A TEST OF THE ROLE OF REFRACTIVE INDEX IN CORRELATIONS BETWEEN SOLVENT EFFECTS ON ELECTRONIC SPECTRA AND SOLVENT EFFECTS ON REACTION EQUILIBRIA AND RATES

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80 correlations have been carried out between the medium-induced changes in equilibrium and kinetic data (Y) and the medium-induced changes in positions of maxima in electronic (both absorption and fluorescence) spectra (Δv) of the Kamlet–Taft type indicators. The correlations have been carried out by means of the equations $Y = Y_0 + k \cdot \Delta v$ and $Y = Y_0 + k' \cdot \Delta v / f(n^2)$ using only the Kamlet–Taft selected solvents (SSS). The equation involving the function of refractive index (n), $f(n^2) = (n^2 - 1)/(2n^2 + 1)$, is better than the simple relation between Y and Δv in 93% of the systems studied. The problem of HBD acidity of nitromethane and the relation of the A and B solvent characteristics by Swain and the characteristics of dipolarity of medium by Kamlet–Taft are discussed.

During the past ten years, an increasing activity can be observed in the field of evaluation of effects of medium on chemical and physical processes[1–10]. More than 50 procedures and solvent scales have been suggested so far in the field of empirical and semiempirical methods which are used almost exclusively for interpretation and prediction. These evaluations are mostly based on the postulate by Scheibe[11] of similar effects of a solvent on chemical equilibria, reaction rates, and spectral parameters. Kamlet and Taft, dealing with the problem of evaluation of the medium effects recently[2,12–18], arrived at the conclusion (based on analysis of published and their own data) that all these empirical characteristics of polarity or dipolarity* of medium are mutually linearly dependent and roughly proportional to the dipole moment of solvent for the set of so called selected solvents (SSS) (which are mono-

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* The terms dipolarity or polarity of the medium are justified in the cases in which this term is interpreted by means of the dipole moment of medium. If, however, these effects of medium are interpreted by means of relative permittivity of refractive index, it would be more appropriate to speak about polarizability — either total (characterized by a function of relative permittivity) or deformational (characterized by a function or refractive index). At present, the term polarizability denotes only the deformation polarizability. The term of polarity of medium is also used in various meanings. Often it is used as a characteristic of the overall effect of medium (inclusive of its effects as an acid, base, *etc.*), or it is recommended that it should be used only for characterization of non-specific interactions — *i.e.* in the context where Kamlet and Taft apply the term dipolarity. To prevent confusion, this paper uses the term dipolarity, although the given interpretation of parameters has been carried out[21] by means of the polarization model.

functional, non-polyhalogenated, aprotic, aliphatic compounds). These authors developed a system of solvent characteristics for evaluation of the dipolar effect (π^*), the effects of the solvent as an acid (α) and base (β). In a previous paper[19] it was shown that applicability of these dipolarity characteristics π^* can be improved (in the field of chemical reactivity) by dividing these parameters by a function of refractive index of the solvent (n), viz. $f(n^2) = (n^2 - 1)/(2n^2 + 1)$. Thus a dipolarity scale π_n^* was formed. Kamlet and Taft[17] suggested an additional term $d\delta$ to improve the applicability of the π^* parameters; the $d\delta$ term is a characteristic of polarizability of certain types of solvents. As the better applicability of the π_n^* parameters (as compared with the π^* parameters, in the field of chemical reactivity) could be considered to be due to mutual correlation between the $\pi^*/f(n^2)$ and $(\pi^* + d\delta)$ terms, we have studied, in this communication, the relations between experimental solvent-induced shifts in electronic spectra of the Kamlet–Taft indicators and some other indicators of this type and the solvent-induced changes in chemical and physical equilibria and reaction rates. Also it is the aim of this communication to discuss the proton-donor character of nitromethane on the basis of its partition coefficients and to discuss the relations between the Swan's A and B solvent parameters and the Kamlet–Taft's parameters.

EXPERIMENTAL

A majority of the data used were taken from literature. In case of 4-nitrotoluene, whose electronic spectra were not available, the measurements were carried out with a Unicam SP 1800 at the conditions described in ref.[20]. For the solvents used, the following values of wave number differences (with respect to cyclohexane) were found: n-hexane (0·14), diethyl ether (−0·57), tetrahydrofurane (−1·24), ethyl acetate (−1·11), dimethylformamide (−1·83). The wave number values are given in 10^3 multiples of cm^{-1}.

