

A STUDY OF THE MEDIUM EFFECT OF MIXED SOLVENTS; THE BENZENE-ACETONITRILE SYSTEM

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Rate constants of the reaction of triethylamine with ethyl iodide (at 293·15, 313·15, 323·15, and 333·15 K) and wave numbers of the longest wavelength band maxima of 4-nitroso-N,N-dimethylaniline, 3-nitro-N,N-dimethylaniline, and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide were measured in benzene, acetonitrile, and their eleven mixtures. Activation characteristics of the reaction of triethylamine with ethyl iodide in these media were calculated, and the correlations of rate constants and spectral data with the functions of relative permittivity and refractive index of the media used and mutually with each other were carried out.

In the framework of an extensive study of the medium effect of mixed solvents on chemical and physical properties and processes, this study of the medium effect of the benzene and acetonitrile mixtures was carried out on the rate of reaction of triethylamine with ethyl iodide and on the wave numbers of the longest wavelength band maxima of 4-nitroso-N,N-dimethylaniline, 3-nitro-N,N-dimethylaniline, and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide. The work resumes our foregoing paper on the medium effect of the acetone-cyclohexane and cyclohexane-nitrobenzene mixtures¹.

The aim of this work has been to investigate the applicability of the functions of relative permittivity and refractive index on evaluating the changes of the above-mentioned properties induced by medium, and in terms of the solvatochromic method by Kamlet and Taft, to judge also the interrelations between the changes induced by medium in kinetic data and electronic spectra of the given indicators.

EXPERIMENTAL

The measurement of reaction rates and electronic spectra was carried out as in our foregoing studies¹. The values of relative permittivities of mixed solvents were taken from literature².

RESULTS AND DISCUSSION

The results obtained are given in Tables I–III. Table I presents, in addition to the wave numbers of the absorption band maxima of the studied indicators found in the media studied, the Kirkwood–Onsager and Block–Walker functions of relative permittivity, $f(D) = (D - 1)/(2D + 1)$, $\Theta(D) = 3D \ln D / (D \ln D - D + 1) - (6/\ln D) - 2$, the Kirkwood–Onsager function of refractive index $f(n^2) = (n^2 -$

$-1)/(2n^2 + 1)$, the product function of relative permittivity and refractive index $f(D, n^2) = (n^2 - 1)(D - 1)/(2n^2 + 1)(2D + 1)$, and the values of the Reichardt E_T^N parameters³ calculated as a ratio of wave numbers of the longest wavelength band maxima of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide in the given medium and in tetramethylsilane as a reference medium.

The Menshutkin reaction of triethylamine with ethyl iodide and electronic spectra of 4-nitroso-N,N-dimethylaniline, 3-nitro-N,N-dimethylaniline, and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide are typical processes and properties of problems of medium effect, and therefore were chosen for this study. The rate of the Menshutkin reaction does not depend on the proton-acceptor capability of medium⁴, therefore for the benzene-acetonitrile system studied it is possible to consider only the effect of the polarity of medium itself (nonspecific interactions) on the course of this reaction. Similarly in case of substances used to study the medium effect on electronic spectra it is not necessary to consider the effect of the medium basicity because the substances are concerned which do not contain acid hydrogen. Benzene and acetonitrile represent, from the point of view of dielectric properties, rather different solvents. So, $f(D)$ function of relative permittivity is for acetonitrile more than double compared to benzene whereas the function of refractive index $f(n^2)$ is for acetonitrile essentially lower than for benzene. This fact manifests itself above all

TABLE I

Functions of relative permittivity and refractive index $f(D)$, $f(n^2)$, and $f(D, n^2)$, wave number $\tilde{\nu}^I$ (cm^{-1}) of the absorption band maximum of 4-nitroso-N,N-dimethylaniline and wave number $\tilde{\nu}^{II}$ (cm^{-1}) of the absorption band maximum of 3-nitro-N,N-dimethylaniline and the Reichardt parameter E_T^N of the benzene-acetonitrile mixtures in dependence on the volume fraction of nitrobenzene v

