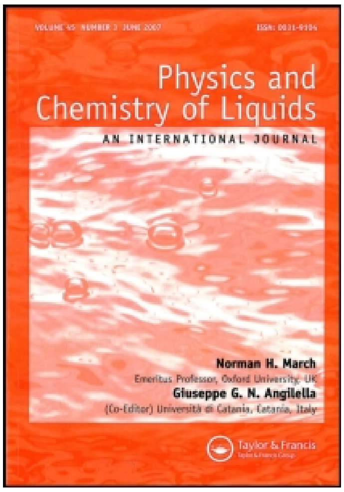

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DIMETHYLSULFOXIDE – N,N-DIMETHYLFORMAMIDE BINARY MIXTURES AND THEIR PHYSICOCHEMICAL PROPERTIES

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Density and refractive indices for mixtures of dimethylsulfoxide (DMSO) with N,N-dimethylformamide were measured over the whole composition range at 298.15 K, as well as the relative permittivities at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15K. From these data the excess molar volumes, apparent and partial molar volumes of DMSO and DMF, 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, $\Delta\delta$(DMSO – DMF) were calculated.

These structural parameters as functions of concentration suggest the formation of the most stable "complexes" of the 2 DMSO•DMF and DMSO•DMF types.

Keywords: Binary liquid mixtures; intermolecular interactions; physicochemical properties

1. INTRODUCTION

The present work is a continuation of series of studies on analysis of intermolecular interactions and internal structures of some liquid binary mixtures, in which dimethylsulfoxide (DMSO) or N,N-dimethylformamide (DMF) is one of two constituents [1 – 4].

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We attempted in this work to resolve the literature controversy regarding the opinion of intermolecular interactions between components of liquid mixtures DMSO – DMF. C. de Visser and G. Somsen [5] on the base of the analysis of changes of densities, molar volumes, partial molar volumes and molar heat capacities as a function of the mole fraction of DMF assumed that the mixture DMSO – DMF can be regarded as almost ideal with lack of intermolecular interactions. The opposite view was expressed in the work of Jonin *et al.*'s [6]. These authors on the base of the analysis of changes of viscosity, density, molar volume and thermodynamic functions of viscous flow suggested the possibility of formation of stable DMSO•DMF type complexes.

In this paper, using the ^{1}H-NMR examinations of liquid DMSO – DMF binary mixtures and changes in their main physicochemical properties the intermolecular interactions in the DMSO – DMF mixtures will be analysed.

2. EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities, densities and refractive index chemical pure DMSO and DMF (Fluka) were used. They were dried and purified according to the known procedures [7]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 K. The proton chemical shifts of DMSO and DMF 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 mesurements was $1 \cdot 10^{-5}$ 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(DMSO – DMF), between the centre of the ^{1}H-NMR signals of the $-CH_3$ groups of DMSO and the centre of the ^{1}H-NMR signal of the formyl proton of DMF molecules within the whole composition range of the binaries determined at 298.15 K presented in Table I.

The measured relative permittivities (ε_{12}) for the DMSO - DMF mixtures at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K are presented in Table II.

3.1. Volumetric Properties of the Dimethylsulfoxide – N, N-dimethylformamide Mixtures

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

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

TABLE I Density (d_{12}), refractive index (n_{12}^D), chemical shift δ(DMSO - DMF), apparent molar volume of the dimethylsulfoxide in DMF ($V_{1,\phi}$) and apparent molar volume of the N,N-dimethyl formamide in DMSO ($V_{2,\phi}$), at 298.15 K