RESULTS AND DISCUSSION

Two procedures were suggested for improvement of applicability of the π^* parameters of dipolarity of medium. Kamlet and Taft[17] suggested to extend this parameter by the term $d\delta$ for some types of solvents (e.g. polyhalogenated and aromatic compounds) and, for evaluation of the dipolar effect of medium, to use the equation in the form:

$$XYZ = XYZ_0 + s \cdot (\pi^* + d\delta), \qquad (1)$$

where XYZ and XYZ_0 mean the investigated property found in a given solvent and in cyclohexane, respectively, δ is different for different types of solvents (e.g. 0·5 for polychlorinated solvents, and 1·0 for aromatics), and d is characteristic for the system studied. The term $d\delta$ was interpreted as a correction for different polarizability of these types of solvents.

On the basis of this polarization model of medium[21] we suggested[19,22] an improvement of applicability of the Kamlet–Taft π^* parameters consisting in dividing these parameters by the above-mentioned function of refractive index. As this improvement of applicability of the π^* parameters in the field of chemical non--spectral properties, achieved in the said way, could seem to be a consequence of mutual correlation between the terms $\pi^*/f(n^2)$ and $(\pi^* + d\delta)$, we carried out this study of the relation of the solvent effects on maxima of electronic spectra of the Kamlet––Taft type of indicators and the solvent effects on chemical and physical equilibria and reaction rates. For this study we only used data found in the Kamlet–Taft selected solvents (SSS), for which the authors introduced $d\delta = 0$. The correlations were carried out with the use of the equations:

$$\Delta G^0 \left(\log K \right) = a + b \cdot \Delta \tilde{v} \tag{2}$$

$$\Delta G^0 \left(\log K \right) = a' + b' \cdot \Delta \tilde{v}/f(n^2) \,. \tag{3}$$

The study was based on the properties independent of basicity of medium and enabling the evaluation for at least four data. The following systems were used (the alphabetical or numerical denotation agrees with Table I): logarithm of the partition coefficient of nitromethane[23] (A), logarithm of solubility of tetraethylammonium iodide[24] (B), logarithm of solubility of tetramethylammonium iodide[24] (C), logarithm of solubility of the dissociated $(C_2H_5)_4N^{(+)}I^{(-)}$ [24] (D,) logarithm of solubility of the dissociated $(CH_3)_4N^{(+)}I^{(-)}$ [24] (E), the Gibbs energy of transition of the ion pair $(CH_3)_4N^{(+)}I^{(-)}$ between methanol and other media[24] (F), the difference in the Gibbs energies of the *cis-trans* isomers of 2-isopropyl-5-methoxy-1,3-dioxane[25] (G), the difference in the Gibbs energies of the *cis-trans* isomers of 2-isopropyl-5-ethoxy--1,3-dioxane[25] (H), logarithm of the solvolysis rate constant of p-methoxyneophyl toluenesulphonate[26] (J), logarithm of rate constant of the reaction of tri-n-propyl-amine with methyl iodide[27] (K). These equilibrium and rate data were correlated by means of Eqs (2) and (3) with electronic spectra of the following indicators: N,N-diethyl-4-nitroaniline[12] (I), 4-nitroanisole[12] (II), N,N-dimethyl-2-nitroani-line[12] (III), N,N-dimethyl-2-nitrotoluidine[12] (IV), N,N-dimethyl-2-nitroanisidine[12] (V), 1,3-diethyl-5-[5-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)-1,3-neo-pentylene-2,4-pentadienylidene]-2-thiobarbituric acid[29] (VI), N-methylacridine[28] (VII), 3-nitro-N,N-dimethylaniline[22] (VIII), 4-nitro-N,N-dimethylaniline[22] (IX), nitromethylpiperidine[22] (X), 4-nitrotoluene (this paper) (XI).

