Excess Volumes of Ternary Mixtures Containing Tetrahydropyran and Decane with 1-Alkanols at the Temperature 298.15 K

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Excess molar volumes (V_m^E) at the temperature 298.15 K of the binary mixture tetrahydropyran + decane and of the ternary mixtures tetrahydropyran + decane + 1-heptanol or 1-octanol have been computed from density measurements. The measured excess volumes have been compared with those predicted from binary data with use of semiempirical equations.

Introduction

This work forms part of a program to determine excess thermodynamic properties for a number of binary and ternary mixtures which include tetrahydropyran or tetrahydrofuran as the common component and *n*-alkanes or 1-alkanols as noncommon components.

In a previous investigation the excess volumes of tetrahydropyran + heptane + 1-heptanol or 1-octanol at the temperature 298.15 K and normal atmospheric pressure were measured (*1*). The purpose of the present study was to investigate the effect of the variation of the alkane chain length on the excess volumes for this kind of ternary mixture, so we have determined the excess molar volumes, V_m^E, of tetrahydropyran + decane + 1-heptanol or 1-octanol at the same temperature and pressure conditions, and we have compared these results with those obtained for the ternary mixtures in which decane was changed by heptane.

Recently we reported the excess volumes for tetrahydropyran + a 1-alkanol (*2*) and an *n*-alkane + a 1-alkanol (*3*). Here, we also report V_m^E of the binary mixture tetrahydropyran + decane. These measurements are needed to evaluate V_m^E in ternary mixtures.

Smooth representations of the results are described and used to construct the curves of constant excess volumes for both ternary mixtures. The possibilities of predicting excess molar volumes of the ternary mixtures using those for the binary mixtures have been analyzed.

Experimental Section

Materials. All the chemicals used in this work were supplied by Fluka and had guaranteed purities of greater than 99.5 mol %. Before use, the chemicals were stored in the dark over molecular sieves (Union Carbide Type 4A) and partially degassed.

Volumetric Measurements. The solutions for the measurements of densities were prepared by mass using a Mettler AT201 balance (precision of 1×10^{-5} g), and airtight stoppered bottles. The possible error in the mole fraction is estimated to be less than 10^{-4}. The densities were measured by an Anton Paar digital precision densimeter (model DMA 60/602) operated in the static mode. The temperature was measured with a digital thermometer (Anton Paar DT 100-30). A Heto circulating thermostat (type 04 PT 623) maintained the temperature constant to within 0.01 K. Bidistilled water and heptane were used as calibrating substances (*4*, *5*). Calibration was carried out before each measurement at the same temperature and pressure conditions.

Densities were measured with a precision of 3×10^{-2} kg m^{-3}. The maximum uncertainty in the excess molar volumes is expected to be less than 3×10^{-3} cm^3 mol^{-1}.

