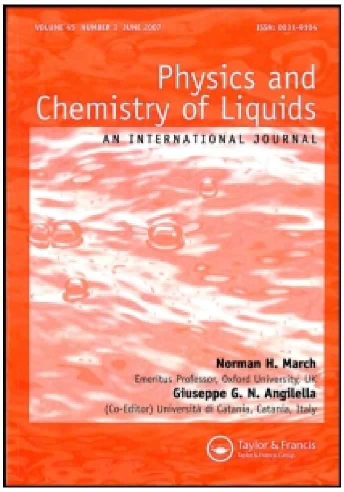

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2-Metoxyethanol-Acetonitrile Binary Mixtures and Their Physicochemical Properties

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2-METOXYETHANOL – ACETONITRILE BINARY MIXTURES AND THEIR PHYSICOCHEMICAL PROPERTIES

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Densities (d_{12}) and relative permittivities (ε_{12}) have been measured for 2-metoxyethanol (ME) and acetonitrile (ACN) binary liquid mixtures over their whole compositions ranges at various temperatures ranging from 288.15 K to 308.15 K. The experimental data were used to test some empirical equations of the type: $y_{12} = y_{12}(t)$ and $y_{12} = y_{12}(X_i)$ (where: $y_{12} - d_{12}$ or ε_{12}). From all these data, the excess molar volumes (V_m^E), temperature coefficients of relative permittivities (α_{12}) and the excess extrathermodynamic parameters ε^E were calculated. The ^{1}H-NMR spectra of liquid binary mixtures of ME and ACN, were recorded at 298 K over almost the whole range of the mixed solvent compositions. From these data the values of the values of the spectral structural parameters were found, $\Delta\delta$(ME – ACN). The values of these structural parameters are discussed in terms of interactions of 2-metoxyethanol with acetonitrile.

Keywords: Binary liquid mixtures; Physicochemical properties; Intermolecular interactions

INTRODUCTION

Systematic investigations of intermolecular interactions and the internal structures of mixed binary liquid mixtures continues to be an area of interest in physical chemistry. Regarding structural studies,

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review of the literature shows that for the analysis of this type of effect in liquid solvent mixtures it is possible to apply a wide range of spectral methods, thermochemical methods, as well as studies on intensive macroscopic properties of solutions (such as density, viscosity, relative permittivity, surface tension, *etc.*) carried out at different temperatures.

Many physicochemical methods may be used to study these specific interactions in solution. However, it is noteworthy that no method can give, alone, a complete understanding of the nature of intermolecular behaviour. The main problem, generally encountered in such studies, is to correlate the thermodynamic properties of the solutes with the physicochemical properties of the corresponding reaction media [1–3].

In this paper, we have investigated the mutual intermolecular interactions in the liquid binary mixtures of 2-metoxyethanol (ME) with acetonitrile (ACN), based on the correlation existing between the ^{1}H-NMR spectral results and measured densities and relative permittivities over a wide temperature range and over the whole composition range, expressed as the mole fraction of ME.

Acetonitrile is a typical example of an aprotic solvent. It exhibits a stronger tendency toward solvation of metallic ions and acceptor molecules in comparison to other solvents with higher donor number (DN) values. 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 a pseudoligand when complexes of acetonitrile are formed [4]. The screenings as well as the charge effects are assigned to this pair [5–7]. The basicity of ACN differs by 5 orders of magnitude from that shown by water [5]. Additionally the presence of proton clathrate was confirmed in pure ACN on the basis of spectroscopic studies [8].

$$\mathrm{CH_3CN}\cdots\mathrm{CH_3CN^{(+)}}\cdots(\mathrm{CH_3CN})_n \xrightarrow{\substack{\text{transfer of}\\ \text{proton}}} \mathrm{CH_3CNH^{(+)}}\cdots(\mathrm{CH_3CN})_n+\mathrm{CH_2CN^{(-)}}$$
$$\Delta\mathrm{H}^{\ominus}=-2.64\ \mathrm{eV}$$

Dielectric and structural results for liquid acetonitrile were reported by Krienke *et al.* [9]. The calculations of the liquid structure were performed using the hypernetted – chain approximation, in which the solvent polarizability was treated, at the self-consistent mean-field level.

Compounds with the general formula $C_mH_{2m.+1}(OCH_2CH_2)_nOH$ have drawn much attention in recent years as the solvent mediums for electrochemical investigations, electroanalytical studies as well as for various industrial processes (galvano-technique, polymers solvents, *etc.*). 2-metoxyethanol (ME) is an ether alcohol showing physicochemical characteristics that are intermediate between protic and dipolar aprotic solvents [10–14]. The molecules of ME contain both hydroxylic and ether groups and in their pure state, they are self – associated and form cyclic dimers in which the hydroxy proton of one ME molecule is bound to the ether oxygen atom of the other [15–17]. They can also form intermolecularly hydrogen-bonded five membered ring monomers [17–19].

