Acetonitrile - 2-Methyl-Propan-1-ol and Acetonitrile - 2-Methyl-Propan-2-ol Binary Mixtures and their Physicochemical Properties

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ACETONITRILE – 2-METHYL-PROPAN-1-OL AND ACETONITRILE – 2-METHYL-PROPAN-2-OL BINARY MIXTURES AND THEIR PHYSICOCHEMICAL PROPERTIES

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The ^{1}H-NMR spectra of liquid binary mixtures of acetonitrile with 2-methyl-propan-1-ol (i-BtOH) and 2-methyl-propan-2-ol (t-BtOH), were recorded at 298 K over almost the whole range of mixed solvent compositions. From these data the values of spectral parameters, $\Delta\delta$(ACN–i-BtOH) and $\Delta\delta$(ACN–t-BtOH) were found. The relative permittivities (ε_{12}) and the densities (d_{12}) of the mixed solvents were measured at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K. The experimental data were used to test some empirical equations of the type: $y_{12} = y_{12}(t)$ and $y_{12} = y_{12}(X_1)$ [where: $y_{12} = d_{12}$ or ε_{12}]. From all these data, the deviations from ideality molar volumes (V_{12}^E), temperature coefficients of relative permittivities (α_{12}) and the excess extrathermodynamic parameters ε_{12}^E were calculated. The values of these structural parameters are discussed in terms of interactions of acetonitrile with both alcohols.

Keywords: Intermolecular interactions; Internal structure; Physicochemical properties; Liquid binary mixtures

INTRODUCTION

Physicochemical and thermodynamic investigations play an important role in helping to understand the nature and the extent of the patterns of molecular aggregation that exist in liquid binary mixtures and their sensitivities to variations in composition and the molecular structure of the pure components.

The specific interaction due to the hydrogen bond between the polar groups of different components is primarily responsible for the non-ideal behaviours of binary associated solutions. When an alcohol is mixed with organic compounds (for example

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acetonitrile), some of the alcohol molecules will tend to dissociate from the polymeric aggregates (formed through the hydrogen bond) to form other kinds of hydrogen bonds with different kinds of molecules and with the geometrical incorporation of the second component into the remaining alcohol structure. On the other hand, there is a possible process of co-operative accommodation of the second component into the alcohol structure, which is accompanied by an interstitial dissolution. As a rough first approximation, these may be the most decisive factors in determining the sign and magnitude of the deviation from the ideal solution law [1–7].

This paper is a continuation of a series of studies on internal structures of some liquid binary mixtures, in which acetonitrile or an aliphatic alcohol is one of the two constituents, based on the correlation existing between the ^{1}H-NMR spectral results and some physicochemical properties of the same binary mixtures [5,6]. In this paper we have analysed the mutual intermolecular interactions in the liquid binary mixtures acetonitrile (ACN) with 2-methyl-propan-1-ol (i-BtOH) and 2-methyl-propan-2-ol (t-BtOH) on variations in the molecular structures of the butanols.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities, densities and refractive indices, chemically pure ACN (Fluka), i-BtOH (Fluka) and t-BtOH (Fluka) were used. They were dried and purified according to known procedures [8].

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, i-BtOH and t-BtOH were measured with an accuracy of *ca.* ± 0.2 Hz with respect to an external standard hexamethyl-disiloxane (HMDS). The relative permittivity measurements were carried out at 3 MHz, with an accuracy of ± 0.4 units, using a bridge of the type OH – 301 (made in Radelcis, Hungary). The thermostatic stainless steel measuring cells are of the covered coaxial capacitors (stainless steel) with vacuum capacitances of 2.5 pF (C3) ($10 < \varepsilon < 25$) and 0.5 pF (C4) ($25 < \varepsilon < 100$). They were calibrated with standard pure liquids, such as acetone, butan-1-ol and dicholoromethane (C3); methanol, ethanol and deionized water (C4). With the exception of the deionized water, all these solvents were of spectrograde quality or higher. The relative permittivity for the standards were taken from literature [8]. Solvent densities were measured, using a glass Lipkin pycnometer of *ca.* 90 cm^3. The maximum error in the density measurements was $4 \cdot 10^{-5}$ g cm^{-3}.

The temperature was maintained constant within ± 0.01 K. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

The experimental data of density (d_{12}), relative permittivity (ε_{12}) and chemical shifts δ(ACN–ROH) obtained from the measurements of the pure solvents and for the analysed binary mixtures at all investigated temperatures are summarized in Tables I, II and III.

TABLE I Densities (d_{12}) and relative permittivities (ε_{12}) for the liquid ACN–i-BtOH mixtures

$X_{i\text{-}BtOH}$	d_{12} [g cm^{-3}]					ε_{12}				
	288.15 [K]	293.15 [K]	298.15 [K]	303.15 [K]	308.15 [K]	288.15 [K]	293.15 [K]	298.15 [K]	303.15 [K]	308.15 [K]
0.0000	0.78724	0.78197	0.77664	0.77128	0.76591	37.58	36.78	35.97	35.09	34.25
0.0509	0.78797	0.78273	0.77745	0.77237	0.76745	35.46	34.74	33.98	33.14	32.33
0.1004	0.78889	0.78371	0.77847	0.77360	0.76902	33.55	32.88	32.17	31.37	30.58
0.1491	0.78997	0.78487	0.77967	0.77494	0.77060	31.83	31.22	30.54	29.76	29.00
0.1996	0.79118	0.78617	0.78102	0.77648	0.77218	30.30	29.72	29.06	28.30	27.58
0.2491	0.79250	0.78759	0.78249	0.77789	0.77376	28.93	28.37	27.74	26.99	26.29
0.3009	0.79389	0.78909	0.78405	0.77944	0.77532	27.72	27.18	26.55	25.80	25.15
0.3506	0.79532	0.79064	0.78566	0.78102	0.77686	26.64	26.11	25.49	24.74	24.12
0.4008	0.79678	0.79221	0.78730	0.78261	0.77836	25.70	25.16	24.54	23.79	23.20
0.4491	0.79822	0.79377	0.78894	0.78418	0.77981	24.87	24.32	23.70	22.93	22.38
0.5003	0.79963	0.79530	0.79054	0.78570	0.78121	24.14	23.58	22.95	22.17	21.64
0.5507	0.80098	0.79675	0.79207	0.78717	0.78254	23.50	22.92	22.28	21.48	20.99
0.6010	0.80223	0.79810	0.79350	0.78855	0.78379	22.94	22.33	21.68	20.87	20.40
0.6491	0.80336	0.79933	0.79481	0.78982	0.78496	22.43	21.80	21.13	20.31	19.84
0.7008	0.80435	0.80039	0.79596	0.79067	0.78604	21.97	21.32	20.63	19.80	19.34
0.7491	0.80515	0.80125	0.79692	0.79196	0.78701	21.55	20.88	20.16	19.33	18.86
0.8007	0.80575	0.80190	0.79765	0.79278	0.78786	21.15	20.46	19.72	18.89	18.41
0.8511	0.80612	0.80229	0.79814	0.79340	0.78859	20.75	20.05	19.28	18.46	17.95
0.9008	0.80623	0.80240	0.79834	0.79380	0.78919	20.35	19.63	18.85	18.04	17.50
0.9491	0.80606	0.80219	0.79823	0.79397	0.78964	19.93	19.21	18.40	17.62	17.02
1.0000	0.80556	0.80164	0.79777	0.79387	0.78994	19.48	18.76	17.93	17.18	16.52