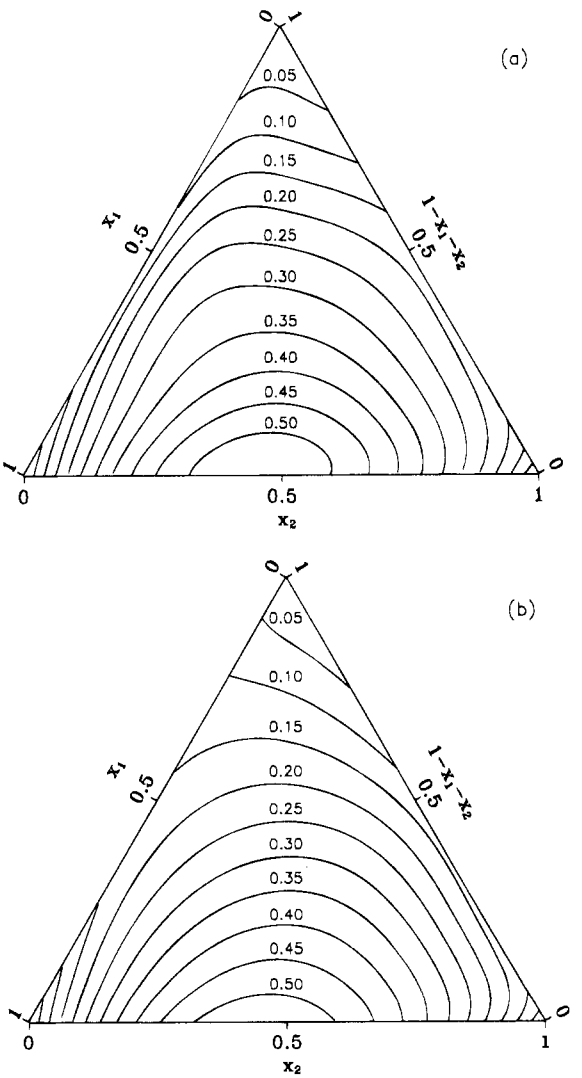

Figure 1. Curves of constant $V_{m,123}^E/(cm^3 mol^{-1})$ for (a) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_5CH_2OH$ and (b) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_6CH_2OH$.

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Table 1. Experimental Excess Molar Volumes for x_1 c-$(CH_2)_5O$ + $(1 - x_1)$ $CH_3(CH_2)_8CH_3$ at 298.15 K

x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})
0.0949	0.1705	0.2741	0.4012	0.5079	0.5359	0.7191	0.4730	0.9485	0.1288
0.1232	0.2102	0.3692	0.4791	0.5790	0.5371	0.8056	0.3827		
0.1965	0.3128	0.4324	0.5134	0.6474	0.5159	0.8776	0.2740		

Table 2. Densities and Excess Molar Volumes for Ternary Mixtures at the Temperature 298.15 K ($\delta V_{m,123}^E = V_{m,123}^E - V_{m,123}^E$ ((a) Eq 2; (b) Eq 3); $\Delta V_{m,123}^E = V_{m,123}^E - V_{m,123}^E$ (Eq 4))

