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Excess molar volumes for binary systems containing toluene, *p*-xylene or pseudo-cumene + five methyl alkyl ketones at 298.15 K. Application of an extended cell model

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Abstract

Excess molar volumes at 298.15 K are reported for the binary systems containing toluene, *p*-xylene or pseudo-cumene +2-propanone, 2-butanone, 2-pentanone, 2-octanone or 2-undecanone. All experimental curves present negative excess volumes, with the sole exception of the pseudo-cumene(1) +2-propanone(2) mixture. The experimental data are examined by an extended cell model.

INTRODUCTION

In this paper, we report the excess molar volumes V^E of binary mixtures containing toluene, *p*-xylene or pseudo-cumene + five methyl alkyl ketones, namely 2-propanone, 2-butanone, 2-pentanone, 2-octanone or 2-undecanone, respectively. In a previous work [1], we reported the excess molar enthalpies H^E of the same binary systems and the aim of this research is to provide more information about the thermodynamic properties of these mixtures.

No literature data could be found for the binary mixtures considered here, with the exception of the toluene or *p*-xylene + 2-propanone systems studied by other authors [2]; these results are reported in Figs. 1 and 2 as dashed lines.

Quin et al. [3] have determined the excess molar volumes of the two above-mentioned systems and of 2-butanone + toluene or +*p*-xylene mixtures but at 293.15 K, whereas our data were all obtained at 298.15 K.

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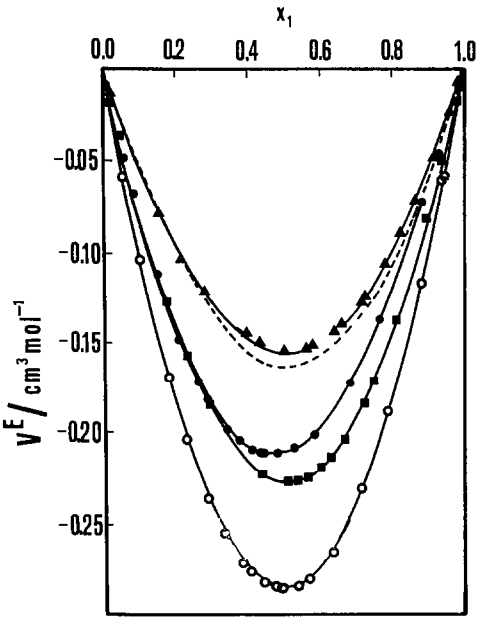

Fig. 1. Excess molar volumes at 298.15 K for toluene + 2-propanone(--) [3], +2-butanone (●), +2-pentanone (○), +2-octanone (■), and +2-undecanone (▲). Solid curves are the least-squares representation of results by eqn. (1).

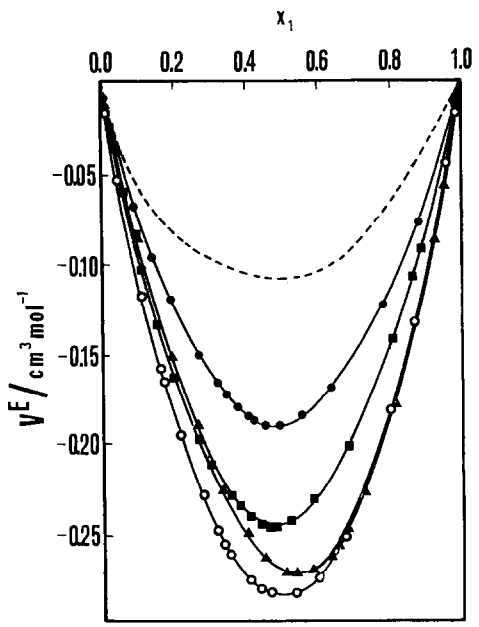

Fig. 2. Excess molar volumes at 298.15 K for *p*-xylene + 2-propanone (--) [3], +2-butanone (●), +2-pentanone (○), +2-octanone (■), and +2-undecanone (▲). Solid curves are the least-squares representation of results by eqn. (1).