TABLE II Densties (d_{12}) and relative permittivities (ε_{12}) for the liquid ACN–t-Bt-OH mixtures

$X_{t\text{-}BtOH}$	d_{12} [g cm^{-3}]				ε_{12}			
	293.15 [K]	298.15 [K]	303.15 [K]	308.15 [K]	293.15 [K]	298.15 [K]	303.15 [K]	308.15 [K]
0.0000	0.78197	0.77664	0.77128	0.76591	36.78	35.97	35.09	34.25
0.0503	0.78108	0.77592	0.77048	0.76526	34.58	33.81	32.98	32.17
0.1007	0.78038	0.77534	0.76985	0.76476	32.54	31.80	31.02	30.24
0.1509	0.77983	0.77488	0.76938	0.76440	30.63	29.92	29.19	28.45
0.2003	0.77943	0.77454	0.76906	0.76417	28.87	28.19	27.49	26.79
0.2496	0.77916	0.77432	0.76887	0.76405	27.24	26.58	25.92	25.25
0.2997	0.77902	0.77419	0.76881	0.76404	25.73	25.09	24.46	23.82
0.3506	0.77899	0.77417	0.76887	0.76413	24.33	23.71	23.10	22.49
0.4002	0.77907	0.77424	0.76902	0.76431	23.04	22.44	21.85	21.26
0.4493	0.77924	0.77439	0.76827	0.76457	21.86	21.26	20.68	20.11
0.5009	0.77951	0.77463	0.76959	0.76489	20.76	20.17	19.60	19.04
0.5511	0.77984	0.77494	0.76998	0.76527	19.76	19.15	18.59	18.04
0.6004	0.78024	0.77531	0.77042	0.76569	18.83	18.21	17.65	17.10
0.6504	0.78070	0.77574	0.77091	0.76616	17.97	17.33	16.77	16.20
0.7006	0.78121	0.77623	0.77143	0.76665	17.18	16.51	15.94	15.36
0.7508	0.78174	0.77676	0.77197	0.76715	16.45	15.74	15.15	14.54
0.7992	0.78231	0.77733	0.77252	0.76767	15.77	15.00	14.40	13.76
0.8491	0.78289	0.77793	0.77306	0.76818	15.12	14.30	13.68	12.98
0.9001	0.78348	0.77856	0.77359	0.76867	14.52	13.62	12.98	12.21
0.9502	0.78406	0.77921	0.77401	0.76914	13.94	12.97	12.29	11.45
1.0000	–	–	0.77455	0.76958	–	–	11.43	10.55

TABLE III Relative ^{1}H-NMR chemical shifts, δ(ACN–ROH), for the liquid ACN–i-BtOH and ACN–t-BtOH mixtures, at 298 K

ROH [mol%]	δ(ACN–i-BtOH) [Hz]	δ(ACN–t-BtOH) [Hz]
0.0100	34.0	28.0
0.0509	42.3	36.9
0.1004	52.3	46.6
0.1491	62.1	56.5
0.1996	71.7	66.1
0.2491	81.3	75.6
0.3009	91.0	84.9
0.3506	100.5	94.3
0.4008	109.9	103.5
0.4491	119.4	112.9
0.5003	128.8	121.6
0.5507	138.1	129.9
0.6010	147.3	137.2
0.6491	156.3	144.8
0.7008	165.3	152.1
0.7491	174.0	159.0
0.8007	182.3	166.4
0.8511	189.0	174.0
0.9008	193.8	181.5
0.9491	195.2	189.1
0.9900	191.0	195.0

The first step of this study involves investigation of the dependence of density (d_{12}) on temperature, and the following relationship was used [9,11]:

$$d_{12}(t) = \sum_0^i \alpha_i T^i \tag{1}$$

where T is the temperature in K.

The polynomial coefficients α_i, for $i = 3$, evaluated through a TSP multilinear regression package [11], are summarized, with the standard deviations [$\sigma(d_{12})$] for each mixture, in Table IV. The suitability of Eq. (1) for this fitting procedure is ascertained on the basis of mean deviation $\overline{\Delta d_{12}} = \pm 0.00003\,\text{g cm}^{-3}$ for ACN–i-BtOH mixtures and $\overline{\Delta d_{12}} = \pm 0.00004\,\text{g cm}^{-3}$ for ACN–t-BtOH mixtures calculated as follows [9,11]:

$$\overline{\Delta d}_{12} = \frac{1}{N} \sum_N \left| d_{12}^{\text{calc.}} - d_{12}^{\text{exp.}} \right| \tag{2}$$

where N is number of experimental data in Table I or Table II.

The second step, of this study, involves investigation of the dependence of density (d_{12}) on molar fraction (X_1) of ROH, and the following relationship was used [9,11]:

$$d_{12}(X_1) = \sum_0^j \beta_j X_1^j \tag{3}$$

The values of β_j coefficients, for $j = 5$, are listed in Table V together with the standard deviations, at each investigated temperature.

