Thermochimica Acta, 204 (1992) 295–302
Elsevier Science Publishers B.V., Amsterdam

Excess molar volumes of benzene with certain isomers of hexanol

J. Ortega [a], M. Chaar [b] and J.S. Matos [b]

[a] *Cátedra de Termodinámica y Fisicoquímica, Escuela Superior de Ingenieros Industriales, 35071-University of Las Palmas de Gran Canaria (Spain)*
[b] *Departamento de Física Aplicada, 35071-University of Las Palmas de Gran Canaria (Spain)*

(Received 3 September 1991)

Abstract

Excess volumes of binary mixtures of several hexanol isomers with benzene were calculated from their density measurements at 298.15 K. The following isomers were used: 3-methylpentan-1-ol, 4-methylpentan-1-ol, 2-ethylbutan-1-ol, 2,2-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, 3,3-dimethylbutan-1-ol, hexan-3-ol, 3,3-dimethylbutan-2-ol and 2,3-dimethylbutan-2-ol. For all mixtures the v^E values are positive over the entire range of composition and the curves show an asymmetrical form whose interpretation is discussed.

INTRODUCTION

This paper is part of a study of binary mixtures of compounds containing hydrogen bonds, designed to improve our understanding of the association effects in such systems. Other work carried out at our laboratory has examined the thermodynamic behavior of *n*-aliphatic and isomeric alkanols and mixtures of such alkanols with hydrocarbons and non-hydrocarbons. The presence of alkanols in the mixtures gives rise to thermodynamic values of magnitudes that are attributable to the breakdown and formation of intermolecular hydrogen bonds in which steric factors, such as the length and/or branching of the alkyl chain and the position of the –OH group on the alkanol, play a major role.

Hexanol was used in our research because its 17 isomers provide the basis for an excellent data-base for analyzing the different cases that may arise.

Many workers have made contributions to research into these aspects, but no systematic program has been carried out. For this reason, recent

---

Correspondence to: J. Ortega, Cátedra de Termodinámica y Fisicoquímica, Escuela Superior de Ingenieros Industriales, 35071-University of Las Palmas de Gran Canaria, Spain.

papers give a complete series of results of the mixing volumes v^E for toluene [1] and cyclohexane [2] with isomers of hexanol. Earlier papers [3,4] gave v^E measurements for binary mixtures of benzene and some hexanol isomers. The intervening time-lapse between the studies stems from the difficulties entailed in obtaining certain of the alkanol isomers.

In the present paper the results for dilution volumes at 298.15 K for benzene and the isomers not considered in the previous studies [3,4] are reported and discussed. These isomers are 3-methylpentan-1-ol (3M-P1), 4-methylpentan-1-ol (4M-P1), 2-ethylbutan-1-ol (2E-B1), 2,2-dimethylbutan-1-ol (2,2DM-B1), 2,3-dimethylbutan-1-ol (2,3-DM-B1), 3,3-dimethylbutan-1-ol (3,3DM-B1), hexan-3-ol (H3), 3,3-dimethylbutan-2-ol (3,3DM-B2) and 2,2-dimethylbutan-2-ol (2,3DM-B2). In addition to these nine isomers (six primaries, two secondaries and one tertiary isomer), new measurements of v^E values were repeated for the mixture of benzene and 2-ethylbutan-1-ol [4], for purposes of comparison.

EXPERIMENTAL

The benzene (puriss p.a. > 99.5 mol.%) used in this study was from Fluka. The source and properties of the hexanols used have been detailed in an earlier paper [1]. However, on this occasion two of the isomers that are not commercially available, 2,3DM-B1 and 2,2DM-B1, were produced by Aldrich on special order to a higher purity specification (98 mol.% and 99 mol.% respectively). As in similar work carried out previously, both the benzene and the hexanol isomers were degassed ultrasonically for several hours and then dried on a molecular sieve (ref. 69828 from Fluka) before any measurements were taken.

