HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 29. pp. 1 - 5 (2001)

REFRACTIVE INDICES, DENSITIES AND DERIVED EXCESS PROPERTIES OF BINARY AND TERNARY SYSTEMS WITH DIMETHYL SULFOXIDE, WATER AND 1,4-DIOXANE

L. M. OMOTA, O. IULIAN and C. MATEESCU

(Department of Applied Physical Chemistry & Electrochemistry, Faculty of Industrial Chemistry, University "POLITEHNICA", 313, Splaiul Independentei, Bucharest, 77206, ROMANIA)

Received: August 9, 2000

Refractive indices and densities for binary dimethyl sulfoxide+water, dimethyl sulfoxide+1,4-dioxane systems and ternary dimethyl sulfoxide+water+1,4-dioxane system have been measured at 298.15 K, over the entire mole fraction scale of the mixture. Changes on molar volume, partial molar volume and molar refraction have been calculated. The experimental data were used to test several mixing rules for estimation of the refractive index.

Keywords: binary and ternary systems with dimethyl sulfoxide, excess properties

Introduction

The properties of liquid mixtures have attracted much attention in the literature from both theoretical and practical viewpoints. The properties of dimethyl sulfoxide (DMSO) and its mixtures have been the subject of considerable interest because of its versatility as a solvent and a plasticizer.

In addition to our studies on the physico-chemical properties of binary and ternary liquid mixtures containing DMSO, 1,4-dioxane and water [1-4], we report in this paper the measurement of refractive indices for binary DMSO+water, DMSO+1,4-dioxane and ternary DMSO+water+1,4-dioxane mixtures. We present the experimental values of refractive indices and calculated changes of molar refraction on mixing over the entire mole fraction range at 298.15 K and at atmospheric pressure. Moreover, experimental data were used to test several mixing rules for refractive indices. The densities, reported earlier [5], were used here to present the calculated excess molar volumes and excess partial molar volumes. The results are discussed in terms of the molecular interactions between the water and organic molecules.

There are less data available concerning the refractive indices for the binary DMSO+water system [6,7]; we mention that refractive indices for the binary DMSO+1,4-dioxane and ternary water+1,4-dioxane+DMSO systems were not found in the literature.

Experimental

Apparatus and Procedure

Refractive indices values for the sodium D-line were measured with a thermostated Abbe refractometer with a precision of ± 0.0001. Temperature is accurate to ± 0.05 K. Density of pure liquids and mixtures was measured using a calibrated pycnometer with an internal diameter of 1 mm. An average of duplicate measurements was considered and these are accurate to ± 0.0002 g cm^{-3}.

Materials

The used substances were purified by distillation. DMSO was distilled under vacuum of 0.8-0.9 kPa at 338.65 K. The analytical-reagent-grade 1,4-dioxane from Merck was distilled at 374.35 K. The water was bidistillated. The impurities were found by GC. A comparison of refractive index and density values of pure liquids with the literature findings is given in Table 1. The mixtures were prepared gravimetrically using a balance with precision of $0.1 \cdot 10^{-6}$ kg. The experimental uncertainties are: $\sigma(X_i) = 0.0001$, $\sigma(\rho)$/kg $m^{-3} = 0.2$ and $\sigma(V^E)/10^{-9} m^3 mol^{-1} = 10$.

Table 1 Densities and refractive indices of pure components at 298.15 K

Compound	ρ , 10^{-3}kg m^{-3}		n_D	
	exptl	Literature	exptl	literature
Water	0.9971	0.99704[8,9]	1.3325	1.3324[9,11]
		0.99705[10]		1.3314[6]
				1.3325[8]
DMSO	1.0957	1.09537[8]	1.4768	1.4768[12]
		1.09547[12]		1.4769[5]
				1.4775[8]
1,4-dioxane	1.0281	1.02797[8]	1.4198	1.4194[5]
		1.02802[13]		
		1.02783[14,15]		

