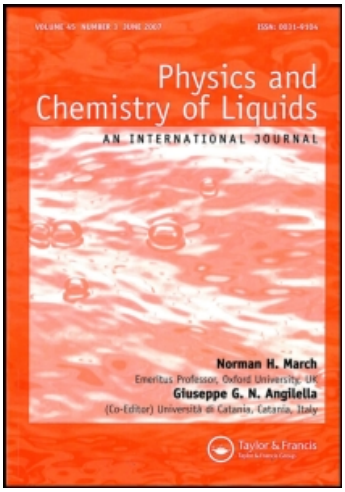

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Studies on Associated Solutions. Part II. Physicochemical Properties of Acetonitrile-Propan-2-ol Mixtures

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STUDIES ON ASSOCIATED SOLUTIONS. PART II. PHYSICOCHEMICAL PROPERTIES OF ACETONITRILE–PROPAN-2-OL MIXTURES

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The ^{1}H-NMR spectra of liquid binary mixtures of acetonitrile and propan-2-ol, were recorded at 298 K over almost the whole range of the mixed solvent compositions. From these data were found the values of the spectral parameter, $\Delta\delta$(ACN–PrOH-2). The densities (d_{12}) and relative permittivities (ε_{12}) of the mixed solvent were measured at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K, as well as refractive indices at 298.15 K. From all these data, the molar volumes (V_m), temperature coefficients of relative permittivities (α_{12}) and their deviations from ideality were calculated. Additionally, the Kirkwood's correlation factors (g_K) were found. The values of these properties are discussed in terms of interactions of acetonitrile with propan-2-ol.

Keywords: Physicochemical properties; intermolecular interactions; binary liquid mixtures

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INTRODUCTION

Previously we have investigated the internal structure in the liquid acetonitrile–methanol, acetonitrile–butan-1-ol and acetonitrile–butan-2-ol binary mixtures, based on the correlation existing between the ^{1}H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures [1, 2]. In the present work, taken into account the published data [3–11] concerning the structure of liquid ACN and alcohols and our results of mixtures of water, methanol, butan-1-ol and butan-2-ol with acetonitrile [1, 2, 12], we have analysed the mutual intermolecular interactions in the liquid mixtures of acetonitrile (ACN)–propan-2-ol (PrOH-2).

EXPERIMENTAL

Presently ^{1}H-NMR spectral studies and the measurements of relative permittivities, densities and refractive indices of mixtures of chemical pure acetonitrile (Fluka) and PrOH-2 (Fluka) were carried. They were dried and purified according to known procedures [13]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The proton chemical shifts of ACN and PrOH-2 were measured with an accuracy of ca. ± 0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were performed with an accuracy of $\pm 0.1\%$, using a bridge of the type OH-301 (made in Hungary). Solvent densities were measured, using a glass Lipkin pycnometer. The maximum error in the density measurements was $3 \cdot 10^{-5}$ g·cm^{-3}. The refractive index measurements for sodium light (λ = 598.55 nm) were performed using the Abbe refractometer. Each temperature was maintained constant with an accuracy of ± 0.01 K. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

From the measured densities (d_{12}) (see Tab. I) the molar excess volumes (V_m^E) and deviations from "ideality" of density [$\Delta(d_{12})_{\text{ideal.}}$]

TABLE I Densities (d_{12}) for the liquid ACN – PrOH-2 mixtures at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