The properties of the hydrocarbon and of the two isomers referred to above at 298.15 K were as follows. For the benzene: $n_D = 1.4978$, 1.4979 [5], 1.4980 [6]; ρ (kg m^{-3}) = 873.45, 873.60 [5], 873.59 [6]. For the 2,3DM-B1, $n_D = 1.4190$, 1.4186 [1], 1.4185 [7]; ρ (kg m^{-3}) = 827.34, 828.6 [1], 825.5 [7]. For the 2,2DM-B1, $n_D = 1.4187$, 1.4188 [1,7]; ρ (kg m^{-3}) = 824.49, 824.3 [1], 824.6 [7].

The v^E values were calculated from the density values for the mixtures, which were prepared by weight. The measuring instruments and procedure have been described previously [8]. The precision of the calculations of the benzene mole fractions was less than $\pm 5 \times 10^{-5}$, and that for the v^E values for the mixtures was less than ± 0.002 cm^3 mol^{-1}.

RESULTS AND DISCUSSION

Table 1 lists the v^E values for the nine systems (x_1 benzene + x_2 hexanol isomer) with the differences δv^E for each mole fraction between

TABLE 1

Excess molar volumes for mixtures of benzene + 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 Benzene + x_2 3-methylpentan-1-ol					
0.06566	0.063	0.61004	0.385	0.83723	0.263
0.14079	0.136	0.64992	0.375	0.87456	0.223
0.24881	0.228	0.66874	0.372	0.92432	0.158
0.35617	0.307	0.69663	0.359	0.93846	0.135
0.44876	0.360	0.77278	0.318	0.97724	0.061
0.51407	0.378	0.81736	0.281	–	–
x_1 Benzene + x_2 4-methylpentan-1-ol					
0.07137	0.063	0.60421	0.347	0.84291	0.237
0.18908	0.153	0.64920	0.344	0.88135	0.197
0.29439	0.232	0.71055	0.323	0.91021	0.165
0.39299	0.293	0.74036	0.312	0.93629	0.129
0.47766	0.331	0.76099	0.299	0.95271	0.104
0.52217	0.341	0.81979	0.257	0.97703	0.056
x_1 Benzene + x_2 2-ethylbutan-1-ol					
0.11314	0.178	0.42287	0.488	0.81717	0.345
0.14912	0.225	0.54014	0.516	0.84846	0.302
0.20904	0.305	0.61894	0.498	0.86760	0.276
0.23221	0.329	0.70074	0.452	0.92351	0.187
0.28602	0.387	0.67456	0.474	0.95181	0.132
0.33083	0.430	0.73586	0.425	0.96426	0.105
0.38767	0.472	0.77226	0.394	–	–
x_1 Benzene + x_2 2,2-dimethylbutan-1-ol					
0.14123	0.321	0.50208	0.647	0.80778	0.428
0.25496	0.495	0.58789	0.626	0.86745	0.333
0.34553	0.595	0.66794	0.579	0.92703	0.218
0.43360	0.637	0.73879	0.510	–	–
x_1 Benzene + x_2 2,3-dimethylbutan-1-ol					
0.15520	0.204	0.51611	0.484	0.81162	0.340
0.26316	0.328	0.59008	0.484	0.88308	0.248
0.33202	0.391	0.66936	0.459	0.92394	0.179
0.42934	0.458	0.75415	0.399	–	–
x_1 Benzene + x_2 3,3-dimethylbutan-1-ol					
0.11186	0.109	0.55893	0.370	0.90694	0.166
0.20150	0.191	0.63136	0.360	0.94377	0.119
0.29851	0.265	0.71286	0.331	0.96773	0.078
0.39413	0.324	0.76592	0.298	0.98029	0.052
0.48241	0.360	0.85466	0.225	–	–
0.51101	0.365	0.88732	0.189	–	–
x_1 Benzene + x_2 hexan-3-ol					
0.04719	0.123	0.57593	0.645	0.85008	0.399
0.14516	0.339	0.67509	0.599	0.87158	0.361
0.25724	0.508	0.70453	0.574	0.91496	0.273
0.33642	0.593	0.78619	0.492	0.93207	0.231
0.48150	0.655	0.81476	0.454	0.97732	0.095