Table I presents the comparison of results of the correlation of these data by Eqs (2) and (3). In 74 cases out of total 80 cases, Eq. (3) is more satisfactory than Eq. (2). Although the standard deviations are, in some cases, by as much as 50% lower for the correlation by Eq. (3) than for that by Eq. (2), the improvement of the correlations is not so distinct as in the case of involvement of the data measured

TABLE I

Comparison of correlations of effects of medium on equilibrium and rate data with effects of medium on electronic spectra by Eqs (2) and (3) for the selected solvents set (SSS)

The system studied	Correlation coefficient		Standard deviation		Number of data
	Eq. (2)	Eq. (3)	Eq. (2)	Eq. (3)	
A–I	0·9822	0·9915	0·143	0·100	13
A–II	0·9853	0·9905	0·142	0·114	7
A–III	0·9725	0·9828	0·243	0·191	5
A–IV	0·9653	0·9768	0·270	0·221	5
A–V	0·9829	0·9901	0·190	0·145	5
A–VI	0·9226	0·9529	0·290	0·228	11
A–VII	0·9541	0·9753	0·262	0·194	9
A–VIII	0·9730	0·9899	0·195	0·120	8
A–IX	0·9361	0·9607	0·298	0·235	8
A–X	0·9485	0·9679	0·268	0·213	8
A–XI	0·9889	0·9958	0·133	0·082	6
B–I	0·9674	0·9958	0·719	0·259	6
B–VI	0·9062	0·9514	1·200	0·873	6
B–VII	0·9561	0·9891	0·957	0·480	5
B–VIII	0·9475	0·9890	0·907	0·419	6
B–IX	0·9502	0·9834	0·884	0·515	6
B–X	0·9557	0·9829	0·835	0·522	6
C–I	0·9870	0·9983	0·516	0·186	6
C–VI	0·9333	0·9662	1·152	0·827	6
C–VII	0·9749	0·9957	0·824	0·344	5
C–VIII	0·9664	0·9909	0·824	0·433	6
C–IX	0·9726	0·9926	0·746	0·389	6
C—X	0·9775	0·9916	0·676	0·416	6
D–I	0·9636	0·9934	2·344	1·003	6
D–VI	0·9068	0·9540	3·691	2·623	6
D–VII	0·9565	0·9895	2·900	1·437	5
D–VIII	0·9451	0·9883	2·863	1·336	6
D–IX	0·9476	0·9817	2·800	1·668	6
D–X	0·9529	0·9792	2·628	1·772	6
E–I	0·9809	0·9973	1·844	0·697	6
E–VI	0·9312	0·9692	3·455	2·336	6
E–VII	0·9737	0·9969	2·482	0·860	5
E–VIII	0·9639	0·9942	2·526	1·021	6
E–IX	0·9673	0·9939	2·404	1·044	6
E–X	0·9703	0·9878	2·294	1·475	6
F–I	0·9935	0·9989	0·659	0·270	8
F–II	0·9986	0·9904	0·300	0·797	5
F–III	0·9947	0·9989	0·788	0·362	4
F–IV	0·9914	0·9970	1·005	0·597	4

TABLE I
(*Continued*)

