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TEMPERATURE DEPENDENCE OF THERMOPHYSICAL PROPERTIES OF OCTANE+1-BUTANOL SYSTEM

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Abstract

The aim of this work is to complete our studies on physical properties of binary mixtures of alkane+1-alkanols. This work reports densities, refractive indices, speeds of sound and isentropic compressibilities of the mixture octane + 1-butanol at different temperatures, from 288.15 to 308.15 K. From the experimental values, the corresponding excess and deviation values were computed (excess molar volumes, changes of refractive index on mixing, changes of speed of sound on mixing and changes of isentropic compressibilities on mixing). The results were fitted to variable-degree polynomials. Excess molar volumes were compared with the predictions of Nitta–Chao Group Contribution Model.

Keywords: excess molar volume, octane + 1-butanol, refractive index, speed of sound

Introduction

Continuing a series of theoretical and experimental works on binary mixtures alkane+1-alkanol, refractive indices, speed of sound and isentropic compressibilities of the binary mixtures of hexane and octane + (1-butanol, 1-hexanol and 1-octanol), at 298.15 K and atmospheric pressure, were published [1, 2]. Recently, a study of the variation of these properties with temperature was performed [3, 4]. As a continuation, this paper reports densities (ρ), refractive indices (n_D), and speeds of sound (u) and the corresponding derived values of octane with 1-butanol, which were measured at the temperatures of 288.15, 293.15, 303.15 and 308.15 K and atmospheric pressure, over the whole range of composition. Values of excess molar volumes for this mixture were found in literature [5, 6] at 298.15 and 303.15 K as well as speeds of sound [7] at 293.15 K and refractive index [8] at 298.15 K.

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Experimental

Octane employed was supplied by Fluka and 1-butanol by Merck. Their mole fraction purities were: octane (>0.995) and 1-butanol (>0.995). These values were checked by gas-liquid chromatography, being in accordance with vendor specifications. The substances were degassed and dried over molecular sieves (Union Carbide, type 0.4 nm). Precautions such as cooling chemicals before sample preparation and minimizing empty space in vessels were taken, in order to avoid evaporation losses during manipulations and then possible errors in calculations.

The refractive index was measured with an automatic refractometer ABBEMAT-HP Dr. Kernchen, with a precision of $\pm 10^{-5}$. In order to keep a constant temperature, the refractometer was thermostated using a PolyScience controller bath model 9510 with a temperature stability of $\pm 10^{-2}$ K. Triply distilled water and air were used for refractometer calibration.

The density and speed of sound of the mixtures and pure liquids were measured with an Anton Paar DSA-48 densimeter and sound analyzer with a precision of $\pm 5 \cdot 10^{-5}$ g cm^{-3} and $\pm 10^{-1}$ m s^{-1}, respectively. The density measuring cell is thermostated with a temperature stability of $\pm 10^{-2}$ K. The apparatus calibration was performed periodically. Triply distilled water was used for calibrating the speed of sound cell. The experimental techniques and operation mode have been described previously [1]. The samples were prepared by mass using a Mettler AE-240 balance with a precision of $\pm 1 \cdot 10^{-4}$ in mole fraction, covering the whole composition range of the mixture.

Results and discussion

Densities, refractive indices and speeds of sound at different temperatures of the pure component liquids are listed in Table 1, together with literature values. The experimental results of refractive index, n_D, at all studied temperatures, are reported in Table 2.

The experimental results of density, ρ, speed of sound, u, and calculated isentropic compressibility, κ_S ($\kappa_S=\rho^{-1}u^{-2}$), are reported in Table 3.

The values of excess molar volumes, were computed using the following equation:

$$V_m^E=\sum_{i=1}^{2} x_i M_i (\rho^{-1}-\rho_i^{-1}) \quad (1)$$

where x is the mole fraction, M the molecular mass, and the corresponding quantities with subscript i referring to pure chemicals.

