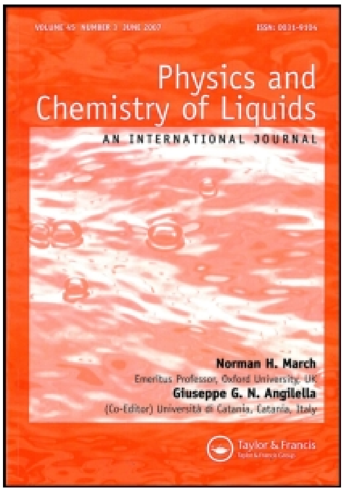

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Cezary M. Kinart[a]; Wojciech J. Kinart[b]; Adam Bald[a]; Andrzej Kolasiński[a]
[a] Department of Chemical Education, University of Łódź, Pomorska, Poland [b] Department of Organic Chemistry, University of Łódź, Narutowicza, Poland

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SOME PHYSICOCHEMICAL PROPERTIES OF ACETONITRYLE-METHANOL BINARY LIQUID MIXTURES

CEZARY M. KINART[a,*], WOJCIECH J. KINART[b], ADAM BALD[a] and ANDRZEJ KOLASIŃSKI[a]

[a]*Department of Chemical Education, University of Łódź, 90-236, Łódź, Pomorska 163, Poland;* [b]*Department of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland*

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Density and refractive indices for mixtures of acetonitryle with methanol were measured over the whole composition range at 298.15 K, as well as the relative permittivities at 288.15 K, 298.15 K and 308.15 K. From these data the excess molar volumes, apparent and partial molar volumes of acetonitryle and methanol, the excess relative permittivity, the temperature coefficients of relative permittivity and Kirkwood's correlation factor for investigated mixtures were calculated. The ^{1}H-NMR spectra of these liquid binary mixtures, were recorded at 298 K and the spectral parameters, $\Delta\delta$(ACN-MeOH) were calculated.

These structural parameters as functions of concentration suggest the formation of the structures such as clathrate and the most stable complexes of the 2 ACN • MeOH and ACN • 3MeOH types.

Keywords: ^{1}H-NMR spectra; binary liquid mixtures; intermolecular interactions

1. INTRODUCTION

Aqueous and alcohols mixtures of acetonitryle are used in chemical and biochemical laboratory practice, as well as in some branches of chemical technology. However, the literature data concerning the physicochemical properties of these systems are rather fragmentary and concern mainly the mixtures of water with acetonitryle. In order to fill this gap, at least partly, we have undertaken the physicochemical

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*Corresponding author.

and ^{1}H-NMR spectroscopic examinations of the mixtures of acetonitryle with methanol.

2. EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities, densities and refractive index chemical pure acetonitryle and methanol (Fluka) were used. They were dried and purified according to the known procedures [1]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 K. The proton chemical shifts of ACN and MeOH 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 ± 0.1%, using a bridge of type OH-301 (made in Hungary). Solvent densities were measured, using a glass Lipkin pycnometer. The maximum error in the density measurements was 1.10^{-5} g.cm^{-3}. The refractive index measurements for sodium light ($\lambda = 598.55$ nm) were performed using the Abbe refractometer. All solutions were prepared by weight.

3. RESULTS AND DISCUSSION

The measured densities (d_{12}), refractive indices (n_{12}^D) and the values of chemical shift differences δ(ACN-MeOH), between the centre of the ^{1}H-NMR signals of the -CH$_3$ group of acetonitryle and the centre of the ^{1}H-NMR signals of the -OH group of CH$_3$OH molecules within the whole composition range of the binaries determined at 298.15 K are presented in Table I.

The measured relative permittivities (ε_{12}) for the ACN-MeOH mixtures at 288.15 K, 298.15 K and 308.15 K are presented in Table II.

