*), the effect of basicity being predominant followed by the solvent polarity. Although in these compounds the basic nature prevails over the acidic properties, the interaction between the nitrogen lone electron pair and solvent obviously is weaker (for sterical reasons) as compared with that between peripheral hydrogen atoms and solvent. This fact explains the low spectral sensitivity to solvents in the case of the indicator No. 55, whose amino hydrogen atoms exhibit a decreased acidity. Aminoanthraquinones (Nos 69–72) provide data which can be correlated with intermittent success, the best results being obtained with Eqs (*12*) and (*13*). The solvent basicity here plays the leading role, the reasons being probably the same as those in the case of the previous indicators.

The replacement of one amino hydrogen atom by alkyl group (Nos 73–82) brings about an increase in the solvent polarity effect to the detriment of the basicity effect, Eq. (*13*) being the most successful one again. Replacement of all amino hydrogen atoms (Nos 83–102) entirely suppresses the solvent basicity effect, and the solvent acidity begins to make itself felt in addition to polarity. At the same time the correlation is slightly worsened. The spectra of azomethine derivatives (Nos 103–105) are preferably affected by the solvent polarity and best interpreted by Eq. (*13*). The hydroxy derivatives (Nos 106–108) – according to the expectation – exhibit spectral bands whose position depends on solvent basicity and polarity, the solvent sensitivity being strongly decreased by intramolecular hydrogen bond (No. 107). If the formation of hydrogen bonds with solvent is prevented by substitution (Nos 109–112), then the spectra predominantly reflect the effect of polarity and partially acidity (which is an analogy with the aniline derivatives), and the correlation is somewhat worsened. Aromatic compounds with bridge groups (Nos 113–114) exhibit solvent-sensitive spectra only if the bridge groups are sterically accessible and sufficiently polarizable (No. 113).

The solvent effects on spectral shifts of fluorescence bands in electronic spectra are similar to those in the absorption spectra, the correlations with the equations tested being somewhat less close. The complex No. 115 exhibits spectra sensitive to the solvent basicity (as it is the case with Nos 32–36). The Py parameter defined with the use of pyrene (No. 116) represents an analogy of the same quantity measured with benzene (No. 42), the solvent sensitivity being greater due to the extensive conjugation. Amino derivatives of naphthalene and anthracene (Nos 117–120) exhibit spectra which are affected predominantly by polarity and partially by basicity. The compounds Nos 121 and 122 show similar behaviour to solvents in both the absorption (Nos 103 and 104) and fluorescence spectra.

4.1.2. *Infrared Spectroscopy*

Table IX summarizes the spectral data selected, Table X gives the statistically significan solvent parameters for the individual models along with the results of the STEPWISE procedure[231], and Table XI presents the multiple correlation coefficients and numbers of the solvents used. According to Table XI, the greatest number of statistically insignificant correlations is observed with Eqs (*8*) and (*19*) (the latter one for a smaller number of the solvents involed) followed by (*18*), (*11*), (*13*), and (*12*). The most successful model (according to the standard deviation) is that with Eq. (*13*) followed stand-offishly by those with Eqs (*11*) and (*12*). If the comparison also includes Eqs (*18*) and (*19*), then the number of the best results is comparable with Eq. (*12*). The combination of parameters in Eq. (*19*) shows a greater applicability to interpretation of solvent effects in infrared spectroscopy than in electronic spectroscopy. As compared with the electronic spectroscopy, all the equations analyzed provide somewhat lower multiple correlation coefficients. The analysis of the last column of Table X supplies data on the frequence of application of the best interpreting parameters which are similar to those obtained in the electronic spectroscopy. The parameters most frequently chosen for description of the solvent polarity are π^* and BASITY (overall the highest frequence), those for basicity are β

TABLE IX

Description of the data tested — wavenumbers ($\tilde{\nu}$) and absorbances (log ε) of selected bonds in infrared spectroscopy; n is the number of solvents

No.	$\tilde{\nu}$	Substrate (indicator), characteristics of process	n	Ref.
123	(O—H)	alcohols, phenols in ether, the G parameter	16	91
124	(O—H)	1,1,1,3,3,3-hexafluoro-2-propanol in tetrachloromethane	8	232
125	(C—H)	chloroform	12	233
126	(C—D)	deuteriochloroform	15	234
127	(N—H)	N-methylaniline	10	235
128	(N—H)	4-nitro-N-methylaniline	12	235
129	(N—H)	2-nitro-N-methylaniline	12	235
130	(C=O)	acetophenone	17	236
131	(C=O)	benzophenone	16	236
132	(C=O)	cyclohexanone	17	236
133	(C=O)	acetone	17	236
134	(C=O)	N,N-dimethylformamide	17	236
135	(C=O)	acetyl chloride	14	236
136	(C=O)	methyl acetate	17	236
137	(S—O)	dimethyl sulphoxide	11	237
138	(S—O)	diphenyl sulphoxide, band II	13	237
139	(S—O)	thionyl chloride	11	237
140	(P=O)	phosphorus oxychloride	8	237
141	(P=O)	dimethyloxophosphorane, band I	12	237
142	(P=O)	dimethyloxophosphorane, band II	12	237
143	(N—O)	*trans*, methyl nitrite	10	237
144	(N—O)	*cis*, methyl nitrite	10	237
145	(N—N)	N-nitrosodimethylamine	9	237
146	(C—Cl)	*trans*, 1,2-dichloroethane	11	238
147	(C—Cl)	*gauche* 1, 1,2-dichloroethane	12	238
148	(C—Cl)	*gauche* 2, 1,2-dichloroethane	13	238
149	(C—Cl)	*trans*, 1-chloropropane	12	239
150	(C—Cl)	*gauche*, 1-chloropropane	12	239
151	(C—Cl)	*trans*, 1-chlorobutane	12	239
152	(C—Cl)	*gauche*, 1-chlorobutane	11	239
153	log ε,	C=O valence vibration, acetone	11	240
154	log ε,	C≡N valence vibration, acetonitrile	9	240

and to a lesser extent B, that for acidity being ACITY. The Y parameter again belongs to those of the least frequence.

A better insight into the solvent participation in vibrational processes is obtained, if the results are classified according to the type of the vibrating bond. The OH

TABLE X

Statistically significant empirical solvent parameters in Eqs *(11)*–*(13)*, *(18)*, *(19)* and results of the STEPWISE procedure — infrared spectroscopy. For numbers see Table IX

No.	*(11)*	*(13)*	*(12)*	*(18)*	*(19)*	STEPWISE
123	AC, BA	π^*, α	Y, P, E	W . f(n^2)	AN	π^*, AC, E_T
124	—	π^*, β	Y, E, B	W, f(n^2), W . f(n^2)	DN	B, β
125	AC, BA	β	P, B	W, f(n^2), W . f(n^2)	DN	β, P
126	—	β	Y, B	—	DN	B, BA
127	BA	β	P, B	—	DN	B, P, E_T, π^*
128	AC, BA	β	B	W, f(n^2), W . f(n^2)	DN	B, P, β
129	—	—	—	—	—	P, BA
130	BA	π^*	Y, P	W, f(n^2)	AN	π^*
131	AC, BA	π^*, α	Y, P, E	W . f(n^2)	AN	π^*, α
132	BA	π^*	Y, P	W, f(n^2)	—	BA, β, B, AC
133	BA	π^*, α	Y, P	W . f(n^2)	—	BA, E_T, AC
134	AC, BA	π^*, α	Y, P, E	W . f(n^2)	AN	AC, BA, E_T
135	AC	π^*, β	Y, P	f(n^2), W . f(n^2)	AN	AC, P, BA, E
136	BA	π^*, β	Y, P	W, f(n^2)	AN	β, AC, E_T, BA, B, π^*
137	BA	π^*, α	Y, P	W . f(n^2)	AN	π^*, α, E
138	AC	π^*, α	Y	W . f(n^2)	AN	AC, E_T, Y
139	BA	π^*, β	Y, P, E	W, W . f(n^2)	AN	π^*, β
140	BA	π^*, β	Y	W, f(n^2)	AN	BA, AC
141	AC, BA	π^*, α	Y, P, B	W, f(n^2)	AN	AC, π^*
142	AC	π^*, α	Y, P, B	W, f(n^2)	AN	AC, P
143	BA	π^*, β	Y, P, E, B	W . f(n^2)	—	BA, β
144	AC, BA	π^*, β, α	P, E, B	—	—	—
145	AC, BA	π^*	Y, E	W	AN	BA, AC
146	BA	π^*, α	Y, P, E, B	W . f(n^2)	—	π^*, Y, β
147	AC	π^*	Y, E	f(n^2), W . f(n^2)	AN	π^*
148	BA	π^*, β	E	W . f(n^2)	AN	π^*, β
149	BA	π^*, β	Y, P, E, B	W . f(n^2)	AN	BA, β
150	BA	π^*	Y, P, E	f(n^2), W . f(n^2)	AN	BA, P
151	BA	π^*	Y, P, E, B	W, f(n^2), W . f(n^2)	AN	BA
152	BA	π^*	Y, E	f(n^2), W . f(n^2)	AN	BA, β
153	AC	—	E	W	—	E, B, BA
154	AC	π^*, α	E	W	AN	AC, E

valence vibration is — in one case (No. 123) — surprisingly dependent on the solvent polarity and acidity, and — in another case (No. 124) — it is basicity-dependent according to expectation. The unexpected behaviour of the system No. 123 can be due to the "inert" solvent used (ether). The C—H and/or C—D vibrations in chloroform (Nos 125 and 126) are only slightly affected by the solvent basicity, due ob-

TABLE XI

The multiple correlation coefficients (R) and numbers of solvents (n) in Eqs (*8*), (*11*)—(*13*), (*18*), (*19*) — infrared spectroscopy. For numbers see Table IX

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
123	0·796 (16)	0·976 (16)	0·981 (14)	0·942 (15)	0·955 (16)	0·956 (12)
124	— —	— —	0·841 (8)	0·998 (8)	0·968 (8)	0·985 (8)
125	— —	0·829 (11)	0·986 (11)	0·974 (12)	0·795 (12)	0·973 (11)
126	— —	— —	0·740 (14)	0·951 (14)	— —	0·947 (7)
127	— —	0·639 (10)	0·901 (10)	0·974 (10)	— —	0·959 (10)
128	— —	0·754 (12)	0·923 (11)	0·967 (12)	0·735 (12)	0·972 (12)
129	— —	— —	— —	— —	— —	— —
130	0·548 (17)	0·922 (17)	0·933 (15)	0·791 (16)	0·936 (16)	0·605 (13)
131	0·760 (16)	0·953 (16)	0·972 (14)	0·945 (15)	0·947 (16)	0·939 (12)
132	— —	0·980 (17)	0·877 (15)	0·767 (16)	0·933 (16)	— —
133	— —	0·928 (17)	0·927 (15)	0·781 (16)	0·946 (16)	— —
134	0·843 (17)	0·989 (17)	0·985 (15)	0·936 (16)	0·954 (16)	0·915 (13)
135	— —	0·631 (14)	0·897 (12)	0·773 (13)	0·758 (14)	0·712 (10)
136	0·573 (17)	0·901 (17)	0·956 (15)	0·772 (16)	0·910 (16)	0·675 (13)
137	0·765 (11)	0·956 (11)	0·983 (10)	0·909 (10)	0·951 (11)	0·973 (7)
138	0·687 (13)	0·920 (13)	0·938 (11)	0·729 (12)	0·857 (13)	0·913 (9)
139	0·737 (11)	0·929 (11)	0·984 (9)	0·982 (10)	0·979 (11)	0·939 (8)
140	0·887 (8)	0·981 (8)	0·996 (7)	0·893 (7)	0·993 (8)	0·969 (5)
141	0·839 (12)	0·989 (12)	0·992 (10)	0·949 (11)	0·964 (12)	0·982 (8)
142	0·799 (12)	0·946 (12)	0·977 (10)	0·943 (11)	0·940 (12)	0·991 (8)
143	0·838 (10)	0·943 (10)	0·977 (9)	0·986 (9)	0·941 (10)	— —
144	— —	0·879 (10)	0·969 (9)	0·911 (9)	— —	— —
145	0·880 (9)	0·981 (9)	0·957 (8)	0·947 (8)	0·960 (9)	0·962 (7)
146	0·683 (11)	0·793 (10)	0·950 (9)	0·984 (10)	0·805 (11)	— —
147	0·827 (12)	0·860 (12)	0·934 (11)	0·910 (11)	0·948 (12)	0·809 (8)
148	0·774 (13)	0·870 (12)	0·972 (12)	0·817 (12)	0·920 (13)	0·807 (8)
149	0·821 (12)	0·991 (11)	0·993 (10)	0·987 (11)	0·954 (12)	0·927 (8)
150	0·861 (12)	0·982 (11)	0·979 (11)	0·964 (11)	0·976 (12)	0·890 (8)
151	0·837 (12)	0·993 (11)	0·990 (10)	0·988 (11)	0·982 (12)	0·943 (8)
152	0·861 (11)	0·988 (11)	0·985 (10)	0·931 (10)	0·978 (11)	0·895 (8)
153	0·742 (11)	0·646 (11)	— —	0·771 (11)	0·732 (11)	— —
154	0·853 (9)	0·988 (9)	0·987 (8)	0·907 (9)	0·911 (9)	0·992 (6)

viously first of all to weak polarization of the respective bond in spite of the electron-acceptor nature of the neighbourhood. Similar situation is encountered with the N—H bonds of N-methylaniline derivatives (Nos 127–129). If there exist intramolecular hydrogen bonds, then the solvent effects on spectra are insignificant as it was the case with the electronic spectra.

The C=O valence vibrations (Nos 130–136) do not give too close correlations in the description by empirical equations, the solvent polarity being the predominant solvent property followed – according to the nature of environment – by the solvent acidity. An increase in the bond polarity increases the dependence on solvent due to more distinct operation of the proton-donor properties of the solvent (Nos 130–132). With methyl acetate (No. 136) the solvent basicity additionally makes itself felt due probably to the polarity change of the C=O bond caused by the interaction between solvent and hydrogen atoms of acetyl group. The valence vibrational frequence of the S—O bond in sulphoxides (Nos 137 and 138) is affected by the solvent acidity and polarity according to expectation, the correlation coefficients being comparable with those of the previous group. The sulfur-oxygen bond in thionyl chloride (No. 139) is affected by the solvent polarity and basicity due to higher electronegativity of chlorine as compared with oxygen. The solvent effects on the P=O valence vibration in oxo derivatives of phosphorus (Nos 140–142) are based on the proton-donor properties and polarity of solvents. The interpretation by empirical equations is very good in some cases. The equation (*13*) appears to be most appropriate for interpretations of solvents effects on the valence vibrational frequences of most polar bonds mentioned.

The valence vibrations of two rotational isomers of methyl nitrite (Nos 143 and 144) are little sensitive to a solvent change, the *s-trans* isomer being affected by basicity. The N—N valence vibration in the N-nitroso derivative No. 145 is affected by polarity and (through the oxygen atom of nitroso group) also acidity of solvents. As in the case of the previous types the correlation coefficients correspond to the average observed for the whole group of infrared spectroscopy. The C—Cl valence vibrational frequences (Nos 146–152) can be correlated with intermittent success, the dominant effects being the solvent polarity and – in some cases – also basicity. The effect of solvent on the bond polarity is transferred to the dipole moment of the molecule and the consequences make themselves felt in the transition moment and absorption intensity as it can be seen in the examples of Nos 153 and 154. The most important is the solvent acidity effect according to expectation.

4.1.3. *Nuclear Magnetic Resonance and Electron Paramagnetic Resonance*

Table XII summarizes the spectral data involving the NMR and EPR spectra, Table XIII presents the statistically significant solvent parameters obtained by application of Eqs (*11*)–(*13*), (*18*), (*19*) and the results of the STEPWISE proce-

TABLE XII

Description of the data tested — nuclear magnetic resonance (Nos 155—207) and electron paramagnetic resonance (Nos 208—218); n is number of solvents

No.	Substrate (indicator), characteristics of the process	n	Ref.
155	δ^1H, methyl group, methyltributylammonium picrate	10	241
156	δ^1H, position 2(6), 1,4-diethylpyridinium iodide, 0·2%	11	242
157	δ^1H, position 2(6), 1,4-diethylpyridinium iodide, 0·5% solution	13	242
158	δ^1H, methyl group, enol form of acetylacetone	12	243
159	δ^1H, methyl group, keto form of acetylacetone	12	243
160	δ^1H, methine group, enol form of acetylacetone	12	243
161	δ^1H, hydroxyl group, enol form of acetylacetone	12	243
162	δ^1H, 1,1-difluoroethene	18	244
163	$\delta^{19}F$, 4-fluoro-2-picoline	25	245
164	$\delta^{19}F$, 2-fluoropyridine	30	245
165	$\delta^{19}F$, 3-fluoropyridine	30	245
166	$\delta^{19}F$, fluorobenzene	17	246
167	$\delta^{19}F$, 4-fluorophenylhydrargyrium acetate	12	247
168	$\delta^{19}F$, 3-fluorophenylhydrargyrium acetate	12	247
169	$\delta^{19}F$, bis(4-fluorophenyl)hydrargyrium	13	247
170	$\delta^{19}F$, bis(3-fluorophenyl)hydrargyrium	13	247
171	$\delta^{19}F$, difference between the chemical shifts in tetrachloromethane and in the presence of solvent, 4-fluorophenol	14	101
172	$\delta^{19}F$, 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane	17	246
173	$\delta^{19}F$, fluorodinitromethane	10	248
174	$\delta^{13}C$, position 4, chlorobenzene	28	249
175	$\delta^{13}C$, position 4, chlorobenzene	24	250
176	$\delta^{13}C$, position 4, methyl phenyl sulphoxide	30	249
177	$\delta^{13}C$, position 3, methyl phenyl sulphoxide	29	249
178	$\delta^{13}C$, position 2, methyl phenyl sulphoxide	28	249
179	$\delta^{13}C$, position 4, phenylsulphur pentafluoride	15	250
180	$\delta^{13}C$, position 3, phenylsulphur pentafluoride	15	250
181	$\delta^{13}C$, position 2, phenylsulphur pentafluoride	15	250
182	$\delta^{13}C$, position 4, benzotrifluoride	30	249
183	$\delta^{13}C$, position 4, benzotrifluoride	26	250
184	$\delta^{13}C$, position 3, benzotrifluoride	30	249
185	$\delta^{13}C$, position 3, benzotrifluoride	26	250
186	$\delta^{13}C$, position 2, benzotrifluoride	30	249
187	$\delta^{13}C$, position 2, benzotrifluoride	26	250
188	$\delta^{13}C$, position 3, (*S*)-1,7-diphenyl-5-hydroxy-3-heptanone	13	251
189	$\delta^{13}C$, position 3, (*S*)-1,7-bis(3,4-dimethoxyphenyl)-5-hydroxy-3-heptanone	12	251
190	$\delta^{13}C$, position 3, (*S*)-5-(1,7-diphenyl-5-hydroxy-3-oxo)heptyl acetate	13	251
191	$\delta^{13}C$, position 3, (*S*)-5-(1,7-bis(3,4-dimethoxyphenyl)-5-hydroxy-3-oxo)-heptyl acetate	13	251
192	$\delta^{15}N$, pyridine	9	252

TABLE XII
(*Continued*)

No.	Substrate (indicator), characteristics of the process	n	Ref.
193	$\delta^{31}P$, tributylphosphine oxide	7	106
194	$\delta^{31}P$, triethylphosphine oxide	25	102
195	$\delta^{23}Na$, sodium iodide	10	253
196	$\delta^{23}Na$, 0·125M sodium iodide	8	254
197	$\delta^{23}Na$, 0·0313M sodium perchlorate	9	254
198	$\delta^{23}Na$, 0·0313M sodium rhodanide	8	254
199	$\delta^{23}Na$, 0·125M sodium tetraphenylborate	10	254
200	$\delta^{23}Na$, 0·5M sodium tetraphenylborate	11	255
201	$J(^{19}F)$, positions 1,1; trifluoroethene	9	256
202	$J(^{19}F)$, positions *Z*-1,2; trifluoroethene	9	256
203	$J(^{19}F)$, positions *E*-1,2; trifluoroethene	9	256
204	$J(^{1}H)$, positions 2,2; 1,1-difluoroethene	18	244
205	$J(^{1}H, ^{19}F)$, positions *Z*; 1,1-difluoroethene	18	244
206	$J(^{1}H, ^{19}F)$, positions *E*; 1,1-difluoroethene	18	244
207	$J(^{19}F)$, positions 1,1; 1,1-difluoroethene	18	244
208	*a*(H2), 1-methyl-4-acetylpyridyl	9	257
209	*a*(H3), 1-methyl-4-acetylpyridyl	9	257
210	*a*(H5), 1-methyl-4-acetylpyridyl	9	257
211	*a*(H6), 1-methyl-4-acetylpyridyl	9	257
212	*a*(H-acetyl), 1-methyl-4-acetylpyridyl	9	257
213	*a*(H3,5), 2,6-dimethyl-semi-1,4-benzoquinone	17	258
214	*a*(H-methyl), 2,6-dimethyl-semi-1,4-benzoquinone	17	258
215	$a(^{14}N)$, ditert.butylaminoxyl	26	107
216	$a(^{14}N)$, 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl	25	107
217	$a(^{14}N)$, 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl	26	107
218	$a(^{13}C)$, 2,2,6,6-tetramethyl-4-piperidon-1-oxyl	9	259

dure[231], and Table XIV gives the multiple correlation coefficients. The interpretability of the given experimental data by the empirical models depends – in the case of NMR – on the type of nucleus. If the dependence is significant, then the correlations are comparable to those of the infrared spectroscopy, i.e. worse than those in electronic spectra. The applications of the equations tested to EPR data give very good correlations. The number of insignificant correlations depends on the number of empirical solvent parameters in the equation and decreases from Eqs (*8*) and (*19*) via (*11*), (*18*), (*13*) to Eq. (*12*). For the NMR data the most successful equation unequivocally is (*13*), for the EPR data Eqs (*13*) and (*12*). The selection of the best interpreting set of parameters (Table XIII) showed that the α parameter is the

TABLE XIII

Statistically significant empirical solvent parameters in Eqs *(11)*–*(13)*, *(18)*, *(19)* and results of the STEPWISE procedure – nuclear magnetic resonance and electron paramagnetic resonance. For numbers see Table XII

