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Excess molar volumes of binary and ternary mixtures of propyl alkanoate, 1-chlorobutane, and *n*-decane at 298.15 K

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Abstract

Excess molar volumes at 298.15 K of the ternary systems propyl propanoate + 1-chlorobutane + *n*-decane and propyl butanoate + 1-chlorobutane + *n*-decane, and of the binary systems propyl propanoate + 1-chlorobutane, propyl butanoate + 1-chlorobutane and 1-chlorobutane + *n*-decane, were determined using an Anton Paar DMA 60/602 densimeter. Different polynomial equations were fitted to experimental results of the ternary systems.

INTRODUCTION

In previous work [1–4], we determined the excess molar volumes of ternary systems at 298.15 K. In this paper we present the excess volumes of propyl propanoate + 1-chlorobutane + *n*-decane and propyl butanoate + 1-chlorobutane + *n*-decane, and of the binary systems propyl propanoate + 1-chlorobutane, propyl butanoate + 1-chlorobutane, and 1-chlorobutane + *n*-decane at 298.15 K.

EXPERIMENTAL

The chemical products were supplied by Fluka: propyl propanoate (puriss., >99 mol.%), propyl butanoate (puriss., >99 mol.%), 1-chlorobutane and *n*-decane (puriss., >99.5 mol.%). All chemical products

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TABLE 1

Densities of the pure liquids at 298.15 K

Substance	$\rho/(\mathrm{g\,cm^{-3}})$	
	Experimental	Literature
Propyl propanoate	0.87563	0.87569 [5] 0.87549 [6]
Propyl butanoate	0.86794	0.86797 [7] 0.86804 [8]
1-Chlorobutane	0.88083	0.88074 [9] 0.88064 [10]
n-Decane	0.72627	0.72614 [11] 0.72615 [12]

were degassed by ultrasound, dried over Fluka type 4 Å molecular sieves, and were otherwise used as supplied. The densities of the pure liquids agree well with the literature values, as shown in Table 1.

Excess molar volumes were determined from the densities of the pure liquids and mixtures measured with an Anton Paar DMA 60/602 densimeter thermostatted at (298.15 ± 0.01) K in a Haake F3 circulating-water bath. The experimental technique had been described elsewhere [5, 13].

RESULTS AND DISCUSSION

Excess molar volumes of the binary mixtures determined in this work are listed in Table 2. A variable-degree Redlich–Kister polynomial of the form

$$V_m^E = x(1-x)\sum_{i=0}^{m} A_i(2x-1)^i \qquad (1)$$

was fitted to each binary system by the unweighted least-squares method. The degree of the polynomial was optimized by applying the *F*-test. The coefficient A_i and the standard deviations s are given in Table 3. Figure 1 shows V_m^E plotted against x and the V_m^E curves calculated from the smoothing equations.

Excess molar volumes of 1-chlorobutane + *n*-decane were measured by Lainez et al. [9] and by Crespo Colin et al. [10]. Our results agree with the first values to within 3% and with the second to within 7%. For the other four binary systems, no published data were found. The results obtained for 1-chlorobutane + *n*-decane are consistent with the general behaviour [2, 9, 10, 14, 15] of the V_m^E values of 1-chloroalkane + *n*-alkane systems which increase when the *n*-alkane chain length increases and when the 1-chloroalkane chain length decreases. The V_m^E values of propyl alkanoate + *n*-alkane mixtures show the same behaviour increases when the *n*-alkane chain length increases and when the propyl alkanoate chain