v	$f(D)$	$\Theta(D)$	$f(n^2)$	$f(D, n^2)$	$\tilde{\nu}^I$	$\tilde{\nu}^{II}$	E_T^N
0.00	0.230	0.129	0.228	0.052	24 190	24 630	0.127
0.05	0.315	0.192	0.226	0.071	23 980	24 390	0.256
0.10	0.361	0.234	0.223	0.081	23 860	24 310	0.290
0.20	0.413	0.295	0.218	0.090	23 770	24 180	0.352
0.30	0.436	0.332	0.213	0.093	23 700	24 160	0.383
0.40	0.450	0.359	0.207	0.093	23 660	24 150	0.410
0.50	0.460	0.382	0.202	0.093	23 660	24 170	0.386
0.60	0.466	0.397	0.196	0.091	23 640	24 150	0.417
0.70	0.472	0.414	0.191	0.090	23 630	24 190	0.429
0.80	0.475	0.426	0.187	0.089	23 640	24 220	0.451
0.90	0.478	0.436	0.181	0.087	23 660	24 290	0.454
0.95	0.479	0.440	0.177	0.085	23 660	24 280	0.460
1.00	0.480	0.444	0.174	0.084	23 650	24 290	0.472

TABLE II

Rate constants of the reaction $(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{I} = (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{I}^-$, k ($10^{-5} \text{ dm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}$) in the benzene-acetonitrile mixtures in dependence on volume fraction of acetonitrile v and temperature T

v	$T, \text{ K}$			
	293.15	313.15	323.15	333.45
0.00	0.372	1.15	2.65	4.28
0.05	1.13	3.26	6.00	11.3
0.10	1.67	5.50	9.55	16.8
0.20	2.92	11.0	21.5	36.2
0.30	4.07	12.7	25.7	50.4
0.40	6.00	22.4	36.5	69.2
0.50	6.51	27.6	41.5	81.7
0.60	8.58	30.7	62.0	101.0
0.70	9.80	37.9	72.4	118.0
0.80	11.5	40.8	74.5	130.0
0.90	13.4	44.0	85.2	143
0.95	14.4	46.4	91.0	152
1.00	17.2	54.3	100.0	190

TABLE III

Activation parameters of the reaction $(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{I} = (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{I}^-$ ($T = 298.15 \text{ K}$) in the benzene-acetonitrile mixtures in dependence on volume fraction of acetonitrile v

v	ΔG^\ddagger kJ mol^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{ K}^{-1}$
0.00	103.52	48.12	-185.92
0.05	100.86	42.38	-196.20
0.10	99.61	44.13	-185.91
0.20	98.29	49.11	-145.95
0.30	97.60	48.22	-165.38
0.40	96.51	46.75	-167.00
0.50	96.22	48.97	-158.56
0.60	95.62	48.24	-159.30
0.70	95.15	48.81	-155.49
0.80	94.92	46.85	-161.30
0.90	94.55	45.93	-163.17
0.95	94.40	45.72	-160.47
1.00	93.86	45.49	-161.32

in the product term, $f(D, n^2)$ whose value in the interval up to 40% acetonitrile increases rapidly and then decreases (Table I). When evaluating the medium effect on electronic spectra by the method of cross term⁵, the contribution of the product function $f(D, n^2)$ in comparison with that of the function of refractive index $f(n^2)$ is decisive (see ref.⁶) – qualitatively reflects this fact also the trend of values of wave numbers of maxima of the indicators studied in the used mixtures of benzene and acetonitrile when $\tilde{\nu}_{\max}$ decrease first and then increase with increasing acetonitrile content.

From the dependence of logarithm of rate constant on $1/T$, the activation parameters of this reaction were calculated. They are given in Table III. The activation parameters exhibit similar dependence on medium as in case of this reaction in the cyclohexane–acetone mixtures¹ and in case of mixtures of aromatic hydrocarbons with dimethyl sulphoxide^{7–9}. The negative activation entropy found in the entire concentration range shows that the transition state of the reaction studied is structurally similar to a ion pair. The calculated values of activation entropy for the mixtures show too large scatter to be able to judge their dependence on composition. As to the dependence of activation enthalpy on composition, it has a similar form as for this reaction studied in the mixtures of dimethyl sulphoxide with aromatic hydrocarbons^{7–9}.

The quantitative evaluation of the effect of mixed media on the rate of the reaction studied was carried out by the procedures used in case of evaluating the medium effect of pure solvents. In addition to the semiempirical methods by Onsager–Kirkwood and Block–Walker, we have used the empirical procedures by Kamlet and Taft and Dimroth and Reichardt. The correlation equations between $\log k$ and the respective parameters have the form (R and σ are the correlation coefficient and standard deviation):

$$\log k = -5.96 + 6.23f(D) \quad R = 0.975, \quad \sigma = 0.11 \quad (1)$$

$$\log k = -5.94 + 4.71\Theta(D) \quad R = 0.993, \quad \sigma = 0.05 \quad (2)$$