EXPERIMENTAL

Chemicals

All pure components considered are the same as used in ref. 1. Before use, the liquids were stored in dark bottles over molecular sieves (Union Carbide, type 4A, 1/16 inch pellets).

Preparation of the mixtures

The mole fractions of the components were weighed out using a Mettler balance AE 160, with a precision of 1×10^{-4} g, and air-tight stoppered bottles. The more volatile component was put inside the bottle and the charged bottle was closed and weighed. The second component was then syringed into the bottle, which avoids possible contamination and minimizes vapor loss; 15 ml bottles were used. Corrections for solvent vaporization revealed a negligible contribution to the mole fraction so that the excess molar volumes are accurate to 0.002 $cm^3\ mol^{-1}$.

Density measurements

Excess molar volumes were calculated from density measurements by means of a digital density meter (Anton Paar DMA 60/602, Austria) at atmospheric pressure, described in ref. 4. The pressure values were read with a digital vacuum-regulator (Normag, Postfach, Germany).

All measurements were performed at 10000 period select switch, and a time gap of 20 min was chosen from one measurement to the next to ensure constancy of temperature and oscillation period stability. The density meter was thermostated at the working temperature to better than ±0.01 K by a Colora bath circulator.

The temperature in the density meter was read with a digital thermometer (Anton Paar DT 100-25) to within ±0.01 K; the densities were reproducible with a precision of 3×10^{-6} g cm^{-3}.

The test system, benzene + cyclohexane [5] at 298.15 K, was used to evaluate the accuracy of the experimental technique and the results were in agreement with those of the literature (discrepancy less than 3×10^{-6} g cm^{-3}).

CORRELATION OF THE VOLUMETRIC DATA

The excess molar volumes V^E of the binary systems studied here have been represented by a Redlich–Kister polynomial

$$V^E/x_1x_2 = \sum_{k=0}^{n-1} A_k(x_1 - x_2)^k \qquad (1)$$

TABLE 1

Experimental excess molar volumes V^E of toluene, *p*-xylene or pseudo-cumene + methyl alkyl ketones mixtures at 298.15 K

X_1	V^E in $cm^3\ mol^{-1}$	X_1	V^E in $cm^3\ mol^{-1}$	X_1	V^E in $cm^3\ mol^{-1}$
Toluene + 2-butanone					
0.0093	−0.0084	0.3433	−0.1991	0.5849	−0.2041
0.0556	−0.0486	0.3786	−0.2054	0.6796	−0.1739
0.0799	−0.0680	0.4065	−0.2110	0.7656	−0.1379
0.1440	−0.1136	0.4420	−0.2126	0.8818	−0.0736
0.2107	−0.1502	0.4466	−0.2129	0.9258	−0.0469
0.2583	−0.1726	0.4807	−0.2123	0.9949	−0.0028
0.2888	−0.1827	0.5205	−0.2091		
Toluene + 2-pentanone					
0.0537	−0.0589	0.4076	−0.2762	0.6292	−0.2664
0.0986	−0.1044	0.4382	−0.2829	0.7129	−0.2311
0.1788	−0.1704	0.4733	−0.2847	0.7863	−0.1892
0.2306	−0.2040	0.4940	−0.2859	0.8763	−0.1169
0.2876	−0.2345	0.5338	−0.2841	0.9416	−0.0594
0.3301	−0.2538	0.5642	−0.2809	0.9913	−0.0098
0.3857	−0.2717				
Toluene + 2-octanone					
0.0202	−0.0175	0.5283	−0.2268	0.7466	−0.1717
0.0454	−0.0379	0.5629	−0.2264	0.8116	−0.1382
0.1707	−0.1271	0.6009	−0.2199	0.8978	−0.0826
0.2350	−0.1579	0.6251	−0.2153	0.9393	−0.0505
0.2959	−0.1851	0.6634	−0.2048	0.9802	−0.0178
0.4272	−0.2239	0.7187	−0.1848	0.9898	−0.0083
0.5107	−0.2269				
Toluene + 2-undecanone					
0.0248	−0.0140	0.5386	−0.1549	0.7750	−0.1067
0.1523	−0.0801	0.5612	−0.1511	0.8253	−0.0877
0.2178	−0.1042	0.5808	−0.1511	0.8652	−0.0724
0.2811	−0.1225	0.6371	−0.1447	0.9146	−0.0489
0.2940	−0.1465	0.6524	−0.1430	0.9601	−0.0288
0.4328	−0.1518	0.7141	−0.1276	0.9919	−0.0048
0.4975	−0.1556	0.7224	−0.1252		
p-Xylene + 2-butanone					
0.0128	−0.0103	0.3423	−0.1808	0.5479	−0.1875
0.0502	−0.0393	0.3717	−0.1853	0.6318	−0.1722
0.0934	−0.0690	0.3982	−0.1889	0.7757	−0.1256
0.1398	−0.0982	0.4176	−0.1912	0.8727	−0.0795
0.1819	−0.1565	0.4494	−0.1928	0.9810	−0.0124
0.2654	−0.1685	0.4831	−0.1903	0.9872	−0.0076
0.3196	−0.1775				