mol.% of DMF	d_{12} [*g.cm*$^{-3}$]	n_{12}^D	δ(*DMSO - DMF*) [*Hz*]	$V_{1,\phi}$ [*cm*^{3}. *mol*$^{-1}$]	$V_{2,\phi}$ [*cm*^{3}. *mol*$^{-1}$]
0.0	1.095576	1.4770	-	71.31	0.00
1.0			16.20	-	
5.0	1.086998	1.4742	16.70	71.34	77.98
10.0	1.078646	1.4715	17.25	71.36	77.86
15.0	1.070482	1.4687	-	71.38	77.77
20.0	1.062472	1.4661	18.20	71.38	77.69
25.0	1.054586	1.4634	18.70	71.39	77.63
30.0	1.046799	1.4608	19.15	71.39	77.58
35.0	1.039090	1.4583	19.40	71.39	77.54
40.0	1.031443	1.4557	19.30	71.39	77.51
45.0	1.023845	1.4532	19.20	71.39	77.49
50.0	1.016288	1.4507	19.10	71.40	77.48
55.0	1.008769	1.4482	19.00	71.41	77.48
60.0	1.001288	1.4458	18.90	71.43	77.47
65.0	0.991850	1.4433	-	71.45	77.47
70.0	0.986466	1.4409	18.80	71.49	77.47
75.0	0.979147	1.4385		71.54	77.47
80.0	0.971914	1.4361	18.70	71.60	77.47
85.0	0.964788	1.4338		71.68	77.46
90.0	0.957796	1.4315	18.60	71.77	77.45
95.0	0.950968	1.4292	18.50	71.89	77.43
96.0		-	18.45		
100.0	0.944341	1.4269	-	0.00	77.40

TABLE II Relative permittivity (ε_{12}) in DMSO – DMF binary mixtures at 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K

mol.% of	ε_{12}				
DMF	*288.15 K*	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*
0.00	–	47.20	46.48	45.83	45.22
5.00	–	46.83	46.09	45.36	44.68
10.00	47.51	46.46	45.70	44.90	44.19
15.00	47.14	46.10	45.30	44.46	43.72
20.00	46.78	45.73	44.90	44.03	43.26
25.00	46.42	45.36	44.48	43.60	42.82
30.00	46.04	44.98	44.06	43.17	42.37
35.00	45.65	44.58	43.62	42.73	41.92
40.00	45.24	44.17	43.18	42.28	41.46
45.00	44.80	43.73	42.72	41.81	40.99
50.00	44.34	43.28	42.25	41.34	40.50
55.00	43.86	42.81	41.77	40.84	39.99
60.00	43.35	42.31	41.28	40.33	39.47
65.00	42.82	41.80	40.78	39.79	38.99
70.00	42.27	41.26	40.25	39.24	38.37
75.00	41.71	40.71	39.72	38.68	37.79
80.00	41.14	40.13	39.16	38.10	37.21
85.00	40.57	39.55	38.59	37.51	36.62
90.00	40.00	38.95	38.00	36.90	36.02
95.00	39.45	38.34	37.38	36.30	35.44
100.00	38.93	37.73	36.74	35.70	34.87

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

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

$$V_i, \phi = V_i^* + V_m^E / x_i \tag{2}$$

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:

$$V_i = V_{i,\phi} + x_i . x_2 \left(\delta V_{i,\phi} / \delta x_i \right) \tag{3}$$

