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Densities and excess molar volumes for binary mixtures containing 2,2,4-trimethylpentane and six different chlorohydrocarbons at 298.15 K

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Abstract

Densities and excess molar volumes for the six binary mixtures containing 2,2,4-trimethylpentane + 1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, +1,2-*trans*-dichloroethylene, +trichloroethylene, or +tetrachloroethylene have been determined at 298.15 K and atmospheric pressure using an Anton Paar density meter. The experimental values have been correlated by the Redlich–Kister equation and the parameters have been evaluated by least-squares analysis. For all mixtures, the V^E values, whose maximum ranges from −0.38 up to 0.65 $cm^3\,mol^{-1}$, decrease with increasing number of chlorine atoms in the molecule. This volume effect is discussed qualitatively in terms of the molecular interactions.

INTRODUCTION

In this paper we report the densites ρ and experimental excess molar volumes V^E of 2,2,4-trimethylpentane (component 1) in six chlorohydrocarbons (component 2), namely 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,2-*trans*-dichloroethylene, trichloroethylene and tetrachlorethylene, respectively.

In a previous work [1], we have determined the molar Gibbs energies at 343.15 K for these same mixtures, with the exception of the 2,2,4-trimethylpentane + 1,2-*trans*-dichloroethylene system, which boils at a lower temperature. The aim of the present work is to measure the volumetric properties, in order to obtain a better understanding of their thermodynamic properties.

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To our knowledge, no volumetric data for these systems are reported in the literature.

EXPERIMENTAL

Apparatus

All the chemicals used were from Aldrich Chem. Co. Ltd., with the exception of the 1,1,1-trichloroethane which was from Fluka. Because they were provided to a high grade of purity ($\geqslant$99%), the products were used as received. Only 1,2-*trans*-dichloroethylene, with a lower stated purity of 98%, was further purified by fractional distillation following the method of Knox and Riddik [2].

Before use, all chemicals were stored in dark bottles and carefully dried with molecular sieves (Union Carbide type 4A, 1/16 in pellets).

The properties of these pure compounds at 298.15 K and atmospheric pressures are listed in Table 1 and compared with literature data [3–8].

Measurements

The densities ρ were determined using an Anton Paar digital density meter (Model DMA 60/602). This determination is based on measuring the oscillation period T of a vibrating U-shaped hollow tube filled with the sample. The operating procedure for determining the densities of mixtures is described in ref. 9.

The precision of the instrument was better than 1.5×10^{-6} g cm^{-3}. The systems are maintained at constant temperature to within 0.005 K by means of a Hetotherm bath circulator (Model 01 DTB 623) and the temperature

TABLE 1

Sources, densities, ρ, and refractive indexes n of the chemicals used in this work

Component	Source	ρ(298.15 K)/(g cm^{-3})		n(D, 298.15 K)	
		Expt.	Lit.	Expt.	Lit.
2,2,4-Trimethylpentane	Aldrich (99.7%)	0.68769	0.68781 [3]	1.3892	1.38899 [3]
1,2-Dichloroethane	Aldrich (99.8%)	1.2468	1.24579 [4]	1.4421	1.4421 [3]
1,1,1-Trichloroethane	Fluka (+99%)	1.32973	1.3299 [3]	1.4361	1.4359 [3]
1,1,2,2-Tetrachloroethane	Aldrich (9%)	1.58785	1.5876 [4]	1.4918	1.4914[3]
1,2-*trans*-Dichloroethylene	Aldrich (98%)	1.25032	1.2502 [5]	1.4436	1.44348 [5]
Trichloroethylene	Aldrich (99%)	1.45572	1.45544 [6] [a]	1.4750	1.4748 [7]
Tetrachloroethylene	Aldrich (99%)	1.61309	1.61432 [3] 1.60682 [8]	1.5037	1.5032 [3]

[a] Interpolated from the density equation.

was measured with a digital thermometer (Anton Paar DT-25) with a precision of 0.01 K.

Degassed, twice distilled water and dry air [10] were prepared daily as the calibrating and reference fluids. Samples were prepared gravimetrically [9] using a Mettler balance (Model AE 160) with a precision of 0.0001 in mole fraction. Each data set was measured within the same day and two or three repetitions were made to determine the reproducibility. After introduction of the samples into the U-tube, time was allowed for thermal equilibrium to be reached, typically 10 min, using a period select switch of 10 000 units.

After measurements, the sample U-tube was washed and dried twice with acetone, until the original calibration value for air was reached. Before measurements, the apparatus was checked with a benzene + cyclohexane mixture, the densities of which are accurately known from the literature [11]: our value for V^E at 0.5 mole fraction is 0.652 $cm^3\ mol^{-1}$ (literature value, 0.6514).

