Journal of Thermal Analysis, Vol. 52 (1998) 815-822

EXCESS MOLAR VOLUMES OF {x_1 BUTYL BUTANOATE +x_2 1-OCTANOL+(1–x_1–x_2) OCTANE} AT 298.15 K

S. García-Garabal[1], *L. Segade*[1], *C. Franjo*[1], *E. Jiménez*[1],
M. M. Piñeiro[2], *J. L. Legido*[2*] *and M. I. Paz Andrade*[3]

[1]Departamento de Física, Facultade de Ciencias, Universidade de A Coruña, A Coruña
[2]Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, Vigo,
[3]Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago, Santiago de Compostela, Spain

Abstract

Excess molar volumes at 298.15 K of the ternary system {$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+ $CH_3(CH_2)_7OH$+$CH_3(CH_2)_6CH_3$} and the binary mixtures {$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+ $CH_3(CH_2)_7OH$}, {$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+$CH_3(CH_2)_6CH_3$} and {$CH_3(CH_2)_7OH$+ $CH_3(CH_2)_6CH_3$} were detemined using an Anton Paar DMA 60/602 densimeter. All experimental values were compared with the results obtained with empirical expressions for estimation of the ternary properties from the binary data. Variable-degree polynomials were fitted to the results.

Keywords: butyl butanoate, empirical equations, excess volume, Nitta-Chao model, ternary mixture

Introduction

Previous papers [1–6] reported experimental excess molar volumes of nonelectrolyte ternary mixtures at 298.15 K. The present paper gives the excess volumes of {butyl butanoate+1-octanol+octane} and of the constituent binary systems {butyl butanoate+1-octanol}, {butyl butanoate+octane} and {1-octanol+ octane} at 298.15 K. The obtained excess molar volumes were used to test the empirical methods of Kohler [7], Jacob and Fitzner [8], Colinet [9], Knobeloch and Schwartz [10], Tsao and Smith [11], Toop [12], Scatchard *et al.* [13], Hillert [14] and Mathieson and Tynne [15]. These methods predict excess properties of the ternary mixtures from those of the binary mixtures involved. The Cibulka [16] and Nagata [17] equations were used to correlate the experimental values of

---

[*] Author to whom all correspondence should be addressed.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publshers, Dordecht

the ternary mixtures. The experimental values were compared with the predictions of the group contribution model of Nitta *et al.*[18].

Experimental

The chemical substances employed, butyl butanoate (Fluka, purity>99%), 1-octanol (Fluka, purity >99.5%) and octane (Aldrich, purity >99%) were degassed by ultrasound, and dried over 4 nm molecular sieves. The measured densities of the pure liquids displayed good agreement with previously published values, as shown in Table 1.

Table 1 Measured densities of pure liquids compared with literature data at 298.15 K

Compound	ρ/g cm^{-3}	
	exp.	lit.
Butyl butanoate	0.86477	0.86485$^{(a)}$ 0.8664 $^{(b)}$
n-octane	0.69882	0.69850$^{(c)}$ 0.69847$^{(d)}$
1-octanol	0.82176	0.82162$^{(d)}$ 0.82161$^{(e)}$

$^{(a)}$ Ilic et al.[1], $^{(b)}$ TRC[22], $^{(c)}$ Franjo et al. [23], $^{(d)}$ Iglesias et al. [24], $^{(e)}$ Amigo et al. [25]

Excess molar volumes were determined from the densities of the pure liquids and mixtures measured with an Anton Paar DMA 60/602 densimeter thermostated at (298.15±0.01) K in a Haake F3 circulating water-bath. Details of the experimental procedure were published previously [1].

Results and discussion

The experimental densities and determined excess molar volumes of the binary mixtures are listed in Table 2. The binary excess volume values were fitted to a variable-degree Redlich-Kister [19] polynomial of the form

$$V^{E}_{m,ij} = x_i x_j \sum_{k=0}^{M} A_k (x_i - x_j)^k \qquad (1)$$

The unweighted least-squares method was employed. The number of coefficients was determined in each case by applying the *F*-test [20]. The coefficients A_k and the standard deviations s are shown in Table 3. Figure 1 presents the binary $V^{E}_{m,ij}$ values plotted against x and the curves calculated from the smoothing equations.