TABLE IV Coefficient α_i and standard deviations $\sigma(d_{12})$ of Eq. (1) for ACN-ROH mixtures

% mol i-BtOH	ACN–i-BtOH				
	$\alpha_3 \cdot 10^7$	$\alpha_2 \cdot 10^5$	$\alpha_1 \cdot 10^4$	$\alpha_0 \cdot 10$	$\sigma(d_{12})$
0.0000	0.3333	− 0.3157	− 9.7448	8.0246	$1.6 \cdot 10^{-5}$
0.0509	1.3333	− 0.7600	− 9.9093	8.0287	$1.8 \cdot 10^{-5}$
0.1004	2.3333	− 1.3014	− 8.0362	8.0309	$1.5 \cdot 10^{-5}$
0.1491	3.2667	− 1.8814	− 6.7295	8.0320	$1.9 \cdot 10^{-5}$
0.1996	2.5333	− 1.3200	− 7.9033	8.0517	$1.9 \cdot 10^{-5}$
0.2491	4.4000	− 2.7114	− 4.5029	8.0388	$1.8 \cdot 10^{-5}$
0.3009	4.8667	− 3.1386	− 3.2038	8.0412	$1.7 \cdot 10^{-5}$
0.3506	5.2000	− 3.5057	− 1.9714	8.0442	$1.0 \cdot 10^{-5}$
0.4008	5.2000	− 3.6543	− 1.2086	8.0506	$1.0 \cdot 10^{-5}$
0.4491	5.1333	− 3.7843	− 0.4219	8.0564	$1.5 \cdot 10^{-5}$
0.5003	5.2000	− 4.0143	0.5914	8.0602	$1.9 \cdot 10^{-5}$
0.5507	4.8000	− 3.8914	0.7571	8.0698	$1.9 \cdot 10^{-5}$
0.6010	4.4000	− 3.7600	0.8900	8.0786	$1.9 \cdot 10^{-5}$
0.6491	4.1333	− 3.7086	1.1795	8.0853	$1.1 \cdot 10^{-5}$
0.7008	7.5333	− 6.2786	7.3595	8.0487	$1.0 \cdot 10^{-5}$
0.7491	2.9333	− 2.9800	3.6667	8.1080	$1.4 \cdot 10^{-5}$
0.8007	2.3333	− 2.5386	− 0.8605	8.1195	$1.1 \cdot 10^{-5}$
0.8511	1.6667	− 1.9786	− 2.1638	8.1324	$0.9 \cdot 10^{-5}$
0.9008	1.0667	− 1.3829	− 3.7124	8.1454	$0.9 \cdot 10^{-5}$
0.9491	0.1333	− 0.4486	− 6.2305	8.1636	$0.8 \cdot 10^{-5}$
1.0000	− 0.5333	0.3857	− 8.6852	8.1790	$1.0 \cdot 10^{-5}$

% mol t-BtOH	ACN–t-BtOH				
	$\alpha_3 \cdot 10^7$	$\alpha_2 \cdot 10^5$	$\alpha_1 \cdot 10^4$	$\alpha_0 \cdot 10$	$\sigma(d_{12})$
0.0000	0.3333	− 0.3157	− 0.9745	8.0246	$1.6 \cdot 10^{-5}$
0.0503	6.6667	− 5.5600	0.4533	7.8892	$1.1 \cdot 10^{-5}$
0.1007	11.3330	− 9.4000	1.4937	7.7904	$1.3 \cdot 10^{-5}$
0.1509	14.2670	− 11.8000	2.1443	7.7273	$1.5 \cdot 10^{-5}$
0.2003	15.7330	− 12.9800	2.4637	7.6949	$1.0 \cdot 10^{-5}$
0.2496	16.5330	− 13.6200	2.6397	7.6762	$1.0 \cdot 10^{-5}$
0.2997	15.4670	− 12.7000	2.3903	7.6964	$1.5 \cdot 10^{-5}$
0.3506	13.8670	− 11.3600	2.0333	7.7267	$1.4 \cdot 10^{-5}$
0.4002	12.0000	− 9.7800	1.6050	7.7646	$1.4 \cdot 10^{-5}$
0.4493	9.2000	− 7.4400	0.9750	7.8214	$1.2 \cdot 10^{-5}$
0.5009	6.6667	− 5.3200	0.4013	7.8743	$1.6 \cdot 10^{-5}$
0.5511	4.1333	− 3.2200	− 0.1613	7.9264	$1.5 \cdot 10^{-5}$
0.6004	1.6000	− 1.1200	− 0.7260	7.9796	$1.3 \cdot 10^{-5}$
0.6504	− 0.6667	0.7600	− 1.2323	8.0284	$1.4 \cdot 10^{-5}$
0.7006	− 2.1333	1.9600	− 1.5527	8.0613	$1.1 \cdot 10^{-5}$
0.7508	− 2.9333	2.5800	− 1.7097	8.0796	$1.0 \cdot 10^{-5}$
0.7992	− 2.8000	2.4400	− 1.6670	8.0813	$0.9 \cdot 10^{-5}$
0.8491	− 1.3333	1.1800	− 1.3197	8.0563	$0.9 \cdot 10^{-5}$
0.9001	1.3333	− 1.1000	− 0.6923	8.006	$1.2 \cdot 10^{-5}$
0.9502	9.0667	− 7.5000	1.0223	7.8636	$1.0 \cdot 10^{-5}$
1.0000	–	–	–	–	–

Equation (3) reproduces the experimental data of d_{12} (see Tables I and II) with $\overline{\Delta d}_{12} = \pm 0.00004 \, \text{g cm}^{-3}$ for ACN–i-BtOH and ACN–t-BtOH mixtures.

In this paper, our investigations of dielectric behaviours as a function of temperature are given by the Eq. (4) [9,11]:

$$\ln \varepsilon_{12} = \alpha_0^* + \alpha_i^* T \qquad (4)$$

where: α_i $(i = 0, 1)$ are empirical constants and T is the absolute temperature.

