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Densities and excess volumes of benzene with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K

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Abstract

Densities of the binary systems of benzene with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene have been measured as a function of the composition, at 298.15 K and atmospheric pressure, using an Anton Paar model DMA 5000 oscillating U-tube densitometer. The calculated excess volumes were correlated with the Redlich–Kister equation and with a series of Legendre polynomials. The excess volumes are positive for all the systems reported here.

Keywords: Densities; Excess volumes; Monomers; Acrylates; Benzene

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1. Introduction

The mixing of different compounds gives rise to properties such as volumes, enthalpies and entropies of mixing, which reflect the extent of the deviations from non-ideality. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and industrially important monomers, in particular the influence of the chemical structure of the solute in the systems under consideration.

Sastry and Dave measured the excess volumes, isentropic compressibilities, and dielectric behavior of 15 binary mixtures of alkyl (methyl, ethyl, and butyl) methacrylate with hexane, heptane, carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene at 308.15 K and found that with aliphatic hydrocarbons the results were controlled by dispersing interactions while with chlorinated solvents the controlling factors were specific interactions (O–Cl and n–π types) [1,2]. Sastry and Valand also measured the excess volumes of mixtures of alkyl (methyl, ethyl, and butyl) acrylates in several alkanols at 298.15 and 308.15 K, and found that they were always positive. These results were explained on the basis of non-specific interactions between the components [3]. Sastry et al. [4] measured the excess volumes of methyl methacrylate (MMA) and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and (*o*, *m*, *p*)-xylenes, at 298.15 and 303.15 K and found that except for benzene all presented positive excess volumes. The excess volume curve for the system benzene + MMA showed a non-symmetric behavior with a

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Table 1
Purity and densities of pure components at 298.15 K

Component	Purity (mass%)	Density ($g\,cm^{-3}$)	
		Measured	Literature
Benzene (1)	99.9	0.873598	0.87370 [10]
BA (2)	99+	0.893666	0.8941 [3]
EA (3)	99	0.925930	0.9163 [3]
MMA (4)	99	0.937669	0.93766 [11]
Styrene (5)	99	0.901972	0.9016 [10]

maximum of $V^E \approx 0.19\,cm^3\,mol^{-1}$ at about $x_{MMA} = 0.40$.

No literature data are available on the excess volumes of the systems with alkyl acrylates analyzed in this work.

2. Experimental

2.1. Materials

Benzene (HPLC grade, 99.9 + mass%) was purchased from Baker, ethyl acrylate, EA (99 + mass%), butyl acrylate, BA (99+mass%), MMA (99+mass%), and styrene (99 mass%), were purchased from Aldrich. EA, BA, and MMA were vacuum distilled previous to use to eliminate the stabilizer (about 0.002 mass% of hydroquinone monomethyl ether). Styrene, containing 10–15 ppm of 4-*tert*-butylcatechol as stabilizer, was not distilled to avoid polymerization but was degassed by freezing and heating. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with the values reported in the literature (Table 1).

2.2. Density measurements

The density of the samples was measured with an Anton Paar model DMA 5000 oscillating U-tube densitometer, provided with automatic viscosity correction, two integrated Pt 100 thermometers (DKD traceable), and a stated accuracy of $5 \times 10^{-6}\,g\,cm^{-3}$. The temperature in the cell was regulated to ±0.001 K with a solid-state thermostat. The apparatus was calibrated once a day with dry air and bi-distilled freshly degassed water.

All liquids were boiled or heated to remove dissolved air. Solutions of different compositions were prepared by mass in a $10\,cm^3$ rubber-stoppered vial to prevent evaporation, using a Mettler AG 204 balance accurate to $\pm 10^{-4}$ g. To minimize the errors in composition, the heavier component was charged first and the sample kept in ice water. Accuracy in the mole fraction is 5×10^{-5}, of the density (duplicate) measurement $\pm 2 \times 10^{-6}\,g\,cm^{-3}$, and of the temperature ±0.002 K.