The system studied	Correlation coefficient		Standard deviation		Number of data
	Eq. (2)	Eq. (3)	Eq. (2)	Eq. (3)	
F–V	0·9991	0·9998	0·332	0·148	4
F–VI	0·9603	0·9836	1·610	1·040	8
F–VII	0·9132	0·9918	2·517	0·790	7
F–VIII	0·9696	0·9861	1·336	0·918	9
F–IX	0·9647	0·9838	1·439	0·980	9
F–X	0·9647	0·9838	1·439	0·980	9
F–XI	0·9993	0·9994	0·228	0·216	5
G–I	0·9639	0·9746	0·158	0·077	5
G–II	0·9991	0·9992	0·010	0·009	4
G–VI	0·9635	0·9725	0·092	0·080	5
G–VII	0·9482	0·9661	0·109	0·089	5
G–VIII	0·9402	0·9547	0·117	0·102	5
G–IX	0·9825	0·9902	0·064	0·048	5
G–X	0·9773	0·9833	0·073	0·063	5
H–I	0·9582	0·9685	0·094	0·082	5
H–II	0·9955	0·9954	0·021	0·021	4
H–VI	0·9564	0·9651	0·096	0·086	5
H–VII	0·9472	0·9648	0·106	0·087	5
H–VIII	0·9333	0·9473	0·118	0·105	5
H–IX	0·9815	0·9891	0·063	0·049	5
H–X	0·9742	0·9800	0·074	0·065	5
J–I	0·9951	0·9865	0·144	0·237	6
J–II	0·9975	0·9887	0·106	0·226	4
J–VI	0·9673	0·9851	0·361	0·250	6
J–VII	0·9751	0·9796	0·322	0·292	6
J–VIII	0·9720	0·9757	0·311	0·320	6
J–IX	0·9927	0·9941	0·175	0·158	6
J–X	0·9967	0·9905	0·180	0·200	6
J–XI	0·9874	0·9889	0·239	0·224	4
K–I	0·99762	0·99767	0·119	0·118	10
K–II	0·9951	0·9934	0·180	0·208	7
K–III	0·9870	0·9927	0·369	0·276	5
K–IV	0·9813	0·9872	0·454	0·367	5
K–V	0·9925	0·9950	0·280	0·230	5
K–VI	0·9772	0·9895	0·364	0·248	10
K–VII	0·9766	0·9866	0·414	0·315	7
K–VIII	0·9917	0·9948	0·241	0·190	8
K–IX	0·9830	0·9868	0·344	0·303	8
K–X	0·9890	0·9895	0·277	0·271	8
K–XI	0·9943	0·9961	0·214	0·176	6

in all the solvents. Of course, this can be understood with respect to lower differences in the $f(n^2)$ function in the selected solvents set.

The more successful correlations between ΔG^0 or $\log K$ and $\Delta \tilde{v}/f(n^2)$ can be considered to confirm justification of our modification of the π^* parameters for the field of equilibria and reaction rates. On the other hand, these results do not decrease the importance of the procedure by Kamlet and Taft (application of the additional parameter $d\delta$ to the π^* parameter). Our modification of the Kamlet–Taft π^* parameters by the $f(n)^2$ function presumes that the extent of vibrational and rotational motions in the Kamlet–Taft indicators is the same for the ground and the excited states and, hence, the additional deformational polarization of completely polarized cybotactic solvent molecules, which accompanies these motions, is the same, too. The effect of medium on such indicators is (within the limits of the Kamlet–Taft selected solvents set) well described by a product function of relative permittivity $(D)^{20,22}$ and refractive index, $f(D, n^2) = (D - 1)/(2D + 1) . (n^2 - 1) :$ $: (2n^2 + 1)$. If, however, the extent of this deformational polarization is different, it is impossible to describe the solvent effect on electronic spectra by a monoparameter equation, but the equation must involve one more parameter characterizing this different deformational polarization, *e.g.* the $f(n^2)$ function. Thus it is generally possible to apply Eq. (4) to the evaluation of the influence of medium on electronic spectra.

$$\Delta \tilde{v} = k . \left[a\pi_n^* + b\, f(n^2) \right] . f(n^2), \tag{4}$$

where the π^* parameter may be replaced (for limited solvent systems) by some function of relative permittivity.

Thus, in the sense of our polarization model[19,21], the effect of medium on the data from the field of chemical reactivity should be evaluable by the relation (for the Gibbs energy change)

$$\Delta\Delta G^0 = k' . a\pi_n^* + b\, f(n)^2 . \tag{5}$$

In Eqs (4) and (5) the term $\left[a\pi_n^* + b\, f(n^2) \right]$ is formally close to the term $\left[\pi^* + d\delta \right]$ by Kamlet and Taft.

Table II gives the results of application of Eq. (5) to some systems from the field of chemical reactivity. The correlation efficiency is evaluated by the overall correlation coefficient and standard deviation, however, also given are the correlation coefficients of partial correlation of the investigated property with the π_n^* parameter and the correlation coefficients between the π_n^* and $f(n^2)$ parameters. From the Table it can be seen that π_n^* has dominant significance in the description of the influence of medium on these properties and that there does not exist a significant correlation between π_n^* and $f(n^2)$.