% *mol.*	$d_{12}[g \cdot cm^{-3}]$				
PrOH-2	288.15 *K*	293.15 *K*	298.15 *K*	303.15 *K*	308.15 *K*
0	0.78726	0.78195	0.77664	0.77128	0.76591
5	0.78668	0.78158	0.77620	0.77090	0.76563
10	0.78637	0.78140	0.77600	0.77072	0.76553
15	0.78626	0.78137	0.77604	0.77071	0.76558
20	0.78631	0.78145	0.77616	0.77083	0.76575
25	0.78646	0.78163	0.77641	0.77106	0.76601
30	0.78669	0.78187	0.77674	0.77136	0.76634
35	0.78695	0.78214	0.77711	0.77170	0.76672
40	0.78723	0.78244	0.77749	0.77208	0.76713
45	0.78751	0.78274	0.77787	0.77246	0.76756
50	0.78777	0.78304	0.77822	0.77284	0.76800
55	0.78799	0.78332	0.77853	0.77322	0.76843
60	0.78818	0.78357	0.77882	0.77358	0.76886
65	0.78833	0.78381	0.77906	0.77392	0.76928
70	0.78845	0.78402	0.77928	0.77426	0.76969
75	0.78856	0.78421	0.77949	0.77459	0.77009
80	0.78866	0.78440	0.77969	0.77493	0.77049
85	0.78878	0.78458	0.77993	0.77529	0.77090
90	0.78895	0.78479	0.78021	0.77570	0.77133
95	0.78920	0.78504	0.78059	0.77617	0.77180
100	0.78957	0.78534	0.78110	0.77673	0.77232

of the mixtures, at the temperature $T = 298.15\,K$, were fitted to the equation:

$$V_m^E = x_1 \cdot M_1 \left(d_{12}^{-1} - d_1^{-1}\right) + x_2 \cdot M_2 \left(d_{12}^{-1} - d_2^{-1}\right) \tag{1}$$

$$\Delta(d_{12})_{\text{ideal.}} = d_{12} - \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{x_1 \cdot (M_1/d_1) + x_2 \cdot (M_2/d_2)} \tag{2}$$

where: M_i, d_i and x_i are the molar mass, density and mole fraction of component i, with $i = 1$ for acetonitrile and $i = 2$ for propan-2-ol while d_{12} is the density of the mixture.

The molar excess volumes (V_m^E) and deviations from "ideality" of density [$\Delta(d_{12})_{\text{ideal.}}$] for all the mixtures were fitted to the equation:

$$y = x(1-x)\sum_{j=0}^{k} a_j (2x-1)^j \tag{3}$$

where: x – mole fraction.

The parameters a_j of Eq. (3) were evaluated by the method of least squares with points weighted and they are listed in Table II along with standard deviations. The values of V_m^E and $\Delta(d_{12})_{\text{ideal.}}$ for the investigated systems are presented graphically as a function of composition in Figure 1.

The analysis of changes of excess values of molar volume and density of liquid binary mixtures ACN–PrOH-2 indicates that for the studied system only one characteristic composition region is observed (see Fig. 1 and Tab. II) from the point of view of changes of these functions. This characteristic composition region for studied mixtures ACN–PrOH-2 corresponds to ca. 25 mol.% of PrOH-2. Within this region the maximum of V_m^E and linked with it the minimum of $(\Delta d_{12})_{\text{ideal.}}$ are observed. These effects can be accounted for by the break-up of PrOH-2 structure and the geometrical fitting of ACN into the remaining alcohol structure. Since the alcohol structure has open cavities, the values of V_m^E should be positive [14, 15].

From the experimental values of relative permittivities (ε_{12}) (see Tab. III), the temperature coefficients of the relative permittivity, denoted α_{12}, *viz.*:

$$\alpha_{12} = \frac{1}{\varepsilon_{12}} \cdot \left[\frac{d\varepsilon_{12}}{d(1/T)} \right] \tag{4}$$

at 298.15 K, were calculated (see Fig. 2). The composition range of liquid binary mixtures within which α_{12} attain their highest values should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic consideration [16]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture.

