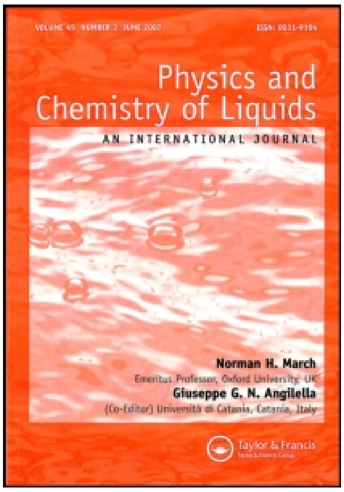

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PHYSICOCHEMICAL PROPERTIES OF ACETONITRILE–BUTAN-1-OL AND ACETONITRILE–BUTAN-2-OL MIXTURES

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The densities (d_{12}) and relative permittivities (ε_{12}) of liquid binary mixtures of acetonitrile–butan-1-ol and acetonitrile–butan-2-ol were measured at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K, as well as refractive indices (n_{12}^D) at 298.15 K and surface tensions (σ_{12}) at 293.15 K, 298.15 K and 303.15 K. From all these data, the molar volumes (V_m), apparent molar volumes ($V_{i,\phi}$), temperature coefficients of relative permittivities (α_{12}) and surface tensions (k) 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 butan-1-ol and butan-2-ol.

Keywords: Physicochemical properties; intermolecular interactions; internal structures

INTRODUCTION

Physicochemical and thermodynamic investigations play an important role in helping to understand the nature and extent of the patterns of molecular aggregation that exist in binary liquid mixtures

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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 acetonitrile), part of alcohol molecules will tend to dissociate from the polymeric aggregates through the hydrogen bond to form other kinds of hydrogen bonds with different kinds of molecules and the geometrical fitting of the second component into the remaining alcohol structure. On the other hand, there is possible a process of cooperative accommodation of the second component into the alcohol structure which is accompanied by an interstitial dissolution. As a rough first approximation, these may by the most decisive factors in determining the sign and magnitude of the deviation from the ideal solution law [1 – 5].

In this paper, our intention is to explore the dependence of the excess molar volume $\left(V_m^E\right)$, apparent molar volume $(V_{i,\phi})$, surface tensions and dielectric properties of liquid binary mixtures of acetonitrile (ACN) with butan-1-ol (BtOH) and butan-2-ol (BtOH-2) on variations in the molecular structures of the butanols. An attempt has been made to obtain information concerning the existence of ordered patterns of molecular aggregation.

EXPERIMENTAL

For the measurements of relative permittivities, densities, surface tensions and refractive indices chemical pure ACN (Fluka), BtOH (Fluka) and BtOH-2 (Fluka) were used. They were dried and purified according to known procedures [23]. The relative permittivities measurements were performed with an accuracy of ±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 $1 \cdot 10^{-5}\,\mathrm{g \cdot cm^{-3}}$. The surface tensions were measured by the maximum bubble pressure method with an accuracy of ±0.2%. The refractive index measurements for sodium light ($\lambda = 598.55\,\mathrm{nm}$) were performed using the Abbe refractometer. Each temperature was maintained constant with an accuracy of ±0.1 K. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

In this work, with the aim of analysing the intermolecular interactions between the components in the ACN–BtOH and ACN–BtOH-2 binary mixtures, we measured densities (d_{12}), relative permittivities (ε_{12}) at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K, surface tensions at 293.15 K, 298.15 K and 303.15 K and refractive indices at 298.15 K within the whole composition range of the binaries.

Volumetric Properties of the Acetonitrile–Butan-1-ol and Acetonitrile–Butan-2-ol Mixtures

From the measured densities (d_{12}) (see Tabs. I and II) the molar excess volumes $\left(V_m^E\right)$ of the mixtures, at the temperature $T = 298.15\,\mathrm{K}$, were fitted to the equation:

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

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

	d_{12} $[g \cdot cm^{-3}]$				
% mol. BtOH	288.15*K*	293.15*K*	298.15*K*	303.15*K*	308.15*K*
0	0.78724	0.78195	0.77664	0.77128	0.76591
5	0.78922	0.78394	0.77864	0.77328	0.76792
10	0.79120	0.78593	0.78062	0.77528	0.76989
15	0.79318	0.78791	0.78259	0.77729	0.77184
20	0.79513	0.78987	0.78454	0.77928	0.77376
25	0.79704	0.79180	0.78645	0.78125	0.77564
30	0.79891	0.79369	0.78833	0.78319	0.77749
35	0.80071	0.79552	0.79015	0.78509	0.77929
40	0.80245	0.79729	0.79191	0.78694	0.78106
45	0.80410	0.79898	0.79361	0.78873	0.78277
50	0.80566	0.80059	0.79524	0.79045	0.78444
55	0.80712	0.80210	0.79679	0.79209	0.78606
60	0.80845	0.80350	0.79824	0.79365	0.78763
65	0.80966	0.80478	0.79960	0.79510	0.78914
70	0.81072	0.80593	0.80085	0.79645	0.79059
75	0.81163	0.80694	0.80199	0.79768	0.79198
80	0.81237	0.80780	0.80300	0.79879	0.79330
85	0.81293	0.80849	0.80389	0.79975	0.79456
90	0.81330	0.80902	0.80463	0.80058	0.79575
95	0.81347	0.80935	0.80523	0.80124	0.79687
100	0.81343	0.80949	0.80568	0.80175	0.79791

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

	d_{12} [$g \cdot cm^{-3}$]				
% mol. BtOH-2	288.15 *K*	293.15 *K*	298.15 *K*	303.15 *K*	308.15 *K*
0	0.78724	0.78195	0.77664	0.77128	0.76591
5	0.78888	0.78328	0.77808	0.77279	0.76729
10	0.79031	0.78471	0.77952	0.77424	0.76876
15	0.79170	0.78611	0.78091	0.77568	0.77021
20	0.79305	0.78782	0.78228	0.77708	0.77165
25	0.79437	0.78878	0.78362	0.77847	0.77306
30	0.79566	0.79007	0.78493	0.77984	0.77446
35	0.79693	0.79133	0.78621	0.78119	0.77584
40	0.79818	0.79255	0.78748	0.78253	0.77721
45	0.79942	0.79375	0.78873	0.78368	0.77856
50	0.80055	0.79493	0.78975	0.78518	0.77990
55	0.80157	0.79608	0.79121	0.78648	0.78122
60	0.80260	0.79721	0.79244	0.78779	0.78253
65	0.80372	0.79832	0.79367	0.78909	0.78383
70	0.80466	0.79942	0.79491	0.79039	0.78511
75	0.80571	0.80050	0.79615	0.79169	0.78639
80	0.80657	0.80158	0.79740	0.79300	0.78765
85	0.80756	0.80264	0.79867	0.79431	0.78920
90	0.80867	0.80385	0.79996	0.79563	0.79074
95	0.80962	0.80505	0.80126	0.79696	0.79218
100	0.81038	0.80639	0.80226	0.79806	0.79369

where: M_1, d_1 and x_1 are the molar mass, density and mole fraction of ACN, respectively; M_2, d_2 and x_2 are the molar mass, density and mole fraction of BtOH and BtOH-2; and d_{12} is the density of the mixture. The values of V_m^E for the investigated systems are reported in Tables III and IV and are presented graphically as a function of composition in Figure 1.

The apparent molar volumes of the acetonitrtile ($V_{\phi,\mathrm{ACN}}$) and the butanols ($V_{\phi,\mathrm{BtOH}}$ or $V_{\phi,\mathrm{BtOH\text{-}2}}$) for the investigated systems were derived from the relations:

$$V_{\phi,\mathrm{ACN}} = \{M_{\mathrm{alcoh.}} \cdot x_{\mathrm{ACN}} \cdot (d_{\mathrm{alcoh.}} - d_{12})/x_{\mathrm{alcoh.}} \cdot d_{12} \cdot d_{\mathrm{alcoh.}}\} + \frac{M_{\mathrm{ACN}}}{d_{12}} \tag{2}$$

$$V_{\phi,\mathrm{alcoh.}} = \{M_{\mathrm{ACN}} \cdot x_{\mathrm{alcoh.}} \cdot (d_{\mathrm{ACN}} - d_{12})/x_{\mathrm{ACN}} \cdot d_{12} \cdot d_{\mathrm{ACN}}\} + \frac{M_{\mathrm{alcoh.}}}{d_{12}} \tag{3}$$

Values of these properties calculated from Eqs. (2) and (3) are given in Tables III and IV.