No.	*(11)*	*(13)*	*(12)*	*(18)*	*(19)*	STEPWISE
155	BA	—	Y, E	W, $f(n^2)$, W . $f(n^2)$	—	π^*
156	—	—	—	[a]	—	Y, α
157	—	—	—		—	Y, B, P
158	—	—	—	—	—	—
159	—	—	—	—	—	—
160	—	—	Y	—	DN	Y
161	AC	π^*, β, α	E	—	—	α, β, AC
162	—	β, α	B	W . $f(n^2)$	DN	β, α
163	AC, BA	π^*, α	Y, E, B	W	AN	AC, BA, β
164	AC	π^*, β, α	Y, E	W . $f(n^2)$	AN	E_T, BA, π^*
165	AC	π^*, α	Y, E, B	W	AN, DN	AC, P, α
166	AC	—	Y, P	$f(n^2)$, W . $f(n^2)$	—	P, π^*
167	—	π^*, β, α	B	W, $f(n^2)$, W . $f(n^2)$	AN, DN	B, α, E_T
168	—	β, α	B	W, $f(n^2)$, W . $f(n^2)$	AN, DN	β, α
169	AC, BA	β	Y, B	W, $f(n^2)$, W . $f(n^2)$	DN	β, E_T
170	AC, BA	β	B	W, $f(n^2)$, W . $f(n^2)$	DN	β
171	AC, BA	β, α	Y, B	—	DN	β, α
172	—	—	P	$f(n^2)$	—	P
173	BA	β	B	W . $f(n^2)$	DN	β
174	BA	π^*, β	Y	W, $f(n^2)$, W . $f(n^2)$	—	BA, β, P
175	AC, BA	π^*, β	Y	W . $f(n^2)$	—	BA, β, P
176	AC	π^*, α	Y, E	W	AN	AC, α, π^*, E
177	AC	π^*, α	Y, E	—	AN	AC, β, B
178	AC, BA	π^*, α, β	E	—	AN	α, β, π^*, P, Y
179	BA	π^*, β	Y	W . $f(n^2)$	—	Y, α, E, β, B
180	BA	π^*, β	Y, B	W . $f(n^2)$	—	Y, β, α, B, E
181	AC, BA	π^*	Y, P	W . $f(n^2)$	—	π^*, E_T
182	BA	π^*, β	Y, B	W, $f(n^2)$, W . $f(n^2)$	—	BA, β, P
183	AC, BA	π^*, β	Y	W . $f(n^2)$	—	BA, β, P
184	BA	π^*, β	Y, B	W . $f(n^2)$	—	Y, AC, E, β, π^*
185	BA	π^*, β	Y	W . $f(n^2)$	—	Y, α, E, β, B
186	AC, BA	π^*, β	Y	W . $f(n^2)$	—	Y, BA
187	AC, BA	π^*, β	Y	W . $f(n^2)$	AN	Y, BA
188	—	π^*, β, α	Y, E, B	W, $f(n^2)$	AN, DN	B, AC, BA, E_T
189	—	β, α	Y, E, B	—	AN, DN	—
190	AC, BA	π^*, α	Y, E, B	W	AN	AC, BA
191	AC, BA	π^*, α	P, E, B	W . $f(n^2)$	AN	AC, α
192	AC, BA	π^*, α	E	W, $f(n^2)$, K . $f(n^2)$	AN	α, π^*
193	AC	π^*, α	P, E	[a]	AN	AC, β

TABLE XIII
(*Continued*)

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
194	AC	π*, α	Y, E	W, f(n^2), W . f(n^2)	AN	AC, α, BA, P
195	—	—	—	f(n^2), W . f(n^2)	—	—
196	—	—	Y, B	W	—	Y, B
197	—	β	E, B	f(n^2)	AN, DN	B, E_T
198	—	—	B	f(n^2)	DN	B
199	—	β	E, B	f(n^2)	AN, DN	B, E_T
200	—	π*	E, B	f(n^2)	AN, DN	B, E, BA
201	—	β	B	—	DN	β
202	AC	β, α	P, E, B	W	—	Y, π*, β
203	BA	—	Y	W	—	Y
204	AC, BA	π*, β	Y, B	f(n^2), W . f(n^2)	DN	β, BA, E, α, Y
205	AC, BA	π*, β	Y, B	f(n^2), W . f(n^2)	DN	β, E, BA, α, P
206	BA	π*, β	Y, B	W . f(n^2)	DN	β, BA, E, α
207	AC, BA	β	Y, P, B	f(n^2), W . f(n^2)	DN	E_T, B, P
208	AC, BA	π*, β, α	Y, P, E, B	W . f(n^2)	AN, DN	E_T, P
209	AC, BA	π*, β, α	Y, P, E	W, W . f(n^2)	AN, DN	E_T, AC, P
210	AC, BA	π*, β, α	Y, P, E	W . f(n^2)	AN, DN	BA, β, E, α
211	AC, BA	π*, α	Y, P, E	W . f(n^2)	AN	AC, BA, P, B
212	AC	π*, α	E, B	W, f(n^2)	AN	AC
213	AC, BA	α	E	—	AN	AC, π*
214	AC	α	E	—	AN	α
215	AC, BA	π*, α	Y, P, E	W	AN	BA, E_T
216	AC, BA	π*, α	Y, P, E	W, f(n^2)	AN	AC, BA, α
217	AC, BA	π*, α	Y, E	W	AN	AC, BA, α
218	BA	π*	P, E	W, W . f(n^2)	—	π*

[a] Insufficient number of data.

acidity parameter of highest frequence, whereas β and BASITY represent the highest-frequence solvent parameters of basicity and polarity, respectively. As compared with the previous spectral models, the occurrence of the π* parameter decreased and that of Y increaed.

A more detailed analysis of the applications of model equations to the data of Table XII gives the following results. The solvent effects on chemical shifts of ^{1}H nuclei (Nos 155–162) are slight and non-interpretable, the greatest changes being observed with the sufficiently acidic protons, which is connected with specific solvation. The solvent effects on the chemical shifts of ^{19}F nuclei (Nos 163–173) are mediated by the interaction with the rest of the molecule as the consequence of changes in shielding of the nuclei measured. If the rest of the molecule contains no

TABLE XIV

The multiple correlation coefficients (R) and numbers of solvents (n) in Eqs (*8*), (*11*)—(*13*), (*18*), (*19*) — nuclear magnetic resonance and electron paramagnetic resonance. For numbers see Table XII

No.	(*8*)		(*11*)		(*13*)		(*12*)		(*18*)		(*19*)	
155	—	—	0·867	(9)	—	—	0·889	(10)	0·984	(9)	—	—
156	—	—	—	—	—	—	—	—	a	a	—	—
157	—	—	—	—	—	—	—	—	—	—	—	—
158	—	—	—	—	—	—	—	—	—	—	—	—
159	—	—	—	—	—	—	—	—	—	—	—	—
160	0·634	(12)	—	—	—	—	0·726	(11)	—	—	0·703	(11)
161	0·721	(12)	0·592	(12)	0·988	(10)	0·700	(11)	—	—	—	—
162	0·566	(18)	—	—	0·845	(15)	0·707	(16)	0·483	(17)	0·724	(14)
163	0·942	(25)	0·994	(25)	0·986	(24)	0·976	(23)	0·749	(19)	0·977	(17)
164	0·864	(30)	0·885	(28)	0·943	(26)	0·872	(28)	0·903	(22)	0·853	(20)
165	0·881	(30)	0·959	(28)	0·969	(26)	0·922	(28)	0·750	(22)	0·965	(20)
166	0·589	(17)	0·566	(16)	—	—	0·855	(16)	0·854	(16)	—	—
167	—	—	—	—	0·981	(10)	0·938	(12)	0·835	(11)	0·924	(12)
168	—	—	—	—	0·981	(10)	0·870	(12)	0·828	(11)	0·893	(12)
169	0·581	(13)	0·924	(13)	0·977	(12)	0·960	(13)	0·906	(13)	0·924	(12)
170	—	—	0·907	(13)	0·969	(12)	0·899	(13)	0·886	(13)	0·890	(12)
171	—	—	0·729	(14)	0·992	(13)	0·898	(14)	—	—	0·683	(12)
172	—	—	—	—	—	—	0·712	(16)	0·673	(16)	—	—
173	—	—	0·835	(8)	0·988	(8)	0·959	(9)	0·743	(9)	0·974	(8)
174	0·530	(28)	0·816	(24)	0·918	(22)	0·848	(27)	0·921	(21)	—	—
175	0·585	(24)	0·847	(23)	0·909	(21)	0·858	(24)	0·884	(18)	—	—
176	0·907	(30)	0·976	(26)	0·991	(24)	0·946	(29)	0·757	(21)	0·984	(23)
177	0·903	(29)	0·952	(25)	0·979	(23)	0·933	(28)	0·799	(20)	0·948	(22)
178	0·661	(28)	0·898	(24)	0·962	(22)	0·804	(27)	—	—	0·831	(21)
179	0·593	(15)	0·721	(15)	0·946	(12)	0·907	(15)	0·859	(11)	—	—
180	—	—	0·635	(15)	0·940	(12)	0·874	(15)	0·771	(11)	—	—
181	0·654	(15)	0·980	(15)	0·987	(12)	0·949	(15)	0·986	(11)	—	—
182	0·477	(30)	0·794	(26)	0·909	(24)	0·849	(29)	0·911	(21)	—	—
183	0·542	(26)	0·825	(25)	0·902	(23)	0·831	(26)	0·867	(18)	—	—
184	0·362	(30)	0·645	(26)	0·849	(24)	0·780	(29)	0·737	(21)	—	—
185	0·453	(26)	0·614	(25)	0·844	(23)	0·756	(26)	0·751	(18)	—	—
186	0·642	(30)	0·870	(26)	0·892	(24)	0·833	(29)	0·886	(21)	—	—
187	0·674	(26)	0·810	(25)	0·895	(23)	0·821	(26)	0·878	(18)	0·448	(21)
188	—	—	—	—	0·937	(13)	0·930	(13)	0·815	(10)	0·887	(12)
189	—	—	—	—	0·858	(12)	0·919	(12)	—	—	0·834	(11)
190	0·857	(13)	0·955	(13)	0·942	(13)	0·918	(13)	0·737	(10)	0·896	(12)
191	0·890	(13)	0·962	(13)	0·932	(13)	0·925	(13)	0·848	(10)	0·912	(12)
192	0·944	(9)	0·995	(9)	0·997	(9)	0·964	(9)	0·992	(7)	0·981	(8)
193	0·985	(7)	0·999	(5)	0·986	(6)	0·990	(7)	a	a	1·000	(4)
194	0·921	(25)	0·984	(25)	0·991	(22)	0·958	(25)	0·858	(19)	1·000	(25)

TABLE XIV
(*Continued*)

No.	(*8*)		(*11*)		(*13*)		(*12*)		(*18*)		(*19*)	
195	—	—	—	—	—	—	—	—	0·855	(8)	—	—
196	—	—	—	—	—	—	0·934	(8)	0·888	(7)	—	—
197	—	—	—	—	0·834	(9)	0·964	(9)	0·861	(8)	0·974	(9)
198	—	—	—	—	—	—	0·898	(8)	0·873	(7)	0·827	(8)
199	—	—	—	—	0·833	(9)	0·971	(10)	0·790	(9)	0·980	(10)
200	—	—	—	—	0·651	(10)	0·967	(11)	0·779	(9)	0·976	(11)
201	—	—	—	—	0·941	(7)	0·919	(8)	—	—	0·965	(7)
202	0·887	(9)	0·864	(9)	0·984	(7)	0·996	(8)	0·942	(9)	—	—
203	—	—	0·671	(9)	—	—	0·712	(8)	0·714	(9)	—	—
204	0·758	(18)	0·844	(16)	0·961	(15)	0·915	(16)	0·881	(17)	0·753	(14)
205	0·707	(18)	0·833	(16)	0·949	(15)	0·906	(16)	0·850	(17)	0·754	(14)
206	0·668	(18)	0·757	(16)	0·956	(15)	0·912	(16)	0·780	(17)	0·774	(14)
207	0·785	(18)	0·779	(16)	0·758	(15)	0·918	(16)	0·952	(17)	0·588	(14)
208	0·989	(9)	0·995	(9)	0·998	(9)	1·000	(9)	0·989	(7)	0·994	(9)
209	0·993	(9)	0·999	(9)	0·999	(9)	0·999	(9)	0·994	(7)	0·998	(9)
210	0·992	(9)	0·999	(9)	0·999	(9)	1·000	(9)	0·976	(7)	0·998	(9)
211	0·983	(9)	0·996	(9)	0·993	(9)	0·999	(9)	0·979	(7)	0·991	(9)
212	0·971	(9)	0·995	(9)	0·995	(9)	0·996	(9)	0·983	(7)	0·994	(9)
213	0·735	(17)	0·937	(15)	0·839	(15)	0·789	(17)	—	—	0·857	(13)
214	0·778	(17)	0·889	(15)	0·870	(15)	0·814	(17)	—	—	0·898	(13)
215	0·932	(26)	0·993	(26)	0·988	(23)	0·961	(25)	0·854	(19)	0·987	(19)
216	0·958	(25)	0·994	(25)	0·991	(23)	0·978	(24)	0·929	(19)	0·981	(18)
217	0·951	(26)	0·993	(26)	0·990	(23)	0·967	(25)	0·901	(19)	0·979	(19)
218	—	—	0·676	(9)	0·710	(9)	0·790	(9)	0·965	(6)	—	—

[a] Insufficient number of data.

groups able of the specific interaction or polarized by the action of electronegative fluorine atom, then the solvent effects are smaller and also worse for interpretation (e.g. Nos 172 and 166). In such cases predominant is the solvent polarizability. In other caes we can observe the absence of polarity effects and operation of solvent acidity or basicity depending on the nature of heteroatoms in the rest of the molecule. The chemical shifts in ^{13}C NMR spectra (Nos 174–191) exhibit a solvent sensitivity particularly in the cases when the respective carbon atom forms a part of an aromatic ring with electron-acceptor sustituents (Nos 174–187). Obviously this phenomenon is connected with the change of electron density at the carbon atom measured mediated by the mesomeric and inductive effects of the solvated electron-acceptor substituent. The solvent effects are the strongest and the correlation is the closest one at the 4 position with respect to the electron-acceptor group; both are worse at the 2 position and still worse at 3 position. This trend can be observed also with benzotrifluoride, which indicates a manifestation of hyperconjugation of the trifluoromethyl group. The solvent acts predominantly electrostatically, also significant being the basicity according to expectation. These effects are interpreted by Eq. (*13*) with excellent results. The chemical shift of ^{13}C in carbonyl group (Nos 188–191) is first of all affected by the solvent acidity in the measure depending on formation of intramolecular hydrogen bonds. The single example given which concerns the solvent effects on the chemical shift of ^{15}N (No. 192) indicates the predominance of solvent acidity followed by solvent polarity. A similar effect can be observed in the case of the chemical shifts of ^{31}P in phosphine oxides (Nos. 193 and 194) and is caused by specific solvation of the bound oxygen. Solvent changes are almost without any effect on the chemical shift of the sodium nuclei ^{23}Na (Nos 195–200) irrespective of the anion present.

The coupling constants $J(H, H)$, $J(H, F)$, and $J(F, F)$ in NMR spectra of fluoroalkanes (Nos 201–207) exhibit changes due especially to the solvent polarity and basicity (particularly the coupling constants between the proton and some other atom) which are caused by polarization of C—H bond and the therewith connected increased acidity of hydrogen atoms. In average, the correlations are very close.

Very close correlations are obtained with the hyperfine splitting constants in the EPR spectra measured for hydrogen (Nos 208–214) and nitrogen (Nos 215–217), those for ^{13}C being distinctly worse (No. 218). In accordance with the structure of models, the dominant solvent effect is determined by the solvent acidity and polarity.

4.2. APPLICATION OF SELECTED EMPIRICAL MODELS TO RATE PROCESSES

Table XV presents the description of the rate processes used for testing of empirical models, Table XVI gives the statistically significant solvent parameters and results of the STEPWISE procedure[231], and Table XVII summarizes the corresponding multiple correlation coefficients. From the tables it follows that rate proceses, represent a more heterogeneous group as compared with the spectral processes and the results of testing correspond thereto. The comparison of the empirical models described by Eqs (*8*), (*11*)–(*13*) shows that Eq. (*8*) completely failed in the greatest number of cases, much better being the other equations in the sequence (*11*), (*13*), and (*12*). The equations (*18*) and (*19*) with a lower number of known parameters also exhibit many cases of complete failure, substantially more cases, however, with Eq. (*19*). In contrast to spectral processes, the most successful equation (according to the residual standard deviations) is Eq. (*11*) followed by Eqs (*13*) and (*12*). The equations (*8*), (*18*), and (*19*) do not participate in the best results to any distinct extent. On the whole it is possible to denote the applicability of the empirical models to the interpretation of solvent effects on rate processes as comparable with general results of the spectral processes, especially so if the lower numbers of experimental

TABLE XV

Description of the data tested — rate processes; n is number of solvents

No.	Substrate, characteristics of the process	n	Ref.
219	log k, solvolysis, 1-bromobutane	4	185, 260
220	log k, solvolysis, isopropyl tosylate	4	261, 262, 263
221	log k, solvolysis, cyklopentyl tosylate	4	263
222	log k, solvolysis, cyclohexyl tosylate	4	263
223	log k, solvolysis, *endo*-norbornyl tosylate	4	263
224	log k, solvolysis, *exo*-norbornyl tosylate	4	263
225	log k, solvolysis, benzyl chloride	4	185, 260
226	log k, solvolysis, tert.butyl chloride	19	264
227	log k, solvolysis, tert.butyl chloride	20	184
228	log k, solvolysis, tert.butyl chloride	7	109
229	log k, solvolysis, tert.butyl chloride	13	265
230	log k, solvolysis, tert.butyl bromide	13	265
231	log k, solvolysis, tert.butyl iodide	13	265
232	log k, solvolysis, 4-methoxyneophyl tosylate	11	110
233	log k, quaternization, ethyl iodide + triethylamine	22	266
234	$\delta \Delta G^{\ddagger}$, quaternization, ethyl iodide + triethylamine	8	17
235	log k, quaternization, methyl iodide + tripropylamine	31	114
236	log k, quaternization, methyl iodide + N,N-dimethyl-N-benzylamine	14	267
237	log k, quaternization, methyl iodide + N,N-dimethyl-N--(3-methylbenzyl)amine	14	267
238	log k, quaternization, butyl iodide + N,N-dimethyl-N--(4-chlorobenzyl)amine	14	267
239	log k, quaternization, methyl iodide + N,N-dimethyl-N--(3-chlorobenzyl)amine	14	267
240	log k, quaternization, methyl iodide + N,N-dimethyl-N--(3-nitrobenzyl)amine	13	267
241	log k, quaternization, methyl iodide + N,N-dimethyl-N--(4-methoxybenzyl)amine	14	267
242	log k, quaternization, methyl iodide + N,N-dimethyl-N--(4-nitrobenzyl)amine	13	267
243	log k, quaternization, ethyl bromoacetate + triethylamine, scale $\mathscr{S}$	15	115
244	log k, quaternization, ethyl iodoacetate + triethylamine, scale $\mathscr{S}$	15	115
245	log k, quaternization, 4-nitrobenzyl chloride + triethylamine	12	268
246	log k, elimination, 1,4-diazabicyclo[2,2,2]octane + 1-chloro--2-phenylethane	22	269
247	log k, elimination, 1,4-diazabicyclo[2,2,2]octane + 1-bromo--2-phenylethane	24	269
248	log k, elimination, 1,4-diazabicyclo[2,2,2]octane + 1-iodo--2-phenylethane	24	269
249	$\Delta G^{\ddagger}$, nucleophilic substitution, methyl iodide + Cl^-	8	17
250	log k, nucleophilic substitution, betaine *II* + methyl iodide	10	270

TABLE XV
(*Continued*)

No.	Substrate, characteristics of the process	n	Ref.
251	log *k*, nucleophilic substitution, 1,3,5-trinitroanisole + 3-nitro-N,N-dimethylaniline	10	271
252	log *k*, nucleophilic substitution, 1,3,5-trinitroanisole + 3-methyl-N,N-dimethylaniline	10 10	271 271
253	log *k*, nucleophilic substitution, 2,4-dinitrochlorobenzene + + piperidine	11	272
254	log *k*, nucleophilic substitution, 2,4-dinitrofluorobenzene + + tyrosine ethyl ester	10	273
255	log *k*, nucleophilic substitution, 4-nitrofluorobenzene + + tetraethylammonium azide	10	274
256	log *k*, nucleophilic substitution, benzoyl chloride + aniline	24	275
257	log *k*, nucleophilic substitution, terephthaloyl chloride + + 3-chloroaniline, k_3	8	275
258	log *k*, nucleophilic substitution, terephthaloyl chloride + + 3-chloroaniline, k_4	8	275
259	log *k*, nucleophilic substitution, carborancarboxylic acid anhydride-chloride + aniline	14	276
260	log *k*, nucleophilic substitution, thiophenesulphonyl chloride + + aniline	11	275
261	log *k*, nucleophilic substitution, thiophenesulphonyl chloride + + 4-methylaniline	10	275
262	log *k*, nucleophilic substitution, thiophenesulphonyl chloride + + 4-chloroaniline	10	275
263	log *k*, nucleophilic substitution, thiophenesulphonyl chloride + + 3-chloroaniline	10	275
264	log *k*, nucleophilic substitution, benzoic acid + + diphenyldiazomethane	26	96, 277, 278
265	log *k*, nucleophilic substitution, 2,4-dinitrophenol + + diphenyldiazomethane	27	278
266	log *k*, nucleophilic substitution, N,N-bis(1-butyl)benzimidamide + + 4-nitrophenylnitromethane	6	279
267	log *k*, cycloaddition, dimerization of pentadiene	14	280
268	log *k*, cycloaddition, maleic anhydride + 1,3-butadiene	7	281
269	log *k*, cycloaddition, acrylaldehyde + cyclopentadiene	14	282
270	log ([*endo*]/[*exo*]), cycloaddition, maleic anhydride + + cyclopentadiene	10	111
271	log ([*endo*]/[*exo*]), cycloaddition, cyclopentadiene + + methyl acrylate	13	282
272	log ([*endo*]/[*exo*]), cycloaddition, cyclopentadiene + + acrylaldehyde	13	282
273	log ([*endo*]/[*exo*]), cycloaddition, cyclopentadiene + + crotonaldehyde	13	282

TABLE XV
(*Continued*)

No.	Substrate, characteristics of the process	n	Ref.
274	log k, cycloaddition, 2-ethyl-1-hexene + chlorosulphonyl isocyanate	9	283
275	log [*cis*-stilbene], addition, chloranil + phenyldiazomethane	19	284
276	log [*trans*-stilbene], addition, chloranil + phenyldiazomethane	19	284
277	log k, addition, chloranil + diphenyldiazomethane	17	285
278	log k, addition, 2,5-dichloro-1,4-benzoquinone + diphenyldiazomethane, product 1	18	285
279	log k, addition, 2,5-dichloro-1,4-benzoquinone + diphenyldiazomethane, product 2	18	285
280	log k, addition, O,O-diethyldithiohypophosphorous acid $(EtO)_2PSSH$ + acrylonitrile	10	286
281	log k, electrophilic addition, 1-pentene + bromine	9	287
282	log k, oxidative dimerization, styrene, palladium(II) acetate	12	288
283	log k, electrophilic substitution, tetramethylstannium + bromine	7	112
284	log k, acid-catalyzed decomposition, 1-phenyl-3-alkyltriazenes	13	289
285	log k, rearrangement, benzoyl azide	9	290
286	log k, rearrangement, allyl 2-nitrobenzenensulphenate	6	291
287	log k, rearrangement, 6-nitrospiropyrane	9	292
288	log k, rearrangement, 2-phenyl-2-propyl peroxybenzoate	8	293
289	log k, *cis-trans* isomerization, 4-nitro-4′-(N,N-diethylamino)-azobenzene	10	294
290	log k, reesterification, sec. butyl chloroacetate and sec. butyl orthotitanate	11	295
291	log k, phenylmethanesulfonyl chloride, diazomethane (triethylamine)	10	296
292	log k, radical decomposition, tert.butyl peroxyformiate (pyridine)	14	297
293	log k, radical decomposition, tert.butyl 2-phenylthioperoxybenzoate	10	298
294	log (k_{tert}/k_{prim}), photochlorination, 2,3-dimethylbutane	16	299
295	log (k_{tert}/k_{prim}), radical chlorination, 2,3-dimethylbutane, tert.butoxy chloride	8	58
296	log $(k_{cHxCl}/k_{acetone})$, photolysis, cyclohexane, tert.butoxy chloride	10	58
297	log k, radical addition, styrene, 4-aminobenzenethienyl	19	300

data in the individual series are taken into account. Out of the individual parameters selected by the STEPWISE procedure, the BASITY parameter exhibited the greatest frequence, the parameter ACITY and the mixed parameter $E_T(30)$ being the most frequent ones of the acidity parameters. The basicity parameters β and B exhibited roughly the same low frequency.