Taking into account the published data concerning the structure of liquid ME and ACN and our results on mixtures of ACN with water and different alcohols it seemed appropriate to extend these structural studies to ME–ACN binary liquid mixtures [20–22].

EXPERIMENTAL

Reagents

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities and densities the solvents ACN and ME high-purity-grade (containing water $<0.02\%$ and $<0.05\%$) from Fluka were used. ACN was dried and purified according to known procedures [23]. 2-metoxyethanol was distilled twice in an all-glass distillation set before use and the middle fraction was collected. The purified ME had a density of $0.96029\,\mathrm{g\,cm^{-3}}$ and a specific conductance of ca. $0.85\cdot 10^{-6}\,\mathrm{S\,cm^{-1}}$ at 298.15 K. These values are in good agreement with the literature values [23, 24].

Apparatus and Procedures

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 ME were measured with an accuracy of ca. ±0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were carried out at 3 MHz, with an accuracy of ±0.1%, using a bridge of the type OH-301 (made in Radelcis, Hungary). The thermostatic stainless steel measuring cells were of C3 ($10 < \varepsilon < 25$) and C4 ($25 < \varepsilon < 100$) type. The sample cells are of the covered coaxial capacitor type with vacuum capacitances of 2.5 pF (C3) and 0.5 pF (C4). The cells were calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane (C3); methanol, ethanol and deionized water (C4). With the exception of the deionized water, all these solvent were of spectrograde quality or higher. The relative permittivity for the standards were taken from literature [24]. Solvent densities were measured, using a glass Lipkin pycnometer of ca. 90 $\mathrm{cm^3}$. The maximum error in the density measurements was $4 \cdot 10^{-5}\,\mathrm{g\,cm^{-3}}$. Each temperature was maintained with an accuracy of ±0.01 K. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

Volumetric Properties of the 2-Metoxyethanol – Acetonitrile Binary Liquid Mixtures

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

The first step of this study involves investigation of the dependence of density (d_{12}) on temperature, and the following relationship was used [24]:

$$d_{12}(t) = \sum_{0}^{i} \alpha_i T^i \tag{1}$$

where T – temperature in K.

The polynomial coefficients α_i, for $i = 2$, are summarized in Table III together with standard deviations [$\sigma(d_{12})$] for each mixture. Equation (1) reproduces the experimental ε_{12} values with an average uncertainty, evaluated by means of the relation:

$$\overline{\Delta d}_{12} = \frac{1}{N} \sum_{N} |d_{12}^{\mathrm{calc}} - d_{12}^{\mathrm{exp}}| \tag{2}$$

where N – number of experimental points.

TABLE I Relative permittivities (ε_{12}) for the liquid ME–ACN mixtures at 291.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

	ε_{12}				
X_{ME}	291.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.0000	37.04	36.78	35.97	35.09	34.25
0.0506	35.84	35.61	34.86	34.04	33.24
0.0992	34.80	34.58	33.86	33.06	32.29
0.1522	33.60	33.40	32.74	32.00	31.26
0.2025	32.47	32.32	31.71	30.99	30.28
0.2472	31.51	31.40	30.80	30.12	29.43
0.3054	30.27	30.19	29.64	28.96	28.32
0.3490	29.39	29.31	28.77	28.12	27.52
0.3964	28.43	28.35	27.82	27.21	26.64
0.4553	27.25	27.19	26.68	26.10	25.55
0.5008	26.34	26.29	25.80	25.25	24.73
0.5531	25.34	25.30	24.83	24.29	23.79
0.5995	24.45	24.43	23.98	23.45	22.97
0.6500	23.51	23.49	23.06	22.56	22.11
0.6972	22.69	22.67	22.24	21.75	21.30
0.7534	21.68	21.66	21.26	20.80	20.35
0.7998	20.88	20.85	20.44	19.99	19.56
0.8451	20.16	20.09	19.67	19.24	18.79
0.9024	19.16	19.06	18.66	18.27	17.85
0.9459	18.42	18.35	17.92	17.51	17.10
1.0000	17.46	17.38	16.95	16.56	16.16

TABLE II Relative ^{1}H-NMR chemical shifts, δ(ME–ACN), measured at 298 K and densities (d_{12}), measured at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