TABLE III Apparent molar volumes ($V_{i,\phi}$) and the deviations from ideality of molar volume (V^E_m) and density (d^E_{12}) for the liquid ACN–BtOH mixtures, at 298.15 K

% mol. BtOH	$V^0_{ACN,\phi}$ [$cm^3 \cdot mol^{-1}$]	$V^0_{BtOH,\phi}$ [$cm^3 \cdot mol^{-1}$]	$V^E_m \cdot 10^2$ [$cm^3 \cdot mol^{-1}$]	$d^E_{12} \cdot 10^4$ [$cm^3 \cdot mol^{-1}$]
0	52.856	–	0.00	0.00
5	52.889	92.623	3.09	–4.40
10	52.914	92.528	5.24	–7.21
15	52.933	92.437	6.50	–8.67
20	52.943	92.352	6.96	–9.02
25	52.946	92.272	6.73	–8.45
30	52.940	92.199	5.88	–7.18
35	52.926	92.132	4.52	–5.37
40	52.903	92.072	2.77	–3.20
45	52.870	92.019	0.72	–0.82
50	52.827	91.937	–1.48	1.62
55	52.774	91.935	–3.70	3.97
60	52.711	91.906	–5.81	6.08
65	52.637	91.884	–7.67	7.85
70	52.552	91.872	–9.13	9.12
75	52.455	91.868	–10.03	9.80
80	52.346	91.875	–10.20	9.74
85	52.225	91.891	–9.46	8.84
90	52.091	91.917	–7.64	6.99
95	51.943	91.954	–4.56	4.09
100	–	92.002	0.00	0.00

TABLE IV Apparent molar volumes ($V_{i,\phi}$) and the deviations from ideality of molar volume (V^E_m) and density (d^E_{12}) for the liquid ACN–BtOH-2 mixtures, at 298.15 K

% mol. BtOH-2	$V^0_{ACN,\phi}$ [$cm^3 \cdot mol^{-1}$]	$V^0_{BtOH\text{-}2,\phi}$ [$cm^3 \cdot mol^{-1}$]	$V^E_m \cdot 10^2$ [$cm^3 \cdot mol^{-1}$]	$d^E_{12} \cdot 10^4$ [$cm^3 \cdot mol^{-1}$]
0	52.856	–	0.00	0.00
5	52.909	93.409	5.08	–7.21
10	52.960	93.335	9.42	–12.93
15	53.012	93.280	13.31	–17.67
20	53.065	93.229	16.73	–21.53
25	53.118	93.181	19.68	–24.58
30	53.173	93.133	22.18	–26.90
35	53.228	93.085	24.20	–28.52
40	53.284	93.037	25.73	–29.50
45	53.342	92.988	26.76	–29.86
50	53.401	92.939	27.26	–29.64
55	53.460	92.888	27.20	–28.84
60	53.519	92.836	26.57	–27.48
65	53.579	92.783	25.32	–25.57
70	53.636	92.728	23.43	–23.11
75	53.689	92.672	20.85	–20.11
80	53.732	92.613	17.54	–16.55
85	53.753	92.552	13.47	–12.43
90	53.711	92.489	8.56	–7.74
95	53.414	92.423	2.79	–2.47
100	–	92.394	0.00	0.00

