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VOLUMETRIC BEHAVIOUR OF BINARY SYSTEMS OF CYCLOHEXANE WITH THE HEXANOL ISOMERS AT 298.15 K

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ABSTRACT

Excess molar volumes, v^E, based on density measurements taken at 298.15 K, were calculated for ten binary mixtures consisting of cyclohexane and the following isomers of hexanol: 3,3-dimethylbutan-1-ol, 2,2-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, 2-ethylbutan-1-ol, 3-methylpentan-1-ol, 4-methylpentan-1-ol, 3,3-dimethylbutan-1-ol, 2-methylpentan-3-ol, hexan-3-ol and 2,3-dimethylbutan-2-ol. The v^E values were positive over the entire range of concentration, except in the case of the binary system of x_1 cyclohexane + x_2 3-methylpentan-1-ol, for which the v^E values were negative for $x_1 < 0.1$. A discussion of the behaviour of these mixtures, based on the experimental results, is included.

INTRODUCTION

The relative influence of the position of the hydroxyl group on the magnitudes of the thermodynamic parameters of mixtures of binary systems that contain isomers of *n*-alkanols has been studied by a large number of researchers. Analysis of the behaviour of such mixtures is most satisfactory when the number of isomers of the *n*-alkanol is relatively large, as is the case for hexanol.

Various workers have reported data on the mixing properties (e.g., h^E, v^E, c_p^E, etc.) of binary systems consisting of certain isomers of hexanol and various solvents, namely, hydrocarbons [1–8], aromatic compounds [9–12] and esters [13] at 298.15 K. Nevertheless, such work was normally carried out for only a limited number of isomers, and thus the analysis of the behaviour of these types of mixtures with respect to a given magnitude has often been incomplete. This fact is still more pronounced in the case of attempts to verify the predictive ability of certain theoretical models, inasmuch as a variety of features or aspects needs to be considered.

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For this reason, a recent paper [14] completed a volumetric study of mixtures of toluene and the isomers of hexanol undertaken by Ortega et al. [12]. Continuing along these same lines, the present paper sets out the v^E values at 298.15 K for ten binary systems composed of cyclohexane and the following isomers of hexanol: 3,3-dimethylbutan-1-ol (3,3DM-B1), 2,2-dimethylbutan-1-ol (2,2DM-B1), 2,3-dimethylbutan-1-ol (2,3DM-B1), 2-ethylbutan-1-ol (2E-B1), 3-methylpentan-1-ol (3M-P1), 4-methylpentan-1-ol (4M-P1), 3,3-dimethylpentan-2-ol (3,3DM-P2), 2-methylpentan-3-ol (2M-P3), hexan-3-ol (H3) and 2,3-dimethylbutan-2-ol (2,3DM-B2). These data complete an earlier paper [6] which reported on mixtures of cyclohexane and the other seven isomers of hexanol: 2-methylpentan-1-ol (2M-P1), hexan-1-ol (H1), 4-methylpentan-2-ol (4M-P2), 3-methylpentan-2-ol (3M-P2), hexan-2-ol (H2), 3-methylpentan-3-ol (3M-P3) and 2-methylpentan-2-ol (2M-P2). The object of these systematic studies is to observe the volumetric behaviour of a series of systems composed of isomers of alkanols and such solvents as benzene and *n*-hexane, in addition to toluene and cyclohexane which are commonly employed in the study of binary systems.

EXPERIMENTAL

A recent paper [14] described the treatments applied to the compounds, cyclohexane and 2M-P3 excepted, and presented the physical properties of the said isomers. This paper, therefore, sets out the properties of these last two components under the same experimental manipulations. Both cyclohexane and 2M-P3 were Fluka A.G. products. The purity as stated by the manufacturer was puriss p.a. > 99.5 mol% for the cyclohexane and purum > 98 mol% for the 2M-P3. The properties of the two compounds, as determined at 298.15 K, were: for the cyclohexane, ρ (kg m^{-3}) = 773.57, 773.89 [15] and 773.7 [16], and n_D = 1.4235, 1.42354 [15] and 1.4233 [16]; for the 2M-P3, ρ (kg m^{-3}) = 820.06 and 819.8 [17], and n_D = 1.4147 and 1.4148 [17].