Changes of refractive index on mixing Δn_D, changes of speed of sound on mixing Δu, and changes of isentropic compressibility on mixing $\Delta\kappa_S$, were evaluated for each composition value, using the following equation:

$$\Delta Q=Q-\sum_{i=1}^{2} x_i Q_i \quad (2)$$

Table 1 Comparison of the density, ρ, refractive index, n_D, and speed of sound, u, of the pure liquids with the available literature data at different temperatures

Compound	T/K	ρ/g cm^{-3}		n_D		u/m s^{-1}	
		exp.	lit.	exp.	lit.	exp.	lit.
Octane	288.15	0.7065	0.70654[a]	1.39937	1.40009[b]	1213	1213.9[b]
	293.15	0.7025	0.70252[c]	1.39755	1.39743[c]	1193	1188.6[d]
	298.15	0.6985	0.69850[e]	1.39510	1.39505[c]	1172	1172[f]
	303.15	0.6944	0.6945[g]	1.39210	1.39196[g]	1152	1151.6[g]
	308.15	0.6904	0.6904[g]	1.38963	1.39052[g]	1131	1132.9[g]
1-Butanol	288.15	0.8132		1.40147		1273	
	293.15	0.8094	0.80965[d]	1.39922	1.3993[c]	1257	1258.8[d]
	298.15	0.8058	0.80580[h]	1.39719	1.39716[h]	1240	1240[i]
	303.15	0.8018	0.80190[j]	1.39510	1.3947[k]	1223	1223[j]
	308.15	0.7979	0.7979[k]	1.39314	1.3927[k]	1206	1208[l]

[a]Ref. [9], [b]Ref. [10], [c]Ref. [11], [d]Ref. [7], [e]Ref. [12], [f]Ref. [13], [g]Ref. [14], [h]Ref. [15],. [i]Ref. [16],. [j]Ref. [17], [k]Ref. [18], [l]Ref. [19].

In these equations, $Q = n_D$, u or κ_S and ΔQ is the change on mixing property (Δn_D, Δu or $\Delta\kappa_S$). The excess molar volumes and change on mixing properties values are given in Tables 2 and 3.

Uncertainty in the changes on mixing was estimated to be better than $\pm 2 \cdot 10^{-5}$ for the refractive index, ± 1.1 m s^{-1} for the speed of sound, ± 2.7 TPa^{-1} for the isentropic compressibilities and $\pm 2 \cdot 10^{-2}$ cm^3 mol^{-1} for excess molar volume.

The values were correlated by means of the Redlich–Kister equation [20] for every binary mixture:

$$\Delta Q = x(1-x)\sum_{p=0}^{M} A_p (2x-1)^p \quad (3)$$

Table 2 Refractive indices, n_D, and changes of refractive indices on mixing, Δn_D, for x octane + (1–x) 1-butanol at different temperatures

x	n_D	Δn_D	x	n_D	Δn_D
	T=288.15 K			T=293.15 K	
0.0474	1.40130	–0.00007	0.0474	1.39903	–0.00011
0.0990	1.40115	–0.00011	0.0990	1.39874	–0.00031
0.1978	1.40081	–0.00024	0.1978	1.39830	–0.00059
0.2991	1.40050	–0.00034	0.2991	1.39797	–0.00075
0.4059	1.40020	–0.00042	0.4059	1.39772	–0.00082
0.4989	1.40000	–0.00042	0.4989	1.39757	–0.00082
0.6004	1.39980	–0.00041	0.6004	1.39750	–0.00072
0.6980	1.39965	–0.00035	0.6980	1.39748	–0.00057
0.7988	1.39954	–0.00025	0.7988	1.39748	–0.00041
0.8993	1.39948	–0.00010	0.8993	1.39747	–0.00025
0.9418	1.39944	–0.00005	0.9418	1.39750	–0.00015
	T=303.15 K			T=308.15 K	
0.0474	1.39500	–0.00021	0.0474	1.39266	–0.00031
0.0990	1.39444	–0.00060	0.0990	1.39220	–0.00059
0.1978	1.39380	–0.00092	0.1978	1.39144	–0.00101
0.2991	1.39330	–0.00108	0.2991	1.39088	–0.00121
0.4059	1.39290	–0.00114	0.4059	1.39033	–0.00139
0.4989	1.39264	–0.00109	0.4989	1.39007	–0.00132
0.6004	1.39242	–0.00098	0.6004	1.38988	–0.00115
0.6980	1.39225	–0.00083	0.6980	1.38975	–0.00094
0.7988	1.39223	–0.00053	0.7988	1.38972	–0.00062
0.8993	1.39221	–0.00022	0.8993	1.38968	–0.00030
0.9418	1.39218	–0.00011	0.9418	1.38965	–0.00018