	d_{12} [$g\ cm^{-3}$]					$\delta(ME-ACN)$ [Hz]
X_{ME}	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	298 K
0.0000	0.78726	0.78197	0.77662	0.77130	0.76589	–
0.0102	–	–	–	–	–	66.0
0.0506	0.80184	0.79661	0.79132	0.78604	0.78078	70.5
0.0992	0.81496	0.80983	0.80456	0.79938	0.79422	75.0
0.1522	0.82915	0.82413	0.81900	0.81387	0.80876	80.0
0.2025	0.84044	0.83554	0.83053	0.82542	0.82035	85.0
0.2472	0.85060	0.84579	0.84088	0.83580	0.83074	90.0
0.3054	0.86316	0.85844	0.85365	0.84862	0.84356	96.0
0.3490	0.87212	0.86745	0.86272	0.85773	0.85268	101.5
0.3964	0.88145	0.87682	0.87214	0.86721	0.86215	108.0
0.4553	0.89066	0.88606	0.88142	0.87655	0.87151	113.5
0.5008	0.90063	0.89603	0.89142	0.88663	0.88162	118.5
0.5531	0.90956	0.90498	0.90039	0.89567	0.89071	122.0
0.5995	0.91713	0.91257	0.90799	0.90332	0.89842	125.0
0.6500	0.92498	0.92046	0.91590	0.91130	0.90645	128.0
0.6972	0.93196	0.92750	0.92298	0.91840	0.91363	130.5
0.7534	0.93983	0.93545	0.93099	0.92643	0.92175	134.0
0.7998	0.94597	0.94168	0.93727	0.93269	0.92809	137.0
0.8451	0.95166	0.94745	0.94308	0.93850	0.93394	140.5
0.9024	0.95846	0.95432	0.94997	0.94537	0.94086	143.0
0.9459	0.96334	0.95919	0.95481	0.95031	0.94569	146.0
0.9903	–	–	–	–	–	148.0
1.0000	0.96925	0.96488	0.96029	0.95576	0.95110	–

TABLE III Coefficients α_i and standard deviations $\sigma(d_{12})$ of Eq. (1) for ME–ACN binary mixtures

X_{ME}	$\alpha_2 \cdot 10^6$	$\alpha_1 \cdot 10^4$	$\alpha_0 \cdot 10^1$	$\sigma(d_{12})$
0.0000	−0.60000	−10.38200	8.02968	$1.6 \cdot 10^{-5}$
0.0506	0.14285	−10.46660	8.17581	$1.4 \cdot 10^{-5}$
0.0992	0.08571	10.4289	8.30604	$3.2 \cdot 10^{-5}$
0.1552	−0.51428	−9.95086	8.44206	$2.0 \cdot 10^{-5}$
0.2025	−1.25714	−9.43143	8.54883	$2.5 \cdot 10^{-5}$
0.2472	−1.91429	−8.98486	8.64516	$2.2 \cdot 10^{-5}$
0.3054	−2.62857	−8.48971	8.76485	$2.2 \cdot 10^{-5}$
0.3490	−2.91429	−8.26286	8.85164	$2.5 \cdot 10^{-5}$
0.3964	−3.17143	−8.05629	8.94235	$2.4 \cdot 10^{-5}$
0.4453	−3.17143	−7.97629	9.03321	$2.5 \cdot 10^{-5}$
0.5008	−2.85714	−8.05543	9.13333	$3.3 \cdot 10^{-5}$
0.5531	−2.54286	−8.13057	9.22305	$3.8 \cdot 10^{-5}$
0.5995	−2.20000	−8.23400	9.92995	$4.5 \cdot 10^{-5}$
0.6500	−2.00000	−8.24400	9.37778	$3.4 \cdot 10^{-5}$
0.6972	−1.94286	−8.18057	9.44657	$2.2 \cdot 10^{-5}$
0.7534	−2.00000	−8.03600	9.52330	$1.0 \cdot 10^{-5}$
0.7998	−2.25714	−7.82143	9.58217	$1.9 \cdot 10^{-5}$
0.8451	−2.60000	−7.57800	9.63626	$3.1 \cdot 10^{-5}$
0.9024	−2.82857	−7.41571	9.70245	$5.2 \cdot 10^{-5}$
0.9459	−3.02857	−7.32171	9.75017	$2.0 \cdot 10^{-5}$
1.0000	−1.48571	−8.34114	9.82112	$3.0 \cdot 10^{-5}$

The value of $\overline{\Delta d}_{12}$ is equal to $\pm 0.00005\,\mathrm{g\,cm^{-3}}$ over the set of the experimental d_{12} values (see Tab. II).

The second step, of this study, involves investigation of the dependence of density (d_{12}) on mole fraction (X_1) of ME, and the following relationship was used [24]:

$$d_{12}(X_1) = \sum_{0}^{i} \beta_j X_1^j \tag{3}$$

The values of β_j coefficients, for $j = 4$, are listed in Table IV together with the standard deviations, at each investigated temperature.

TABLE IV Coefficients β_j and standard deviations $\sigma(d_{12})$ of Eq. (3) for ME–ACN binary mixtures

T [K]	$\beta_4 \cdot 10^2$	$\beta_3 \cdot 10$	$\beta_2 \cdot 10$	$\beta_1 \cdot 10$	$\beta_0 \cdot 10$	$\sigma(d_{12})$
288.15 K	−3.0029	0.8980	−1.7118	2.9313	7.8738	$8.5 \cdot 10^{-5}$
293.15 K	−3.1949	0.9574	−1.7440	2.9651	7.8202	$6.0 \cdot 10^{-5}$
298.15 K	−3.8443	1.0725	−1.8481	2.9976	7.7659	$3.3 \cdot 10^{-5}$
303.15 K	−3.8209	1.0555	−1.8321	3.0037	7.7130	$2.0 \cdot 10^{-5}$
308.15 K	−5.0651	1.3032	−1.9874	3.0432	7.6588	$1.4 \cdot 10^{-5}$

Equation (3) reproduces the experimental data of d_{12} (see Tab. II) with $\overline{\Delta d_{12}} = \pm 0.00007\,\mathrm{g\,cm^{-3}}$.

