

## A STUDY OF THE MEDIUM EFFECT OF MIXED SOLVENTS; THE CYCLOHEXANE-NITROBENZENE SYSTEM

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Rate constants of the reaction of triethylamine with ethyl iodide (at 293·15, 313·15, 323·15, and 333·45 K) and wavenumbers of the longest wavelength band maxima of 4-nitroso-N,N-dimethylaniline and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide were measured in nitrobenzene and thirteen mixtures of nitrobenzene with cyclohexane. The activation characteristics of the reaction of triethylamine with ethyl iodide in these media were calculated, and the correlations of rate constants and spectral data were carried out with functions of relative permittivity and refractive index of the media used and mutually with each other.

Thanks to the extensive work of Kamlet and Taft, a systematic characterization of a great many solvents has been carried out in the last ten years which makes it possible to achieve hitherto the most reliable prediction and interpretation of the medium effect on chemical and physical properties and processes<sup>1,2</sup>. The region of evaluating the effect of mixed media, which are very widespread in practical chemistry, remains, however, at the border of interest. The studies of the effect of mixed media carried out up to now have not required a more general validity, and the interpretation of experimental data has been carried out more or less successfully in terms of functions of relative permittivity.

The aim of this work was to study the medium effect of the cyclohexane-nitrobenzene mixture on the rate of reaction of triethylamine with ethyl iodide and on the electronic spectra of 4-nitroso-N,N-dimethylaniline and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide in the entire concentration range of the solvents given, and to carry out a correlation of the medium effect on the obtained experimental data with functions of relative permittivity and refractive index and mutually with each other in terms of the Kamlet-Taft method of evaluating the medium effect.

### EXPERIMENTAL

The electronic spectra were measured on an SP 1800 Unicam apparatus in quartz measuring cells 1 cm thick (2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide) and in sodium chloride measuring cells of thickness 0·1 mm (4-nitroso-N,N-dimethylaniline). The measurement of reaction rates was carried out at the temperatures of 293·15, 313·15, 323·15, and 333·45 K with an accuracy of  $\pm 0\cdot02$  K. Identical amounts of freshly prepared  $0\cdot2$  mol dm<sup>-3</sup> solutions of tri-

ethylamine and ethyl iodide in corresponding solvent were got into 5 cm<sup>3</sup> glass ampoules which were placed after sealing into a thermostat. In given time intervals, the ampoules were taken out of the thermostat and placed into an ice bath.

The content of unreacted triethylamine was determined by titration. 3 cm<sup>3</sup> solution from the ampoule were inserted into 15 cm<sup>3</sup> 0.025 mol dm<sup>-3</sup> hydrochloride acid solution. The excess of acid was then titrated visually with 0.016 mol dm<sup>-3</sup> sodium hydroxide solution free of carbonates on using bromothymol blue as an indicator. The triethylamine content was determined in this way with an accuracy of 1%. The rate constant was calculated from the relation  $kt = 1/(a-x) - 1/a$ , where  $a$  is the initial triethylamine concentration and  $(a-x)$  is the instantaneous triethylamine concentration. The activation parameters were calculated by the least-squares method from the temperature dependence of the rate constant. The values of relative permittivity were taken from literature<sup>3</sup>, the refractive index of these mixtures was measured using a refractometer RL Nr 2611. The regression analysis of the data obtained was performed by means of a computer. The solvents were freed of water by anhydrous sodium sulphate and dried up by double treatment of freshly activated molecular sieve Nalcit 4.

## RESULTS AND DISCUSSION

The results obtained are given in Tables I–III. Table I presents, besides the functions of relative permittivity ( $D$ ) and refractive index ( $n$ ),  $f(D) = (D-1)/(2D+1)$ ,

TABLE I

Functions of relative permittivity and refractive index  $f(D)$ ,  $\theta(D)$ ,  $f(n^2)$ , and  $f(D, n^2)$ , wave number  $\tilde{\nu}_{\max}$  (in cm<sup>-1</sup>) of the absorption band maximum of 4-nitroso-N,N-dimethylaniline, and  $E_T(30)$  parameter of the cyclohexane–nitrobenzene mixture in dependence on the volume fraction of nitrobenzene  $v$  (in kJ mol<sup>-1</sup>)