3.1. Volumetric Properties of the Acetonitryle-Methanol Mixtures

From the measured densities (see Tab. I) the molar excess volumes V_m^E of the mixtures were calculated according to:

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

TABLE I Density (d_{12}), refractive index (n_{12}^{D}), chemical shift δ(ACN-MeOH) and apparent molar volume of ACN in MeOH ($V_{1,\omega}$) and MeOH in ACN($V_{2,\omega}$) at 298.15 K

mol. % of MeOH	d_{12} [$g \cdot cm^{-3}$]	n_{12}^{D}	δ(*ACN-MeOH*) [*Hz*]	$V_{1,\omega}$ [$cm^3 \cdot mol^{-1}$]	$V_{2,\omega}$ [$cm^3 \cdot mol^{-1}$]
0.0	0.776641	1.34159		52.86	0.00
0.5	-	—	62.50	-	
5.0	0.777419	1.34099	67.50	52.83	40.21
10.0	0.778121	1.34038	75.00	52.81	40.27
15.0	0.778771	1.33975	81.00	52.79	40.32
20.0	0.779388	1.33911	87.50	52.76	40.36
25.0	0.779989	1.33845	94.00	52.74	40.40
30.0	0.780584	1.33778	101.00	52.72	40.43
35.0	0.781184	1.33709	107.00	52.70	40.45
40.0	0.781792	1.33639	113.50	52.67	40.46
45.0	0.782410	1.33567	120.00	52.64	40.48
50.0	0.783034	1.33493	126.50	52.60	40.49
55.0	0.783660	1.33419	133.00	52.56	40.50
60.0	0.784275	1.33342	139.50	52.51	40.51
65.0	0.784868	1.33265	146.00	52.45	40.53
70.0	0.785419	1.33186	153.50	52.38	40.54
75.0	0.785907	1.33105	159.50	52.31	40.56
80.0	0.786309	1.33023	167.50	52.23	40.59
85.0	0.786594	1.32939	174.00	52.13	40.62
90.0	0.786731	1.32854	181.50	52.03	40.65
95.0	0.786682	1.32767	180.50	51.91	40.70
99.5		—	179.50	—	--
100.0	0.786410	1.32679		0.00	40.74

where M_i, x_i and d_i are the molar mass, density and mole fraction of component i with $i = 1$ for acetonitryle and $i = 2$ for methanol while d_{12} is density of the mixture. The values of V_m^E for the investigated system are presented in Figure 1 as a function of composition.

The apparent molar volumes $V_{i,\Phi}$ of both components of the mixtures are determined from:

$$V_{i,\Phi} = V_i^* + V_m^E / x_i \qquad (2)$$

where V_i^* is the molar volume of pure component. The obtained values are given in Table I. The values of $V_{1,\Phi}$ and $V_{2,\Phi}$ as a function of x_i were used to calculate the partial molar volumes V_i of the components according to:

$$V_i = V_{i,\Phi} + x_i \cdot x_2 (\partial V_{i,\Phi} / \partial x_i) \qquad (3)$$

TABLE II Relative permittivity of acetonitryle-methanol mixtures at 288.15 K, 298.15 K and 308.15 K

mol. % of	ε_{12}		
MeOH	288.15 K	298.15 K	308.15 K
0.0	37.61	35.96	34.30
2.0	37.86	36.15	34.53
5.0	38.14	36.42	34.77
8.0	38.31	36.54	34.90
10.0	38.37	36.57	34.93
12.0	38.39	36.57	34.93
15.0	38.38	36.51	34.87
20.0	38.25	36.34	34.67
25.0	38.04	36.09	34.39
30.0	37.79	35.82	34.09
35.0	37.53	35.54	33.78
40.0	37.28	35.28	33.48
45.0	37.06	35.05	33.22
50.0	36.85	34.84	32.97
55.0	36.67	34.64	32.74
60.0	36.49	34.44	32.52
65.0	36.32	34.24	32.30
70.0	36.14	34.02	32.07
75.0	35.95	33.79	31.82
80.0	35.73	33.53	31.55
85.0	35.50	33.27	31.26
90.0	35.26	33.01	30.98
95.0	35.03	32.75	30.73
100.0	34.84	32.66	30.56

The values of $(\delta V_{i,\phi}/\delta x_i)$ were obtained by the local fitting procedure similar to that described by Zegers and Somsen [2]. The partial molar volumes V_1 of acetonitryle in the mixtures and the corresponding data that refer to the methanol are presented in Table III.