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 Benzene + x_2 3,3-dimethylbutan-2-ol					
0.08638	0.161	0.44642	0.549	0.82050	0.420
0.11524	0.206	0.48296	0.562	0.84458	0.390
0.15927	0.274	0.54348	0.573	0.89296	0.307
0.27149	0.423	0.64853	0.558	0.90177	0.287
0.33401	0.482	0.67230	0.547	0.93248	0.220
0.40323	0.530	0.73788	0.503	0.97831	0.081
x_1 Benzene + x_2 2,3-dimethylbutan-2-ol					
0.10628	0.206	0.45195	0.631	0.84679	0.447
0.17487	0.327	0.57861	0.658	0.86993	0.404
0.21325	0.386	0.63453	0.647	0.91021	0.319
0.26287	0.461	0.71516	0.601	0.95066	0.205
0.29203	0.498	0.74684	0.571	0.96408	0.158
0.33632	0.548	0.78745	0.526	0.97814	0.106
0.39207	0.597	0.82457	0.482	–	–

the values calculated from the densities and those obtained using the fitting equation, which for all the mixtures was

$$v^E\ (\mathrm{cm^3\ mol^{-1}}) = x_1x_2\sum_{i=0}^{n} A_i[x_1/(x_1+kx_2)]^i \qquad (1)$$

Table 2 presents the values of the coefficients A_i and k, which were calculated by least squares to obtain the best fit with the lowest standard deviation $s(v^E)$, also given in the table. Although eqn. (1) exhibited good correlation with the experimental data at extreme concentrations, the greatest percentage differences were recorded for values of x_1 in the vicinity of zero and unity; even so, with a few exceptions, the overall mean

TABLE 2

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

Benzene +	k	A_0	A_1	A_2	A_3	$s(v^E)$
3-Methylpentan-1-ol	3.256	0.965	3.300	−5.343	4.102	0.001
4-Methylpentan-1-ol	3.625	0.827	3.343	−5.276	3.982	0.001
2-Ethylbutan-1-ol	2.292	1.515	3.001	−5.992	4.817	0.002
2,2-Dimethylbutan-1-ol	2.787	2.652	−0.170	−0.813	2.260	0.002
2,3-Dimethylbutan-1-ol	2.310	1.352	3.134	−5.181	3.751	0.001
3,3-Dimethylbutan-1-ol	3.784	1.004	3.231	−6.294	5.132	0.001
Hexan-3-ol	3.201	2.766	−1.254	2.885	–	0.002
3,3-Dimethylbutan-2-ol	1.944	1.972	1.159	−1.729	2.688	0.002
2,3-Dimethylbutan-2-ol	2.229	2.049	2.938	−5.279	5.468	0.002

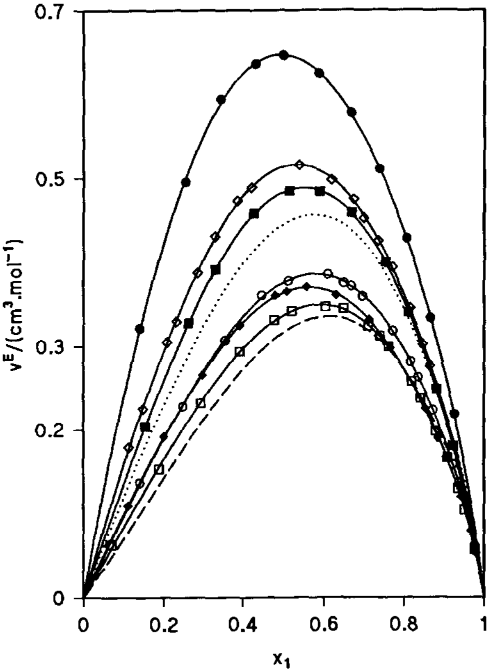

Fig. 1. Plot of experimental v^E values and those from a previous paper for x_1 benzene + x_2 primary isomers of hexanol. All curves were obtained with eqn. (1): – – –, H1 [3]; · · ·, 2M-P1 [3]; ○, 3M-P1; □, 4M-P1; ◇, 2E-B1; ●, 2,2DM-B1; ■, 2,3DM-B1; ◆, 3,3DM-B1.