$v$	$f(D)$	$\theta(D)$	$f(n^2)$	$f(D, n^2)$	$\tilde{\nu}_{\max}$	$E_T(30)$
0.00	0.2020	0.115	0.2044	0.0410	25 316	7.93
0.05	0.2860	0.166	0.2067	0.0591	25 063	—
0.095	0.3247	0.206	0.2093	0.0680	24 876	9.25
0.20	0.3908	0.267	0.2132	0.0833	24 450	9.58
0.26	0.4116	0.299	0.2179	0.0897	24 213	9.75
0.32	0.4286	0.314	0.2185	0.0936	24 155	9.82
0.40	0.4412	0.345	0.2213	0.0976	24 010	9.78
0.45	0.4489	0.358	0.2231	0.1001	23 923	9.80
0.55	0.4593	0.378	0.2281	0.1048	23 781	9.94
0.60	0.4621	0.384	0.2298	0.1062	23 781	9.87
0.70	0.4684	0.403	0.2330	0.1091	23 641	10.40
0.76	0.4717	0.416	0.2358	0.1112	23 585	10.04
0.80	0.4728	0.4	0.2378	0.1124	23 474	10.25
0.90	0.4766	0.430	0.2406	0.1144	23 364	10.04
1.00	0.4793	0.439	0.2430	0.1165	23 256	10.04

$f(n^2) = (n^2 - 1)/(2n^2 + 1)$ ,  $f(D, n^2) = (n^2 - 1)(D - 1)/(2n^2 + 1)(2D + 1)$ , and the Block-Walker function of relative permittivity  $\Theta(D) = 3D \ln D / [(D \ln D - D + 1) - (6/\ln D) - 2]$ , the wavenumber of the absorption band maximum of 4-nitroso-N,N-dimethylaniline and  $E_T(30)$  parameter found in the given mixtures cyclohexane-nitrobenzene. Table II summarizes the rate constants of the reaction of triethylamine with ethyl iodide measured in the cyclohexane-nitrobenzene mixtures at the temperatures of 293.15, 313.15, 323.15, and 333.45 K and the relative rate constants in the given mixture with regard to the rate constant of this reaction found in nitrobenzene ( $k/k_{Nb}$ ). In Table III there are the activation parameters of the reaction studied as found for the temperature of 298.15 K in the mixed solvents. The Dimroth-Reichardt parameters were calculated from the wavenumber of the absorption band maximum of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide according to the relation  $E_T(30) = a \cdot \tilde{\nu}$ , where  $a = 1.196 \cdot 10^{-2} \text{ kJ cm mol}^{-1}$ . The value of  $E_T(30)$  for cyclohexane was taken from literature<sup>4</sup>.

Similarly to our foregoing work<sup>5</sup>, we used in this study the Menshutkin reaction of triethylamine with ethyl iodide and electronic spectra of 4-nitroso-N,N-dimethyl-

TABLE II

Rate constants  $k$  ( $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of the reaction  $(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{I} = (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{I}^-$  and relative rate constants related to the rate of reaction in pure nitrobenzene ( $k_{Nb}$ ) and in the cyclohexane-nitrobenzene mixtures in dependence on volume fraction of nitrobenzene  $v$  and temperature  $T$

$v$	$k^a$	$k/k_{Nb}^a$	$k^b$	$k/k_{Nb}^b$	$k^c$	$k/k_{Nb}^c$	$k^d$	$k/k_{Nb}^d$
0.00	0.003	0.00014	0.010	0.00015	0.019	0.00017	0.036	0.00019
0.05	0.018	0.00086	0.050	0.00076	0.090	0.00080	0.178	0.0009
0.10	0.053	0.0026	0.196	0.0030	0.369	0.0033	0.655	0.0034
0.20	0.161	0.0078	0.573	0.0090	1.30	0.0092	2.27	0.012
0.26	0.273	0.013	1.18	0.040	2.34	0.021	3.94	0.021
0.32	0.433	0.021	1.48	0.023	3.38	0.030	5.59	0.029
0.40	0.784	0.038	2.85	0.043	4.88	0.044	8.91	0.047
0.45	0.80	0.040	2.88	0.043	5.38	0.048	10.08	0.053
0.55	1.54	0.074	5.58	0.085	10.92	0.097	19.15	0.100
0.60	2.48	0.120	12.0	0.183	21.7	0.194	32.5	0.170
0.70	3.34	0.161	12.7	0.194	24.8	0.221	47.2	0.231
0.76	5.36	0.259	20.1	0.306	37.0	0.330	61.8	0.324
0.80	8.20	0.396	29.3	0.447	49.6	0.443	83.2	0.436
0.90	13.5	0.652	36.9	0.563	64.0	0.571	113.0	0.590
1.00	20.7	1.000	65.6	1.000	112.0	1.000	191.0	1.000

<sup>a</sup>  $T = 293.15 \text{ K}$ ; <sup>b</sup>  $T = 313.15 \text{ K}$ ; <sup>c</sup>  $T = 323.15 \text{ K}$ ; <sup>d</sup>  $T = 333.45 \text{ K}$ .

aniline and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide as a typical processes and properties of problems of study of the medium effect. The cyclohexane–nitrobenzene system was used for that reason that cyclohexane pertains to the Kamlet–Taft set of selected solvents ( $\delta = 0$ ), whereas nitrobenzene belongs to aromatic solvents ( $\delta = 1$ ) with conspicuous dipole moment which in the studies of medium effect behaves often inconsistently<sup>1,6</sup>.

