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Excess molar volumes of ternary mixtures di-*n*-butyl ether+1-pentanol+*n*-dodecane at 298.15 K

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Abstract

Excess molar volumes of {$x_1$di-*n*-butyl ether+$x_2$1-pentanol+$(1-x_1-x_2)$*n*-dodecane} and the binary mixtures {$x$di-*n*-butyl ether+$(1-x)$*n*-dodecane} and {x1-pentanol+$(1-x)$*n*-dodecane} were measured at 298.15 K using an Anton Paar DMA 60/602 densimeter. All the experimental values were compared with the results obtained by empirical expressions for estimating ternary properties from binary results. Variable-degree polynomials have been fitted to the results. The experimental excess molar volumes were compared with the results obtained with the Nitta–Chao model. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Di-*n*-butyl ether; *n*-Dodecane; Nitta–Chao model; 1-pentanol; Excess molar volumes

1. Introduction

In previous works [1–3], we have reported experimental excess molar volumes of ternary systems at 298.15 K containing di-*n*-butyl ether+alcohol+*n*-alkanes as components. In this paper, we continue our studies and we present the excess volumes of {di-*n*-butyl ether+1-pentanol+*n*-dodecane} and the binary systems {di-*n*-butyl ether+*n*-dodecane} and {1-pentanol+*n*-dodecane} at 298.15 K. The excess molar volumes obtained were used to test the empirical methods of Kohler [4], Jacob–Fitzner [5], Colinet [6], Tsao–Smith [7], Toop [8], Scatchard et al. [9] and Hillert [10]. These methods predict excess properties of the ternary mixtures from those of involved binary mixtures. The Cibulka [11] equation has been used to correlate the experimental values of ternary mixtures. The experimental excess molar volumes were compared with the results obtained with the Nitta–Chao model [12] based on the Carnahan–Starling hard-sphere equation of state [13].

2. Experimental

The experimental excess molar volumes were determined from densities of the pure liquids and mixtures, measured with an Anton Paar DMA 60/602 vibrating-tube densimeter thermostated in a Schott-Geräte CT 1450 circulating-water bath, the uncertainty in measurements does not exceed $\pm 1\times 10^{-5}$ g cm^{-3}. The substances employed were supplied by Fluka and

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Table 1
Densities in g cm^{-3} of the pure liquids at 298.15 K

Substance	ρ	
	Experimental	Literature
Di-*n*-butyl ether	0.76411	0.7641[a]
n-Dodecane	0.74588	0.74572[b]
1-Pentanol	0.81091	0.8109[c]

[a] From Ref. [14].
[b] From Ref. [15].
[c] From Ref. [16].

Aldrich. Their mole-fraction purities were: di-*n*-butyl ether (Fluka)>0.995, 1-pentanol (Fluka)>0.99 and *n*-dodecane (Aldrich)>0.99. All chemical products were degassed by ultrasound, dried over Sigma type 0.4 nm molecular sieves, but otherwise used as supplied. Densities of pure liquids agrees with the literature values as Table 1 shows.

3. Results and discussion

Excess molar volumes for binary mixtures are reported in Table 2, and graphical representations are given in Fig. 1. A variable degree of the form

$$V^{\mathrm{E}}_{\mathrm{m},ij} = x_i x_j \sum_{p=0}^{n} A_p (x_i - x_j)^p \tag{1}$$

was fitted to the results. A least-squares method was employed in all the cases. The number of parameters was determined using a F-test [17]. Parameters and standard deviations are listed in Table 3. The experimental excess molar volumes of the ternary system, $V^{\mathrm{E}}_{\mathrm{m},123}$, are shown in Table 4. The Cibulka equation has been fitted to the experimental values:

$$V^{\mathrm{E}}_{\mathrm{m},123} = V^{\mathrm{E}}_{\mathrm{bin}} + x_i x_j (1 - x_i - x_j)(B_0 + B_1 x_i + B_2 x_j), \tag{2}$$

where

$$V^{\mathrm{E}}_{\mathrm{bin}} = V^{\mathrm{E}}_{\mathrm{m},12} + V^{\mathrm{E}}_{\mathrm{m},13} + V^{\mathrm{E}}_{\mathrm{m},23}, \tag{3}$$

