

Intermolecular Interactions in Water-Ethanol Mixtures, Studied by Ultrasound Technique

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Containing -OH groups with non-participant electrons, water and primary alcohols, form clusters by hydrogen bonds. Mixtures of water and ethanol and their ternary solutions containing small amounts of a spectrally active substance were studied by ultrasound techniques in order to determine the coefficient of adiabatic compressibility considered as being an indicator of the strength of intermolecular interactions in hydroxy liquids. A linear dependence between the adiabatic compressibility of solution and the wavenumber in the maximum of the solute electronic absorption band was evidenced in our experiments.

Keywords: ultrasound, adiabatic compressibility, water-ethanol mixtures, 2,2-diphenyl-1-picril-hydrazyl (DPPH), p-Phenyl-Pyridazinium-(acetyl-p-nitro-benzoyl) methylid (PPANiBM), electronic absorption spectra (EAS)

Water and ethanol are non-toxic liquids with important implications for life. Water is named “matrix of life” because it is an essential component of all systems lying to the life origins. For example, lipid bilayers with important role in cell membranes are separated by water layers consisting from free or hydrogen bonded molecules [1,2]. Water is a very good solvent; it assures the nutrients’ transport into human body and eliminates the toxic components from the organism.

Ethanol is soluble in water in various portions and in a wide range of temperatures. The behavior of the binary solvent water + ethanol components is very interesting and it was studied by various techniques, such as spectroscopy and ultrasonography [3-5].

Water and ethanol are non-toxic liquids frequently used for biochemical and biophysical researches [6,7] and also in pharmaceutical or food industry.

Water is a protic, polar and polarizable molecule and so, in liquid alcohol solutions its molecules can coexist into hydrogen bonded complexes (of the type water-water, water-alcohol; water-water-alcohol), or as free ones.

The possibility of hydrogen bonds appearance between water molecules with cluster formation was studied in [8,9].

Recently some pyridazinium [10-14] and hydrazyl [15-17] derivatives were tested from pharmacological point of view. So, the interactions between these types of substances and the solvents such as water, ethanol, or their mixtures, must be known when solutions of these substances are used in pharmacological purposes.

2,2 Diphenyl-1-picril-hydrazyl (DPPH) is an important standard in RES spectrometry [15-19] and it is also used in order to determine the antioxidant character of active biochemical compounds. Being insoluble in water, DPPH can be used as antioxidant controller [20] only in ethanol-water mixtures. The best results were obtained for 1:1 volumetric concentrations of the two solvents [19] in water-ethanol mixture.

p-Phenyl-pyridazinium-acetyl-p-nitro-benzoyl-methylid (PPANiBM) has been tested as antimicrobial and antifungal agent [12-14]. This substance can be prepared and it is usually used in solutions.

One of the experimental methods very well suited for investigating structure of liquids is the ultrasound speed

which can be determined with a very good precision. The liquid density is also easily measurable with a very good accuracy [21-24]. So, the acoustic measurements are widely applied in investigating solvation phenomena.

The ultrasounds permit to evaluate the adiabatic compressibility of the water-alcohols mixtures, by measuring their density and the velocity of the ultrasound waves for different alcohol concentrations in solutions. The ultrasound velocity increases and the adiabatic compressibility (defined by relation (1)) decreases with the degree of association in the binary solvent [23,24].

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (1)$$

The study of ultrasound propagation in aqueous solutions is of great interest, especially when these mixtures contain biological active substances. So, the molar apparent volume and the adiabatic compressibility of some antibiotics such as: sodium cloxacillin penicillin, or sodium dicloxacillin penicillin in water, were determined by the studies regarding the ultrasound propagation through their aqueous solutions [3, 4]. The compressibility of some solutions with biological interest was also determined in [5]. For ultrasound propagation in organic liquids some theoretical models were proposed [25].

The structure of the water mixtures with different polar, non-polar, hydroxy or non-hydroxy solvents was theoretically [26] described or studied by using various means, such as microwaves [9], ultrasounds [27, 28], or spectral techniques, namely NMR [29], or IR [30,31].

In simple liquids, the energy of the intermolecular interactions has the same order of magnitude as the energy of the thermal motion [32]. Consequently, only a local order extended to a few molecular diameters was evidenced in liquids. The local order in dipolar liquids or in ionic solutions is determined by the stronger electrical interactions, compared with non-polar liquids. The dipolar liquids are more ordered compared with the last up-mentioned.

