A STUDY OF THE MEDIUM EFFECT OF MIXED SOLVENTS; THE CYCLOHEXANE–ACETONE SYSTEM

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Wavenumbers of the S—O bond valence vibration of dimethyl sulphoxide, wavenumbers of the longest wavelength band maxima of 3-nitro-N,N-dimethylaniline and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide and rate constants of the reaction of triethylamine with ethyl iodide measured in mixtures of cyclohexane and acetone were correlated with functions of relative permittivity and refractive index of these media and mutually with each other.

The use of mixed solvents is very popular when studying the course of chemical reactions. These studies are mostly carried out in mixtures of water with alcohols and some aprotic solvents as dioxane, dimethylformamide, and dimethyl sulphoxide, the studies performed in mixtures of aprotic solvents only being very rare (e.g.[1-11]). A question, which is rather seldom solved, is the problem of quantitative evaluation of the effect of mixed media, not taking into account the frequent attempts to interpret experimental data by means of the functions of relative permittivity irrespective of the fact that the medium is considered, where, besides the influence of polarity itself, the medium exerts an influence through its acidity or basicity.

The aim of this work was to study the medium effect of the cyclohexane–acetone mixture in the entire concentration range on the rate of reaction of triethylamine with ethyl iodide, and further the effect of this medium on the valence vibration of S – O bond in dimethyl sulphoxide and on the position of the longest wavelength band of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide ($E_T(30)$ parameters of polarity) and 3-nitro-N,N-dimethylaniline in the visible region of light.

EXPERIMENTAL

The infrared spectra were measured on an IR-75 apparatus (Zeiss, Jena) in sodium chloride measuring cells of thickness 0·3 mm, the concentration of solutions measured was 10^{-4} mol dm^{-3}. The electronic spectra were measured on an SP 1800 Unicam apparatus in quartz measuring cells 1 cm thick, the concentration of solutions was 10^{-5} mol dm^{-3}. The measurement of reaction rates was carried out at the temperatures of 292·65, 313·45, 322·65, and 333·45 K with an accuracy of $\pm 0·02$ K. Identical amounts of freshly prepared 0·2 mol dm^{-3} solutions of triethylamine and ethyl iodide were placed into 5 cm^3 glass ampoules which were placed after sealing into a thermostat. In 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^3 solution from the ampoule were inserted into 15 cm^3 0·025 mol dm^{-3} hydrochloride acid solution. The excess of acid was titrated visually with 0·016 mol dm^{-3} 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

$$kt = 1/(a - x) - 1/a, \qquad\qquad (1)$$

where a is the initial triethylamine concentration (0·1 mol dm^{-3}) 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 of the cyclohexane–acetone mixtures were taken from the literature[12], the refractive index of these mixtures was measured using a refractometer RL Nr 2611. The regresion analysis of the data obtained was performed by means of a computer. The solvents used were dehydrated by anhydrous sodium sulphate and dried up by double treatment of 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 : $f(D) = (D - 1)/(2D + 1)$, $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ and $f(D, n^2) = (D - 1)(n^2 - 1)/(2D + 1)(2n^2 + 1)$, the wavenumber of valence vibration of S–O bond of dimethyl sulphoxide $(\tilde{\nu}_{S-O})$, the wavenumber of the absorption band maximum of 3-nitro-N,N-dimethylaniline and $E_T(30)$ parameter found in the given mixtures cyclohexane–acetone. Table II summarizes the rate constants of the reaction of triethylamine with ethyl iodide measured in the cyclohexane–acetone mixture at four temperatures along with the relative rate constant in the given mixture with regard to the rate constant of this reaction found in acetone (k/k_{AC}). In Table III there are the activation parameters of the studied reaction calculated for the temperature of 298·15 K in single mixed solvents. The values of the Dimroth–Reichardt parameter $E_T(30)$ 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 $E_T(30) = 2·889 . 10^{-3}\tilde{\nu}$.