From the measured densities (d_{12}) (see Tab. I) the molar excess mixing volumes (V_m^E) of the mixtures, at each investigated temperature, were fitted in the equation [22]:

$$V_m^E = X_1 \cdot M_1(d_{12}^{-1} - d_1^{-1}) + X_2 \cdot M_2(d_{12}^{-1} - d_2^{-1}) \tag{4}$$

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

The molar excess mixing volumes (V_m^E) values have been fitted in a Redlich–Kister equation of the type [25]:

$$V_m^E = X_1 X_2 \sum_{j=0}^{k} a_j (2X_2 - 1)^j \tag{5}$$

where X_i – mole fraction.

The parameters a_j of Eq. (5) were evaluated by the method of least squares with points weighted and they are listed in Table V along with standard deviations $\sigma(V_m^E)$. The results of calculations for the investigated systems are presented graphically as a function of mole fraction of ME (X_1) in Figure 1.

As we can see, V_m^E is always negative at all the temperatures investigated and for the whole composition range and it has an absolute minimum at $X_{\mathrm{ME}} = 0.5$ (this composition range corresponds to the most dense and packed mixed solvent). These properties have been used as a qualitative as well as quantitative guide to the extent of complexing in analysing binary liquid mixtures [26–31].

TABLE V Parameters (a_j) and standard deviations $\sigma(V_m^E)$ for least squares representations by Eq. (5) of V_m^E for ME–ACN mixtures at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

T [K]	α_0	α_1	α_2	α_3	α_4	$\sigma(V_m^E)$
288.15	−1.1189	−0.2183	−0.4217	0.4425	0.1965	0.001
293.15	−1.1952	−0.0925	−0.5091	0.00143	0.0787	0.003
298.15	−1.3256	−0.0700	−0.5218	−0.2283	0.0376	0.003
303.15	−1.3888	−0.1278	−0.4546	−0.1437	−0.1400	0.002
308.15	−1.4170	−0.1108	−0.7516	−0.2108	−0.0418	0.001

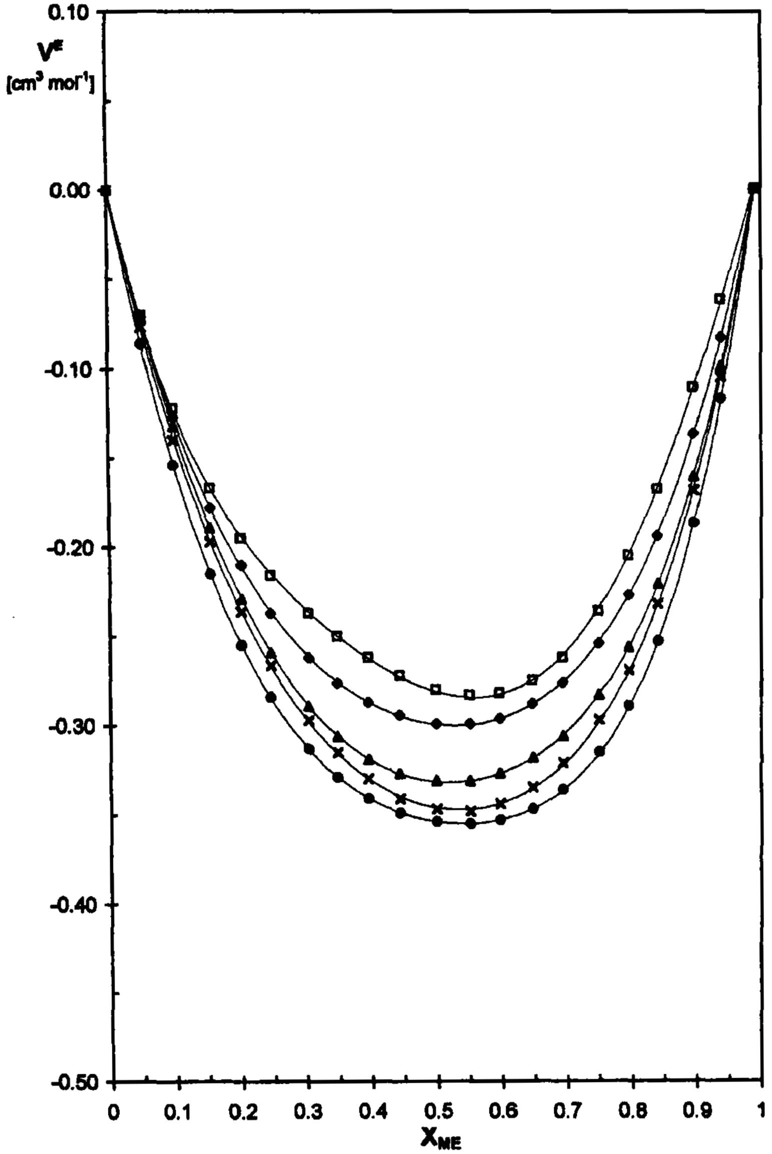

FIGURE 1 Changes in the excess molar volumes (V_m^E) for the liquid ME–ACN mixtures, at 288.15 K (□), 293.15 K (◆), 298.15 K (▲), 303.15 K (×) and 308.15 K (•).