Table 3 Densities, ρ, speeds of sound, u, isentropic compressibilities, κ_S, excess molar volumes, V_m^E, changes of speeds of sound on mixing, Δu, and changes of isentropic compressibilities on mixing, $\Delta\kappa_S$, for x octane + (1–x) 1-butanol at different temperatures

x	ρ/g cm^{-3}	u/m s^{-1}	κ_S/TPa^{-1}	V_m^E/cm^3 mol^{-1}	Δu/m s^{-1}	$\Delta\kappa_S$/TPa^{-1}
			T=288.15 K			
0.0500	0.8041	1264.9	777.3	–0.001	–5.1	8.3
0.0992	0.7953	1257.2	795.5	0.057	–9.8	16.6
0.2039	0.7791	1243.8	829.7	0.104	–17.0	29.5
0.2930	0.7669	1234.8	855.2	0.160	–20.7	37.0
0.4038	0.7537	1225.9	882.9	0.202	–23.0	42.3
0.5044	0.7431	1219.7	904.5	0.245	–23.2	43.5
0.6135	0.733	1214.7	924.7	0.269	–21.8	41.6
0.7053	0.7255	1211.8	938.6	0.261	–19.1	36.9
0.8058	0.7182	1210.4	950.4	0.219	–14.6	28.4
0.8791	0.7133	1210.1	957.4	0.188	–10.5	20.5
0.9299	0.7103	1210.5	960.8	0.121	–7.1	13.6
			T=293.15 K			
0.0498	0.8001	1248.0	802.5	0.024	–5.6	9.4
0.0947	0.7922	1240.7	820.0	0.056	–9.9	17.1
0.1995	0.7757	1226.4	857.1	0.124	–17.6	31.4
0.2958	0.7626	1216.0	886.8	0.167	–21.9	40.1
0.3980	0.7504	1207.3	914.2	0.204	–24.1	45.4
0.5004	0.7395	1200.4	938.5	0.254	–24.5	47.3
0.6048	0.7297	1195.3	959.1	0.287	–22.9	45.3
0.7087	0.7212	1191.9	975.9	0.274	–19.7	39.4
0.8042	0.7142	1190.4	988.0	0.248	–15.2	30.7
0.8826	0.7091	1190.2	995.6	0.185	–10.5	21.2
0.9323	0.706	1190.4	999.5	0.156	–7.1	14.4
			T=303.15 K			
0.0538	0.7916	1212.2	859.8	0.040	–6.7	11.9
0.0930	0.7848	1205.2	877.3	0.054	–10.9	19.6
0.1967	0.7682	1189.5	920.0	0.140	–19.2	36.2
0.2962	0.7545	1177.5	956.0	0.198	–24.1	47.1
0.4033	0.7418	1167.4	989.2	0.223	–26.6	53.5
0.4966	0.7317	1160.3	1015.1	0.294	–27.0	55.8
0.5236	0.7290	1158.7	1021.8	0.310	–26.8	55.7
0.6964	0.7139	1150.9	1057.4	0.327	–22.2	47.9

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	κ_S/TPa^{-1}	V_m^E/cm^3 mol^{-1}	Δu/m s^{-1}	$\Delta\kappa_S$/TPa^{-1}
			T=303.15 K			
0.7765	0.7080	1149.1	1069.7	0.284	–18.3	39.9
0.8831	0.7008	1148.5	1081.8	0.231	–11.4	25.2
0.9333	0.6978	1148.5	1086.4	0.171	–7.8	17.2
			T=308.15 K			
0.0461	0.7891	1196.3	885.4	0.034	–5.8	10.8
0.0970	0.7801	1186.9	910.0	0.069	–11.5	21.6
0.1998	0.7638	1170.7	955.3	0.142	–20.1	39.2
0.2987	0.7501	1158.3	993.7	0.218	–25.1	50.8
0.4036	0.7375	1147.7	1029.3	0.273	–27.8	58.1
0.5022	0.7270	1140.1	1058.2	0.327	–28.1	60.4
0.6037	0.7175	1134.3	1083.2	0.353	–26.3	58.0
0.7013	0.7094	1130.5	1103.0	0.354	–22.9	51.5
0.8033	0.7020	1128.2	1119.2	0.300	–17.5	40.1
0.8833	0.6967	1127.6	1128.9	0.253	–12.2	28.2
0.9329	0.6939	1127.9	1132.8	0.156	–8.2	18.7

where x is the molar fraction of octane, A_p stands for the fitting parameters and M is the degree of the polynomial expansion. An unmassed least-squares method was used to fit the data. The degree of the polynomials was optimized by applying the F-test

