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ACETONITRYLE – WATER BINARY MIXTURES AND THEIR ASSUMED INTERNAL STRUCTURES

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The ¹H-NMR spectra of liquid binary mixtures, acetonitrile (ACN) – water (H₂O), were recorded at 298 K and the spectral parameters, $\Delta\delta$ (ACN-H₂O) were evaluated. The surface tensions (σ_{12}) were measured at 298.15 K. From literature values of density (d_{12}), viscosity (η_{12}), relative permittivities (ϵ_{12}) and measured surface tensions the values of molar volumes (V_{12}) and their deviations from “ideality” were calculated. Further on the temperature coefficients of relative permittivity, $\alpha_{12} = (1/\epsilon_{12}) \cdot [d\epsilon_{12}/d(1/T)]$, were evaluated. These structural parameters as functions of concentration suggest the formation of the intermolecular “complexes” of the ACN • 2H₂O, ACN • H₂O, 2 ACN • 3H₂O and 2 ACN • 3 H₂O types.

Keywords: Intermolecular interactions; ¹H-NMR spectra; binary liquid mixtures

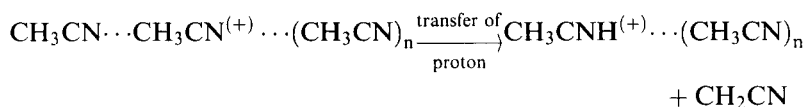
1. INTRODUCTION

This paper is a continuation of the series of studies on internal structures of some liquid binary mixtures, in which H₂O or a organic solvent is one of two constituents, based on the correlation existing between the ¹H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures [1–3]. In the present work we have analysed the mutual interactions in the liquid mixtures of ACN and H₂O.

Acetonitrile (ACN) is a typical example of the aprotic solvent. It exhibits the stronger tendency of solvation of metallic ions and

acceptor molecules in comparison to other solvents with higher values of donor number (DN). Undoubtedly, it is favoured by its advantageous steric properties, whereas the nitrogen atom with a free electron pair is responsible for solvation of acceptor bonds. This pair may be even regarded as a pseudoligand [4] when complexes of acetonitrile are formed. The screening as well as the charge effects are assigned to this pair [5–7].

Acetonitrile exhibits higher affinity towards proton in comparison to water. The basicity of ACN differs by 5 orders of magnitude from this shown by water. For small concentrations of H₂O and ACN the equilibrium states were monitored which indicate stronger donor properties of water [5]. Additionally the presence of proton clathrate was confirmed in pure ACN on the base of spectroscopic studies [8].



$$\Delta H^0 = -2,64 \text{ eV}$$

2. EXPERIMENTAL

For the present ¹H-NMR spectral studies and the measurements of surface tensions chemical pure ACN (Fluka) was used. It was dried and purified according to known procedure [9]. Water was prepared for measurements as previously [1]. The ¹H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The proton chemical shifts of ACN and H₂O were measured with an accuracy of ca. ± 0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The surface tensions measurements were performed with an accuracy of ± 0.1% using a stalagmometr. All the solutions were prepared by weight.

3. RESULTS AND DISCUSSION

Moreau [10], Cunningham [11], Grant-Taylor [12], Lühra [13], Mahgoub [14] and Benson [15] measured viscosity, relative permitti-

vity and density for the binary mixtures. However, they did not interpret their results in terms of internal structure of intermolecular "complexes" formed by molecules of ACN and H₂O. Also, measurements of density, relative permittivity and refractive index of the liquid mixtures of ACN and H₂O, carried out by Himienko [16] are only available in the monograph by Krestov *et al.* [17] in the form of numerical values collected in tables. As in these works, no analysis of the intermolecular interactions in the binary mixtures studied here is given. In this work, with the aim of analysing the intermolecular interactions between the components in the binary liquid ACN-H₂O mixtures, we measured the values of chemical shift differences δ (ACN-H₂O) at 298 K, between the center of the ¹H-NMR signals of the -OH group of water and the center of the ¹H-NMR signals of -CH₃ group of ACN molecules over a wide range of solvent compositions, i.e. from 2.00 to 98.00 mol.% of ACN (see Tab. I). From these new spectral data the spectral parameter $\Delta\delta$ (ACN-H₂O)

TABLE I Relative ¹H-NMR chemical shifts; δ (ACN-H₂O) and surface tensions (σ_{12}) for binary liquid mixtures ACN-H₂O, measured at 298.15 K