x_1	x_2	ϱ/(g·cm^3)	$V_{m,123}^E$/(cm^3·mol^{-1})	$\delta V_{m,123}^E$/(cm^3·mol^{-1})	$\Delta V_{m,123}^E$/(cm^3·mol^{-1})	x_1	x_2	ϱ/(g·cm^3)	$V_{m,123}^E$/(cm^3·mol^{-1})	$\delta V_{m,123}^E$/(cm^3·mol^{-1})	$\Delta V_{m,123}^E$/(cm^3·mol^{-1})
(a) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_5CH_2OH$											
1.0000	0.0000	0.878 91				0.3090	0.3174	0.790 02	0.3222	0.0000	−0.0180
0.0000	1.0000	0.726 30				0.3456	0.3550	0.786 70	0.3637	−0.0040	0.0225
0.0000	0.0000	0.818 78				0.3603	0.1566	0.811 85	0.2691	0.0013	0.0303
0.0729	0.1760	0.799 67	0.0921	0.0002	−0.0021	0.3629	0.0290	0.830 50	0.1430	0.0000	0.0236
0.1095	0.2644	0.790 54	0.1665	0.0027	−0.0021	0.3736	0.3837	0.784 16	0.3969	0.0045	−0.0223
0.1377	0.1415	0.805 93	0.1148	−0.0042	0.0003	0.3993	0.4101	0.781 85	0.4273	0.0000	−0.0207
0.1466	0.3540	0.781 67	0.2392	0.0026	−0.0093	0.4041	0.1756	0.810 99	0.2962	−0.0005	0.0194
0.1628	0.3930	0.777 97	0.2642	0.0004	−0.0156	0.4262	0.4378	0.779 39	0.4663	−0.0019	−0.0101
0.1750	0.4226	0.775 20	0.2833	0.0010	−0.0182	0.4454	0.4574	0.777 66	0.4941	−0.0029	−0.0011
0.1808	0.0786	0.815 54	0.1105	−0.0005	0.0112	0.4607	0.0368	0.834 10	0.1840	0.0020	0.0348
0.1812	0.1861	0.801 81	0.1748	0.0005	0.0076	0.4931	0.2143	0.809 24	0.3465	0.0025	−0.0061
0.2022	0.4882	0.769 22	0.3206	0.0002	−0.0232	0.4935	0.2145	0.809 24	0.3466	0.0023	−0.0063
0.2113	0.5102	0.767 25	0.3343	0.0011	−0.0221	0.5313	0.0424	0.836 89	0.2070	0.0042	0.0377
0.2286	0.0994	0.814 58	0.1511	−0.0019	0.0190	0.5657	0.2459	0.807 80	0.3839	−0.0056	−0.0255
0.2362	0.0189	0.826 15	0.0882	−0.0003	0.0079	0.5872	0.0469	0.839 25	0.2163	0.0032	0.0328
0.2382	0.5752	0.761 52	0.3779	0.0039	−0.0123	0.6136	0.2667	0.806 74	0.4240	−0.0060	−0.0187
0.2572	0.2642	0.794 76	0.2633	−0.0053	−0.0075	0.6336	0.2754	0.806 28	0.4419	−0.0065	−0.0136
0.2593	0.6261	0.757 16	0.4111	0.0046	−0.0006	0.6447	0.0515	0.841 84	0.2176	−0.0001	0.0221
0.2628	0.1142	0.813 87	0.1835	−0.0012	0.0257	0.6946	0.0554	0.844 17	0.2172	0.0000	0.0143
0.2693	0.2766	0.793 65	0.2765	−0.0053	−0.0108	0.7473	0.0597	0.846 76	0.2134	0.0003	0.0061
0.2723	0.6575	0.754 55	0.4233	0.0019	0.0030	0.8191	0.0654	0.850 46	0.2041	0.0007	−0.0008
0.3071	0.1335	0.812 96	0.2229	−0.0020	0.0293	0.8707	0.0695	0.853 28	0.1934	−0.0002	−0.0026