error in the fits did not exceed 10%. The values presented herein for the system x_1 benzene + x_2 2-ethylbutan-1-ol matched almost exactly the values reported in a previous paper [4], yielding an absolute difference of 0.011 cm^3 mol^{-1} at $x_1 = 0.5$ and a mean error for all points of around 3%.

Figures 1, 2 and 3 depict the curves for the v^E values for the primary, secondary, and tertiary isomers, respectively, using the correlations for eqn. (1). The broken lines represent v^E curves for isomers taken from earlier papers [3,4]. The maximum values were calculated for the curves $v^E = \Psi(x_1)$, yielding the following sequence for the mixtures of x_1 benzene + x_2 hexanol isomer, in descending order: 2,2DM-B1 > 2M-P2 > 2,3DM-B2 > H3 > 3M-P3 > 3M-P2 > 4M-P2 > 2M-P3 > H2 > 3,3DM-B2 > 2E-B1 > 2,3DM-B1 > 2M-P1 > 3M-P1 > 3,3DM-B1 > 4M-P1 > H1; this order can be seen to be independent of isomer type. Except for the alkanols 2,2DM-B1 and 2,3DM-B2, the results corroborated the descending order established in earlier works [3,4] in accordance with isomer type, namely, tertiary > secondary > primary. Despite the cases mentioned above, this sequence of interaction with benzene was to be expected, chiefly on account of the rigidity of the aromatic ring and the degree of association of the alkanols in accordance with isomer type.

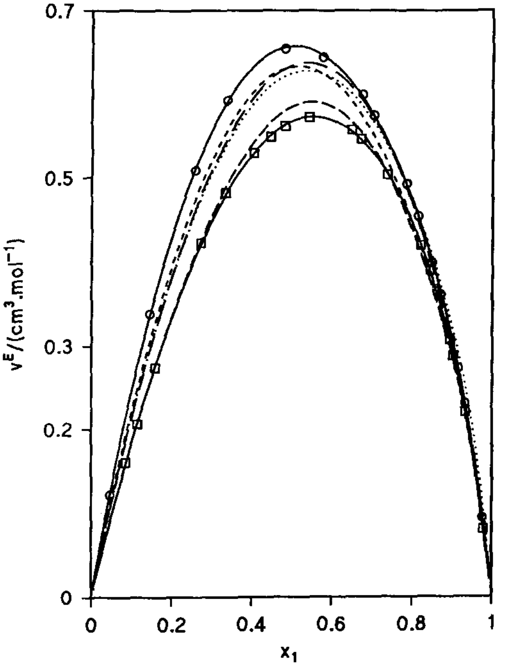

Fig. 2. Plot of experimental v^E values and those of previous papers for x_1 benzene + x_2 secondary isomers of hexanol. All curves were obtained with eqn. (1): – – –, H2 [3]; ————, 3M-P2 [3]; - - -, 4M-P2 [3]; ···, 2M-P3 [4]; ○, H3; □, 3,3DM-B2.