Table 2 Experimental densities ρ and excess molar volume value $V^{E}_{m,ij}$ for the binary mixtures involved

x	ρ/ g cm^{-3}	$V^{E}_{m,123}$/ $\text{cm}^3\ \text{mol}^{-1}$	x	ρ/ g cm^{-1}	$V^{E}_{m,123}$/ $\text{cm}^3\ \text{mol}^{-1}$
$x\text{CH}_3(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3+(1-x)\text{CH}_3(\text{CH}_2)_7\text{OH}$					
0.0418	0.82342	0.0345	0.5351	0.84407	0.2353
0.1050	0.82592	0.0994	0.6105	0.84728	0.2259
0.1541	0.82795	0.1314	0.6888	0.85074	0.2104
0.1905	0.82938	0.1562	0.7146	0.85186	0.1968
0.2736	0.83290	0.1981	0.7541	0.85366	0.1705
0.3332	0.83540	0.2140	0.8672	0.85867	0.1137
0.3838	0.83758	0.2259	0.9429	0.86210	0.0539
0.4865	0.84197	0.2370			
$x\text{CH}_3(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3+(1-x)\text{CH}_3(\text{CH}_2)_6\text{CH}_3$					
0.0609	0.70858	0.1204	0.6868	0.81213	0.2820
0.1275	0.71943	0.2051	0.7209	0.81779	0.2684
0.1756	0.72725	0.2670	0.7885	0.82912	0.2207
0.2236	0.73516	0.2946	0.8137	0.83343	0.1838
0.2941	0.74675	0.3413	0.8356	0.83706	0.1744
0.3513	0.75621	0.3600	0.8784	0.84426	0.1324
0.4727	0.77639	0.3600	0.9672	0.85923	0.0397
0.6219	0.80125	0.3177			
$x\text{CH}_3(\text{CH}_2)_7\text{OH}+(1-x)\text{CH}_3(\text{CH}_2)_6\text{CH}_3$					
0.0145	0.70029	0.0426	0.3826	0.74056	–0.0319
0.0166	0.70054	0.0444	0.4410	0.75229	–0.0436
0.0187	0.70077	0.0477	0.4482	0.75315	–0.0468
0.0189	0.70080	0.0462	0.5341	0.76383	–0.0707
0.0240	0.70139	0.0521	0.6423	0.77731	–0.0830
0.0412	0.70339	0.0598	0.6846	0.78259	–0.0888
0.0707	0.70697	0.0688	0.8219	0.79967	–0.0733
0.1337	0.71458	0.0559	0.8957	0.80882	–0.0490
0.2364	0.72079	0.0450	0.9470	0.81516	–0.0249
0.2824	0.73271	–0.0009			

Table 3 Coefficients A_k and B_i for Eqs (1), (4) and (5), and standard deviations s

Equation 1	A_0	A_1	A_2	A_3	A_4	A_5	s
$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+ $CH_3(CH_2)_7OH$	0.9517	–0.0282	0.0883				0.004
$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+ $CH_3(CH_2)_6CH_3$	1.432	–0.4076	–0.2500				0.005
$CH_3(CH_2)_7OH$+ $CH_3(CH_2)_6CH_3$	–0.2352	–0.5439	–0.1863	0.6273	1.281	–1.742	0.008

Equation 4	B_0	B_1	B_2	s
$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$+$CH_3(CH_2)_7OH$+ $CH_3(CH_2)_6CH_3$	0.2712	1.5912	–1.8660	0.01

Equation 5	B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
$CH_3(CH_2)_2CO_2(CH_2)_3CH_3$ +$CH_3(CH_2)_7OH$ +$CH_3(CH_2)_6CH_3$	0.0012	0.0003	0.0077	0.0054	–0.0157	–0.0037	–0.0088	0.0118	0.009

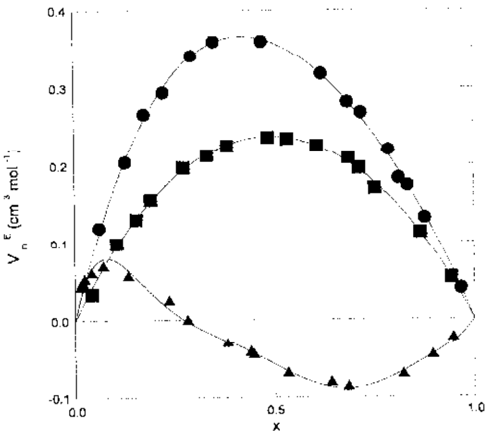

Fig. 1 Excess molar volumes $V^E_{m,ij}$ at 298.15 K of the binary mixtures:
● – $xCH_3(CH_2)_2CO_2(CH_2)_3CH_3$+(1–$x$) $CH_3(CH_2)_6CH_3$; ▲– $xCH_3(CH_2)_7OH$+(1–x)$CH_3(CH_2)_6CH_3$, ■– $xCH_3(CH_2)_2CO_2(CH_2)_3CH_3$+(1–$x$)$CH_3(CH_2)_7OH$

