

## A CONTRIBUTION TO EVALUATION OF INFLUENCE OF MEDIUM IN ELECTRONIC AND INFRARED SPECTROSCOPY

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Dependence of  $E_T(30)$  of solvent parameters on relative permittivity ( $\epsilon$ ) and refractive index ( $n$ ) of solvent has been found for forty solvents in the form  $E_T(30) = 29.87 + 72.03 (\epsilon - 1)/(2\epsilon + 1) - 29.16(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1)$ , the correlation coefficient being 0.958. Relation has been discussed between  $E_T(30)$  and  $\pi^*$  solvent parameters and significance of the term  $(\epsilon - 1) \cdot (n^2 - 1)/(2\epsilon + 1)(2n^2 + 1)$  has been tested for evaluation of solvent effects in electronic spectra.

Great number (about 40) of suggested empirical medium polarity scales as well as great number of models and equations derived theoretically from them indicate complex nature of the problem called generally solvent effect. For adjusting empirical scales of polarity of medium as well as for verification of applicability of theoretically derived equations, kinetic and equilibrium chemical data and especially spectral data (IR, UV-VIS, NMR, ESR) have been used. Special attention was also paid to the problem of mutual relation of the individual empirical parameters and to their interpretation by theoretical methods.

In our previous papers<sup>1,2</sup> we showed that for evaluation of solvent-induced shifts in IR and electronic spectra the main effect is due to the cross-term  $f(\epsilon, n^2) = (\epsilon - 1)(n^2 - 1)/(2\epsilon + 1) \cdot (2n^2 + 1)$ . We found a very good correlation between this cross term and the Taft-Kamlet solvent parameters and suggested a model of solvent effect on electronic and infrared spectra of the molecules<sup>3</sup>.

The aim of the present study is application of this model to interpretation of one of the most used characteristics of medium – the  $E_T(30)$  parameter suggested by Dimroth and Reichardt<sup>4,5</sup>, discussion of relation between these  $E_T(30)$  parameters and the  $\pi^*$  solvent parameters by Taft and Kamlet<sup>6-10</sup>, estimation of the  $E_T(30)$  and  $\pi^*$  parameters of some solvents, comparison of applicability of the equation suggested with that by Bilot-Kawski-Bachshiev<sup>11-15</sup> and testing of applicability of the equation suggested to evaluation of solvent shifts in fluorescence spectra.

### EXPERIMENTAL

The  $E_T(30)$ ,  $\pi^*$  and electronic spectra of 4-nitroanisole and 4-nitro-N,N-diethylaniline as well as fluorescence spectra of N-methylacridone were taken from refs<sup>4,7,16</sup>. Electronic spectra of 3-nitro-N,N-dimethylaniline, 4-nitroso-N,N-dimethylaniline, and N-(2-nitrophenyl)piperi-

dine were measured in the given solvents (Table II) using an SP 1800 Unicam apparatus and 1 mm cells. The IR spectra of 2-nitrophenol and acetone were measured with a Specord IR-75 spectrometer (Zeiss, Jena). The regression analysis of the data was carried out with a Tesla 2000 computer.

