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Excess molar volumes of binary mixtures containing isooctane + six methyl-*n*-alkyl ketones at 298.15 K

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Abstract

Excess molar volumes V^E of binary mixtures containing isooctane + six methyl-*n*-alkyl ketones have been determined using a digital density meter at 298.15 K and atmospheric pressure.

The experimental values were correlated by the Redlich–Kister equation. V^E decreases with an increase in the chain length of the ketone, from the highly positive values of isooctane + 2-propanone ($V^E \approx 1.0\,\mathrm{cm^3\,mol^{-1}}$) up to the markedly negative values of isooctane + 2-undecanone ($V^E \approx -0.4\,\mathrm{cm^3\,mol^{-1}}$). The volume effect is discussed qualitatively in terms of the molecular interactions.

INTRODUCTION

We are engaged in a systematic study of the thermodynamic properties of methyl-alkyl ketones with several organic solvents. So far we have determined excess molar enthalpies or excess molar volumes of ketones + 1-methylnaphthalene [1, 2], + 1-chloronaphthalene [3], + halothane [4], and + some benzene-substituted compounds [5–7]. In this paper, we report the excess molar volumes V^E of isooctane (component 1) + six methyl-*n*-alkyl ketones (component 2) namely 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-octanone, and 2-undecanone, at 298.15 K and atmospheric pressure. The aim of this systematic research is to obtain a better understanding of the connection between the molecular structure and properties of these mixtures. We are not aware of any V^E data reported in the literature for these systems.

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EXPERIMENTAL

Materials

Isooctane (2,2,4-trimethylpentane), an Aldrich product, analytical grade 99.7 mol.%, was used as received.

The methyl-*n*-alkyl ketones were the same as in our previous papers; their purifications are described in detail in refs. 1 and 4.

Before use, all the compounds were stored in dark bottles over suitable molecular sieves (Union Carbide type 4A, 1/16 in pellets).

Measurements

A digital density meter (Anton Paar, Graz, Austria, model 60 equipped with a measuring mixing cell, type 602) was used for the determination of the densities of the pure components and of the mole fractions of the binary mixtures. The densities of the pure components are very accurate, as demonstrated in the comparison with literature data reported in Table 1.

Water and dry air were taken as calibrating fluids because their densities are known to a high degree of precision. All measurements were carried out at atmospheric pressure, measured by a precision digital manometer manufactured by Fritz GmbH (Normag) Hofheim (Germany), with accuracies of 0.02 kPa.

A Heto constant-temperature bath circulator (Hetotherm type 01 DBT 623) was used with a temperature control interval of ±0.005 K. The temperature was detected with a digital thermometer (Anton Paar, type DT 100-25) with a precision of 0.01 K. The precision of the instrument is reported to be 1×10^{-6} g cm^{-3}. Samples were prepared gravimetrically using a Mettler analytical balance (model A 160) with a precision of 0.0001 in mole fraction; all weights were corrected to account for the partial evaporation of the liquid. This procedure is described in ref. 10. The partial

TABLE 1

Experimental densities ρ in g cm^{-3} at 298.15 K and comparison with literature data

Component	This study	Literature
Isooctane	0.68770	0.68781 [8]
2-Propanone	0.78501	0.78440 [8]
2-Butanone	0.79970	0.7997 [8]
2-Pentanone	0.80151	0.8015 [8]
2-Hexanone	0.80637	0.8067 [8]
2-Octanone	0.81436	0.8143 [8]
2-Undecanone	0.82230	0.82216 [8]

evaporation and impurities of the materials are considered to be the major causes of experimental errors.

Three repetitions of each data set were made to ensure repeatability and, after each measurement, the sample U-tube of the density meter was washed with propanone and dried repeatedly until the original calibration volume for air was achieved. The accuracy of the density measurements is estimated as 2×10^{-6} g cm^{-3} and the average error in V^E for all systems was smaller than 2×10^{-4} cm^3 mol^{-1}.

