Excess Molar Volumes in Systems Alkane—1-Chloroalkane

J. LINEK and É. KOVÁCS

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, CZ-165 02 Prague

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Densities of binary liquid mixtures pentane—1-chloropropane, —1-chlorobutane, —1-chloropentane, —1-chlorohexane, hexane—1-chloropropane, —1-chlorobutane, —1-chloropentane, —1-chlorohexane, heptane—1-chloropropane, —1-chlorobutane, —1-chloropentane, —1-chlorohexane, and octane—1-chloropropane, —1-chlorobutane, —1-chloropentane, —1-chlorohexane have been measured at 298.15 K by a vibrating tube densimeter. Excess molar volumes, V^E, calculated from the density data, are negative for the pentane—1-chloropentane, pentane—1-chlorohexane, and hexane—1-chlorohexane systems over the entire range of composition. The pentane—1-chlorobutane, hexane—1-chloropentane, and heptane—1-chlorohexane systems exhibit an S-shaped V^E dependence. For all the other systems, V^E is 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.

Excess molar volumes, V^E, for 16 binary liquid mixtures containing alkanes and 1-chloroalkanes have been measured by the vibrating tube densimeter at 298.15 K and atmospheric pressure. The purpose of this investigation is to examine the excess molar volume changes accompanying the mixing of various alkanes with the series of 1-chloroalkanes with the aim to form the basis for testing modern theories (equations of state) of liquid mixtures.

Dahmani and *Linek* [1] and *Lainez et al.* [2] have reported V^E for heptane—1-chlorobutane system. As far as we know, no V^E data have been published for the other mixtures.

EXPERIMENTAL

Materials

Hydrocarbons and 1-chloroalkanes used for the experiments were products of the best quality from the Fluka catalogue. In order to check the purity of the compounds, their density values and refractive indices were determined at 298.15 K and compared with literature data [3—5]. The agreement was, in general, good. The purity of all chemicals was checked by GLC. The found contents of substances are: pentane 99.91 %, hexane 99.99 %, heptane 99.95 %, octane 99.91 %, 1-chloropropane 99.96 %, 1-chlorobutane 99.90 %, 1-chloropentane 99.85 %, 1-chlorohexane 99.53 %. All these chemicals were not degassed prior to use.

Apparatus and Procedure

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

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

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

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, the densities, ρ_i, and molar masses, M_i, of pure components i (i = 1, 2) from the relation

$$V^E=[xM_1+(1-x)M_2]/\rho-[xM_1/\rho_1+(1-x)M_2/\rho_2] \qquad (2)$$

Subscript 1 refers to alkane and 2 to 1-chloroalkane and x stands for the mole fraction of alkane.

The experimental uncertainty of composition is less than $\pm 1 \times 10^{-4}$ in mole fraction, of the density measurement it is approximately $\pm 1 \times 10^{-5}$ g cm^{-3}, and of V^E it is estimated to be about $\pm 2 \times 10^{-3}$ cm^3 mol^{-1}.

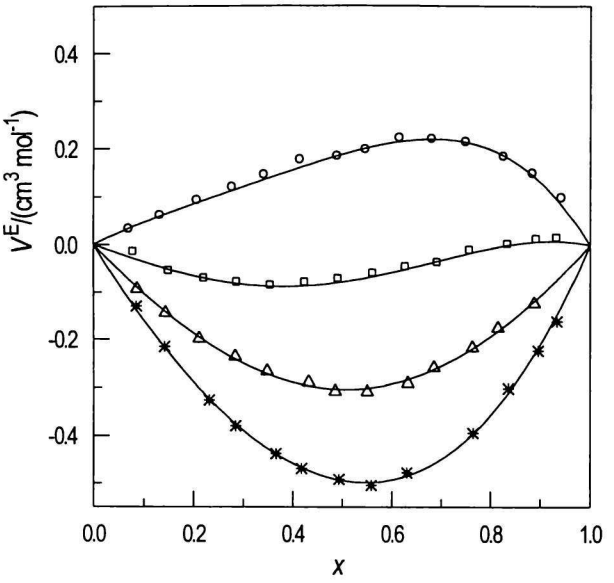

Fig. 1. Excess molar volumes, V^E, for the pentane—1-chloroalkane systems at 298.15 K. Experimental results: ○ 1-chloropropane, □ 1-chlorobutane, Δ 1-chloropentane, ∗ 1-chlorohexane.

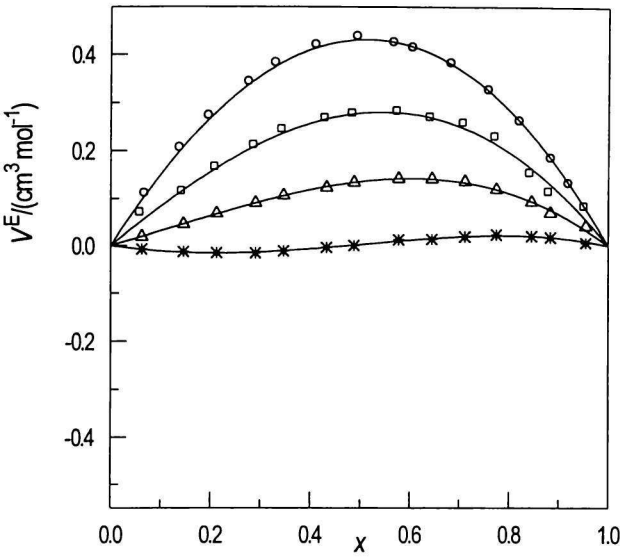

Fig. 3. Excess molar volumes, V^E, for the heptane—1-chloroalkane systems at 298.15 K. Experimental results: ○ 1-chloropropane, □ 1-chlorobutane, Δ 1-chloropentane, ∗ 1-chlorohexane.

