DENSITIES AND EXCESS VOLUMES IN BINARY MIXTURES OF HEPTANE WITH 1-CHLOROPROPANE, 1-CHLOROBUTANE, 1-CHLOROPENTANE, OR 1-CHLOROHEXANE AT 298.15 K

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Densities and excess molar volumes, V^E, of heptane–1-chloropropane, heptane–1-chlorobutane, heptane–1-chloropentane, and heptane–1-chlorohexane systems are reported at 298.15 K and atmospheric pressure over the whole composition range. Value of V^E was found to be slightly negative at lower mole fractions and slightly positive at higher mole fractions in case of the heptane–1-chlorohexane system. For all the other systems, V^E was positive. The V^E results were correlated using the fourth-order Redlich–Kister equation, the maximum likelihood procedure being applied for evaluating the adjustable parameters.

Key words: 1-Chloroalkanes; Heptane; Binary mixtures; Densities; Excess volumes.

In this paper, the excess molar volumes, V^E, at 298.15 K and atmospheric pressure are presented for four binary liquid mixtures of heptane with 1-chloroalkanes in order to examine the variation of V^E with the chain length of the compounds. With the exception of the heptane–1-chlorobutane system[1,2], no V^E data have been published for the binary mixtures of heptane with 1-chloroalkanes mentioned.

EXPERIMENTAL

Materials

Heptane, Fluka AG (Buchs, Switzerland), puriss., p.a. material of stated GC purity ≥99.5% was used without further purification. It was stored over molecular 4 Å sieves. The specification of the 1-chloroalkanes used was as follows: 1-Chloropropane (propyl chloride), Fluka AG (Buchs, Switzerland), purum material of stated GC purity ≥97%, 1-chlorobutane (butyl chloride), Fluka AG (Buchs, Switzerland), puriss., p.a. material of stated GC purity ≥97%, 1-chloropentane (pentyl chloride), Fluka AG (Buchs, Switzerland), puriss. material of stated GC purity ≥99%, 1-chlorohexane (hexyl chloride), Fluka AG (Buchs, Switzerland), puriss.

material of stated GC purity ≥99%. All the chloroalkanes were used as received without further purification.

All these chemicals were not degassed prior to use. In order to check the purity of the compounds, their density values and refractive indices were determined at 298.15 K. They are given in Table I and compared with literature data[3–5] (if available).

Apparatus and Procedure

The vibrating tube density meter, DMA 58 (Anton Paar, Graz, Austria) was used for the measurement. The temperature of the density-measuring cell was controlled to better than 0.005 K against ITS-90 and measured to within ±0.01 K by means of a built-in thermostat (a semiconductor Peltier element and a resistance thermometer temperature control system). The mixture samples were prepared by weighing covering the whole interval of mole fractions and were not degassed prior to use.

Density of the sample, ρ_m, was calculated from the measured period of vibration, τ, by using the following relation:

$$\rho_m = a + b\tau^2 \ . \qquad (1)$$

Constants a and b were determined by calibration using bidistilled water and heptane of special purity.

Values of V^E were calculated from the mixture densities, ρ_m, and the densities, ρ_i, and molar masses, M_i, of pure components i (i = 1, 2) by the relation:

$$V^E = [x\, M_1 + (1 - x)\, M_2]/\rho_m - [x\, M_1/\rho_1 + (1 - x)\, M_2/\rho_2] \ , \qquad (2)$$

where subscript 1 refers to heptane and 2 to chloroalkane and x stands for the mole fraction of heptane.

TABLE I
Densities, ρ, and refractive indices, n_D, at 298.15 K of pure components and comparison with literature values

Component	ρ, g cm^{-3}			n_D		
	exp.	lit.	ref.	exp.	lit.	ref.
Heptane	0.67961	0.67943–0.67963	4	1.3851	1.38510–1.38521	4
1-Chloropropane	0.88409	0.8850	3	1.3858	1.3858	3
1-Chlorobutane	0.88073	0.8809	3	1.3999	1.4001	3
1-Chloropentane	0.87694	0.8769	3	1.4099	1.4100	3
1-Chlorohexane	0.87333	0.8745	5	1.4172	–	

The experimental uncertainty of composition is less than ±1·10^{-4} in mole fractions, that of the density measurement is approximately ±1·10^{-5} g cm^{-3}, and of V^E is estimated to be about ±2·10^{-3} cm^3 mol^{-1}.