The mixtures were prepared by weighing, and the v^E values were calculated indirectly from the density measurements. The measurement technique and the precision of the results were as descibed in earlier papers [13,18].

EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 gives the v^E values calculated for the ten systems considered in the present study, x_1 cyclohexane + x_2 isomer of hexanol. The experimental values were correlated using the polynomial expression

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

TABLE 1

Excess molar volumes for mixtures of cyclohexane + an isomer of hexanol 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 cyclohexane + x_2 3,3-dimethylbutan-1-ol					
0.06655	0.034	0.39700	0.194	0.70744	0.256
0.13908	0.070	0.46858	0.224	0.75216	0.242
0.17038	0.089	0.50698	0.238	0.85442	0.190
0.21440	0.106	0.55329	0.250	0.90098	0.157
0.31680	0.158	0.60438	0.258	0.91907	0.141
0.35782	0.178	0.67811	0.260	0.96956	0.085
x_1 cyclohexane + x_2 2,2-dimethylbutan-1-ol					
0.10930	0.187	0.43838	0.468	0.85136	0.276
0.20642	0.317	0.53596	0.461	0.90926	0.216
0.29519	0.404	0.65831	0.410	–	–
0.37261	0.452	0.77637	0.330	–	–
x_1 cyclohexane + x_2 2,3-dimethylbutan-1-ol					
0.08729	0.089	0.41881	0.367	0.75223	0.351
0.14230	0.144	0.46785	0.394	0.81394	0.306
0.19511	0.195	0.52011	0.409	0.87120	0.248
0.25701	0.251	0.59093	0.416	0.90795	0.203
0.32679	0.305	0.67009	0.398	0.97039	0.092
x_1 cyclohexane + x_2 2-ethylbutan-1-ol					
0.05200	0.064	0.43222	0.465	0.83004	0.332
0.08547	0.102	0.50248	0.497	0.86979	0.284
0.12132	0.147	0.55894	0.502	0.89167	0.251
0.17463	0.212	0.59331	0.499	0.91862	0.211
0.21327	0.263	0.62452	0.492	0.96646	0.118
0.29920	0.356	0.70798	0.449	–	–
0.34173	0.398	0.74598	0.419	–	–
x_1 cyclohexane + x_2 3-methylpentan-1-ol					
0.02241	−0.031	0.39037	0.275	0.65721	0.383
0.04697	−0.032	0.41775	0.290	0.67781	0.382
0.08595	−0.005	0.46011	0.318	0.79098	0.324
0.12906	0.037	0.51570	0.351	0.82829	0.288
0.22186	0.126	0.54441	0.368	0.91914	0.166
0.25299	0.157	0.59115	0.383	0.96951	0.070
0.36863	0.255	0.64041	0.389	–	–
x_1 cyclohexane + x_2 4-methylpentan-1-ol					
0.05689	0.063	0.34384	0.328	0.67069	0.405
0.08652	0.096	0.38306	0.349	0.76909	0.354
0.12464	0.137	0.42105	0.372	0.81981	0.313
0.15293	0.166	0.51559	0.409	0.86539	0.262
0.22312	0.232	0.56057	0.418	0.92485	0.184
0.26013	0.263	0.58451	0.419	0.96680	0.109
0.29929	0.292	0.66920	0.406	–	–
x_1 cyclohexane + x_2 3,3-dimethylbutan-2-ol					
0.04034	0.050	0.39925	0.320	0.70023	0.352
0.13463	0.150	0.45743	0.338	0.78276	0.332
0.21627	0.216	0.56612	0.361	0.86212	0.288
0.30670	0.276	0.62969	0.361	0.92555	0.224