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 [8]. The partial molar

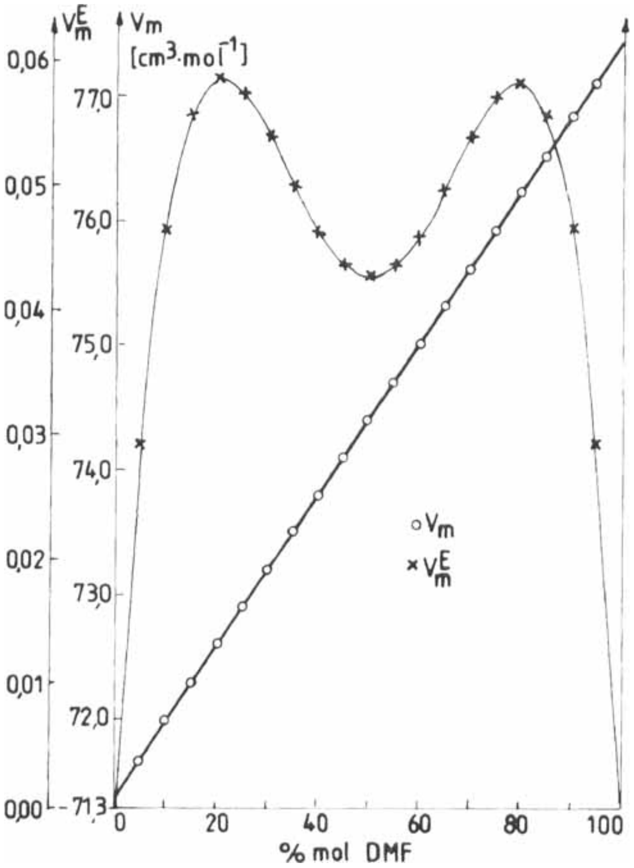

FIGURE 1 Molar Volumes (V_m^E) and excess volumes (V_m^E) of DMSO – DMF mixtures vs. DMF content, at 298.15 K.

volumes (V_0^1) of DMSO in the mixtures and the corresponding data that refer to the N, N-dimethylformamide (V_0^2) are presented in Table III.

As it can be seen in Figure 1, the excess molar volumes curves exhibit positive values over the whole composition range with the maximum within ca. 20 mol. % DMF and ca. 80 mol. % of DMF. According to the authors mentioned above the V_m^E maximum position points at the mixture composition which has the most stable or ordered structure [9, 10].

TABLE III Partial molar volume of DMSO (V_1) and DMF (V_2) in dimethylsulfoxide - N, N-dimethylformamide mixtures, at 298. 15 K

mol. % of DMF	V_0^1 [$cm^3 . mol^{-1}$]	V_0^2 [$cm^3 . mol^{-1}$]
0.0	71.31	78.11
5.0	71.32	77.86
10.0	71.33	77.68
15.0	71.35	77.55
20.0	71.37	77.47
25.0	71.38	77.42
30.0	71.39	77.40
35.0	71.38	77.40
40.0	71.38	77.41
45.0	71.37	77.42
50.0	71.36	77.44
55.0	71.34	77.46
60.0	71.32	77.47
65.0	71.31	77.48
70.0	71.31	77.48
75.0	71.33	77.47
80.0	71.38	77.45
85.0	71.46	77.44
90.0	71.59	77.42
95.0	71.77	77.41
100.0	72.02	77.40

An analogous conclusion can be drawn from the analysis of concentration dependencies of the partial (or apparent) molar volumes of dimethylsulfoxide in N, N-dimethylformamide (V_0^1) and N, N-dimethylformamide in dimethylsulfoxide (V_0^2) (see Tab. III). The excess of this functions V_0^{1E} and V_0^{2E} exhibits the maximum at the composition having ca. 20 mol. % of DMF and ca. 80 mol. % of DMF (Fig. 2). It was suggested that the decrease of the V_1 and V_2 of the solute with increasing of concentration are due to the solvophobic solvatation of the solute [11 – 14].

The region of the composition corresponding to ca. 50 mol.% of DMF is very interesting from the point of view of volumetric changes. V_m^E achieves here the minimum value (see Fig. 1) and the difference of the excess partial molar volumes, $V_0^{1E} - V_0^{2E}$, is equal to zero (see Fig. 2). Therefore, it is necessary to assume that the intermolecular association leading to formation of DMSO•DMF type complexes is responsible for it. This suggestion is in agreement with conclusions drawn by Jonin [3].