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 2-metoxyethanol and acetonitrile molecules and formed the stable ME·ACN 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 geometrical effect). As these differences increase the more negative should be the contribution to V_m^E. In these mixtures, the ME and ACN molecules have different molar volumes as pure species (molar volume: $V_{ME} = 79.25\,\mathrm{cm^3\,mol^{-1}}$ and $V_{ACN} = 52.86\,\mathrm{cm^3\,mol^{-1}}$), therefore this effect should be large and very important. The difference in the free volumes between ME and ACN could facilitate the penetration of one component (ACN) into the other (ME).

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

^{1}H-NMR Spectroscopic and Dielectric Properties of the 2-Metoxyethanol–Acetonitrile Mixtures

The relative permittivities data obtained from the measurements of the pure solvents and for binary mixtures at all the investigated temperatures are summarized in Table I.

In this paper, our investigations of dielectric behaviours as a function of temperature are given by the Eq. (5) [32]:

$$\ln\varepsilon_{12} = \alpha_0 + \alpha_1 T \tag{6}$$

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

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

Equation (6) reproduces the experimental ε_{12} values with an average uncertainty, evaluated by means of the relation (7):

$$\overline{\Delta\varepsilon}_{12} = \frac{1}{N}\sum_N |\varepsilon_{12}^{\mathrm{calc}} - \varepsilon_{12}^{\mathrm{exp}}| \tag{7}$$

where N is the number of experimental points, $\overline{\Delta\varepsilon}_{12} = \pm\ 0.04$ units of over relative permittivity values (see Tab. VI).

TABLE VI Coefficients α_i and standard deviations $\sigma(\ln\varepsilon_{12})$ of Eq. (6) for ME–ACN binary mixtures

X_{ME}	$\alpha_1 \cdot 10^3$	α_0	$\sigma(ln\varepsilon_{12})$
0.0000	−4.6497	4.9673	$1.2 \cdot 10^{-3}$
0.0506	−4.4724	4.8830	$1.4 \cdot 10^{-3}$
0.0992	−4.4493	4.8469	$1.4 \cdot 10^{-3}$
0.1522	−4.2818	4.7631	$1.6 \cdot 10^{-3}$
0.2025	−4.1661	4.6960	$2.2 \cdot 10^{-3}$
0.2472	−4.0933	4.6452	$2.4 \cdot 10^{-3}$
0.3054	−4.0220	4.5848	$2.8 \cdot 10^{-3}$
0.3490	−3.9771	4.5420	$2.6 \cdot 10^{-3}$
0.3964	−3.9327	4.4956	$2.4 \cdot 10^{-3}$
0.4553	−3.9056	4.4457	$2.6 \cdot 10^{-3}$
0.5008	−3.8323	4.3904	$2.6 \cdot 10^{-3}$
0.5531	−3.8463	4.3560	$2.7 \cdot 10^{-3}$
0.5995	−3.8258	4.3147	$3.0 \cdot 10^{-3}$
0.6500	−3.7639	4.2573	$2.9 \cdot 10^{-3}$
0.6972	−3.8712	4.2531	$2.9 \cdot 10^{-3}$
0.7534	−3.8568	4.2036	$3.1 \cdot 10^{-3}$
0.7998	−3.9789	4.2012	$2.8 \cdot 10^{-3}$
0.8451	−4.2233	4.2364	$2.2 \cdot 10^{-3}$
0.9024	−4.2080	4.1800	$1.5 \cdot 10^{-3}$
0.9459	−4.4832	4.2215	$2.0 \cdot 10^{-3}$
1.0000	−4.6483	4.2157	$1.7 \cdot 10^{-3}$

The variation of relative permittivity with binary composition was analyzed by using the following equation [32]:

$$\ln\varepsilon_{12} = \sum_{0}^{J} \beta_j X_1^j \tag{8}$$

which could be fitted to the experimental data at each temperature using a least-squares method. The values of β_j coefficients, for $j = 2$, and the standard deviations $\sigma(\ln\varepsilon_{12})$ are summarized in Table VII. Equation (7) reproduces the experimental data of ε_{12} (see Tab. I) with $\overline{\Delta\varepsilon_{12}} = \pm\ 0.04$ units.