The success of mathematical interpretation depends on the mechanism type, particularly on structure of the activated complex inclusive of its charge distribution.

TABLE XVI

Statistically significant empirical solvent parameters of Eqs (*11*)—(*13*), (*18*), (*19*) and results of the STEPWISE procedure — rate processes. For numbers see Table XV

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
219	BA	[a]	[a]	[a]	—	[a]
220	BA	[a]	[a]	[a]	—	[a]
221	AC, BA	[a]	[a]	[a]	—	[a]
222	—	[a]	[a]	[a]	—	[a]
223	AC, BA	[a]	[a]	[a]	—	[a]
224	AC, BA	[a]	[a]	[a]	—	[a]
225	BA	[a]	[a]	[a]	—	[a]
226	AC, BA	π^*, β, α	Y, P, E	$f(n^2)$, W . $f(n^2)$	AN	E_T, β, π^*
227	AC, BA	π^*, α	Y, E	$f(n^2)$, W . $f(n^2)$	AN	E_T, BA, E, β
228	AC, BA	π^*	Y, B	[a]	—	π^*
229	AC, BA	π^*, α	Y, P, E	W, $f(n^2)$, W . $f(n^2)$	AN	E_T
230	AC, BA	π^*, α	Y, E	W, $f(n^2)$	AN	BA, AC
231	AC, BA	π^*, α	Y, E	W, $f(n^2)$	AN	BA, AC, P
232	AC, BA	π^*, β, α	Y, E	W . $f(n^2)$	AN	E_T, E
233	BA	π^*, β	Y, P, E, B	W, $f(n^2)$	AN, DN	BA, π^*, E_T
234	AC, BA	π^*	Y, E	W · $f(n^2)$	—	π^*, BA
235	BA	π^*	Y, P	W, $f(n^2)$	—	π^*, BA
236	AC, BA	π^*	Y	$f(n^2)$, W . $f(n^2)$	—	BA, α, B
237	BA	π^*	Y	W . $f(n^2)$	—	BA, AC
238	AC, BA	π^*	Y	W	—	BA, E, P
239	AC, BA	π^*, β	Y	$f(n^2)$, W . $f(n^2)$	—	BA, α, B
240	AC, BA	π^*, β	Y	W, $f(n^2)$, W . $f(n^2)$	—	BA, α, B
241	AC, BA	π^*	Y	$f(n^2)$, W . $f(n^2)$	—	BA, α, B
242	AC, BA	π^*, β	Y	W, $f(n^2)$, W . $f(n^2)$	—	BA, α, B
243	AC, BA	π, α	Y, P, E	W, W . $f(n^2)$	AN	BA, AC
244	AC, BA	π^*, α	Y, P, E, B	W, $f(n^2)$	AN	BA, AC, Y
245	BA	π^*	Y, B	W . $f(n^2)$	—	π^*, P
246	AC, BA	π^*, β	Y	W, W . $f(n^2)$	—	BA, E_T
247	AC, BA	π^*, β, α	Y, E	W . $f(n^2)$	—	BA, E_T, α, β
248	BA	π^*, β, α	Y, E	W . $f(n^2)$	—	BA
249	AC	α	E	W	AN	α
250	AC	α	P, E	—	AN	α, P, E
251	AC, BA	π^*, β	Y, E	$f(n^2)$, W . $f(n^2)$	—	Y, E_T
252	AC, BA	π^*, β, α	Y, B	W . $f(n^2)$	—	[a]
253	BA	π^*, β	Y, B	W, $f(n^2)$, W . (n^2)	DN	E_T, α, Y, AC, B
254	AC, BA	π^*, β	Y, B	W . $f(n^2)$	DN	B, Y
255	AC, BA	β, α	E, B	—	AN, DN	AC, Y
256	BA	π^*, β, α	Y, P, E, B	$f(n^2)$, W . $f(n^2)$	AN, DN	β, E, π^*
257	AC	β, α	E	$f(n^2)$	—	β, P, AC
258	AC	β, α	E	$f(n^2)$	—	β, P, AC
259	BA	π^*, β	Y	W	AN, DN	BA, β, E
260	AC, BA	β, α	E	[a]	AN	BA, π^*, AC

TABLE XVI
(*Continued*)

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
261	AC, BA	β, α	E	[a]	AN	E_T, BA, π^*
262	AC	β, α	E	[a]	AN	E_T
263	AC	β, α	E	[a]	AN	E
264	AC	π^*, β, α	Y, P, E, B	—	AN, DN	B, E_T, Y
265	AC, BA	π^*, α	Y, P, B	W	AN, DN	AC, B, Y, P, α
266	AC	π^*	Y, E	$f(n^2)$, $W \cdot f(n^2)$	[a]	Y, α
267	—	—	P, E	$f(n^2)$	—	—
268	—	β	E, B	—	DN	B, E
269	AC	α	P, E	W, $f(n^2)$	AN	P, AC
270	AC, BA	π^*, α	E	W	AN	E_T
271	AC, BA	π^*, α	Y, E	W	AN	E_T, BA
272	AC, BA	α	E	—	AN	α, B
273	AC	α	E	—	AN	α
274	BA	π^*	Y, P, E	$W \cdot f(n^2)$	AN	π^*, Y
275	—	π^*, β	Y, B	—	DN	β, E_T
276	BA	π^*	Y, E	W	AN	E_T
277	AC	π^*	Y, E, B	W, $f(n^2)$	AN	AC, BA, Y, α
278	AC	π^*, α	Y, E, B	W, $f(n^2)$	AN	AC, B, E_T
279	AC	π^*, α	Y, E, B	W, $f(n^2)$	AN	AC, π^*
280	—	—	—	$f(n^2)$, $W \cdot f(n^2)$	—	—
281	AC, BA	π^*, α	E	[a]	AN	E, BA
282	AC	π^*, β	E, B	—	AN, DN	α
283	AC, BA	π^*, β, α	Y	$W \cdot f(n^2)$	DN	Y, β
284	—	β	B	W, $f(n^2)$, $W \cdot f(n^2)$	DN	B
285	AC	π^*, α	Y, E	W	AN	AC
286	AC, BA	π^*, α	E	—	AN	AC, α, E_T
287	BA	β	Y	$W \cdot f(n^2)$	DN	E_T, E
288	AC, BA	π^*, α	E, B	[a]	AN	E_T
289	AC	π^*, β	Y, P, E	$W \cdot f(n^2)$	AN	AC
290	AC	π^*	Y, E	W	AN	AC
291	AC	π^*, β, α	E	W, $f(n^2)$	AN	β, BA, α, E_T, E, Y
292	BA	π^*, β	Y, P, E, B	$W \cdot f(n^2)$	AN	π^*, β, E_T, AC
293	AC, BA	π^*, α	Y, P, E	W	AN	E_T, P, π^*
294	—	—	P	$f(n^2)$	—	—
295	AC	—	—	—	—	AC
296	AC	α	E	W	AN	E_T
297	BA	π^*, β	Y, E, B	$f(n^2)$, $W \cdot f(n^2)$	AN, DN	E_T, β

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[a] Insufficient number of data.

TABLE XVII

The multiple correlation coefficients (R) and numbers of solvents (n) in Eqs (*8*), (*11*)—(*13*), (*18*), (*19*) — rate processes. For numbers see Table XV

No.	(*8*)		(*11*)		(*13*)		(*12*)		(*18*)		(*19*)	
219	—	—	0·972	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
220	0·990	(4)	0·973	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
221	0·987	(4)	1·000	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
222	0·978	(4)	—	—	[a]	[a]	[a]	[a]	[a]	[a]	—	—
223	0·962	(4)	1·000	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
224	0·965	(4)	1·000	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
225	—	—	0·988	(4)	[a]	[a]	[a]	[a]	[a]	[a]	—	—
226	0·972	(19)	0·979	(19)	0·978	(17)	0·983	(19)	0·970	(12)	0·944	(16)
227	0·982	(20)	0·989	(19)	0·976	(18)	0·978	(20)	0·967	(12)	0·930	(15)
228	0·948	(7)	0·999	(7)	0·999	(5)	0·895	(7)	[a]	[a]	—	—
229	0·973	(13)	0·995	(13)	0·993	(13)	0·983	(13)	0·990	(8)	0·955	(12)
230	0·957	(13)	0·996	(13)	0·993	(13)	0·946	(13)	0·976	(8)	0·910	(12)
231	0·909	(13)	0·993	(13)	0·992	(13)	0·896	(13)	0·981	(8)	0·834	(12)
232	0·977	(11)	0·982	(11)	0·997	(9)	0·975	(11)	0·983	(6)	0·922	(10)
233	0·884	(22)	0·994	(22)	0·989	(21)	0·985	(21)	0·994	(22)	0·908	(17)
234	—	—	0·996	(17)	0·993	(15)	0·935	(17)	0·997	(12)	—	—
235	0·444	(31)	0·945	(28)	0·962	(28)	0·804	(31)	0·990	(26)	—	—
236	—	—	0·998	(14)	0·926	(13)	0·591	(13)	0·968	(11)	—	—
237	—	—	0·954	(14)	0·922	(13)	0·562	(13)	0·915	(11)	—	—
238	—	—	0·979	(14)	0·882	(13)	0·631	(13)	0·952	(11)	—	—
239	—	—	0·995	(14)	0·947	(13)	0·635	(13)	0·963	(11)	—	—
240	—	—	0·974	(13)	0·800	(12)	0·594	(12)	0·985	(10)	—	—
241	—	—	0·998	(14)	0·930	(13)	0·569	(13)	0·970	(11)	—	—
242	—	—	0·981	(13)	0·836	(12)	0·645	(12)	0·987	(10)	—	—
243	0·920	(15)	0·995	(13)	0·985	(13)	0·995	(15)	0·990	(14)	0·899	(8)
244	0·911	(15)	0·997	(13)	0·988	(13)	0·995	(15)	0·997	(14)	0·884	(8)
245	0·605	(12)	0·904	(11)	0·895	(11)	0·945	(12)	0·927	(9)	—	—
246	—	—	0·962	(21)	0·853	(20)	0·665	(22)	0·963	(16)	—	—
247	—	—	0·967	(22)	0·896	(22)	0·701	(24)	0·939	(18)	—	—
248	—	—	0·952	(22)	0·887	(22)	0·685	(24)	0·904	(18)	—	—
249	0·944	(8)	0·948	(8)	0·987	(6)	0·952	(8)	0·899	(5)	0·957	(8)
250	0·756	(10)	0·895	(10)	0·926	(10)	0·984	(10)	—	—	0·929	(8)
251	0·853	(10)	0·896	(10)	0·927	(9)	0·982	(9)	0·977	(9)	—	—
252	0·784	(10)	0·929	(10)	0·980	(9)	0·971	(9)	0·977	(9)	—	—
253	0·908	(11)	0·858	(11)	0·956	(10)	0·955	(11)	0·956	(11)	0·679	(9)
254	—	—	0·779	(10)	0·955	(10)	0·979	(10)	0·810	(7)	0·828	(10)
255	0·819	(9)	0·994	(9)	0·972	(8)	0·967	(9)	—	—	0·981	(8)
256	0·773	(24)	0·721	(22)	0·939	(21)	0·953	(24)	0·872	(23)	0·912	(13)
257	0·789	(8)	0·812	(8)	0·979	(7)	0·774	(8)	0·795	(8)	—	—
258	0·769	(8)	0·792	(8)	0·980	(7)	0·776	(8)	0·789	(8)	—	—

TABLE XVII
(*Continued*)

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
259	0·708 (14)	0·723 (14)	0·849 (13)	0·602 (14)	0·765 (14)	0·898 (11)
260	0·947 (11)	0·971 (9)	0·962 (10)	0·930 (11)	[a] [a]	0·928 (8)
261	0·954 (10)	0·978 (9)	0·971 (10)	0·937 (10)	[a] [a]	0·910 (8)
262	0·974 (10)	0·959 (9)	0·961 (10)	0·970 (10)	[a] [a]	0·951 (8)
263	0·975 (10)	0·958 (9)	0·963 (10)	0·977 (10)	[a] [a]	0·953 (8)
264	0·500 (26)	0·479 (21)	0·938 (23)	0·970 (26)	— —	0·921 (14)
265	0·648 (27)	0·803 (23)	0·626 (25)	0·927 (26)	0·660 (26)	0·723 (18)
266	0·951 (6)	0·866 (6)	0·838 (6)	0·997 (6)	0·988 (6)	[a] [a]
267	— —	— —	— —	0·724 (14)	0·944 (10)	— —
268	— —	— —	0·903 (5)	0·996 (6)	— —	0·887 (6)
269	0·738 (14)	0·922 (14)	0·874 (13)	0·910 (14)	0·784 (10)	0·950 (12)
270	0·938 (10)	0·974 (10)	0·969 (8)	0·910 (10)	0·888 (7)	0·935 (9)
271	0·981 (13)	0·973 (13)	0·956 (11)	0·984 (13)	0·973 (10)	0·900 (12)
272	0·628 (13)	0·930 (13)	0·902 (12)	0·808 (13)	— —	0·713 (12)
273	0·661 (13)	0·745 (13)	0·820 (12)	0·763 (13)	— —	0·783 (12)
274	0·903 (9)	0·986 (9)	0·984 (8)	0·990 (9)	0·989 (9)	0·818 (6)
275	— —	— —	0·903 (16)	0·823 (18)	— —	0·747 (15)
276	0·865 (18)	0·789 (17)	0·808 (16)	0·812 (18)	0·776 (18)	0·639 (15)
277	0·741 (17)	0·877 (15)	0·838 (15)	0·995 (16)	0·861 (17)	0·887 (11)
278	0·802 (18)	0·899 (16)	0·912 (16)	0·958 (17)	0·883 (18)	0·895 (12)
279	0·801 (18)	0·912 (16)	0·917 (16)	0·924 (17)	0·911 (18)	0·933 (12)
280	— —	— —	— —	— —	0·983 (7)	— —
281	0·913 (9)	0·992 (8)	0·995 (7)	0·935 (8)	[a] [a]	0·809 (7)
282	— —	0·786 (11)	0·787 (10)	0·886 (11)	— —	0·933 (10)
283	0·768 (7)	0·994 (7)	1·000 (6)	0·952 (7)	0·995 (5)	0·929 (6)
284	— —	— —	0·959 (13)	0·984 (13)	0·799 (13)	0·949 (10)
285	0·916 (9)	0·977 (9)	0·946 (9)	0·951 (9)	0·968 (9)	0·985 (6)
286	0·909 (6)	0·998 (6)	0·994 (6)	0·880 (6)	— —	0·942 (6)
287	0·911 (9)	0·737 (9)	0·836 (9)	0·907 (9)	0·782 (9)	0·868 (8)
288	0·921 (8)	0·996 (8)	0·995 (5)	0·990 (8)	[a] [a]	0·993 (5)
289	0·953 (10)	0·978 (10)	0·967 (10)	0·982 (10)	0·972 (10)	0·991 (8)
290	0·822 (11)	0·949 (10)	0·881 (10)	0·938 (9)	0·908 (11)	0·929 (8)
291	0·864 (10)	0·910 (10)	0·979 (9)	0·821 (10)	0·995 (5)	0·946 (9)
292	0·877 (14)	0·978 (14)	0·997 (13)	0·996 (14)	0·996 (14)	0·794 (9)
293	0·970 (10)	0·986 (10)	0·983 (10)	0·988 (10)	0·888 (6)	0·921 (7)
294	0·563 (16)	— —	— —	0·616 (15)	0·620 (15)	— —
295	— —	0·898 (9)	— —	— —	— —	— —
296	0·926 (8)	0·972 (7)	0·761 (7)	0·941 (7)	0·859 (7)	0·987 (5)
297	0·841 (19)	0·707 (17)	0·859 (19)	0·940 (18)	0·805 (19)	0·813 (14)

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[a] Insufficient number of data.

Solvolyses proceeding unequivocally by the S_N2 mechanism (Nos 219 and 220) exhibit sensitivity to the solvent polarity, although this conclusion must be considered preliminary because of the small number of points. The solvolyses with possible participation of the monomolecular mechanism (Nos 221–225) in most cases exhibit the acidity effects, too (this statement being similarly restricted as above). The solvolyses with unequivocal S_N1 mechanism (Nos 226–231) are accelerated by both increased polarity and increased acidity. The reason probably lies in the stabilization of the polar transition state as well as in the increased solvation of the leaving group, which prevents the recombination. The same reasons apply to the interpretation of solvent effects on the elimination reaction No. 232 which goes by the E1 mechanism with the same rate-limiting step. In all the cases given the correlations can be denoted as very good. The quaternization reactions of the type of the Menshutkin reaction with the S_N2 mechanism (Nos 233–245) exhibit – according to expectation – predominant sensitivity to the solvent polarity, the solvent basicity (stabilization by solvation of the ammonium ion) and acidity (in a positive way, hence also the stabilization of anion and charge separation) making also themselves felt according to the nature of reactants. The way of stabilization shows that the electron transfer is considerably advanced in the activated complex. The reactions Nos 246–248 are denoted as quaternizations, but a more detailed analysis of solvent effects[37] indicates at least a contribution (if not the exclusive presence) of the elimination reactions. Every quaternization reaction exhibits a high sensitivity to solvent effects and good correlation with its quantitative description by empirical parameters. In this respect a somewhat worse situation is encountered with further nucleophilic substitution reactions (Nos 249–266) irrespective of their taking place at aliphatic carbon, aromatic ring, with participation of carbonyl or sulphonyl groups, or at hydrogen atom. The bimolecular nucleophilic substitutions S_N2 (Nos 249–250) exhibit, first of all, a positive effect of acidity, which indicates a greater localization of the negative charge at the leaving group. The reactions Nos 251 and 252 are originally declared[340] as substitutions at the methyl group of methoxyl group and quaternizations, but – with regard to the nature of the reactants – the nucleophilic aromatic substitution is also likely. From the observed magnitudes of the regression coefficients it follows that the reaction discussed is roughly three times less sensitive to the solvent polarity than the typical quaternization reaction, being almost equally sensitive as the following typical aromatic nucleophilic substitutions. These results throw doubt upon the original classification of the reaction (in the least). The nucleophilic aromatic substitution reactions (Nos 253–255) exhibit sensitivity to solvent polarity and basicity, if the nucleophilic reagent involves amino group (the transition state is polar, the basicity facilitates the splitting off of the proton from the nucleophilic group; the addition of nucleophilic reagent is rate-limiting), or they are negatively affected by the solvent basicity and positively affected by the acidity (the solvation of ammonium ions facilitating the departure of the leaving group in the same way as the acidity; the decomposition of the adduct is rate-limiting). The nucleophilic substitution reaction at carbonyl group (Nos 256–259) – out of the reactions given – is predominantly dependent on the basicity, since in this way the solvent facilitates the splitting off of the proton from the attacking amino group. A partial contribution of acidity is connected with the stabilization of the negative charge at the oxygen atom of the carbonyl group whose polarization is thereby increased. This effect becomes dominant in the reactions of sulphonyl chloride (Nos 260–263) with nucleophiles. The reaction of hydroxyl group (Nos 264–265) with diazomethane, which can be considered a nucleophilic reaction at hydrogen, is affected by solvent in a complex way. The analogous substitution at hydrogen (No. 266) is positively affected by acidity due obviously to stabilization of the charge formed at the leaving conjugated base.

The cycloaddition reactions (Nos 267–274) usually are little sensitive to solvent effects, and empirical parameters provide poor correlations, which is a consequence of the synchronous mechanism and low polarity of reactants in the transition state. In the reactions of chloranil with diazoalkanes (Nos 275 – 277) the effect of polarity is accompanied by a positive effect of solvent acidity, which is probably a consequence of the facilitation of the attack by the nucleophile. The same situation is also encountered with the reactions of diazoalkanes with other electron acceptors (Nos 278 and 279). The solvent effects on the Michael addition (No. 280) cannot be well interpreted by empirical relations. A classical example of electrophilic addition to double bond (No. 281) indicates positive effects of solvent polarity and acidity (facilitation of polarization of Br—Br bond during its interaction with the π^*-electrons of the double bond). The correlation with empirical solvent parameters is very good. The complex reaction No. 282 is affected by solvents only little. The electrophilic substitution of bromine atom by a Lewis acid (No. 283) is accelerated – according to expectation – by increased solvent polarity and basicity (formation of charges, stabilization of the leaving group). The negative influence of solvent basicity on the acid-catalyzed decomposition of triazene (No. 284) is caused by solvation of the proton which is transferred on the substrate in the rate-limiting step (general acid catalysis). The possibilities of qualitative and quantitative interpretations of solvent effects on rearrangements (Nos 285–288), isomerizations (No. 289), and other complex reactions (Nos 290 – 297) are variable and depend on more detailed studies. The fit in the correlations varies from a very good to bad one. The same applies to interpretation of solvent effects in the radical reactions, their reactants and transition states being very little polarized.

