ANALYSIS OF EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF TOLUENE WITH THE HEXANOL ISOMERS AT 298.15 K

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ABSTRACT

Excess molar volumes v^E at 298.15 K were obtained for eight binary systems formed by toluene with the following hexanol isomers: 4-methylpentan-1-ol, 3-methylpentan-1-ol, 3,3-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, 2-ethylbutan-1-ol, 2,2-dimethylbutan-1-ol, hexan-3-ol, 3,3-dimethylbutan-2-ol and 2,3-dimethylbutan-2-ol. The volumes were determined from measurements of the density with a vibrating-tube densimeter. The v^E values are positive over the entire range of composition for all cases except for the system toluene + 4-methylpentan-1-ol, where an inversion of the sign of v^E is observed at $x \approx 0.1$. The values are represented by rather asymmetrical curves of different shapes depending on whether the alkanol is primary, secondary, or tertiary.

INTRODUCTION

The thermodynamic properties of binary mixtures that contain isomers of alcohols are uncommon in the literature, even more so in the case of long-chain alcohols. Interpretation of the behaviour of systems that contain such isomers is therefore difficult, particularly when applying certain current theoretical models to predict mixing volumes.

The interest in studying systems that contain branched alcohols lies in observing the influence of the OH group on the mixing properties. The literature consulted contained considerations of different excess properties of binary mixtures of isomers of hexanol and various solvents, such as enthalpies [1], volumes [2–8], and heat capacities [3,9]. One paper [8] presented the v^E values for toluene with eight isomers of hexanol at 298.15 K; this paper presents data for the other nine isomers, that is for mixtures of toluene + 4-methylpentan-1-ol, 3-methylpentan-1-ol, 3,3-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, 2-ethylbutan-1-ol, 2,2-dimethylbutan-1-ol, hexan-3-

TABLE 1

Characteristics of pure compounds at 298.15 K and their comparison with literature values

Compound	Supplier and specifications	n_D		ρ (k g m^{-3})	
		Experi-mental	Litera-ture	Experi-mental	Litera-ture
Toluene	BDH > 99.95 mol%	1.4940	1.49413 [10]	862.10	862.19 [10]
4-Methylpentan-1-ol	Fluka, purum ≈ 97 mol%	1.4125	1.4135 [11]	811.51	809.5 [11]
3-Methylpentan-1-ol	Fluka, purum ≈ 99 mol%	1.4175	1.4175 [11]	820.80	820.0 [11]
3,3-Dimethylbutan-1-ol	Fluka, purum ≈ 98 mol%	1.4121	1.4118 [11]	807.86	809.7 [11]
2,3-Dimethylbutan-1-ol	Ferak, ≈ 97 mol%	1.4190	1.4185 [11]	828.57	825.5 [11]
2-Ethylbutan-1-ol	Fluka, purum > 98 mol%	1.4203	1.4205 [11]	829.09	829.5 [11]
2,2-Dimethylbutan-1-ol	Ferak, ≈ 95 mol%	1.4188	1.4188 [11]	824.27	824.6 [11]
Hexan-3-ol	Fluka, pract. ≈ 95 mol%	1.4136	1.4140 [11]	814.85	814.4 [11]
3,3-Dimethylbutan-2-ol	Fluka, purum > 97 mol%	1.4132	1.4132 [11]	813.94	813.9 [11]
2,3-Dimethylbutan-2-ol	Aldrich, > 99 mol%	1.4146	1.4150 [11]	819.99	818.2 [11]

ol, 3,3-dimethylbutan-2-ol, and 2,3-dimethylbutan-2-ol. In combination with the data published previously, the results presented herein will provide a basis for better analyses of the volumetric behaviour of such systems. To this end, information obtained using IR spectroscopy has been included, in addition to the information yielding the mixing volumes.

EXPERIMENTAL SECTION

Prior to use all chemicals were degassed ultrasonically and dried on a molecular sieve (Union Carbide type 4A by Fluka). The commercial characteristics and the values of the physical properties, as determined at 298.15 K, are given in Table 1 and compared with the data from the literature cited. Because these alcohol isomers are not in particularly common use and commercial availability is limited, Table 1 presents new values that complement the values contained in the literature; some differences were recorded.

The excess molar volumes, v^E, were calculated indirectly from the densities of the pure components and the mixtures. The details concerning the procedures employed to prepare the mixtures as well as the measuring techniques and equipment have been described in an earlier paper [5]. The v^E values were estimated with a precision of better than ± 0.002 cm^3 mol^{-1}, and the concentration, x, data with a precision of better than ± 0.0001.