As it can be seen in Figure 1, the molar volumes of the mixtures of acetonitryle with methanol deviate significantly from additivity. The excess volume curves show negative values over the whole composition range. It is known that the negative values of V_m^E connected with the phenomenon of concentration are characteristic for the mixtures of liquids associated by the hydrogen bonds and they reflect an increase in association [3]. According to the authors mentioned above the V_m^E minimum position points at the mixture composition which has the most stable or ordered structure [4, 5]. In our case, the position of the V_m^E minimum corresponds to ca. 67 mol. % of ACN. Thus, at this composition the strongest interactions between components involving

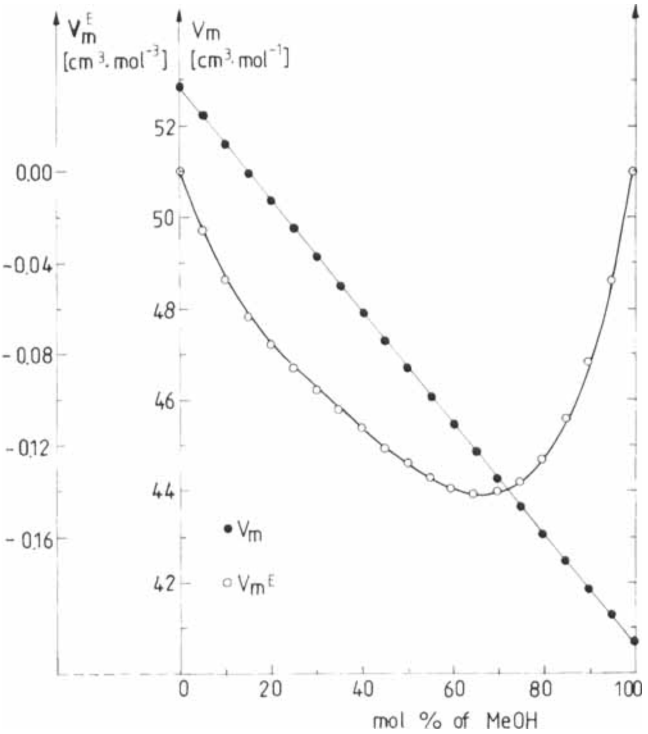

FIGURE 1 Molar Volume (V_m) and excess molar volume (V_m^E) of acetonitryle-methanol mixtures, at 298.15 K.

hydrogen bonds, are observed, and the stable "complex" is 2 ACN • MeOH.

An analogous conclusion can be drawn from the analysis of concentration dependencies of the apparent (or partial) molar volumes of acetonitryle in methanol (V_1) and methanol in acetonitryle (V_2) (Table III). The excess of partial volumes V_1^E and V_2^E exhibits the maximum at the composition having ca. 70 mol.% and 25 mol.% of MeOH (Fig. 2). Thus, the conclusion would be drawn that at these compositions the strongest interactions between components with involved hydrogen bonds are displayed [6–9], and the stable "complexes" are of the 2 ACN • MeOH and ACN • 3 MeOH types.

TABLE III Partial molar volume of acetonitryle (V_1) and of methanol (V_2) in ACN-MeOH mixtures at 298.15 K

mol. % of MeOH	V_1 [$cm^3 \cdot mol^{-1}$]	V_2 [$cm^3 \cdot mol^{-1}$]
0.0	52.86	40.13
5.0	52.85	40.27
10.0	52.84	40.37
15.0	52.83	40.44
20.0	52.82	40.48
25.0	52.82	40.50
30.0	52.81	40.52
35.0	52.81	40.53
40.0	52.81	40.53
45.0	52.80	40.54
50.0	52.80	40.54
55.0	52.78	40.55
60.0	52.76	40.57
65.0	52.73	40.59
70.0	52.68	40.61
75.0	52.61	40.64
80.0	52.51	40.67
85.0	52.38	40.69
90.0	52.22	40.72
95.0	52.02	40.73
100.0	51.78	40.74