Proper safety measures were taken when handling all the materials, particularly benzene, a possible carcinogenic material.

3. Results and discussion

At least 21 density measurements were performed (with repetition) for each binary system, in the full concentration range ($0 \leq x \leq 1$).

The excess volumes V^E of the solutions of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = \left[\frac{xM_1 + (1-x)M_2}{\rho}\right] - \left[\frac{xM_1}{\rho_1} + \frac{(1-x)M_2}{\rho_2}\right] \qquad (1)$$

where ρ, ρ_1, and ρ_2 are the densities of the solution and pure components 1 and 2, respectively, and M_1 and M_2 the molar masses of the pure components. The corresponding values of ρ and V^E are reported in Tables 2–5 and Fig. 1. The values of V^E were correlated with composition using the following two procedures:

(a) The Redlich–Kister expression [5]:

$$V^E = x_1 x_2 \sum_{k=0}^{N} A_k (x_1 - x_2)^k \qquad (2)$$

where the A_k's are the adjustable parameters of the model.

The Redlich–Kister regressor is very powerful and frequently used to correlate vapor–liquid equilibrium data and excess properties. Notwithstanding, it suffers from the important drawback that

Table 2
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system benzene (1) + BA (2) at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$ cm^3 mol^{-1})	V^E ($\times 10^2$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})[a]
0.0000	0.893938	1.4338	0.0000	0
0.0561	0.893158	1.4036	0.8421	1
0.1014	0.892512	1.3792	1.3785	−1
0.1497	0.891789	1.3532	2.0803	−2
0.2002	0.890981	1.3260	3.1414	0
0.2511	0.890123	1.2987	4.3419	2
0.2994	0.889291	1.2727	5.2597	2
0.3499	0.888392	1.2455	6.0964	1
0.4001	0.887465	1.2185	6.8329	−2
0.4502	0.886505	1.1915	7.4969	−4
0.5007	0.885454	1.1644	8.6544	0
0.5509	0.884405	1.1373	9.2308	0
0.6005	0.883317	1.1106	9.8072	2
0.6498	0.882227	1.0840	9.8318	1
0.7001	0.881098	1.0568	9.3927	−1
0.7498	0.879918	1.0299	8.9987	0
0.8003	0.878707	1.0026	8.0293	0
0.8500	0.877475	0.9756	6.7637	0
0.9001	0.876223	0.9484	4.8522	−1
0.9499	0.874924	0.9213	2.7458	0
1.0000	0.873598	0.8940	0.0000	0

[a] $\delta V^E = V^E_{\text{expt}} - V^E_{\text{calc}}$.

Table 3
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system benzene (1) + EA (3) at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$ cm^3 mol^{-1})	V^E ($\times 10^2$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})[a]
0.0000	0.915930	10.931	0	0
0.0253	0.915005	10.881	0.5266	−2
0.0506	0.914072	10.831	1.0830	−2
0.1000	0.912218	10.734	2.1630	−3
0.1538	0.910159	10.628	3.3996	3
0.2019	0.908298	10.533	4.3524	−2
0.2501	0.906397	10.438	5.2864	−3
0.3003	0.904384	10.339	6.2452	5
0.3496	0.902390	10.242	6.9628	2
0.4003	0.900310	10.142	7.5749	0
0.4500	0.898243	10.043	8.0210	−2
0.5012	0.896081	9.941	8.3519	2
0.5502	0.893990	9.844	8.4465	1
0.6002	0.891840	9.744	8.2782	−6
0.6498	0.889670	9.645	8.0624	2
0.7001	0.887449	9.545	7.5247	−1
0.7498	0.885223	9.445	6.8488	3
0.8001	0.882953	9.344	5.8419	−3
0.8500	0.880662	9.243	4.6985	−2
0.9002	0.878324	9.142	3.3854	5
0.9500	0.875981	9.041	1.7951	2
0.9751	0.874795	8.990	0.8732	−3
1.0000	0.873598	8.940	0	0

[a] $\delta V^E = V^E_{\text{expt}} - V^E_{\text{calc}}$.