Not involved in this study are the data found in acetonitrile and nitromethane. Kamlet and Taft originally included these solvents among SSS, but later on they reject them due to their hydrogen-bond donor effect. With regard to acidity of nitromethane it is noteworthy that there exists an interesting relation between the partition coefficient of nitromethane and spectral solvent shifts in electronic spectra. From Table I it is obvious that for the 13 solvents used (inclusive of the strongly basic ones, as *e.g.* dimethyl sulphoxide and amides) the relation between $\log k$ and $\Delta \tilde{\nu}$: : $f(n^2)$ is very close in case of A–I system, and the correlation characteristics are not improved significantly by introduction of the second term which characterizes the basicity of medium. In case of ethanol as the solute, the basicity of medium has a substantial effect on its partition coefficient[30]. This finding throws doubt upon the acidic character of nitromethane which should be distinct just in basic solvents.

In terms of our evaluation of the influence of medium the problem of HBD-effect of nitromethane and acetonitrile appears as a consequence of low refractive index

TABLE II

Evaluation of influence of medium on reaction rates by Eq. (*5*)

Reaction[a]	n	R	s	$r (\log k - \pi_n^*)$	$r(\pi_n^* - f(n^2))$
I	50	0·9892	0·160	0·9840	0·0082
II	12	0·9909	0·396	0·9880	0·3241
III	10	0·9903	0·347	0·9899	0·4453
IV	10	0·9904	0·320	0·9903	0·4454
V	11	0·9920	0·073	0·9917	0·0557
VI	10	0·9895	0·174	0·9880	0·3373
VII	22	0·9680	0·236	0·9664	0·0959
VIII	22	0·9758	0·200	0·9747	0·2283
IX	19	0·9880	0·144	0·9880	0·0005
X	19	0·9802	0·176	0·9802	0·0001
XI	17	0·9813	0·155	0·9801	0·2034
XII	15	0·9800	0·139	0·9784	0·2342

[a] I Rate of the reaction of tri-n-propylamine with methyl iodide[27], II rate of decomposition of tert-butyl chloride[32], III rate of decomposition of tert-butyl bromide[32], IV rate of decomposition of tert-butyl iodide[32], V rate of oxidation of styrene[33], VI rate of solvolysis of p-methoxyneophyl toluenesulphonate[26], VII rate of the reaction of ethyl bromoacetate with ethyl iodide[34], VIII rate of the reaction of ethyl iodoacetate with ethyl iodide[34,35], IX rate of the reaction of 1,4-diazabicyclo[2,2,2]octane with 2-bromoethylbenzene[36], X rate of the reaction of 1,4-diazabicyclo[2,2,2]octane with 2-iodoethylbenzene[36], XI rate of the reaction of 1,4-diazabicyclo[2,2,2]octane with 2-chloroethylbenzene[36], XII rate of decomposition of butyl peroxoformate[35], n number of solvents, s standard deviation.

of these solvents (the $f(n^2)$ function is 0·188 and 0·174 for nitromethane and aceto-nitrile, respectively) and, hence, of the great difference in relative effects of these solvents on electronic spectra and on equilibria and reaction rates. The original α values were determined from the solvent effects on electronic spectra of five indicators and on the solvolysis rates of tert-butyl chloride[17]. In case of four out of these five indicators the electronic transitions are accompanied with charge transfer. In our previous paper[19] it was shown that the overall influence of medium on this transition can be quantitatively interpreted very well as a sum of two opposite effects. One of them is identical with the solvent effect in the Kamlet–Taft indicators (the batho-chromic shift described by the term $\Delta\tilde{v} = \pi_n^* \cdot f(n^2)$), the other, more significant hypsochromic effect is described by the term $\pi_n^* \cdot f(D)$. Thus *e.g.* for the most popular empirical solvent scale $E_T(30)$, which is based on the solvatochromism of 2,6-di-phenyl-4-(2,4,6-triphenyl-1-pyridinium) phenoxide, the correlation equation for 23 SSS had the form[19]

$$E_T(30) = 31·84 + 10·61\pi_n^* \cdot f(D^2) - 10·85\pi_n^* \cdot f(n^2), \quad R = 0·984 \qquad (6)$$