The test system, benzene + cyclohexane [11], was used to calibrate the apparatus and the results obtained are in agreement with those of the literature over the entire range of concentration (the discrepancy is less than 2×10^{-6} g cm^{-3}).

RESULTS AND DISCUSSION

The excess molar volumes for isooctane mixtures at 298.15 K are listed in Table 2 as a function of composition, and are represented graphically in Fig. 1. For each mixture, the V^E values are fitted to the Redlich–Kister equation by the method of least squares

$$V^E/x_1x_2 = \sum_{k \geq 0} a_k(x_1 - x_2)^k \tag{1}$$

where x_1, x_2 refer to the mole fraction of isooctane and ketones, respectively. The adjustable parameters a_k and the standard deviations $\sigma(V^E)$ are reported in Table 3. The values of $\sigma(V^E)$ were obtained using

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

where $\phi_{\min}$ is the minimum value of the objective function defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{3}$$

with N being the number of experimental points, $\eta_k = V^E_{\text{calc}} - V^E$ and V^E_{calc} being determined from the right-hand-side of eqn. (1) and n being the number of adjustable parameters.

Figure 2 shows $V^E_{0.5}$, the equimolar volume of V^E, plotted against n_C, the number of carbon atoms of the methyl-n-alkyl ketone.

Observing the patterns of the curves of Figs. 1 and 2 and the data of Table 2, it can be seen that the V^E values for isooctane + 2-propanone, +2-butanone, +2-pentanone, and +2-hexanone are positive over the entire range of mole fractions, and decrease with increasing ketone chain-length. A sign inversion in V^E can be noted for the isooctane + 2-octanone mixture, while markedly negative values in V^E for isooctane + 2-undecanone are displayed.

For a qualitative point of view, it may be conceived that mixing isooctane

TABLE 2

Experimental excess molar volumes V^E in $cm^3 mol^{-1}$ for isooctane(1) + methyl-*n*-alkyl ketone(2) systems at 298.15 K

x_1	V^E	x_1	V^E	x_1	V^E
Isooctane + 2-propanone					
0.0083	0.0402	0.2332	0.7676	0.5333	1.0475
0.4435	0.1907	0.2704	0.8390	0.6114	1.0198
0.0843	0.3439	0.2784	0.8499	0.6315	1.0047
0.1086	0.4311	0.3059	0.8976	0.8051	0.7398
0.1589	0.5857	0.3588	0.9645	0.9003	0.4502
0.1779	0.6389	0.3844	0.9882	0.9717	0.1481
0.2128	0.7227	0.4708	1.0401		
Isooctane + 2-butanone					
0.0106	0.0240	0.3039	0.5099	0.5264	0.6443
0.0509	0.1096	0.3373	0.5416	0.5715	0.6474
0.1276	0.2589	0.3482	0.5498	0.6310	0.6349
0.1769	0.3406	0.3937	0.5891	0.7439	0.5650
0.2102	0.3925	0.4441	0.6167	0.8073	0.4882
0.2474	0.4480	0.4605	0.6261	0.9687	0.1160
0.2796	0.4824				
Isooctane + 2-pentanone					
0.0374	0.0484	0.3093	0.3266	0.5184	0.4409
0.0653	0.0828	0.3394	0.3494	0.5650	0.4446
0.1089	0.1321	0.3740	0.3696	0.6112	0.4472
0.1648	0.1950	0.3889	0.3787	0.7094	0.4252
0.2024	0.2344	0.4386	0.4073	0.8131	0.3497
0.2267	0.2542	0.4695	0.4199	0.7951	0.0691
0.2463	0.2744				
Isooctane + 2-hexanone					
0.0155	0.0080	0.3674	0.1924	0.5932	0.2796
0.0758	0.0393	0.4056	0.2101	0.6507	0.2804
0.1375	0.0725	0.4286	0.2198	0.7079	0.2756
0.2160	0.1132	0.4764	0.2382	0.7578	0.2700
0.2734	0.1463	0.5316	0.2583	0.9099	0.1606
0.3001	0.1613	0.5501	0.2629	0.9722	0.0589
0.3370	0.1792				
Isooctane + 2-octanone					
0.0111	−0.0069	0.3987	−0.0853	0.6836	−0.0103
0.0771	−0.0383	0.4442	−0.0802	0.7808	0.0197
0.1219	−0.0556	0.4498	−0.0773	0.7932	0.0230
0.1455	−0.0692	0.4902	−0.0724	0.9065	0.0391
0.2845	−0.0894	0.5424	−0.0571	0.9557	0.0259
0.3100	−0.0928	0.6116	−0.0344	0.9729	0.0168
0.3758	−0.0879				
Isooctane + 2-undecanone					
0.0183	−0.0244	0.4632	−0.3830	0.7489	−0.2848
0.0991	−0.1281	0.4906	−0.3905	0.8281	−0.2104
0.1938	−0.2300	0.5209	−0.3878	0.8984	−0.1293
0.2814	−0.3011	0.5543	−0.3852	0.9144	−0.1128
0.3277	−0.3336	0.6160	−0.3662	0.9429	−0.0745
0.3774	−0.3585	0.6678	−0.3419	0.9844	−0.0288
0.4299	−0.3777				