TABLE V Coefficients β_j and standard deviations $\sigma(d_{12})$ of Eq. (3) for ACN–i-BtOH and ACN–t-BtOH mixtures

T [K]	$\beta_5 \cdot 10^{14}$	$\beta_4 \cdot 10^{12}$	$\beta_3 \cdot 10^8$	$\beta_2 \cdot 10^6$	$\beta_1 \cdot 10^4$	$\beta_0 \cdot 10$	$\sigma(d_{12})$
				ACN–i-BtOH			
288.15	− 2.4423	7.8711	− 3.8138	4.3354	1.2564	7.8724	$6.9 \cdot 10^{-5}$
293.15	− 12.8820	35.8850	− 4.4410	4.8767	1.3014	7.8197	$7.2 \cdot 10^{-5}$
298.15	− 3.2333	8.1225	− 4.1901	4.8713	1.3828	7.7664	$5.1 \cdot 10^{-5}$
303.15	− 84.7530	20.7680	− 4.6434	3.6781	1.9949	7.7128	$3.8 \cdot 10^{-5}$
308.15	− 1.3516	6.1234	− 1.3977	0.7016	3.0513	7.6591	$2.5 \cdot 10^{-5}$

T [K]	$\beta_5 \cdot 10^3$	$\beta_4 \cdot 10^3$	$\beta_3 \cdot 10^2$	$\beta_2 \cdot 10^2$	$\beta_1 \cdot 10^2$	$\beta_0 \cdot 10$	$\sigma(d_{12})$
				ACN–t-BtOH			
293.15	− 2.3327	5.2810	− 1.7436	3.6444	− 1.9314	7.8197	$6.6 \cdot 10^{-5}$
298.15	− 3.6307	9.1389	− 1.7326	3.1388	− 1.6419	7.7670	$7.1 \cdot 10^{-5}$
303.15	1.4821	4.2100	− 1.1434	3.5002	− 1.7595	7.7128	$2.4 \cdot 10^{-5}$
308.15	− 0.3594	0.5185	− 1.3550	3.1531	− 1.4473	7.6591	$1.9 \cdot 10^{-5}$

TABLE VI Coefficients α_1^* and α_0^* standard deviations $\sigma(\ln \varepsilon_{12})$ of Eq. (4) for ACN–i-BtOH and ACN–t-BtOH mixtures

$X_{i\text{-}BtOH}$	$\alpha_1^* \cdot 10^3$	α_0^*	$\sigma(\ln \varepsilon_{12})$	$X_{t\text{-}BtOH}$	$\alpha_1^* \cdot 10^3$	α_0^*	$\sigma(\ln \varepsilon_{12})$
0.0000	− 4.6540	3.6975	$1.3 \cdot 10^{-3}$	0.0000	− 4.6540	3.6975	$1.3 \cdot 10^{-3}$
0.0509	− 4.6400	3.6398	$1.4 \cdot 10^{-3}$	0.0503	− 4.8360	3.6407	$1.1 \cdot 10^{-3}$
0.1004	− 4.6480	3.5848	$1.6 \cdot 10^{-3}$	0.1007	− 4.8960	3.5811	$1.2 \cdot 10^{-3}$
0.1491	− 4.6820	3.5333	$1.8 \cdot 10^{-3}$	0.1509	− 4.9280	3.5211	$1.6 \cdot 10^{-3}$
0.1996	− 4.7380	3.4849	$2.2 \cdot 10^{-3}$	0.2003	− 4.9920	3.4632	$1.4 \cdot 10^{-3}$
0.2491	− 4.8240	3.4402	$2.0 \cdot 10^{-3}$	0.2496	− 5.0580	3.4063	$2.1 \cdot 10^{-3}$
0.3009	− 4.9340	3.3991	$2.1 \cdot 10^{-3}$	0.2997	− 5.1420	3.3508	$1.8 \cdot 10^{-3}$
0.3506	− 5.0540	3.3612	$2.7 \cdot 10^{-3}$	0.3506	− 5.2380	3.2967	$1.9 \cdot 10^{-3}$
0.4008	− 5.2120	3.3274	$2.3 \cdot 10^{-3}$	0.4002	− 5.3560	3.2445	$2.1 \cdot 10^{-3}$
0.4491	− 5.3980	3.2972	$2.5 \cdot 10^{-3}$	0.4493	− 5.5620	3.1959	$2.4 \cdot 10^{-3}$
0.5003	− 5.6100	3.2704	$2.8 \cdot 10^{-3}$	0.5009	− 5.7640	3.1483	$2.0 \cdot 10^{-3}$
0.5507	− 5.8180	3.2462	$2.4 \cdot 10^{-3}$	0.5511	− 6.0600	3.1045	$2.0 \cdot 10^{-3}$
0.6010	− 6.0480	3.2250	$2.9 \cdot 10^{-3}$	0.6004	− 6.4100	3.0631	$2.6 \cdot 10^{-3}$
0.6491	− 6.3240	3.2065	$3.2 \cdot 10^{-3}$	0.6504	− 6.8820	3.0256	$2.4 \cdot 10^{-3}$
0.7008	− 6.5780	3.1892	$3.5 \cdot 10^{-3}$	0.7006	− 7.4180	2.9911	$2.5 \cdot 10^{-3}$
0.7491	− 6.8780	3.1743	$3.4 \cdot 10^{-3}$	0.7508	− 8.1680	2.9625	$2.4 \cdot 10^{-3}$
0.8007	− 7.1460	3.1593	$3.0 \cdot 10^{-3}$	0.7992	− 8.9960	2.9362	$3.4 \cdot 10^{-3}$
0.8511	− 7.4480	3.1448	$3.4 \cdot 10^{-3}$	0.8491	− 10.0440	2.9151	$3.6 \cdot 10^{-3}$
0.9008	− 7.7260	3.1295	$1.8 \cdot 10^{-3}$	0.9001	− 11.3540	2.9004	$2.8 \cdot 10^{-3}$
0.9491	− 8.0400	3.1137	$1.4 \cdot 10^{-3}$	0.9502	− 12.8840	2.8904	$1.7 \cdot 10^{-3}$
1.0000	− 8.3520	3.0960	$1.1 \cdot 10^{-3}$	1.0000	−	−	−

The empirical coefficients a_0^* and α_1^* of this fitting procedure are listed in Table VI, along with the standard deviations $\sigma(\ln \varepsilon_{12})$ for each solvent system.