## RESULTS AND DISCUSSION

Extensive treatment of effects of medium on physico-chemical processes carried out by Kamlet, Taft and coworkers<sup>6-10,17-24</sup> revealed a broad applicability of their  $\pi^*$  indexes of polarity of medium. However, some difficulties were encountered when applying these  $\pi^*$  factors to evaluation of the solvent-induced shifts in electronic spectra of betains, especially those of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide whose solvatochromic behaviour was chosen as basic for empirical solvent parameters  $E_T(30)$ . In contrast to the standards used for construction of the  $\pi^*$  scale and in contrast to all the compounds studied by Kamlet and Taft, charge-transfer process is operating in the case of electronic excitation of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide. With respect to the model approach to the influence of solvent on the excitation process of solute molecule<sup>3</sup> it must be emphasized that negative charge is localized at oxygen in the ground state of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide, whereas in the excited state this charge is delocalized over the extensive aromatic system of the molecule. As compared with solvent effects on the Taft-Kamlet indicators, the solvent molecules of cybotactic sphere have another function. Not only they undergo additional electronic and atomic polarization during the excitation course (effect of this polarization on position of absorption bands is evaluated by the  $f(\epsilon, n^2)$  term), but, in addition to it, they affect facility of the charge-transfer process by their total polarizability. The greater is the total polarizability of these molecules the greater are the energy requirements of the transfer of localized charge from oxygen to the  $\pi$  system of the molecule, which results in hypsochromic shift of the corresponding band. Presuming the lifetime of the solute molecule in its ground state before excitation to be sufficiently long for reorientation of solvent molecules of cybotactic sphere to be possible, effect of these molecules on energetical facility of the charge transfer will be proportional to their polarizability and, hence, also to their reaction field and to the term  $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$ . Increasing  $f(\epsilon)$  of solvent increases energy requirements of the charge transfer, the band is shifted hypsochromically, and  $E_T(30)$  is increased. As this effect of solvent molecules depends on distance between solute molecule and molecules of cybotactic sphere (the latter being connected with the formed reaction field and, hence, with the  $f(\epsilon)$  function), the overall influence of polarizability of solvent molecules on facility of the charge transfer should be proportional to  $f^2(\epsilon)$ . The overall effect of medium on position of the absorption band should then be a sum of the bathochromic effect characterized by  $f(\epsilon, n^2)$  (which reflects well the behaviour of the Taft-Kamlet indicators) and the hypsochromic effect characterized

by the  $f^2(\varepsilon)$  function. As the position of absorption maximum of the longest-wave band of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide  $\lambda_{\max}$  [nm] is immediately connected with the  $E_T(30)$  parameters by relation  $E_T(30) = 28\,590/\lambda_{\max}$ , we used these  $E_T(30)$  parameters direct in the correlation. The correlation was carried out for 40 aprotic aliphatic solvents whose  $E_T(30)$  values, relative permittivities and refractive indexes are known. In addition we found experimentally the  $E_T(30)$  values of dibromomethane and diiodomethane. All these data are given in Table I. The correlation function between  $E_T(30)$  and the functions  $f(\varepsilon)$  and  $f(\varepsilon, n^2)$  reads as follows:

$$E_T(30) = 29.87 + 72.02f^2(\varepsilon) - 29.16f(\varepsilon, n^2) \quad (1)$$

$$R = 0.957, \quad SD = 1.332, \quad r_{E_T-f(\varepsilon)} = 0.957,$$

where  $R$  and  $SD$  mean correlation coefficient and standard deviation, respectively. From magnitude of the regression coefficients and magnitude of partial correlation coefficient between  $E_T(30)$  and  $f(\varepsilon)$  it is obvious that the  $f(\varepsilon)$  term has a predominant influence on the  $E_T(30)$  parameters. According to expectation the signs of the two regression coefficients are opposite, which agrees with the mentioned model presumption. Dibromomethane and diiodomethane were included in this set, because they represent solvents with high refractive index, and, hence, their presence thus interferes with possibly significant correlation between  $f(\varepsilon)$  and  $f(\varepsilon, n^2)$ . With these solvents it is also possible to expect only non-specific interactions with solute. The problem of nature and extent of interactions between solute and solvent molecules is very delicate in these studies. In this context various sets of solvents were suggested for studies of effects of medium. When studying the medium effects on IR spectra we arrived, in this respect, at the following conclusion concerning a suitable solvent set: hexane, cyclohexane, tetrachloromethane, tetrachloroethylene, carbon disulphide, trichloroethylene, dichloromethane, 1,2-dichloroethane, dibromomethane, and diiodomethane. With these solvents non-specific interactions in solutions can only be expected in most cases (except for diiodomethane, which can, sometimes, form charge-transfer complexes), the differences between their refractive indexes and relative permittivities being great enough. We carried out a correlation between  $E_T(30)$  and  $f(\varepsilon)$  and  $f(\varepsilon, n^2)$  for the mentioned solvents only, and the resulting relation is:

$$E_T(30) = 29.83 + 81.98f^2(\varepsilon) - 40.14f(\varepsilon, n^2) \quad (2)$$

$$R = 0.994, \quad SD = 0.49.$$

In contrast to electronic spectra, the solvent-induced shifts of IR absorption bands are, in most cases, characterized well by the one-parameter equation containing the  $f(\varepsilon, n^2)$  term only<sup>1,2</sup>. Here the excitation of molecule is not accompanied by a change

TABLE I

Dependence of the  $E_T(30)$  parameters on relative permittivity and refractive index of aprotic aliphatic solvents