(b) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_6CH_2OH$											
1.0000	0.0000	0.878 91				0.3328	0.0420	0.827 51	0.3130	−0.0026	−0.0160
0.0000	1.0000	0.726 30				0.3328	0.3127	0.793 49	0.3130	0.0001	−0.0357
0.0000	0.0000	0.821 61				0.3501	0.3290	0.791 95	0.3279	−0.0069	−0.0424
0.0734	0.1616	0.804 94	0.0793	0.0000	−0.0088	0.3672	0.1479	0.815 44	0.2150	−0.0030	−0.0385
0.1013	0.2229	0.798 67	0.1173	0.0002	−0.0132	0.3933	0.3696	0.787 95	0.3881	−0.0016	−0.0336
0.1205	0.2652	0.794 35	0.1468	0.0005	−0.0156	0.4097	0.1651	0.814 59	0.2456	−0.0014	−0.0407
0.1368	0.3010	0.790 73	0.1698	−0.0038	−0.0216	0.4200	0.3947	0.785 45	0.4267	0.0033	−0.0246
0.1526	0.3360	0.787 13	0.2089	0.0068	−0.0119	0.4202	0.0531	0.830 64	0.1803	0.0041	−0.0148
0.1629	0.3586	0.784 87	0.2222	0.0011	−0.0179	0.4394	0.0555	0.831 13	0.1870	0.0049	−0.0151
0.1679	0.1578	0.807 93	0.1320	0.0000	−0.0195	0.4515	0.1819	0.813 74	0.2769	−0.0002	−0.0417
0.1729	0.1625	0.807 51	0.1365	0.0000	−0.0203	0.4525	0.4252	0.782 42	0.4639	0.0003	−0.0205
0.1859	0.4092	0.779 75	0.2657	0.0015	−0.0170	0.4934	0.0623	0.832 58	0.2048	0.0068	−0.0161
0.1880	0.0757	0.818 61	0.1109	−0.0002	−0.0136	0.4972	0.2003	0.812 78	0.3100	−0.0014	−0.0435
0.1959	0.4311	0.777 56	0.2841	0.0016	−0.0163	0.5001	0.4700	0.777 91	0.5205	0.0004	−0.0056
0.2091	0.1965	0.804 43	0.1705	−0.0001	−0.0261	0.5369	0.2163	0.811 92	0.3395	−0.0026	−0.0430
0.2280	0.0288	0.826 08	0.1110	0.0000	−0.0071	0.5694	0.0719	0.834 80	0.2190	0.0000	−0.0256
0.2284	0.5027	0.770 44	0.3403	0.0021	−0.0122	0.5742	0.2313	0.811 09	0.3669	−0.0044	−0.0411
0.2310	0.0931	0.817 88	0.1353	−0.0001	−0.0190	0.6169	0.0779	0.836 21	0.2376	0.0067	−0.0195
0.2356	0.5184	0.768 89	0.3516	0.0020	−0.0111	0.6294	0.2536	0.809 83	0.4079	−0.0067	−0.0336
0.2367	0.2225	0.802 02	0.2034	0.0042	−0.0255	0.6589	0.0832	0.837 55	0.2461	0.0059	−0.0199
0.2672	0.2511	0.799 37	0.2324	−0.0007	−0.0337	0.6703	0.2701	0.808 81	0.4463	0.0001	−0.0156
0.2814	0.1134	0.817 00	0.1644	0.0000	−0.0256	0.7213	0.0911	0.839 65	0.2582	0.0069	−0.0163
0.2867	0.0362	0.827 43	0.1269	−0.0057	−0.0161	0.7738	0.0977	0.841 54	0.2637	0.0066	−0.0121
0.2928	0.2752	0.797 11	0.2596	−0.0038	−0.0387	0.8721	0.1101	0.845 50	0.2560	0.0000	−0.0035
0.3320	0.1338	0.816 11	0.1904	−0.0049	−0.0366						

