Thermochimica Acta, 217 (1993) 301–308 301
Elsevier Science Publishers B.V., Amsterdam

Excess molar volumes of *n*-hexane with some hexanol isomers at 298.15 K

J. Ortega * and E. Gonzalez

Laboratorio de Termodinámica y Fisicoquímica, Escuela Superior de Ingenieros Industriales, Universidad de Las Palmas de Gran Canaria, 35071 Las Palmas, Canary Islands (Spain)

(Received 3 August 1992)

Abstract

Excess molar volumes measured at 298.15 K using a vibrating-tube densimeter are reported for ten binary mixtures formed by *n*-hexane with the hexanol isomers: 3-methylpentan-1-ol, 4-methylpentan-1-ol, 2,2-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, hexan-2-ol, hexan-3-ol, 2-methylpentan-3-ol, 3,3-dimethylbutan-2-ol, 2-methylpentan-2-ol and 2,3-dimentylbutan-2-ol. The results are compared with previous excess volumes for mixtures of *n*-hexane and the other hexanol isomers.

INTRODUCTION

The literature contains a number of studies on the thermodynamic properties of normal alkanols in various solvents. However, systematic studies on branched alkanols are less common. These mixtures offer an interesting opportunity to observe the relationship between the thermodynamic properties of the mixtures and the isomer type (primary, secondary, or tertiary), as well as the influence of the position of the hydroxyl group on the alkanol.

In a recent series of papers, our laboratory has reported the mixing enthalpy values of mixtures of *n*-nonane with isomers of hexanol [1] and the excess volumes of isomers of hexanol with several different components, such as toluene [2] cyclohexane [3] and benzene [4]. The purpose of this research has been to study the effect of molecular shape on the thermodynamic magnitudes of systems consisting of binary mixtures consisting of isomers of hexanol together with a second component, in this case a hydrocarbon, *n*-hexane. The literature has divulged a considerable quantity of v^E values for mixtures of *n*-hexane with several different isomers of hexanol, namely, hexan-1-ol (H1) [5, 6], 2-methylpentan-1-ol (2M-P1) [6, 7], 2-ethylbutan-1-ol (2E-B1) [8], 3,3-dimethylbutan-1-ol

---

* Corresponding author.

(3,3DM-B1) [9], 4-methylpentan-2-ol (4M-P2) [6], 3-methylpentan-2-ol (3M-P2) [6] and 3-methylpentan-3-ol (3M-P3) [6].

As a further investigation in this series, we have measured the excess volumes at 298.15 K for mixtures of *n*-hexane with the other isomers of hexanol not previously considered, namely, the primary isomers 3-methylpentan-1-ol (3M-P1), 4-methylpentan-1-ol (4M-P1), 2,2-dimethylbutan-1-ol (2,2DM-B1), and 2,3-dimethylbutan-1-ol (2,3DM-B1), the secondary isomers hexan-2-ol (H2), hexan-3-ol (H3), 2-methylpentan-3-ol (2M-P3), and 3,3-dimethylbutan-2-ol (3,3DM-B2), and the tertiary isomers 2-methylpentan-2-ol (2M-P2), and 2,3-dimethylbutan-2-ol (2,3DM-B2).

EXPERIMENTAL

Values for the physical properties of hexanol isomers have been published in several previous papers [2–4]. The *n*-hexane (puriss p.a. > 99.5, Fluka) employed in this experiment was degassed with ultrasound and then dried on a molecular sieve (ref. 69828, Fluka). The values of the physical properties, namely, the density and the refractive index, determined at 298.15 K were: $\rho = 654.78$, 654.81 [6] and 654.84 [10] (kg m^{-3}); and $n_D = 1.3723$, 1.37226 [10].

An Anton Paar model DMA 60/602 vibrating-tube densimeter was used to determine the changes in volume on mixing the liquid components under constant pressure and temperature. Temperature was regulated at 298.15 ± 0.01 K and the densimeter was calibrated at this temperature using water at a setting of $\rho = 997.043$ kg m^{-3} and *n*-nonane at a setting of $\rho = 713.855$ kg m^{-3}, as previously reported by one of the authors [11]. The binary mixtures were prepared by weight; the imprecision in the determinations of the mole fraction of the hydrocarbon was estimated at $\pm 5 \times 10^{-5}$ over the entire range of concentrations. Excess molar volumes v^E were determined indirectly from the density values; the imprecision in the v^E calculations was estimated at less than ±0.002 cm^3 mol^{-1}.