The system acetone–cyclohexane was chosen for that reason that both the solvents are aprotic, differing considerably in polarity, and furthermore, that they pertain to the Kamlet–Taft set of selected solvents (SSS), where it is sufficient to use the Kirkwood functions of relative permittivity and refractive index[13,14] for evaluating the influence of medium on both the spectral and equilibrium and kinetic data. The reason for selecting the properties studied was the fact that we deal with the properties which have privileged position in the region of empirical methods of evaluating the medium effect. So, the reaction rate of the Menschutkin reaction is dependent expressively on medium and the logarithm of rate constant of the reaction of tripropylamine with methyl iodide is designated as a polarity scale φ. It is a classical S_N2 reaction when from the initial tertiary amine and alkyl iodide, ions are formed,

in case of $(C_2H_5)_3N$ and $(C_2H_5)I$ in terms of the equation

$$(C_2H_5)_3N \ + \ C_2H_5I \ = \ (C_2H_5)_4N^+ \ + \ I^- \ . \qquad\qquad (A)$$
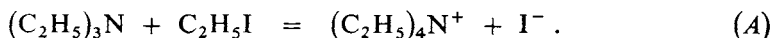
From the point of view of distinguishing single contributions to the effect of medium, the Menschutkin reaction is significantly influenced by the polarity of medium (the reaction is accelerated with increasing polarity) and its acidity (the reaction is decelerated with increasing protondonation ability), and does not show influencing by the medium basicity. A number of works[15-19] was devoted to the study of the influence of single solvents upon the rate of the Menschutkin reaction. As to the effect of mixed solvents on the rate of the Menschutkin reaction, studies were performed of the effect of the mixtures acetone–benzene[3], acetone–dioxane[3], acetone–tetrahydrofuran[4], dimethyl sulphoxide–benzene[5], dimethyl sulphoxide–cyclohexane–benzene[6], dimethyl sulphoxide–toluene[7], dimethyl sulphoxide–p-xylene[8], dimethyl sulphoxide–mesitylene[8] and propionitrile–cyclohexane[15].

The wavenumber of the valence vibration of S–O bond was used to construct an "infrared" scale of polarity[20] G. This adsorption of dimethyl sulphoxide in infrared region is moreover substantially more sensitive towards the effect of medium than the vibration of carbonyl groups, and it is possible to carry out comparison of the solvent--induced changes with the gaseous state, when $f(D) = f(n^2) = f(D, n^2) = 0$.

TABLE I

Functions of relative permittivity and refractive index $f(D)$, $f(n^2)$ and $f(D, n^2)$, wavenumber $\tilde{v}_{S-O}$ of the valence vibration of S—O bond of dimethyl sulphoxide, wavenumber $\tilde{v}_{max}$ of the absorption band maximum of 3-nitro-N,N-dimethylaniline and $E_T(30)$ parameter of the cyclohexane–acetone mixtures in dependence on volume fraction of acetone v

v	$f(D)$	$f(n^2)$	$f(D, n^2)$	$\tilde{v}_{S-O}$	$\tilde{v}_{max}$	$E_T(30)$
0·00	0·202	0·204	0·0412	1 084·0	26 530	—
0·05	0·255	0·203	0·0518	1 077·0	26 300	
0·10	0·300	0·202	0·0606	1 073·2	26 200	37·5
0·15	0·335	0·201	0·0673	1 072·0	26 150	—
0·20	0·355	0·200	0·0710	1 071·0	26 030	38·4
0·30	0·386	0·198	0·0762	1 069·8	25 960	39·3
0·40	0·413	0·194	0·0802	1 068·0	25 940	39·9
0·50	0·425	0·191	0·0812	1 068·0	26 900	40·2
0·60	0·441	0·188	0·0829	1 066·7	25 800	40·5
0·70	0·450	0·186	0·0837	1 066·2	25 750	40·8
0·80	0·456	0·184	0·1839	1 065·5	25 730	41·2
0·90	0·460	0·182	0·0837	1 065·2	25 710	41·6
1·00	0·465	0·180	0·0837	1 065·3	25 710	42·2