The experimental densities, ρ and calculated excess volumes $V^E_{m,123}$ of the ternary system are listed in Table 4. The ternary excess volume values were fitted to the following equation:

$$V^E_{m,123} = V^E_{m,bin} + \Delta_{123} \tag{2}$$

where $V^{\mathrm{E}}_{\mathrm{m,bin}}$ is the binary contribution to the excess ternary volumes given by the equation:

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

The $V^{\mathrm{E}}_{\mathrm{m,ij}}$ values were fitted by means of Eq. (1). The ternary contribution Δ_{123} was correlated by using the equation suggested by Cibulka [16]:

$$\Delta_{123} = B_0 + B_1x_1 + B_2x_2 \tag{4}$$

and the expression due to Nagata-Tamura [17]:

Table 4 Experimental densities, ρ, and excess molar volumes values $V^{\mathrm{E}}_{\mathrm{m,123}}$ for the ternary mixture $CH_3(CH_2)_2CO_2(CH_2)_3CH_3 + CH_3(CH_2)_7OH + CH_3(CH_2)_6CH_3$

x_1	x_2	ρ/ g cm^{-3}	$V^{\mathrm{E}}_{\mathrm{m,123}}$/ cm^3 mol^{-1}	x_1	x_2	ρ/ g cm^{-3}	$V^{\mathrm{E}}_{\mathrm{m,123}}$/ cm^3 mol^{-1}
0.0117	0.0694	0.70817	0.0881	0.0715	0.0503	0.71616	0.1648
0.0192	0.1142	0.71544	0.0698	0.2169	0.1526	0.75250	0.2634
0.0372	0.2211	0.73137	0.0664	0.2938	0.2066	0.77195	0.2601
0.0744	0.4421	0.76480	0.0231	0.3144	0.2211	0.77711	0.2728
0.0927	0.5511	0.78128	0.0324	0.3618	0.2544	0.78912	0.2670
0.1300	0.7724	0.81493	0.0778	0.4353	0.3062	0.80774	0.2663
0.0343	0.0824	0.71398	0.1155	0.4476	0.3148	0.81080	0.2749
0.0361	0.0866	0.71478	0.1143	0.0647	0.0224	0.71171	0.1502
0.1111	0.2667	0.74912	0.1311	0.0923	0.0320	0.71738	0.1779
0.1655	0.3973	0.77428	0.1298	0.1841	0.0638	0.73620	0.2805
0.1883	0.4519	0.78471	0.1495	0.3669	0.1272	0.77425	0.3243
0.2246	0.5390	0.80163	0.1379	0.4621	0.1602	0.79412	0.3216
0.2580	0.6193	0.81719	0.1505	0.5560	0.1928	0.81381	0.2931
0.0373	0.0477	0.71031	0.1127	0.6487	0.2249	0.83332	0.2461
0.0531	0.0679	0.71534	0.1299	0.0717	0.0083	0.71126	0.1322
0.1092	0.1396	0.73320	0.1768	0.1150	0.0133	0.71887	0.2013
0.1631	0.2085	0.75051	0.2020	0.3292	0.0381	0.75704	0.3599
0.2236	0.2858	0.77005	0.2057	0.4472	0.0517	0.77834	0.3557
0.2408	0.3077	0.77558	0.2117	0.4917	0.0569	0.78640	0.3489
0.2772	0.3543	0.78744	0.2084	0.5556	0.0642	0.79792	0.3387
0.3348	0.4279	0.80609	0.2169	0.6792	0.0785	0.82034	0.2807
0.3889	0.4970	0.82372	0.2134	0.7903	0.0914	0.84058	0.2004

$$\Delta_{123}/RT = B_0 - B_1x_1 - B_2x_2 - B_3x_1^2 - B_4x_2^2 - B_5x_1x_2 - B_6x_1^3 - B_7x_2^3 \qquad (5)$$

In both cases, the parameters B_i were calculated by the unweighted least-squares method by using a non-linear optimization parameter due to Marquardt [21]. Table 3 presents the values of the parameters B_i for Eqs (4) and (5) and the corresponding standard deviations s.