TABLE 1 (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 cyclohexane + x_2 2-methylpentan-3-ol					
0.05250	0.095	0.40286	0.507	0.79272	0.473
0.07721	0.140	0.46512	0.537	0.85391	0.409
0.13877	0.236	0.56179	0.562	0.93329	0.273
0.22054	0.342	0.62399	0.555	0.96792	0.165
0.31287	0.439	0.65104	0.545	–	–
x_1 cyclohexane + x_2 hexan-3-ol					
0.05418	0.138	0.39123	0.661	0.77710	0.546
0.08846	0.215	0.47898	0.700	0.86355	0.418
0.13780	0.319	0.54974	0.702	0.92633	0.291
0.22818	0.476	0.63844	0.671	0.97010	0.156
0.30681	0.581	0.70763	0.621	–	–
x_1 cyclohexane + x_2 2,3-dimethylbutan-2-ol					
0.07985	0.102	0.37910	0.362	0.78502	0.398
0.08065	0.104	0.48098	0.409	0.85765	0.348
0.15479	0.184	0.54521	0.429	0.94168	0.237
0.23371	0.261	0.61917	0.436	0.95886	0.195
0.33051	0.333	0.69886	0.429	–	–

and the values of the coefficient A_i were calculated by a method of least-squares, with optimisation of the degree of the polynomial obtained by using an F-test. Table 2 shows the values for the parameters in eqn. (1) for each of the ten systems, along with the standard deviation, $s(v^E)$, values for the differences between the experimental data and the theoretical results calculated for each system using eqn. (1). Graphical representation of the functions $v^E = f(x_1)$ made possible analysis of the behaviour of these systems and both quantitative and qualitative evaluation of all the results.

TABLE 2

Parameters of eqn. (1) and standard deviations, $s(v^E)$, in cm^3 mol^{-1} for data in Table 1

x_1 cyclohexane +	k	A_0	A_1	A_2	A_3	A_4	$s(v^E)$
x_2 3,3-dimethylbutan-1-ol	3.00	0.542	0.656	7.565	−18.597	13.631	0.002
x_2 2,2-dimethylbutan-1-ol	2.42	1.871	1.262	−6.443	7.484	–	0.001
x_2 2,3-dimethylbutan-1-ol	2.21	1.054	1.635	3.246	−11.672	9.553	0.001
x_2 2-ethylbutan-1-ol	3.00	1.162	5.610	−11.615	9.137	–	0.002
x_2 3-methylpentan-1-ol	0.23	−2.340	12.191	−17.221	9.748	–	0.002
x_2 4-methylpentan-1-ol	2.50	1.197	0.927	4.594	−11.864	9.134	0.002
x_2 3,3-dimethylbutan-2-ol	2.00	1.347	−1.406	8.338	−14.669	11.413	0.002
x_2 2-methylpentan-3-ol	2.00	1.980	−0.653	7.665	−15.344	12.636	0.002
x_2 hexan-3-ol	2.50	2.674	0.018	3.580	−9.196	9.195	0.002
x_2 2,3-dimethylbutan-2-ol	3.00	1.401	−0.116	7.663	−14.950	12.953	0.001

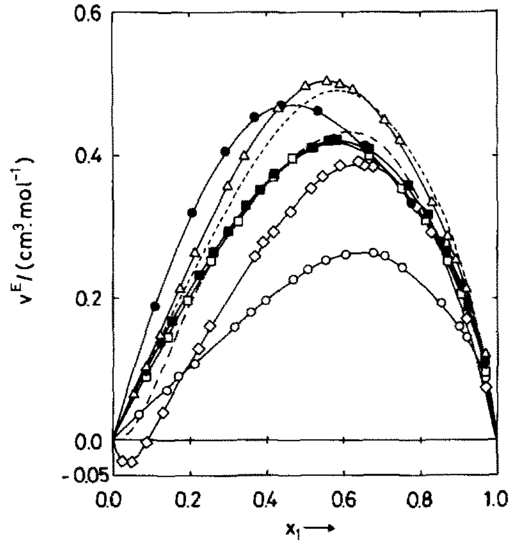

Fig. 1. Plot of experimental values of v^E and comparison of fitting curves for x_1 cyclohexane $+ x_2$ primary hexanol isomers: - - - - - -, 2M-P1 (see ref. 6); — — —, H1 (see ref. 6); ○, 3,3DM-B1; ◇, 3M-P1; □, 2,3DM-B1; ■, 4M-P1; ●, 2,2DM-B1; △, 2E-B1.

