

# Characterization of the solvation spheres of some dipolar spectrally active molecules in binary solvents

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When two solvents very different from the point of view of intermolecular interactions are used to obtain ternary solutions of a spectrally active molecule, the competition of the solvent molecules can be characterized by estimating the average statistic weights of the two solvents in the first solvation sphere of the studied molecule. The model of the ternary solutions was used to estimate the content of the first solvation sphere of some zwitterionic molecules.

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## 1. Introduction

The energy corresponding to the thermal motion in liquids [1-4] equalises the potential energy due to the intermolecular interactions. The radial symmetry of the interactions determines a radial distribution of particles in simple liquids. The ordered systems formed around one molecule are of the sizes of a few molecular diameters and have short life time. Spectrally active molecules are introduced as sonds in liquids, in order to obtain information regarding the internal fields of forces. These molecules measure the intensity of the internal fields by the modifications registered in their electronic (absorption or fluorescence) spectra.

Van der Waals intermolecular interactions are unsaturated and oriented to the center of the particle.

In solutions, the electronic levels of the spectrally active molecules are modified by the energy of interactions between these molecules and the rest of the solution. The spectrally active molecules concentration in solutions is very small ( $10^{-4}$  –  $10^{-5}$  mol/L) and so, one can replace the solution by subsystems consisting from a single molecule surrounded by their solvation spheres. The number of these subsystems is proportional to the concentration of the spectrally active molecules in solution and influences only the intensity in the maximum of the spectral band. The wavenumber in the maximum of the electronic spectra is determined by the interaction energies of the spectrally active molecule (in the electronic states participating to the transition) and the solvent molecules surrounding it. The interaction energy between the spectrally active molecule, placed in the centers of the solvent spheres and these spheres gradually diminishes when the radius of the solvation spheres increases. The interaction energy of the central molecule and its first solvation sphere is bigger than the interaction energy with the second, or the third solvation sphere [5]. The strenght of the intermolecular forces depends on the chemical

structure of the interacting molecules. When the studied solution contains spectrally active molecules and two types of solvent molecules, a competition between the solvent molecules for the places more convenient from the point of view of energy minimization, takes place. In the ternary solutions, the first solvation sphere composition differs from the rest of the solution.

## 2. Experimental

Some zwitterionic compounds [6-12], 3-phenyl-pyridazinium-anilido-benzoyl-methylid ( $I_1$ ), 3-cumyl-pyridazinium-anilido-benzoyl-methylid ( $I_2$ ), and benzo-[f]-quinolinium-anilido-benzoyl-methylid ( $I_3$ ), were considered as spectrally active molecules. They were prepared and purified by the methods described in [6,7]. The used solvents, spectrally grade, were achieved from Merck Company.

The electronic spectra were recorded at a Specord UV VIS Carl Zeiss Jena spectrophotometer with a data aquisition system. The volumetric concentrations were used for solutions' achieving and the molar fractions of the two solvents were estimated by using formula (4). The average weights of  $s_1$  and  $s_2$  molecules in the first solvation sphere of the spectrally active molecule were estimated on the basis of formula (2) and (3).

The studied cycloimmonium ylids have a visible absorption band that appears by charge transfer from the carbanion to the heterocycle [9,10] very sensitive to the solvent action. This band diminishes or even disappears in acid solvents, shifts to blue when passes from non-polar to polar solvents, or from the aprotic to protic ones [8-12]. Van der Waals interactions take place between the non-protic solvents and the cycloimmonium ylids. Specific interactions of the type of proton donor – acceptor, additionally act in protic solvents, determining a

supplementary spectral shift to blue of the visible electronic band of cycloimmonium ylids [12].

### 3. Theoretical notions

In T. Abe model of a simple liquid [5,4] the solution is modeled as a system consisting from a central spectrally active molecule and a great number of solvation spheres surrounding the central molecule. The centers of the solvation spheres are placed in the symmetry center of the spectrally active molecule. Abe demonstrates in his model that the interaction energies between the central molecule and its first three solvation spheres are in the ratios: 1;1/16; 1/81. So, the solution can be approximated by the spectrally active molecule and its first solvation sphere. This approximation was used and in Mazurenko model [13] for the ternary solutions in which the spectral changes in the electronic spectra of a spectrally active molecule are described by the interaction between it and its first solvation sphere.

A cell model of the ternary solutions [13-15] permits to evaluate the pair potential energy of interactions between the solute molecules and the active solvent molecules from the intermolecular forces point of view. In this model two solvents are used. They do not absorb in the spectral range where the spectrally active molecules absorb. Let be  $u$  - the spectrally active molecule,  $s_1$  a molecule of the active solvent and  $s_2$  a molecule of the inactive solvent from the point of view of intermolecular interactions. The concentration of the spectrally active molecules in the studied solutions is very small ( $10^{-5}$  mol/l).