RESULTS AND DISCUSSION

Experimental values of the molar excess volumes v^E obtained by us for the binary mixtures of *n*-hexane with ten hexanol isomers at 298.15 K are listed in Table 1. In all cases, x_1 denotes the mole fraction of the hydrocarbon. These results are also plotted in Figs. 1, 2 and 3 according to the type of isomer namely, primary, secondary, or tertiary, respectively, for clarity of presentation.

Each set of results was fitted with a polynomial equation of the form

$$v^E\,(\mathrm{cm^3\,mol^{-1}}) = x_1x_2\sum_i A_i[x_1/(x_1 + kx_2)]^i \tag{1}$$

TABLE 1

Excess molar volumes at 298.15 K for the mixtuers x_1 *n*-hexane + x_2 isomer of hexanol and $\delta v^E = v^E_{exp} - v^E_{cal}$

x_1	v^E ($cm^3\ mol^{-1}$)	$\delta v^E \times 10^3$ ($cm^3\ mol^{-1}$)	x_1	v^E ($cm^3\ mol^{-1}$)	$\delta v^E \times 10^3$ ($cm^3\ mol^{-1}$)	x_1	v^E ($cm^3\ mol^{-1}$)	$\delta v^E \times 10^3$ ($cm^3\ mol^{-1}$)
x_1 *n*-hexane + x_2 3-methylpentan-1-ol								
0.9382	0.021	−1	0.6545	−0.128	−1	0.2950	−0.258	−8
0.9054	0.017	4	0.5819	−0.168	−2	0.2682	−0.245	−1
0.8571	−0.017	−9	0.4999	−0.203	2	0.1782	−0.192	8
0.8163	−0.025	8	0.4136	−0.236	2	0.1080	−0.140	−4
0.7139	−0.095	−1	0.3403	−0.251	1	0.0362	−0.049	−0
x_1 *n*-hexane + x_2 4-methylpentan-1-ol								
0.9823	0.013	0	0.6360	0.021	14	0.2999	−0.182	−3
0.9652	0.025	1	0.5967	0.010	27	0.2076	−0.162	10
0.9240	0.043	−2	0.5651	−0.028	9	0.1218	−0.117	1
0.8617	0.051	−11	0.5492	−0.054	6	0.1123	−0.107	2
0.8177	0.055	−9	0.5132	−0.090	−19	0.0459	−0.046	−7
0.7210	0.041	−4	0.4245	−0.140	−13	–	–	–
x_1 *n*-hexane + x_2 2,2-dimethylbutan-1-ol								
0.9752	0.081	−0	0.6871	0.102	2	0.4069	0.079	−0
0.9563	0.096	0	0.6011	0.094	−1	0.3337	0.069	−1
0.9075	0.104	−0	0.5913	0.093	−1	0.2534	0.061	1
0.8581	0.106	1	0.5026	0.090	3	0.1628	0.045	2
0.7717	0.104	−1	0.4403	0.081	−2	0.0737	0.018	−4
x_1 *n*-hexane + x_2 2,3-dimethylbutan-1-ol								
0.9371	0.033	−0	0.6789	−0.011	5	0.3249	−0.158	1
0.8602	0.036	1	0.5718	−0.052	−4	0.2440	−0.172	−3
0.7742	0.010	−4	0.4936	−0.091	−1	0.1606	−0.140	3
0.7516	0.007	0	0.4311	−0.117	2	0.0744	−0.074	−1
x_1 *n*-hexane + x_2 hexan-2-ol								
0.9627	0.099	2	0.5093	0.101	0	0.2962	0.021	5
0.8903	0.127	−3	0.4646	0.079	−5	0.2439	0.002	3
0.8210	0.135	1	0.4171	0.061	−4	0.1936	−0.015	−3
0.7820	0.139	3	0.3923	0.054	−1	0.1264	−0.025	−5
0.6576	0.136	−1	0.3537	0.041	2	0.0807	−0.021	−2
0.5706	0.121	1	0.3136	0.028	6	0.0261	−0.010	−2