Equation 4 reproduces the experimental ε_{12} values with an average uncertainty, evaluated by the means of the relation (5):

$$\overline{\Delta \varepsilon}_{12} = \frac{1}{N} \sum_N \left| \varepsilon_{12}^{\text{calc.}} - \varepsilon_{12}^{\text{exp.}} \right| \tag{5}$$

TABLE VII   Coefficients β_j^* and standard deviations $\sigma(\ln \varepsilon_{12})$ of Eq. (6) for ACN–i-BtOH and ACN–t-BtOH mixtures

T [K]	$\beta_4^* \cdot 10$	$\beta_3^* \cdot 10$	$\beta_2^* \cdot 10$	β_1^*	β_0^*	$\sigma(\ln \varepsilon_{12})$
			ACN–i-BtOH			
288.15	− 6.3011	8.3943	3.1495	− 1.1848	3.6277	$2.4 \cdot 10^{-3}$
293.15	− 3.9087	4.5745	4.2817	− 1.1695	3.6054	$2.2 \cdot 10^{-3}$
298.15	− 3.8235	4.4820	4.0167	− 1.1643	3.5831	$2.9 \cdot 10^{-3}$
303.15	− 3.5179	4.4943	3.4998	− 1.1620	3.5582	$3.2 \cdot 10^{-3}$
308.15	− 4.0648	4.6107	3.9687	− 1.1811	3.5341	$1.8 \cdot 10^{-3}$
			ACN–t-BtOH			
293.15	− 2.0814	4.0770	1.8102	− 1.2280	3.6051	$1.9 \cdot 10^{-3}$
298.15	− 2.5616	3.9395	2.9939	− 1.2386	3.5830	$1.8 \cdot 10^{-3}$
303.15	− 5.5322	8.6556	− 2.3479	− 1.1933	3.5569	$2.1 \cdot 10^{-3}$
308.15	− 6.2964	8.7632	− 2.1261	− 1.2065	3.5327	$2.0 \cdot 10^{-3}$

where: N is the experimental points; $\overline{\Delta\varepsilon_{12}} = \pm 0.04$ units of over relative permittivity values for ACN–i-BtOH mixtures and $\overline{\Delta\varepsilon_{12}} = \pm 0.03$ units for ACN–t-BtOH mixtures (see Tables I and II).

The variation of relative permittivity with binary composition was analyzed by using the following equation [9,11]:

$$\ln \varepsilon_{12} = \sum_0^j \beta_j^* X_1^j \tag{6}$$

which could be fitted to the experimental data at each temperature using a least-squares method. The values of β_j^* coefficients, for $j = 4$ and the standard deviations $\sigma(\ln \varepsilon_{12})$ are summarized in Table VII. Equation (6) reproduces the experimental data of ε_{12} (see Tables I and II) with $\overline{\Delta\varepsilon_{12}} = \pm 0.04$ units for ACN–i-BtOH and ACN–t-BtOH mixtures.

In this work, with the aim of analyzing the intermolecular interactions between the components in the liquid binary ACN–i-BtOH and ACN–t-BtOH mixtures, we measured the values of chemical shift differences δ(ACN–i-BtOH) and δ(ACN–t-BtOH), at 298 K, between the centre of ^{1}H-NMR signals of the -OH group of i-BtOH or t-BtOH and the centre of the ^{1}H-NMR signal of –CH$_3$ group of acetonitrile molecules over a wide range of solvent compositions i.e. from 0.0100 to 0.9900 mole fraction of ROH. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(ACN–i-BtOH) and δ(ACN–t-BtOH), shown in Table III, and explained above, their deviations from the additive properties, *viz*. $\Delta\delta$(ACN–i-BtOH) and $\Delta\delta$(ACN–t-BtOH) values, have been calculated. The procedure to fit these values has been discussed in detail previously [5]. The values of these structural parameters or, more precisely, the locations of their maximum values correspond to the compositions with the strongest intermolecular interactions between the components, where hydrogen bonds are involved [5–7]. The $\Delta\delta$(ACN–i-BtOH) and $\Delta\delta$(ACN–t-BtOH) values are visualized in Fig. 1 as a function of the mixture compositions.
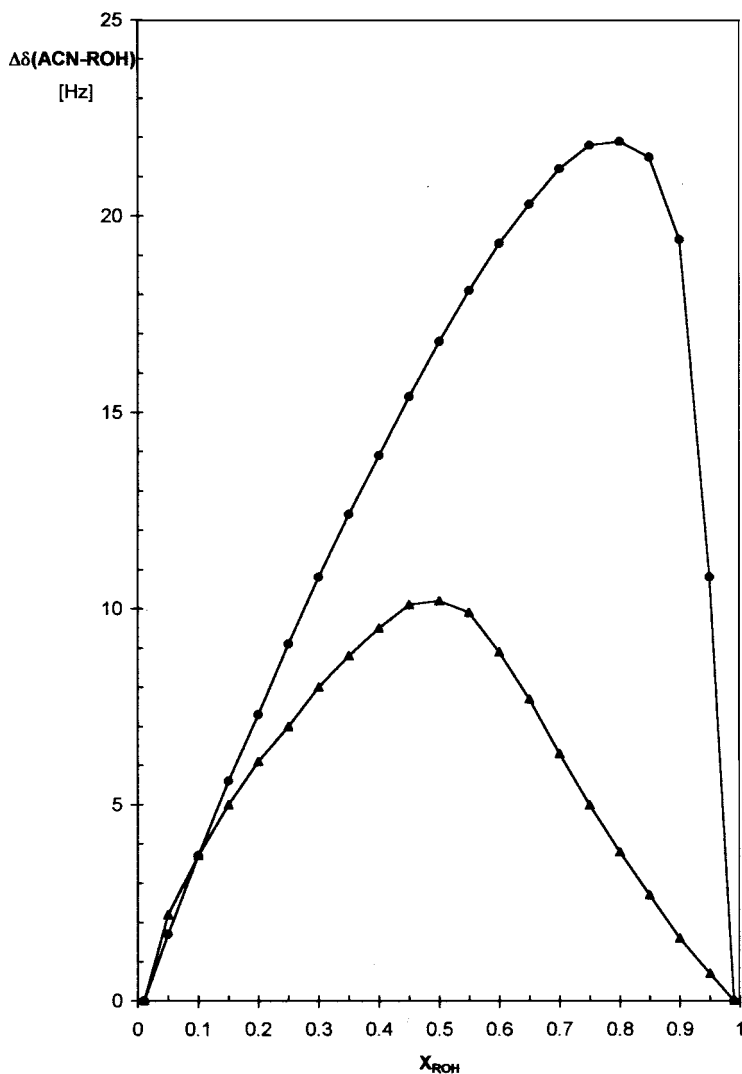
FIGURE 1   Changes in the spectral structural parameter, $\Delta\delta$(ACN–ROH), in the liquid ACN–i-BtOH mixtures at 298 K (●) and for ACN–t-BtOH mixtures at 303.15 K (▲).