RESULTS AND CORRELATION

The densities and excess molar volumes of heptane–1-chloroalkane systems at the temperature 298.15 K and at atmospheric pressure are presented in Tables II–V. The dependences of excess molar volumes on mole fraction of heptane are illustrated in Fig. 1 for all the systems. The data were fitted to the fourth-order Redlich–Kister equation:

$$V^E = x(1 - x)[a_0 + a_1(1 - 2x) + a_2(1 - 2x)^2] , \qquad (3)$$

where a_0, a_1, and a_2 are parameters of the Redlich–Kister equation which were determined by the maximum likelihood method. The coefficients and standard deviations of the fit are summarized in Table VI.

DISCUSSION

In case of the systems of heptane with 1-chloropropane, 1-chlorobutane or 1-chloropentane, the excess molar volumes are positive with fairly symmetrical V^E *vs* x curves. The values of V^E decrease with the increasing number of carbon atoms in the aliphatic chain of chloroalkanes. On increasing the

TABLE II
Densities, ρ_m, and excess molar volumes, V^E, for heptane–1-chloropropane binary system at 298.15 K

x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}	x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}
0.0718	0.85985	0.1065	0.5707	0.74084	0.4207
0.1418	0.83835	0.2020	0.6085	0.73432	0.4103
0.2000	0.82192	0.2687	0.6860	0.72170	0.3781
0.2802	0.80126	0.3389	0.7612	0.71041	0.3221
0.3343	0.78840	0.3782	0.8238	0.70164	0.2578
0.4146	0.77077	0.4158	0.8874	0.69326	0.1803
0.4975	0.75421	0.4335	0.9234	0.68874	0.1276

number of carbon atoms, the difference between the molecular size of heptane and 1-chloroalkane decreases and so does the geometrical packing effect.

TABLE III
Densities, ρ_m, and excess molar volumes, V^E, for heptane–1-chlorobutane binary system at 298.15 K

x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}	x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}
0.0760	0.85940	0.0658	0.5463	0.75276	0.2780
0.1401	0.84248	0.1108	0.6478	0.73432	0.2651
0.2122	0.82440	0.1621	0.6941	0.72632	0.2535
0.2816	0.80793	0.2075	0.7571	0.71587	0.2250
0.3549	0.79154	0.2403	0.8704	0.69817	0.1489
0.4218	0.77735	0.2634	0.9089	0.69249	0.1098
0.4770	0.76617	0.2734	0.9393	0.68810	0.0781

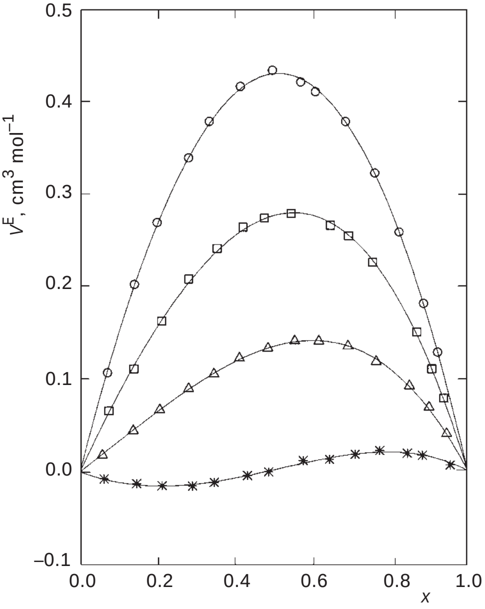

FIG. 1
Excess molar volumes, V^E, for the heptane–1-chloroalkane systems at 298.15 K; experimental results: ❍ 1-chloropropane, ❒ 1-chlorobutane, Δ 1-chloropentane, ∗ 1-chlorohexane. Solid curves represent the values calculated from Eq. (*3*)

For the heptane–1-chlorohexane system, the V^E values are rather small. The excess molar volumes show, however, a distinct S-shaped curve, V^E being slightly negative at lower mole fractions and slightly positive at higher mole fractions of heptane.