TABLE 2

Experimental excess molar volumes V_m^E in $cm^3\,mol^{-1}$ at 298.15 K

x	V_m^E	x	V_m^E	x	V_m^E	x	V_m^E
xPropyl propanoate + $(1+x)$1-chlorobutane							
0.1555	0.0586	0.3648	0.0940	0.5760	0.0931	0.8463	0.0481
0.1928	0.0682	0.4216	0.0978	0.6290	0.0884		
0.2614	0.0821	0.4653	0.0974	0.6767	0.0797		
0.3052	0.0885	0.5206	0.0964	0.7866	0.0619		
xPropyl butanoate + $(1-x)$1-chlorobutane							
0.0500	0.0075	0.2954	0.0293	0.5907	0.0302	0.8797	0.0101
0.0998	0.0141	0.3421	0.0319	0.6493	0.0272	0.9353	0.0057
0.1514	0.0197	0.4590	0.0326	0.6680	0.0254		
0.2088	0.0245	0.5082	0.0318	0.7294	0.0222		
0.2548	0.0274	0.5373	0.0320	0.7891	0.0168		
x1-Chlorobutane + $(1-x)n$-decane							
0.1042	0.1536	0.4994	0.4098	0.7581	0.3057	0.9219	0.1243
0.2060	0.2694	0.5708	0.4003	0.7940	0.2736	0.9664	0.0573
0.2972	0.3417	0.6153	0.3896	0.8282	0.2389		
0.3449	0.3697	0.6857	0.3564	0.8584	0.2069		
0.4274	0.3995	0.7172	0.3359	0.8933	0.1638		

length decreases [5, 7, 11, 16, 17]. The V_m^E values of propyl alkanoate + 1-chlorobutane mixtures increase when the propyl alkanoate chain length decreases.

The experimental excess volumes V_{123}^E of the ternary systems are shown in Tables 4 and 5. The Cibulka equation [18] has been fitted to the experimental values

$$V_{m,123}^E = V_{m,bin}^E + x_1x_2(1+x_1-x_2)(B_1+B_2x_1+B_3x_2) \quad (2)$$

where

$$V_{m,bin}^E = V_{m,12}^E + V_{m,13}^E + V_{m,23}^E \quad (3)$$

Table 6 presents the parameters and the standard deviations between

TABLE 3

Coefficients A_i of eqn. (1) and standard deviations s

System	A_0	A_1	A_2	A_3	s
xPropyl propanoate + $(1-x)$1-chlorobutane	0.3882	−0.0593	0.0373		0.0007
xPropyl butanoate + $(1-x)$1-chlorobutane	0.1296	−0.0371	−0.0090		0.0004
xPropyl propanoate + $(1-x)n$-decane [5]	3.258	−0.084	0.210		0.002
xPropyl butanoate + $(1-x)n$-decane [7]	2.712	−0.038	0.156		0.004
x1-Chlorobutane + $(1-x)n$-decane	1.6348	0.0118	0.0720	0.0481	0.0007

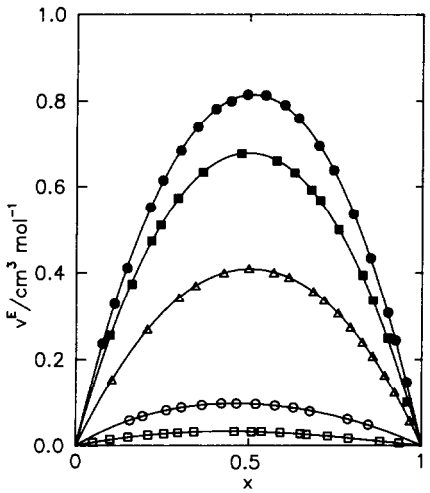

Fig. 1. Excess molar volumes at 298.15 K of: ○, $x$propyl propanoate + $(1-x)$1-chlorobutane; □, $x$propyl butanoate + $(1-x)$1-chlorobutane; ●, $x$propyl propanoate + $(1-x)n$-decane [5]; ■, $x$propyl butanoate + $1-xn$-decane; △, x1-chlorobutane + $(1-x)n$-decane.