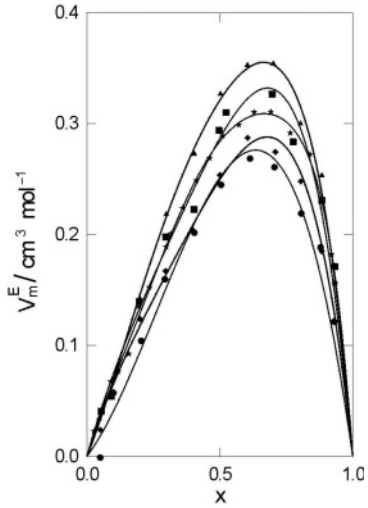

Fig. 1 Excess molar volume for x octane + (1–x) 1-butanol : • – 288.15 K; ◆ – 293.15 K; ★– 298.15 K; ■ – 303.15 K; ▲ – 308.15 K; — Eq. 3

[21]. These parameters are compiled in Table 4 as well as the root mean square deviations calculated according to the expression:

$$\sigma = \left(\sum_{i}^{N} \frac{(z_{exp} - z_{cal})^2}{N - n} \right)^{1/2} \quad (4)$$

where z_{exp} is the experimental value, z_{cal} is the calculated value, N is the number of experimental data values and n is the number of fitting parameters A_p, used in Eq. 3.

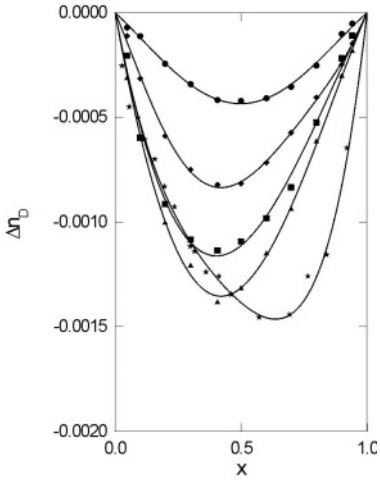

Fig. 2 Changes of refractive index on mixing for x octane + (1–x) 1-butanol:
• – 288.15 K; ◆ – 293.15 K; ★ – 298.15 K; ■ – 303.15 K; ▲ – 308.15 K;
— Eq. 3

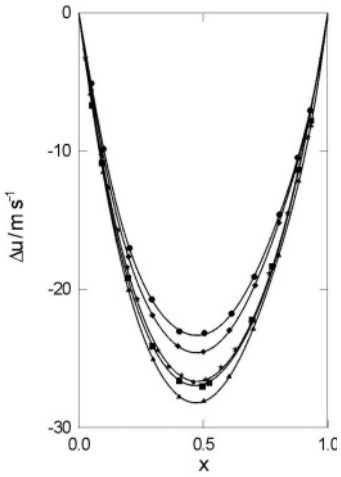

Fig. 3 Changes of speed of sound on mixing for x octane + (1-x) 1-butanol:
• – 288.15 K; ◆ – 293.15 K; ★ – 298.15 K; ■ – 303.15 K; ▲ – 308.15 K;
— Eq. 3

Table 4 Parameters A_P in Eq. (3) and standard deviations σ for x octane + (1–x) 1-butanol