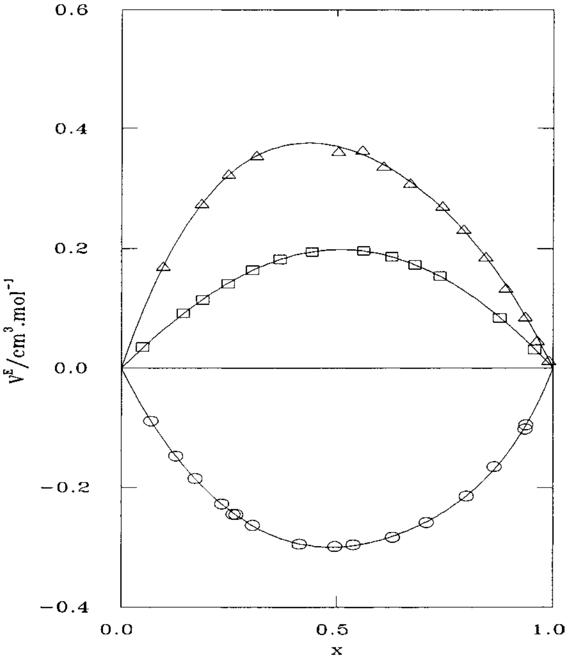

Fig. 1. Excess molar volumes $V^{\mathrm{E}}_{\mathrm{m}}$ at 298.15 K of: (O) {*x*di-*n*-butyl ether+(1−*x*)1-pentanol} [1]; (□) {*x*di-*n*-butyl ether+(1−*x*)*n*-dodecane}; (△) {*x*1-pentanol + (1−*x*)*n*-dodecane}.

Table 2
Experimental excess molar volumes $V^{\mathrm{E}}_{\mathrm{m}}$ in cm^3 mol^{-1} at 298.15 K

x	$V^{\mathrm{E}}_{\mathrm{m}}$	x	$V^{\mathrm{E}}_{\mathrm{m}}$	x	$V^{\mathrm{E}}_{\mathrm{m}}$	x	$V^{\mathrm{E}}_{\mathrm{m}}$
*x*Di-*n*-butyl ether+(1−*x*)*n*-dodecano							
0.0486	0.0351	0.3037	0.1636	0.6268	0.1860	0.9577	0.0312
0.1425	0.0916	0.3673	0.1813	0.6811	0.1726		
0.1873	0.1136	0.4417	0.1942	0.7382	0.1531		
0.2466	0.1410	0.5617	0.1955	0.8764	0.0846		
*x*1-Pentanol + (1−*x*)*n*-dodecano							
0.0958	0.1702	0.5023	0.3622	0.7442	0.2711	0.9357	0.0862
0.1852	0.2749	0.5583	0.3644	0.7936	0.2324	0.9631	0.0460
0.2476	0.3249	0.6075	0.3379	0.8440	0.1863	0.9896	0.0131
0.3126	0.3553	0.6692	0.3096	0.8905	0.1342		

Table 3
Parameters A_k and B_k for Eqs. (1) and (2) and standard deviations s in cm^3 mol^{-1}

xDi-n-butyl ether+(1−x)1-pentanol[a]					
A_0=−1.1975	A_1=−0.0499	A_2=−0.2413	A_3=−0.0239	A_4=−0.2275	s=0.002
xDi-n-butyl ether+(1−x)n-dodecane					
A_0=0.7917	A_1=−0.0279	A_2=−0.0557	–	–	s=0.0009
x1-Pentanol+(1−x)n-dodecane					
A_0=1.4827	A_1=−0.3325	A_2=0.3276	–	–	s=0.004
x_1Di-n-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)n-dodecane					
B_0=−0.0755	B_1=0.3624	B_2=2.1043	–	–	s=0.007

[a] From Ref. [1].

Table 4
Experimental excess molar volumes of ternary mixtures in $V^E_{m,123}$ cm^3 mol^{-1} $x_1$di-n-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)n-dodecane at 298.15 K