Results and Discussion

The values of V_m^E for the binary mixture tetrahydropyran + decane are reported in Table 1. The polynomial function

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{k=0}^{2}A_k(x_1 - x_2)^k \quad (1)$$

was fitted to the results by the method of least squares with all points weighted equally.

The experimental excess molar volumes $V_{m,123}^E$ of the ternary mixtures are shown in Table 2. The dependence of experimental ternary values on composition is expressed by the polynomial

$$V_{m,123}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = V_{m,12}^E + V_{m,13}^E + V_{m,23}^E + x_1x_2x_3\{A_0 + A_1x_1(x_2 - x_3) + A_2x_1^2(x_2 - x_3)^2\} \quad (2)$$

for tetrahydropyran + decane + 1-heptanol and

$$V_{m,123}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = V_{m,12}^E + V_{m,13}^E + V_{m,23}^E + x_1x_2x_3\{A_0 + A_1x_1 + A_2x_2\} \quad (3)$$

for tetrahydropyran + decane + 1-octanol, where $V_{m,ij}^E$ are the polynomials representing the excess molar volumes for the binary mixtures. Table 3 presents the values of the

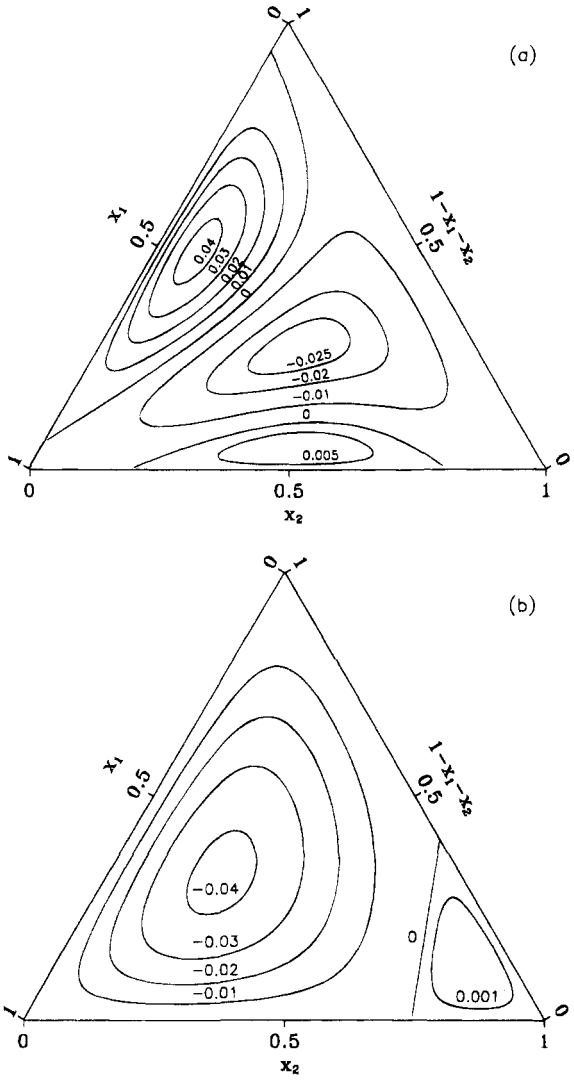

Figure 2. Curves of constant ternary contribution ($V^E_{m,123} - V^E_{m,12} - V^E_{m,13} - V^E_{m,23}$)/(cm^3·mol^{-1}) to the excess molar volumes of (a) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_5CH_2OH$ and (b) x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_6CH_2OH$.

parameters of eqs 1–3, fitted to the experimental values using a nonlinear regression algorithm due to Marquardt (*6*), and the corresponding standard deviations.

We are not aware of any volumetric data in the literature for the systems presented in this study.

Curves of constant $V^E_{m,123}$ have been plotted in Figure 1, and the ternary contributions, given by $V^E_{m,123} - V^E_{m,12} - V^E_{m,13} - V^E_{m,23}$, in Figure 2.

The experimental ternary excess volumes are positive over the entire range of composition. These values suggest that the structure-breaking effect of the components is dominant in the mixtures analyzed.

The behavior of the present systems is quite different from that of the ternary mixtures in which decane was changed by heptane (*1*). By comparing the results for the ternary mixtures containing decane with those containing heptane, it can be observed that when the alkane chain length decreases, the packing effect in the mixture increases and therefore the values of V^E_m decrease, even reaching negative values.

Table 3. Parameters A_i of Eqs 1–3 and Standard Deviations

A_0	A_1	A_2	s/cm^3·mol^{-1}
	x_1 c-$(CH_2)_5O$ + $(1 - x_1)$ $CH_3(CH_2)_8CH_3$		
2.1384	0.3758	0.2028	0.0013
	x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_5CH_2OH$		
−0.6235	−6.3705	67.573	0.0031
	x_1 c-$(CH_2)_5O$ + x_2 $CH_3(CH_2)_8CH_3$ + $(1 - x_1 - x_2)$ $CH_3(CH_2)_6CH_2OH$		
−1.2204	−1.1763	2.0440	0.0037

The excess molar volumes of mixtures of more than two components may be estimated, from binary results, using the expression (*7*, *8*)

$$V^E_{m,123}/(\text{cm}^3\cdot\text{mol}^{-1}) = \sum_{i<j}(x_i x_j / x_i' x_j')V^E_{m,ij}(x_i', x_j') \quad (4)$$

where the mole fractions x_i' and x_j' are defined so that $x_i' + x_j' = 1$. For a ternary mixture the mole fractions x_i' and x_j' may be obtained from a triangular diagram by projecting the point representing the ternary mixture onto the corresponding binary axis. In this paper we have used the normal projection with $x_i' = (1 + x_i - x_j)/2$ and $x_j' = (1 - x_i + x_j)/2$.

Table 2 also lists the deviations $\delta V^E_{m,123}$ between the experimental and the fitted excess molar volumes, together with the discrepancies $\Delta V^E_{m,123}$ between experimental and predicted values.

Registry Numbers Supplied by Author. Tetrahydropyran, 142-68-7; decane, 124-18-5; 1-heptanol, 111-70-6; 1-octanol, 143-08-8.

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