Table 4
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system benzene (1) + MMA (4) at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$ cm^3 mol^{-1})	V^E ($\times 10^2$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})[a]
0	0.937608	1.0678	0	0
0.0250	0.936121	1.0636	1.5885	1
0.0502	0.934656	1.0594	2.7431	−2
0.1007	0.931623	1.0509	5.6072	0
0.1500	0.928664	1.0425	7.8901	1
0.1999	0.925639	1.0341	10.0187	2
0.2503	0.922595	1.0255	11.4459	−2
0.3007	0.919473	1.0169	13.1309	0
0.3502	0.916423	1.0084	14.1232	−2
0.4000	0.913267	0.9998	15.4069	2
0.4508	0.910063	0.9911	16.0382	1
0.5003	0.906908	0.9825	16.3547	1
0.5504	0.903696	0.9738	16.2850	−1
0.6004	0.900452	0.9651	16.0046	−1
0.6502	0.897175	0.9564	15.5519	0
0.7001	0.893879	0.9476	14.6529	0
0.7500	0.890556	0.9388	13.3882	1
0.7999	0.887200	0.9300	11.7608	1
0.8499	0.883845	0.9210	9.3850	−1
0.9000	0.880446	0.9121	6.7781	−1
0.9499	0.877033	0.9031	3.7060	0
0.9753	0.875288	0.8985	1.9163	0
1	0.873598	0.8940	0	0

[a] $\delta V^E = V^E_{\text{expt}} - V^E_{\text{calc}}$.

the values of the adjustable parameters change as the number of terms in the series is increased.

(b) A series of Legendre polynomials $L_k(x_1)$:

$$V^E = x_1 x_2 \sum_{k=0}^{N} a_k L_k(x_1) \tag{3}$$

which for the first three terms ($k = 0, 1, 2$) is

$$V^E = x_1 x_2 [a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1)] \tag{4}$$

Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, and

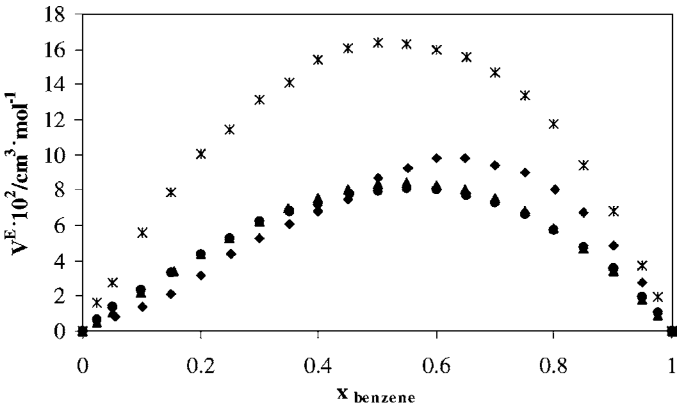

Fig. 1. Excess volumes at 298.15 K: (∗) benzene + MMA; (●) benzene + EA; (◆) benzene + BA; (▲) benzene + styrene.

Table 5
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system benzene (1) + styrene (5) at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$ cm^3 mol^{-1})	V^E ($\times 10^2$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})[a]
0	0.901972	1.1547	0	0
0.0254	0.901363	1.1481	0.6117	0
0.0519	0.900708	1.1413	1.3847	2
0.1002	0.899532	1.1288	2.3619	0
0.1503	0.898287	1.1158	3.3177	−1
0.2009	0.896993	1.1028	4.3681	−1
0.2499	0.895722	1.0901	5.2399	−1
0.3001	0.894385	1.0771	6.2052	1
0.3501	0.893049	1.0641	6.8206	0
0.4001	0.891693	1.0511	7.2530	−1
0.4519	0.890248	1.0377	7.7845	1
0.5002	0.888896	1.0251	7.9194	0
0.5506	0.887450	1.0120	8.0728	0
0.6000	0.886017	0.9991	7.9878	0
0.6502	0.884537	0.9860	7.7174	0
0.7005	0.883030	0.9728	7.2783	0
0.7502	0.881517	0.9598	6.6660	0
0.7997	0.880001	0.9468	5.7369	−1
0.8506	0.878396	0.9334	4.7774	0
0.8998	0.876827	0.9205	3.5557	1
0.9499	0.875216	0.9073	1.9713	1
0.9751	0.874400	0.9006	1.0646	1
1	0.873598	0.8940	0	0