The analysis of the data indicates the presence of a maximum $\Delta\delta$(ACN–i-BtOH) at *ca.* $X_{i-BtOH} \approx 0.80$ and a maximum $\Delta\delta$(ACN–t-BtOH) at *ca.* $X_{i-BtOH} \approx 0.50$. Thus, at these compositions the strongest interactions between components involving hydrogen bonds, are observed, and the most stable "complexes" are ACN · 4i-BtOH and ACN · t-BtOH.

From the experimental values of relative permittivities (ε_{12}) (see Tables I and II), the temperature coefficients of the relative permittivity, denoted α_{12}, viz.:

$$\alpha_{12} = \frac{1}{\varepsilon_{12}} \cdot \left[\frac{d\varepsilon_{12}}{d(1/T)} \right] \tag{7}$$

for ACN–i-BtOH mixtures at 298.15 K and ACN–t-BtOH mixtures at 303.13 K, were calculated.

The composition range of liquid binary mixtures within which α_{12} or its excess (α_{12}^E) attain their highest values should be interpreted (as shown in Reätzsch et al.'s thermo-dynamic consideration [12]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture [5,7].

In our studies on intermolecular interactions in liquid mixtures of ACN with both butanols we have carried out an analysis of the changes of values of α_{12} as a function of the composition of the mixed solvent (see Fig. 2).
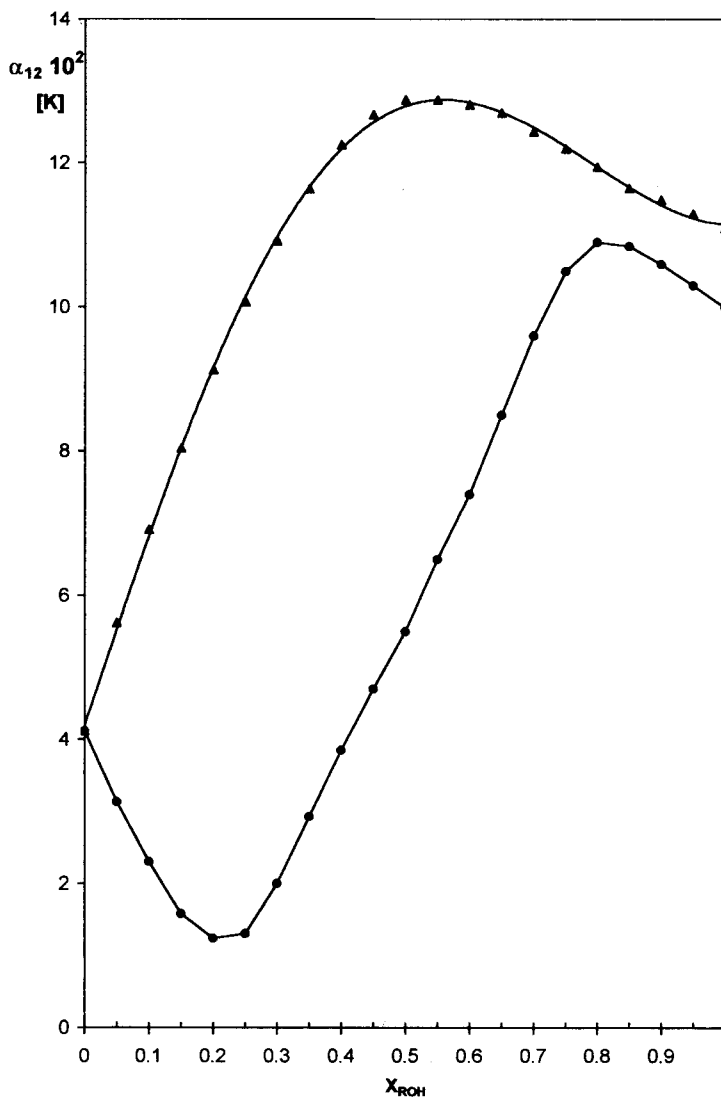
FIGURE 2   Changes in the temperature coefficient of the relative permittivity in the liquid ACN–i-BtOH mixtures at 298.15 K (●) and for ACN–t-BtOH mixtures at 303.15 K (▲).

In the case of ACN–i-BtOH mixtures, we observed the tendency to achieve the maximum by the function α_{12} at *ca.* $X_{i-BtOH} \approx 0.80$, which is the same composition range where the maximum $\Delta\delta(\text{ACN–i-BtOH})$ is observed (see Fig. 1). This effect can be accounted for by maximal intermolecular interactions between ACN and i-BtOH, which lead to the formation of stable $\text{ACN} \cdot 4\text{i-BtOH}$ intermolecular complexes [5,12].

The detailed analysis of the functions $\alpha_{12} = f(X_{i\text{-BtOH}})$ indicates that increasing addition of i-BtOH to ACN up to *ca.* $X_{i-BtOH} \approx 0.20$, where the minimum is reached, causes the rapid drop in α_{12}. Further addition of i-BtOH to this mixture causes an increase in α_{12} which results in the maximum at *ca.* $X_{i-BtOH} \approx 0.80$. The break-up of i-BtOH structure, the geometrical incorporation of ACN into the remaining alcohol structure and the complex, $4\text{ACN} \cdot \text{i-BtOH}$, formation can account for this effect. The addition of i-BtOH, up to *ca.* $X_{i-BtOH} \approx 0.80$, stabilizes the internal structure increasingly by maximal intermolecular interactions between ACN and i-BtOH, which lead to the formation of the above mentioned stable $\text{ACN} \cdot 4\text{i-BtOH}$ intermolecular complex in the analyzed liquid binary mixtures.

The course of changes of α_{12} as a function of the composition of the mixed solvent ACN–t-BtOH may appear unexpected. This parameter achieves a maximum for the composition range corresponding to *ca.* $X_{i-BtOH} \approx 0.50$, which is the same composition range where the maximum of $\Delta\delta(\text{ACN–t-BtOH})$ is observed (see Fig. 1). It is most likely linked with formation here of a complex of $\text{ACN} \cdot \text{t-BtOH}$ which exists in spite of loosening of the internal structure of liquid ACN–t-BtOH mixtures characterized by the highest stability in comparison with other possible intermolecular structures.

In our studies on intermolecular interactions in liquid mixtures of ACN with butanols we have carried out the analysis of changes of deviations from ideality values of ε_{12} as a function of the composition of the mixed solvents. The study of this extrathermodynamic structural parameter of liquid binary mixtures represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometric composition. Therefore, a very slight shift ε_{12} from the linear behavior of a non-interacting "ideal" system should correspond to very weak complexes [13–15].