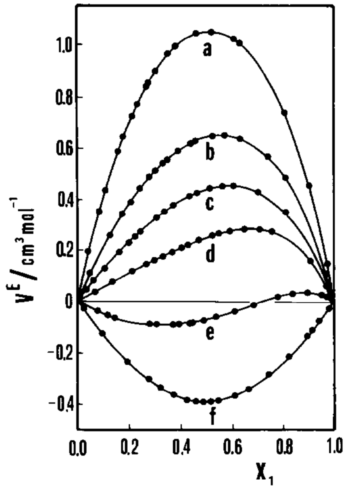

Fig. 1. Excess molar volumes V^E at 298.15 K for the binary mixtures of isooctane + 2-propanone (a); +2-butanone (b); +2-pentanone (c); +2-hexanone (d); +2-octanone (e); +2-undecanone (f).

TABLE 3

Coefficients a_k of the polynomial function eqn. (1) for binary mixtures of isooctane(1) + methyl-*n*-alkyl ketone(2)

Ketones	a_0	a_1	a_2	a_3	$\sigma(V^E)/cm^3 mol^{-1}$
2-Propanone	4.1889	0.2353	0.9035	0.2089	0.0020
2-Butanone	2.5534	0.5221	0.5149	0.2999	0.0017
2-Pentanone	1.7283	0.6720	0.3213		0.0026
2-Hexanone	0.9907	0.6819	0.3711	0.2306	0.0023
2-Octanone	−0.2750	0.4772	0.3089	0.1990	0.0021
2-Undecanone	−1.5508	−0.0220	0.1972		0.0026

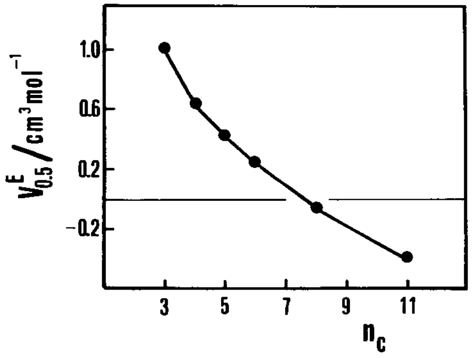

Fig. 2. Values of equimolar volumes $V^E_{0.5}$ at 298.15 K as a function of the number of carbon atoms in the ketone n_C, for the binary mxtures of isooctane + methyl-*n*-alkyl ketones.

and ketone, in which mixture the latter presents molecular association, will produce partial dissociation and hence a volume increase, whereas the interactions between dissimilar molecules or interstitial accomodation of small molecules in associated aggregates will lead to a volume decrease [12]. It seems reasonable that this last effect is prevalent when large ketone molecules are implied.

These remarks are in agreement with the curves of Fig. 2, showing decreased V^E values when the number of carbon n_C is increased.

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