[a] $\delta V^E = V^E_{\mathrm{expt}} - V^E_{\mathrm{calc}}$.

> Chebyshev, which have the important characteristic that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series is increased. This is an important property because if a physical explanation can be assigned to one of its coefficients, its value remains constant. For the case of discrete measurements, such as determination of volumes of mixing, the values of the coefficients will vary, but slightly.

In addition, as shown in Table 6, the series of Legendre polynomials have the important characteristic that the structure of its first four terms is the same as that of the first four terms of the Redlich–Kister expression.

Eqs. (2) and (3) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{1}^{N} (V^E_{i,\mathrm{expt}} - V^E_{i,\mathrm{calc}})^2 \tag{5}$$

where N is the number of observations. The values of the different adjustable parameters, A_k and a_k, are reported in Tables 7 and 8 for different values of k,

Table 6
Expressions for Legendre polynomials and the Redlich–Kister expression

Polynomial order, k	L_k (see Eq. (3))	Redlich–Kister (see Eq. (2))
0	1	1
1	$2x_1 - 1$	$2x_1 - 1$
2	$6(x_1^2 - x_1 + \frac{1}{6})$	$4(x_1^2 - x_1 + \frac{1}{4})$
3	$20(x_1^3 - \frac{3}{2}x_1^2 + \frac{3}{5}x_1 - \frac{1}{20})$	$8(x_1^3 - \frac{3}{2}x_1^2 + \frac{3}{4}x_1 - \frac{1}{8})$
4	$70(x_1^4 - 2x_1^3 + \frac{9}{7}x_1^2 - \frac{2}{7}x + \frac{1}{70})$	$16(x_1^4 - 2x_1^3 + \frac{3}{2}x_1^2 - \frac{1}{2}x + \frac{1}{16})$

Table 7
Coefficients A_k (Eq. (2)), standard deviation s (Eq. (6)), Durbin–Watson statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	$A_0 \times 10$	$A_1 \times 10^2$	$A_2 \times 10^3$	$A_3 \times 10^2$	$s \times 10^3$	d[a]	$(V^E)_{x=0.5}$ (cm^3 mol^{-1})	$\bar{V}_1^{E,\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{E,\infty}$ (cm^3 mol^{-1})
1 + 2	3.447	27.30	15.95	−4.74	1.6	1.43	0.0862	0.1351	0.5863
1 + 3	3.317	8.01	−39.7		0.3	2.45	0.0833	0.2086	0.3776
1 + 4	6.517	9.15	55.1		1.1	2.37	0.1629	0.6153	0.7983
1 + 5	3.180	6.60	7.27	2.496	0.7	1.73	0.0795	0.2344	0.4162

[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})^2 / \sum_{u=1}^{N} e_u^2$, $e_u = V_{u,\text{calc}}^E - V_{u,\text{expt}}^E$.