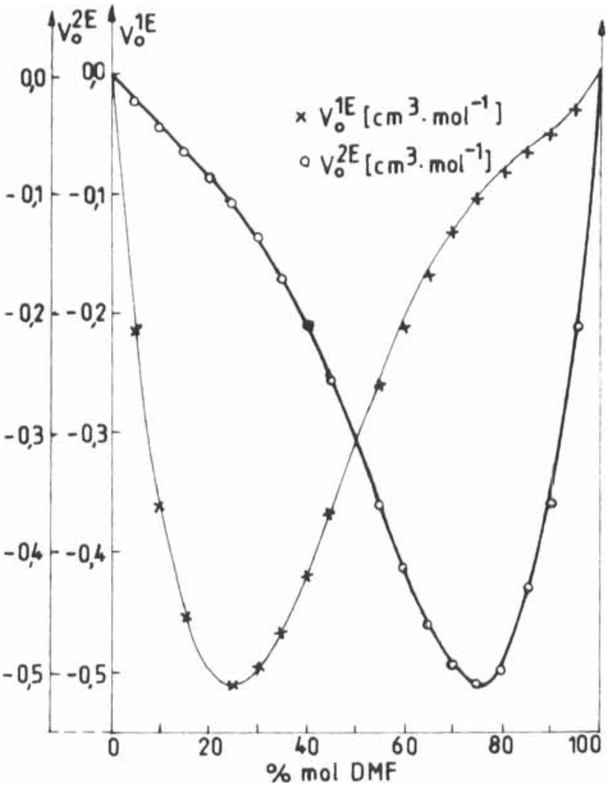

FIGURE 2 Excess partial molar volume of dimethylsulfoxide (V_0^{1E}) and of N,N-dimenthylformamide (V_0^{2E}) in DMSO – DMF mixtures vs. DMF content, at 298.15 K.

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 DMSO – DMF mixtures, we measured the values of chemical shifts differences δ(DMSO – DMF) at 298 K, between the centre of the ^{1}H-NMR signals of the —CH$_3$ group of DMSO and the centre of the ^{1}H-NMR signals of the formyl proton of DMF molecules over a wide range of solvent compositions, i.e. from 1.00 to 96.00 mol. % of DMF. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(DMSO – DMF), shown in Table I and explained above, their deviations from the additive properties, viz. Δδ(DMSO − DMF) values, have been calculated. The procedure to find these values has been discussed in detail previously [1]. The values of this structural parameter or, more precisely, the location of its maximum values [1 − 4], are located at the composition with the strongest intermolecular interactions between the components, where hydrogen bonds are involved. The Δδ(DMSO − DMF) values are visualized in Figure 3 as a function of the mixture compositions.

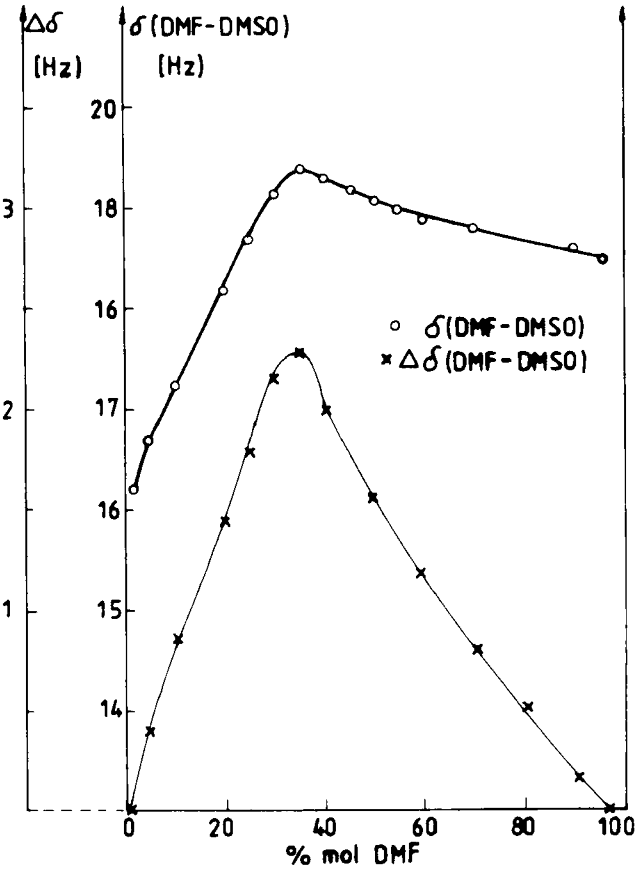

FIGURE 3 Changes in the function δ(DMSO − DMF) and Δδ(DMSO − DMF) in DMSO − DMF mixtures vs. DMF content, at 298 K.