When ionic or dipolar molecules are introduced in water, a hydration process determines modifications in the local order and contributes to the appearance of some clathrate shells around the ions or dipoles. Consequently,

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a pronounced polarization of the solvent is produced [33,34] in the presence of ions or dipoles.

In homogeneous mixtures of solvents [35], the polar solvent molecules are in competition with the non-polar ones in order to occupy the (favoured from energetic point of view) places neighbouring the solute particles. So, it is evidently that the ultrasound velocity in a pure liquid differs from that in a solution. The measurements of the ultrasound velocity in various liquids at different temperatures were also used in order to evaluate the thermal fields in fluids [36].

Experimental part

p-Phenyl-pyridinium-acetyl-*p*-nitro-benzoyl-methylid (PPANiBM) and 2,2-diphenyl-1-picril-hydrazyl (DPPH), were prepared as previously described [10,16]. They are of pharmaceutical interest, being potential pharmaceutical compounds [11-13]. The study of the aqueous solutions of ylids is important because these compounds are prepared *in situ* and are used in solutions [14]. The chemical structure of the studied spectrally active substances is illustrated in figures 1a and b.

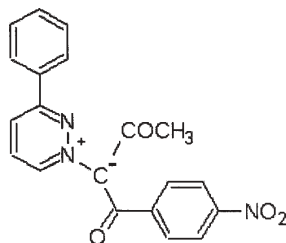


Fig.1a. PPANiBM chemical structure

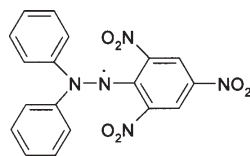


Fig.1b. DPPH chemical structure

Water was double distilled. Ethanol achieved from Merck Company was spectrally grade and used without supplementary purification.

The ultrasound velocity was determined interferometrically, as it was described in [5,24]. The density of solutions was measured with a 25 mL pycnometer, using a Mettler MDB-5 balance ($\pm 10^{-5}$ g). Determination of ϵ at 25°C was made using a Wayne Kerr Autobalance Universal Bridge B-641 (300MHz) coupled with a Telmes TR-970 dielectric cell for liquids, thermostated with a U-10 Ultrathermostat ($\pm 0.2^\circ\text{C}$ precision). The refractive index of solutions was measured with a RPL Carl Zeiss Jena immersion refractometer ($\pm 10^{-5}^\circ\text{C}$ precision) thermostated at 25°C with the same thermostat used in ϵ -determination.

Results and discussions

Some results regarding the ultrasound propagation in water-solvent mixtures and in their solutions realized with two dipolar organic compounds are presented here.

The molar fraction, x_{et} , of ethanol, the empirical polarities, $Z(\text{kcal/mol})$, defined by Kosower [37,38] (as a measure of the intermolecular interactions in a given solvent), the function, $f(n, \epsilon)$, describing the intermolecular interactions in liquids, all estimated for various alcohol molar fractions in ethanol+water solutions are listed in table1. This table also contains the adiabatic compressibilities, β_s , and the wavenumbers, $\bar{\nu}_s$ in the maximum of the visible electronic absorption band for the ternary solutions achieved from the binary solvent and the

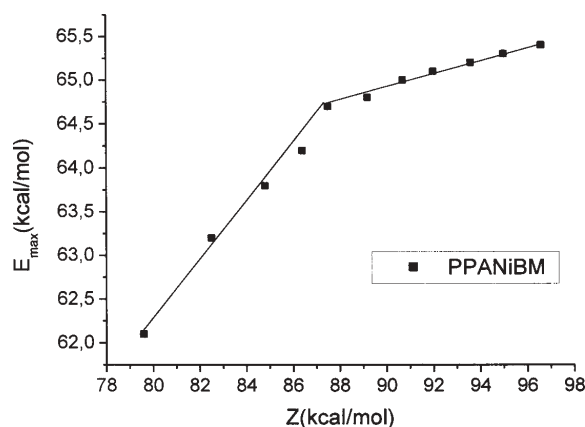


Fig.2a. Energy in the maximum of the visible band of PPANiBM versus empirical polarities defined by Kosower

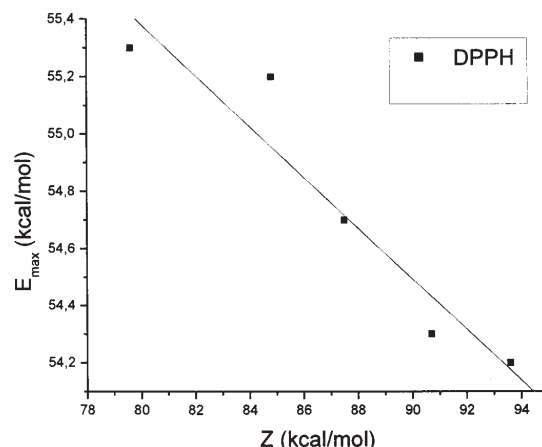


Fig.2b. Energy in the maximum of the visible band of DPPH versus empirical polarities defined by Kosower