From Eq. (6) it can be deduced that *e.g.* in the pair dimethyl sulphoxide–nitromethane (which have very close π_n^* and $f(D)$ values but different $f(n^2)$ values) the calculated $E_T(30)$ will be greater for nitromethane than for dimethyl sulphoxide. The calculated difference is 1·3 units, which agrees with the difference found experimentally. Similar situation is encountered also with the remaining three indicators with the transitions of the charge-transfer nature. In case of solvolysis of butyl chloride the solvent effect is described by the π_n^* parameter. The π_n^* parameters of nitromethane and aceto-nitrile are much closer to the π_n^* parameter of dimethyl sulphoxide as compared with the corresponding π^* parameters. The sixth indicator for adjustment of the α scale was the Brooker's merocyanine[29] whose solvatochromic behaviour is similar to that of the Kamlet–Taft indicators. Using this indicator, Kamlet and Taft obtained $\alpha = 0$ for acetonitrile. The given facts indicate that the published values of the α characteristics cannot be considered definitive and that our modification of these α parameters by the $f(n^2)$ function was meaningless[19].

As far as the problem is concerned of number of the solvent characteristics or num-ber of terms in the correlation equations evaluating the influence of medium, the hitherto experience shows that in spite of all objections it will be useful to retain the multi-parameter equations containing besides the acidity and basicity terms also one or two terms of dipolarity. Although the $E_T(30)$ parameters exhibit a high degree of aplicability and will undoubtedly remain one of the most used empirical solvent characteristics (particularly in the prediction), their theoretical analysis and experience have shown that they do not reflect the influence of the medium as a base and that they fail in cases when dipolarity and acidity of medium affect the process investigated in opposite sense (*e.g.* the Menshutkin reaction).

Objections must also be raised to the approach by Swain and coworkers[10]. These authors suggested two-parameter equations for evaluation of the influence of medium, the suggested characteristics of medium being its ability to solvate cations (an equivalent of basicity, the B constant) and ability to solvate anions (an equivalent of acidity, the A constant). The authors started from the idea that the overall solvent effect on any property is composed from these two basic effects, and so-called dipolarity or own polarity can be expressed by a sum of these effects $(A + B)$. We carried out correlation of this sum with the π_n^* parameters; the correlation equations are

$$A + B = 0.081 + 0.278\pi_n^*, \quad R = 0.957, \quad SD = 0.12 \qquad (7)$$

for 45 solvents inclusive of alcohols and water, and

$$A + B = 0.048 + 0.274\pi_n^*, \quad R = 0.988, \quad SD = 0.06 \qquad (8)$$

for 37 aprotic solvents of the same set.

Of course, not only this sum $(A + B)$ but also the B constants alone show a close relation with the π_n^* parameters. Thus for the 37 aprotic solvents the correlation between B and π_n^* reads

$$B = 0.046 + 0.207\pi_n^*, \quad R = 0.978. \quad SD = 0.06 \qquad (9)$$

Eq. (9) shows that the B parameter is rather a dipolarity characteristic than a basicity characteristic. Qualitatively this can be seen *e.g.* in low value of the B parameter in the case of triethyalmine whose solvation effects with respect to the proton belong to the most distinct ones.

For comparison, we carried out the correlation of rate constant of the reaction of aniline with benzoyl chloride measured in 22 solvents[31] with the A and B parameters and with the π_n^* and β parameters. The correlation equations read as follows:

$$\log k = -0.86 - 3.4iA + 5.05B, \quad R = 0.801, \quad SD = 0.65 \qquad (10)$$

$$\log k = -0.79 + 0.552\pi_n^* + 2.910\beta, \quad R = 0.957, \quad SD = 0.33 \qquad (11)$$

The Swain's statement about mutual independence of the A and B parameters applies to the whole set of the solvents studied and for some selections. However, for a great number of solvents there exists a relation between A and B, *e.g.* for 22 solvents, in which the reaction of aniline with benzoyl chloride was studied, the correlation coefficient between the A and B constants equals 0.857. After all, the

possible existence of the relation between the A and B constants for some sets of solvents is obvious from Fig. 1 of the Swain's report[10], too.

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Note added in proof: The transformation of π^* to π_n^* supposes the deformational polarization to obey the $f(n^2)$. An improvement can be expected when replacing the $f(n^2)$ function by some empiric characteristic of the media deformational polarization.