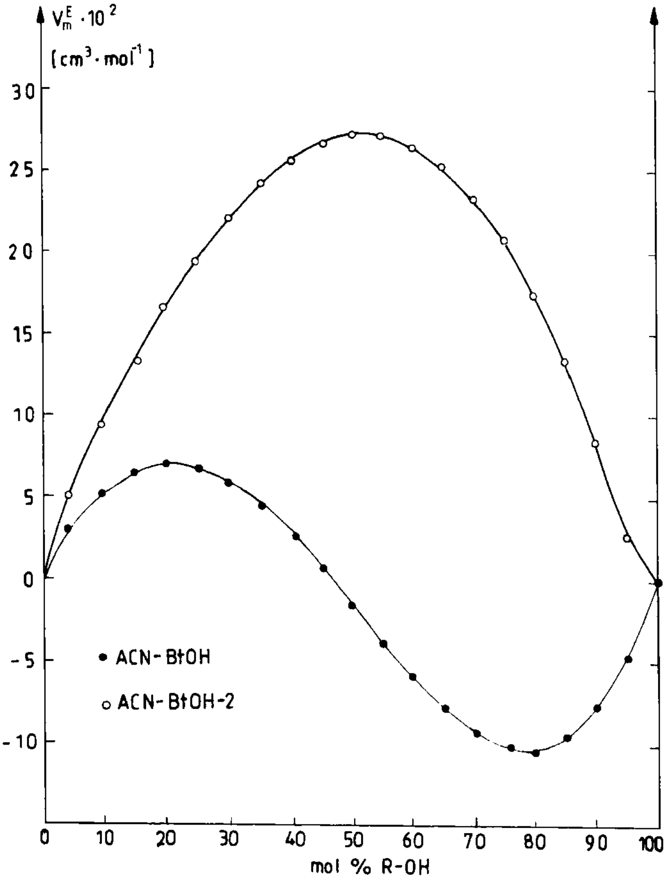

FIGURE 1 Changes in the excess molar volumes (V_m^E) for the liquid ACN-BtOH and ACN-BtOH-2 mixtures, at 298.15 K.

Additional information about intermolecular interactions in binary liquid mixtures are provided by the analysis of deviations from "ideality" of density (d_{12}). In this study, using experimental values of density at 298.15 K, the deviations from "ideality" of the function involved have been calculated from the following equation:

$$d_{12}^E = d_{12} - \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{x_1 \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{M_2}{d_2}} \tag{4}$$

where M is the molar weight.

Values calculated from the above equation over a range of the composition of ACN–alcohols mixtures are shown in Tables III and IV.

It can be seen from Figure 1 that the variation of excess molar volumes of ACN–BtOH and ACN–BtOH-2 binary liquid mixtures are to be poles asunder.

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

First of them corresponds to ca. 20 mol.% of BtOH. Within this region the maximum of V_m^E are linked with it the minimum of d_{12}^E (see Tab. III) are observed. These effects can be accounted for by the break-up of BtOH 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 [6, 7].

The second characteristic composition region for studied mixtures of ACN with BtOH corresponds to ca. 80 mol.% of BtOH. Additionally, the analysis of the courses of studied excess functions (V_m^E and d_{12}^E) indicates that this composition range corresponds to the most dense and packed mixed solvent. In the cases where the excess volume changes sign, there is always a volume contraction in alcohol-rich region [2]. These properties have been used as a qualitative as well as quantitative guide to extend of complexing in analysing binary liquid mixtures [6–10].

The analysis of changes of excess values of molar volume and density of liquid binary mixtures ACN–BtOH-2 indicates that for the studied system only one characteristic composition region is observed (see Fig. 1 and Tab. IV) from the point of view of changes of these functions. This characteristic composition region for studied mixtures ACN–BtOH-2 corresponds to ca. 50 mol.% of BtOH-2. Within this region the maximum of V_m^E and linked with it the minimum of d_{12}^E are observed. These effects, in reference to the internal structure of ACN and BtOH-2, should be interpreted in the analogous way as it has been done above while discussing changes of V_m^E and d_{12}^E for the composition range corresponding to ca. 20 mol.% of BtOH in the binary mixture ACN–BtOH.

Observed by us different courses of analysed curves for various composition ranges of studied liquid mixtures are presumably associated with a size and shape of formed intermolecular complexes by ACN with studied alcohols which is result of a different structure and H-donors properties of alcohols molecules [11–15].

The analysis of changes of obtained values of $V_{i,\phi}$ as a function of the composition for studied mixtures (see Tabs. III and IV) points at the existence of extremes at mentioned functions. However, the interpretation of these results from the point of view of intermolecular interactions is difficult. Values of these extremes are small and they exceed the measuring error only by an order of magnitude.

Dielectric and Surface Tension Properties of the Acetonitrile – Butan-1-ol and Acetonitrile – Butan-2-ol Mixtures

From the experimental values of relative permittivities (ε_{12}) (see Tabs. V and VI), the temperature coefficients of the relative permittivity,

TABLE V Relative permittivities (ε_{12}), temperature coefficients of the relative permittivity (α_{12}) and refractive indices (n^D_{12}) for the liquid ACN – BtOH mixtures