Table 1
PARAMETERS OF THE TERNARY SOLUTIONS OF PPANiBM AND DPPH IN WATER+ETHANOL SOLUTIONS OF CONCENTRATION $10^{-3}(\text{mol/L})$; THE WAVENUMBERS OF VISIBLE ELECTRONIC ABSORPTION

x_{et}	Z (kcal/mol)	$f(n, \epsilon)$	PPANiBM		DPPH	
			$10^{10} \cdot \beta_s$ (Pa^{-1})	$\bar{\nu}(cm^{-1})$	$10^{10} \cdot \beta_s$ (Pa^{-1})	$\bar{\nu}(cm^{-1})$
0.00	96.6	0.757	4.15	22890	4.04	
0.0332	95.0	0.751	4.47	22830	4.44	
0.0717	93.6	0.745	4.44	22810	4.41	18980
0.1168	92.0	0.740	4.61	22780	4.54	
0.1707	90.7	0.732	4.70	22740	4.66	19010
0.2359	89.2	0.725	5.02	22670	4.96	
0.3165	87.5	0.717	5.39	22620	5.29	19120
0.4187	86.4	0.707	5.76	22450	6.68	
0.5526	84.8	0.695	6.33	22310	6.14	19310
0.7354	82.5	0.668	7.15	22120	6.96	
1.0000	79.6	0.666	8.18	21730	7.96	19350

spectrally active molecules PPANiBM and DPPH, respectively.

From this table one can see that the coefficient of adiabatic compressibility has a minimum value at about $x_e = 0.0717$ ethanol molar fraction in water (for a volumetric concentration near 20%). The minimum value of the adiabatic compressibility could be induced by the changes in the liquid mixture network at the above mentioned concentration, compared to the smaller concentrations.

The dependence of the visible electronic absorption band wavenumbers (expressed in kcal/mol) on the empirical polarities [37] are plotted in figures 2a and b for the two studied solutes in binary solvents. These dependences offer information about the difference between the spectral sensitivity of the active molecule (1-ethyl-4-carbomethoxy-pyridinium ylid) used as standard in Kosower scale of the solvents, and the solutes here studied. One can observe a slope change of the linear dependence when the molar fraction of the ethanol increases. This change could be induced by the changes in the composition of the solvation sphere of the complex formed by hydrogen bond between the studied molecules and the molecules of the protic solvent, or even by the substitution of the solute-water complex by solute-ethanol complex. The dependence from Fig.2a shows us that the complexes of PPANiBM are more sensitive to the ethanol action compared to the water action. From these graphs it results changes in intermolecular interaction nature. An example could be the replacing of the solute-water complex by the solute-ethanol complex, when the ethanol molar fraction increases in the solvent mixture.

A linear dependence between the energy in the maximum of the visible absorption band of DPPH versus empirical polarities of the solvents was also evidenced (fig.2b). The energy in the maximum of the visible band of this substance decreases when the solvent polarity increases.

When the spectral data are used in order to put in evidence the intermolecular interactions between a spectrally active molecule and the solvent molecules, beside empirical scales of the solvents, some theories regarding the intermolecular interactions in the simple liquids must be considered.

If one takes into consideration the Bakhshiev theory [39,40] on the homogeneous solutions, considered as infinite continuous dielectric media, a dependence of the wavenumber in the maximum of the electronic bands on the functions corresponding to the universal interactions and [35-37], defined by the relations (2) or (3) can be established.

(2)

$$\Delta \bar{\nu} = \bar{\nu}_s - \bar{\nu}_v = C_1 \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + C_2 \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

$$\Delta \bar{\nu} = C_1 f(n, \epsilon) + C_2 f(n)$$

The dependence of the type (2), expressing the spectral shift versus the solvent macroscopic parameters is given in figures 3a and b for the two types of the spectrally active molecules studied in this paper. The dependences obtained in figures 3a and b are quite linear and are obtained when $C_2 = 0$.