Table 2 Densities, excess molar volumes and excess partial molar volumes. Binary systems at T= 298.15 K

X_1	ρ, 10^{-3}kg m^{-3}	V^E, 10^{-6}m^{3}mol^{-1}	$\overline{V}_1^E$, 10^{-6}m^{3}mol^{-1}	$\overline{V}_2^E$, 10^{-6}m^{3}mol^{-1}
DMSO(1)+WATER(2)				
1.0000	1.0957	0.0000	0.0000	-2.5890
0.9085	1.0966	-0.2035	0.0267	-2.4893
0.8287	1.0979	-0.4032	-0.0010	-2.3487
0.7585	1.0989	-0.5626	-0.0509	-2.1698
0.6962	1.0997	-0.6938	-0.1310	-1.9836
0.6406	1.1001	-0.7921	-0.2297	-1.7945
0.5205	1.0996	-0.9411	-0.5664	-1.3479
0.4331	1.0973	-0.9826	-0.9415	-1.0140
0.3459	1.0922	-0.9526	-1.4441	-0.6927
0.2979	1.0876	-0.9000	-1.7810	-0.5263
0.2158	1.0756	-0.7466	-2.4697	-0.2724
0.1363	1.0563	-0.5145	-3.2856	-0.0772
0.0782	1.0361	-0.3079	-4.0031	0.0056
0.0351	1.0166	-0.1406	-4.6136	0.0221
0.0000	0.9971	0.0000	-5.1674	0.0000
DMSO(1)+1,4-DIOXANE(2)				
1.0000	1.0957	0.0000	0.0000	-1.5916
0.9581	1.0934	-0.0708	-0.0115	-1.4273
0.8938	1.0895	-0.1504	-0.0276	-1.1845
0.7829	1.0825	-0.2547	-0.0937	-0.8353
0.6906	1.0764	-0.3074	-0.1755	-0.6017
0.5950	1.0699	-0.3335	-0.2816	-0.4099
0.5459	1.0665	-0.3361	-0.3421	-0.3288
0.4959	1.0630	-0.3313	-0.4066	-0.2571
0.3929	1.0558	-0.3069	-0.5527	-0.1478
0.2861	1.0482	-0.2493	-0.7016	-0.0680
0.1750	1.0403	-0.1650	-0.8520	-0.0193
0.0888	1.0343	-0.0924	-0.9670	-0.0072
0.0470	1.0313	-0.0443	-1.0095	0.0033
0.0000	1.0281	0.0000	-1.0658	0.0000

Results and discussion

Binary Systems

Tables 2 and 3 list the measured densities (ρ) and refractive indices (n_D) together with the calculated values of excess molar volumes (V^E), excess partial molar volumes of the components ($\overline{V}_1^E, \overline{V}_2^E$) and, respectively, changes of molar refraction on mixing (ΔR). Table 3 includes also the results of prediction of

Table 3 Refractive indices, changes of molar refraction on mixing and refractive indices deviations calculated with several mixing rules. Binary systems at T=298.15 K