Solvent	$f^2(\epsilon)$	$f(\epsilon, n^2)$	$E_T(30)$	
			exptl.	calc.
n-Hexane	0.034	0.034	30.9	31.3
Cyclohexane	0.041	0.041	31.2	31.6
Tetrachloroethylene	0.054	0.053	31.9	32.2
Cyclohexene	0.050	0.047	32.3	32.1
Tetrachloromethane	0.051	0.048	32.5	32.1
Carbon disulphide	0.068	0.068	32.6	32.8
Triethylamine	0.059	0.048	33.3	32.7
Di-n-butyl ether	0.084	0.056	33.4	34.3
Diisopropyl ether	0.108	0.060	34.0	35.9
Diethyl ether	0.117	0.061	34.6	36.5
Trichloroethylene	0.095	0.068	35.9	34.8
Ethyl carbonate	0.075	0.052	36.2	33.8
Tetrahydrofuran	0.163	0.080	37.4	39.3
Ethyl acetate	0.148	0.071	38.1	38.5
Diiodomethane	0.138	0.106	36.5	36.7
Ethyl bromide	0.181	0.087	37.6	40.3
Chloroform	0.127	0.075	39.1	36.8
Tri-n-butyl phosphate	0.169	0.083	39.6	39.6
Methyl acetate	0.157	0.073	40.0	39.1
Cyclopentanone	0.199	0.093	40.3	41.5
Cyclohexanone	0.212	0.097	40.8	42.3
Ethyl formate	0.162	0.073	40.9	39.4
Dichloromethane	0.176	0.085	41.1	40.1
2-Butanone	0.213	0.086	41.3	42.7
1,2-Dichloroethane	0.197	0.090	41.9	41.4
Acetone	0.217	0.084	42.2	43.0
1-Methyl-2-pyrrolidone	0.228	0.104	42.2	43.3
Propionitrile	0.224	0.087	43.7	43.5
N,N-Dimethylacetamide	0.230	0.099	43.7	43.6
N,N-Dimethylformamide	0.230	0.098	43.8	43.6
Acetanhydride	0.216	0.090	43.9	42.8
Sulfolan	0.233	0.107	44.0	43.5
Dimethyl sulfoxide	0.235	0.106	45.0	43.7
Hexamethylphosphorustriamide	0.226	0.090	40.9	43.6
4-Butyrolactone	0.231	0.100	44.3	43.6
Nitroethane	0.226	0.091	43.6	43.5
Nitropropane	0.221	0.091	42.8	43.1
Dibromomethane	0.162	0.096	39.4	38.7
Acetonitrile	0.230	0.084	46.0	44.0
Nitromethane	0.230	0.090	46.3	43.8

of direction of dipole moment of the bond studied, the change of dipole moment being small. Thus the orientation of molecules of the cybotactic sphere cannot undergo any changes during the excitation process. Exceptions are here the systems

TABLE II

Effect of medium on position of the longest-wave bands in electronic spectra of 3-nitro-N,N-dimethylaniline (*I*), 4-nitroso-N,N-dimethylaniline (*II*), N-(2-nitrophenyl)piperidine (*III*), 4-nitroanisole (*IV*), and 4-nitro-N,N-diethylaniline, fluorescence spectrum of N-methylacridine (*VI*) and IR valence vibration of O—H bond in 2-nitrophenol (*VII*) and C=O bond in acetone (*VIII*). The maxima of absorption bands of 4-nitroanisole and 4-nitro-N,N-dimethylaniline were taken from ref.<sup>6</sup>, the fluorescence spectrum was taken from ref.<sup>24</sup>