The lines of constant ternary excess molar volume $V^E_{m,123}$ calculated via Eqs (2) and (3) are shown in Fig. 2. The ternary excess molar volume presents a maximum of 0.364 cm^3 mol^{-1} at x_1=0.420 and x_2=0.000, and a minimum of

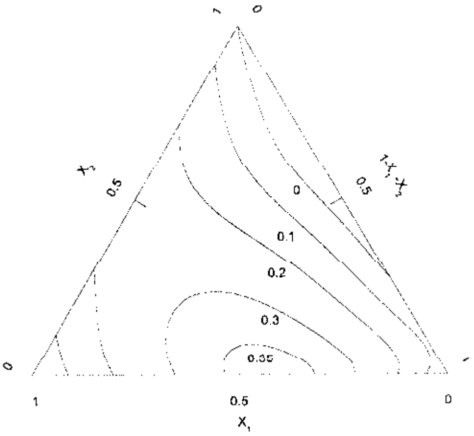

Fig. 2 Curves of constant $V^E_{m,123}$ / (cm^3 mol^{-1}) for the ternary mixture $\{x_1CH_3(CH_2)_2CO_2(CH_2)_3CH_3+x_2CH_3(CH_2)_7OH+(1-x_1-x_2)CH_3(CH_2)_6CH_3\}$, calculated with Eq. (4), at 298.15 K

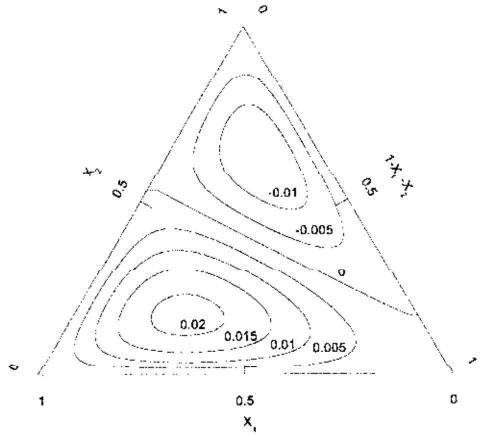

Fig. 3 Curves of constant ternary contribution Δ_{123}/(cm^3 mol^{-1}) to the excess molar volume $V^E_{m,123}$ of the ternary mixture $\{x_1CH_3(CH_2)_2CO_2(CH_2)_3CH_3+x_2CH_3(CH_2)_7OH+(1-x_1-x_2)CH_3(CH_2)_6CH_3\}$; at 298.15 K, correlated through use of Eq. (4)

-0.0903 cm^3 mol^{-1} at x_1=0.000 and x_2=0.680. Figure 3 depicts lines of constant ternary contribution Δ_{123}. This contribution shows a maximum of 0.0217 cm^3 mol^{-1} at a concentration x_1=0.560 and x_2=0.169, and a minimum of -0.0138 cm^3 mol^{-1} at x_1=0.150 and x_2=0.625.

Table 5 Average percentage deviations from the ternary experimental values obtained with the empirical predictive methods. For the asymmetric equations, three numberings of the components were compared, in the orders 123, 231 and 312

Predictive method	Percentage deviation		
Kohler		8.7	
Jacob and Fitzner		7.6	
Colinet		6.3	
Knobeloch and Schwartz		33.9	
Tsao and Smith	9.6	39.7	23.7
Toop	9.2	12.3	22.3
Scatchard	8.6	11.7	22.2
Hillert	235	10.8	22.1
Mathieson and Tynne	8.1	8.0	10.1

Several empirical predictive methods have been suggested to estimate ternary excess properties from experimental results on the corresponding constituent binaries. These methods are asymmetric when the predictions depend on the arbitrary designation of the numbering, and symmetric otherwise. The symmetric equations tested were those of Kohler [7], Jacob and Fitzner [8], Colinet [9] and Knobeloch and Schwartz [10]. The asymmetric expressions were those of Tsao and Smith [11], Toop [12], Scatchard [13], Hillert [14] and Mathieson and Tynne [15]. For the asymmetric equations, three numberings of the components were considered to check the differences in the predicted values. Table 5 shows the average percentage deviations of the predictions of these equations. The numberings considered for the asymmetric equations were:

123: x_1 butyl butanoate+x_2 1-octanol+x_3 octane
231: x_1 octane+x_2 1-octanol+x_3 butyl butanoate
312: x_1 octane+x_2 butyl butanoate+x_3 1-octanol

The best result in the prediction was achieved with the symmetric equation of Colinet, with a deviation of 6.3%. The best agreement for the asymmetric equation was achieved with that of Mathieson and Tynne, with a 8.0% deviation using the ordering 213.