X_1	n_D	ΔR, 10^{-6} m^{3}mol^{-1}	Δn_D			
			L-L	G-D	A-B	EDW
DMSO(1)+WATER(2)						
1.0000	1.4768	0.0000	0.0000	0.0000	0.0000	0.0000
0.9085	1.4739	-0.0272	-0.0008	-0.0008	-0.0038	-0.0011
0.8287	1.4713	-0.0474	-0.0015	-0.0014	-0.0079	-0.0021
0.7585	1.4685	-0.0661	-0.0022	-0.0020	-0.0118	-0.0031
0.6962	1.4658	-0.0767	-0.0028	-0.0025	-0.0152	-0.0038
0.6406	1.4630	-0.0833	-0.0032	-0.0029	-0.0183	-0.0044
0.5205	1.4552	-0.0915	-0.0040	-0.0037	-0.0246	-0.0056
0.4331	1.4475	-0.0892	-0.0043	-0.0041	-0.0285	-0.0060
0.3459	1.4371	-0.0821	-0.0044	-0.0044	-0.0312	-0.0060
0.2979	1.4298	-0.0754	-0.0044	-0.0045	-0.0317	-0.0058
0.2158	1.4135	-0.0634	-0.0042	-0.0046	-0.0305	-0.0051
0.1363	1.3914	-0.0494	-0.0037	-0.0044	-0.0251	-0.0040
0.0782	1.3701	-0.0352	-0.0029	-0.0037	-0.0177	-0.0028
0.0351	1.3505	-0.0225	-0.0020	-0.0026	-0.0096	-0.0018
0.0000	1.3325	0.0000	0.0000	0.0000	0.0000	0.0000
DMSO(1)+1,4-DIOXANE(2)						
1.0000	1.4768	0.0000	0.0000	0.0000	0.0000	0.0000
0.9581	1.4741	-0.0124	-0.0003	-0.0003	-0.0013	-0.0004
0.8938	1.4698	-0.0324	-0.0009	-0.0008	-0.0029	-0.0011
0.7829	1.4628	-0.0519	-0.0014	-0.0013	-0.0048	-0.0016
0.6906	1.4572	-0.0593	-0.0015	-0.0015	-0.0056	-0.0018
0.5950	1.4515	-0.0641	-0.0016	-0.0016	-0.0059	-0.0019
0.5459	1.4487	-0.0619	-0.0015	-0.0015	-0.0059	-0.0019
0.4959	1.4458	-0.0621	-0.0015	-0.0015	-0.0058	-0.0018
0.3929	1.4401	-0.0549	-0.0013	-0.0013	-0.0052	-0.0016
0.2861	1.4343	-0.0449	-0.0011	-0.0011	-0.0041	-0.0012
0.1750	1.4284	-0.0337	-0.0008	-0.0008	-0.0028	-0.0009
0.0888	1.4241	-0.0188	-0.0004	-0.0004	-0.0015	-0.0005
0.0470	1.4220	-0.0113	-0.0003	-0.0003	-0.0008	-0.0003
0.0000	1.4198	0.0000	0.0000	0.0000	0.0000	0.0000

refractive indices by various mixing rules: Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Arago-Biot (A-B), Edwards (EDW). The deviations between experimental and predicted values of the refractive indices were represented by Δn.

Excess molar volumes and changes of molar refraction on mixing were calculated from:

$$V^E = \sum X_i M_i \left(\rho^{-1} - \rho_i^{0^{-1}}\right) \quad (1)$$

$$\Delta R = R - \sum X_i R_i \quad (2)$$

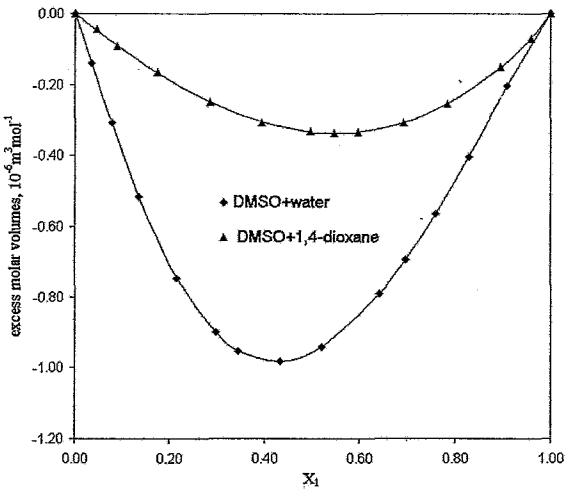
$$R = V \frac{n_D^2 - 1}{n_D^2 + 2} \quad (3)$$

where X_i is the mole fraction of component i; ρ and R are the density and molar refraction of the mixture, respectively; M_i, ρ_i^0 and R_i are the molar mass, density and molar refraction of pure components. The molar refractions were calculated from the Lorentz-Lorenz equation (eq.3), V being the molar volume.