As can be seen from Table II, the reaction rate of the Menschutkin reaction studied increases with temperature and polarity of medium. Previous studies of this reaction showed<sup>1,7,8</sup> that the rate of this reaction does not depend on the basicity of medium so that in case of the mixed media used, the rate of reaction is influenced only by polarity of medium. Therefore we carried out a correlation of the rate constants found at 293.15 K with the Kirkwood  $f(D)$  function, the Block–Walker  $\Theta(D)$  function, the Dimroth–Reichardt  $E_T(30)$  parameters, with the changes of the position of adsorption maximum of 4-nitroso-N,N-dimethylaniline  $\Delta\tilde{\nu}$  induced by solvent, and with the ratio of  $\Delta\tilde{\nu}$  and the function of refractive index,  $\Delta\tilde{\nu}/f(n^2)$ ; the correlation equations have the form ( $R$  is correlation coefficient,  $\sigma$  is standard deviation):

$$\log k = -10.40 + 12.63 f(D) \quad R = 0.950, \sigma = 0.34 \quad (1)$$

TABLE III

Activation parameters of the reaction  $(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4N^+ + I^-$  (298.15 K) in the cyclohexane–nitrobenzene mixtures in dependence on volume fraction of nitrobenzene  $v$

$v$	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>
0.00	113.81	45.09	-230.6
0.05	111.37	43.17	-228.7
0.095	108.49	48.87	-200.0
0.20	105.73	52.13	-179.8
0.26	104.28	52.67	-173.1
0.32	103.25	50.48	-176.9
0.40	101.73	46.58	-185.0
0.45	101.71	49.00	-176.8
0.55	100.02	49.00	-171.1
0.60	98.58	50.97	-159.7
0.70	97.95	50.23	-160.1
0.76	96.70	44.41	-165.3
0.80	95.85	44.71	-171.5
0.90	94.62	40.22	-182.5
1.00	93.62	42.72	-170.7

$$\log k = -8.67 + 10.69 \Theta(D) \quad R = 0.989, \sigma = 0.16 \quad (2)$$

$$\log k = -20.24 + 1.561 E_T(30) \quad R = 0.893, \sigma = 0.45 \quad (3)$$

$$\log k = -7.23 + 1.73 \Delta\bar{v} \quad R = 0.993, \sigma = 0.13 \quad (4)$$

$$\log k = -7.44 + 0.417 \Delta\bar{v}/f(n^2) \quad R = 0.987, \sigma = 0.17. \quad (5)$$

As it is evident from the correlation equations, the Block-Walker function of relative permittivity suits much better the evaluation of media used than the Kirkwood function (half standard deviation). It is a consequence of medium effect in the region of higher relative permittivities, for  $f(D) = 0.45-0.48$ . For the region  $0.20-0.45$ , the Kirkwood function suits very well and the correlation equation has the form

$$\log k = -9.51 + 9.73 f(D) \quad R = 0.997, \sigma = 0.07. \quad (6)$$

Better applicability of the Block-Walker function for evaluating the medium effect in the entire region is usually interpreted by the fact that the Block-Walker function considers also the effect of dielectric saturation which is acute just in the region of higher relative permittivity. The Block-Walker function evaluates also very well the medium effect of the studied mixtures of nitrobenzene and cyclohexane and the mixtures of cyclohexane and acetone<sup>5</sup>; for 27 these mixed solvents, the correlation equation between  $\log k$  and this function has the form

$$\log k = -8.49 + 10.23 \Theta(D) \quad R = 0.988, \sigma = 0.15.$$

Unlike the cyclohexane-acetone system<sup>5</sup>, in case of the nitrobenzene-cyclohexane mixtures we have found the best correlation between  $\log k$  and the solvent-induced changes in position of adsorption band of 4-nitroso-N,N-dimethylaniline. The  $E_T(30)$  parameters failed completely to correlate. This might be connected with the fact that the cyclohexane-nitrobenzene system exhibits just in the region of anomalous behaviour of the Dimroth-Reichardt indicator ( $v = 0.70$ ) the limited miscibility (the mixture forms two phases at 15°C), and also the isothermal vapour-liquid equilibrium data which are available<sup>9</sup> for this system show a conspicuous deviation from ideal behaviour in this region.

The activation parameters of the studied Menschutkin reaction show analogous dependence on medium as in the cyclohexane-acetone mixtures<sup>5</sup>. The negative activation entropy found in the entire concentration range indicates that the transition state of this reaction is structurally similar to ion pair. The fact that activation entropy increases with increasing nitrobenzene concentration in the mixtures gives further evidence that the solvation of the formed charges of transition state is not an only reason of negative activation entropy of this reaction. It is further worth

noting that the activation entropy has its maximum value in the above-mentioned region about 70 vol. % nitrobenzene.

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