The group contribution model of Nitta and Chao was applied to predict the ternary excess molar volumes, using the parameters calculated by Legido *et al.*, [26] Fernández *et al.* [27] and Ortega *et al.* [28], yielding a standard deviation of 0.11 $cm^3 mol^{-1}$.

References

1 P. V. Ilic, E. Jiménez, J. L. Legido, J. Fernández and M. I. Paz Andrade, J. Chem. Thermodynamics, 22 (1990) 865.
2 M. J. Souza, E. Jiménez, J. L. Legido, J. Fernández, E. Perez-Martell and M. I. Paz Andrade, J. Chem. Thermodynamics, 24 (1992) 119.
3 T. Lorenzana, E. Jiménez, J. L. Legido, J. Fernández and M. I. Paz Andrade, J. Chem. Thermodynamics, 25 (1993) 1041.
4 C. Franjo, M. T. Lorenzana, J. L. Legido, M. I. Paz Andrade and E. Jiménez, J. Chem. Thermodynamics, 26 (1994) 1025.
5 C. Franjo, M. T. Lorenzana, L. Segada, E. Jiménez, J. L. Legido and M. I. Andrade, Chem. Thermodynamics, 27 (1995) 1197.
6 E. Jiménez, C. Franjo, L. Segade, J. L. Legido and M. I. Paz Andrade, J. Chem. Eng. Data 42 (1997) 262.
7 F. Kohler, Monatsh. Chem., 91 (1997) 738.
8 K. T. Jacob and K. Fitzner, Thermochim. Acta, 18 (1997) 197.
9 C. Colinet, D. E. S. University of Grenoble, Grenoble, France, 1967.
10 J. B. Knobeloch and C. E. Schwartz, J. Chem. Eng. Data, 7 (1962) 386.
11 C. Tsao and J. Smith, Appl. Thermodyn. Chem. Eng. Prog. Symp. Ser., 49 (1953) 107.
12 G. W. Toop, Trans TMS AIME 223 (1965) 850.
13 G. Scatchard, L. B. Ticknor, J. R. Goates and E. R. McCartney, J. Am. Chem. Soc., 74 (1952) 3721.
14 M. Hillert, Calphad, 4 (1980) 1.
15 A. R. Mathieson, and C. J. Tynne, J. Chem. Soc., (1956) 3713.
16 I. Cibulka, Collect. Czech. Chem. Commun., 47 (1982) 1414.
17 I. Nagata and K. Tamura, J. Chem. Thermodynamics, 22 (1990) 279.
18 T. Nitta, E. Turek, R. A. Greenkorn and K. C. Chao, AIChE. J., 23 (1977) 144.
19 O. Redlich and A. T. Kister, Ind. Eng. Chem., 40 (1948) 341.
20 P. Bevington, Data Reduction and Error Analysis for the Physical Sciences. McGraw-Hill, New York 1969.
21 D. W. Marquardt, J. Soc. Indust. Appl. Math., 2 (1963) 431.
22 Selected Values of Properties of Hydrocarbons and Related Compounds. Thermodynamics Research Center: Texas A&M University, College Station, Texas. 1976.
23 C. Franjo, C. P. Menaut, E. Jiménez, J. L. Legido and M. I. Paz Andrade, J. Chem. Eng. Data, 40 (1995) 992.
24 T. P. Iglesias, J. L. Legido, L. Romaní, J. Peleteiro and M. I. Paz Andrade, Phys. Chem. Liq., 30 (1995) 159.
25 A. Amigo, R. Bravo and M. J. Pintos, Chem. Eng. Data, 38 (1993) 141.
26 J. L. Legido, J. Vijande, B. E. de Cominges, J. García, T. P. Iglesias, S. García-Garabal and J. Fernández, Fluid Phase Eq. 1998 (in press).
27 J. Fernández, J. L. Legido, M. I. Paz Andrade and L. Pías, Fluid Phase Eq. 55 (1990) 293.
28 J. Ortega and J. L. Legido, Fluid Phase Eq. 95, (1994) 175.