TABLE 1 (continued)

X_1	V^E in $cm^3\ mol^{-1}$	X_1	V^E in $cm^3\ mol^{-1}$	X_1	V^E in $cm^3\ mol^{-1}$
p-Xylene + 2-pentanone					
0.0116	−0.0156	0.3164	−0.2483	0.5919	−0.2745
0.0486	−0.0552	0.3327	−0.2566	0.688	−0.2509
0.1136	−0.1177	0.3494	−0.2616	0.7989	−0.1781
0.1622	−0.1578	0.4092	−0.2769	0.8626	−0.1335
0.1733	−0.1649	0.4371	−0.2817	0.9571	−0.0441
0.2163	−0.1916	0.4592	−0.2835	0.9846	−0.0162
0.2740	−0.2289	0.5318	−0.2842		
p-Xylene + 2-octanone					
0.0109	−0.0109	0.3507	−0.2293	0.5874	−0.2316
0.0614	−0.0614	0.3766	−0.2354	0.6882	−0.2014
0.1130	−0.1044	0.4078	−0.2401	0.8041	−0.1420
0.1527	−0.1337	0.4426	−0.2452	0.8565	−0.1081
0.1990	−0.1637	0.4592	−0.2454	0.8787	−0.0932
0.2652	−0.1985	0.4803	−0.2457	0.9818	−0.0154
0.2973	−0.2125	0.5230	−0.2432		
p-Xylene + 2-undecanone					
0.0288	−0.0250	0.5074	−0.2727	0.6770	−0.2499
0.1009	−0.0847	0.5271	−0.2722	0.7300	−0.2276
0.1939	−0.1517	0.5779	−0.2711	0.8166	−0.1811
0.2632	−0.1917	0.5917	−0.2703	0.9207	−0.0877
0.3301	−0.2312	0.6279	−0.2641	0.9492	−0.0584
0.3936	−0.2512	0.6535	−0.2575	0.9906	−0.0110
0.4520	−0.2640				
Pseudo-cumene + 2-propanone					
0.0080	−0.0004	0.2527	0.0068	0.4594	−0.0059
0.0509	−0.0023	0.2680	−0.0072	0.5601	−0.0046
0.0691	−0.0048	0.2980	−0.0074	0.6437	−0.0039
0.0952	−0.0052	0.3477	−0.0069	0.7784	−0.0004
0.1411	−0.0056	0.3671	−0.0067	0.8475	0.0019
0.1814	−0.0065	0.3966	−0.0063	0.9693	0.0003
0.2059	−0.0066	0.4290	−0.0059		
Pseudo-cumene + 2-butanone					
0.0187	−0.0107	0.2562	−0.0649	0.5289	−0.0715
0.0612	−0.0235	0.2769	−0.0675	0.6092	−0.0655
0.0971	−0.0342	0.3116	−0.0704	0.6775	−0.0579
0.1121	−0.0387	0.3401	−0.0727	0.8020	−0.0390
0.1589	−0.0499	0.3893	−0.0752	0.8651	−0.0261
0.1921	−0.0559	0.4466	−0.0748	0.9790	−0.0056
0.2054	−0.0584	0.4859	−0.0738		