The IR spectra of the mixtures were determined using a Nicolet model 60SX spectrometer with a resolution of 2 cm^{-1}. Different cells were used, depending on the concentration of toluene: potassium bromide cells with a thickness of 400 μm for low concentrations and variable-thickness cells for concentrated solutions.

RESULTS AND DISCUSSION

A polynomial equation of the form

$$v^E \text{ (cm}^3 \text{ mol}^{-1}) = x_1 x_2 \sum_{i=0} A_i \left[x_1/(x_1 + kx_2) \right]^i \tag{1}$$

was used to fit the v^E values for the mixtures listed in Table 2, where x_1 is the mole fraction of toluene. The coefficients A_i were calculated by a least-squares procedure, and the values for each of the systems are shown in Table 3, together with the optimum values of k and the standard deviation, $s(v^E)$. In order to visualise better the v^E values for the 17 systems of toluene plus an isomer of hexanol, Figs. 1, 2 and 3 depict the curves obtained using eqn. (1) for the primary, secondary, and tertiary isomers respectively; the solid lines represent the curves obtained in the present study, and the broken lines the curves from a previous paper [8].

As in the case of other toluene + alcohol systems [12,13], the excess molar volumes were positive for all the systems except for toluene + hexan-1-ol and toluene + 4-methylpentan-1-ol, in which mixing volumes underwent contraction at high alcohol concentrations and consequently v^E values were negative.

A comparative quantitative analysis of the v^E results was made, the sequence of v^E values being observed. For all the isomers of hexanol, the order found, from lowest to highest, was hexan-1-ol < 4-methylpentan-1-ol < 3-methylpentan-1-ol < 2-methypentan-1-ol < 3,3-dimethylbutan-1-ol < 2,3-dimethylbutan-1-ol < 2-ethylbutan-1-ol < hexan-2-ol < 4-methylpentan-2-ol < hexan-3-ol < 2-methylpentan-2-ol < 2-methylpentan-3-ol < 3-methylpentan-2-ol < 3,3-dimethylbutan-2-ol < 3-methylpentan-3-ol < 2,3-dimethylbutan-2-ol < 2,2-dimethylbutan-1-ol. This did not exactly agree with the findings presented in ref. 4, which indicated that v^E values decreased in accordance with the position of the OH group, in other words, tertiary > secondary > primary.

TABLE 2

Excess molar volumes for toluene + isomer of hexanol mixtures at 298.15 K

x_1	v^E (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})
x_1 toluene + x_2 4-methylpentan-1-ol					
0.02156	−0.0033	0.36256	0.0783	0.75665	0.1267
0.04689	−0.0038	0.41041	0.0926	0.80840	0.1167
0.06438	−0.0059	0.49044	0.1142	0.86910	0.0989
0.11306	0.0023	0.54595	0.1218	0.93309	0.0674
0.15682	0.0149	0.61321	0.1297	0.96287	0.0468
0.21013	0.0300	0.63831	0.1311	0.98697	0.0200
0.29367	0.0580	0.72163	0.1290		
x_1 toluene + x_2 3-methylpentan-1-ol					
0.06423	0.0143	0.39609	0.1538	0.70721	0.1897
0.09168	0.0238	0.46330	0.1773	0.71789	0.1855
0.13443	0.0392	0.49949	0.1859	0.81994	0.1506
0.19148	0.0643	0.57153	0.1991	0.82680	0.1474
0.24519	0.0881	0.58901	0.2001	0.92999	0.0864
0.33482	0.1291	0.64029	0.1988	0.98694	0.0244
x_1 toluene + x_2 3,3-dimethylbutan-1-ol					
0.02154	0.0186	0.36001	0.2025	0.82850	0.1673
0.04473	0.0376	0.42863	0.2271	0.86697	0.1456
0.06343	0.0515	0.48852	0.2378	0.92550	0.0984
0.10671	0.0823	0.56981	0.2453	0.94228	0.0854
0.15382	0.1099	0.62492	0.2413	0.97582	0.0445
0.21152	0.1412	0.69982	0.2261	0.98746	0.0246
0.29489	0.1777	0.75326	0.2056		
x_1 toluene + x_2 2,3-dimethylbutan-1-ol					
0.03773	0.0257	0.46286	0.3096	0.92186	0.1287
0.13199	0.1056	0.59377	0.3167	0.96233	0.0747
0.21783	0.1783	0.70335	0.2878		
0.33207	0.2555	0.81707	0.2236		
x_1 toluene + x_2 2-ethylbutan-1-ol					
0.04766	0.0433	0.37448	0.2983	0.74742	0.2624
0.10148	0.1003	0.46664	0.3211	0.82877	0.2115
0.12259	0.1193	0.53657	0.3250	0.86313	0.1831
0.20039	0.1878	0.59078	0.3196	0.89762	0.1536
0.31528	0.2686	0.67371	0.2975	0.93253	0.1154
0.34617	0.2851	0.71447	0.2776	0.96843	0.0654
x_1 toluene + x_2 2,2-dimethylbutan-1-ol					
0.09860	0.2006	0.39679	0.5440	0.79171	0.3552
0.20035	0.3623	0.52212	0.5248	0.87161	0.2647
0.28502	0.4624	0.58567	0.4997	0.94964	0.1346
0.36666	0.5106	0.71257	0.4244		