TABLE VII Coefficients β_j and standard deviations $\sigma(\ln\varepsilon_{12})$ of Eq. (8) for ME–ACN binary mixtures

T [K]	$\alpha_2 \cdot 10^{-1}$	$\alpha_1 \cdot 10^{-1}$	α_0	$\sigma(ln\varepsilon_{12})$
291.15 K	−1.37543	−6.06300	3.60997	$2.0 \cdot 10^{-3}$
293.15 K	−1.56713	−5.83920	3.60200	$2.2 \cdot 10^{-3}$
298.15 K	−1.76824	−5.65442	3.57957	$2.5 \cdot 10^{-3}$
303.15 K	−1.83431	−5.57251	3.55512	$2.6 \cdot 10^{-3}$
308.15 K	−1.97944	−5.42070	3.53012	$2.7 \cdot 10^{-3}$

In our studies on intermolecular interactions in liquid mixtures of ME with ACN 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 solvent. 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 behaviour of a non-interacting "ideal" system should correspond to very weak complexes.

The values of ε_{12}^E have been evaluated by means of the equation [22, 33]:

$$\varepsilon_{12}^E = \varepsilon_{12} - (\varepsilon_1 X_1 + \varepsilon_2 X_2) \tag{9}$$

The values of ε_{12}^E have been fitted in a Redlich–Kister equation of the type [25]:

$$\varepsilon_{12}^E = X_1 X_2 \sum_{j=0}^{k} a_j (2X_2 - 1)^j \tag{10}$$

where X_i – molar fraction.

The parameters a_j of Eq. (10) were evaluated by the method of least squares with weighted points and they are listed in Table VIII along with standard deviations $\sigma(\varepsilon^E)$ [25]. The results of ε_{12}^E calculations for the investigated systems are presented graphically as a function of mole fraction of ME (X_1) in Figure 2.

As we can see, the excess of this extra-thermodynamic parameter (ε_{12}^E) is always negative over the whole composition range. In Figure 2, the excess relative permittivity is plotted against the ME mole fraction (X_1). As a major feature, this plot show a minimum centred at $X_1 = 0.5$ at all investigated temperatures.

TABLE VIII Parameters (a_j) and standard deviations $\sigma(\varepsilon_{12}^E)$ for least squares representations by Eq. (10) of ε_{12}^E for ME–ACN mixtures at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

T [K]	α_0	α_1	α_2	α_3	α_4	$\sigma(\varepsilon_{12}^E)$
291.15	−3.55630	0.20070	0.18978	0.85030	0.88440	0.022
293.15	−3.06510	0.24420	0.67969	0.86140	−0.27060	0.016
298.15	−2.54240	0.15640	1.20449	0.82540	−0.84720	0.010
303.15	−2.24350	0.09230	1.04889	0.79740	−0.2386	0.007
308.15	−1.83420	0.25890	0.53478	0.44330	0.16780	0.006