In conclusion it can be stated that the individual aspects of the solvent effect on a reaction course are unequivocally operating as a consequence of the mechanism. On the other hand, the analysis of solvent effects can provide important indications for suggestion or improvement of the reaction mechanism. However, this approach is used relatively little, as compared with other tools of mechanistic studies.

4.3. APPLICATION OF SELECTED EMPIRICAL MODELS TO EQUILIBRIUM PROCESSES

Equilibrium processes represent a very extensive field. This review includes, under this heading, tautomeric equilibria, conformational equilibria, equilibria of formation of associates either with solvent or between the compounds measured, solvation equilibria (differences of the Gibbs energy for the transfer of a compound from the reference solvent to a general one), and distribution coefficients between phases. The dissociation equilibria are not tested here, because the pK values are not only functions of solvent properties, but also functions of the measurement system and acidity scale, and they are often considerably different when taken from different sources. Table XVIII gives the equilibrium processes used for the testing, Table XIX summarizes the selected statistically significant solvent parameters of Eqs (*11*)–(*13*), (*18*), (*19*), and the results of the STEPWISE procedure[231], and Table XX presents the respective correlation coefficients. From Table XX it can be seen that the correlations are less close than those of the previous processes. It is also possible to observe a greater number of failures of the empirical models, most often with Eqs (*19*), (*8*), and (*18*). On the other hand, the relatively most successful models are characterized by Eqs (*13*), (*12*), and (*11*) (in decreasing order). There can exist several reasons of these results. One of them consists in the process itself, since the characterizing quantity ($\log K$, ΔG) reflects the difference in solvation energies of (usually) little charged and (hence also) solvated species. Structural differences between the two equilibrium forms are usually slight, which makes itself felt in small solvation differences, too. Last but not least, also the indirect way of the measurements (by means of some other quantity, e.g. spectral one) introduces an additional error into the results. Also some internal reasons not connected with solvent (e.g. in the conformational but also tautomeric equilibria) can make themselves felt. This whole situation affects the selection of the best parameters by the STEPWISE method: except a slight preference of the π^* and BASITY parameters to the Y parameter, no distinct differences can be observed between the other aspects of the solvent effects.

The analysis of the individual types of equilibrium processes leads to the following conclusions. The tautomeric equilibria (Nos 298–305) are only poorly described quantitatively by means of the empirical methods. If the enol form can form the intramolecular hydrogen bond, the dominant effect is the solvent polarity, and the solvent basicity acts to a little extent only. If the hydrogen bond is impossible, then only the basicity and acidity effects are observed (they control the stabilization of both forms). The conformational equilibrium of 1,3-dioxane derivatives (Nos 306 and 307) is affected by the solvent polarity (differences in charge dislocation) and acidity (differences in the possibility of mutual approach of the solvent molecule and the compound tested). The correlation coefficients in these interpretations can

TABLE XVIII

Description of data tested — equilibrium processes, n is number of solvents

No.	Substrate (indicator), characteristics of the process	n	Ref.
298	log K, tautomerism, acetylacetone	12	243
299	log K, tautomerism, ethyl acetoacetate	13	243
300	log K, tautomerism, 6-chloro-2-pyridone	16	301
301	log K (NMR), tautomerism, 5,5-dimethyl-1,3-cyclohexanedione	10	302
302	log K (NMR), tautomerism, 8-oxabicyclo[4,3,0]nonane-2,9-dione	17	302
303	log K (NMR), tautomerism, 2,4-pentanedione	15	302
304	log K (NMR), tautomerism, ethyl 3-oxobutanoate	14	302
305	ΔG, tautomerism, 5,5-dimethyl-1,3-cyclohexanedione	15	302
306	ΔG, conformation, 2-isopropyl-5-methoxy-1,3-dioxane	14	126
307	ΔG, conformation, 2-isopropyl-5-ethoxy-1,3-dioxane	13	126
308	log K, formation of complex between iodine and solvent, heptane	16	303, 304
309	log K, association, benzoic acid	7	305
310	log K (NMR), association, 5-fluoroindole — solvent, tetrachloromethane	10	306
311	log K (solvent basicity), association, 4-fluorophenol, tetrachloromethane	20	177
312	log K (NMR), association, 4-fluorophenol, tetrachloromethane	14	101
313	ΔG, transfer of K^+ from water to the solvent	11	307
314	ΔG, transfer of Ag^+ from water to the solvent	11	307
315	ΔG, transfer of Cl^- from water to the solvent	11	307
316	ΔG, transfer of Br^- from water to the solvent	11	307
317	ΔG, transfer of I^- from water to the solvent	11	307
318	ΔG, transfer of ClO^- from water to the solvent	11	307
319	ΔG, transfer of $(CH_3)_4N^+ + I^-$ from methanol to the solvent	21	308
320	ΔG, transfer of $(C_2H_5)_4N^+ + I^-$ from methanol to the solvent	24	308
321	ΔG, transfer of tetraphenylmethane from water to the solvent	10	309
322	ΔG, transfer of tetraphenylgermanium from water to the solvent	10	309
323	ΔG, transfer of complex tetraphenylarsenium–tetraphenylborium from water to the solvent	10	309
324	log K, distribution between water and the solvent, 2-nitrophenol	9	310
325	log K, distribution between water and the solvent, 2-amino-4,6-dinitrophenol	11	310
326	log K, distribution between water and the solvent, 1-nitroso-2-naphthol	9	310
327	log K, distribution between water and the solvent, 2-nitroso-1-naphthol	9	310
328	log K, distribution between water and the solvent 2-hydroxy-3-methoxybenzaldehyde	11	311
329	log K, distribution between water and the solvent, 5-methylfurfural	7	311
330	log K, distribution between water and the solvent, 2-hydroxybenzaldehyde	15	311
331	log K, distribution between water and the solvent, acetylacetone	15	311

be denoted as average. The differences in the constants of formation of the complex between iodine and solvent (No. 308) cannot be interpreted by means of the empirical

TABLE XIX

Statistically significant empirical solvent parameters in Eqs (*11*)—(*13*), (*18*), (*19*) and results of the STEPWISE procedure — equilibrium processes. For numbers see Table XVIII

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
298	AC, BA	π^*	Y	$W . f(n^2)$	AN	E_T, BA
299	AC, BA	π^*, β	Y	$f(n^2)$, $W . f(n^2)$	AN	π^*, β
300	AC	β, α	E, B	—	AN, DN	AC, B
301	—	β, α	—	$W . f(n^2)$	DN	β, B, AC, P
302	BA	π^*	Y	W	—	π^*
303	AC, BA	π^*, β	Y	W	—	π^*, β
304	AC, BA	π^*	Y	W	—	π^*, E
305	—	β, α	E, B	—	DN	β, E
306	AC, BA	π^*, α	Y, E, B	W	AN	π^*, AC
307	AC	π^*	Y, P, E, B	$W . f(n^2)$	AN	E_T, π^*, β
308	—	—	B	—	DN	B
309	BA	π^*	Y, P, E	W, $f(n^2)$	—	BA
310	AC, BA	π^*, β	Y, B	—	—	B, Y
311	AC, BA	π^*, β, α	Y, B	W, $f(n^2)$, $W . f(n^2)$	AN, DN	β, α, E, P
312	AC, BA	π^*, β, α	Y, B	—	DN	β, α, E
313	—	π^*, β	B	$f(n^2)$	AN, DN	P, BA
314	BA	π^*	B	—	AN, DN	BA, α
315	AC	π^*, α	E	—	AN	E_T
316	AC	α	E	—	AN	E_T
317	AC, BA	—	E	$f(n^2)$, $W . f(n^2)$	AN	AC, BA
318	BA	—	Y	—	—	B, Y
319	AC, BA	π^*, β, α	Y, B	$f(n^2)$, $W . f(n^2)$	AN	Y, π^*, E_T
320	AC, BA	π^*, β, α	Y, P, E	W, $f(n^2)$	AN	Y, π^*, α
321	AC	α	E	—	AN	AC
322	AC	α	E	$f(n^2)$, $W . f(n^2)$	AN	E_T
323	AC	α	Y, E	$f(n^2)$	AN	α
324	AC, BA	π^*, β, α	Y, P, E	W, $f(n^2)$	—	BA, AC
325	BA	π^*	P, E	W, $f(n^2)$	—	π^*, B
326	BA	π^*	Y, P, E	W, $f(n^2)$	—	BA
327	AC, BA	π^*	Y, P, E	W, $f(n^2)$	—	BA, P, Y
328	BA	π^*, β	Y, P, E	W, $f(n^2)$, $W . f(n^2)$	—	BA, β, α
329	AC	π^*	[a]	W	[a]	π^*
330	BA	π^*	Y	W, $f(n^2)$	AN	π^*
331	AC	π^*, β, α	—	W, $f(n^2)$, $W . f(n^2)$	AN	AC

[a] Insufficient number of data.

equations. Benzoic acid forms strongly hydrogen-bonded dimers in solvents (No. 309), the respective equilibrium constant being affected only by the solvent polarity.

TABLE XX

The multiple correlation coefficients (R) and numbers of solvents (n) in Eqs (*8*), (*11*),—(*13*), (*18*), (*19*) — equilibrium processes. For numbers see Table XVIII

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
298	0·786 (12)	0·901 (12)	0·857 (10)	0·749 (11)	0·875 (9)	0·668 (11)
299	0·742 (13)	0·908 (13)	0·968 (11)	0·741 (12)	0·983 (10)	0·721 (12)
300	0·765 (16)	0·827 (16)	0·938 (16)	0·929 (16)	— —	0·965 (13)
301	— —	— —	0·917 (10)	— —	0·875 (7)	0·747 (9)
302	— —	0·765 (17)	0·816 (17)	0·623 (17)	0·790 (14)	— —
303	0·570 (15)	0·863 (15)	0·902 (15)	0·719 (15)	0·872 (11)	— —
304	— —	0·824 (14)	0·780 (14)	0·535 (14)	0·725 (11)	— —
305	0·545 (15)	— —	0·790 (15)	0·802 (15)	— —	0·666 (14)
306	0·842 (14)	0·973 (13)	0·961 (14)	0·957 (14)	0·927 (13)	0·823 (11)
307	0·946 (12)	0·941 (12)	0·916 (13)	0·993 (13)	0·993 (13)	0·892 (10)
308	— —	— —	— —	0·796 (16)	— —	0·717 (15)
309	0·765 (7)	0·994 (7)	0·993 (7)	0·998 (7)	0·996 (7)	— —
310	— —	0·838 (10)	0·978 (9)	0·865 (10)	— —	— —
311	— —	0·680 (18)	0·993 (19)	0·891 (20)	0·661 (20)	0·799 (15)
312	— —	0·764 (14)	0·995 (13)	0·868 (14)	— —	0·633 (12)
313	— —	— —	0·962 (8)	0·816 (11)	0·711 (8)	0·832 (11)
314	— —	0·644 (10)	0·859 (8)	0·816 (11)	— —	0·826 (11)
315	0·980 (11)	0·957 (10)	0·975 (8)	0·975 (11)	— —	0·989 (11)
316	0·963 (11)	0·954 (10)	0·883 (8)	0·954 (11)	— —	0·971 (11)
317	0·877 (11)	0·949 (10)	— —	0·851 (11)	0·814 (8)	0·870 (11)
318	— —	0·686 (10)	— —	0·799 (11)	— —	— —
319	0·719 (21)	0·800 (21)	0·857 (20)	0·981 (21)	0·964 (15)	0·577 (16)
320	0·769 (24)	0·938 (24)	0·964 (23)	0·967 (24)	0·994 (18)	0·688 (18)
321	0·937 (10)	0·911 (10)	0·862 (9)	0·927 (10)	— —	0·918 (9)
322	0·939 (10)	0·901 (10)	0·855 (9)	0·926 (10)	0·906 (6)	0·920 (9)
323	0·925 (10)	0·920 (10)	0·962 (9)	0·975 (10)	0·894 (6)	0·931 (9)
324	0·835 (9)	0·999 (9)	0·998 (9)	0·990 (9)	0·987 (9)	— —
325	0·730 (11)	0·804 (11)	0·969 (9)	0·930 (9)	0·942 (11)	— —
326	0·846 (9)	0·999 (9)	0·988 (9)	0·982 (9)	0·988 (9)	— —
327	0·880 (9)	0·998 (9)	0·980 (9)	0·985 (9)	0·992 (9)	— —
328	0·839 (11)	0·993 (11)	0·988 (10)	0·979 (10)	0·993 (11)	— —
329	0·833 (7)	0·809 (7)	0·973 (5)	[a] [a]	0·980 (7)	[a] [a]
330	0·622 (15)	0·897 (14)	0·967 (14)	0·539 (15)	0·965 (14)	0·771 (7)
331	— —	0·893 (14)	0·975 (14)	— —	0·937 (14)	0·971 (6)

[a] Insufficient number of data.

The equilibria of formation of hydrogen bonds with solvents can be described very well by means of empirical parameters (Nos 310–312): in these cases the solvent polarity and also basicity are significant. The differences in the Gibbs solvation energies (Nos 313–323), according to the nature of the compounds examined, depend on the solvent polarity and basicity (cations), or polarity and acidity (small or polar anions), or are governed by the nature of the particle accessible for the solvent (ionic pairs). The correlation coefficients of these interpretations by empirical equations mostly are average. Better results are obtained in the correlations of the distribution coefficients, although most compounds used for the measurements contain an intramolecular hydrogen bond (Nos 324–331).

4.4. APPLICATION OF SELECTED EMPIRICAL MODELS TO OTHER PROCESSES

Table XXI gives the description of the selected experimental data not included in the previous categories, Table XXII presents a survey of statistically significant empirical solvent parameters from Eqs (*11*)–(*13*), (*18*), and (*19*) along with the results of the STEPWISE procedure[231], Table XXIII summarizes the corresponding multiple correlation coefficients. The comparison of the results of Table XXIII with the previous ones shows that the processes assembled in Table XXI provide correlations of substantially lower quality in the empirical solvent models. Sporadic successful cases can rather be considered exceptions. One of the reasons obviously consists in the model processes used for the parametrization: they reflect different properties of solvents. The applications of the equations (*8*), (*11*)–(*13*), (*18*), and (*19*) led to failure most frequently with Eqs (*18*) and (*8*) and most rarely with Eqs (*12*), (*13*), and (*19*). Also the fact that the usual location of Eq. (*19*) changed indicates a different character of the data of Table XXI. The best result was obtained (according to the minimum residual standard deviation) most frequently with Eqs (*12*), (*13*), and (*11*). The priority of Eq. (*12*) is due to the more universal character of multiparameter equations. In the selection of the best parameters set the most frequent parameters were B, BASITY, ACITY, β, and Y.

A more detailed insight can be obtained by separate analyses of the individual process types. The thermodynamic quantities (Nos 332–339) belong to the best correlatable ones in the whole set. The formation of adducts with the Lewis acids is a function of the solvent basicity as expected. The partial molar dissolution heats depend on the solvent in various ways: they depend on the solvent basicity in the case of acidic solutes (No. 335), on the solvent acidity for basic solutes (No. 334), and predominantly on the solvent polarity in the cases of ionic solutes (Nos 336 to 339). The C_B and E_B parameters derived by Drago[315] (Nos 340 and 341) also from thermochemical data stand in accordance first of all with the function of basicity.

Another region is represented by electrochemical quantities. The half-wave potential of cyclic volt-amperometry of ferrocene (No. 342) depends only slightly on the

TABLE XXI

Description of the data tested — other processes; n is number of solvents

No.	Substrate (indicator), characteristics of the process	n	Ref.
332	$-\Delta H$, formation of adduct between antimony(V) chloride and solvent, 1,2-dichloroethane	50	15
333	$-\Delta H$, formation of adduct between boron trifluoride and solvent, dichloromethane	14	312, 313
334	$-\Delta H$, 4-fluoroanisole, partial molar dissolution heats	13	314
335	$-\Delta H$, 4-fluorophenol, partial molar dissolution heats	13	314
336	ΔG, dissolution of $(CH_3)_4N^+ + I^-$	17	308
337	ΔG, dissolution of $(CH_3)_4N^+I^-$	17	308
338	ΔG, dissolution of $(C_2H_5)_4N^+ + I^-$	21	308
339	ΔG, dissolution of $(C_2H_5)_4N^+I^-$	20	308
340	Parameter C_B, Drago	14	315, 316
341	Parameter E_B, Drago	14	315, 316
342	$E_{1/2}$, cyclic volt-amperometry, ferrocene	12	317
343	E_p^{red}, 2-nitroaniline	10	318
344	E_p^{red}, 4-nitroaniline	10	318
345	E_p^{red}, 2-nitro-4-methylaniline	10	318
346	E_p^{red}, 4-nitro-N-methylaniline	10	318
347	E_p^{red}, 2-nitro-N,N-dimethylaniline	10	318
348	E_p^{red}, 4-nitro-N,N-dimethylaniline	10	318
349	$E_{1/2}$, oxidation of tetraphenylporphyrinecarbonylruthenium(II), the first step	10	319
350	Λ, equivalent conductivity, H^+	14	320
351	$\ln \gamma$, activity coefficient, 4-nitrobenzyl chloride	14	268
352	Solubility, HCl	13	321
353	δ, solubility parameter	41	137
354	δ_0, solubility parameter	41	137
355	δ_d, solubility parameter	41	137
356	δ_p, solubility parameter	41	137
357	δ_h, solubility parameter	41	137
358	δ, solubility parameter	33	138
359	χ_e, selectivity, ethanol	40	139
360	χ_d, selectivity, dioxane	40	139
361	χ_n, selectivity, nitromethane	40	139
362	χ_t, selectivity, toluene	39	139
363	χ_m, selectivity, 2-butanone	36	139
364	S, aromatic selectivity, $K_{toluene}/K_{octane}$	40	138
365	P', polarity parameter	44	139
366	V_m, molar volume	44	138
367	$\hat{\eta}$, a parameter derived from the activation viscosity data	28	144
368	The proton activity from mass spectrometry	21	171

TABLE XXII

Statistically significant empirical solvent parameters in Eqs (*11*)–(*13*), (*18*), (*19*) and results of the STEPWISE procedure — other processes. For numbers see Table XXI

No.	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)	STEPWISE
332	—	β	E, B	—	AN, DN	B, α, E, β
333	—	β	B	—	DN	B, BA
334	AC	π*, α	Y, E	W . $f(n^2)$	AN	AC
335	—	β	B	—	DN	B
336	AC, BA	π*, β, α	Y	W, W . $f(n^2)$	AN	Y, π*, E
337	AC, BA	π*, α	Y	W, $f(n^2)$	AN	Y, β
338	AC, BA	π*, β, α	Y, B	$f(n^2)$, W . $f(n^2)$	AN	Y, β, E_T
339	AC, BA	π*, α	Y, E, B	W, W . $f(n^2)$	AN	Y, B, E_T
340	—	π*, β	Y, B	—	AN, DN	B, β, E
341	BA	π*, β	Y, E, B	W . $f(n^2)$	AN, DN	β, E
342	—	α	B	—	AN, DN	B
343	AC, BA	π*	P, E	—	AN	AC, BA
344	AC	π*, β	E	—	AN	AC
345	AC, BA	π*	P, E	W	AN	E_T
346	AC	—	E	—	AN	AC, BA
347	AC, BA	π*	P, E	—	AN	AC, BA, α
348	AC, BA	π*, α	E	W	AN	E_T, AC, B
349	AC, BA	π*, β	B	—	AN, DN	β, Y
350	AC	—	Y, P, E	W, $f(n^2)$, W . $f(n^2)$	AN	—
351	AC, BA	π*, α	Y, E	W, $f(n^2)$	—	BA, E_T, B, AC
352	—	—	B	—	—	B, β, BA, P
353	AC, BA	π*, α	Y, E	W, $f(n^2)$	AN	E_T, Y, BA
254	AC, BA	π*, α	Y, E	W, $f(n^2)$	AN	E_T, β, B, Y, π*, AC
355	AC, BA	π*, α	P	$f(n^2)$	—	P, BA
356	AC, BA	π*, β	Y	$f(n^2)$, W . $f(n^2)$	AN	Y
357	AC	π*, α	E, B	$f(n^2)$, W . $f(n^2)$	AN, DN	E, B, BA
358	AC, BA	π*, α	Y, E	W, $f(n^2)$	AN	E, BA, α
359	BA	π*, β, α	P, B	W, $f(n^2)$, W . $f(n^2)$	DN	β, BA, B, α, P
360	—	π*, β, α	P, E, B	W, $f(n^2)$, W . $f(n^2)$	AN, DN	B, π*, Y, AC
361	AC	β, α	E, B	—	AN, DN	α, B, E_T
362	AC, BA	π*, β, α	P, B	W, $f(n^2)$	DN	β, α, π*
363	AC	π*, β, α	P, E, B	W, $f(n^2)$, W . $f(n^2)$	AN, DN	B, π*
364	BA	π*	Y	W . $f(n^2)$	—	BA
365	AC, BA	π*, β, α	Y, E	$f(n^2)$, W . $f(n^2)$	AN	BA, E, B, P, AC
366	AC	π*, α	Y, E, B	W	AN	AC, α, B
367	AC	α	P, E	W, W . $f(n^2)$	DN	E, P, π*, BA, Y
368	AC	β, α	E, B	—	AN, DN	B, E

TABLE XXIII

The multiple regression coefficients (*R*) and numbers of solvents (n) in Eqs (*8*), (*11*)—(*13*), (*18*), (*19*) — other processes. For numbers see Table XXI