TABLE 1
(continued)

x_1	v^E (cm^3 mol^{-1})	$\delta v^E \times 10^3$ (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})	$\delta v^E \times 10^3$ (cm^3 mol^{-1})	x_1	v^E (cm^3 mol^{-1})	$\delta v^E \times 10^3$ (cm^3 mol^{-1})
x_1 *n*-hexane + x_2 hexan-3-ol								
0.9433	0.143	1	0.7618	0.180	−1	0.2208	0.117	−1
0.9265	0.152	−2	0.5986	0.176	−1	0.1944	0.108	−2
0.8699	0.170	−0	0.4127	0.158	2	0.1090	0.075	1
0.8841	0.175	1	0.3173	0.140	−1	0.0919	0.064	−0
0.7939	0.179	1	0.2619	0.130	1	0.0401	0.033	2
x_1 *n*-hexane + x_2 2-methylpentan-3-ol								
0.9618	0.145	3	0.6177	0.124	2	0.2999	0.020	2
0.9058	0.189	−8	0.5642	0.098	−2	0.2725	0.017	4
0.8635	0.203	1	0.5435	0.089	−3	0.2087	0.005	2
0.8509	0.206	4	0.5198	0.084	1	0.1442	−0.001	1
0.7815	0.187	1	0.4688	0.063	−2	0.0863	−0.006	−2
0.6915	0.153	1	0.4383	0.052	−3	0.0402	−0.001	1
0.6690	0.145	2	0.3597	0.030	−2	–	–	–
x_1 *n*-hexane + x_2 3,3-dimethylbutan-ol								
0.9420	0.173	3	0.6753	0.161	−5	0.2258	0.018	−1
0.8996	0.199	−6	0.5837	0.138	4	0.1894	0.012	0
0.8515	0.215	3	0.4709	0.094	1	0.0918	−0.004	−3
0.7873	0.203	2	0.3866	0.058	−7	0.0462	−0.003	−2
0.7379	0.186	−0	0.2703	0.038	9	–	–	–
x_1 *n*-hexane + x_2 2-methylpentan-2-ol								
0.9269	0.281	5	0.5514	0.301	8	0.2691	0.035	1
0.8997	0.344	−1	0.5116	0.237	−7	0.1764	0.005	1
0.8132	0.459	−4	0.4685	0.189	−4	0.1461	−0.004	−3
0.7140	0.456	−3	0.4199	0.139	−3	0.0786	−0.007	2
0.6637	0.421	1	0.3875	0.113	1	–	–	–
0.6334	0.395	5	0.3409	0.079	4	–	–	–
x_1 *n*-hexane + x_2 2,3-dimethylbutan-2-ol								
0.9833	0.103	−0	0.6596	0.149	−0	0.3500	0.008	3
0.9510	0.185	0	0.7420	0.189	2	0.2781	−0.014	1
0.9175	0.211	0	0.5359	0.082	−4	0.1652	−0.032	−5
0.8206	0.210	−1	0.4321	0.038	2	0.0736	−0.016	3