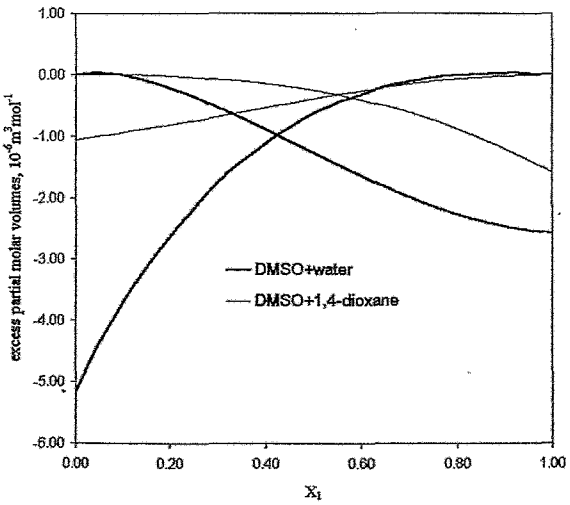
V^E and ΔR for the binary systems were fitted with Redlich-Kister polynomials [16] to derive the binary coefficients, A_k, and standard deviation, σ, between the observed and calculated quantities:

Table 4 Coefficients and standard deviations for excess molar volumes and changes of molar refraction on mixing. Binary systems at T=298.15 K

Coefficients	DMSO+water		DMSO+1,4-DIOXANE		DMSO+WATER+ +1,4-DIOXANE	
	V^E, $10^{-6}m^3mol^{-1}$	ΔR, $10^{-6}m^3mol^{-1}$	V^E, $10^{-6}m^3mol^{-1}$	ΔR, $10^{-6}m^3mol^{-1}$	V^E, $10^{-6}m^3mol^{-1}$	ΔR, $10^{-6}m^3mol^{-1}$
A0	-3.8264	-0.3679	-1.3339	-0.2449	-22.8351	-1.9693
A1	1.3438	-0.0305	-0.2614	-0.0821	-7.7350	-0.4168
A2	0.1426	0.0815	0.0079	-0.0611	-2.3061	-2.0049
A3	-0.3202	0.1833	0.0015	0.0366	5.4136	2.8996
A4	0.7828	-0.2069	-0.0746		-39.8483	-2.3964
A5			-0.1443		-20.1031	-2.9990
A6					-69.6860	-5.1973
A7					-84.2652	
A8					-74.7347	
A9					4.6162	
$\sigma, 10^{-6}m^3mol^{-1}$	0.0013	0.0013	0.0024	0.0009	0.0945	0.0186



a)



b)

Fig.1 Excess molar volume (a) and excess partial molar volume (b) vs. mole fraction of DMSO. Binary systems at T=298.15 K.

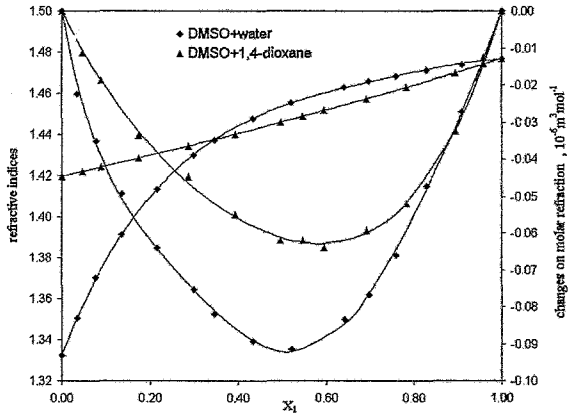


Fig.2 Refractive indices and changes of molar refraction on mixing vs. mole fraction of DMSO. Binary systems at T=298.15 K.

$$Z = X_i X_j \sum_k A_k (2X_i - 1)^{k-1} \quad (4)$$

$$\sigma = \left[\frac{\sum (Z_{exp} - Z_{calc})^2}{N_{exp} - N_{par}} \right]^{0.5} \quad (5)$$

where Z represents the experimental and calculated excess values (V^E or ΔR), N_{exp} is the number of experimental data and N_{par} is the number of parameters. No significant better standard deviation was obtained by trying various models to correlate the excess values. The parameters of the fitting equation (4) and the corresponding standard deviations are presented in Table 4.