<i>mol.% of ACN</i>	δ (ACN-H ₂ O) [Hz]	$\sigma_{12} \cdot 10^{-3}$ [N · m ⁻¹]
0.00	—	71.97
2.00	128.4	71.11
5.00	125.4	74.25
10.00	120.5	76.79
15.00	115.6	73.79
20.00	111.0	62.61
25.00	116.5	56.95
30.00	112.1	52.90
35.00	98.2	50.05
40.00	94.1	49.61
45.00	90.3	48.73
50.00	86.7	47.29
55.00	83.6	45.62
60.00	81.0	43.65
62.00	80.0	—
64.00	78.9	—
66.00	78.2	—
70.00	71.5	39.55
75.00	55.6	—
80.00	45.0	35.81
85.00	37.5	—
90.00	25.5	31.78
98.00	22.3	—
100.00	—	27.64

has been found (using the same method as previously [1-3]). The values of this parameter or, more precisely, the location of its maximum values, are located at the composition with the strongest intermolecular interactions between the components, where hydrogen bonds are involved 1-3). The $\delta\Delta(\text{ACN-H}_2\text{O})$ values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta(\text{ACN-H}_2\text{O})$ at ca. 67 mol. % of ACN. Thus, at this composition the strongest interactions between components involving hydrogen bonds, are observed, and the most stable "complex" is 2 ACN • H₂O.

From the literature values of the relative permittivity [12], the temperature coefficients of the relative permittivity, denoted α_{12} , viz. $\alpha_{12} = (1/\epsilon_{12}) \cdot [d\epsilon_{12}/d(1/T)]$ were calculated. The composition range of

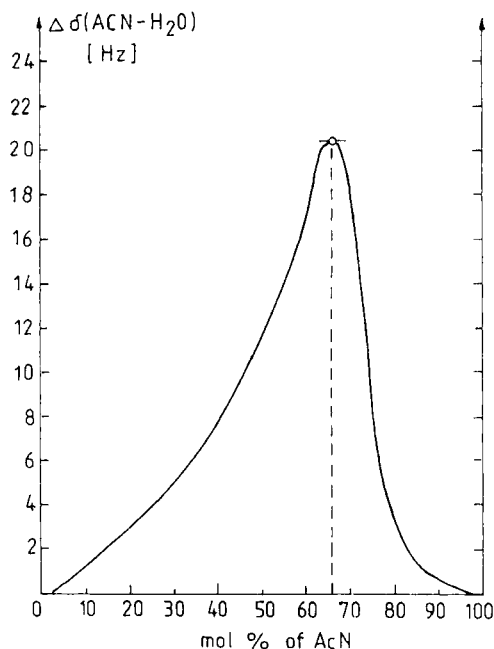


FIGURE 1 Changes in $\Delta\delta(\text{ACN-H}_2\text{O})$ for liquid ACN-H₂O mixtures, at 298 K.

binary liquid mixtures within which α_{12} attains its highest value should be interpreted (as shown in our previous works [1-3]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Changes in α_{12} vs. composition of liquid ACN mixtures are shown in Figure 2.

The maximum value of α_{12} is found at ca. 67 mol. % of ACN. This confirms the conclusion from $^1\text{H-NMR}$ spectral data concerning the formation of a "complex" of 2 ACN \bullet H_2O .

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physicochemical properties of these mixtures, i.e. density (d_{12}), viscosity (η_{12}), relative permittivity (ϵ_{12}), surface tension (σ_{12}) and molar volumes (V_{12}) [1-3]. A thorough review of the literature justifies the correctness of using these parameters in the analysis of intermolecular interactions [1]. In this paper, using the

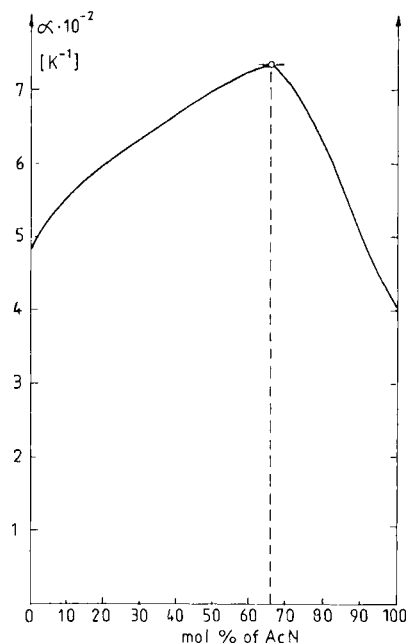


FIGURE 2 Changes in the temperature coefficient of relative permittivity as a function of composition for the liquid ACN- H_2O mixtures, at 298.15 K.

experimental values of surface tension at 295.15 K (see Tab. I) and the literature values of density, viscosity, speed of propagation of ultrasound and relative permittivity [10, 12, 15] the values of deviations from "ideality" of analysed physicochemical properties were calculated using equations discussed in our previous works [1–3]. This values are shown in Figure [3].