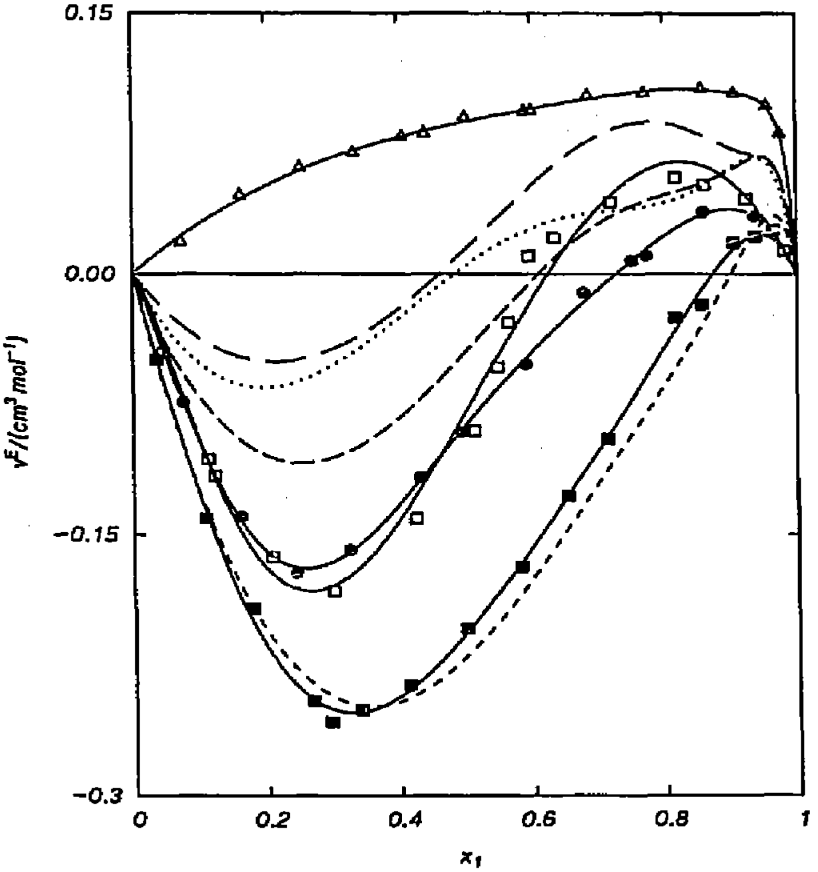

Fig. 1. Representation of experimental v^E values and those calculated using eqn. (1) along with the curves of previous papers for the mixture x_1 n-hexane + x_2 primary isomers of hexanol: - - - -, hexan-1-ol [5]; · · · · · ·, 3,3-dimethylbutan-1-ol [9]; — — —, 2-methypentan-1-ol [7]; ————, 2-ethylbutan-1-ol; △, 2,2-dimethylbutan-1-ol; □, 4-methylpentan-1-ol; ●, 2,3-dimethylbutan-1-ol; ■, 3-methylpentan-1-ol.

Values of the coefficients A_i and the parameter k, and standard deviations by the least-squares method with all points weighted equally, are given in Table 2. The curves (solid lines) corresponding to our experiment data in Figs. 1–3 were calculated from eqn. (1) with these values of A_i and k. The broken lines represent the curves of v^E derived from the literature for the other isomers not included in Table 1. So, in this paper a comparative analysis of the n-hexane mixtures with the seventeen hexanol isomers is shown.

As revealed by the figures, the v^E curves for most of the mixtures were sigmoidal. However, the behaviour of the primary alkanols is clearly distinguishable from that of the rest of the isomers. Thus, in Fig. 1 the curves for the primary isomers generally have values of $v^E > 0$ at low alkanol concentrations and $v^E < 0$ at higher concentrations, and contraction effects tend to decrease with isomer type, although there are exceptions. Rupture of the hydrogen bonds at high values of x_1 reflected the positive v^E values which provided a partial basis for the order followed in the figures.