We have also calculated excess partial molar volumes, $\overline{V}_i^E$, as follows:

$$\overline{V}_i^E = \overline{V}_i - V_i^0 \quad (6)$$

Table 5 Refractive indices, changes of molar refraction on mixing and refractive indices deviations calculated with several mixing rules. Ternary system at T=298.15 K

X_1	X_2	ρ 10^3, kg m^{-3}	n_D	ΔR 10^6, m^{3}mol^{-1}	Δn_D			
					L-L	G-D	A-B	EDW
0.0999	0.8001	1.0376	1.4242	-0.0208	-0.0005	-0.0004	-0.0043	-0.0008
0.1000	0.5998	1.0535	1.4358	-0.0433	-0.0011	-0.0010	-0.0075	-0.0016
0.0998	0.4001	1.0691	1.4480	-0.0548	-0.0015	-0.0014	-0.0091	-0.0021
0.1000	0.1999	1.0838	1.4602	-0.0686	-0.0020	-0.0018	-0.0088	-0.0026
0.1997	0.6000	1.0490	1.4300	-0.0238	-0.0007	-0.0005	-0.0088	-0.0013
0.1998	0.4020	1.0662	1.4420	-0.0721	-0.0021	-0.0019	-0.0123	-0.0029
0.2000	0.2001	1.0835	1.4572	-0.0371	-0.0011	-0.0009	-0.0118	-0.0021
0.1998	0.1000	1.0927	1.4632	-0.0876	-0.0028	-0.0025	-0.0136	-0.0038
0.3002	0.5999	1.0442	1.4220	-0.0518	-0.0016	-0.0013	-0.0121	-0.0025
0.3000	0.4000	1.0627	1.4364	-0.0459	-0.0015	-0.0012	-0.0143	-0.0025
0.3000	0.2000	1.0835	1.4508	-0.0947	-0.0032	-0.0028	-0.0187	-0.0046
0.2999	0.1002	1.0918	1.4582	-0.0908	-0.0032	-0.0028	-0.0175	-0.0044
0.3997	0.5001	1.0465	1.4200	-0.0526	-0.0018	-0.0015	-0.0149	-0.0028
0.4000	0.4002	1.0573	1.4275	-0.0659	-0.0023	-0.0020	-0.0173	-0.0035
0.4002	0.1998	1.0812	1.4436	-0.1085	-0.0040	-0.0036	-0.0233	-0.0057
0.3998	0.1002	1.0911	1.4522	-0.0979	-0.0038	-0.0034	-0.0226	-0.0054
0.5000	0.4001	1.0503	1.4170	-0.0744	-0.0028	-0.0025	-0.0201	-0.0042
0.5001	0.3000	1.0629	1.4256	-0.0863	-0.0034	-0.0031	-0.0231	-0.0049
0.5002	0.1998	1.0751	1.4348	-0.0850	-0.0035	-0.0032	-0.0246	-0.0051
0.4998	0.1002	1.0884	1.4440	-0.1030	-0.0044	-0.0040	-0.0272	-0.0062
0.5997	0.3002	1.0528	1.4130	-0.0728	-0.0032	-0.0029	-0.0236	-0.0047
0.6001	0.1997	1.0685	1.4232	-0.0857	-0.0039	-0.0036	-0.0281	-0.0057
0.6000	0.1000	1.0826	1.4352	-0.0529	-0.0025	-0.0023	-0.0282	-0.0044
0.7000	0.2001	1.0564	1.4082	-0.0582	-0.0030	-0.0027	-0.0278	-0.0047
0.6998	0.1000	1.0734	1.4200	-0.0590	-0.0032	-0.0030	-0.0310	-0.0050
0.8001	0.1500	1.0466	1.3928	-0.0388	-0.0024	-0.0022	-0.0269	-0.0039
0.7990	0.0500	1.0645	1.4042	-0.0569	-0.0037	-0.0039	-0.0299	-0.0049
0.9000	0.0500	1.0366	1.3732	-0.0377	-0.0029	-0.0031	-0.0223	-0.0036
0.9000	0.0250	1.0407	1.3765	-0.0331	-0.0026	-0.0031	-0.0213	-0.0030