	ε_{12}						
% mol. BtOH	288.15 *K*	293.15 *K*	298.15 *K*	303.15 *K*	308.15 *K*	$\alpha_{12} \cdot 10^{-2}$ [*K*] 298.15 *K*	n^D_{12} 298.15 *K*
0	37.58	36.78	35.97	35.09	34.25	4.120	1.34162
5	35.44	34.70	33.94	33.11	32.29	4.840	1.34603
10	33.52	32.82	32.11	31.32	30.51	5.400	1.35030
15	31.80	31.14	30.45	29.69	28.92	5.806	1.35442
20	30.26	29.63	28.97	28.23	27.49	6.074	1.35839
25	28.89	28.29	27.65	26.91	26.21	6.157	1.36219
30	27.68	27.10	26.47	25.73	25.06	6.140	1.36584
35	26.61	26.04	25.42	24.67	24.05	6.071	1.36932
40	25.67	25.11	24.49	23.73	23.14	5.950	1.37262
45	24.84	24.28	23.66	22.89	22.34	5.782	1.37575
50	24.11	23.54	22.92	22.14	21.61	5.565	1.37871
55	23.46	22.89	22.26	21.46	20.97	5.318	1.38147
60	22.89	22.30	21.66	20.85	20.37	5.116	1.38405
65	22.37	21.76	21.11	20.30	19.83	5.018	1.38644
70	21.89	21.26	20.60	19.78	19.32	4.980	1.38862
75	21.44	20.79	20.12	19.30	18.82	4.987	1.39061
80	21.00	20.32	19.65	18.84	18.34	5.059	1.39239
85	20.56	19.85	19.17	18.38	17.84	5.309	1.39396
90	20.10	19.36	18.68	17.92	17.33	5.714	1.39532
95	19.62	18.85	18.16	17.44	16.78	6.240	1.39646
100	19.07	18.28	17.56	16.91	16.31	6.900	1.39737

TABLE VI Relative permittivities (ε_{12}), temperature coefficients of the relative permittivity (α_{12}) and refractive indices (n_{12}^{D}) for the liquid ACN – BtOH-2 mixtures

% *mol.*	ε_{12}					$\alpha_{12}\cdot 10^{-2}$ [*K*]	n_{12}^{D}
BtOH-2	288.15*K*	293.15*K*	298.15*K*	303.15*K*	308.15*K*	298.15*K*	298.15*K*
0	37.58	36.78	35.97	35.09	34.25	4.120	1.34163
5	35.53	34.77	34.01	33.16	32.36	4.651	1.34552
10	33.63	32.90	32.20	31.37	30.59	5.172	1.34921
15	31.86	31.16	30.50	29.70	28.95	5.660	1.35271
20	30.24	29.55	28.93	28.16	27.42	6.133	1.35604
25	28.74	28.05	27.47	26.73	26.01	6.611	1.35919
30	27.36	26.68	26.13	25.41	24.70	7.070	1.36220
35	26.11	25.42	24.89	24.19	23.49	7.482	1.36506
40	24.97	24.27	23.76	23.08	22.38	7.851	1.36780
45	23.94	23.22	22.72	22.07	21.37	8.203	1.37042
50	23.02	22.28	21.78	21.14	20.44	8.494	1.37294
55	22.20	21.43	20.93	20.31	19.59	8.661	1.37537
60	21.47	20.68	20.17	19.55	18.83	8.810	1.37773
65	20.83	20.02	19.48	18.86	18.13	8.951	1.38002
70	20.28	19.44	18.88	18.25	17.51	9.092	1.38226
75	19.80	18.95	18.34	17.71	16.94	9.201	1.38447
80	19.40	18.53	17.87	17.22	16.44	9.310	1.38665
85	19.07	18.18	17.46	16.79	15.99	9.423	1.38881
90	18.81	17.90	17.11	16.41	15.59	9.520	1.39098
95	18.60	17.69	16.82	16.07	15.24	9.611	1.39316
100	18.45	17.54	16.58	15.78	14.93	9.700	1.39537

denoted α_{12}, *viz.*:

$$\alpha_{12} = \frac{1}{\varepsilon_{12}}\cdot\left[\frac{d\varepsilon_{12}}{d(1/T)}\right] \tag{5}$$

at 298.15 K, were calculated (see Tabs. V and VI). 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 Räetzsch *et al.*'s thermodynamic consideration [16]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture.

In our studies on intermolecular interactions in liquid mixtures of ACN with both butanols we have carried out the analysis of changes of excess values of α_{12}^{E} as a function of the composition of the mixed solvent (see Fig. 2).