Solvent	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>
Perfluorohexane	368.0	380.0	—	—	—	—	3 242	1 729
n-Pentane	378.0	390.5	384.0	—	—	—	3 236	1 723
n-Hexane	379.5	392.5	385.0	34.31	27.71	25.12	3 235	1 722
n-Heptane	381.0	393.0	388.0	—	—	—	3 234	1 722
Cyclohexane	383.0	395.0	391.0	34.13	27.40	25.06	3 234	1 721
Tetrachloromethane	390.5	402.0	399.0	33.56	26.70	24.75	3 240	1 719
Tetrachloroethylene	391.0	—	401.0	—	—	24.78	3 237	1 720
Trichloroethylene	399.0	—	409.0	—	25.76	—	3 245	1 716
Carbon disulphide	402.0	413.5	409.0	—	—	—	3 231	1 716
Diethyl ether	393.5	399.5	395.0	33.45	26.52	24.84	—	1 720
Tetrahydrofuran	405.0	410.0	406.0	32.79	25.61	24.39	—	1 718
Ethyl acetate	399.5	408.5	405.5	32.79	25.74	24.57	—	—
Ethyl formate	401.0	411.0	408.5	—	—	—	—	—
Acetone	407.0	416.5	414.0	—	25.22	24.33	—	—
Methyl isobutyl ketone	405.0	412.5	409.5	—	—	—	—	—
Dichloromethane	410.0	419.0	420.0	32.25	24.96	24.33	3 252	1 713
1,2-Dichloroethane	411.0	419.0	419.5	32.36	25.06	24.27	3 255	1 713
Acetonitrile	409.0	421.0	420.0	—	—	24.27	—	1 713
Nitromethane	413.5	—	422.5	—	—	—	—	1 712
Cyclopentanone	411.0	419.0	415.0	—	—	—	—	—
Dibromomethane	415.5	425.0	425.5	—	—	—	3 245	1 710
N,N-Dimethylformamide	415.0	423.0	420.0	32.05	24.66	24.04	—	—
Dimethyl sulphoxide	420.0	431.0	428.0	31.70	24.60	23.87	—	1 709
Diiodomethane	423.0	436.5	435.5	—	—	—	3 237	1 707
N,N-Dimethylacetamide	—	—	—	32.05	24.75	24.04	—	—
Hexamethylphosphorotriamide	—	—	—	31.90	24.75	24.33	—	—
Triethylamine	—	—	—	—	27.14	24.87	—	—
N-Methylpyrrolidone	—	—	—	31.90	24.60	—	—	—
4-Butyrolactone	—	—	—	31.95	24.60	—	—	—
n-Butyl ether	—	—	—	33.56	26.85	—	—	—

involving dynamic equilibrium between two states which are rapidly interconverted (*e.g.* acetylacetone enol form or acetic acid dimer<sup>27</sup>) and systems with intramolecular hydrogen bond. IR spectroscopy is very sensitive to existence of hydrogen bond, and there is a rough relation between increasing strength of the hydrogen bond and decreasing wave number of the group bound by this bond. The solvent molecules of the cybotactic sphere play two roles again: they undergo additional polarization during excitation (shift of the absorption band to lower wavenumbers) and affect the strength of intramolecular hydrogen bond (shift of the absorption band to higher wave numbers as compared with its position found for the molecule in gaseous phase). Both these effects are antagonistic, and relation in the form of Eq. (1) can again be expected. We measured IR spectra of 2-nitrophenol in 13 solvents (Table II) and carried out their correlation with the  $f(\epsilon, n^2)$  and  $f(\epsilon)$  terms according to Eq. (1). The resulting equation reads as follows:

$$\begin{aligned} \nu_{\text{O-H}} &= 3\,241 - 327.5f(\epsilon, n^2) + 226.0f^2(\epsilon) & (3) \\ R &= 0.926, \quad SD = 2.89. \end{aligned}$$

Correlation of these data with only the  $f(\epsilon, n^2)$  term was low, similarly the empirical parameters *e.g.*  $G$  factors by Allerhand & Schleyer,  $\pi^*$  parameters by Taft and Kamlet, or the  $E_{\text{T}}(30)$  solvent factors are quite unsatisfactory for evaluation of effect of medium in this case.

As far as relation of  $E_{\text{T}}(30)$  and  $\pi^*$  solvent parameters is considered, it can be obtained in quantitative form for systems involving only non-specific interactions by solving Eq. (1) with the correlation equation between  $\pi^*$  and  $f(\epsilon, n^2)$  which for 29 aliphatic aprotic solvents reads as follows<sup>3</sup>:

$$\pi^* = 14.65f(\epsilon, n^2) - 0.573; \quad R = 0.989; \quad SD = 0.049. \quad (4)$$

The final relation between  $E_{\text{T}}(30)$  and  $\pi^*$  parameters has the form:

$$E_{\text{T}}(30) = 28.73 - 1.99\pi^* + 72.02f^2(\epsilon). \quad (5)$$

Electronic spectra of 3-nitro-*N,N*-dimethylaniline, 4-nitroso-*N,N*-dimethylaniline and *N*-(2-nitrophenyl)piperidine and IR spectra of acetone were used for calculation of the  $\pi^*$  solvent parameters of perfluorohexane, dibromomethane and diiodomethane (-0.40, 0.92 and 1.12, respectively).