We observed the tendency to achieve the maximum by the function α_{12} at ca. 25 mol.% of PrOH-2. This effect can be accounted by maximal intermolecular interactions between ACN and PrOH-2,

TABLE II Parameters (a_j) and standard deviations (s) for least squares representations by Eq. (3) of V_m^E and $\Delta(d_{12})_{\text{ideal.}}$ for studied mixtures, at 298.15 K

Functions	a_0	a_1	a_2	a_3	a_4	a_5	s
V_m^E	0.35593	−0.33480	0.70120	0.12440	−0.00910	0.02870	$3.4 \cdot 10^{-4}$
$\Delta(d_{12})_{\text{ideal.}}$	−0.00430	0.00480	−0.00940	0.00010	0.00030	0.00009	$6.2 \cdot 10^{-6}$

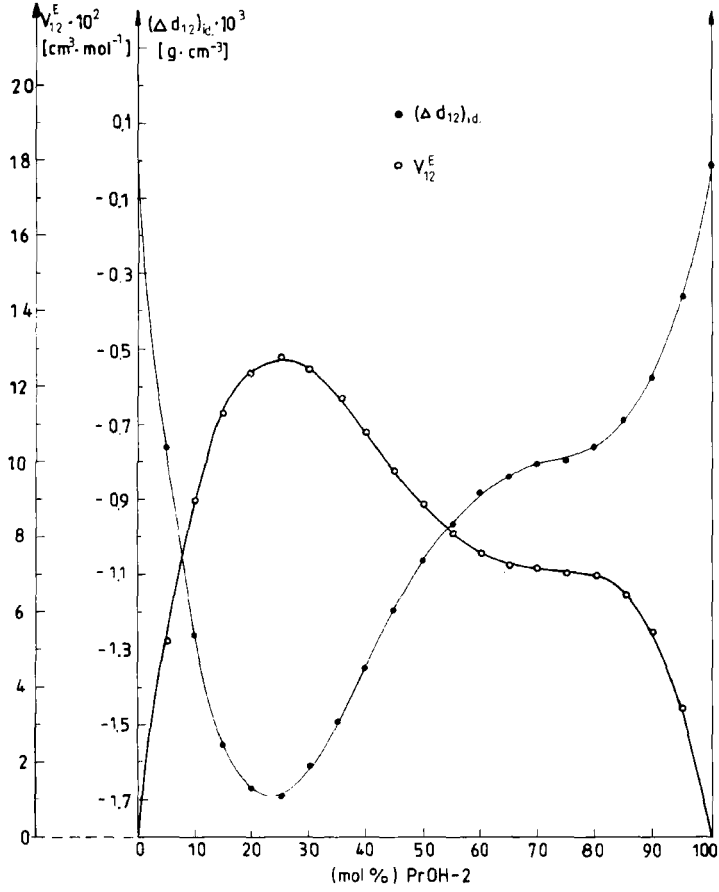

FIGURE 1 Changes in the excess molar volumes (V_m^E) and the deviations from "ideality" of density [$(\Delta d_{12})_{ideal.}$] for the liquid ACN–PrOH-2 mixtures.

which lead to formation of stable intermolecular complexes [1–3]. This effect (similarly as for the interpretation of maximum values of V_m^E) can be accounted for by the break-up of alcohol structure and the geometrical fitting of ACN into the remaining alcohol structure.

In this work with the aim of analysing the intermolecular interactions between the components in the binary liquid ACN–PrOH-2 mixtures, we measured the values of chemical shifts differences δ(ACN–PrOH) at 298 K, between the centre of the ^{1}H-NMR signals

TABLE III Relative permittivities (ε_{12}), chemical shifts δ(ACN – PrOH-2) and refractive indices (n_{12}^D) for the liquid ACN – PrOH-2 mixtures