x_1	x_2	$V^E_{m,123}$	x_1	x_2	$V^E_{m,123}$
0.0281	0.1463	0.2500	0.3330	0.4079	0.0887
0.0370	0.1926	0.2837	0.3742	0.4583	−0.0189
0.0629	0.3276	0.3302	0.4140	0.5070	−0.1545
0.0868	0.4520	0.3081	0.2884	0.1994	0.2251
0.1051	0.5471	0.2480	0.3571	0.2468	0.1709
0.1131	0.5888	0.2130	0.4311	0.2979	0.1001
0.1233	0.6422	0.1512	0.4874	0.3368	−0.0250
0.1370	0.7130	0.0493	0.5410	0.3739	−0.1549
0.1499	0.7807	−0.0610	0.2472	0.0882	0.2191
0.1113	0.2628	0.3052	0.3469	0.1237	0.2059
0.1543	0.3643	0.2859	0.6018	0.2147	−0.0055
0.1906	0.4500	0.2230	0.6855	0.2445	−0.1452
0.2043	0.4823	0.1886	0.2845	0.0311	0.1912
0.2247	0.5302	0.1240	0.4166	0.0456	0.1969
0.2500	0.5901	0.0219	0.5271	0.0577	0.1748
0.2750	0.6491	−0.1056	0.5641	0.0617	0.1616
0.1593	0.1951	0.2679	0.6307	0.0690	0.1306
0.2784	0.3410	0.1893	0.7302	0.0799	0.0538
0.3042	0.3726	0.1477	0.8196	0.0897	−0.0295

where the $V^E_{m,ij}$ is given by Eqs. (1) and (2). Table 3 presents the parameters and the standard deviation between experimental and fitted values. The lines of constant ternary excess molar volume $V^E_{m,123}$ calculated by using Eqs. (2) and (3), are shown in Fig. 2, with a minimum of −0.2801 cm^3 mol^{-1} at x_1=0.51, x_2=0.48. Fig. 3 shows lines of constant "ternary contribution". The so-called "ternary contribution" represents the difference between the experimental value and that predicted from binary mixtures ($V^E_{m,123} - V^E_{bin}$). The ternary contribution shows a maximum for 0.0335 cm^3 mol^{-1} at x_1=0.27 and x_2=0.48. The minimum of Fig. 2 is due to the fact that one of the binary systems present negative values, as Fig. 1 shows, and the ternary contribution is little significative and positive in the whole range. In Fig. 3 exists a maximum lightly shifted towards the region rich in propanol, probably due to the strong polar effect of the alkanol.

The results for binary and ternary mixtures were compared with those of the Nitta–Chao theory using the interaction parameters of references [12,18–21]. Curves obtained are represented in Figs. 4 and 5 by dashed lines.

Several methods have been proposed to estimated ternary excess properties from experimental results on constituent binaries [4–10]. These methods have been described previously [22]. For asymmetrical equations

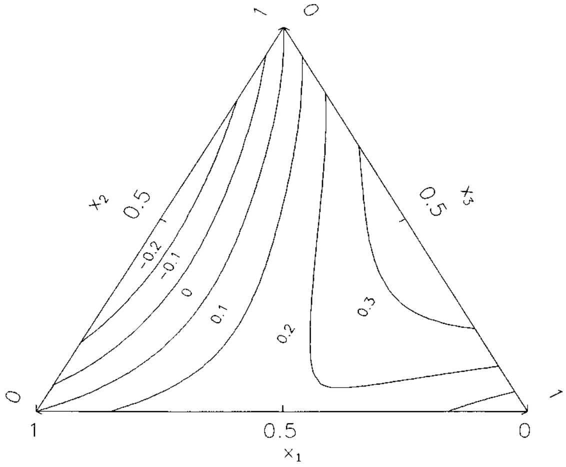

Fig. 2. Curves of constant $V^{E}_{m,123}/\mathrm{cm^3\,mol^{-1}}$ for {$x_1$di-*n*-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)*n*-dodecane}.

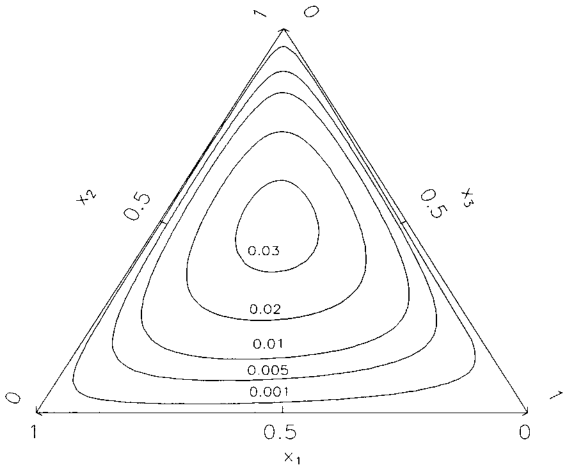

Fig. 3. Curves of constant $(V^{E}_{m,123} - V^{E}_{m,bin})/\mathrm{cm^3\,mol^{-1}}$ for {$x_1$di-*n*-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)*n*-dodecane}.