In the case of ACN – BtOH mixtures, we observed the tendency to achieve the maximum by the function α_{12}^{E} at ca. 80 mol.% of BtOH. This effect can be accounted by maximal intermolecular interactions between ACN and BtOH, which lead to the formation of stable

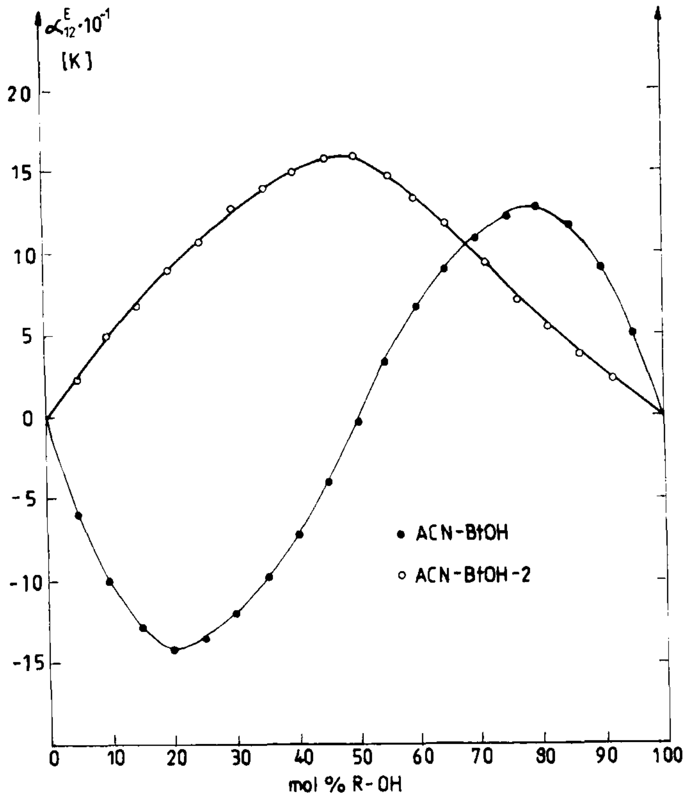

FIGURE 2 Changes in the excess temperature coefficient of relative permittivities (α^E_{12}) in the liquid ACN-BtOH and ACN-BtOH-2 mixtures, at 298.15 K.

intermolecular complexes [5, 16]. Further interesting result, for these mixtures, can be obtained by detailed analysis of the functions α^E_{12} = f(mol.% BtOH). This indicates that increasing addition of BtOH to ACN up to ca. 20 mol.% BtOH, where the minimum is reached, causes the rapid drop in α^E_{12}. Further addition of BtOH to the mixtures causes an increase in α^E_{12} which results in the maximum at ca. 80 mol.% BtOH. This effect can be accounted for by the break-up of BtOH structure and the geometrical fitting of ACN into the remaining alcohol structure. Whereas, further addition of BtOH, up to ca. 80 mol.% of BtOH, stabilizes the internal structure increasingly by complexing in the analysed binary liquid mixtures.

The course of changes of α_{12}^E as a function of the composition of the mixed solvent ACN – BtOH-2 may appear unexpected. This parameter achieves maximum for the composition range corresponding to ca. 50 mol.% of BtOH-2, which means for the same composition range where the maximum of V_m^E is observed (see Fig. 1). It is most likely linked with formation here of a "complex" of ACN · BtOH-2 which exists inspite of loosening of the internal structure of liquid ACN – BtOH-2 mixtures characterized by the highest stability in comparison with other possible intermolecular structures.

Presently, in purpose to gain further information regarding intermolecular interactions in liquid mixtures of ACN with BtOH and BtOH-2, we have applied measurements of temperature dependances of the surface tension (σ_{12}) of these systems (see Tabs. VII and VIII).

The analysis of changes of the surface tension and its temperature coefficients, denoted k [or more precisely its negative value, *viz.* $k = -(d\sigma_{12}/dT)$] within the whole compositions range enables the assessment of intermolecular interactions between components of binary

TABLE VII Surface tension (σ_{12}) for the liquid ACN – BtOH mixtures at 293.15 K, 298.15 K and 303.15 K