% *mol. PrOH-2*	ε_{12}					$\delta(ACN-PrOH\text{-}2)$ [*Hz*]	n_{12}^D
	288.15 *K*	293.15 *K*	298.15 *K*	303.15 *K*	308.15 *K*	298 *K*	298.15 *K*
0	37.58	36.78	35.97	35.09	34.25	–	1.3416
1	–	–	–	–	–	67.0	–
5	36.28	35.43	34.59	33.79	32.95	74.8	1.3438
10	35.01	34.11	33.26	32.52	31.68	84.0	1.3459
15	33.76	32.85	32.00	31.29	30.46	93.3	1.3480
20	32.54	31.63	30.81	30.11	29.28	102.1	1.3500
25	31.38	30.48	29.67	28.98	28.15	109.8	1.3519
30	30.26	29.38	28.60	27.90	27.07	115.7	1.3538
35	29.20	28.34	27.59	26.88	26.05	121.8	1.3556
40	28.20	27.37	26.64	25.91	25.08	127.3	1.3574
45	27.27	26.47	25.75	25.00	24.17	133.0	1.3591
50	26.41	25.63	24.91	24.16	23.32	138.5	1.3608
55	25.62	24.85	24.14	23.37	22.53	144.1	1.3624
60	24.89	24.14	23.41	22.64	21.80	149.5	1.3639
65	24.23	23.49	22.75	21.97	21.13	155.1	1.3655
70	23.64	22.90	22.13	21.35	20.51	160.6	1.3669
75	23.11	22.36	21.57	20.79	19.94	166.3	1.3684
80	22.63	21.88	21.05	20.28	19.42	171.8	1.3698
85	22.20	21.44	20.59	19.81	18.94	177.5	1.3712
90	21.82	21.04	20.16	19.38	18.50	183.6	1.3725
95	21.47	20.67	19.78	18.98	18.10	199.4	1.3738
99	–	–	–	–	–	194.0	–
100	21.14	20.33	19.45	18.62	17.73	–	1.3750

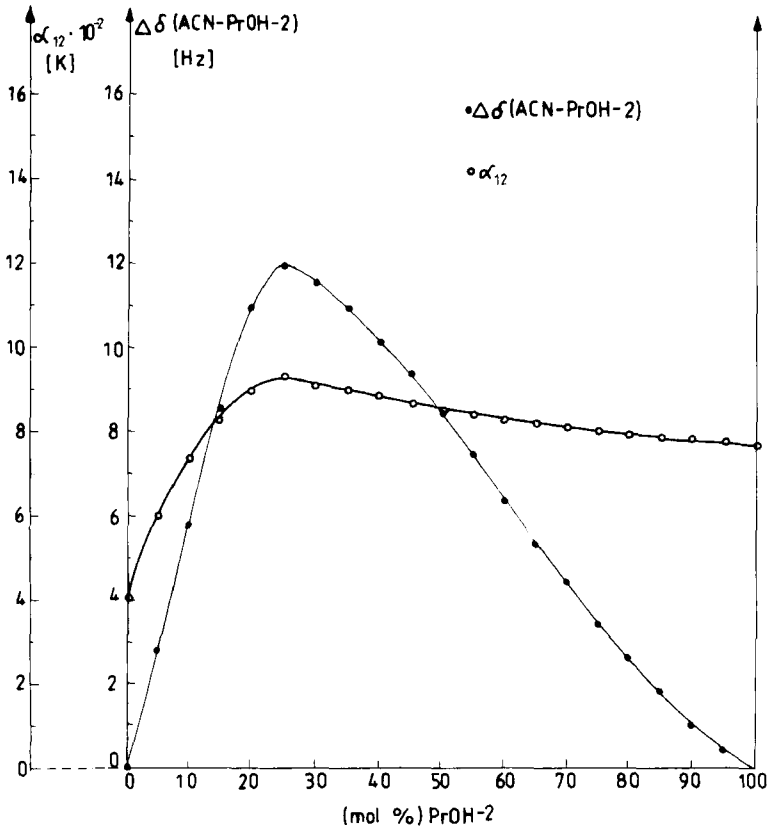

FIGURE 2 Changes in $\Delta\delta$(ACN – PrOH-2) and the temperature coefficient of relative permittivities (α_{12}) for the liquid ACN – PrOH-2 mixtures.

of the $-CH_3$ group of acetonitrile and the centre of the ^{1}H-NMR signals of the —OH group of PrOH-2 molecules over a wide range of solvent compositions, *i.e.*, from 1.0 to 99.0 mol.% of PrOH-2. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(ACN – PrOH-2), shown in Table III and explained above, their deviations from the additive properties, *viz.* $\Delta\delta$(ACN – PrOH-2) values, have been calculated. The procedure to find these values has been discussed in detail previously [1]. The values of this structural parameter or, more precisely, the location of its maximum values [1 – 3], are located at the composition with the

strongest intermolecular interactions between the components, where hydrogen bonds are involved.