where $\overline{V_i}$ represents the partial molar volumes and V_i^0 the molar volumes of the pure components.

The curves of excess molar volumes (eq.1), of excess partial molar volumes and of changes of molar refraction on mixing (eq.2) are given in Figs. 1 and 2; Fig.2 contants also the refractive index as function of mole fraction. The values of V^E are negative for both binary systems, the magnitude of minimum value of V^E observed in the case of DMSO+water is approximately three times larger than that observed in DMSO+1,4-dioxane mixture. The excess partial molar volumes of components are mostly negative and decrease with X_i, for both systems. Negative excess volumes are characteristic of polar nonelectrolyte mixtures.

The negative ΔR values for binary systems vary almost identically throughout the composition scale with the values of V^E. The ΔR for DMSO+water system is greater than ΔR for DMSO+1,4-dioxane system. More negative V^E, $\overline{V_i}^E$ and ΔR observed for DMSO+water mixture compared to those for DMSO+1,4-dioxane is supported by the published results refering to η^E and G^E of the mixtures [2-4].

Negative values of V^E, $\overline{V_i}^E$ and ΔR suggest the presence of specific interactions between the mixing components. Because of three distinctive functional groups, DMSO is capable to exhibit intra and intermolecular interactions. The main effect in DMSO+water system is the strong H-bonding between DMSO and water, reflected by the negative values of V^E. Smaller negative values of V^E for DMSO+1,4-dioxane are due to unlike dipole-dipole interactions between SO groups of DMSO and O group of 1,4-dioxane. The addition of 1,4-dioxane (dipole moment μ = 0.4 D) to the DMSO (μ = 4.06 D) tends to destroy the strong polar type interaction between DMSO molecules.

Our studies agree with other studies in the literature [6] for DMSO+water system.

Several methods to predict refractive indices of mixtures were applied to test their validity in high polar mixtures. The refractive indices were predicted by mixing rules proposed in literature [17,18]. The results are presented in Table 3. It can be seen from this Table that for these binary systems, the Lorentz-Lorenz mixing rule was the most suitable; the Arago-Biot mixing rule gave in both cases poor predictions of the refractive index. A close similarity was observed between the Lorentz-Lorenz and Gladstone-Dale relations.

Ternary Systems

Experimental densities, refractive indices and changes of molar refraction of mixing are given in Table 5.

Excess molar volumes and changes of molar refraction of mixing were fitted using equation (7):

$$Z = X_1X_2X_3[A_0 + A_1(X_1 - X_2) + A_2(X_1 - X_3) + A_3(X_2 - X_3) + A_4(X_1 - X_2)^2 + A_5(X_1 - X_3)^2 + A_6(X_2 - X_3)^2 + ...] \quad (7)$$

where Z represents V^E or ΔR.

The results of fitting equation (7), parameters and standard deviations, are given in Table 4. The values of ΔR are negative over the entire composition range. The binary mixtures DMSO+water, DMSO+1,4-dioxane present negative ΔR values with a minimum of –0.09 cm^3mol^{-1} and –0.064 cm^3mol^{-1}, respectively. The ΔR values of ternary system are also negative with a minimum of - 0.136 cm^3mol^{-1}. The values of ternary V^E, reported previously [5], are likewise negative for all compositions.