TABLE 4

Excess molar volumes in $cm^3\ mol^{-1}$ of $x_1$propyl propanoate + $x_2$1-chlorobutane + x_3n-decane at 298.15 K

x_1	x_2	V_m^E	x_1	x_2	V_m^E
0.0190	0.1073	0.1964	0.2179	0.1295	0.6281
0.0377	0.0988	0.2578	0.2490	0.0895	0.6455
0.0531	0.3005	0.4313	0.2516	0.6594	0.2530
0.0591	0.3343	0.4450	0.2532	0.3751	0.5977
0.0596	0.1562	0.3680	0.2980	0.4415	0.5247
0.0781	0.4419	0.4919	0.3038	0.1806	0.6899
0.0830	0.1230	0.3861	0.3367	0.4987	0.4096
0.0853	0.0306	0.3094	0.3524	0.1266	0.7255
0.0950	0.5375	0.4624	0.3730	0.5515	0.2580
0.1047	0.2744	0.5005	0.3863	0.2296	0.6863
0.1133	0.6408	0.4013	0.4134	0.2457	0.6595
0.1199	0.0713	0.4267	0.4488	0.1612	0.7094
0.1272	0.7195	0.3056	0.4562	0.2711	0.6032
0.1344	0.0483	0.4329	0.4831	0.1736	0.6965
0.1392	0.7875	0.1883	0.5191	0.3085	0.4711
0.1426	0.3736	0.5624	0.5351	0.1923	0.6244
0.1476	0.2186	0.5609	0.5742	0.3412	0.3021
0.1879	0.4925	0.5285	0.6017	0.2162	0.4953
0.2016	0.2988	0.6162	0.6689	0.2404	0.3099
0.2072	0.5430	0.4539			

TABLE 5

Excess molar volumes in $cm^3 mol^{-1}$ of $x_1$propyl butanoate + $x_2$1-chlorobutane + x_3n-decane at 298.15 K

x_1	x_2	V_m^E	x_1	x_2	V_m^E
0.0073	0.9527	0.0679	0.1235	0.7218	0.2497
0.0121	0.9215	0.1085	0.1260	0.5811	0.3937
0.0156	0.9482	0.0618	0.1496	0.5088	0.4248
0.0240	0.8440	0.2012	0.1634	0.7313	0.2007
0.0285	0.9052	0.1126	0.1688	0.6287	0.3250
0.0304	0.9331	0.0712	0.1851	0.5928	0.3556
0.0317	0.9479	0.0416	0.1881	0.3746	0.4860
0.0362	0.9518	0.0366	0.2072	0.7247	0.1498
0.0377	0.7552	0.2857	0.2231	0.5090	0.4111
0.0384	0.9154	0.0875	0.2295	0.6226	0.2740
0.0422	0.9306	0.0555	0.2389	0.2058	0.5351
0.0477	0.9463	0.0146	0.2530	0.7154	0.0851
0.0510	0.8303	0.1902	0.2565	0.5782	0.3091
0.0546	0.6450	0.3769	0.2865	0.3696	0.4890
0.0631	0.5897	0.3955	0.2952	0.5146	0.3444
0.0747	0.5142	0.4245	0.3351	0.5547	0.2438
0.0775	0.7424	0.2737	0.3571	0.2142	0.5744
0.0791	0.8258	0.1704	0.3853	0.3663	0.4358
0.0950	0.3827	0.4555	0.4032	0.5464	0.1342
0.1076	0.8231	0.1368	0.4848	0.4546	0.1604
0.1101	0.6339	0.3538	0.5007	0.1765	0.5456

experimental and fitted values. The lines of constant ternary excess molar volume $V_{m,123}^E$ calculated by eqns. (2) and (3) are shown in Fig. 2. The $V_{m,123}^E$ values of propyl alkanoate + 1-chlorobutane + n-decane systems increase when the propyl alkanoate chain length decreases, as was found for other ternary systems containing propyl alkanoate + 1-chlorobutane + n-decane [3].

Figure 3 show the lines of the ternary contributions, $V_{m,123}^E - V_{m,bin}^E$. This contribution shows a maximum of $0.017\ cm^3 mol^{-1}$, $x_1 = 0.51$, $x_2 = 0.34$, and a minimum of $-0.020\ cm^3 mol^{-1}$, $x_1 = 0.18$, $x_2 = 0.21$, for propyl

TABLE 6

Coefficients B_i of eqn. (2) and standard deviations s

System	B_1	B_2	B_3	s
x_1Propyl propanoate + $x_1$1-chlorobutane + x_2n-decane	0.9398	2.5484	−0.4699	0.007
x_1Propyl butanoate + $x_2$1-chlorobutane + x_3n-decane	−2.0875	3.4866	2.8365	0.004