Variations in temperature of the batch and minor impurities in the materials are considered to be the major sources of experimental errors. All measurements were corrected for bouyancy and for evaporation of components. For this reason, the vapour pressures at room temperature of the pure components, a knowledge of which is necsesary for determining such corrections, were evaluated using an equilibrium still manufactured by Fritz and Gmbh (Normag, Hoffheim, Germany): for details and operation procedure, see ref. 12.

The estimated uncertainty in V^E, calculated from variance analysis [13], is 3×10^{-3} $cm^3\ mol^{-1}$ for the four mixtures exhibiting larger values of V^E, rising to 6×10^{-3} $cm^3\ mol^{-1}$ for trichloroethylene and 1,1,2,2-tetrachloroethane.

RESULTS AND CONCLUSIONS

Densities values ρ ($g\ cm^{-3}$) and experimental excess molar volumes V^E (cm^3/mol^{-1}) are reported in Table 2 and graphical representations are given in Fig. 1. The Redlich–Kister equation

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

was fitted to each set of results by the method of least-squares with all points weighted equally.

Table 3 summarizes the values of the parameters a_k and the standard deviations $\sigma(V^E)$. Figure 2 shows V^E ($x = 0.5$), the equimolar volume of V^E, plotted against the number n_{Cl} of Cl atoms in the chlorohydrocarbons.

Figure 1 shows that double-bonded molecules have V^E values smaller than the corresponding alkanes with the same number of Cl atoms.

Replacing H atoms with Cl atoms leads to a decrease in V^E for both alkenes and alkanes.

TABLE 2

Densities ρ and experimental excess molar volumes V^E for 2,2,4-trimethylpentane(1) + chlorohydrocarbons(2)

x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
2,2,4-Trimethylpentane + 1,2-dichloroethane					
0.0082	1.23599	0.013	0.3118	0.96990	0.478
0.0450	1.19459	0.072	0.3768	0.92956	0.547
0.0886	1.14960	0.141	0.4086	0.91134	0.581
0.1311	1.10933	0.209	0.4887	0.86922	0.640
0.1552	1.08790	0.248	0.5212	0.85354	0.656
0.1953	1.05440	0.312	0.6439	0.80052	0.656
0.2231	1.03265	0.352	0.7103	0.77536	0.622
0.2467	1.01497	0.387	0.7774	0.75212	0.543
0.2892	0.98497	0.449	0.9694	0.69554	0.104
0.2941	0.98169	0.452			
2,2,4-Trimethylpentane + 1,1,1-trichloroethane					
0.0117	1.31722	0.016	0.3599	1.01762	0.310
0.0829	1.24497	0.097	0.3952	0.99352	0.324
0.1504	1.18247	0.165	0.4049	0.98709	0.327
0.1830	1.15404	0.195	0.4436	0.96189	0.339
0.2016	1.13832	0.211	0.4978	0.92835	0.349
0.2224	1.12123	0.226	0.6759	0.83006	0.314
0.2731	1.08109	0.266	0.7630	0.78776	0.263
0.2909	1.06760	0.274	0.8200	0.76177	0.217
0.3390	1.03240	0.298	0.9813	0.69488	0.027
2,2,4-Trimethylpentane + 1,1,2,2-tetrachloroethane					
0.0098	1.57426	−0.010	0.3901	1.13793	−0.146
0.0642	1.50113	−0.060	0.4372	1.09419	−0.136
0.0768	1.48474	−0.067	0.5159	1.02509	−0.117
0.1228	1.42680	−0.100	0.5770	0.97474	−0.098
0.2124	1.32149	−0.139	0.6159	0.94400	−0.083
0.2404	1.29044	−0.144	0.6599	0.91044	−0.068
0.2764	1.25170	−0.150	0.7568	0.84074	−0.037
0.3003	1.22681	−0.154	0.8872	0.75510	−0.003
0.3422	1.18438	−0.152	0.9728	0.70343	0.001
2,2,4-Trimethylpentane + 1,2-*trans*-dichloroethylene					
0.0499	1.19228	0.077	0.3383	0.95302	0.360
0.0886	1.15157	0.132	0.3726	0.93215	0.374
0.1188	1.12209	0.172	0.3953	0.9189	0.383
0.1550	1.08909	0.214	0.4398	0.89449	0.390
0.2132	1.04070	0.272	0.4628	0.88246	0.395
0.2511	1.01198	0.307	0.5910	0.82264	0.380
0.2668	1.00067	0.320	0.6837	0.78570	0.335
0.2989	0.97856	0.340	0.7600	0.75849	0.280
0.3198	0.96477	0.354	0.9686	0.69587	0.047