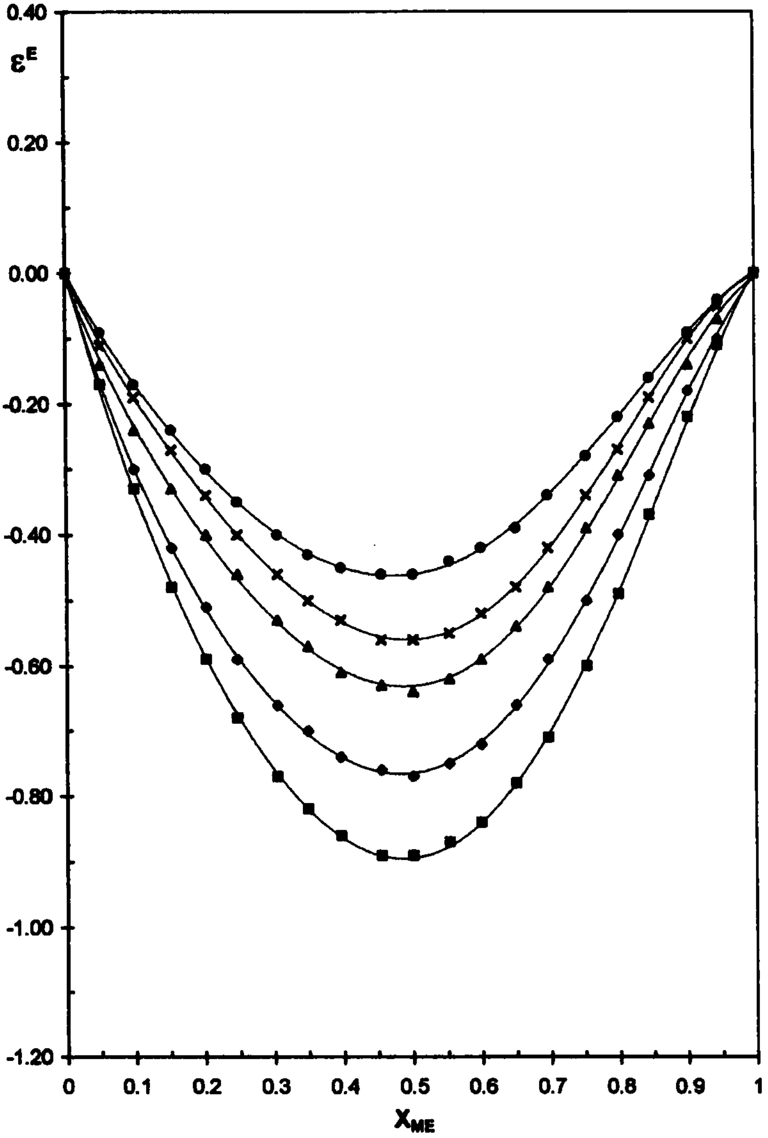

FIGURE 2 Changes in the deviations from "ideality" values of relative permittivity for the liquid ME–ACN mixtures, at 291.15 K (■), 293.15 K (◆), 298.15 K (▲), 303.15 K (×) and 308.15 K (●).

It have been pointed out in the literature [34, 35] and our previous papers [20–22] that the small negative ε^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.

In our opinion, for ME–ACN mixtures, appropriate negative contributions may be expected to originate in hydrogen bonding between 2-metoxyethanol and acetonitrile molecules and formation of the stable ME·ACN adduct in this binary solvent system. In the case examined here, evidence for the existence of a complex with the stoichiometry ME : ACN = 1 : 1 has been obtained at all the investigated temperatures.

Furthermore, the sign and the magnitude of the quantity ε_{12}^E should help in establishing the nature and relative strength of specific interactions between unlike molecules. Thus, attractive forces such as hydrogen bonds and dipole–dipole interactions are related to negative ε_{12}^E quantities, and confirm the present findings.

These results fully confirm the conclusions regarding structural aspects derived from densimetric measurements.

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

$$\alpha_{12} = \frac{1}{\varepsilon_{12}} \cdot \left[\frac{d\varepsilon_{12}}{d(1/T)}\right] \tag{11}$$

at 298.15 K, were calculated (see Fig. 3).

The composition range of liquid binary mixtures within which α_{12} or its excess (α_{12}^E) attain their highest values (minimum or maximum) should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic consideration [35]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture.

In the case of ME–ACN mixtures, we observed the tendency to achieve the minimum by the function α_{12} at ca. $X_{\mathrm{ME}} = 0.55$. This effect can be accounted for by maximal intermolecular interactions between ACN and ME molecules, which lead to the formation of stable ME·ACN intermolecular complex [34, 36, 37].

We also measured the values of chemical shift differences δ(ME–ACN) at 298 K, between the centre of ^{1}H-NMR signals of the —OH group of ME 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.*,