The values of ε_{12}^E have been evaluated by means of the equation [14]:

$$\varepsilon_{12}^E = \varepsilon_{12} - (\varepsilon_1 X_1 + \varepsilon_2 X_2) \tag{8}$$

where X_i is the molar fraction.

The results of ε_{12}^E calculations for the investigated systems are presented graphically as a function of molar fraction of ROH (X_1) in Fig. 3.

As we can see, the excess of this extra-thermodynamic parameter (ε_{12}^E) is always negative over the whole composition range for both studied mixtures. As a major feature, these plots show a minimum centered at *ca.* $X_1 \approx 0.50$ molar fraction of both butanols.

As suggested by other authors, the small negative ε_{12}^E value for various solvent systems may be attributed either to homoconjugation phenomena of the more polar component induced by the presence of an apolar or quasi-apolar one, and/or to associations between unlike molecules in the mixtures [13–16].

In the analyzed ACN–ROH mixtures, we have to very polar components $(\mu_{\text{ACN}}^{298.15K} = 3.53D, \ \mu_{i-\text{BtOH}}^{298.15K} = 1.79D$ and $\mu_{t-\text{BtOH}}^{303.15K} = 1.66D)$ [8], therefore it is likely that there are homoconjugations between similar molecules but more likely that there
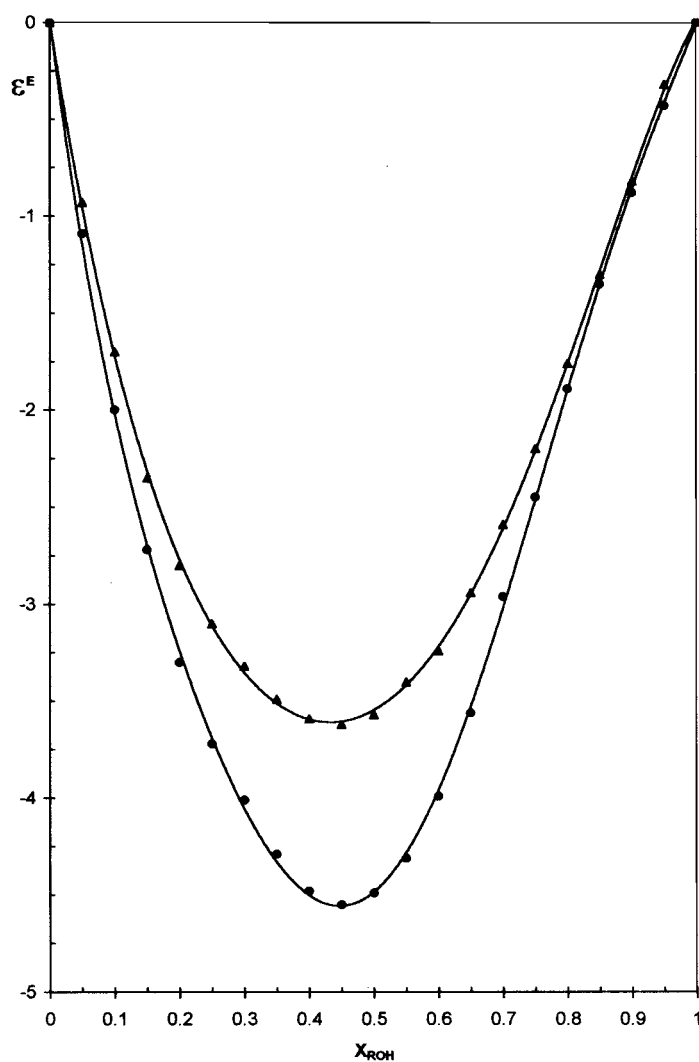
FIGURE 3   Changes in the deviations from ideality of relative permittivity (ε_{12}^E) for the liquid ACN–i-BtOH mixtures at 298.15 K ($\bullet$) and for ACN–t-BtOH mixtures 303.15 K ($\blacktriangle$).

are weak dipolar associations between unlike molecules and/or appropriate negative contributions may be expected to originate in hydrogen bonding between ACN and ROH molecules and formation of the stable ACN · ROH adducts in these binary solvent systems.

Analogous conclusions can be drawn from the analysis of the volumetric properties of the studies of binary mixtures.

From the measured densities (d_{12}) (see Tables I and II) the molar excess volumes (V_m^E) of the mixtures, for ACN–i-BtOH mixtures at 298.15 K and ACN–t-BtOH mixtures at 303.15 K, were fitted to the equation [10,15]:

$$V_m^E = X_1 \cdot M_1(d_{12}^{-1} - d_1^{-1}) + X_2 \cdot M_2(d_{12}^{-1} - d_2^{-1}) \tag{9}$$

TABLE VIII   Parameters (a_j) and standard deviations, $\sigma(V_m^E)$, for least-squares representations by Eq. (10) of V_m^E for studied mixtures

Functions	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma(V_m^E)$	T [K]
V_m^E (ACN–i-BtOH)	− 15.7240	− 223.1700	− 47.7720	− 0.2185	− 1.6074	− 0.1806	$2.52 \cdot 10^{-3}$	298.15
V_m^E (ACN–t-BtOH)	148.5040	− 36.7440	− 33.8360	− 13.0676	15.0407	14.4930	$2.53 \cdot 10^{-3}$	303.15

where: M_1, d_1 and X_1 are the molar mass, density and molar fraction of ACN, respectively; M_2, d_2 and X_2 are the molar mass, density and molar fraction of i-BtOH or t-BtOH; and d_{12} is the density of the mixture.

The calculated V_m^E quantities were fitted by least-squares method to a smoothing equation due to Redlich–Kister [9];

$$V_m^E = X_1 X_2 \sum_{j=0}^{k} a_j (2X_2 - 1)^j \tag{11}$$

whose coefficients a_j, for $k = 5$, are listed in Table VIII with the standard deviations $\sigma(V_m^E)$ at 298.15 K. This function reproduces the V_m^E values with an average deviation $\overline{\Delta V_m^E} = \pm 0.038 \, \text{cm}^3 \, \text{mol}^{-1}$ for ACN–i-BtOH mixtures and $\overline{\Delta V_m^E} = \pm 0.045 \, \text{cm}^3 \, \text{mol}^{-1}$ for ACN–t-BtOH mixtures. The values of V_m^E for the systems investigated are presented graphically as a function of composition in Fig. 4.