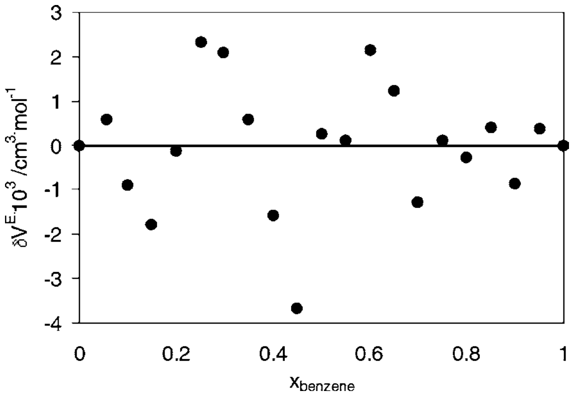

Fig. 2. Residual distribution plot for the system benzene + BA according to the fit given in Table 6.

together with the pertinent statistics. The standard deviation s was calculated as

$$s = \left[\frac{\sum (V_{i,\text{expt}}^E - V_{i,\text{calc}}^E)^2}{N - k}\right]^{1/2} \tag{6}$$

where k is the number of adjustable parameters. The statistical significance of adding one or more terms after the third was examined using a χ^2-based test, coupled to the requirement that the residues be randomly distributed, as suggested by Wisniak and Polishuk [6]. It was not deemed necessary to perform a step-wise regression.

The values of the function V^E/x_1x_2 at infinite dilution represent the values of the partial excess volume at infinite dilution, $\bar{V}_i^{E,\infty}$ [7] and can be calculated from the adjustable parameters as follows:

(a) Redlich–Kister:

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - \cdots = \bar{V}_1 - V_1^0 \tag{7}$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + \cdots = \bar{V}_2 - V_2^0 \tag{8}$$

(b) Legendre:

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - \cdots = \bar{V}_2 - V_2^0 \tag{9}$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + \cdots = \bar{V}_2 - V_2^0 \tag{10}$$

where V_i^0 is the molar volume of pure component i. The pertinent values of $\bar{V}_i^{E,\infty}$ are also shown in Tables 6 and 7. Eqs. (7) and (8) or (9) and (10) yield the same values of $\bar{V}_i^{E,\infty}$.

Fig. 2 shows a typical distribution of the residuals, which is random as declared by the Durbin–Watson statistic.

Inspection of the results of Tables 2–5 and Fig. 1 indicates that the excess volumes for the four systems

Table 8
Coefficients a_k (Eq. (3)), standard deviation s (Eq. (6)), Durbin–Watson statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	$a_0 \times 10$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$s \times 10^3$	d[a]	$(V^E)_{x=0.5}$ (cm^3 mol^{-1})	$\bar{V}_1^{E,\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{E,\infty}$ (cm^3 mol^{-1})
1 + 2	3.500	24.46	1.063	−1.896	1.6	1.43	0.0863	0.1351	0.5863
1 + 3	3.199	8.01	−2.65		0.3	2.45	0.0833	0.2134	0.3736
1 + 4	6.700	9.15	3.67		1.1	2.37	0.1630	0.6153	0.7983
1 + 5	3.204	8.092	0.485	0.999	0.8	1.73	0.0795	0.2344	0.4162

[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})^2 / \sum_{u=1}^{N} e_u^2$, $e_u = V_{u,\text{calc}}^E - V_{u,\text{expt}}^E$.

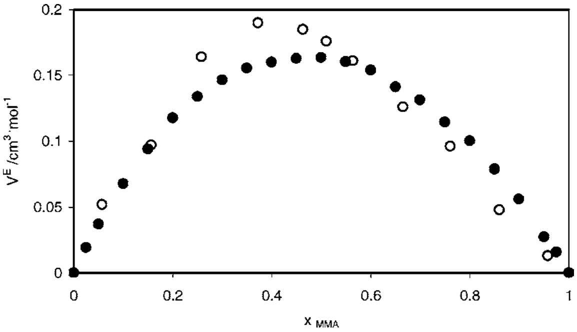

Fig. 3. Comparison of the results for the system MMA + toluene: (●) this work; (○) Sastry et al. [4].

studied here are positive for the whole composition range. As shown in Fig. 3, the results for the system benzene + MMA obtained in this work are very similar to those of Sastry et al. [4]. The difference may be attributed to the fact that Sastry et al. used MMA as purchased, with the stabilizer, and here the monomer was freshly distilled before the measurements. In addition, the small difference between the two sets of results may also be due to the difference in the experimental equipment (pyknometer against oscillating U-tube densitometer), and the background error.