Figures 1 (for primary isomers), 2 (for secondary isomers) and 3 (for tertiary isomers) depict the curves for the mixtures studied in the present experiment using eqn. (1) and the parameters from Table 2 (solid lines), together with the experimental data points for these same mixtures (Table 1); the broken

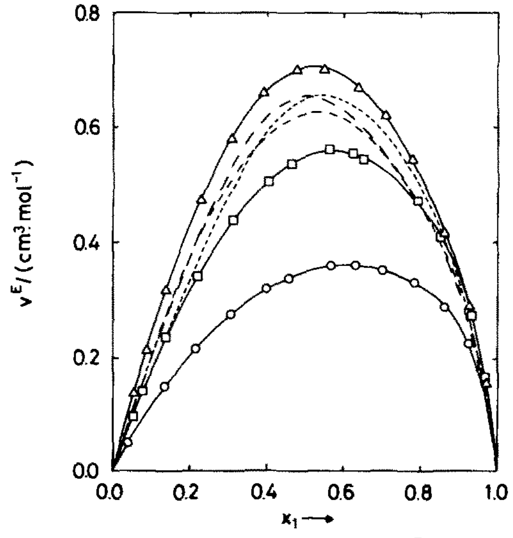

Fig. 2. Plot of experimental values of v^E and comparison of fitting curves for x_1 cyclohexane $+ x_2$ secondary hexanol isomers: - - - - - -, 4M-P2 (see ref. 6); — — —, 3M-P2 (see ref. 6); — — —, 4M-P2 (see ref. 6); ○, 3,3DM-B2; □, 2M-P3; △, H3.

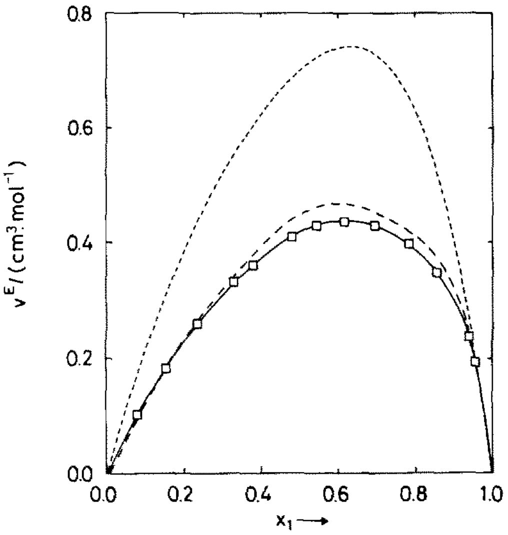

Fig. 3. Plot of experimental values of v^E and comparison of fitting curves for x_1 cyclohexane + x_2 tertiary hexanol isomers: - - - - - -, 2M-P2 (see ref. 6); — — —, 3M-P3 (see ref. 6); □, 2,3DM-B2.

lines represent the curves for the remaining systems taken from the literature [6].

The v^E values for the set of all seventeen systems were all positive, except those for the primary alkanols H1 and 3M-P1, which presented negative values for the regions of cyclohexane concentration of $x_1 < 0.04$ for H1 and $x_1 < 0.1$ for 3M-P1. The curves were quite asymmetrical and displayed a variety of shapes, even for the same type of isomer, and the $v^E_{\max}$ values were shifted towards regions rich in cyclohexane in some cases and those rich in the isomer of the alkanol in others.