The $\Delta\delta$(ACN–PrOH-2) values are visualized in Figure 2 as a function of the mixture compositions. The analysis of the data indicates the presence of a maximum $\Delta\delta$(ACN–PrOH-2) at ca. 25 mol.% of PrOH-2.

Thus, the conclusion can be drawn that at this composition the strongest interactions between PrOH-2 and ACN molecules are displayed and it suggests the formation of the structure such as clathrates.

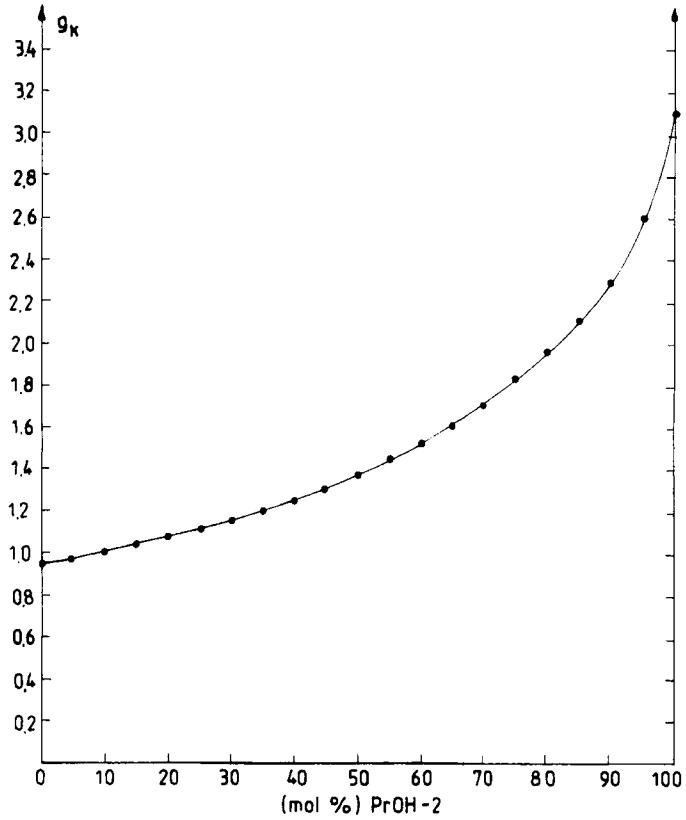

FIGURE 3 Changes in the Kirkwood's correlation factors (g_K) for the liquid ACN–PrOH-2 mixtures.

Presently obtained results fully confirm our previous conclusions regarding structural aspects derived from densimetric and dielectrometric measurements.

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of Kirkwood's correlation factor g_K [17]. Its values reflect mutual orientation of neighbouring molecular dipoles and they can provide information of associates present in solution [17, 18]. From the experimental values of relative permittivity, refractive index (see Tab. III) and literature values of dipole moment of ACN and PrOH-2 [13] the Kirkwood's correlation factors, at 298.15 K, were calculated. The procedure to find these values has been discussed in detail previously [1]. The g_K values for ACN–PrOH-2 binary mixtures as a function of the mixture composition are presented in Figure 3.

The analysis of g_K values within the whole composition range of ACN–PrOH-2 mixtures suggests that acetonitrile–alcohol open dimers and multimers exist in the system.

As observed by us, different courses of all analysed curves for various composition ranges of ACN–PrOH [2] and ACN–PrOH-2 liquid mixtures are presumably associated with a size and shape of intermolecular complexes formed by ACN with studied alcohols as a result of different structure of these molecules [3–9].

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