It is extremely difficult to explain adequately the volumetric behavior of these mixtures, because none of the available theoretical models provides satisfactory quantitative data on the various opposing factors contributing to the v^E values, e.g. expansions and contractions due to the rupture and formation of hydrogen bonds, interstitial accommodations between molecules, and interactions between the π electrons in the benzene ring and the –OH groups on the alkanol [9,10]. Nevertheless, it is interesting to point out certain qualitative aspects for the mixtures considered that are reflected in the figures. The volume–composition curves are asymmetrical and are shifted slightly towards regions richer in benzene. This may have been caused by accommodation between the benzene molecules and the alkanol molecules at $x_1 \ll 0.5$, where rupture of the hydrogen bonds decreases while, conversely, association effects of the alkanol increase, producing lower v^E values. The v^E values for the different isomers depicted in Figs. 1, 2 and 3 reflect the different degrees of interaction between the isomer and the benzene according to the position and aggregation of the –OH groups and alkyl side-chains on the alkanol.

Maximum v^E values, v^E_{max}, for the mixtures x_1 (benzene or toluene) + x_2 hexanol isomer were compared, because of the similar structural characteristics of the benzene and toluene molecules. For a given isomer, the v^E_{max}

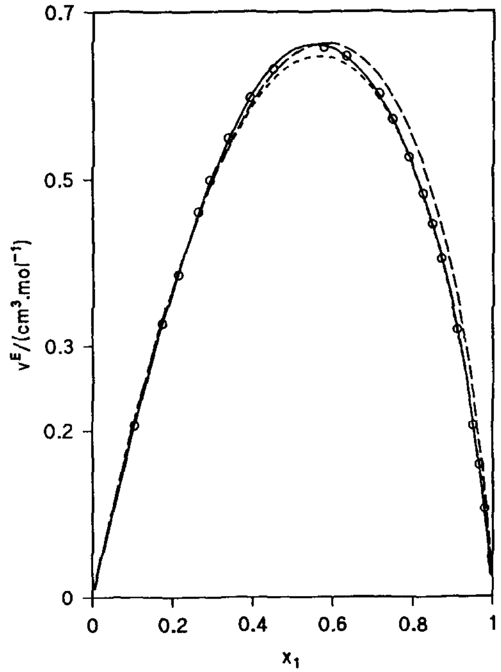

Fig. 3. Plot of experimental v^E values and those of a previous paper for x_1 benzene + x_2 tertiary isomers of hexanol. All curves were obtained with eqn. (1): ---, 2M-P2 [3]; - - -, 3M-P3 [3]; ○, 2,3DM-B2.

values followed the sequence benzene > toluene; the presence of the methyl group on the aromatic ring increases the polarity of the toluene molecule, because the arrangement of the π electrons in the aromatic ring is less ordered when methyl groups are added to the ring, which, moreover, decreases the ionization potential. Therefore, interactions with the -OH groups on the alkanol arise, resulting in lower v^E values than those for the corresponding benzene-containing mixture.

ACKNOWLEDGMENTS

One of us (J.O.) is indebted to Canarias Government for the financial support to the project 08/90.

REFERENCES

1 J.S. Matos, J. Ortega and M.V. Garcia, Thermochim. Acta, 168 (1990) 127.
2 J. Ortega, J.S. Matos and E. Perez, Thermochim. Acta, 180 (1991) 1.
3 J. Ortega, J.A. Peña, M.I. Paz-Andrade, M. Pintos and L. Romani, J. Chem. Thermodyn., 17 (1985) 321.
4 J. Ortega, M.I. Paz-Andrade and R. Bravo, J. Chem. Thermodyn., 17 (1985) 1199.

5 J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, Techniques of Chemistry, Vol. II, 4th edn., Wiley–Interscience, New York, 1986.

6 J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1965.

7 T.R.C., Thermodynamic Tables of Hydrocarbons, Thermodynamic Research Center, Texas A&M University, 1967, p. a-5090.

8 J. Ortega, J.S. Matos, M.I. Paz-Andrade and E. Jimenez, J. Chem. Thermodyn., 17 (1985) 1127.

9 G.C. Benson, M.K. Kumaran, C.J. Halpin and P.J. D'Arcy, J. Chem. Thermodyn., 18 (1986) 1007.

10 I. Brown, W. Fock and F. Smith, J. Chem. Thermodyn., 1 (1969) 273.