It can be see from Fig. 4 that the variation of excess molar volumes of ACN–i-BtOH and ACN–t-BtOH liquid binary mixtures are poles apart.

In the case of ACN–i-BtOH binaries, the analysis of the course of changes of V_m^E as a function of the composition of the studied mixtures points to two characteristic composition regions of mixed solvent within which the appearance of strong intermolecular interactions may be expected (see Fig. 4).

The first of them corresponds to *ca.* $X_{\text{i−BtOH}} \approx 0.20$ molar fraction of i-BtOH. Within this region the maximum of V_m^E is observed. This volume behaviour is the result of several opposing effects accompanying the differences in the molecular size and the shape of the components, breaking of hydrogen bonds of the self-associated i-BtOH by the addition of ACN, and the complex, $4\text{ACN} \cdot \text{i-BtOH}$, formation between -OH group of i-BtOH and nitrogen (N≡) in acetonitrile. Since the alcohol structure has open cavities, the values of V_m^E should be positive [17,18].

The second characteristic composition region for mixtures of ACN with i-BtOH studied corresponds to *ca.* $X_{\text{i−BtOH}} \approx 0.80$. Additionally, the analysis of the course of studied excess function V_m^E indicates that this composition range corresponds to the most dense and packed mixed solvent. In cases where the excess volume changes sign, there is always a volume contraction in the alcohol-rich region [19]. These properties have been used as a qualitative as well as quantitative guide to the extent of complexing in analysing liquid binary mixtures [17–22]. Since both components of these binary mixtures have a considerable proton-donating and proton-accepting ability, appropriate negative contributions may be expected to originate in hydrogen bonding between i-BtOH and ACN molecules and from the stable $\text{ACN} \cdot 4\text{i-BtOH}$ adduct in this binary solvent system.

Another effect, which should give a negative contribution to the excess volume, is the difference in molecular size between the components in the mixture (this is a geometrical effect). As these differences increase, the more negative should be the contribution
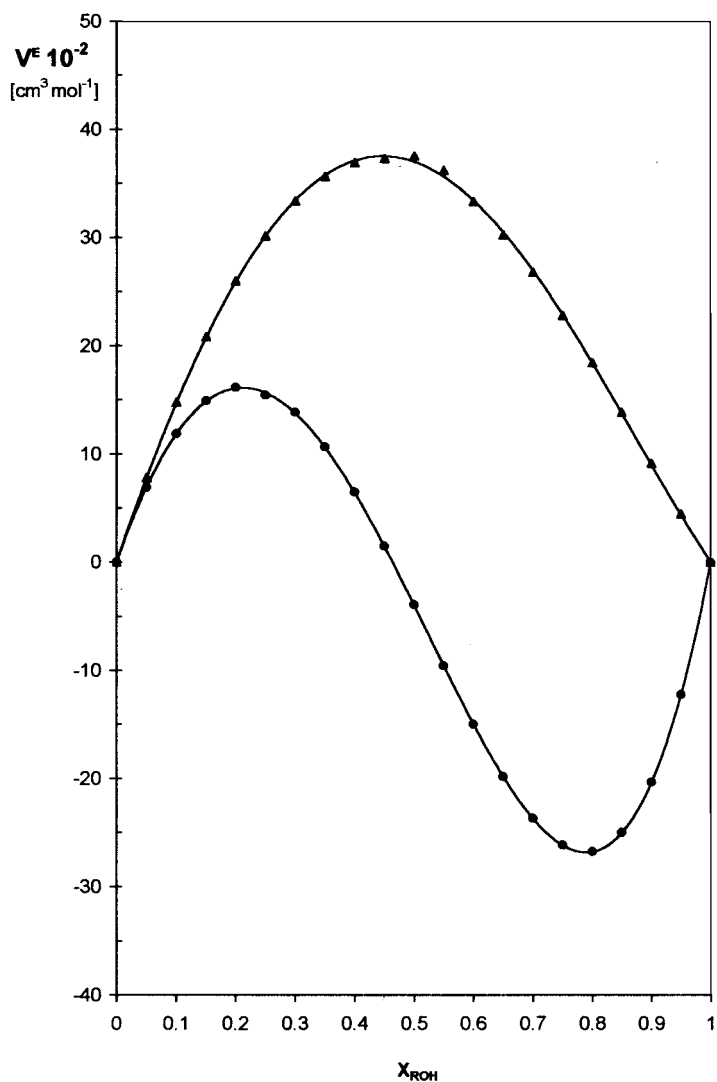
FIGURE 4   Changes in the excess molar volumes (V_m^E) for the liquid ACN–i-BtOH mixtures at 298.15 K (●) and for ACN–t-BtOH mixtures 303.15 K (▲).

to V_m^E. In the mixtures studied, the i-BtOH and ACN molecules have different molar volumes as pure species (molar volume: $V_{\text{i-BtOH}} = 92.91\,\text{cm}^3\,\text{mol}^{-1}$ and $V_{\text{ACN}} = 52.86\,\text{cm}^3\,\text{mol}^{-1}$), therefore this effect should be large and very important. The difference in the free volumes between i-BtOH and ACN could facilitate the penetration of one component (ACN) into the other (i-BtOH).

After these considerations, we may assume that in the ACN–i-BtOH liquid mixtures all the effects discussed above should be taken into account and may contribute to V_m^E values.

The analysis of changes of excess values of molar volume of liquid binary mixtures ACN–t-BtOH indicates that for the system studied only one characteristic composition

region is observed (see Fig. 3) from the point of view of changes of this function. This characteristic composition region for ACN–t-BtOH mixtures studied corresponds to *ca*. $X_{t-BtOH} \approx 0.50$. Within this region the maximum of V_m^E is observed. This effect, in reference to the internal structure of ACN and t-BtOH, should be interpreted in the analogous way as it has been done above while discussing the change of V_m^E for the composition range corresponding to *ca*. $X_{i-BtOH} \approx 0.20$ molar fraction of i-BtOH in the binary ACN–i-BtOH mixtures.

Different courses of analysed curves for various composition ranges of liquid mixtures studied observed by us are presumably associated with the size and shape of intermolecular complexes formed by ACN with alcohols studied which is a result of a different structure and H-donors properties of the alcohol molecules [23–27].

The conclusion to be drawn from all these results is that the molecules of these mixed solvents may be joined as dipolar and/or hydrogen bonds to form stable adducts of 4ACN · i-BtOH, ACN · 4i-BtOH and ACN · t-BtOH.

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