The binary solvent is achieved from different volumetric ratios of the two solvents. Let be  $x_1$  and  $x_2$  the molar ratios of the two solvents in the solution and  $p_1$  and  $p_2$  [16,17] the average weights of the active and inactive solvents respectively in the first solvation sphere of the spectrally active molecule.

In the model of ternary solution the following relation is established [5, 15]:

$$\ln \frac{x_1}{1-x_1} = \ln \frac{p_1}{1-p_1} + \frac{w_2 - w_1}{kT} \quad (1)$$

In relation (1),  $w_1$  and  $w_2$  are the pair potential energies for interactions between a spectrally active molecule  $u$  and one molecule of the type  $s_1$  or  $s_2$ , respectively. The statistical average weight of the active

solvent in the first solvation sphere can be expressed as function of  $v_1$  and  $v_2$ , the wavenumbers of the electronic absorption band registered in the binary solutions achieved in each type of solvent, and of  $v_t$ , corresponding to the ternary solution achieved in the solvent mixture [16,17].

$$P_1 = \frac{v_t - v_2}{v_1 - v_2} \quad (2)$$

$$p_1 + p_2 = 1 \quad (3)$$

The molar fractions were estimated by the formula:

$$x_1 = \frac{\frac{C_1 V \rho_1}{M_1}}{\frac{C_1 V \rho_1}{M_1} + \frac{C_2 V \rho_2}{M_2}} \quad (4)$$

In (4),  $V$  is the solution volume,  $C_j, j = 1,2$  are the solvent volumetric ratios,  $\rho_j, j = 1,2$ , the  $j$ -solvent density and  $M_j, j = 1,2$  the  $j$ -solvent molecular weight. The molar fractions of the two solvents satisfy the relation (5).

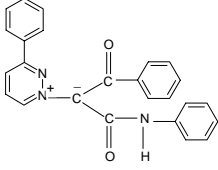
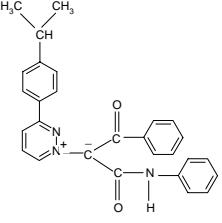
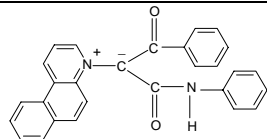
$$x_1 + x_2 = 1 \quad (5)$$

Generally, in the ternary solutions the composition of the first solvation sphere differs from the solution composition, because between the two type of solvent molecules a competition occurs in order to occupy the places that assure the system stability.

If relation (1) is applicable for the studied ternary solution and the intermolecular interactions in the inactive solvent could be neglected, the energy  $w_1$  between a pair  $u - s_1$  of the solute and the active solvent molecules can be estimated.

In ternary solutions having a protic and one non-protic solvent as component, the protic molecules will compete to occupy the places favoring the proton changes; the solvation spheres will be enriched in protic molecules comparing with the rest of the solution. Consequently,  $p_1 > x_1$  and in the first solvation sphere of the spectrally active molecule are more active molecules from the point of view of the intermolecular interactions compared with the rest of the solution.

Table 1. The structural features of the studied cycloimmonium ylids.

I <sub>1</sub>		3-phenyl-pyridazinium anilido-benzoyl methylid
I <sub>2</sub>		3-cumyl-pyridazinium anilido-benzoyl methylid
I <sub>3</sub>		Benzo-[f]-quinolinium anilido-benzoyl methylid

#### 4. Results and discussion

The data regarding the molar fractions  $x_1$  and  $x_2$  of the protic solvent in the ternary solution (computed from the volumetric ratios of the two solvents in the ternary solutions) and the average statistic weights of the protic solvent in the first solvation sphere of the spectrally active molecule (computed by using relation (2) and the experimentally obtained wavenumbers in the maximum of the intramolecular charge transfer band) for the spectrally active compounds

I<sub>1</sub> – I<sub>3</sub> in three mixtures of solvents are given in Tables 2 - 4.

In Figures 1-3 the dependences of the quantities  $\ln \frac{x_1}{1-x_1}$  and  $\ln \frac{p_1}{1-p_1}$  are illustrated. The slopes of the lines (1) are quite equal to the unity for the solutions having as protic solvent one alcohol and differ from the unity when the protic solvent is an acid.

Table 2. The molar ratios for the active solvent in the ternary solution of propionic acid + chloroform + I<sub>j</sub> (j = 1, 2, 3) and its average statistic weight in the first solvation sphere.