The values of the speed of propagation of ultrasound $\Delta(\nu_{12})_{id}^{(x)}$ and viscosity $\Delta(\eta_{12})_{id}^{(x)}$ have minimum at ca. 50 mol. % of ACN what suggest the formation of the "complex" of $ACN \bullet H_2O$ type. The values of $\Delta(V_{12})_{id}^{(x)}$ and $\Delta(\sigma_{12})_{id}^{(x)}$ have minimum at ca. 33 mol. % of ACN what suggest the formation of the "complex" of $ACN \bullet 2 H_2O$ type. The values of $\Delta(\epsilon_{12})_{id}^{(x)}$ have minimum at ca. 40 mol. % of ACN what suggest the formation of the "complex" of $2 ACN \bullet 3 H_2O$ type. The concentration area corresponding to the content of ACN equal to ca. 8 – 12 mol. % of ACN is very interesting to study due to the present here structural effects. The maximum deviations from "ideality" of density, viscosity, the speed of propagation of ultrasound and the surface tension are observed in this region (see Fig. 3). In our

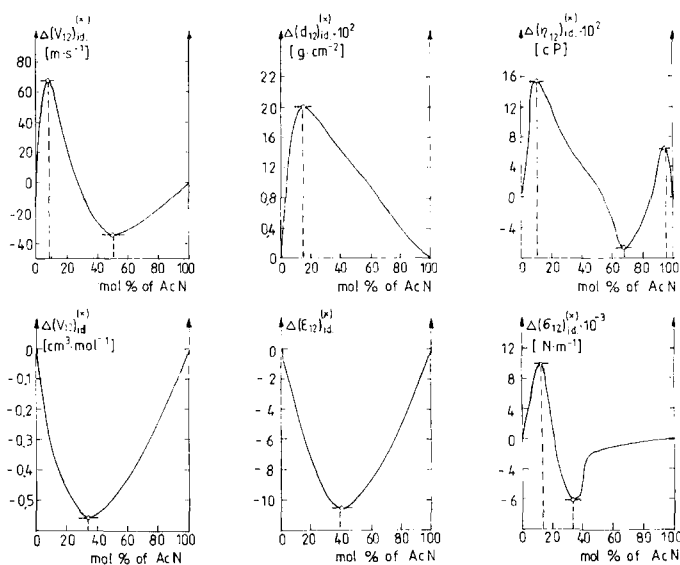
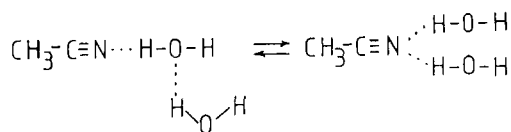
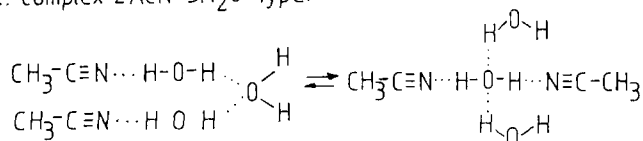


FIGURE 3 The course of changes of deviations from "ideality" of physicochemical properties of ACN-H₂O mixtures as a function of composition for the liquid ACN-H₂O mixtures, at 298.15 K.

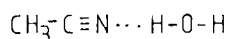
1. complex $\text{ACN} \cdot \text{H}_2\text{O}$ type:



2. complex $2\text{ACN} \cdot 3\text{H}_2\text{O}$ type:



3. complex $\text{ACN} \cdot \text{H}_2\text{O}$ type:



4. complex $2\text{ACN} \cdot \text{H}_2\text{O}$

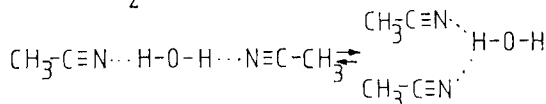


FIGURE 4

opinion, the most satisfying interpretation lies in the cooperative, specific participation of the solute molecules with water to form a clathrate type of structure.

The hypothetical structures of intermolecular "complexes" formed in the liquid $\text{ACN-H}_2\text{O}$ system shown in Figure 4.

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