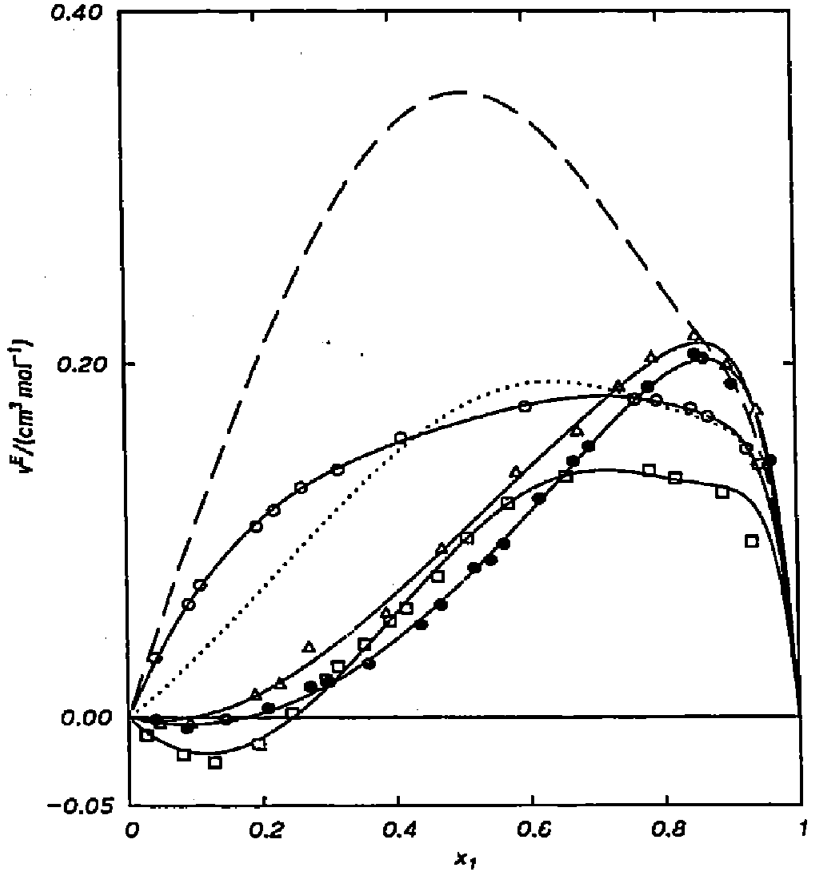

Fig. 2. Representation of experimental v^E values and those calculated using eqn. (1) along with the curves of previous papers for the mixtures x_1 *n*-hexane + x_2 secondary isomers of hexanol: · · · · · ·, 3-methylpentan-2-ol [6]; ———, 4-methylpentan-2-ol [6]; ○, hexan-3-ol; △, 3,3-dimethylbutan-2-ol; ●, 2-methylpentan-3-ol; □, hexan-2-ol.

As alkanol concentration increased, the bonds ruptured more easily, because there was a smaller quantity of hydrocarbon. However, the interstitial accommodation effects increased, resulting in contraction of the volume of the mixture. 2,2DM-B1, whose v^E values were positive over the entire range of concentrations, was the exception among the primary isomers. Contraction effects decreased in the secondary and tertiary alkanols, suggesting an increase in the rupture of the hydrogen bonds as the –OH group assumed a more central position in the molecule, coupled with an opposing decrease in the effects of interstitial accommodation between the hydrocarbon and alkanol molecules. In other words, there was an increase in the physical effects of steric hindrance arising when branched alkanols are present in the mixtures.

Contrasting the volumetric behaviour of the systems considered here (*n*-hexane + hexanol isomers) with that of systems containing mixtures of cyclohexane and hexanol isomers [3], the following variation for the v^E values was found: cyclohexane > hexane; this was attributable to the differing extent of the interactions between the alkanol isomers and