The experimental results indicate that the expansive rupture [19–21] of the hydrogen bonds within the alkanol molecules is one of the main factors responsible for the excess volumes in these systems. The maximum values of the curves, $v^E_{\max}$, were calculated for use as indices for the comparative analysis of the set of all the binary systems. In ascending order, the sequence obtained, with $v^E_{\max}$ values expressed as $\mathrm{cm}^3\,\mathrm{mol}^{-1}$, was as follows: 3,3DM-B1 (0.262) < 3,3DM-B2 (0.362) < 3M-P1 (0.386) < 2,3DM-B1 (0.416) < 4M-P1 (0.419) < H1 (0.432) < 2,3DM-B2 (0.437) < 3M-P3 (0.468) < 2,2DM-B1 (0.471) < 2M-P1 (0.491) < 2E-B1 (0.504) < 2M-P3 (0.560) < 3M-P2 (0.627) < 4M-P2 (0.654) < H2 (0.656) < H3 (0.706) < 2M-P2 (0.739).

An interpretation of this sequence should take into account the various contributions that occur during the mixing process, which include the rupture and formation of new hydrogen bonds in the alkanols, the interstitial sites of the cyclohexane molecules within the branching structures of the isomers of hexanol, the flexibility and relative sizes of the molecules being

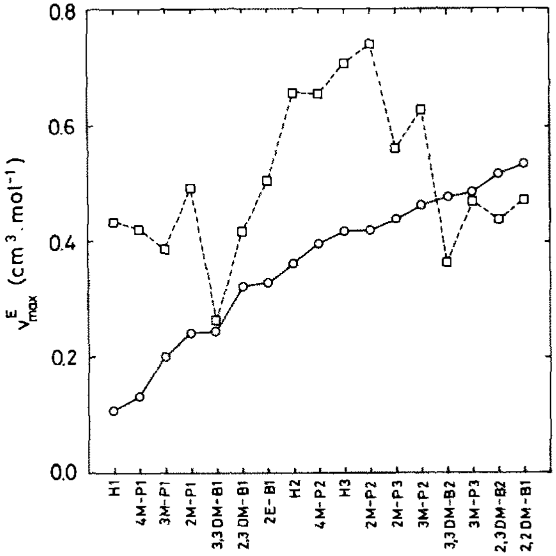

Fig. 4. Comparison of v^E_{max} for the binary systems: o——o, toluene + hexanol isomers; and □- - - - -□, cyclohexane + hexanol isomers.

mixed, and the intensity of the electrostatic interactions between the chains of the components. However, the net balance of the contributions would be extremely difficult to calculate, unless each of the above contributions could be quantified accurately.

Because of similarities between the molecules of toluene and cyclohexane such as size and the high density of the energies of cohesion, the v^E_{max} values were used to compare the mixing volumes of mixtures of these two solvents with isomers of hexanol. The sequence of v^E_{max} values for the two series differed. Figure 4, therefore, presents the isomers of hexanol along the x-axis in ascending order of the v^E_{max} values obtained for the series of binary systems of toluene + an isomer of hexanol [14]. Figure 4 shows that the v^E_{max} values for the mixtures of cyclohexane + an isomer of hexanol are higher than those for the mixtures in which toluene was used as the solvent, except for the mixtures containing the isomers 3,3DM-B2, 3M-P3, 2,3DM-B2, and 2,2DM-B1. In general the differences between the behaviour for these two sets of systems is explicable in terms of the negative contribution to the v^E values of the interactions between the hydroxyl groups and the π-electrons of the toluene. The exception in the case of the isomers just referred to above, can be due to the negative contributions because those isomers are even smaller than those in the mixtures containing cyclohexane.

A comprehensive analysis of the results contained herein and an interpretation of the different series would require a theoretical model capable of quantifying the different positive and negative contributions occurring during the mixing process. Unfortunately, the most widely applied theoretical models do not adequately represent the mixing volumes for systems containing isomers of alkanols.

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