	$\sigma_{12} \cdot 10^3$ $[N \cdot m^{-1}]$		
% mol. BtOH	293.15 *K*	298.15 *K*	303.15 *K*
0	29.20	28.16	27.71
5	27.28	26.17	25.70
10	26.50	25.41	24.81
15	26.07	24.97	24.36
20	25.76	24.70	24.07
25	25.56	24.53	23.90
30	25.36	24.37	23.75
35	25.17	24.22	23.61
40	25.00	24.09	23.48
45	24.83	23.95	23.36
50	24.68	23.84	23.26
55	24.54	23.72	23.15
60	24.43	23.64	23.06
65	24.34	23.58	23.00
70	24.27	23.54	22.94
75	24.24	23.52	22.90
80	24.23	23.53	22.89
85	24.28	23.56	22.92
90	24.35	23.67	22.99
95	24.49	23.84	23.12
100	24.67	24.23	23.78

TABLE VIII Surface tension (σ_{12}) for the liquid ACN–BtOH-2 mixtures at 293.15 K, 298.15 K and 303.15 K

	$\sigma_{12} \cdot 10^3 [N \cdot m^{-1}]$		
% mol. BtOH-2	293.15 *K*	298.15 *K*	303.15 *K*
0	29.20	28.16	27.71
5	28.47	27.42	26.97
10	27.83	26.78	26.31
15	27.26	26.23	25.73
20	26.77	25.76	25.22
25	26.35	25.36	24.78
30	25.98	25.03	24.40
35	25.67	24.76	24.09
40	25.40	24.54	23.82
45	25.17	24.36	23.60
50	24.97	24.22	23.42
55	24.80	24.10	23.27
60	24.65	24.00	23.15
65	24.52	23.92	23.06
70	24.38	23.84	22.99
75	24.25	23.75	22.92
80	24.12	23.65	22.87
85	23.96	23.54	22.82
90	23.79	23.39	22.76
95	23.60	23.21	22.69
100	23.36	22.99	22.61

mixtures the more so as it has been shown by Landau [17] and Torianik [18] that the fluctuation of *k* values should be interpreted as changes of entropies of aggregates forming the free surface of the studied mixture.

The temperature coefficients of surface tension *k*, $T = 298.15\,\mathrm{K}$, are presented graphically as a function of ACN–BtOH and ACN–BtOH-2 composition in Figure 3. The course of their changes indicates that they achieve maximum values for the composition range corresponding to ca. 20 mol.% of BtOH and 50 mol.% of BtOH-2. It corresponds also to the maximum positive values of entropies of aggregates forming the free surface of studied mixtures. These results fully confirm earlier conclusions that in a case of composition ranges corresponding ca. 20 mol.% of BtOH and 50 mol.% of BtOH-2 in studied binary mixtures we deal with the most loose structure of mentioned systems.

It may be explained in the analogous way as previously by decomposition of long linear associates of BtOH and BtOH-2 by molecules of ACN and formation of intermolecular associates linked with each

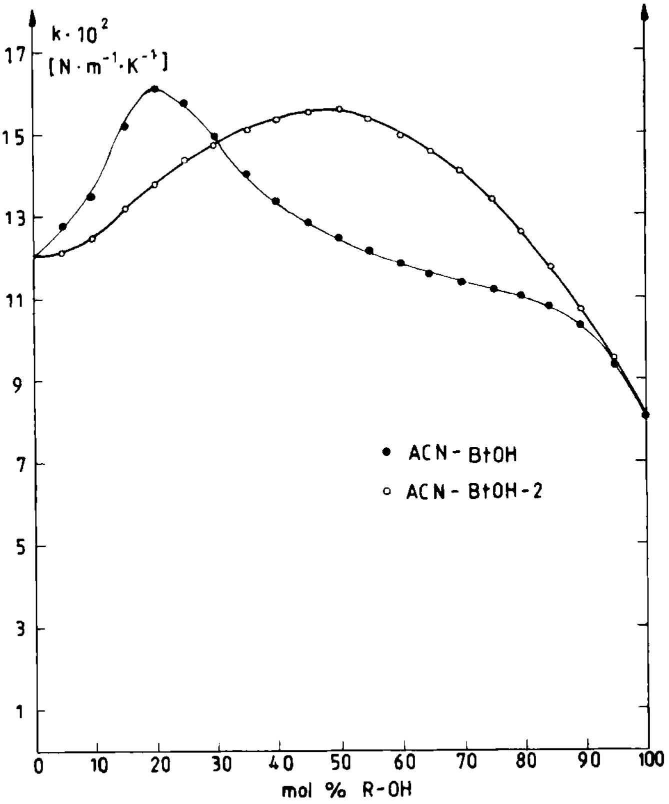

FIGURE 3 Changes in the temperature coefficient of surface tensions (k) in the liquid ACN - BtOH and ACN - BtOH-2 mixtures, at 298.15 K.

other in a loose way. Such structure is characterized by big number of free cavities which has been pointed out while analysing changes of V_m^E.