The specific interactions, such as hydrogen bonding or intermolecular charge transfer, are neglected in Bakhshiev's theory. Their contribution to the spectral shift can be taken into consideration by adding an empirical

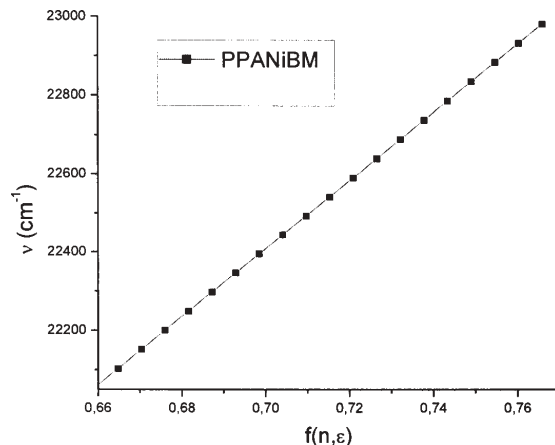


Fig.3a. Wavenumber in the maximum of the visible band of PPANiBM versus $f(n, \epsilon)$ of the binary solvent

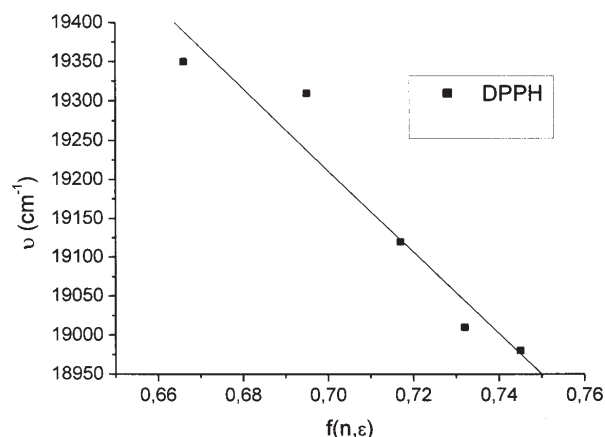


Fig.3b. Wavenumber in the maximum of the visible band of DPPH versus the binary solvent

supplementary term [32,41] in relation (3). This term must describe the local modifications induced by specific interactions.

Both empirical scales and theoretical models inform us about the strength of intermolecular interactions in liquid solutions [41-44].

Because in our study all spectra were recorded into protic solvents or in their mixtures, the specific interactions take place in all solutions and all spectra will be shifted in the wavenumber scale compared with those obtained in aprotic solvents.

The coefficient of the adiabatic compressibility determined for the ternary solutions of the type water+ethanol+DPPH or water+ethanol+PPANiBM and the wavenumber in the maximum of the visible electronic band (figs.4a and b) depend linearly, showing us that the compressibility is directly correlated with internal interactions in liquid. It also can be deduced the fact that the local structure of liquid becomes enhanced and more rigid, i.e. less compressible, when water is added in the non-electrolytic liquid.

The coefficient of adiabatic compressibility increases when the ethanol molar fraction increases (fig.4).

The adiabatic compressibility can be considered as an indicator of the intermolecular interactions strength. In the same time the visible electronic spectra of the organic compounds can offer information about the strength of the intermolecular interactions between the solvent and the spectrally active molecule in electronic states participating to the transition to which the electronic absorption band is attributed.

In figures 4a and b a linear dependence between the ternary solution adiabatic compressibility and the visible

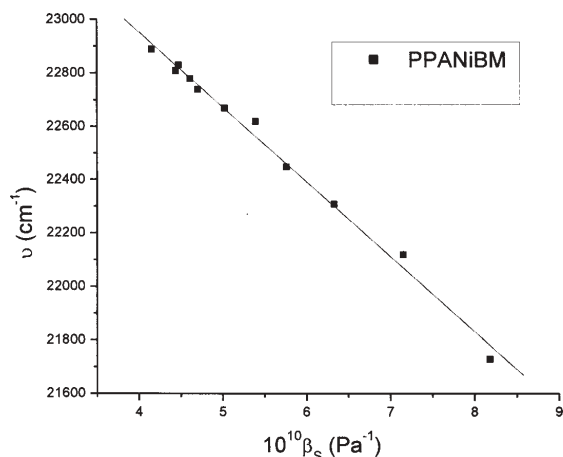


Fig.4a.Wavenumber in the maximum of the visible band of PPANiBM versus the coefficient of adiabatic compressibility

band wavenumbers of the two compounds (DPPH and PPANiBM), considered as spectrally active molecules, is illustrated.