TABLE 1 (continued)

X_1	V^E in $cm^3 mol^{-1}$	X_1	V^E in $cm^3 mol^{-1}$	X_1	V^E in $cm^3 mol^{-1}$
Pseudo-cumene + 2-pentanone					
0.0114	−0.0121	0.3144	−0.1768	0.6683	−0.1770
0.0347	−0.0293	0.3541	−0.1868	0.7361	−0.1541
0.0817	−0.0638	0.3762	−0.1906	0.7867	−0.1328
0.1339	−0.0987	0.4407	−0.1999	0.8743	−0.0873
0.1870	−0.1259	0.4874	−0.2012	0.9059	−0.0670
0.2354	−0.1489	0.5255	−0.2001	0.9766	−0.0181
0.2948	−0.1700	0.5689	−0.1967		
Pseudo-cumene + 2-octanone					
0.0120	−0.0117	0.4146	−0.2287	0.6951	−0.2120
0.0487	−0.0428	0.4446	−0.2331	0.7822	−0.1724
0.0846	−0.0696	0.4596	−0.2349	0.8646	−0.1194
0.1884	−0.1364	0.5043	−0.2427	0.9052	−0.0882
0.2075	−0.1486	0.5276	−0.2405	0.9457	−0.0535
0.2609	−0.1763	0.5798	−0.2363	0.9833	−0.0178
0.3201	−0.2005	0.6619	−0.2206		
Pseudo-cumene + 2-undecanone					
0.0219	−0.0180	0.4337	−0.2237	0.7138	−0.2075
0.0922	−0.0662	0.5160	−0.2341	0.7883	−0.1801
0.1390	−0.0977	0.5439	−0.2363	0.8172	−0.1605
0.1904	−0.1292	0.6098	−0.2329	0.9151	−0.0879
0.2217	−0.1459	0.6198	−0.2309	0.9449	−0.0612
0.3197	−0.1896	0.6548	−0.2250	0.9854	−0.0199
0.3718	−0.2075				

where n is the number of the parameters A_k, and x_1 and x_2 are the mole fractions of components 1 (substituted benzene) and 2 (methyl alkyl ketone).

The method of least squares was used to determine the values of the parameters A_k, $\sigma(V^E)$ is the standard deviation of the fit

$$\sigma(V^E) = (\phi_{min}/(N-n))^{0.5} \quad (2)$$

where ϕ_{min} is the minimum value of the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \quad (3)$$

with N the number of experimental points, $\eta_k = V^E_{calc} - V^E$, and V^E_{calc} determined from the right-hand-side of eqn. (1). Values of V^E are listed in Table 1 and are represented graphically in Figs 1–3. The parameters A_k, together with the standard deviations $\sigma(V^E)$, are reported in Table 2. Figure 4 shows the correlation of values of V^E for $x_1 = 0.5$, and n_c, the number of carbon atoms of the linear methyl alkyl ketones.