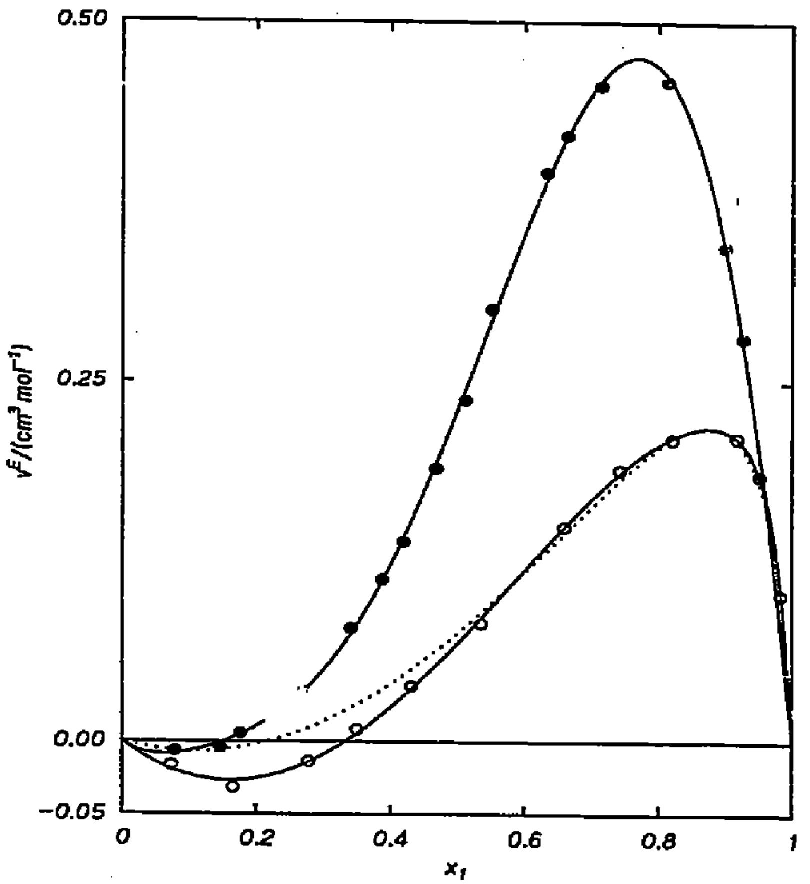

Fig. 3. Representation of experimental v^E values and those calculated using eqn. (1) along with the curves of previous papers for the mixtures x_1 n-hexane + x_2 tertiary isomers of hexanol: · · · · · ·, 3-methylpentan-3-ol [6]; ○, 2,3-dimethylbutan-2-ol; ●, 2-methylpentan-2-ol.

TABLE 2

Parameters of eqn. (1) and standard deviation $s(v^E)$

x_1 n-hexane + x_2	k	A_0	A_1	A_2	A_3	A_4	$10^3 \times s(v^E)$
3-Methylpentan-1-ol	1.296	−1.372	−1.562	14.067	−23.033	12.860	5
4-Methylpentan-1-ol	0.293	−0.513	−3.292	4.580	–	–	1
2,2-Dimethylbutan-1-ol	8.113	0.318	−0.377	7.317	−13.331	12.494	2
2,3-Dimethylbutan-1-ol	0.895	−0.866	−3.944	21.181	−30.269	14.789	3
Hexan-2-ol	4.282	−0.367	−6.055	−13.080	11.905	–	3
Hexan-3-ol	3.470	0.840	−2.989	14.235	−23.052	16.182	1
2-Methylpentan-3-ol	10.000	−9.064	4.325	−6.917	2.438	–	3
3,3-Dimethylbutan-2-ol	3.751	−7.524	2.778	−3.324	5.822	–	5
2-Methylpentan-2-ol	0.596	−0.345	2.515	−6.521	9.146	–	4
2,3-Dimethylbutan-2-ol	7.680	−0.342	6.014	−7.007	9.793	–	3

hydrocarbon type. The results obtained when other solvents, such as benzene and toluene, were used do not appear to be comparable.

REFERENCES

1 J. Ortega, Int. Data Ser. A, 2 (1990) 94–110.
2 J.S. Matos, J. Ortega and M.V. Garcia, Thermochim. Acta, 168 (1990) 127.
3 J. Ortega, J.S. Matos and E. Perez, Thermochim. Acta, 180 (1991) 1.
4 J. Ortega, M. Chaar and and J.S. Matos, Thermochim. Acta, 204 (1992) 295.
5 A.J. Treszczanowicz and G.C. Benson, J. Chem. Thermodyn., 12 (1980) 173.
6 R. Bravo, M. Pintos, M.C. Baluja, M.I. Paz-Andrade, G. Roux-Desgranges and J.-P.E. Grollier, J. Chem. Thermodyn., 16 (1984) 73.
7 F. Kimura and G.C. Benson, J. Chem. Eng. Data, 29 (1984) 72.
8 F. Kimura and G.C. Benson, Fluid Phase Equil. 16 (1984) 77.
9 G.C. Benson, M.K. Kumaran, C.J. Halpin and P.J. D'Arcy, J. Chem. Thermodyn., 18 (1986) 1007.
10 J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, Techniques of Chemistry, Vol. II, 4th edn., Wiley Interscience, New York, 1986.
11 J. Ortega, J.S. Matos, M.I. Paz-Amdrade and E. Jimenez, J. Chem. Thermodyn., 17 (1985) 1127.