The analysis of the obtained data indicates the presence of a maximum $\Delta\delta$(DMSO – DMF) at ca. 33 mol. % of DMF.

Thus the conclusion can be drawn that at this composition the strongest interactions between DMSO and DMF molecules are observed and the most stable "complex" is 2 DMSO•DMF.

Form the relative permittivity data (Tab. II), the temperature coefficient of the relative permittivity, denoted α_{12} viz. $\alpha_{12} = (1/\varepsilon_{12})[d\varepsilon_{12}/d(1/T)]$, were calculated. The composition range of liquid binary mixtures within which α_{12} attains its highest value should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic consideration [15]) 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

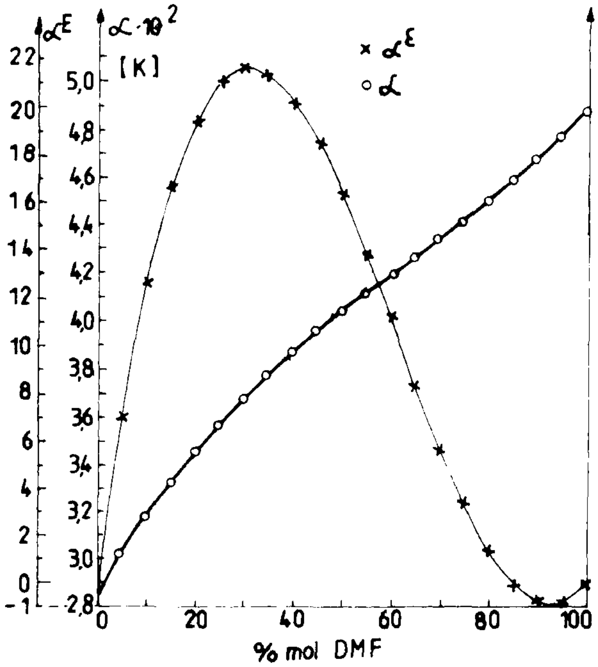

FIGURE 4 Changes in the temperature coefficient of dielectric permittivity (α_{12}) and excess of the temperature coefficient (α^{E}_{12}) in DMSO – DMF mixtures vs. DMF content, at 298.15 K.

α_{12} are fully consistent [1–4]. Changes in α_{12}vs. composition of liquid DMSO – DMF mixtures are shown in Figure 4.

The maximum of α_{12} is found at ca. 33 mol.% of DMF. This confirms the conclusion from ^{1}H-NMR spectral data concerning the formation of a "complex" of 2 DMSO•DMF.

One of the tools for the investigation of molecular interactions in liquids is an analysis of the Kirkwood's correlation factor g_k [16]. 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