No.	(*8*)	(*11*)	(*13*)	(*12*)	(*18*)	(*19*)
332	0·545 (15)	— —	0·790 (15)	0·802 (15)	— —	0·666 (14)
333	— —	— —	0·786 (13)	0·930 (14)	— —	0·896 (13)
334	0·881 (13)	0·929 (12)	0·900 (11)	0·859 (13)	0·761 (13)	0·913 (12)
335	— —	— —	0·730 (11)	0·966 (13)	— —	0·933 (12)
336	0·726 (17)	0·869 (17)	0·928 (16)	0·972 (17)	0·993 (12)	0·600 (14)
337	0·725 (17)	0·904 (17)	0·876 (16)	0·888 (17)	0·979 (12)	0·626 (14)
338	0·703 (21)	0·774 (21)	0·833 (20)	0·988 (21)	0·944 (15)	0·561 (16)
339	0·751 (20)	0·845 (20)	0·830 (19)	0·930 (20)	0·959 (14)	0·677 (15)
340	— —	— —	0·818 (14)	0·967 (14)	— —	0·956 (14)
341	0·628 (14)	0·755 (13)	0·949 (14)	0·925 (14)	0·766 (14)	0·835 (14)
342	— —	— —	0·728 (9)	0·877 (12)	— —	0·852 (12)
343	0·856 (10)	0·970 (10)	0·661 (10)	0·920 (10)	— —	0·963 (10)
344	0·727 (10)	0·877 (10)	0·750 (10)	0·741 (10)	— —	0·917 (10)
345	0·910 (10)	0·906 (10)	0·677 (10)	0·910 (10)	0·722 (10)	0·910 (10)
346	0·780 (10)	0·812 (10)	— —	0·703 (10)	— —	0·944 (10)
347	0·880 (10)	0·951 (10)	0·703 (10)	0·876 (10)	— —	0·944 (10)
348	0·887 (10)	0·950 (10)	0·852 (10)	0·737 (10)	0·646 (10)	0·930 (10)
349	— —	0·908 (10)	0·940 (9)	0·821 (10)	— —	0·941 (10)
350	— —	0·570 (14)	— —	0·824 (14)	0·900 (9)	0·668 (11)
351	— —	0·936 (13)	0·913 (13)	0·692 (14)	0·886 (11)	— —
352	— —	— —	— —	0·758 (13)	— —	— —
353	0·847 (41)	0·826 (36)	0·870 (34)	0·848 (39)	0·802 (31)	0·748 (27)
354	0·864 (41)	0·850 (36)	0·878 (34)	0·858 (39)	0·852 (31)	0·756 (27)
355	— —	0·624 (36)	0·600 (34)	0·783 (39)	0·758 (31)	— —
356	0·732 (41)	0·810 (36)	0·785 (34)	0·792 (39)	0·884 (31)	0·501 (27)
357	0·906 (41)	0·850 (36)	0·914 (34)	0·933 (39)	0·822 (31)	0·849 (27)
358	0·902 (33)	0·895 (30)	0·900 (29)	0·907 (31)	0·841 (25)	0·828 (19)
359	— —	0·369 (35)	0·951 (34)	0·805 (39)	0·846 (28)	0·806 (24)
360	— —	— —	0·845 (34)	0·812 (39)	0·849 (28)	0·714 (24)
361	0·646 (40)	0·681 (35)	0·871 (34)	0·800 (39)	— —	0·831 (24)
362	— —	0·634 (34)	0·898 (33)	0·678 (38)	0·699 (27)	0·499 (24)
363	— —	0·379 (31)	0·884 (30)	0·832 (35)	0·850 (25)	0·781 (22)
364	0·410 (40)	0·631 (35)	0·613 (34)	0·519 (38)	0·645 (31)	— —
365	0·792 (44)	0·911 (39)	0·906 (37)	0·832 (42)	0·924 (32)	0·611 (26)
366	0·645 (44)	0·693 (39)	0·658 (37)	0·737 (42)	0·461 (32)	0·662 (26)
367	0·580 (28)	0·610 (26)	0·645 (26)	0·778 (27)	0·658 (23)	0·541 (21)
368	0·521 (21)	0·554 (19)	0·778 (20)	0·948 (20)	— —	0·910 (15)

solvent basicity. Similarly the potential of reduction of nitroanilines (Nos 343 – 348) is only slitghly correlated with the solvent acidity, for the *ortho* derivatives also with the solvent polarity. The half-wave potential of a ruthenium complex (No. 349) is indistinctly connected with the solvent basicity and polarity. The equivalent conductivity of the proton (No. 350) is practically independent of the solvent characteristics at the levels tested. The activity coefficient of 4-nitrobenzoyl chloride (No. 351) is affected by all properties of solvents in a complex way, but the correlations are not too significant.

The solubility of hydrogen chloride (No. 352) correlates only very slightly with the solvent basicity and/or polarity, the process cannot be described by the solvent parameters used, and the same is true of the other solubility parameters (Nos 353 to 358) which – on the other hand – are sometimes used as additional components of empirical equations (see e.g. refs[27,190]). Not much different is the situation with the characteristics obtained from the chromatographic and allied methods (Nos 359 – 366) and other measurements (Nos 367 and 368).

4.5. Evaluation of Applicability of Empirical Models

Although the solvent effects on processes in solutions are dealt with in a number of monographs focused either directly on solvents[2–6] or on some aspects of their action[7–13,321] as well as in a number of reviews (e.g. refs[14–17,27,34,105,157,160,172,322–334]), only little attention has been given to systematic evaluation of applicability of the solvent parameters. The applicability range is best studied for the parameters π^*, α, and β by Kamlet & Taft, which is documented by many original papers and reviews (for a survey see refs[16,27], further e.g. in refs[51,99,333–342]). Also relatively well evaluated is the applicability of the $E_T(30)$ parameter[6,10,14,30,69,70,343]. A rough idea about the applicability of the individual parameters can also be obtained from the tests carried out for the parameters newly suggested (e.g. refs[34,37,50]). No comparison of significant empirical solvent scales on the basis of an extensive data set including various processes in solutions has been carried out so far.

The evaluation of applicability of the equations by Reichardt & Dimroth (*8*), Swain et al. (*11*), Kamlet & Taft (*13*), Koppel & Palm (*12*), and of the parameter scales suggested by Bekárek et al. (*18*), Gutmann & Mayer (*19*) can make use of the results given in Parts 4.1. through 4.4. The equations mentioned were applied to interpretation of 368 experimental data series (122 electronic absorption and fluorescence spectroscopy, 32 infrared spectroscopy, 53 nuclear magnetic resonance spectroscopy, 11 electron paramagnetic resonance spectroscopy, 79 rate processes, 34 equilibrium processes, 37 other processes) including 5 828 data, which represents about 16 points per one series (17 electronic absorption and fluorescence spectroscopy, 13 IR spectroscopy, 17 NMR and EPR spectroscopy, 13 kinetics, 13 equilibria, 25 other processes). These data provide a rough survey of application of the individual experimental techniques to studies of the solvent effects and of the extent of the studies undertaken. The average numbers of the data used for one successful calculation (at least one statistically significant parameter) decrease in the sequence of the correlation equations: (*8*) – 16 points, (*12*) – 16 points, (*11*) – 15 points, (*13*) – 15 points, (*18*) – 13 points, and (*19*) – 12 points. With a sufficiently uniform selection of solvents within the solvent scale, the numbers given are sufficient (see Part 2.2.) for significant conclusions about all the correlation equations tested. Due to lack of parameters the calculation could not be carried out in 5·7% of cases with Eq. (*18*), 2·2% with Eq. (*12*), 1·9% with Eq. (*13*), 0·8% with Eq. (*19*), whereas the calculations with Eqs (*8*) and (*11*) were not limited by the parameters. The statistically insignificant correlation was found most frequently with Eq. (*8*) (25·3%) and Eq. (*19*) (25·2%) followed by Eqs (*18*) (15·0%), (*11*) (13·6%), and (*13*) (8·0%), the lowest proportion of failures was observed with Eq. (*12*) (3·6%). Except Eqs (*18*) and (*19*), the sequence given is a function of the number of regression parameters. From this point of view Eqs (*18*) and (*19*) appear to be of lower quality, which was also indicated by the previous analyses focused on the process type (Part 4.1. through 4.4.). According to the success determined by the standard deviations the average sequence reads as follows: Eq. (*13*) – 1·87, Eq. (*12*) – 2·18, Eq. (*11*) – 2·37, and Eq. (*8*) – 3·58.

The STEPWISE procedure failed in 2·7% of the cases, whereas in 2·4% of the cases there were not enough data available (with respect to the number of degrees of freedom) in the data set. The following sequence of frequences (%) of the individual solvent parameters has been found in the successful calculations: BASITY 17·5, π^* 16·3, ACITY 14·6, $E_T(30)$ 11·2, β 10·9, Y 9·8, B 8·6, α 4·3, P 3·4, E 3·4. On the basis of physical meaning of the parameters given it can be stated that the solvent effect on processes in solutions consists first of all of the solvent polarity followed by roughly the same contributions of acidity and basicity. The parameters by Swain et al. (ACITY, BASITY) and those by Kamlet & Taft (π^*, β) belong to the best ones. This conclusion is also confirmed by the order of measurements arranged according to the frequence of the first parameter selected by the STEPWISE method (the data in %): BASITY 14·5, β 13·0, π^* 11·6, ACITY 11·5, $E_T(30)$ 9·4, B 9·0, P 8·6, α 8·2, Y 8·1. Average number of the parameters selected by the STEPWISE method is 2·5. If it is taken into account that emprical correlation equations use a certain set of parameters in a selected combination chosen from several (in our case ten) parameters, then the number of the solvent parameters equal to three appears reasonable (see also Chap. 2.).

The significance of parameters in the individual empirical models can inter alia be evaluated from their shares in the resulting regression equation. The parameters ACITY and BASITY (Eq. (*11*)) occur roughly equally often (73·9 and 76·4%). The parameter π^* was statistically significant in 82·5% of the cases, whereas the α and β parameters in 51·2 and 51·5% of the cases, respectively (Eq. (*13*)). Thereform it can be concluded that the π^* parameter brings a great contribution to the overall success of this model. In the model equation (*12*) the occurrence of parameters was following: Y 68·6%, P 38·9%, E 57·1%, and B 39·5%, i.e. the polarity parameter is dominant again. In Eq. (*18*) the parameter W . f(n^2) prevailed in its frequence (60·3%) over the two remaining ones (W 48·5% and f(n^2) 47·5%), which indicates a good interpretation quality of the product term. In Eq. (*19*) the parameter AN was statistically significant in 78·4% of the cases in contrast to the lower occurrence of the DN parameter (44·7%), which is probably due also to a certain share of polarity involed in the AN parameter as compared with DN.

From the analysis carried out and from the results of the former Parts (4.1.–4.4.) it follows that the most appropriate model for interpretation of solvent effects on processes in solutions is that by Kamlet & Taft represented by Eq. (*13*), i.e. the basic version without the additional correction parameters. Very good results can be expected with application of the parameters ACITY and BASITY by Swain et al. (Eq. (*11*)) provided the equation is extended by a term describing the basicity (the β parameter of Eq. (*13*) being the best one for this purpose). The interpretation abilities of the other model equations tested, with regard to the number of parameters, are not comparable with the above-given two equations.

The evaluation presented depends undoubtedly on the data set used for testing. Therefore, the empirical correlation equations based on the empirical parameters obtained from spectral data will be preferred. As, however, the selection used reflects the frequence of studies of the solvent effect in the dependence on the type of processes, the conclusions given here are valid in the sense of practical applicability of the relations tested.

5. EMPIRICAL MODELS FOR DESCRIPTION OF PROCESSES IN MIXED SOLVENTS

A mixture of two or more individual solvents represents a medium which in its action does not behave additively in accordance with its composition but exhibits additional effects as a consequence of mutual interactions between the individual components of the solvent. This fact causes many difficulties during description and interpretation of effects of changes in composition of mixed solvents on processes in solutions, and therefore this field has been less studied than the effect of individual solvents. A survey can be found in some monographs[2,4,7,12,344] and other communications[332,345–349]. Most original papers are focused on measurements of dissociation constants and rate constants in binary (especially aqueous–organic) mixtures.

The description and interpretation of effect of a change in composition of binary solvent mixtures on processes in solutions are based, beside the theoretical approach, on two different concepts. The first one is derived from LFER in similar way as with individual solvents (see Part 2.1.). The methods based on this concept can be denoted as methods with empirical solvent parameters, these parameters being dependent on the components and composition of the mixture. Linear models are used for the correlations preferably. The second, more universal concept is based on the description of the result of a process in dependence on the composition of mixture. The application leads to linear or non-linear models having always a single variable – the composition of mixture. These methods can be denoted as methods without empirical solvent parameters.

5.1. METHODS WITH EMPIRICAL SOLVENT PARAMETERS

The empirical models for description of processes in mixed solvents which are based on the parameters characterizing the solvent have a great drawback as compared with those for the individual solvents: whereas there exist several tens of practically important individual solvents, the number of only binary mixtures of the most important solvents is substantially greater. In addition it is necessary to parametrically describe a sufficient number of concentration ratios. Determination of such an amount of parameters by means of model processes is almost impossible, and therefore semiempirical characteristics are often used, most often functions of relative permittivity (for tables see e.g. ref.[350]) or refractive index. If there is no significant mutual interaction between components of a binary solvent, then the results of measurements of a process in this solvent represent an additive function of the results obtained at the individual concentrations. As under these conditions the dielectrical and optical properties are additive, too, in principle it makes no difference whether the interpretation uses parameters adjusted with some model or semiempirical characteristics or even concentrations of one component. Such behaviour can be expected with the solvent mixtures unable of specific interactions. In the opposite case the function of relative permittivity represents an insufficient characteristics as it was shown e.g. by the measurements in "isodielectric" mixtures[351-354].

The first instance of definition of empirical parameters in description of effect of changes of binary solvents on the rate of solvolytic reactions was that by Grunwald & Winstein[108]. The form of the dependence is given in Eq. (*6*). The empirical parameter Y_{GW} exclusively describing the properties of the mixed solvent was defined as logarithm of the rate constant of solvolysis of tert.butyl chloride in the mixture of ethanol and water ($m = 1$), the standard state being represented by 80% aqueous ethanol ($Y_{GW} = 0$). A number of papers[109,110,116,117,179-184] studied the scope and limitations of Eq. (*6*) and analyzed the model reaction. Various modifications were also described in literature[121,355-358], particularly the combination with nucleophilicity according to Eq. (*7*). These facts indicate the importance of the equations mentioned for correlations of rate constants of solvolyses. The more general Eq. (*9*) by Swain et al.[185] and its special variant[359] have similar basis, but these equations did not prove practical.

The spectral methods used for parametrizations of individual solvents were also applied to binary mixtures. The values of Kosower's Z are known e.g. for the mixtures[52] water–organic solvent (methanol, ethanol, isopropyl alcohol, tert.butyl alcohol, acetone, dioxane), water–ethanol and water–dimethyl sulphoxide[360], methanol–2-methyl-2-butanol, methanol–pyridine, ethanol–2,2,2-trifluoroethanol[106]. Brownstein[61] determined the parameters for several mixtures with the same indicator. The parameters $E_T(30)$ and/or E_T^N by Reichardt & Dimroth are known for a large number of binary solvents[48,62,64,68,360–362]. The χ_R parameter defined by Brooker et al.[73] with merocyanines was determined for 7 mixtures (water–2,6-lutidine, water–pyridine, water–methanol, water–dioxane, 2,6-lutidine–methanol, 2,6-lutidine–methylcyclohexane, and dioxane–isooctane). The basicity parameter β by Kamlet & Taft, denoted also B_{KT} in mixed solvents, is known for a series of aqueous–organic mixtures[80,174,349,362–364]. The sum of the E_T^N and B_{KT} parameters denoted as IPP (ionizing power parameter) was also suggested[174,364] as a suitable characteristic of binary mixtures. Several examples of application of the DN parameter determined from calorimetric measurements to the interpretation of processes in mixed solvents can be found in ref.[4] (p. 133).

The attempts at linearization of the dependence of the $E_T(30)$ parameter on logarithm of molar concentration of the more polar component of binary solvent resulted in suggestion of Eq. (*20*) by Langhals[346,365]

$$E_T(30) = E_D \ln (c_p/c^* + 1) + E_T^0(30)\,, \qquad (20)$$

where E_D, c^*, and $E_T^0(30)$ are parameters and c_p is the concentration of more polar component of mixed binary solvent. The author generalized Eq. (*20*) to the form (*21*)

$$P_G = E_D \ln (c_p/c^* + 1) + P_G^0\,, \qquad (21)$$

where c^* is the parameter with the values determined from Eq. (*20*), P_G is the result of the process in mixed solvent, and P_G^0 and E_D are regression parameters. Although some aspects of this approach were criticized[366], the validity of Eq. (*21*) was demonstrated on 60 examples with mostly excellent results. Non-linear dependences were found for the mixtures water–dioxane ($E_T(30)$), water–ethanol ($E_T(30)$, Y, π^*), and 1-butanol–nitromethane ($E_T(30)$). The c^* parameter depends on the indicator used, which is a drawback[346] which can be removed by replacing the c^* parameter by the adjustable c^* parameter, of course, the linear equation is thereby transformed into a non-linear one. Instead of the linear regression, a non-linear one must be used with optimization of parameters. At the same time, Eq. (*21*) is transformed into an equation without empirical solvent parameters. Langhals[347] also showed the existence of a linear dependence between the function of refractive index and density in several aqueous–organic mixtures.

Numert[367] used the validity of relations of LFER type, particularly of the Brönsted equation, for prediction of pK of acids in any arbitrary medium. Benzoic acid and water were used as the standard acid and standard medium, respectively, and the results of these predictions were very good.

5.2. METHODS WITHOUT EMPIRICAL SOLVENT PARAMETERS

Methods of this type adopt the concentration of one component of binary mixture as the single variable (generally, the number of variables equals the number of components minus one). The aim of the methods is to find such a function which reflects the non-ideality of behaviour of the mixture in comparison with the ideal non-interacting mixture of the components. Experience shows (and this fact was also used by Langhals[346] when suggesting his equation) that behaviour of a mixture is predominantly governed by the more polar component within a large range. Therefore, e.g. it is possible to find relatively good linear dependences between logarithm of solvolysis rate constants and logairthm of water concentration in mixtures with high content of water and low content of organic component. These dependences, which can be described by Eq. (*22*)

$$\log k = \log k_0 + \bar{n} \log [H_2O] , \qquad (22)$$

where $[H_2O]$ means the actual water concentration and $\log k_0$ and $\bar{n}$ are the regression parameters, were used for interpretations of both kinetic[368-378] and equilibrium data[360,379,380].

Sytilin[345,381-383] based his approach on the idea of the existence of solvation equilibria between reactants and both components of binary solvent. The expression for the reaction rate constant has the form (*23*) under the presumption of formation of a 1 : 1 complex between the reactant and a solvent component

$$k_{obs} = k_P + (k_D - k_P) K[D]/(K[D] + [P]) , \qquad (23)$$

where k_{obs} denotes the rate constant observed in the mixture and k_D, k_P are the rate constants in pure components. K represents the equilibrium constant defined by Eq. (*24*)

$$K = [AD] [P]/([AP] [D]) , \qquad (24)$$

where $[P]$, $[D]$ are the concentrations of pure components in the mixture, and $[AD]$, $[AP]$ are concentrations of the respective complexes. The unknown parameters K, k_D, and k_P can be determined by optimization or, less precisely, by the linear regression of the reciprocal relation. Eq. (*23*) interprets the data of the several examples given very well.

Recently Achumov[384] published a study dealing with solubility of compounds as a function of composition of binary solvent. The equation derived has the form (*25*)

$$y = y_1^0 x_1^{n_1} + y_2^0 x_2^{n_2}\,, \tag{25}$$

where y means the solubility in the mixture, y_1^0 and y_2^0 denote the solubilities in the pure components, x_1 and x_2 are mole fractions (or %) of the components, and n_1, n_2 are parameters. From the mathematical point of view, Eq. (*25*) appears to be flexible and able of good interpretation of experimental data. The success of the equation is documented with only one example. This approach appears to be more appropriate than the solution of the same problem in ref.[385].

Nagy & Herzfeld[386] suggested Eq. (*26*) for interpretation of the dependence of logarithm of rate constant of the exchange of amine in Schiff bases,

$$\log k = x_1 \log k_1 + x_2 \log k_2 + (a_k + b_k \gamma_1)\, x_1 x_2\,, \tag{26}$$

where k, k_1, and k_2 are the rate constants in the mixture and in pure components, x_1 and x_2 are mole fractions, γ_1 stands for the activity coefficient of the component 1, and a_k, b_k are parameters. The equation (*26*) gave the correlation coefficients close to 1 when applied to the empirical parameters E_T^N and B_{KT} in ethanol–cyclohexane and ethanol–benzene mixtures.

A non-parametrical description of effects of changes in composition of a binary (but also general) solvent can be based on the following presumptions[387]. Any physical or chemical process in solution is described by the difference of the Gibbs energy between the initial and final states. As there are less molecules undergoing the process as compared with the number of solvent molecules, in the first approximation it is possible to neglect the effect of the process on the solvent. If the process and the solvent are taken as two systems, then the effect of solvent on the process can be taken as the change of chemical potential during the process, hence

$$\mu^{\mathrm{after}} - \mu^{\mathrm{before}} = \bar{\alpha}\, \mu^{\mathrm{solvent}} \tag{27}$$

where the left hand side concerns the process, the right hand side concerns the solvent, and $\bar{\alpha}$ represents the coefficient of proportionality. By expressing the chemical potentials as the Gibbs energy changes with changes of composition, and after further modifications, it is possible to rewrite the above equation in the form (*28*)

$$\Delta G^{\mathrm{process}} = \bar{\alpha}\, \Delta G^{\mathrm{solvent}}\,. \tag{28}$$

This equation (*28*) expresses the dependence of the Gibbs energy change during the process on the change in composition of the solvent mixture. If we start from the pure components of the mixture as the standard state, then the Gibbs energy change during the process in the ideal mixture is a function of only the composition of mixture, and the non-ideality of the solution can be expressed by the so-called additional change of the Gibbs function.

The whole situation is expressed in Eq. (*29*)

$$\Delta G^{\text{process}} = \sum_{i=1}^{t} n_i \, \Delta G_{0i}^{\text{process}} + \bar{\alpha} \, \Delta G^{E} , \qquad (29)$$

where $\Delta G^{\text{process}}$ means the change of the Gibbs function during the process (given e.g. by $\log k$, $\log K$, $\tilde{\nu}$), $\Delta G_{0i}^{\text{process}}$ means the same value in the pure component i, n_i denotes the number of moles of the component i, t stands for the number of components, and ΔG^E is the additional change of the Gibbs function. The additional change of the Gibbs function in the dependence on composition of the liquid phase can be expressed by the Wohl empirical expansion[388] which generalizes a number of equations (Margules[389], van Laar[390], Null[391], Redlich–Kister[392] and others). Application of these classical equations to a series of experimental data[387] showed that, from practical point of view, it is the most advantageous to use the 3rd order linear equation by Margules (*30*)

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 (x_1 \, A_{21} + x_2 \, A_{12}) \qquad (30)$$

or the more perfect (but multiparameter) equation of the 4th order by Margules (*31*)

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 (x_1 \, A_{21} + x_2 \, A_{12} - x_1 x_2 \, D_{12}) \, . \qquad (31)$$

In Eqs (*30*) and (*31*) ΔG_{10} and ΔG_{20} concern the results of the process in pure components of the mixed binary solvent (they need not be known), A_{21}, A_{12}, D_{12} are parameters, x_1, x_2 are mole fractions of the components of the solvent.