TABLE II

Rate constants of the reaction $(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4N^+ + I^-$ $(k, 10^7 \ dm^3 \ mol^{-1} \ s^{-1})$ and relative rate constants related to the rate of reaction in pure acetone (k_{Ac}) in the cyclohexane--acetone mixture in dependence on volume fraction of acetone v and temperature T

v	k^a	k/k_{Ac}^a	k^b	k/k_{Ac}^b	k^c	k/k_{Ac}^c	k^d	k/k_{Ac}^h
0·00	0·30	0·0009	0·99	0·0008	1·86	0·0007	3·6	0·0007
0·05	1·05	0·003	3·5	0·003	6·1	0·0025	11·1	0·0022
0·10	3·96	0·013	13·8	0·011	23·6	0·010	45·6	0·009
0·15	5·10	0·015	17·0	0·014	31·0	0·013	70·0	0·014
0·20	13·0	0·037	46·9	0·038	85·0	0·035	151	0·031
0·30	18·7	0·053	64·0	0·051	122	0·050	280	0·057
0·40	40·0	0·114	165	0·132	292	0·119	508	0·104
0·50	65·0	0·186	266	0·213	382	0·156	955	0·195
0·60	83·5	0·239	351	0·280	556	0·227	1 200	0·245
0·70	124·0	0·354	508	0·406	860	0·351	1 650	0·337
0·80	188·0	0·557	640	0·522	1 120	0·457	2 390	0·489
0·90	277·0	0·790	959	0·767	1 710	0·698	2 730	0·558
1·00	350·0	1·000	1 250	1·000	2 450	1·000	4 890	1·000

^{a} $T = 292 \cdot 65$ K; ^{b} $T = 313 \cdot 45$ K; ^{c} $T = 322 \cdot 65$ K; ^{d} $T = 333 \cdot 45$ K.

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–acetone mixtures in dependence on volume fraction of acetone v

v	$\Delta G^{\ddagger}$ kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
0·00	113·81	45·09	−200·6
0·05	111·47	44·45	−225·0
0·10	108·06	43·36	−217·0
0·15	106·75	49·67	−200·0
0·20	104·88	45·28	−200·0
0·30	104·50	49·97	−182·9
0·40	102·78	47·62	−185·0
0·50	100·99	47·83	−178·3
0·60	100·24	47·62	−176·5
0·70	99·83	47·83	−174·4
0·80	98·75	46·13	−176·5
0·90	97·59	42·50	−184·8
1·00	96·38	45·27	−163·8

The Dimroth–Reichardt $E_T(30)$ parameters are doubtless the most popular empirical characteristics of medium. Up to now they have been published for more than 250 pure solvents[1,21] and for a number of solvent mixtures[9-11].

Finally, in case of 3-nitro-N,N-dimethylaniline, an indicator of the Kamlet–Taft type is considered. Kamlet and Taft, on the basis of the solvatochromism of aromatic mostly nitroaminoderivatives, defined a scale of dipolarity π^*, a scale of basicity β and a scale of acidity α of a great number of solvents, and used these parameters successfully to interpret the solvent-induced changes both in the spectral manifestations of lots of substances and in the region of chemical equilibria and reaction rates[2,22-26].

As it is evident from Table II, the reaction rate of the Menschutkin reaction studied increases with temperature and polarity of medium. The activation entropy of this reaction is negative, which is in agreement with the opinion of Arnet and Reich[27] that the transition state of the Menschutkin reactions is structurally close to an ion pair and with the conclusion of further authors[28,29] which consider the transition state of this reaction structurally closer to initial compounds than to ionic products. However, from Table III is also apparent that the activation entropy of the reaction increases with increasing content of acetone in the reaction medium. Therefore it is not possible to consider only the solvation of the charges formed of transition state as the only reason of negative activation entropy.