C <sub>1</sub> %	x <sub>1</sub>	P <sub>1</sub>			w <sub>2</sub> – w <sub>1</sub> (× 10 <sup>-21</sup> J)		
		I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>
0	0	0	0	0	5.147	3.8126	7.3399
5	0.053	0.298	0.244	0.221			
10	0.109	0.473	0.341	0.362			
25	0.263	0.668	0.563	0.634			
50	0.517	0.706	0.722	0.862			
75	0.763	0.908	0.856	0.962			
100	1	-	-	-			

Table 3. The molar ratios for the active solvent in the ternary solution of octanol + 1,2-dichloroethane +  $I_j$  ( $j = 1, 2, 3$ ) and its average statistic weight in the first solvation sphere.

C <sub>1</sub> %	x <sub>1</sub>	P <sub>1</sub>			w <sub>2</sub> - w <sub>1</sub> (× 10 <sup>-21</sup> J)		
		I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>
0	0	0	0	0	7.17199	5.763	7.9381
5	0.025	0.124	0.180	0.135			
10	0.052	0.268	0.260	0.245			
25	0.141	0.438	0.460	0.520			
50	0.330	0.699	0.727	0.790			
75	0.597	0.915	0.847	0.910			
100	1	-	-	-			

Table 4. The molar ratios for the active solvent in the ternary solution of 1,2-propanediol + benzene +  $I_j$  ( $j = 1, 2, 3$ ) and its average statistic weight in the first solvation sphere.

C <sub>1</sub> %	x <sub>1</sub>	P <sub>1</sub>			w <sub>2</sub> - w <sub>1</sub> (× 10 <sup>-21</sup> J)		
		I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>
0	0	0	0	0	4.5351	4.1417	2.6988
5	0.064	0.111	0.114	0.089			
10	0.126	0.265	0.265	0.194			
25	0.303	0.609	0.588	0.419			
50	0.566	0.841	0.806	0.722			
75	0.796	0.908	0.904	0.897			
100	1	-	-	-			

From the data in Tables 2 – 4 one can estimate the difference  $w_2 - w_1$ . The data for  $w_2 - w_1$  were estimated at  $T = 20^\circ\text{C}$  ( $kT = 4,0474 \times 10^{-21}$  J). Taking into account the results obtained by Abe, in whose theory the number of the molecules composing the first solvation sphere is approximated by  $4\pi$ , one can estimate the energy of interaction between one spectrally active molecule and its first solvation sphere.

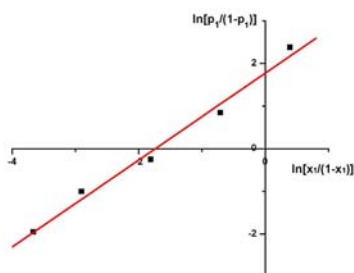


Fig. 1. Dependence of  $\ln \frac{p_1}{1-p_1}$  on  $\ln \frac{x_1}{1-x_1}$  for  $I_1$  in octanol + dichloroethane ternary solution.

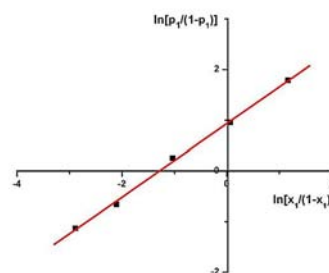


Fig. 2. Dependence of  $\ln \frac{p_1}{1-p_1}$  on  $\ln \frac{x_1}{1-x_1}$  for  $I_2$  in propionic acid + chloroform ternary solution.

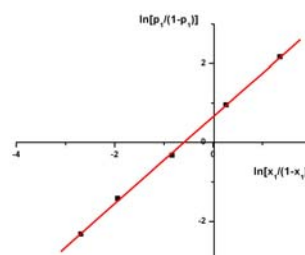


Fig. 3. Graph of  $\ln \frac{p_1}{1-p_1}$  vs.  $\ln \frac{x_1}{1-x_1}$  for  $I_3$  in propanediol + benzene ternary solution.

## 5. Conclusions

The cell model of the ternary solution can be applied to the cycloimmonium ylids solutions in binary solvent in which the active solvent is a protic one.

The difference between the interaction energies of the pairs  $u - s_1$  and  $u - s_2$  of molecules was estimated from the cut at origin and then the energy between the spectrally active molecules and their first solvation sphere was also estimated.

For a negligible contribution of the interactions between the spectrally active molecule and a molecule of the type  $s_2$ , the energy  $w_1$  can be approximated. Fig. 3.

Graph of  $\ln \frac{p_1}{1-p_1}$  vs.  $\ln \frac{x_1}{1-x_1}$  for  $I_3$  in propanediol + benzene ternary solution.

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