3.2. ^{1}H-NMR Spectroscopic and Dielectric Properties

Presently with the aim of analysing the intermolecular interactions between the components in the binary liquid ACN-MeOH mixtures, we measured the values of chemical shifts differences δ(ACN-MeOH) at 298 K, between the centre of the ^{1}H-NMR signals of the -CH_3 group of acetonitryle and the centre of the ^{1}H-NMR signals of the -OH group of methanol molecules over a wide range of solvent compositions, i.e. from 0.50 to 99.50 mol. % of MeOH. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(ACN-MeOH), shown in Table I and explained above, their deviations from the additive properties, viz. $\Delta\delta$(ACN-MeOH) values, have been calculated. The procedure to find these values has been discussed in detail previously [10]. The values of this structural parameter or, more precisely, the location of its maximum values [10–12], are located at the composition with the strongest inter-

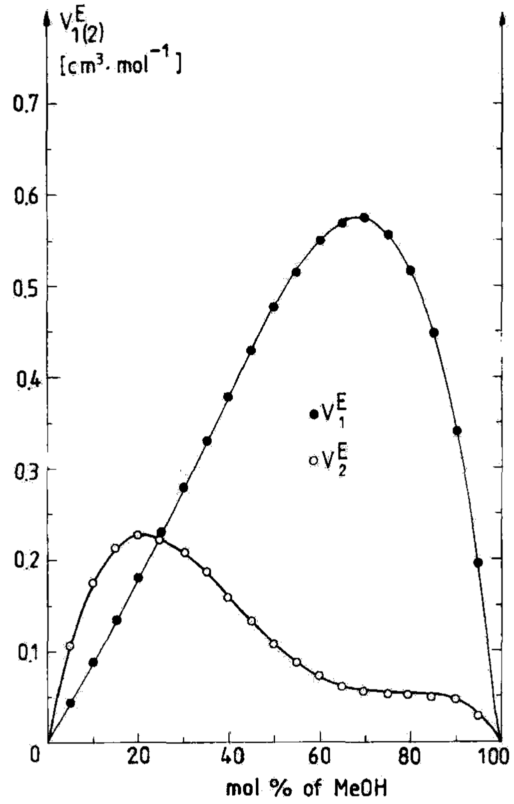

FIGURE 2 Excess partial molar volume of acetonitryle (V_1) and of methanol (V_2) in acetonitryle-methanol mixtures, at 298.15 K.

molecular interactions between the components, where hydrogen bonds are involved. The $\Delta\delta$(ACN-MeOH) values are visualized in Figure 3 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta$(ACN-MeOH) at ca. 90 mol. % of MeOH.

Thus, the conclusion can be drawn that at this composition the strongest interactions between MeOH and ACN molecules are displayed and suggest the formation of the structure such as clathrates.

From the relative permittivity data (Table II), the temperature coefficient of the relative permittivity, denoted α_{12}, viz. $\alpha_{12} = (1/\epsilon_{12})[d\epsilon_{12}/d(1/T)]$, were calculated. The composition range of liquid binary