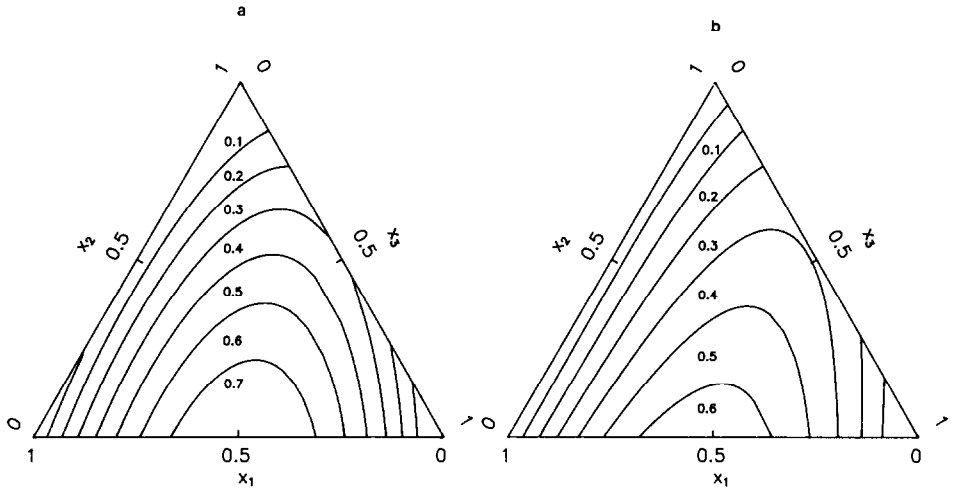

Fig. 2. Ternary contributions $\Delta V^{E}_{m,123} = V^{E}_{m,123} - V^{E}_{m,bin}$ for: a, $x_1$propyl propanoate + $x_2$1-chlorobutane + x_3n-decane; b, $x_1$propyl butanoate + $x_2$1-chlorobutane + x_3n-decane.

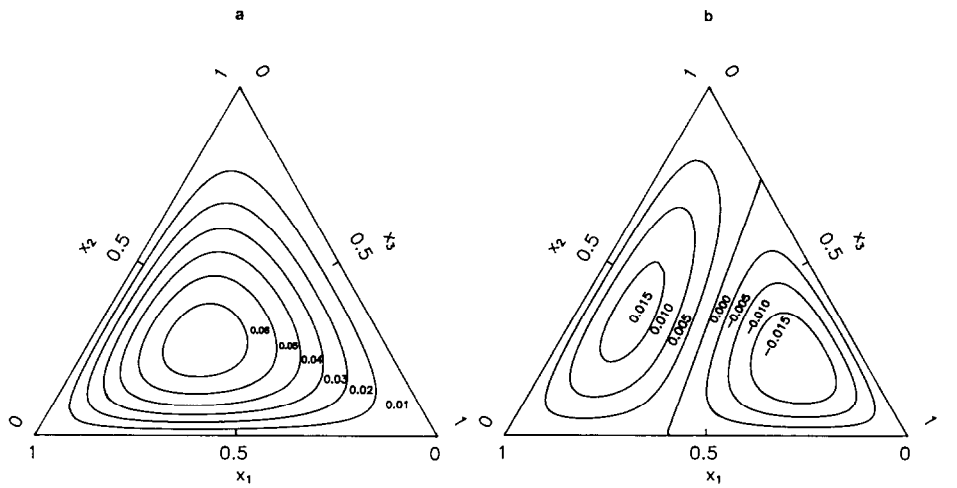

Fig. 3. Curves of constant $V^{E}_{m,123}$ ($cm^3\,mol^{-1}$) for: a, $x_1$propyl propanoate + $x_2$1-chlorobutane + x_3n-decane; b, $x_1$propyl butanoate + $x_2$1-chlorobutane + x_3n-decane.

butanoate + 1-chlorobutane + n-decane, and a maximum of 0.067 cm^3 mol^{-1}, $x_1 = 0.45$, $x_2 = 0.28$, for propyl propanoate + 1-chlorobutane + n-decane.

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