A number of papers has been devoted to the problem of theoretic evaluation of the solvent-induced shifts in electronic spectra; the suggested equations were tested with respect to their applicability to experimental data and to applicability to calcula-

tion of dipole moment of the studied molecule in its excited state. The problem is reviewed in ref.<sup>16</sup>. The most suitable for these studies proved to be the equation suggested by Bilot and Kawski and Bachshiev<sup>11-16,24</sup>, which, for these purposes, is used in the form:

$$\nu = A + B(n^2 - 1)/(n^2 + 2) + C(2n^2 + 1)/(n^2 + 2) [(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)] \quad (6)$$

With the aim to test the applicability of the suggested model and the product term for evaluation of solvent effects in electronic spectroscopy, we carried out correla-

TABLE III

Regression coefficients and correlation characteristics of dependences of electronic (*I-V*), fluorescence (*VI*) and infrared spectra (*VIII*) of the studied compounds on medium (using Eqs (6)-(8))

Value	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VIII</i>
Eq. (6)							
<i>A</i>	28.90	28.03	28.64	36.13	30.34		
<i>B</i>	-11.49	-11.09	-12.32	- 8.62	-12.68		
<i>C</i>	- 2.38	- 1.99	- 2.29	- 2.34	- 2.89		
<i>R</i>	0.9918	0.983	0.967	0.987	0.978		
<i>SD</i>	0.12	0.17	0.22	0.15	0.23		
Eq. (7)							
<i>A'</i>	27.74	26.94	27.39	35.60	29.19		
<i>B'</i>	-35.48	-29.58	-33.89	-34.40	-44.43		
<i>C'</i>	- 5.31	-10.87	-10.33	- 4.70	- 2.32		
<i>R</i>	0.995	0.987	0.971	0.991	0.984		
<i>SD</i>	0.10	0.15	0.21	0.13	0.20		
Eq. (8)							
<i>A</i>	27.61	26.69	27.07			25.63	1 730.6
<i>B</i>	-36.70	-32.40	-35.60			-15.35	-204.6
<i>R</i>	0.9923	0.975	0.960	0.991	0.984	0.963	0.968
<i>SD</i>	0.12	0.20	0.24	0.13	0.20	0.10	1.5
<i>n</i>	24	21	23	15	18	16	19

tion of position of the longest-wave bands of 3-nitro-N,N-dimethylaniline, 4-nitroso-N,N-dimethylaniline, N-(2-nitrophenyl)piperidine, 4-nitroanisole, and 4-nitro-N,N-diethylaniline using both Eq. (6) and equation containing the product term in the form:

$$\nu = A' + B'(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1) + C'(n^2 - 1)/(2n^2 + 1). \quad (7)$$

The investigation involved 30 aprotic aliphatic solvents (Table II); the found regression coefficients and correlation characteristics are given in Table III. Comparison of the correlation coefficients and standard deviations shows that Eq. (7) fits the experimental data in all cases better (the only monoparameter Eq. (8) in three cases better) than the equation by Bilot-Kawski-Bachshiev.

$$\nu = A + B(\epsilon - 1)(n^2 - 1)/(2\epsilon - 1)(2n^2 + 1). \quad (8)$$

Table III also gives results of regression analysis of dependence of position of fluorescence maximum of N-methylacridone on relative permittivity and refractive index of the solvents carried out by Eq. (8). The fluorescence spectra were taken from ref.<sup>24</sup> and the values obtained by analysis are given in Table II. The results obtained show that application of the product term can be expected to be suitable to evaluation of solvent shifts in fluorescence spectra.

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*Note added in proof:* When replacing  $f(e)$  part of the  $f(e, n^2)$  term by some solvent parameter say  $P$ , new empiric solvent polarity scale is obtained which is related to the solvent induced spectral shifts in the form  $P.f(n^2)$  and these  $P$  solvent parameters are directly applicable to the correlation of solvent effects on chemical kinetic and equilibrium data in a better way than any other polarity parameters. Examples of the application of these new polarity parameters are given in our next communication.