Table 5
Standard deviations in $\mathrm{cm^3\,mol^{-1}}$ of the models for the mixtures $x_1$di-*n*-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)*n*-dodecane

Jacob and Fitzner		0.0206	
Kohler		0.0220	
Colinet		0.0215	
Tsao and Smith	0.0406[a]	0.0180[b]	0.0700[c]
Toop	0.0246[a]	0.0154[b]	0.0261[c]
Scatchard	0.0248[a]	0.0152[b]	0.0244[c]
Hillert	0.0232[a]	0.0156[b]	0.0269[c]

[a] x_1Di-*n*-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)*n*-dodecane.
[b] $x_1$1-Pentanol+$x_2$di-*n*-butyl ether+(1−x_1−x_2)*n*-dodecane.
[c] x_1*n*-Dodecane+$x_2$1-pentanol+(1−x_1−x_2)di-*n*-butyl ether.

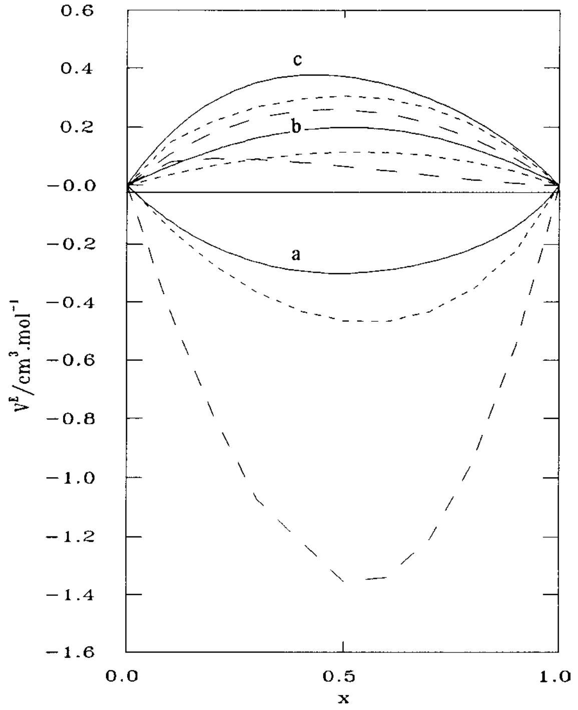

Fig. 4. Excess molar volumes V^{E}_{m} of: (a) {*x*di-*n*-butyl ether+(1−*x*)1-pentanol}; (b) {*x*di-*n*-butyl ether+(1−*x*)*n*-dodecane}; (c) {*x*1-pentanol+(1−*x*)*n*-dodecane}; (—) Eq. (1); (— — —) Nitta–Chao model with parameters from [18]; (- - -) Nitta–Chao model with parameters from [12,19–21].

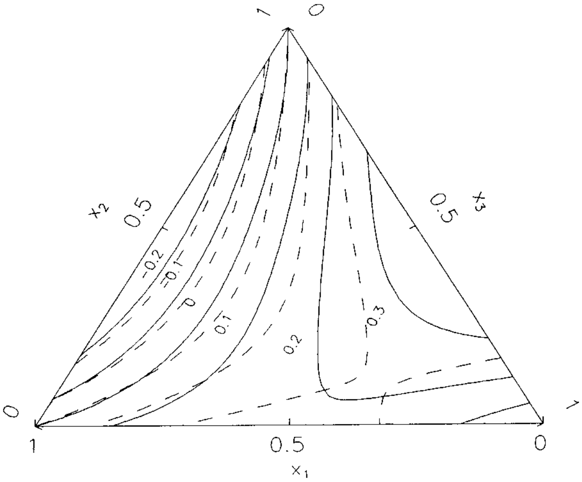

Fig. 5. Curves of constant $V^{E}_{m,123}/\mathrm{cm^3\,mol^{-1}}$ for {$x_1$di-*n*-butyl ether+$x_2$1-pentanol+(1−x_1−x_2)*n*-dodecane}. (—) Eqs. (2) and (3); (- - -) Nitta–Chao model with parameters from [18].

the numerical predictions depend on the arbitrary designation of components-numbering. Table 5 shows the standard deviations between experimental and predicted values.

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