5.3. EVALUATION OF APPLICABILITY OF EMPIRICAL MODELS TO DESCRIPTION OF PROCESSES IN MIXED SOLVENTS

For the reasons summarized in Part 5.1. it is impossible to mutually compare the methods with empirical parameters with a larger set of experimental data. Evaluation of the indiviudal methods can be found in the references quoted.

Mutual comparisons of some methods given in Part 5.2. are made possible by the results of Table XXIV obtained from a selected set of processes involving spectral (E_T^N, $\beta = B_{KT}$), kinetic ($\log k$ of solvolysis and quaternization), and equilibrium (pK_A) characteristics. The equations (*22*) and (*25*) were used in more general form (*32*) and (*33*)

$$\Delta G = \Delta G_0 + \bar{n} \log x(H_2O) , \quad x(H_2O) \geqq 0{\cdot}1 \qquad (32)$$

TABLE XXIV

The residual dispersion variances (s^2) and numbers of points (n) in the regression equations (*32*), (*33*), (*26*), and (*31*) obtained by application of spectral (Nos 1—20), kinetic (Nos 21—24), and equilibrium data (Nos 25—29) about processes in binary solvents

No.	Characteristics of the process[a]	Mixture components[b]	Residual dispersion variances, s^2					n	Ref.
			(*32*)	(*33*)	(*26*)	(*30*)	(*31*)		
1	E_T^N	MeOH–W	$2{\cdot}279 . 10^{-3}$	$3{\cdot}396 . 10^{-5}$	$1{\cdot}958 . 10^{-4}$	$3{\cdot}674 . 10^{-5}$	$1{\cdot}204 . 10^{-5}$	11	362
2	E_T^N	EtOH–W	$5{\cdot}654 . 10^{-3}$	$4{\cdot}632 . 10^{-4}$	$9{\cdot}043 . 10^{-4}$	$2{\cdot}176 . 10^{-4}$	$2{\cdot}261 . 10^{-5}$	11	362
3	E_T^N	PrOH–W	$8{\cdot}414 . 10^{-3}$	$2{\cdot}103 . 10^{-3}$	$3{\cdot}249 . 10^{-3}$	$1{\cdot}650 . 10^{-3}$	$6{\cdot}664 . 10^{-4}$	11	362
4	E_T^N	i-PrOH–W	$8{\cdot}613 . 10^{-3}$	$1{\cdot}722 . 10^{-3}$	$2{\cdot}619 . 10^{-3}$	$1{\cdot}004 . 10^{-3}$	$2{\cdot}310 . 10^{-4}$	11	362
5	E_T^N	AN–W	$2{\cdot}406 . 10^{-3}$	$3{\cdot}577 . 10^{-4}$	$2{\cdot}845 . 10^{-3}$	$2{\cdot}840 . 10^{-4}$	$2{\cdot}558 . 10^{-4}$	11	362
6	E_T^N	DMSO–W	$9{\cdot}679 . 10^{-3}$	$3{\cdot}435 . 10^{-4}$	$4{\cdot}451 . 10^{-4}$	$1{\cdot}031 . 10^{-4}$	$3{\cdot}170 . 10^{-5}$	11	362
7	E_T^N	DMF–W	$8{\cdot}699 . 10^{-3}$	$6{\cdot}458 . 10^{-4}$	$9{\cdot}419 . 10^{-4}$	$2{\cdot}238 . 10^{-4}$	$3{\cdot}714 . 10^{-5}$	11	362
8	E_T^N	A–W	$5{\cdot}483 . 10^{-3}$	$1{\cdot}229 . 10^{-3}$	$2{\cdot}530 . 10^{-4}$	$3{\cdot}352 . 10^{-3}$	$8{\cdot}905 . 10^{-5}$	11	362
9	E_T^N	THF–W	$1{\cdot}053 . 10^{-2}$	$4{\cdot}071 . 10^{-3}$	$6{\cdot}709 . 10^{-3}$	$1{\cdot}223 . 10^{-3}$	$7{\cdot}348 . 10^{-4}$	11	362
10	E_T^N	D–W	$9{\cdot}109 . 10^{-3}$	$1{\cdot}955 . 10^{-3}$	$3{\cdot}010 . 10^{-3}$	$7{\cdot}361 . 10^{-4}$	$2{\cdot}644 . 10^{-4}$	11	362
11	β	MeOH–W	$7{\cdot}569 . 10^{-3}$	$6{\cdot}304 . 10^{-4}$	$7{\cdot}186 . 10^{-4}$	$3{\cdot}944 . 10^{-4}$	$2{\cdot}063 . 10^{-4}$	11	362
12	β	EtOH–W	$1{\cdot}324 . 10^{-2}$	$8{\cdot}787 . 10^{-4}$	$1{\cdot}983 . 10^{-3}$	$6{\cdot}668 . 10^{-4}$	$6{\cdot}798 . 10^{-4}$	11	362
13	β	PrOH–W	$1{\cdot}661 . 10^{-2}$	$1{\cdot}551 . 10^{-4}$	$5{\cdot}930 . 10^{-3}$	$2{\cdot}272 . 10^{-3}$	$1{\cdot}142 . 10^{-3}$	11	362

14	β	i-PrOH-W	1·632 . 10^{-2}	1·513 . 10^{-4}	4·022 . 10^{-3}	1·790 . 10^{-3}	1·997 . 10^{-4}	11	362
15	β	AN-W	4·299 . 10^{-3}	1·146 . 10^{-4}	1·023 . 10^{-3}	8·302 . 10^{-4}	1·709 . 10^{-4}	11	362
16	β	DMSO-W	9·059 . 10^{-3}	9·600 . 10^{-5}	6·197 . 10^{-4}	6·411 . 10^{-4}	9·324 . 10^{-5}	11	362
17	β	DMF-W	1·395 . 10^{-2}	1·418 . 10^{-2}	1·546 . 10^{-3}	3·719 . 10^{-4}	2·171 . 10^{-4}	11	362
18	β	A-W	1·028 . 10^{-2}	1·506 . 10^{-4}	2·016 . 10^{-3}	6·540 . 10^{-4}	4·935 . 10^{-4}	11	362
19	β	THF-W	1·013 . 10^{-2}	1·065 . 10^{-3}	1·006 . 10^{-2}	5·593 . 10^{-3}	2·339 . 10^{-3}	11	362
20	β	D-W	1·012 . 10^{-2}	7·359 . 10^{-4}	7·127 . 10^{-4}	6·548 . 10^{-4}	3·023 . 10^{-4}	11	362
21	Y_{GW}	EtOH-W	2·059 . 10^{-1}	1·368 . 10^{-2}	1·616 . 10^{-2}	8·202 . 10^{-3}	4·627 . 10^{-3}	11	108
22	Y_{GW}	MeOH-W	9·575 . 10^{-2}	4·585 . 10^{-4}	1·164 . 10^{-3}	5·607 . 10^{-4}	2·328 . 10^{-4}	11	108
23	log k_S	A-W	2·385 . 10^{-1}	1·596 . 10^{-2}	1·713 . 10^{-1}	9·486 . 10^{-3}	8·459 . 10^{-3}	17	368
24	log k_M	c-Hx-A	—	1·479 . 10^{-1}	1·035 . 10^{0}	4·602 . 10^{-1}	2·324 . 10^{-1}	13	393
25	pK_{AA}	MeOH-W	2·602 . 10^{-2}	9·386 . 10^{-1}	9·829 . 10^{-2}	4·233 . 10^{-2}	1·526 . 10^{-2}	40	367, 394—397
26	pK_{AA}	EtOH-W	3·535 . 10^{-2}	7·491 . 10^{-2}	9·125 . 10^{-2}	1·735 . 10^{-2}	6·525 . 10^{-3}	41	367, 394, 395, 398—400
27	pK_{AA}	DMSO-W	1·131 . 10^{-1}	2·921 . 10^{-3}	4·917 . 10^{-2}	4·684 . 10^{-3}	1·485 . 10^{-3}	23	401—408
28	pK_{AA}	DMF-W	1·511 . 10^{-1}	1·179 . 10^{-1}	1·494 . 10^{-1}	1·609 . 10^{-1}	1·764 . 10^{-1}	15	401—404, 409—210
29	pK_{AA}	A-W	8·525 . 10^{-2}	4·884 . 10^{-1}	4·951 . 10^{-1}	1·374 . 10^{-1}	6·516 . 10^{-2}	22	395, 409, 411, 412

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[a] E_T^N, Y_{GW} see Part 5·1., k_S solvolysis rate constant of isopropyl benzenesulphonate, k_M rate constant of the reaction of triethylamine with ethyl iodide at 333·45 K, pK_{AA} is pK_a of acetic acid; [b] MeOH — methanol, W — water, EtOH — ethanol, PrOH — 1-propanol, i-PrOH — 2-propanol, AN — acetonitrile, DMSO — dimethyl sulphoxide, DMF — dimethylformamide, A — acetone, THF — tetrahydrofurane, D — 1,4-dioxane, c-Hx — cyclohexane.

$$\Delta G = G_1^0 x_1^{n_1} + G_2^0 x_2^{n_2}\,, \qquad (33)$$

where x means the mole fraction of the solvent. As it can be seen from Table XXIV Eq. (*31*) provides the best results and Eq. (*32*) the worst ones. This statement can be documented with the average order of successfulness: Eq. (*31*) 1·4, Eq. (*33*) 2·5, Eq. (*30*) 2·6, Eq. (*26*) 3·9, and Eq. (*32*) 4·6.

The results provided by Eqs (*22*) and (*32*) within the mole fraction range up to $x = 0{\cdot}9$ of the organic solvent show the dominant role of the more polar component (water) in the process. At higher concentrations of the organic solvent the results become worse, and the calculations with the values valid in the pure organic solvent cannot be carried out (logarithm of zero). These drawbacks are removed to a certain extent by Eq. (*21*) whose quantity c* represents a further adjustable parameter c^*. However, its application to the processes of Table XXIV exhibited, in some cases, a high correlation between the parameters E_D and c^*, which prevented the optimization, and therefore the results are not given. The optimization of parameters in Eq. (*25*) presented no difficulties with the test data. Eqs (*26*), (*30*), and (*31*) form a group based on the description making use of the additional Gibbs function. According to expectation, the success depends on the number of the regression parameters[387]. The undoubted advantage of this description lies in the linearity of the dependence which enables (after multiplication) application of multiple linear regression. The equation (*23*) was tested with kinetic data (Nos 21–24, Table XXIV). In all the cases either the k_D parameter or the k_P parameter was negative, which is physically nonsensical. Fitting of experimental points with a regression curve exhibited bad quality in the criterion of regular alternation of positive and negative deviations. The optimization ensuring positive values of all parameters led to a further increase of residual variance.

From the analysis given it follows that the method based on empirical interpretation of the Gibbs additional function is the most appropriate one for description of the change of the process result with the change of composition of a mixed solvent. Out of the possible equations adopting this approach the linear equations (after multiplication) (*26*), (*30*) or (*31*) can be recommended. The choice should respect the required quality of interpretation in combination with the number of experimental points (see Part 2.2.).

LIST OF SYMBOLS AND ABBREVIATIONS

A	regression parameter
$\bar{A}$	result of a process in solvent
$\bar{A}_0$	regression parameter
A_{12}, A_{21}	regression coefficients
$\mathscr{A}_N$	also a^{14N}, solvent parameter (Knauer, Napier, Paragraph 3.1.3.)
AC, ACITY	solvent parameter (Swain et al., Part 3.5.)

AN	solvent parameter (Mayer, Gutmann et al., Paragraph 3.1.3.)
AP	solvent parameter (Svoboda et al., Part 3.5.)
a	regression coefficient
$a(\mathrm{H})$, $a(^{14}\mathrm{N})$	hyperfine splitting constants in EPR
$\mathrm{a_k}$	solvent parameter of mixed solvent (Nagy, Herzfeld, Part 5.2.)
$\mathrm{a^{14N}}$	also $\mathscr{A}_\mathrm{N}$, solvent parameter (Knauer, Napier, Paragraph 3.1.3.)
B	solvent parameter (Koppel, Palm, Paragraph 3.1.2)
B	regression coefficient
$\mathrm{B_{KT}}$	also β, solvent parameter (Kamlet, Taft, Paragraph 3.1.1.)
BA, BASITY	solvent parameter (Swain et al., Part 3.5.)
BC(DEF)	solvent parameter (Cramer, Part 3.5.)
BP	solvent parameter (Svoboda et al., Part 3.5.)
b	regression coefficient
$\mathrm{b_k}$	solvent parameter of mixed solvent (Nagy, Herzfeld, Part 5.2.)
C	regression coefficient
$\mathrm{C_B}$	solvent parameter (Drago)
CT	charge transfer
c	regression coefficient
c*	solvent parameter of mixed solvent (Langhals, Part 5.1.)
c^*	regression coefficient (Langhals, Part 5.1.)
c_p	the concentration of more polar component of a binary solvent (Langhals, Part 5.1.)
$\mathrm{c_1}$, $\mathrm{c_2}$	sensitivity parameters (Swain et al., Paragraph 3.7.2.)
D	regression coefficient
$\mathrm{D_{I,II}}$	solvent parameter (Selbin, Chap. 3.1.1.)
$\mathrm{D_1}$	also $-\Delta G^0_{\mathrm{OCH_3}}$, solvent parameter (Eliel et al., Part 3.3.)
D_{12}	regression coefficient
DN	solvent parameter (Gutmann, Part 3.4.)
d	regression coefficient
$\mathrm{d_1}$, $\mathrm{d_2}$	solvent parameters (Swain et al., Paragraph 3.7.2.)
E	solvent parameter (Koppel, Palm, Paragraph 3.7.3.)
$\mathrm{E_B}$	solvent parameter (Drago)
$\mathrm{E_{CT}}$	solvent parameter (Davis, Paragraph 3.1.1.)
E_D	regression coefficient (Langhals, Part 5.1.)
$\mathrm{E_k}$	solvent parameter (Walther, Paragraph 3.1.1.)
$E_\mathrm{p}^\mathrm{red}$	reduction potential of polarized electrode
$\mathrm{E_T}$, $\mathrm{E_T(30)}$	solvent parameter (Reichardt, Dimroth, Paragraph 3.1.1.)
$E_\mathrm{T}^0(30)$	regression parameter (Langhals)
$\mathrm{E_T(MPI)}$, $\mathrm{E_T(SB)}$	solvent parameters (Štrop et al., Paragraph 3.1.1.)
$\mathrm{E_T^{SO}}$	solvent parameter (Walther, Paragraph 3.1.1.)
$E_{1/2}$	half-wave potential
EP	solvent parameter (Svoboda et al., Part 3.5.)
EPR	electron paramagnetic resonance
ETR	extrathermodynamic relationships
e	regression coefficient
F	also Φ, solvent parameter (Dubois, Paragraph 3.1.1.)
FA	factor analysis
$f(\ )$	function
$\mathrm{f(n^2)}$	solvent parameter, $\mathrm{f(n^2)} = (n^2 - 1)/(2n^2 + 1)$
G	solvent parameter (Allerhand, Schleyer, Paragraph 3.1.2.)

ΔG, $\Delta G^{\mathrm{process}}$	change in energy of a system during a process; change in the Gibbs energy during a process
ΔG^{E}	additional change of the Gibbs energy (function)
ΔG^{solv}	change of the Gibbs energy of solvent with the composition change
ΔG_0	change in the energy of a system during a process in the standard state; the Gibbs energy change in the standard state
ΔG^0_{vp}	standard Gibbs energy of evaporation
$\Delta G^{\ddagger}$	activation Gibbs energy
$\mathit{\Delta}\,\Delta G$	change in the Gibbs energy with a change in conditions
$-\Delta \mathrm{G}^0$	solvent parameter (Llor, Cortijo, Part 3.3.)
$-\Delta \mathrm{G}^0_{\mathrm{OCH_3}}$	also D_1, solvent parameter (Eliel, Part 3.3.)
ΔH	enthalpy change during a process
I	retention index
$\Delta \mathrm{I}^{\mathrm{Cl/Br}}_{50}$	solvent parameter (Kováts, Part 3.4.)
IR	infrared spectroscopy
i	index
J	coupling constant in NMR spectroscopy
K	equilibrium constant
k	rate constant
$\log k_0$	regression parameter
LFER	linear free energy relationships
LSER	linear solvation energy relationships
l	regression coefficient
m	regression coefficient (Grunwald, Winstein, Paragraph 3.7.1.)
N	number of conditions of a process
N	nucleophilicity parameter
NMR	nuclear magnetic resonance
n	number of solvents in regression calculations
n	refractive index
$\bar{n}$	regression coefficient
(n)	the n-th total differential
n_{i}	mole number of the i-th component in a mixed solvent
n_1, n_2	power parameters
P	solvent parameter, $\mathrm{P} = (n^2 - 1)/(n^2 + 1)$ (Koppel, Palm, Paragraph 3.7.3.)
P	condition of a process
P	general solvent parameter
P′	solvent parameter (Rohrschneider, Part 3.4.)
$\mathit{\Delta} P$	process condition change
P_{G}	process result in mixed solvent (Langhals, Part 5.1.)
P^0_{G}	regression parameter (Langhals, Part 5.1.)
PCA	principal component analysis
PLS	partial least squares method
PP	solvent parameter (Svoboda et al., Part 3.5.)
Py	solvent parameter (Dong, Paragraph 3.1.1.)
p	regression coefficient
Q	process result in solvent
q_0, q_1	regression parameters
R	multiple correlation coefficient
RPM	solvent parameter (Dähne, Paragraph 3.1.1.)

r	correlation coefficient
S	entropical term (Krygowski, Fawcet, Paragraph 3.7.2.)
S	aromatic selectivity
S_1	solvent parameter (Zelinskii, Paragraph 3.1.1.)
S_2	solvent parameter (Brownstein, Paragraph 3.1.1.)
$\mathcal{S}$	solvent parameter (Drougard, Decroock, Part 3.2.)
STEPWISE	a statistical regression method (Chap. 4.)
s	regression coefficient
s^2	residual dispersion variance
T	temperature
t	number of components in mixed solvents
V_m	molar volume
VARIMAX	a criterion and method of transformation of variables
W	solvent parameter (Bekárek, Paragraph 3.1.1.)
X	solvent parameter (Gielen, Nasielski, Part 3.2.)
XYZ	process result in solvent
XYZ_0	regression parameter
x	mole fraction
Y	solvent parameter (Koppel, Palm, Paragraph 3.7.3.)
Y	process result in solvent
Y_{GW}	solvent parameter (Grunwald, Winstein, Parts 3.2. and 5.1.)
$\mathrm{y}, \mathrm{y}_1^0, \mathrm{y}_2^0$	solubilities of solutes in binary solvent
y	regression coefficient
Z	solvent parameter (Kosower, Paragraph 3.1.1.)
α	solvent parameter (Kamlet, Taft, Paragraph 3.1.1.)
α	regression coefficient
$\bar{\alpha}$	coefficient of proportionality
α_m	solvent parameter α for solvents acting as monomers
β	solvent parameter (Kamlet, Taft, Paragraph 3.1.1.)
β	regression coefficient
β_m	solvent parameter β for solvents acting as monomers
γ	activity coefficient
Δ	a change with a change in conditions
δ	solvent parameter of solubility (Part 3.4.)
δ	polarizability correction term (Kamlet, Taft, Paragraph 3.1.1.)
δ_H	solvent parameter (Hildebrand, Part 3.4.)
$\delta^1\mathrm{H}, \delta^{19}\mathrm{F}$	chemical shifts in NMR spectra
δ^2	solvent parameter (Makitra, Pirig, Part 3.6.)
ε	relative permittivity
$\varepsilon_0, \varepsilon_{\mathrm{Al_2O_3}}$	solvent parameter (Snyder, Part 3.4.)
$\hat{\eta}$	solvent parameter (Kupfer, Part 3.4.)
ϑ_1, ϑ_2	statistical quantities characterizing solvent (Sjöström, Wold, Part 3.5.)
Λ	equivalent conductivity
λ	wavelength
μ	chemical potential
$\tilde{\nu}$	wavenumber in IR spectra
ξ	correction term of a parameter (Kamlet, Taft, Paragraph 3.1.2.)
π^*	solvent parameter (Kamlet, Taft, Paragraph 3.1.1.)
π_m^*	solvent parameter π^* for solvents acting as monomers

σ^*	substitution parameter for inductive contribution
Φ	also F, solvent parameter (Dubois, Paragraph 3.1.1.)
χ_B, χ_R	solvent parameters (Brooker, Paragraph 3.1.1.)
χ_e, χ_d, χ_n, χ_t, χ_m	selectivity
χ^n	the *n*-th order connectivity
Ω	solvent parameter (Berson, Part 3.2.)
ω	solvent parameter (Taft, Paragraph 3.7.3.)
$\int_H^{p\text{-}NO}$	solvent parameter (Taft, Table III)
^{0}	standard state

REFERENCES

1. Menschutkin N.: Z. Phys. Chem. *6*, 41 (1890).
2. Amis E. S., Hinton J. F.: *Solvent Effects on Chemical Phenomena*, Vol. 1. Academic Press, New York 1973.
3. Buckingham A. D., Lippert E., Bratos S. (Eds): *Organic Liquids. Structure Dynamics, and Chemical Properties.* Wiley, New York 1978.
4. Gutmann V.: *The Donor-Acceptor Approach to Molecular Interactions.* Plenum Press, New York 1978.
5. Popovych O., Tomkins R. P. T.: *Nonaqueous Solution Chemistry.* Wiley, New York 1981.
6. Reichardt C.: *Solvent Effects in Organic Chemistry.* Verlag Chemie, Weinheim 1979.
7. Schwetlik K.: *Kinetische Methoden zur Untersuchung von Reaktionsmechanismen*, Chap. 5. VEB Deutscher Verlag der Wissenschaften, Berlin 1971.
8. Palm V. A.: *Osnovy kolichestvennoi teorii organicheskikh reaktsii.* Khimiya, Leningrad 1977.
9. Kamlet M. J., Abboud J. L. M., Taft R. W.: Prog. Phys. Org. Chem. *13*, 485 (1981).
10. Reichardt C. in the book: *Molecular Interactions* (H. Ratajczak and W. J. Orville-Thomas, Eds), Vol. 3. Wiley, New York 1982.
11. Shorter J.: *Correlation Analysis of Organic Reactivity*, Chap. 5. Wiley, New York 1982.
12. Burger K.: *Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents.* Akadémiai Kiadó, Budapest 1983.
13. Modena G., Paradisi C., Scorano G. in the book: *Studies in Organic Chemistry* (F. Bernardi, I. G. Csizmadia and A. Mangini, Eds), Vol. 19, p. 568. Elsevier, Amsterdam 1985.
14. Reichardt C.: Pure Appl. Chem. *54*, 1867 (1982).
15. Marcus Y.: J. Solution Chem. *13*, 599 (1984).
16. Taft R. W., Abboud J.-L. M., Kamlet M. J., Abraham M. H.: J. Solution Chem. *14*, 153 (1985).
17. Abraham M. H.: Pure Appl. Chem. *57*, 1055 (1985).
18. Born M.: Z. Phys. *1*, 45 (1920).
19. Buttcher C. J. F.: *Theory of Electric Polarization* (revised by O. C. Van Belle, P. Bordewijk). Elsevier, Amsterdam 1973.
20. Block M., Walker S. M.: Chem. Phys. Lett. *19*, 363 (1973).
21. Liptay W.: Z. Naturforsch., A *20*, 272 (1965).
22. Abraham R. J.: J. Phys. Chem. *73*, 1192 (1969).
23. Bakhshiev N. G.: *Spektroskopiya mezhmolekulyarnych vzaimodeistvii.* Nauka, Leningrad 1972.
24. Došen-Mićović L., Žigman V.: J. Chem. Soc., Perkin Trans. 2, *1985*, 625.
25. Bekárek V.: J. Phys. Chem. *85*, 722 (1981).
26. Sjöström M., Wold S.: Acta Chem. Scand., B *35*, 537 (1981).
27. Kamlet M. J., Taft R. W.: Acta Chem. Scand., B *39*, 611 (1985).