In terms of our previous works[13,14,30], we carried out the correlation of the solvent-induced changes in the properties studied with the functions of relative permittivity $f(D) = (D - 1)/(2D + 1)$ and the product term $f(D, n^2) = f(D) \cdot f(n^2) = (D - 1)(n^2 - 1)/(2D + 1)(2n^2 + 1)$. For the rate constant found at 292.65 K, the correlation equations had the form

$$\log k = -9.84 + 11.08 f(D), \quad r = 0.991, \quad \sigma = 0.14, \quad N = 13 \qquad (2)$$

$$\log k = -10.45 + 66.20 f(D, n^2), \quad r = 0.968, \quad \sigma = 0.25, \quad N = 13. \qquad (3)$$

From the correlation coefficients r and standard deviations σ found for N points is evident that the simple function of relative permittivity complies better with evaluating the effect of medium on the rate of this reaction than the product term which is similar to the case of evaluating the influence of medium on non-spectral properties studied in pure solvents.

Even if the difference in the function of refractive index for acetone and cyclohexane is small, we have found even for the studied system acetone–cyclohexane better dependence between the logarithm of rate constant k of this reaction and the wavenumber of energetically lowest transition in 3-nitro-N,N-dimethylaniline measured in identical media $(\Delta \tilde{\nu})$ divided by the function of refractive index of this

media $f(n^2)$ than the simple dependence between $\log k$ and $\Delta\tilde{v}$ (ref.[30]). The correlation equations $\log k$ versus $\Delta\tilde{v}$, $\Delta\tilde{v}/f(n^2)$ and the respective $E_T(30)$ parameters found for the system cyclohexane–acetone have taken the form

$$\log k = -7\cdot67 + 3\cdot70\,\Delta\tilde{v}, \qquad r = 0\cdot991, \quad \sigma = 0\cdot13, \quad N = 13 \qquad (4)$$

$$\log k = -7\cdot56 + 0\cdot66\,\Delta\tilde{v}/f(n^2), \quad r = 0\cdot994, \quad \sigma = 0\cdot11, \quad N = 13 \qquad (5)$$

$$\log k = -22\cdot43 + 0\cdot43\,E_T(30), \qquad r = 0\cdot993, \quad \sigma = 0\cdot09, \quad N = 10. \qquad (6)$$

It was not possible to determine the value of $E_T(30)$ for cyclohexane and 5% solution of acetone in cyclohexane because of an insufficient solubility of the indicator used.

The determined $E_T(30)$ parameters of the cyclohexane–acetone mixtures were correlated with the functions $f(D)$ and $f(D, n^2)$ in terms of our previous interpretation of $E_T(30)$ parameters. The correlation equation has taken the form

$$E_T(30) = 34\cdot4 + 61\cdot0f(D) - 247\cdot6f(D, n^2), \quad r = 0\cdot993, \quad \delta = 0\cdot18,$$
$$N = 10. \qquad (7)$$

In a similar way to the case of pure solvents[14], the parity of regression coefficients for the $f(D)$ and $f(D, n^2)$ functions is opposite. The product term $f(D, n^2)$ complies very well with evaluating the influence of medium of the cyclohexane–acetone mixture upon the position of maxima of IR spectrum of dimethyl sulphoxide $(\tilde{v}_{s-o})$ and electronic spectrum of 3-nitro-N,N-dimethylaniline. The correlation equation has taken here the form for 3-nitro-N,N-dimethylaniline

$$\tilde{v} = 27\,280 - 17\,882f(D, n^2), \quad r = 0\cdot975, \quad \sigma = 59\cdot3, \quad N = 13 \qquad (8)$$

and for dimethyl sulphoxide

$$\tilde{v}_{s-o} = 1\,099 - 385\cdot5f(D, n^2), \quad r = 0\cdot984, \quad \sigma = 1\cdot00, \quad N = 13. \qquad (9)$$

The value of the absolute term $1\,099$ is not too different from $\tilde{v}_{s-o}$ measured in the gaseous state $-1\,103\,\mathrm{cm}^{-1}$ (see ref.[31]) when $f(D, n^2) = 0$. The correlations performed show that in the studied system cyclohexane–acetone it is possible to use very well the correlation equations proposed for evaluating the medium effect of pure solvents. This finding witnesses that the ratio of the solvents in the solvation sphere is close to that in solution.

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