The predictive mixing rules for the refractive indices were used. The differencies between the experimental and calculated values (Δn_D in Table 5) show that the better results were obtained by Lorentz-Lorenz and Gladstone-Dale equations.

Conclusion

Excess values of molar volumes, partial molar volumes and molar refraction supported by earlier reported properties indicate the presence of molecular interactions in binary and ternary studied systems. Lorentz-Lorenz and Gladstone-Dale mixing rules for refractive indices lead to the best results.

Acknowledgements

This work was financed by CNCSIS (National Council for Academic Scientific Research ROMANIA) grant.

SYMBOLS

A_k	coefficients in Redlich-Kister equation
G^E	excess Gibbs free energy
k	degree of the Redlich-Kister polynomials
M_i	molar mass of component i
N_{exp}	number of experimental points
N_{par}	number of parameters in Redlich-Kister equation
n_D	refractive index
R_i	molar refractivity of component i
R	molar refractivity of mixture
ΔR	changes of molar refractivity on mixing
V_i^0	molar volume of the pure components i
V^E	excess molar volume
$\overline{V}_i$	partial molar volume of component i
$\overline{V}_i^E$	excess partial molar volume of component i
V	molar volume of mixture
X_i	mole fraction of component i
Z	experimental and calculated excess values for V^E or ΔR

Greek Letters

ρ_i^0	density of pure component i
ρ	density of mixture
η^E	excess viscosity
μ	dipole moment
σ	standard deviation

REFERENCES

1. IULIAN O., JINESCU G., ILIUTA M. and HAMPLEA L., Hung.J.Ind.Chem., *1994*, 22(2), 95-100
2. IULIAN O., MATEESCU C. and ILIUTA M.: Rev.Roum.Chim., *1995*, 40(3), 235-239
3. IULIAN O., HAMPLEA L. and JINESCU G., Hung.J.Ind.Chem.: *1997*, 25(4), 249-253
4. LANDAUER O., MATEESCU C., IULIAN O., ILIUTA M., HAMPLEA L.: Rev.Chim. (Bucharest), *1993*, 44, 26-30
5. ILIUTA M., IULIAN O. and OMOTA L.M., ELDATA: Int.Electron.J.Phys.-Chem.Data, *1998*, 4, 121-128
6. AMINABHAVI T.M. and GOPALAKRISHNA B.: J.Chem.Eng.Data, *1995*, 40, 856-861
7. LE BEL R.G. and GORING D.A.: J.Chem.Eng.Data, *1962*, 7, 100-101
8. RIDDICK J.A., BUNGER W.B. and SAKANO T.K.: Techniques of Chemistry, vol. II, Organic Solvents, 4th Ed. John Wiley & Sons, New York, 1986
9. ARCE A., AGEITOS J.M., MENDOZA J. and SOTA A.: J.Chem.Eng.Data, *1995*, 40, 647-649
10. LIDE D.R.: CRC Handbook of Physics and Chemistry, 78th Ed. CRC Press, Florida, 1997
11. ARCE A., BLANCO A., SOTO A. and VIDAL I.: J.Chem.Eng.Data, *1993*, 38, 336-340
12. ARALAGUPPI M., AMINABHAVI T.M., HAROGOPPAD S.B. and BALUNDGI R.H.: J.Chem.Eng.Data, 1992, 37, 298-303
13. TIEMERMANS J.: Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950
14. SAKURAI M.: J.Chem.Eng.Data, *1992*, 37, 492-496
15. ACEVEDO I.J., PEDROSA G.C. and KATZ M.: Can.J.Chem., *1991*, 69, 1906-1910
16. REDLICH O. and KISTER A.T.: Ind.Eng.Chem., *1948*, 40, 345-348
17. TASIC A.Z., DJORDJEVIC B.D. and GROZDANIC D.K.: J.Chem.Eng.Data, *1992*, 37, 310-313
18. 18. BOTTCHER C.J.F.: Theory of Electric Polarization, Elsevier, Amsterdam, 1952