TABLE 2 (continued)

x_1	v^E (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})
x_1 toluene + x_2 hexan-3-ol					
0.02320	0.0455	0.41150	0.4172	0.84103	0.2768
0.06646	0.1205	0.49232	0.4288	0.84898	0.2696
0.11309	0.1914	0.52015	0.4255	0.89147	0.2224
0.17447	0.2713	0.59471	0.4111	0.91431	0.1920
0.22808	0.3242	0.66869	0.3927	0.95953	0.1106
0.28328	0.3621	0.71697	0.3651	0.98606	0.0421
0.35210	0.3985	0.77281	0.3337		
x_1 toluene + x_2 3,3-dimethylbutan-2-ol					
0.07357	0.1243	0.38383	0.4273	0.79919	0.3720
0.09558	0.1581	0.48414	0.4643	0.84323	0.3252
0.11063	0.1782	0.54955	0.4678	0.92965	0.1984
0.20288	0.2919	0.64185	0.4582	0.97102	0.0967
0.30810	0.3827	0.70950	0.4321		
x_1 toluene + x_2 2,3-dimethylbutan-2-ol					
0.05347	0.0949	0.47918	0.5030	0.84498	0.3708
0.12630	0.2051	0.55810	0.5163	0.92932	0.2267
0.21551	0.3204	0.63528	0.5118	0.96108	0.1417
0.30954	0.4042	0.70736	0.4819		
0.38787	0.4625	0.77712	0.4385		

TABLE 3

Equation (1) parameters and standard deviations $s(v^E)$ for data in Table 2

| System	k	A_0	A_1	A_2	A_3	$10^3 s(v^E)$
x_1 toluene + x_2 4-methylpentan-1-ol	1.738	−0.1514	3.0153	−4.9383	3.5194	1.8
x_1 toluene + x_2 3-methylpentan-1-ol	2.976	0.1798	3.5885	−6.4544	4.6549	0.8
x_1 toluene + x_2 3,3-dimethylbutan-1-ol	7.484	0.7955	1.6311	−2.5948	2.6056	2.5
x_1 toluene + x_2 2,3-dimethylbutan-1-ol	1.896	0.7249	3.0983	−5.8922	4.3494	1.8
x_1 toluene + x_2 2-ethylbutan-1-ol	2.072	0.9938	2.1084	−4.8519	4.0705	1.8
x_1 toluene + x_2 2,2-dimethylbutan-1-ol	1.458	2.1967	1.2429	−5.7954	5.5331	2.1
x_1 toluene + x_2 hexan-3-ol	2.684	1.9812	−1.8262	3.0019	−2.7636	2.3
x_1 toluene + x_2 3,3-dimethylbutan-2-ol	3.276	1.8102	−0.3063	2.2487	–	2.1
x_1 toluene + x_2 2,3-dimethylbutan-2-ol	4.056	1.8288	0.6470	1.9147	–	2.2
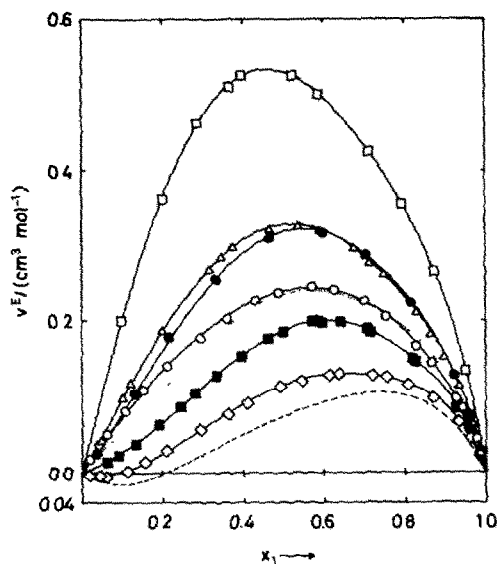
Fig. 1. Plot of experimental v^E values and those of a previous paper for x_1 toluene $+ x_2$ primary isomer of hexanol. All curves were obtained with eqn. (1): — — —, hexan-1-ol [8]; $\diamond$, 4-methylpentan-1-ol; ■, 3-methylpentan-1-ol; $\cdots\cdots$, 2-methylpentan-1-ol [8]; $\circ$, 3,3-dimethylpentan-1-ol; ●, 2,3-dimethylbutan-1-ol; $\triangle$, 2-ethylbutan-1-ol; □, 2,2-dimethylbutan-1-ol.
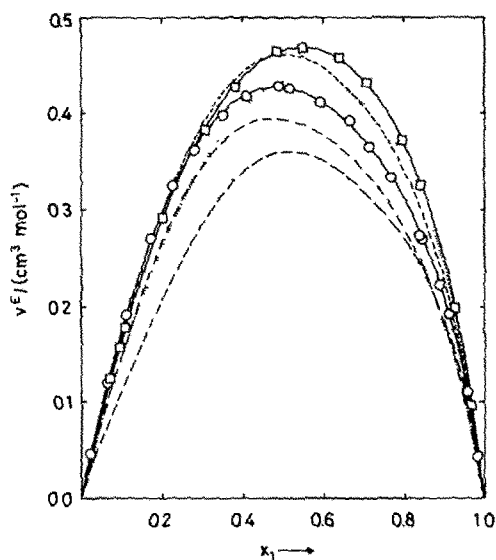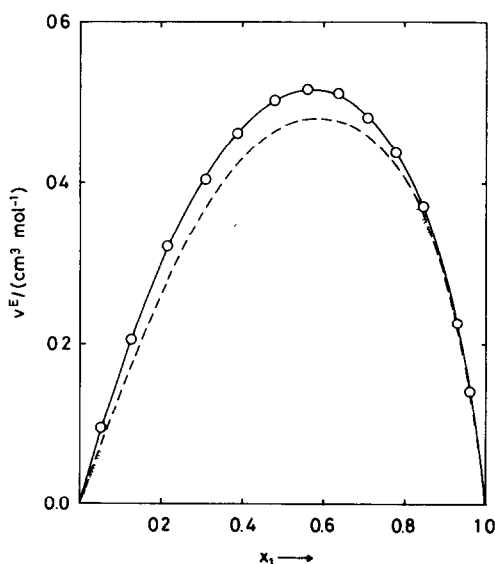