As regards to the symmetry of the excess function, Fig. 1 shows that the function $V^E(x)$ is symmetric only for the system benzene + MMA indicating that the maximum specific interaction occurs at about equimolar composition, with $(V^E)_{x=0.5} \approx 0.165\,\mathrm{cm^3\,mol^{-1}}$. For the other three systems the minimum of the curve deviates slightly to the right of $x = 0.5$, pointing to a small amount of self-association of the solute (monomer).

The sign and intensity of the volume changes that take place during mixing is the result of several effects that operate in the same or opposite directions. The most important ones are: (a) a positive one due to the break-up of the structure of one or both components (originating from non-chemical or chemical interactions such as hydrogen bonding or complex-forming interactions such as self-association) and (b) a negative one due to physical interactions (for example, heteroassociation) or geometric fitting of one component into the second, leading to a more compact packing (interstitial accommodation). The second contribution becomes more and more important with increasing sphericicity of the solute molecule and higher molar volume of the solvent [9].

Structurally benzene may be considered the homomorph of cyclohexane, aprotic, and non-polar. Interactions between a polar component and an aromatic compound such as benzene is considered to occur via complex formation between the two species, or n–π interaction [8].

The magnitude and sign of V^E is a reflection of the type of interactions taking place in the mixture. This is very well exhibited by the mixtures studied here, with the maximum value of V^E ranging from about $+0.08$ to $+0.17\,\mathrm{cm^3\,mol^{-1}}$. The V^E curves are positive, their relative intensity depending on the nature of the solute (monomer) and the solvent. The overall magnitude of V^E is a result of the effect of breaking the ester's dipole–dipole association being larger than a net packing effect contributed by structural effects arising from interstitial accommodation. n–π interactions between an aromatic hydrocarbon (such as benzene and styrene) and an ester are much stronger than those between a cyclic hydrocarbon (such as cyclohexane) and an ester. As shown in Fig. 1, the system benzene + styrene presents the smallest expansion effect. This fact is a result of the inductive effect of the vinyl group in styrene enhancing the electron density of its ring and the electrostatic interaction with the benzene ring. This packing effect decreases the break-up of the structure of the components.

Anyhow, it is clear that there is a substantial difference in packing of benzene with the esters and with styrene. The value of $(V^E)_{x=0.5}$ for the latter is about two times smaller than that for MMA.

References

[1] N.V. Sastry, P.N. Dave, Int. J. Thermophys. 17 (1996) 1289–1304.
[2] N.V. Sastry, P.N. Dave, Proc. Indian Acad. Sci. (Chem. Sci.) 109 (1997) 211–220.
[3] N.V. Sastry, M.K. Valand, Phys. Chem. Liq. 3 (2000) 61–72.
[4] N.V. Sastry, S.R. Patel, M.C. Patel, J. Chem. Thermodyn. 3 (1999) 797.
[5] O. Redlich, A.T. Kister, Ind. Eng. Chem. 4 (1948) 345–351.
[6] J. Wisniak, A. Polishuk, Fluid Phase Equilibria 16 (1999) 61–82.

[7] H.C. Van Ness, M.M. Abbott, Classical Thermodynamics of Nonelectrolyte Solutions, McGraw-Hill, New York, 1982.

[8] S.C. Sharma, R. Kaur, J. Singh, J. Chem. Thermodyn. 2 (1992) 1171–1174.

[9] R. Tanaka, M. Adachi, J. Chem. Thermodyn. 23 (1991) 1023–1027.

[10] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Techniques of Chemistry, vol. II, 4th ed., Wiley/Interscience, New York, 1991.

[11] L. Beichen, S.E.M. Hamam, B.C.-Y. Lu, J. Chem. Thermodyn. 18 (1986) 1043–1046.