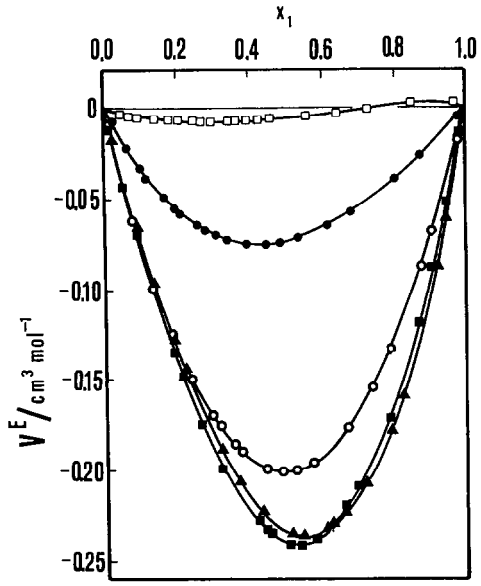

Fig. 3. Excess molar volumes at 298.15 K for pseudo-cumene + 2-propanone (□), +2-butanone (●), +2-pentanone (○), +2-octanone (■), and +2-undecanone (▲). Solid curves are the least-squares representation of results by eqn. (1).

TABLE 2

Redlich–Kister parameters A_k and the standard deviation $\sigma(V^E)$ (both in $cm^3\ mol^{-1}$) of the excess molar volume according to eqn. (1), and the empirical factor c in eqn. (6)

Mixture	A_0	A_1	A_2	$\sigma(V^e)$	c
Toluene+					
2-butanone	−0.4844	0.1256	0.0484	0.0009	2.07
2-pentanone	−1.1420	0.0212		0.0012	3.40
2-octanone	−0.9121	−0.0245	0.0487	0.0012	0.73
2-undecanone	−0.6186	−0.0098		0.0012	0.82
p-Xylene+					
2-butanone	−0.7541	0.0674		0.0012	1.20
2-pentanone	−1.1400	0.0245		0.0015	2.03
2-octanone	−0.9788	0.1087	0.0421	0.0006	1.10
2-undecanone	−1.0878	−0.1671	0.0329	0.0013	0.56
Pseudo-cumene+					
2-propanone	−0.0212	0.0333		0.0007	0.30
2-butanone	−0.2927	0.0936	−0.0290	0.0010	0.70
2-pentanone	−0.8072	0.0318		0.0010	1.00
2-octanone	−0.9574	−0.0934		0.0012	1.79
2-undecanone	−0.9329	−0.1921	−0.0570	0.0014	0.69

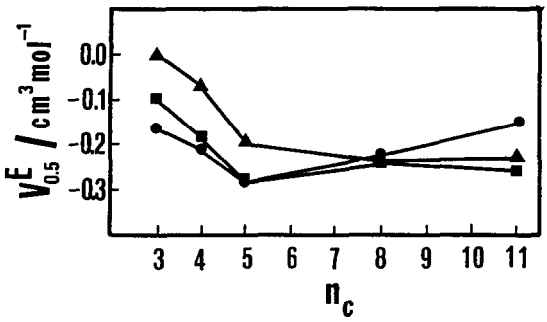

Fig. 4. Values of $V^E_{0.5} = V^E(x = 0.5)$ at 298.15 K as a function of n_c for the binary mixtures of methyl alkyl ketones + toluene (●), +*p*-xylene (■), and +pseudo-cumene (▲).

THE CELL MODEL

An extension of the Prigogine cell model [6] has been used here to represent the excess molar volumes V^E. The same model was applied in our previous paper [1] to calculate excess molar enthalpies H^E for the same mixtures, and the results obtained in ref. 1 allow calculation of V^E.

The expressions for H^E and V^E below are according to the extended cell model

$$H^E = x_1x_2E_{11}z[-1.44\theta + 10.76(RT/zE_{11})^2(-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1x_2\theta^2)] \quad (4)$$

$$V^E = 2.03V^*x_1x_2RT/E_{11}(-2\theta - \delta^2 + 4\theta\delta x_2 + 4x_1x_2\theta^2) \quad (5)$$

where z is the number of first neighbors in the quasi-lattice model and E_{11}, E_{22}, E_{12} are interaction energies between molecules

$$\delta = (E_{22} - E_{11})/E_{11}$$

$$\theta = (E_{12} - (E_{11} + E_{22})/2)E_{11}$$

$$V^* = (cr_{av})^3 \quad (6)$$

where c is an empirical factor accounting for approximations involved in evaluating r_{av}. The characteristic volume V^* [6] may be calculated from the molecular distance corresponding to the minimum of potential energy for each component and the geometrical arrangement of molecules in the solution.