	A_0	A_1	A_2	A_3	A_4	A_5	σ
			T=288.15 K				
V_m^E/cm^3 mol^{-1}	1.005	0.691	–	–	–	–	0.001
Δn_D	–0.0017	0.00003	0.0007	–	–	–	0.0001
Δu/m s^{-1}	–93.1	8.1	–14.1	20.6	–8.5	–40.2	0.1
$\Delta\kappa_S$/TPa^{-1}	174.5	1.6	15.9	–33.3	14.2	71.2	0.1
			T=293.15 K				
V_m^E/cm^3 mol^{-1}	0.998	0.729	0.487	–	–	–	0.013
Δn_D	–0.0032	0.0013	0.0003	–0.0014	–	–	0.0001
Δu/m s^{-1}	–98.1	9.96	–8.9	19.9	–15.9	–36.9	0.1
$\Delta\kappa_S$/TPa^{-1}	188.2	1.5	24.9	–	–		0.5
			T=298.15 K				
[a]V_m^E/cm^3 mol^{-1}	1.136	0.604	0.206	0.602	0.701	–	0.005
[a]Δn_D	–0.0056	–0.0019	–0.0028	–	–	–	0.0001
[a]Δu/m s^{-1}	–106.3	9.0	–17.7	–	–	–	0.3
[a]$\Delta\kappa_S$/TPa^{-1}	211.0	5.4	23.4	–	–	–	0.6
			T=303.15 K				
V_m^E/cm^3 mol^{-1}	1.147	0.849	0.564	–	–	–	0.016
Δn_D	–0.0045	0.0019	–	–	–	–	0.0001
Δu/m s^{-1}	–107.5	11.3	–19.9	–	–	–	0.3
$\Delta\kappa_S$/TPa^{-1}	221.7	–5.7	30.3	30.1	–	–	0.5
			T=308.15 K				
V_m^E/cm^3 mol^{-1}	1.284	0.747	0.457	0.400	–	–	0.008
Δn_D	–0.0053	0.0019	0.0005	–	–	–	0.0001
Δu/m s^{-1}	–90.7	–29.5	7.73	–23.4	–18.5	–	0.1
$\Delta\kappa_S$/TPa^{-1}	–116.6	83.7	15.6	62.5	66.3	–	0.5

[a]Ref. [2]

Figure 1 shows excess molar volumes for octane+1-butanol and the smoothed curves at five temperatures. The excess molar volumes are positive for the whole composition at all temperatures. Changes of refractive index (Fig. 2), show an opposite trend with excess molar volumes, and do not present a systematic variation with temperature. Changes of speed of sound are negative showing a symmetric behaviour with x=0.5 concentration and decrease with temperature (Fig. 3). Changes of isentropic compressibilities on mixing, (Fig. 4) present the same qualitative behaviour as excess molar volumes curves, becoming both magnitudes more positive when

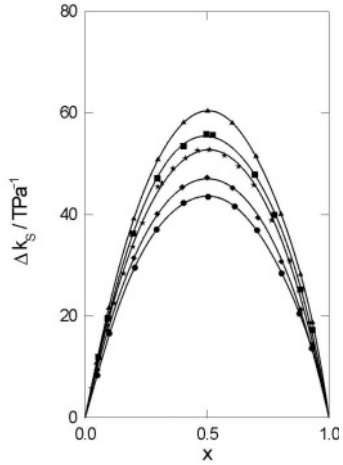

Fig. 4 Changes of isentropic compressibilities on mixing for *x* octane + (1–*x*) 1-butanol: ● – 288.15 K; ◆ – 293.15 K; ⋆– 298.15 K; ■ – 303.15 K; ▲ – 308.15 K; — Eq. 3