One of the tools for the investigation of molecular interactions in liquids is an analysis of the Kirkwood's correlation factor (g_K) [19]. Its values reflect mutual orientation of neighbouring molecular dipoles and they can inform about the possible kind of associates present in the solution [20]. According to Cole [20, 21], the Kirkwood's correlation factor for binary liquid mixtures can be calculated from the equation:

$$g_K = \left[9kT(M_1 \cdot x_1/d_1 + M_2 \cdot x_2/d_2)/4\Pi L(\mu_1^0 \cdot x_1 + \mu_2^0 \cdot x_2)^2\right] \cdot \left[(\varepsilon_{12} - \varepsilon_\infty)(2\varepsilon_{12} + \varepsilon_\infty)/\varepsilon_{12}(\varepsilon_\infty + 2)^2\right]$$

where: k and L are respectively Boltzmann's and Avogadro's constants; M_i, x_i, d_i and μ_i^0 represent respectively the molar mass, mole fraction, density and gas-phase dipole moment; $i = 1$ denotes acetonitrile, while $i = 2$ denotes BtOH or BtOH-2. T is temperature of the mixture, ε_{12} – relative permittivity of solution, while $\varepsilon_\infty = 1.1 \cdot n_D^2$ represent the mixture relative permittivity at high frequency [21].

From the experimental values of relative permittivity, refractive index (see Tabs. V and VI) and literature values of dipole moment of ACN, BtOH and BtOH-2 ($\mu_{ACN} = 3.37$ D, $\mu_{BtOH} = 1.70$ D and $\mu_{BtOH\text{-}2} = 1.64$ D [22]) the Kirkwood's correlation factors, at 298.15 K,

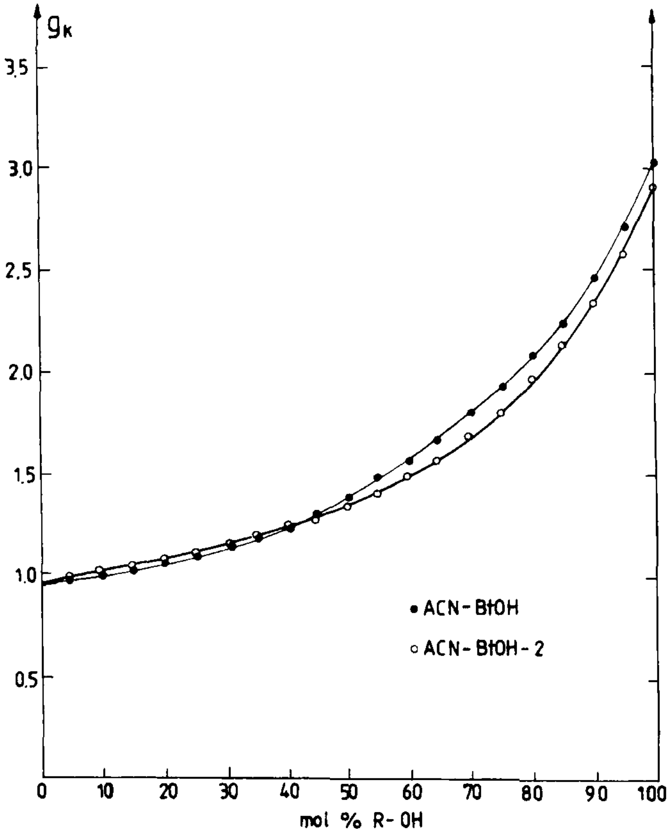

FIGURE 4 Changes in the Kirkwood's correlation factors (g_K) in the liquid ACN–BtOH and ACN–BtOH-2 mixtures, at 298.15 K.

were calculated. The g_K values for ACN–BtOH and ACN–BtOH-2 binary mixtures as a function of the mixture composition is presented in Figure 4.

The g_K values in all mixtures investigated here are following: $0.96 \leq g_K \leq 3.08$ for ACN–BtOH-2 mixtures and for ACN–BtOH $0.96 \leq g_K \leq 2.94$ –2, which suggests that the acetonitrile–alcohols open dimers and multimers exist in the systems.

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