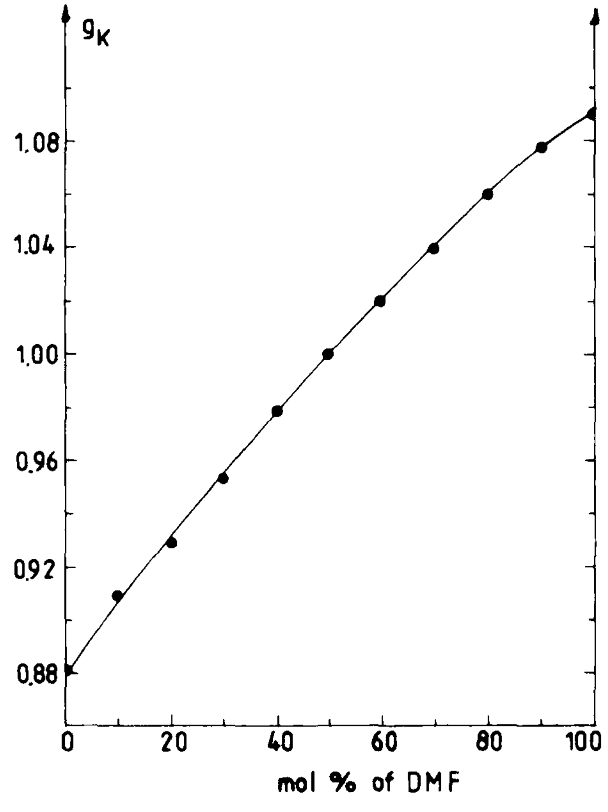

FIGURE 5 Kirkwood's correlation parameter g_K as a function of DMF content for DMSO – DMF mixtures, at 298.15 K.

case of open dimers and multimers the values of $g_k > 1$ suggest parallel dipols orientation while $0 < g_k < 1$ point at the antiparallel orientation of neighbouring dipoles, hence mixed associated structures are present [17]. According to Cole [18], the Kirkwood's correlation factor for binary liquid mixtures, can be calculated from the equation:

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

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 DMSO, while $i = 2$ denotes DMF. T is a temperature of the mixture, ε_{12} – relative permittivity of the solution, while $e_\infty/\varepsilon_\infty = 1.1n_D^2$ represents the mixture relative permittivity at high frequency [17]. The Kirkwood's correlation factor g_k for DMSO – DMF mixtures as a function of the mixture composition is presented in Figure 5.

Values of the Kirkwood's correlation factor within the whole composition range of DMSO – DMF mixtures are closed to unity. The linear increase of g_k values with the gradual addition of DMF to DMSO seems to indicate that with the increase of the concentration of DMF in the studies system the linear associates start to predominate.

References

[1] Romanowski, S. J., Kinart, W. J. and Kinart, C. M. (1995). *J. Chem. Soc. Faraday Trans.*, **91**(1), 65.

[2] Kinart, C. M. and Kinart, W. J. (1996). *Phys. Chem. Liq.*, **31**, 1.

[3] Kinart, C. M. and Kinart, W. J. (1996). *Phys. Chem. Liq.*, **33**, 151.

[4] Kinart, C. M., Kinart, W. J., Skulski, L. and Kolasiński, A. (1997). *Phys. Chem. Liq.*, **34**, 181.

[5] De Visser, C. and Somsen, G. (1979). *J. Solution Chem.*, **8**(8), 593.

[6] Jonin, M. and Rogozina, M. (1979). *Zh. Fiz. Khem.*, **3**, 695.

[7] Roddick, J. A., Bunger, W. B. and Sakano, T. K. (1988). *Organic Solvents, Physical Properties and Method of Purification*, Ed. J. Wiley and Sons, New York.

[8] Zegers, H. C. and Somsen, G. (1984). *J. Chem. Thermodyn.*, **16**, 225.

[9] Nakanishi, K., Kato, N. and Maruyama, M. (1967). *J. Phys. Chem.*, **71**, 814.

[10] Gallant, R. W. (1967). *Hydrocarbon Processing*, **46**, 201.

[11] Benson, G. C., D'Arcy, P. J. and Kiyohara, O. (1980). *J. Solution Chem.*, **9**, 931.

[12] Jolicoeur, C. and Lacroix, G. (1976). *Can. J. Chem.*, **54**, 624.

[13] Roux, G., Roberts, D., Perron, G. and Desnoyers, J. E. (1980). *J. Solution Chem.*, **9**, 629.

[14] Franks, F. (1977). *J. Chem. Soc. Faraday Trans.*, **73**(1), 830.

[15] Räetzsch, M. T., Kehlen, H. and Rosner, H. (1974). *Z. phys. Chem. (Leipzig)*, **255**, 115.
[16] Kirkwood, J. C. (1939). *J. Phys. Chem.*, **7**, 911.
[17] D'Aprano, A., Donato, D. J. and Livieri, V. T. (1989). *J. Solution Chem.*, **18**, 785.