Because this information is not available, V^* was obtained by the approximate eqn. (6) where r_{av} is the arithmetical mean of the distances r_1 and r_2 of molecules in pure liquids 1 and 2, as determined by the formula

$$r_i = (\gamma_i/N_a)^{1/3}$$

where γ_i is the molar liquid volume and N_a is Avogadro's constant. This procedure was used by Kohler [7] in the calculation of the interchange energy in the lattice theory of solutions.

The values of c are discussed below; they are obtained by the following procedure.

The values of θ allowing for the best calculated values of H^E were determined in ref. 1, whereas δ and E_{11} were obtained from vaporization data and z was chosen as 8. The same set of θ, δ, E_{11} and z values were introduced into eqn. (5) and the calculated values of V^E obtained. The factor c was chosen so as to match the calculated and experimental values of V^E at the minimum.

RESULTS AND DISCUSSION

As can be seen from Figs. 1–3, the excess volume data at 298.15 K for all the binary mixtures are negative over the entire range of composition, with the exception of the pseudo-cumene + 2-propanone system, which undergoes a sign inversion. However, the latter system shows very small values of $|V^E|$, not exceeding 0.01 $cm^3\ mol^{-1}$.

The other mixtures also exhibit quasi-symmetric curves over the entire range of composition, with a minimum value of around 0.45–0.55 mole fraction of component 1.

Figure 5 compares the Redlich–Kister fits of V^E wiht the V^E curves calculated by the cell model, for the mixtures 2-undercanone + toluene +p-xylene, and +pseudo-cumene. All other mixtures give approximately

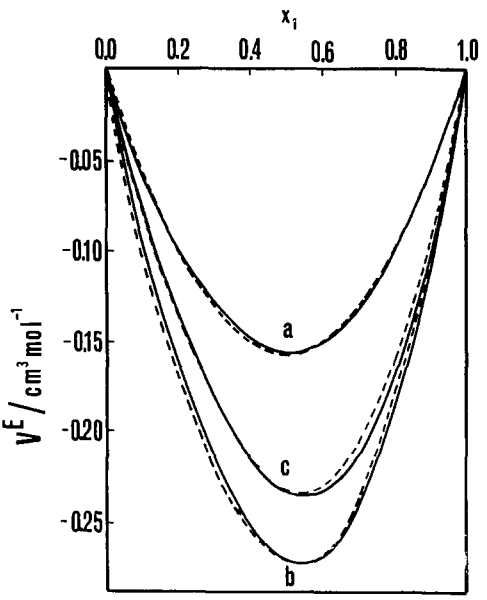

Fig. 5. Example of comparison between the Redlich-Kister fit (—) and the cell model (– – –) for V^E at 298.15 K for the 2-undecanone + toluene (a), +p-xylene (b), and +pseudo-cumene (c) systems.

the same agreement between the smoothed experimental and calculated V^E curves and are not represented.

The values of c which yield this agreement are 0.82, 0.56 and 0.69 for the three mixtures of Fig. 5; the values of c for the other mixtures are listed in Table 2.

However, the mixtures toluene + 2-butanone or +2-pentanone, and p-xylene + 2-pentanone show large values of c (up to 3.4), indicating for these systems a poor representation in terms of r_{av} (eqn. (6)), whereas the cell model provides the right sign for V^E.

Finally, it is clear that an increase in chain length of the ketones is accompanied by decreased values of V^E, except for long-chained ketones, which show an inverted effect.

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