As mentioned above, authors[1,2] measured the V^E data for the heptane–1-chlorobutane system at the temperature 298.15 K, too. Their

TABLE IV
Densities, ρ_m, and excess molar volumes, V^E, for heptane–1-chloropentane binary system at 298.15 K

x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}	x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}
0.0583	0.86303	0.0182	0.5549	0.75739	0.1402
0.1372	0.84474	0.0447	0.6172	0.74562	0.1398
0.2058	0.82931	0.0670	0.6918	0.73191	0.1347
0.2805	0.81303	0.0895	0.7647	0.71895	0.1178
0.3458	0.79921	0.1051	0.8503	0.70418	0.0918
0.4119	0.78558	0.1219	0.9003	0.69579	0.0688
0.4856	0.77085	0.1326	0.9456	0.68836	0.0401

TABLE V
Densities , ρ_m, and excess molar volumes, V^E, for heptane–1-chlorohexane binary system at 298.15 K

x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}	x	ρ_m, g cm^{-3}	V^E cm^{-3} mol^{-1}
0.0623	0.86054	–0.0077	0.5769	0.75844	0.0113
0.1463	0.84345	–0.0131	0.6442	0.74558	0.0125
0.2120	0.83020	–0.0155	0.7106	0.73301	0.0179
0.2905	0.81450	–0.0158	0.7740	0.72110	0.0221
0.3465	0.80337	–0.0120	0.8449	0.70794	0.0190
0.4327	0.78641	–0.0047	0.8834	0.70083	0.0167
0.4873	0.77577	–0.0009	0.9550	0.68777	0.0599

data along with our experimental values and calculated curve are plotted in Fig. 2. A very good agreement is evident from the comparison of all three data sets.

TABLE VI
Parameters a_i (in cm^3 mol^{-1}) of Eq. (*3*) and standard deviations $\sigma(x)$ and $\sigma(V^E)$ (in cm^3 mol^{-1}) evaluated by the maximum likelihood procedure for the heptane–1-chloralkane binary systems at 298.15 K

Chloroalkane	a_0	a_1	a_2	$\sigma(x) . 10^6$	$\sigma(V^E) . 10^2$
1-Chloropropane	1.7203	–0.8372	0.5966	0.74	0.25
1-Chlorobutane	1.1051	–0.2307	0.2968	0.69	0.26
1-Chloropentane	0.5381	–0.2346	0.2615	0.19	0.13
1-Chlorohexane	0.5068	–0.1881	0.2549	0.62	0.15

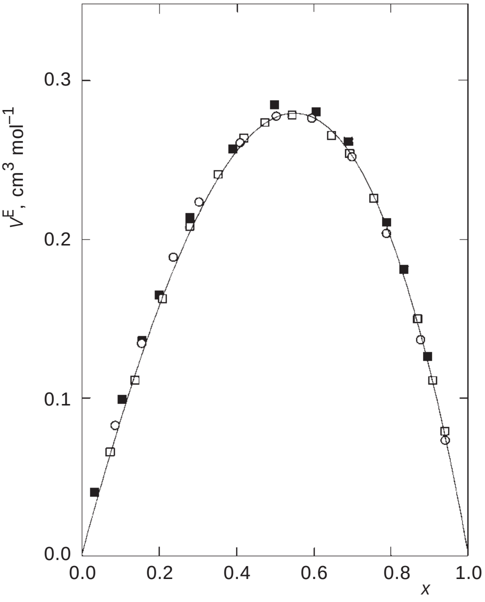

FIG. 2
Comparison of excess molar volumes, V^E, of the heptane–1-chlorobutane system at 298.15 K; ■ Dahmani *et al.*[1], ❍ Lainez *et al.*[2], ❐ this work. Solid line calculated from the data of this work

SYMBOLS

a	parameter of Eq. (*1*), g cm^{-3}
a_0, a_1, a_2	parameters of Redlich–Kister equation (Eq. (*3*)), cm^3 mol^{-1}
b	parameter of Eq. (*1*), g cm^{-3} s^{-2}
M_1, M_2	molar masses of pure compounds 1and 2, g mol^{-1}
n_D	refractive index
V^E	excess molar volume, cm^3 mol^{-1}
x	mole fraction of heptane
ρ	density, g cm^{-3}
ρ_m	density of binary mixture, g cm^{-3}
ρ_1, ρ_2	densities of pure components 1, 2, g cm^{-3}
σ	standard deviation
τ	period of vibration, s

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