Fig. 2. Plot of experimental v^E values and those of a previous paper, for x_1 toluene $+ x_2$ secondary isomer of hexanol. All curves were obtained with eqn. (1): — — —, hexan-2-ol [8]; — · — · —, 4-methylpentan-2-ol [8]; $\circ$, hexan-3-ol, $\cdots\cdots$, 2-methylpentan-3-ol [8]; - - - - - -, 3-methylpentan-2-ol [8]; □, 3,3-dimethylbutan-2-ol.

Fig. 3. Plot of experimental v^E values and those of a previous paper, for x_1 toluene $+ x_2$ tertiary isomer of hexanol. All curves were obtained with eqn. (1): $\cdots\cdots$, 2-methylpentan-2-ol; $-\,-\,-$, 3-methylpentan-3-ol; $\bigcirc$, 2,3-dimethylbutan-2-ol.

The infrared spectra were also obtained at various concentrations of the different mixtures. The results showed that cleavage of the hydrogen bonds in the alcohols was complete, even at low toluene concentrations, and faint bands of weak association (possibly dimers) were discernible. However, since similar IR observations were recorded for all the isomers, the steric hindrance associated with the radical attached to the OH-group of the alcohol was probably one factor that played an important role in the sequence of v^E_{max} values observed for these systems. Steric hindrance values for the radicals considered in the present paper are few and far between in the literature [14]. Consequently, in the light of the fact that the sequence of v^E_{max} values given above did not match the findings reported in the literature, since the values for the secondary and tertiary isomers were mixed in with those for the primary isomers, explanation of the behaviour of the systems studied was extremely difficult.

Nevertheless, when, instead of considering the entire group of isomers as a whole, the v^E_{max} values were analysed according to isomer type, there appeared individual sequences for the primary, secondary, and tertiary isomers which could readily be extracted from the order set out above. On the basis of this, in combination with the data on steric hindrances from ref. 14, it became evident that for a given isomer group, e.g. the primary isomers, the ν^E_{max} values increased with the value associated with the steric hindrance of the radical attached to the OH-group, as was to be expected, since, by affording more protection to the OH-group on the isomer, the π–OH

interaction weakens and the v_{max}^E value rises. The same applied to the secondary and tertiary alcohols.

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