The ylid is a dipolar molecule and it has the ability to form molecular complexes by hydrogen bonds with the protic solvents as water or ethanol. The hydrogen bonded complexes are realized by a proton transfer between a water molecule and the ylid carbanion [32, 41]. Such complexes exist in all studied solutions under study. At low ethanol molar fractions, the complexes of the type water-ylid are predominant. This complex is surrounded by solvation spheres containing smaller or bigger quantities of ethanol, depending on its molar fraction into binary solvent.

When ethanol becomes predominant (for concentrations), the probability of existence of (PPANiBM)-ethanol, or DPPH-ethanol complexes has great values and the energy of interactions between these complexes and solution is reflected in their electronic absorption spectra.

If one estimate the number of water molecules corresponding to a single alcohol molecule and if the first solvation shell is considered filled with about 12 molecules, according to T. Abe results [43,44], one can observe that for the ethanol molar concentration of , the ethanol molecules begin to penetrate into the first solvation sphere of the solute-water complex. At this concentration the changes in the composition of the first solvation sphere induce modifications in the adiabatic compressibility of the solution. When the ethanol molar fraction increases in the ternary solutions, the alcohol molecules penetrate the first solvation shell, modifying the strength of the interactions between the formed by hydrogen bond complex and its first solvation sphere.

When an organic non-electrolyte molecule is added in small concentrations in water+ethanol mixtures, three mechanisms could influence the solution compressibility [21]:

- formation of less or more strong hydrogen bonds;
- compression of neighbouring water by electrostatic forces originating from the charged parts of the solute molecules;
- formation of cages around hydrophobic parts of molecules.

The molecules engaged in hydrogen bonds become almost completely incompressible, but such building does not affect the original water-ethanol network on longer distance.

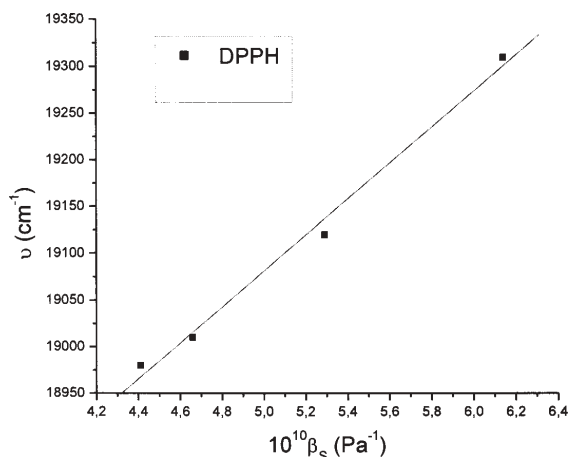


Fig.4b.Wavenumber in the maximum of the visible band DPPH versus the coefficient of adiabatic compressibility

Because of low charge density of the charged fragments of typical polar non-electrolyte molecules, the second mechanism contributing to the solution compressibility is much weaker than the first.

The third mechanism is known as hydrophobic hydration. It causes an increase in the rigidity of the solvent network affecting its compressibility, in the sense of its decrease. This effect is suspected to be much longer in range than the first one [21].

It was found from theoretical calculations that water organization is only locally sensitive to the structural details of the non-polar solutes [48].

From the above described mechanisms it results that the hydroxy molecules could exist in various forms:

- those belonging to original bulk structure of the hydroxy solvent;
- hydroxy molecules belonging to the hydrophobic hydration shells (cage-like);
- some molecules whose number is proportional to the solute concentration should be engaged in hydrophilic hydration.

Normally the concentration of the three forms of hydroxy molecules in ternary solutions of the type DPPH+water+ethanol or PPANiBM+water+ethanol is sensitive to the ethanol content in the binary hydroxy solvent.

At small molar fractions of ethanol in the binary solvent, complexes of type solute-water are predominant. If the ethanol molar fraction is higher than 0.5, the solute ethanol complexes could be considered as being predominantly.

Conclusions

Ultrasound measurements can offer information about the intermolecular interactions in liquid solutions. The coefficient of adiabatic compressibility of the ternary solutions water+ ethanol+ DPPH and water+ ethanol +PPANiBM can be considered as indicator of the intermolecular interactions strength between spectrally active molecules and the hydroxy liquids.

As empirical characteristic of the solvent, the Z-parameter defined by Kosower informs us about the global action of the binary solvent on the valence electronic cloud of the solute molecule, but does not permit to appreciate the contribution of each type of interaction to the total spectral shift of the electronic absorption band in a given solvent, comparatively to its position in gaseous phase.

The total spectral shift caused by the protic solvent mixtures linearly depends on the theoretically established solvent functions from Bakhshiev theory.

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