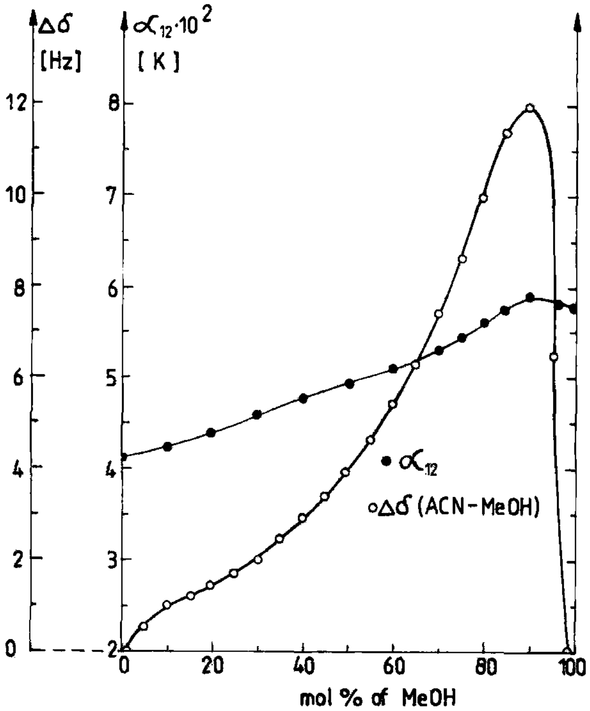

FIGURE 3 Changes in the temperature coefficient of relative (α_{12}) and the function $\Delta\delta$(ACN-MeOH) drawn as a function of composition for the liquid acetonitryle-methanol mixtures, at 298.15 K.

mixtures within which α_{12} attains its highest value should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic consideration [13]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Conclusions drawn from the analysis of changes in $\Delta\delta$ and α_{12} are fully consistent [10–12]. Changes in α_{12} vs. composition of liquid ACN-MeOH mixtures are shown in Figure 3. We observed the tendency to achieve the maximum by the function α_{12} at ca. 90 mol. % of MeOH. This confirms the conclusion from ^{1}H-NMR spectral data concerning the formation of the structure such as clathrates.

One of the tools for the investigation of molecular interactions in liquids is an analysis of the Kirkwood's correlation factor g_K [14]. Its values reflect mutual orientation of neighbouring molecular dipoles and they can inform about the possible kind of associates present in the solution. For monomers $g_K = 1$ and for cyclic dimers $g_K = 0$. In the case of open dimers and multimers the values of $g_K > 1$ suggest parallel dipoles orientation while $0 < g_K < 1$ point at the antiparallel orientation of neighbouring dipoles, hence mixed associated structures [15]. According to Cole [16], the Kirkwood's correlation factor for binary liquid mixtures, can be calculated from the equation:

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

where: k and L are respectively Boltzmann's and Avogadro's constants; M_i, x_i, d_i and μ_i^o represent respectively, the molar mass, mole fraction, density and gas-phase dipole moment; $i = 1$ denotes

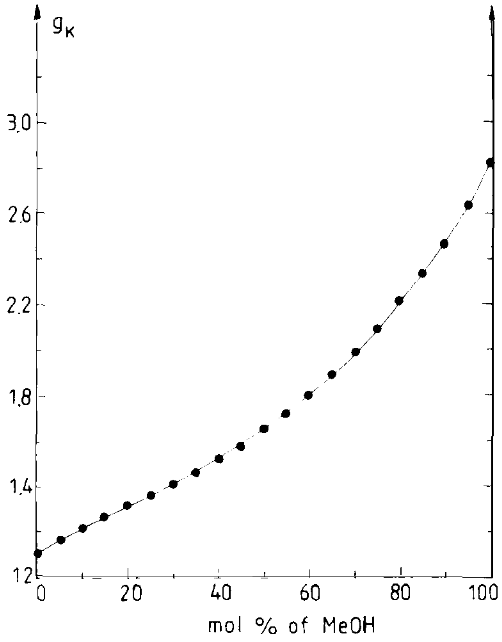

FIGURE 4 Krikwood correlation parameter (g_K) as a function of methanol content for acetonitryle-methanol mixtures, at 298.15 K.

acetonitryle, while $i = 2$ denotes a methanol. T is a temperature of the mixture, ε_{12}- relative permittivity of the solution, while $\varepsilon_{\infty} = 1.1 n_D^2$ represents the mixture relative permittivity at high frequency [17]. The Kirkwood's correlation factor g_K for ACN - MeOH mixtures as a function of the mixture composition is presented in Figure 4.

The g_K values in all mixtures investigated here are above unity $1.11 < g_K < 2.82$, which suggests that the acetonitryle - methanol open dimers and multimers exist in the system.

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