$$\log k = -5.54 + 2.76 \cdot 10^{-3} \Delta\tilde{\nu} \quad R = 0.945, \quad \sigma = 0.16 \quad (3)$$

$$\log k = -5.46 + 5.16 \cdot 10^{-4} \Delta\tilde{\nu}/f(n^2) \quad R = 0.988, \quad \sigma = 0.08 \quad (4)$$

$$\log k = -5.98 + 4.67E_T^N \quad R = 0.987, \quad \sigma = 0.08 \quad (5)$$

From the comparison of the correlation characteristics follows that the Block–Walker function suits essentially better the evaluations than the Kirkwood–Onsager one. Better applicability of the Block–Walker function is usually interpreted as a consequence of the fact that this function includes also the effect of dielectric saturation of the solvent molecules in the vicinity of the solute molecules^{4,10}. The dependence

of $\log k$ on the Kirkwood–Onsager and Block–Walker functions is plotted in Figs 1 and 2. On the other hand it is, however, known¹¹ that the rate of the Menshutkin reaction depends also on the deformation polarizability of solvent molecules, and this effect is evaluated by the Kirkwood–Onsager function of refractive index. The extension of correlation equations (1) and (2) by this term leads to an increase of correlation coefficients of these dependences up to 0.998.

The comparison of effectiveness of the correlation of $\log k$ with the changes of position of absorption maximum of 4-nitroso-N,N-dimethylaniline induced by medium and with the ratio of this change and the function of refractive index $f(n^2)$ is also interesting. The correlation with the ratio is significantly better (half standard deviation) and indicates so that a modification of the Kamlet–Taft solvatochrome method¹² is perspective even in the region of the effect of the mixed solvent medium, naturally especially in the cases when components of a mixture differ considerably in their refractive indices.

As to the evaluation of medium effect on the position of absorption maxima of 4-nitroso-N,N-dimethylaniline and 3-nitro-N,N-dimethylaniline, we have used the method of a product function, that is the correlations of wave numbers with a two-parameter equation with terms $f(D, n^2)$ and $f(n^2)$; the equations have had the form:

$$\bar{\nu} = 23\,910 - 10\,740 f(D, n^2) + 3\,690 f(n^2) \quad R = 0.998, \quad \sigma = 12 \quad (6)$$

$$\bar{\nu} = 25\,440 - 12\,010 f(D, n^2) - 827 f(n^2) \quad R = 0.989, \quad \sigma = 19. \quad (7)$$

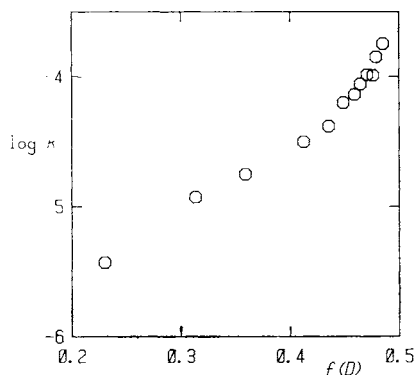


FIG. 1

Dependence of logarithm of rate constant of the reaction of triethylamine with ethyl iodide at the temperature of 293.15 K on the Kirkwood–Onsager function of relative permittivity

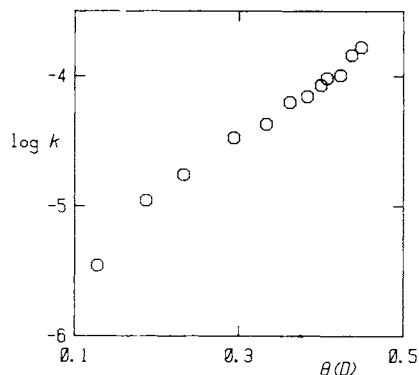


FIG. 2

Dependence of logarithm of rate constant of the reaction of triethylamine with ethyl iodide at the temperature of 293.15 K on the Block–Walker function of relative permittivity

Similarly to the case of pure solvents¹³, also in the case of the mixtures studied, their E_T^N parameter depends mainly on the function of relative permittivity of medium:

$$E_T^N = 0.05 + 1.73f^2(D) + 0.065f(D, n^2)$$
$$R = 0.984, \quad \sigma = 0.015. \quad (8)$$

It is well known that the manifestation of aromatic hydrocarbons as a medium does not correspond to their relative permittivity but it is higher⁴. The performed correlations of studied properties in the used mixed media showed that also the effective manifestation of orientational polarization of benzene is, in the mixtures studied, a function of composition, similarly to relative permittivity.

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