28. Grunwald E.: J. Am. Chem. Soc. *106*, 5414 (1984).
29. Wold S.: Chem. Scr. *5*, 97 (1974).
30. Reichardt C.: Wiadomosci Chem. *35*, 339 (1981).
31. Fawcett W. R., Krygowski T. M.: Can. J. Chem. *54*, 3283 (1976).
32. Sjöström M., Wold S.: J. Chem. Soc., Perkin Trans. 2, *1981*, 104.
33. Carlson R., Lundstedt T., Albano C.: Acta Chem. Scand., B *39*, 79 (1985).
34. Swain C. G., Swain M. S., Powel A. L., Alunni S.: J. Am. Chem. Soc. *105*, 502 (1983).
35. Elguero J., Fruchier A.: Ann. Quim., C *79*, 72 (1983).
36. Chastrette M., Rajzmann M., Chanon M., Purcell K. F.: J. Am. Chem. Soc. *107*, 1 (1985).
37. Svoboda P., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *48*, 3287 (1983).
38. Coetzee J. F., Ritchie C. D. (Eds): *Solute-Solvent Interactions*, Vol. I. 1969; Vol. II, 1976. Dekker, New York.
39. Gordon J. E.: *The Organic Chemistry of Electrolyte Solutions*. Wiley, New York 1975.
40. Koppel I. A., Palm V. A. in the book: *Advances in Linear Free Energy* (N. B. Chapman and J. Shorter, Eds), p. 203. Plenum Press, London 1972.
41. Swain C. G.: J. Org. Chem. *49*, 2005 (1984).
42. Marcus Y.: Pure Appl. Chem. *57*, 1103 (1985).
43. Bekárek V., Stolařová M.: Collect. Czech. Chem. Commun. *48*, 1237 (1983).
44. Bekárek V.: J. Chem. Soc., Perkin Trans. 2, *1983*, 1293.
45. Bekárek V.: Collect. Czech. Chem. Commun. *49*, 2332 (1984).
46. Bekárek V.: J. Chem. Soc., Perkin Trans. 2, *1986*, 1425.
47. Dixon W. J. (Ed.): *BMDP — Biomedical Computer Programs*. University of California Press, Los Angeles 1983.
48. Reichardt C., Harbusch-Görnert E.: Liebigs Ann. Chem. *1983*, 721.
49. Kamlet M. J., Abboud J.-L. M., Abraham M. H., Taft R. W.: J. Org. Chem. *48*, 2877 (1983).
50. Bekárek V., Bekárek V.: Collect. Czech. Chem. Commun. *52*, 287 (1987).
51. Abboud J.-L. M., Taft R. W., Kamlet M. J.: J. Chem. Soc., Perkin Trans. 2, *1985*, 815.
52. Kosower E. M.: J. Am. Chem. Soc. *80*, 3252 (1958).
53. Kosower E. M.: J. Chim. Phys. *61*, 230 (1964).
54. Kosower E. M.: Prog. Phys. Org. Chem. *3*, 81 (1965).
55. Kosower E. M., Mohamad M.: J. Am. Chem. Soc. *90*, 3271 (1968).
56. Mohamad M., Kosower E. M.: J. Phys. Chem. *74*, 1153 (1970).
57. Kosower E. M., Mohamad M.: J. Am. Chem. Soc. *93*, 2713 (1971).
58. Walling C., Wagner P. J.: J. Am. Chem. Soc. *86*, 3368 (1964).
59. Griffiths T. R., Pugh D. C.: J. Solution Chem. *8*, 247 (1979).
60. Griffiths T. R., Symons M. C. R.: Trans. Faraday Soc. *56*, 1125 (1960).
61. Brownstein S.: Can. J. Chem. *38*, 1590 (1960).
62. Dimroth K., Reichardt C., Siepman T., Bohlman F.: Liebigs Ann. Chem. *661*, 1 (1963).
63. Reichardt C.: Angew. Chem. *77*, 30 (1965).
64. Dimroth K., Reichardt C.: Z. Anal. Chem. *215*, 344 (1966).
65. Reichardt C., Dimroth K.: Fortschr. Chem. Forsch. *11*, 1 (1968).
66. Dimroth K., Reichardt C.: Liebigs Ann. Chem. *727*, 93 (1969).
67. Reichardt C.: Liebigs Ann. Chem. *752*, 64 (1971).
68. Maksimovič Z. B., Reichardt C., Spirič A.: Z. Anal. Chem. *270*, 100 (1974).
69. Reichardt C.: Angew. Chem. *91*, 119 (1979).
70. Johnson B. P., Gabrielsen B., Matulenko M., Dorsey J. G., Reichardt C.: Anal. Lett. *19*, 939 (1986).
71. Dubois J. E., Goetz E., Bienvenüe A.: Spectrochim Acta *20*, 1815 (1964).

72. Dubois J.-E., Bienvenüe A.: J. Chim. Phys. *65*, 1259 (1968).
73. Brooker L. G. S., Craig A. C., Heseltine D. W., Jenkins P. W., Lincoln L. L.: J. Am. Chem. Soc. *87*, 2443 (1965).
74. Davis K. M. C.: J. Chem. Soc., B *1967*, 1128.
75. Selbin J.: Chem. Rev. *65*, 153 (1965).
76. Walther D.: J. Prakt. Chem. *316*, 604 (1974).
77. Dähne S., Shob F., Nolte K.-D., Radeglia R.: Ukr. Khim. Zh. *41*, 1170 (1975).
78. Štrop P., Mikeš F., Kálal J.: J. Phys. Chem. *80*, 694 (1976).
79. Walter W., Bauer O. H.: Liebigs Ann. Chem. *1977*, 421.
80. Kamlet M. J., Taft R. W.: J. Am. Chem. Soc. *98*, 377 (1976).
81. Kamlet M. J., Jones M. E., Taft R. W., Abboud J.-L. M.: J. Chem. Soc., Perkin Trans. 2, *1979*, 342.
82. Taft R. W., Kamlet M. J.: J. Am. Chem. Soc. *98*, 2886 (1976).
83. Taft R. W., Kamlet M. J.: J. Chem. Soc., Perkin Trans. 2., *1979*, 1723.
84. Kamlet M. J., Abboud J.-L. M., Taft R. W.: J. Am. Chem. Soc. *99*, 6027 (1977).
85. Abboud J.-L. M., Kamlet M. J., Taft R. W.: J. Am. Chem. Soc. *99*, 8325 (1977).
86. Kamlet M. J., Hall T. N., Boykin J., Taft R. W.: J. Org. Chem. *44*, 2599 (1979).
87. Taft R. W., Abboud J.-L. M., Kamlet M. J.: J. Am. Chem. Soc. *103*, 1080 (1981).
88. Zhmyreva I. A., Zelinskii V. V., Kolobkov V. P., Krasnitskaya I. D.: Dokl. Akad. Nauk SSSR, Ser. Khim. *129*, 1089 (1959).
89. Davis K. M. C.: Nature *223*, 728 (1969).
90. Dong D. C., Winnik M. A.: Photochem. Photobiol. *35*, 17 (1982).
91. Allerhand A., Schleyer P.v.R.: J. Am. Chem. Soc. *85*, 371 (1963).
92. Allerhand A., Schleyer P.v.R.: J. Am. Chem. Soc. *86*, 5709 (1963).
93. Koppel I. A., Palm V. A.: Reakts. Sposobnost Organ. Soedin. (Tartu) *8*, 291 (1971).
94. Burden A. G., Collier G., Shorter J.: J. Chem. Soc., Perkin Trans. 2, *1976*, 1627.
95. Koppel I. A., Paju A. I.: Org. Reactiv. *11*, 121 (1904).
96. Aslam M. H., Collier G., Shorter J.: J. Chem. Soc., Perkin 2, *1981*, 1572.
97. Kamlet M. J., Solomonovici A., Taft R. W.: J. Am. Chem. Soc. *101*, 3734 (1979).
98. Taft R. W., Gramstad T., Kamlet M. J.: J. Org. Chem. *47*, 4557 (1982).
99. Kamlet M. J., Gal J. F., Maria P. C., Taft R. W.: J. Chem. Soc., Perkin Trans. 2, *1985*, 1583.
100. Taft R. W., Klingensmith G. B., Price E., Fox I. R.: *Pap. Symp.: Linear Free Energy Correlations, Durham 1964.*
101. Gurka D., Taft R. W.: J. Am. Chem. Soc. *91*, 4794 (1969).
102. Mayer V., Gutmann V., Gerger W.: Monatsh. Chem. *106*, 1235 (1975).
103. Mayer V., Gutmann V., Gerger W.: Monatsh. Chem. *108*, 489 (1977).
104. Gutmann V.: CHEMTECH *1977*, 255.
105. Mayer V.: Pure Appl. Chem. *51*, 1697 (1979).
106. Elias H., Dreher M., Neitzel S., Volz H.: Z. Naturforsch., B *37*, 684 (1982).
107. Knauer B. R., Napier J. J.: J. Am. Chem. Soc. *98*, 4395 (1976).
108. Grunwald E., Winstein S.: J. Am. Chem. Soc. *70*, 846 (1948).
109. Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *78*, 2770 (1956).
110. Smith S. G., Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *83*, 618 (1961).
111. Berson J. A., Hamlet Z., Mueller W. A.: J. Am. Chem. Soc. *84*, 297 (1962).
112. Gielen M., Nasielski J.: J. Organomet. Chem. *1*, 173 (1963).
113. Gielen M., Nasielski J.: J. Organomet. Chem. *7*, 273 (1967).
114. Lassau C., Jungers J.-C.: Bull. Soc. Chim. Fr. *1968*, 2678.
115. Drougard Y., Decroock D.: Bull. Soc. Chim. Fr. *1969*, 2972.

116. Winstein S., Grunwald E., Jones H. W.: J. Am. Chem. Soc. *73*, 2700 (1951).
117. Winstein S., Fainberg A. H., Grunwald E.: J. Am. Chem. Soc. *79*, 4146 (1957).
118. Bentley T. W., Schadt F. L., Schleyer P. v. R.: J. Am. Chem. Soc. *94*, 992 (1972).
119. Bentley T. W., Schleyer P. v. R.: J. Am. Chem. Soc. *98*, 7658 (1976).
120. Schadt F. L., Bentley T. W., Schleyer P. v. R.: J. Am. Chem. Soc. *98*, 7667 (1976).
121. Bentley T. W., Carter G. E.: J. Org. Chem. *48*, 579 (1983).
122. Peterson P. E., Vidrine D. W., Waller F. J., Henrichs P. M., Magaha S., Stevens B.: J. Am. Chem. Soc. *99*, 7968 (1977).
123. Llor J., Cortijo M.: J. Chem. Soc., Perkin Trans. 2, *1977*, 1111.
124. Eliel E. L.: Pure Appl. Chem. *25*, 509 (1971).
125. Eliel E. L., Enanoza R. M.: J. Am. Chem. Soc. *94*, 8072 (1972).
126. Eliel E. L., Hofer O.: J. Am. Chem. Soc. *95*, 8041 (1973).
127. Gutmann V., Wychera E.: Inorg. Nucl. Chem. Lett. *2*, 257 (1966).
128. Gutmann V.: Coord. Chem. Rev. *2*, 239 (1967).
129. Gutmann V., Scherhaufer A.: Monatsh. Chem. *99*, 335 (1968).
130. Gutmann V.: Chimia *23*, 285 (1969).
131. Gutmann V.: Electrochim. Acta. *21*, 661 (1976).
132. Olofson G., Lindquist I., Sunner S.: Acta Chem. Scand. *17*, 259 (1963).
133. Olofson G.: Acta Chem. Scand. *18*, 11 (1964).
134. Olofson G.: Acta Chem. Scand. *18*, 1022 (1964).
135. Olofson G., Olofson I.: J. Am. Chem. Soc. *95*, 7231 (1973).
136. Hildebrand J. H., Prausnitz J. M., Scott R. L.: *Regular and Related Solutions.* Van Nostrand-Reinhold, Princeton 1970.
137. Barton A. F. M.: Chem. Rev. *75*, 731 (1975).
138. Rohrschneider L.: Anal. Chem. *45*, 1241 (1973).
139. Snyder L. R.: J. Chromatogr. Sci. *16*, 223 (1978).
140. Snyder L. R. in the book: *Techniques of Chemistry* (E. S. Perry and A. Weissberger, Eds), Vol. 12, Chap. 2. Wiley, New York 1978.
141. Kováts E.: Z. Anal. Chem. *181*, 351 (1961).
142. Kováts E., Weis P. B.: Ber. Bunsenges. Phys. Chem. *69*, 812 (1965).
143. Kuss E.: Z. Angew. Phys. *7*, 372 (1955).
144. Kupfer M., Abraham W.: J. Prakt. Chem. *325*, 95 (1983).
145. Malinowski E. R., Howery D. G.: *Factor Analysis in Chemistry.* Wiley, New York 1980.
146. Überla K.: *Faktorenanalyse.* Springer, Berlin 1971.
147. Blahuš P.: *Faktorová analýza a její zobecnění.* SNTL, Praha 1985.
148. Lorber A., Wanger L. E., Kowalski B. R.: J. Chemometr. *1*, 19, (1987).
149. Wold S., Geladi P., Esbensen K., Öhman J.: J. Chemometr. *1*, 57 (1987).
150. De Ligny C. L., Van der Veen N. G.: Ind. Eng. Chem., Fundam. *15*, 336 (1976).
151. Bohle M., Kollecker W., Martin D.: Z. Chem. *17*, 161 (1977).
152. Chastrette M.: Tetrahedron *35*, 1441 (1979).
153. Chastrette M., Carretto J.: Tetrahedron *38*, 1615 (1982).
154. Chastrette M., Carretto J.: Can. J. Chem. *63*, 3492 (1985).
155. Cramer R. D.: J. Am. Chem. Soc. *102*, 1837 (1980).
156. Cramer R. D.: J. Am. Chem. Soc. *102*, 1879 (1980).
157. Maria P.-C., Gal J.-F., Franceschi J., Fargin E.: J. Am. Chem. Soc. *109*, 483 (1987).
158. Kirkwood J. G.: J. Chem. Phys. *2*, 351 (1934).
159. Taft R. W., Abboud J.-L. M., Kamlet M. J.: J. Org. Chem. *49*, 2001 (1984).
160. Fowler F. W., Katritzky A. R., Rutheford R. J. D.: J. Chem. Soc., B *1971*, 460.
161. Krygowski T. M., Czerminski J. B.: Wiadomosci Chem. *32*, 597 (1978).

162. Brady J. E., Carr P. W.: Anal. Chem. *54*, 1751 (1982).
163. Brady J. E., Carr P. W.: J. Phys. Chem. *86*, 3053 (1982).
164. Abboud J.-L. M., Taft R. W., Kamlet M. J.: J. Phys. Chem. *88*, 4414 (1984).
165. Bekárek V., Juřina J.: Collect. Czech. Chem. Commun. *47*, 1060 (1982).
166. Ehrenson S.: J. Am. Chem. Soc. *103*, 6036 (1981).
167. Kamlet M. J., Taft R. W.: J. Chem. Soc., Perkin Trans. 2, *1979*, 349.
168. Kamlet M. J., Carr P. W., Taft R. W., Abraham M. H.: J. Am. Chem. Soc. *103*, 6062 (1981).
169. Taft R. W., Pienta N. J., Kamlet M. J., Arnett E. M.: J. Org. Chem. *46*, 661 (1981).
170. Abraham M. H., Kamlet M. J., Taft R. W.: J. Chem. Soc., Perkin Trans. 2, *1982*, 923.
171. Kolling O. W.: Anal. Chem. *54*, 260 (1982).
172. Reichardt C. in the book: *Organic Liquids. Structure, Dynamics, and Chemical Properties* (A. D. Buckingham, E. Lippert and S. Bratos, Eds), Chap. 16. Wiley, New York 1978.
173. Krygowski T. M., Fawcett W. R.: J. Am. Chem. Soc. *97*, 2143 (1975).
174. Krygowski T. M., Radomski J. P., Rzeszowiak A., Wrona P. K., Reichardt C.: Tetrahedron *37*, 119 (1981).
175. Makitra R., Pirig J.: Org. Reactiv. *16*, 103 (1979).
176. Kier L. B., Hall L. H.: Eur. J. Med. Chem. *12*, 307 (1977).
177. Taft R. W., Gurka D., Joris L., Schleyer P. v. R., Rakshys J. W.: J. Am. Chem. Soc. *91*, 4801 (1969).
178. Joris L., Mitski J., Taft R. W.: J. Am. Chem. Soc. *94*, 3438 (1972).
179. Winstein S., Fainberg A. H.: J. Am. Chem. Soc. *79*, 5937 (1957).
180. Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *79*, 1597 (1957).
181. Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *79*, 1602 (1957).
182. Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *79*, 1608 (1957).
183. Winstein S., Fainberg A. H., Grunwald E.: J. Am. Chem. Soc. *79*, 5937 (1957).
184. Koppel I. A., Palm V. A.: Reakts. Sposobnost Organ. Soedin. (Tartu) *6*, 504 (1969).
185. Swain C. G., Mosely R. B., Bown D. E.: J. Am. Chem. Soc. *77*, 3731 (1955).
186. Krygowski T. M., Fawcett W. R.: Aust. J. Chem. *28*, 2115 (1975).
187. Koppel I. A., Paju A. I.: Org. Reactiv. *11*, 137 (1974).
188. Dougherty R. C.: Tetrahedron Lett. *1975*, 385.
189. Mayer U.: Monatsh. Chem. *109*, 775 (1978).
190. Mayer U.: Monatsh. Chem. *109*, 421 (1978).
191. Dimroth K., Arnoldy G., von Eicken S., Schiffler G.: Liebigs Ann. Chem. *604*, 221 (1957).
192. Mac Kay R. A., Poziomek E. J.: J. Am. Chem. Soc. *94*, 6107 (1972).
193. Kaminski L. S., Lamchen M.: J. Chem. Soc., B *1968*, 1085.
194. Ahmed W.: J. Chem. Educ. *56*, 795 (1979).
195. Blandamer M. J., Fox M. F.: Chem. Rev. *70*, 59 (1970).
196. Le Rosen A. L., Reid C. E.: J. Chem. Phys. *20*, 233 (1952).
197. Kolling O. W.: Anal. Chem. *53*, 54 (1981).
198. Mostasalvskii M. A., Ismailskii V. A.: Dokl. Akad. Nauk SSSR *142*, 600 (1962).
199. Davis M. M., Hetzer H. B.: Anal. Chem. *38*, 451 (1966).
200. Launay G., Wojtkowiak B.: Bull. Soc. Chim. Fr. *1969*, 3036.
201. Hayes W. P., Timmons C. J.: Spectrochim. Acta *21*, 529 (1965).
202. Burgess J.: Spectrochim. Acta A *26*, 1957 (1970).
203. Nagy O. B., Nagy J. B., Bruylants A.: J. Chem. Soc., Perkin Trans. 2, *1972*, 968.
204. Dupire S., Mulindabyuma J. M., Nagy J. B., Nagy O. B.: Tetrahedron *31*, 135 (1975).
205. Manuta D. M., Lees A. J.: Inorg. Chem. *22*, 3825 (1983).
206. Macovei V.: Rev. Roum. Chim. *20*, 1413 (1975).
207. Macovei V.: Rev. Roum. Chim. *21*, 193 (1976).