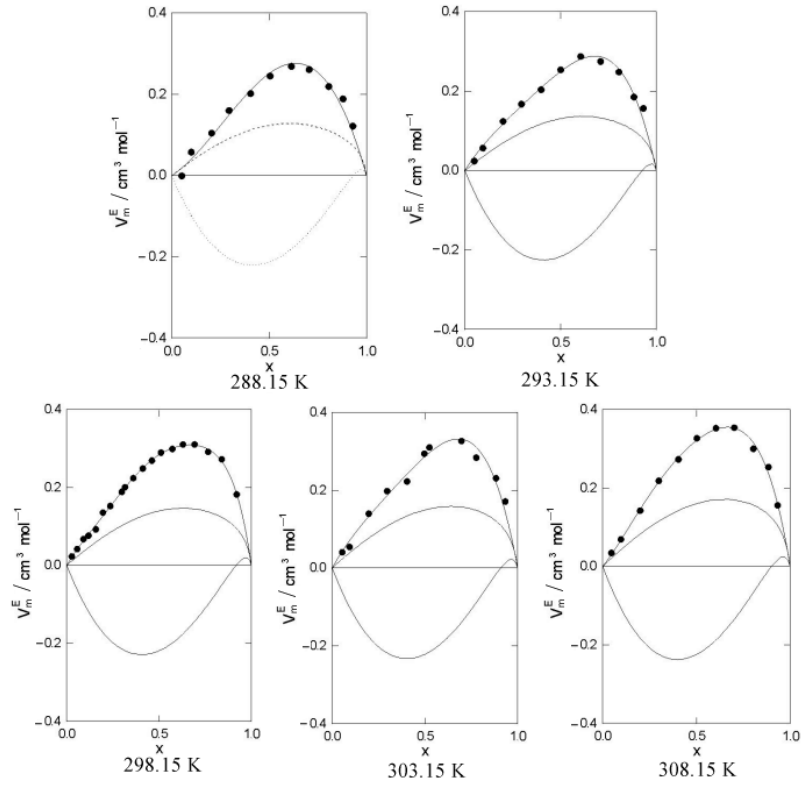

Fig. 5 Excess molar volumes for *x* octane + (1–*x*) 1-butanol at 288.15, 293.15, 298.15, 303.15 and 308.15 K. • – experimental values; — Eq. 3; — — Nitta–Chao model with parameters of Fernández *et al*.[23]; - - - Nitta –Chao model with parameters of Nitta *et al*. [22]

the temperature increases. Excess molar volumes were compared in Fig. 5 with the predictions of Nitta–Chao group contribution model, using the old set of parameters obtained by Nitta *et al*. [22], and the ones recalculated by Fernández *et al*. [23]. As shown in this figure, the predictions with the parameters of Fernández *et al*. are better than those obtained using the old set of parameters. The Nitta–Chao model predictions of Fernández *et al*. present positive values and a maximum shifted towards the dilute region of 1-butanol, in agreement with the experimental curves, and describe this behaviour.

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References

1 B. E. de Cominges, M. M. Piñeiro, T. P. Iglesias, J. L. Legido and M. I. Paz Andrade, J. Chem. Thermodyn., 30 (1998) 1147.
2 B. E. de Cominges, M. M. Piñeiro, T. P. Iglesias, J. L. Legido and M. I. Paz Andrade, Phys. Chem. Liq., 37 (1999) 683.
3 B. E. de Cominges, M. M. Piñeiro, E. Mascato, T. P. Iglesias and J. L. Legido, High Temperatures-High Pressures, 32 (2000) 653.
4 B. E. de Cominges, M. M. Piñeiro, L. Mosteiro, T. P. Iglesias, J. L. Legido and M. I. Paz Andrade, J. Chem. Eng. Data, 46/5 (2001) 1206.
5 T. P. Iglesias, J. L. Legido, J. Peleteiro, L. Romaní and M. I. Paz Andrade, J. Chem. Thermodyn., 25, (1993) 1325.
6 B. M. C. V. Gupta, P. R. Naidu and M. V. P. Rao, J. Chem. Thermodyn., 8 (1976) 191.
7 J. Nath, J. Chem. Thermodyn., 29 (1997) 853.
8 J. Nath and J. G. Pandey, J. Chem. Eng. Data, 42 (1997) 128.
9 J. M. Pardo, Ph. D. University of Vigo, Spain, 1999.
10 Engineering Chemistry Laboratory, University of Vigo, Spain 2000.
11 J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents, Tecniques of Chemistry, Wiley, New York 1986.
12 C. Franjo, C. P. Menaut, E. Jiménez, J. L. Legido and M. I. Paz Andrade, J. Chem. Eng. Data, 40 (1995) 992.
13 S. Junguera, J. Tardajos and E. Aicart, J. Chem. Thermodyn., 20 (1998) 1461.
14 B. Orge, A. Rodriguez, J. M. Canosa, G. Marino, M. Iglesias and J. Tojo, J. Chem. Eng. Data, 44 (1999) 1041.
15 T. P. Iglesias, J. L. Legido, J. Peleteiro, L. Romaní and M. I. Paz Andrade, Phys. Chem. Liq. , 30 (1995) 159.
16 T. M. Aminabhavi, V. B. Patil, M. I. Aralaguppi and H. T. S. Phayde, J. Chem. Eng. Data, 41 (1996) 521.
17 S. L. Oswal and K. D. Prajapati, J. Chem. Eng. Data, 43 (1998) 367.
18 J. Ortega, J. Chem. Eng. Data, 27 (1982) 312.
19 TRC Thermodynamics Tables, Thermodynamic Research Center, Texas A&M University, College Station, TX 1994.

20 O. Redlich and A. T. Kister, Ind. Eng. Chem., 40 (1948) 345.
21 P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences; McGraw-Hill, New York 1969.
22 T. Nitta, E. Turek, R. A. Greenkorn and K. C. Chao, AIChE. J., 23 (1977) 144.
23 J. Fernández, J. L. Legido, M. I. Paz Andrade, L. Pías and J. Ortega, Fluid Phase Equilibria, 55 (1990) 293.