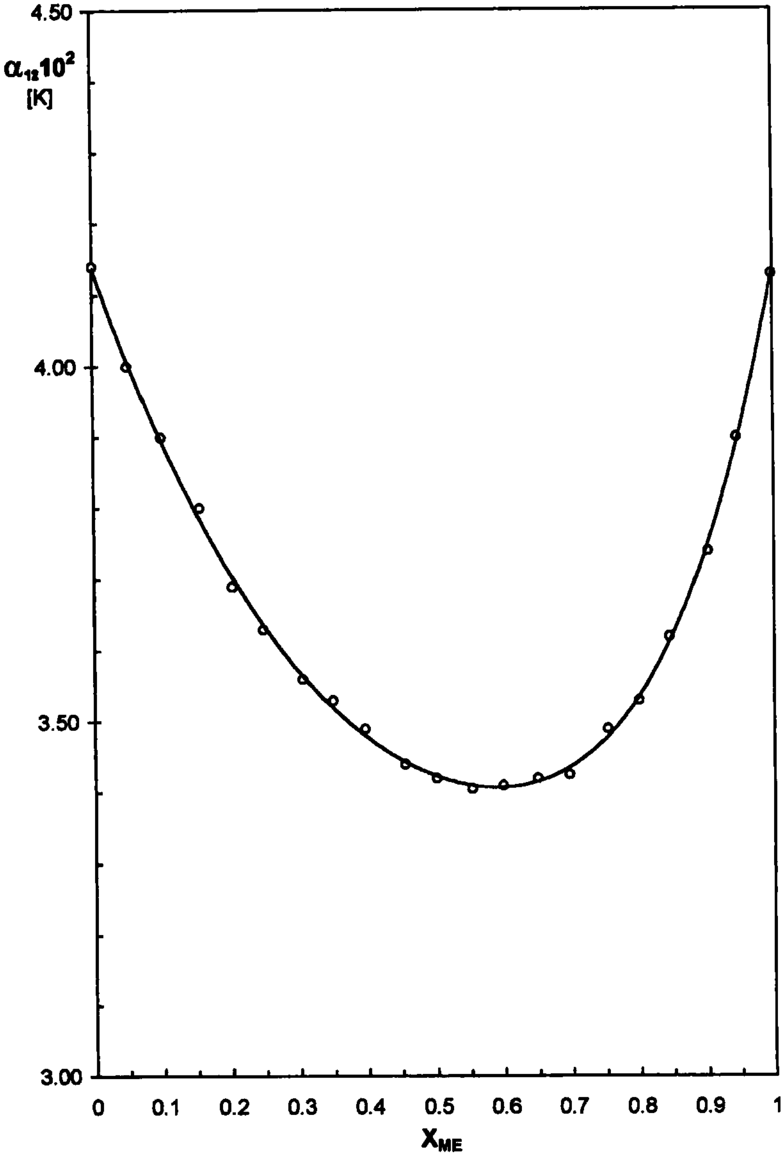

FIGURE 3 Changes in the temperature coefficient of the relative permittivity in the liquid ME–ACN mixtures, at 298.15 K.

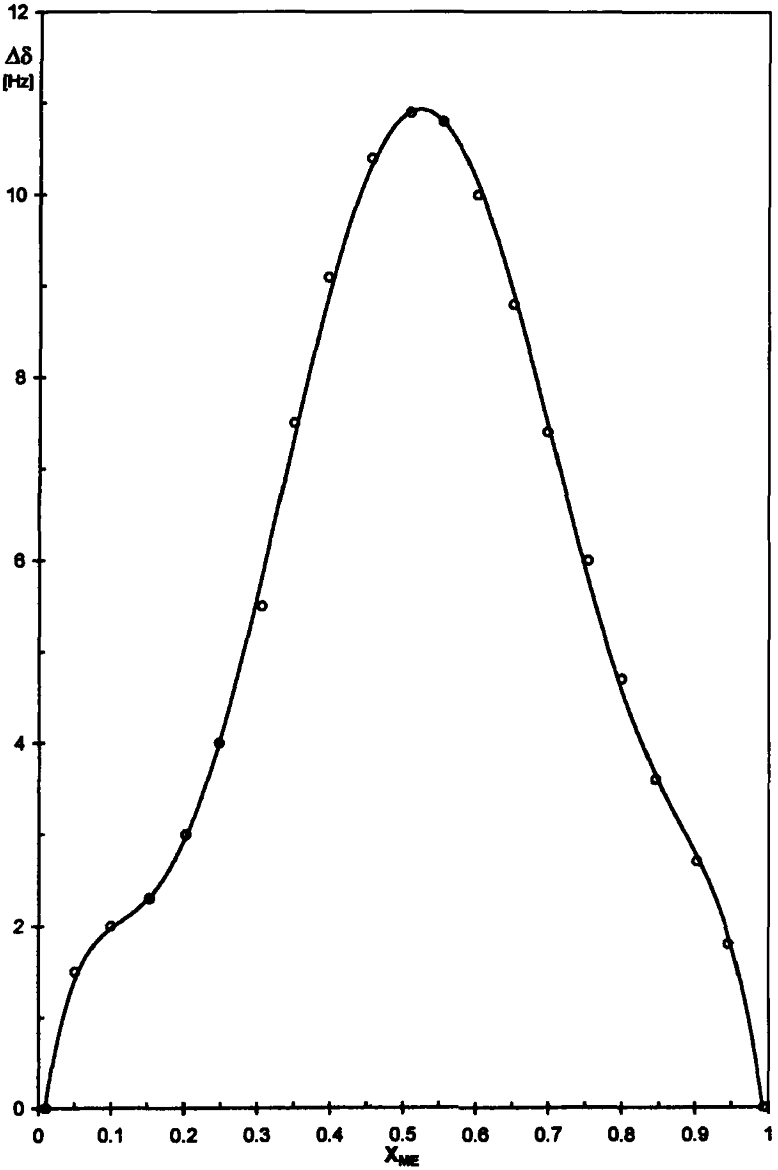

FIGURE 4 Changes in the spectral structural parameter, Δδ(ME–ACN), in the liquid ME–ACN mixtures, at 298 K.

from $0.0102 \leq X_{\mathrm{ME}} \leq 0.9903$. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(ME–ACN), shown in Table II and explained above, their deviations from the additive properties, *viz.* $\Delta\delta$(ME–ACN) values, have been calculated. The procedure to fit these values has been discussed in detail previously [36]. 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 [3, 20–22, 36]. The $\Delta\delta$(ME–ACN) values are visualised in Figure 4 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta$(ME–ACN) at ca. $X_{\mathrm{ME}} = 0.5$. Thus, at this composition the strongest interactions between components involving hydrogen bonds, are observed, and the most stable complex is ME·ACN.

The results presently obtained fully confirm our previous conclusions regarding structural aspects derived from dielectric measurements and by considering the excess volumes of mixing (V_m^E) where the maximum degree of molecular packing is observed at all the investigated temperatures.

The conclusion to be drawn from all these results is that the molecules of this mixed solvent may be joined as dipolar and/or hydrogen bonds to form stable adducts of 1:1 stoichiometry.

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