208. Macovei V.: Rev. Roum. Chim. *21*, 1137 (1976).
209. Macovei V.: Anal. Sti. Univ. „Al. I. Cuza", Iasi, Sect. Ib, *22*, 51 (1976).
210. Macovei V.: Anal. Sti. Univ. „Al. I. Cuza", Iasi, Sect. Ib, *22*, 61 (1976).
211. Macovei V.: Rev. Roum. Chim. *25*, 651 (1980).
212. Macovei V.: Rev. Roum. Chim. *26*, 1405 (1981).
213. Bayliss N. S., Mc. Rae E. G.: J. Phys. Chem. *58*, 1002 (1954).
214. Launay G., Wojtkowiak B., Krygowski T. M.: Can. J. Chem. *57*, 3065 (1979).
215. Suppan P.: J. Chem. Soc., A *1968*, 3125.
216. Yokoyama T., Taft R. W., Kamlet M. J.: Aust. J. Chem. *36*, 701 (1983).
217. Yokoyama T., Taft R. W., Kamlet M. J.: J. Am. Chem. Soc. *98*, 3233 (1976).
218. Minesinger R. R., Jones M. E., Taft R. W., Kamlet M. J.: J. Org. Chem. *42*, 1929 (1977).
219. Lutskii A. E., Bokharova U. U., Kanevskaya Z. I.: Zh. Obshch. Khim. *45*, 2731 (1975).
220. Fain V. Ya., Kliot L. Ya., Ivanov Ya. V., Zaitsev B. E.: Org. Reactiv. *20*, 467 (1983).
221. Fain V. Ya., Kliot L. Ya., Zaitsev B. E.: Org. Reactiv. *23*, 19 (1986).
222. Yokoyama I.: Aust. J. Chem. *29*, 1469 (1976).
223. Lutskii A. E., Bokharova V. V., Kreslavskaya M. R.: Zh. Obshch. Khim. *45*, 2276 (1975).
224. Kamlet M. J., Minesinger R. R., Kayser E. G., Aldridge M. H., Eastes J. W.: J. Org. Chem. *36*, 3852 (1971).
225. Lippert E.: Z. Elektrochem. *61*, 962 (1957).
226. Cowley D. J.: J. Chem. Soc., Perkin Trans. 2, *1975*, 287.
227. Moskal J., Moskal A., Pietrzycki W.: J. Chem. Soc., Perkin Trans 2, *1977*, 1893.
228. Popovych O., Rogers L. B.: J. Am. Chem. Soc. *81*, 4469 (1959).
229. Dilling W. L.: J. Org. Chem. *31*, 1045 (1966).
230. Rosenberg H. M., Eimutis E.: Spectrochim. Acta *22*, 1751 (1966).
231. Afifi A. A., Azen S. P.: *Statistical Analysis. A Computer Oriented Approach*, 2nd ed., Chap. 3.3. Academic Press, New York 1979.
232. Purcell K. F., Stikeleather J. A., Brunk S. D.: J. Am. Chem. Soc. *91*, 4019 (1969).
233. Agami C., Caillot M.: Bull. Soc. Chim. Fr. *1969*, 1990.
234. Josien M.-L., Leicknam J.-P., Fuson N.: Bull. Soc. Chim. Fr. *1958*, 188.
235. Gonzáles G., Clavijo E.: J. Chem. Soc., Perkin Trans. 2, *1985*, 1751.
236. Bellamy L. J., Williams R. L.: Trans. Faraday Soc. *55*, 14 (1959).
237. Bellamy L. J., Conduit C. P., Pace R. J., Williams R. L.: Trans. Faraday Soc. *55*, 1677) 1959).
238. Oi N., Coetzee J. F.: J. Am. Chem. Soc. *91*, 2478 (1969).
239. Oi N., Coetzee J. F.: J. Am. Chem. Soc. *91*, 2473 (1969).
240. Tanaka S., Tanabe K., Kamada H.: Spectrochim. Acta, A *23*, 209 (1967).
241. Taylor R. P., Kuntz I. D.: J. Am. Chem. Soc. *92*, 4813 (1970).
242. Anderson R. G., Symons M. C. R.: Trans. Faraday Soc. *65*, 2537 (1969).
243. Rogers M. T., Burdett J. L.: Can. J. Chem. *43*, 1516 (1965).
244. Mac Donald C. J., Schaefer T.: Can. J. Chem. *45*, 3157 (1967).
245. Giam C. S., Lyle J. L.: J. Am. Chem. Soc. *95*, 3235 (1973).
246. Taft R. W., Price E., Fox I. R., Lewis I. C., Anderson K. K., Davis G. T.: J. Am. Chem. Soc. *85*, 709 (1963).
247. Kravtsov D. N., Kvasov B. A., Fedin E. I., Faingor B. A., Golovtchenko L. S.: Izv. Akad. Nauk SSSR *1969*, 536.
248. Ochlobystina L. V., Chutoreckii V. M., Naumov A. D., Kessenych A. V.: Izv. Akad. Nauk SSSR *1972*, 545.
249. Uschold R. E., Taft R. W.: Org. Magn. Reson. *1*, 375 (1969).
250. Chawla B., Pollack S. K., Lebrilla C. B., Kamlet M. J., Taft R. W.: J. Am. Chem. Soc. *103*, 6924 (1981).

251. Ohta S.: Bull. Chem. Soc. Jpn. *59*, 1181 (1986).
252. Duthaler R. O., Roberts J. D.: J. Am. Chem. Soc. *100*, 4969 (1978).
253. Bloor E. G., Kidd R. G.: Can. J. Chem. *46*, 3425 (1968).
254, Erlich H. R., Popov A. I.: J. Am. Chem. Soc. *93*, 5620 (1971).
255. Erlich H. R., Roach E., Popov A. I.: J. Am. Chem. Soc. *92*, 4989 (1970).
256. Smith S. L., Ihrig A. M.: J. Chem. Phys. *46*, 1181 (1967).
257. Kubota S., Ikegami Y.: J. Phys. Chem. *82*, 2739 (1978).
258. Oakes J., Symons M. C. R.: Trans. Faraday Soc. *64*, 2579 (1968).
259. Brière R., Lemaire H., Rassat A.: Bull. Soc. Chim. Fr. *1965*, 3273.
260. Swain C. G., Dittmer D. C.: J. Am. Chem. Soc. *77*, 3924 (1955).
261. Peterson P. E., Kelley R. E., Belloli R., Sipp K. A.: J. Am. Chem. Soc. *87*, 5169 (1965).
262. Schleyer P. v. R., Fry J. L., Lam L. K. M., Lancelot C. J.: J. Am. Chem. Soc. *92*, 2542 (1970).
263. Brown H. C., Ravindranathan M., Chloupek F. J., Rothberg I.: J. Am. Chem. Soc. *100*, 3143 (1978).
264. Koppel I. A., Palm V. A.: Reakts. Sposobnost Organ. Soedin. (Tartu) *4*, 862 (1967).
265. Abraham M. H., Taft R. W., Kamlet M. J.: J. Org. Chem. *46*, 3053 (1981).
266. Abraham M. H., Grellier P. L.: J. Chem. Soc., Perkin Trans. 2, *1976*, 1735.
267. Matsui T., Tokura N.: Bull. Chem. Soc. Jpn *44*, 756 (1971).
268. von Halban H.: Z. Phys. Chem. *84*, 129 (1913).
269. Auriel M., Hoffmann E.: J. Am. Chem. Soc. *97*, 7433 (1975).
270. Reichardt C., Müller R.: Liebigs Ann. Chem. *1976*, 1953.
271. Kondo Y., Matsui T., Tokura N.: Bull. Chem. Soc. Jpn. *42*, 1037 (1969).
272. Mancini P. M. E., Martinéz R. D., Vottero L. R., Nudelman N. S.: J. Chem. Soc., Perkin Trans. 2, *1984*, 1133.
273. Zhu Zhong-Yuan, Sun Cheng-E, Han Te-Kang: J. Chem. Soc., Perkin Trans. 2, *1985*, 929.
274. Miller J., Parker A. J.: J. Am. Chem. Soc. *83*, 117 (1961).
275. Makitra R. G., Pirig Ya. N.: Org. Reactiv. *15*, 346 (1978).
276. Vorobev N. K., Tshishova E. A., Korshak V. V., Bekasova N. I., Komarova L. G.: Kinet Katal. *17*, 1420 (1976).
277. Chapman N. B., Dack M. R. J., Newman D. J., Shorter J., Wilkinson R.: J. Chem. Soc., Perkin Trans. 2, *1974*, 962.
278. Burden A. G., Chapman N. B., Duggua H. F., Shorter J.: J. Chem. Soc., Perkin Trans. 2, *1978*, 296.
279. Hubbard C. D., Harris Ill. D. L., Hooper D. W., Tucci A. F.: J. Chem. Soc., Faraday Trans. 1, *78*, 3619 (1982).
280. Cöster G., Pfeil E.: Chem. Ber. *101*, 4248 (1968).
281. Wong K. F., Eckert C. A.: Trans. Faraday Soc. *66*, 2313 (1970).
282. Blankenburg B., Fiedler H., Hampel M., Hauthal H. G., Just G., Kahlert K., Korn J., Müller K.-H., Pritzkow W., Reinhold Y., Röllig M., Sauer E., Schnurpfeil D., Zimmermann G.: J. Prakt. Chem. *316*, 804 (1974).
283. Clauss K.: Liebigs Ann. Chem. *722*, 110 (1969).
284. Oshima T., Nishioka R., Nagai T.: Bull. Chem. Soc. Jpn. *55*, 904 (1982).
285. Oshima T., Nagai T.: Bull. Chem. Soc. Jpn. *55*, 555 (1982).
286. Cherkasov R. A., Kutyrev G. A., Ovchinikov V. V., Pudovik A. N.: Zh. Obshch. Khim. *46*, 963 (1976).
287. Garnier F., Dubois J. E.: Bull. Soc. Chim. Fr. *1968*, 3797.
288. Yatsimirsky A. K., Ryabor A. D., Zogorodnikov V. P., Sakodinskaya I. K., Kavetskaya O. I., Berezin I. V.: Inorg. Chim. Acta *48*, 163 (1981).

289. Isaacs N. S., Rannala E.: J. Chem. Soc., Perkin Trans. 2, *1977*, 902.
290. Newman M. S., Lee S. H., Garret A. B.: J. Am. Chem. Soc. *69*, 113 (1947).
291. Tang R., Msilow K.: J. Am. Chem. Soc. *92*, 2100 (1970).
292. Sveishi Y., Ohcho M., Nishimura N.: Bull. Chem. Soc. Jpn. *58*, 2608 (1985).
293. Jablokova N. V., Jablokov V. A., Badyanova A. V.: Kinet. Catal. (Engl. Transl.) *8*, 40 (1967).
294. Marcandelli B., Pellicciardi-Di Liddo L., Di Fede C., Bellobono I. R.: J. Chem. Soc., Perkin Trans. 2, *1984*, 589.
295. Uri A., Tuulmets A.: Org. Reactiv. *20*, 578 (1983).
296. Bordwell F. G., Williams J. M., Hoyt E. B., Jarvis B. B.: J. Am. Chem. Soc. *90*, 429 (1968).
297. Pincock E. R.: J. Am. Chem. Soc. *86*, 1820 (1924).
298. Tuleen D. L., Bentrude W. G., Martin J. C.: J. Am. Chem. Soc. *85*, 1938 (1963).
299. Russel G. A.: J. Am. Chem. Soc. *80*, 4987 (1958).
300. Ito O., Matsuda M.: J. Am. Chem. Soc. *104*, 568 (1982).
301. Beak P., Covington J. B., White J. M.: J. Org. Chem. *45*, 1347 (1980).
302. Mills S. G., Beak P.: J. Org. Chem. *50*, 1216 (1985).
303. Laurence C., Guiheneuf G., Wojtkowiak B.: J. Am. Chem. Soc. *101*, 4793 (1979).
304. Panchenko B., Oleinik N., Sadovsky Yu., Dadali V., Litvinenko L.: Org. Reactiv. *17*, 65 (1980).
305. Fujii Y., Sobue K., Tanaka M.: J. Chem. Soc., Faraday Trans. 1, *1978*, 1467.
306. Mitsky J., Joris L., Taft R. W.: J. Am. Chem. Soc. *94*, 3442 (1972).
307. Glikberg S., Marcus Y.: J. Solution Chem. *12*, 255 (1983).
308. Abraham M. H.: J. Chem. Soc., Perkin Trans. 2, *1972*, 1343.
309. Kim J. I.: J. Phys. Chem. *82*, 191 (1978).
310. Makitra R. G., Pirig Ja. N.: Org. Reactiv. *16*, 84 (1979).
311. Makitra R. G., Pirig Ja. N.: Org. Reactiv. *15*, 355 (1978).
312. Maria P.-C., Gal J. F.: J. Phys. Chem. *89*, 1296 (1985).
313. Maria P.-C., Gal J. F., Elegant L., Azzaro M.: Thermochim. Acta *115*, 67 (1987).
314. Arnet E. M., Mitchell E. J., Murty T. S. S. R.: J. Am. Chem. Soc. *96*, 3875 (1974).
315. Drago R. S.: Struct. Bond. *15*, 73 (1973).
316. Doan P. E., Drago R. S.: J. Am. Chem. Soc. *104*, 4524 (1982).
317. Alexander R., Parker A. J., Sharp J. H., Waghorne W. E.: J. Am. Chem. Soc. *95*, 1148 (1972).
318. Santa-Ana M. A., Chadwik I., Gonzáles G.: J. Chem. Soc., Perkin Trans. 2, *1985*, 1755.
319. Kadish K. M., Chang D.: Inorg. Chem. *21*, 3614 (1982).
320. Karelson M. M., Haldna U. L., Palm V. A.: Reakts. Sposobnost Organ. Soedin. (Tartu) *10*, 163 (1973).
321. Gerrard W., Macklen E. D.: Chem. Rev. *59*, 1105 (1959).
322. Abraham M. H.: Prog. Phys. Org. Chem. *11*, 1 (1974).
323. Ritchie C. D. in the book: *Solute.Solvent Interactions* (Coetzee J. F. and Ritchie C. D., Eds), Vol. 2, p. 229. Dekker, New York, 1976.
324. Golub A. M.: Usp. Khim. *45*, 961 (1976).
325. Bentley T. W., Schleyer P. v. R.: Adv. Phys. Org. Chem. *14*, 1 (1977).
326. Parker A. J., Mayer U., Schmid R., Gutmann V.: J. Org. Chem. *43*, 1843 (1978).
327. Cox B. G., Waghorne W. E.: Chem. Soc. Rev. *9*, 381 (1980).
328. Buncel E., Wilson H.: J. Chem. Educ. *57*, 629 (1980).
329. Rodriguez Velasco J., Piazza Molini C., Teyera Quijano J. I.: Acta Cient. Compostel. *22*, 413 (1985).
330. Karelson M.: Org. Reactiv. *22*, 373 (1985).

331. Blandamer M. J., Scott J. M. W., Robertson R. E.: Prog. Phys. Org. Chem. *15*, 149 (1985).
332. Holba V., Grančičová O.: Chem. Listy *79*, 449 (1985).
333. Abraham M. H., Doherty R. M., Kamlet M. J., Taft R. W.: Chem. Br. *22*, 551 (1986).
334. Abraham M. H.: Acta Chim. Hung. *121*, 11 (1986).
335. Taft R. W., Abraham M. H., Doherty R. M., Kamlet M. J.: J. Am. Chem. Soc. *107*, 3105 (1985).
336. Kamlet M. J., Doherty R. M., Abraham M. H., Taft R. W.: Carbon *23*, 549 (1985).
337. Taft R. W., Abraham M. H., Doherty R. M., Kamlet M. J.: Nature *313*, 384 (1985).
338. Kamlet M. J., Doherty R. M., Abboud J.-L. M., Abraham M. H., Taft R. W.: J. Pharm. Sci. *75*, 338 (1986).
339. Begtrup M., Taft R. W., Kamlet M. J.: J. Org. Chem. *51*, 2130 (1986).
340. Kamlet M. J., Doherty R. M., Abboud J.-L. M., Abraham M. H., Taft R. W.: CHEMTECH *16*, 566 (1986).
341. Leahy D. E., Carr P. W., Pearlman R. S., Taft R. W., Kamlet M. J.: Chromatographia *21*, 473 (1986).
342. Kamlet M. J., Doherty R. M., Abraham M. H., Carr P. W., Doherty R. F., Taft R. W,: J. Phys. Chem. *91*, 1996 (1987).
343. Laurence C., Nicolet P., Reichardt C.: Bull. Soc. Chim. Fr. *1987*, 125.
344. Krestov G. A., Vinogradov V. I., Kessler Ju. M., Abrosimov V. K., Kolker A. M., Mishustin A. I., Pirogov A. I.: *Sovremenniye problemy khimii rastvorov.* Nauka, Moskva 1986.
345. Morozov A. I., Sytilin M. S.: Zh. Org. Khim. *14*, 2471 (1978).
346. Langhals H.: Angew. Chem., Int. Ed. *21*, 724 (1982).
347. Langhals H.: Z. Phys. Chem. (Leipzig) *266*, 775 (1985).
348. Langhals H.: Tetrahedron Lett. *27*, 339 (1986).
349. Krygowski T. M., Reichardt C., Wrona P. K., Wyszomirska C., Zielkowska V.: J. Chem. Res., Synop. *1983*, 116.
350. Achadov Ya. Yu.: *Dielektricheskiie svoistva binarnych rastvorov.* Nauka. Moskva 977.
351. Kundu K. K., De A. L., Das M. N.: J. Chem. Soc., Dalton Trans. *1972*, 373.
352. Kundu K. K., De A. L., Das M. N.: J. Chem. Soc., Dalton Trans. *1972*, 378.
353. Kundu K. K., Rakshit A. K., Das M. N.: J. Chem. Soc., Dalton Trans. *1972*, 381.
354. Kundu K. K., De A. L., Das M. N.: J. Chem. Soc., Dalton Trans. *1972*, 386.
355. Bentley T. W., Roberts K.: J. Org. Chem. *50*, 4821 (1985).
356. Kevill D. N., Lin G. M. L.: J. Am. Chem. Soc. *101*, 3916 (1979).
357. Kevill D. N., Rissmann T. J.: J. Org. Chem. *50*, 3062 (1985).
358. Kevill D. N., Anderson S. W.: J. Org. Chem. *50*, 3330 (1985).
359. Swain C. G., Dittmer D. C., Kaiser L. E.: J. Am. Chem. Soc. *77*, 3737 (1955).
360. Gowland J. A., Schmid G. H.: Can. J. Chem. *47*, 2953 (1969).
361. Langhals H., Fritz E., Mergelsberg I.: Chem. Ber. *113*, 3662 (1980).
362. Krygowski T. M., Wrona P. K., Zielkowska U., Reichardt C.: Tetrahedron *41*, 4519 (1985).
363. Krygowski T. M., Milczarek E., Wrona P. K.: J. Chem. Soc., Perkin Trans. *2*, *1980*, 1563.
364. Wrona P. K.: J. Electroanal. Chem. *108*, 153 (1980).
365. Langhals H.: Nouv. J. Chim. *5*, 97 (1981).
366. Suppan P.: Nouv. J. Chim. *6*, 285 (1982).
367. Nummert V.: Org. Reactiv. *20*, 279 (1983).
368. Tommila E.: Acta Chem. Scand. *9*, 975 (1955).
369. Tommila E., Tiilikainen M., Voipio A.: Ann. Acad. Sci. Fennicae AII, 65 (1955). Chem. Abstr. *50*, 4601 (1955).
370. Pekkarinen L., Tommila E.: Acta Chem. Scand. *13*, 1019 (1959).
371. Tommila E., Murto M.-L.: Acta Chem. Scand. *16*, 63 (1962).

372. Tommila E., Murto M.-L.: Acta Chem. Scand. *17*, 1957 (1963).
373. Popov A. F., Tokarev V. J., Litvinenko L. M., Troyanik A. I.: Reakts. Sposobnost Organ. Soedin. (Tartu) *4*, 658 (1967).
374. Sadek H., Khalil F. Y.: Z. Phys. Chem. (Frankfurt am Main) *57*, 306 (1968).
375. Sadek H., Khalil F. Y.: Z. Phys. Chem. (Frankfurt am Main) *61*, 63 (1968).
376. Henderson J. W., Haake P.: J. Org. Chem. *42*, 3989 (1977).
377. Salem S. M., Sidahmed I. M.: J. Chin. Chem. Soc. (Taipei) *32*, 451 (1985).
378. Stewart R., Van Dyke J. D.: Can. J. Chem. *50*, 1992 (1972).
379. Woolley E. M., Hurkot D. G., Hepler L. G.: J. Phys. Chem. *74*, 3908 (1970).
380. Fiordiponti P., Rallo F., Rodante F.: Z. Phys. Chem. (Frankfurt am Main) *88*, 149 (1974).
381. Sytilin M. S.: Zh. Fiz. Khim. *50*, 1075 (1976).
382. Sytilin M. S.: Zh. Fiz. Khim. *50*, 1306 (1976).
383. Sytilin M. S.: Zh. Fiz. Khim. *51*, 266 (1977).
384. Achumov E. I.: Zh. Fiz. Khim. *59*, 1423 (1985).
385. Chen Show-An: Chem. Eng. Sci. *30*, 575 (1975).
386. Nagy P., Herzfeld R.: Acta Phys. Chem. Szeged *32*, 33 (1986).
387. Pytela O., Ludwig M.: Collect. Czech. Chem. Commun. *53*, 671 (1988).
388. Wohl K.: Trans. Am. Inst. Eng. *42*, 215 (1946).
389. Margules M.: Sitzber. Akad. Wiss. Wien, Math. Naturw. Kl. II, *104*, 1243 (1895).
390. Van Laar J. J.: Z. Phys. Chem. *72*, 723 (1910); *185*, 35 (1929).
391. Null H. R.: *Phase Equilibrium in Process Design*. Wiley, New York 1970.
392. Redlich O., Kister A. T.: Ind. Eng. Chim. *40*, 345 (1948).
393. Bekárek V., Nevečná T.: Collect. Czech. Chem. Commun. *50*, 1928 (1985).
394. Izmailov N. A.: Zh. Fiz. Khim. *24*, 321 (1950).
395. Douheret G.: Bull. Soc. Chim. Fr. *1967*, 1412.
396. Juillard J.: *Thesis*. Université de Clermont-Ferrand 1967.
397. Vozňáková Z., Štráfelda F.: Coll. Czech. Chem. Commun. *36*, 2993 (1971).
398. Konovalov O. M.: Zh. Fiz. Khim. *39*, 693 (1965).
399. Bowden K., Hardy M. Parkin D. C.: Can. J. Chem. *46*, 2929 (1968).
400. Grunwald E., Berkowitz B. J.: J. Am. Chem. Soc. *73*, 4939 (1951).
401. Kolthoff I. M., Chantooni M. K.: J. Am. Chem. Soc. *93*, 3843 (1971).
402. Kolthoff I. M., Chantooni M. K., Bhownik S.: J. Am. Chem. Soc. *90*, 23 (1968).
403. Kolthcff I. M., Chantooni M. K.: J. Am. Chem. Soc. *90*, 5961 (1968).
404. Kolthoff I. M., Chantooni M. K., Smagowski H.: Anal. Chem. *42*, 1622 (1970).
405. Balash N. M., Robertson E. B., Sokolowski M. D.: J. Chem. Soc., Faraday Trans. *66*, 2622 (1970).
406. Courtot-Coupez J., Demezet M.: Bull. Soc. Chim. Fr. *1969*, 1033.
407. Halle J. C., Gabariaud R., Shall R.: Bull. Soc. Chim. Fr. *1970*, 2047.
408. Morell J. P.: Bull. Soc. Chim. Fr. *1967*, 1405.
409. Reynaud R.: Bull. Soc. Chim. Fr. *1967*, 4597.
410. Petrov S. M., Umanskii Y. Y., Golikova N. D., Khabibova F. S., Safiulina L. A.: Zh. Fiz. Khim. *43*, 2964 (1969).
411. Ludwig M.: *Thesis*. Institute of Chemical Technology, Pardubice 1984.
412. Morel J. P.: Bull. Soc. Chim. Fr. *1966*, 2112.

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