TABLE 2 (continued)

x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
2,2,4-Trimethylpentane + trichlorethylene					
0.0100	1.44176	−0.003	0.3828	1.04686	−0.063
0.0587	1.37696	−0.021	0.4103	1.02502	−0.061
0.1016	1.32381	−0.031	0.4125	1.02328	−0.060
0.1279	1.29302	−0.040	0.5464	0.92674	−0.047
0.2140	1.19999	−0.055	0.5821	0.90354	−0.045
0.2488	1.16545	−0.059	0.6289	0.87438	−0.038
0.2770	1.13872	−0.061	0.7100	0.82732	−0.029
0.2876	1.12891	−0.061	0.8193	0.76996	−0.020
0.3179	1.10175	−0.062	0.9762	0.69774	−0.001
2,2,4-Trimethylpentane + tetrachloroethylene					
0.0089	1.60012	−0.014	0.4138	1.12318	−0.364
0.0729	1.51035	−0.109	0.4339	1.10419	−0.369
0.1490	1.41160	−0.204	0.5138	1.03232	−0.371
0.1613	1.39637	−0.216	0.5488	1.00244	−0.361
0.2045	1.34454	−0.256	0.5846	0.97281	−0.353
0.2383	1.30549	−0.282	0.6887	0.89186	−0.310
0.2995	1.23831	−0.323	0.7490	0.84812	−0.265
0.3227	1.21385	−0.332	0.8658	0.76951	−0.160
0.3511	1.18475	−0.347	0.9836	0.69724	−0.022
0.3746	1.16125	−0.356			

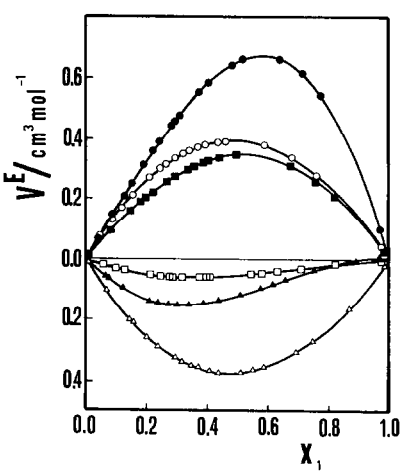

Fig. 1. Excess molar volumes V^E for the binary mixtures 2,2,4-trimethylpentane(1) +: ●, 1,2-dichloroethane(2); ■, 1,1,1-trichloroethane(2); ▲, 1,1,2,2-tetrachloroethane(2); ○, 1,2-*trans*-dichloroethylene(2); □, trichloroethylene(2); △, tetrachloroethylene(2) at 298.15 K. Solid curves are least-squares representation of results by eqn. (1).

TABLE 3

Adjustable parameters a_k and standard deviations $\sigma(V^E)$ of the polynomial function eqn. (1) for binary liquid mixtures of 2,2,4-trimethylpentane + chlorohydrocarbons at 298.15 K

Chlorohydrocarbon	a_0	a_1	$\sigma(V^E)$
1,2-Dichloroethane	2.5879	0.9992	0.0017
1,1,1-Trichloroethane	1.3863	0.1327	0.0012
1,1,2,2-Tetrachloroethane	−0.4890	0.5807	0.0012
1,2-*trans*-Dichloroethylene	1.5833	−0.0822	0.0016
Trichloroethylene	−0.2194	0.1806	0.0017
Tetrachloroethylene	−1.4829	0.1490	0.0018

These experimental features may be explained, almost qualitatively, by considering the one-dimensional model of solutions in the extension discussed by Prigogine and Lafleur [14], remembering that many results of this simplified model were confirmed by the cell model, for molecules of the same size.

According to the one-dimensional model, the sign of the excess volume is given by $2/E_{12} - 1/E_{11} - 1/E_{22}$, with E_{ij} being the interaction energy for an ij pair of molecules. Furthermore, a volume expansion on mixing is predicted when $E_{11} \geqslant E_{22} \simeq E_{12}$, whereas a contraction is expected for an interaction parameter E_{ij} of comparable magnitude.

In effect, if E_{11} is taken as the energy of the alkanes, the greater rigidity of the double bond should give rise to a smaller interaction between similar molecules of alkenes ($E_{22} \leqslant E_{11}$), and, hence, contraction in passing from alkanes to alkenes.

The substitution of H atoms with Cl atoms leads, moreover, to molecules that show more and more negative charge on their outer surface, due to the large electronegative Cl atoms, which cannot but reduce interactions between similar molecules with the consequent trend to negative V^E values.

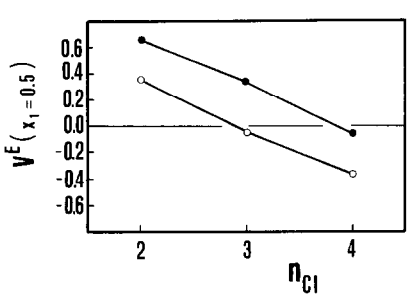

Fig. 2. Values of equimolar volumes V^E ($x_1 = 0.5$) at 298.15 K and atmospheric pressure as a function of the number of chlorine atoms n_{Cl} for the binary mixtures of 2,2,4-trimethylpentane + chlorohydrocarbons: ●, chloroalkanes; ○, chloroalkenes.

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