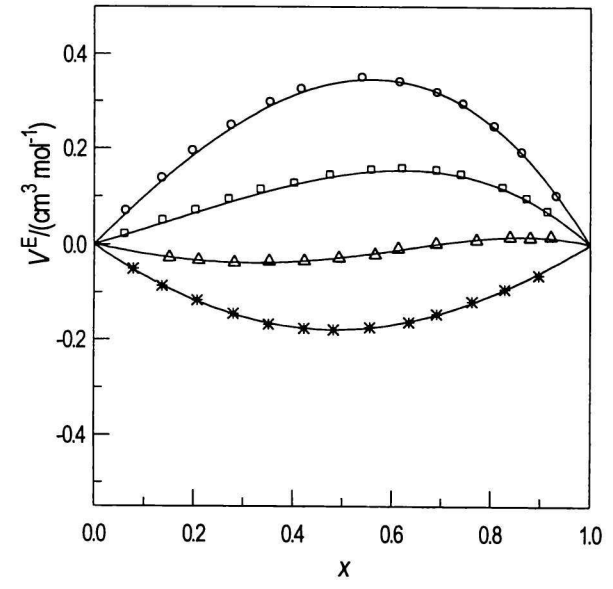

Fig. 2. Excess molar volumes, V^E, for the hexane—1-chloroalkane systems at 298.15 K. Experimental results: ○ 1-chloropropane, □ 1-chlorobutane, Δ 1-chloropentane, ∗ 1-chlorohexane.

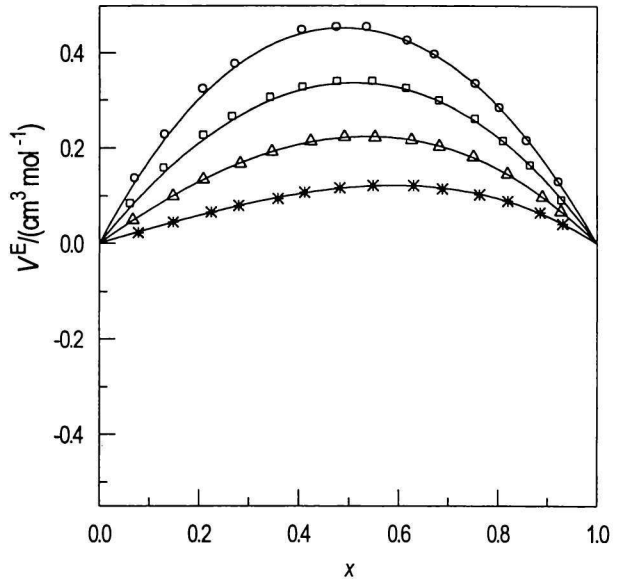

Fig. 4. Excess molar volumes, V^E, for the octane—1-chloroalkane systems at 298.15 K. Experimental results: ○ 1-chloropropane, □ 1-chlorobutane, Δ 1-chloropentane, ∗ 1-chlorohexane.

RESULTS AND CORRELATION

Dependences of excess molar volume on mole fraction of alkane are illustrated in Figs. 1—4 for all the systems. The data were fitted to the fourth-order Redlich—Kister equation

$$V^E/(\mathrm{cm^3 mol^{-1}}) = x(1-x)[a_0 + a_1(1-2x) + a_2(1-2x)^2] \quad (3)$$

where a_0, a_1, and a_2 are parameters of the Redlich—Kister equation which were determined by using the maximum likelihood method. Coefficients and standard deviations of the fit are summarized in Table 1.

Table 1. Coefficients a_i of Eqn (*3*) and Standard Deviations σ (V^E) Evaluated by the Maximum Likelihood Procedure for the Alkane—1-Chloroalkane Binary Mixtures at 298.15 K

	$a_0/(\text{g cm}^{-3})$	$a_1/(\text{g cm}^{-3})$	$a_2/(\text{g cm}^{-3})$	$\sigma(V^E)$ $10^2/(\text{cm}^3\ \text{mol}^{-1})$
		Pentane—1-Chloroalkane Systems		
C_3H_7Cl	0.7520	−0.5945	0.3721	0.72
C_4H_9Cl	−0.3109	−0.3051	0.2325	0.51
$C_5H_{11}Cl$	−1.2163	0.0349	0.0769	0.61
$C_6H_{13}Cl$	−1.9777	0.3602	−0.1227	0.70
		Hexane—1-Chloroalkane Systems		
C_3H_7Cl	1.3613	−0.3340	0.0019	0.24
C_4H_9Cl	0.5730	−0.3170	0.0477	0.15
$C_5H_{11}Cl$	−0.1080	−0.2327	0.1305	0.19
$C_6H_{13}Cl$	−0.7160	−0.0404	−0.0326	0.26
		Heptane—1-Chloroalkane Systems		
C_3H_7Cl	1.7203	−0.0837	0.0060	0.25
C_4H_9Cl	1.1051	−0.2307	0.0297	0.26
$C_5H_{11}Cl$	0.5381	−0.2346	0.0261	0.13
$C_6H_{13}Cl$	0.5068	−0.1881	−0.0255	0.15
		Octane—1-Chloroalkane Systems		
C_3H_7Cl	1.8111	0.0775	0.0802	0.24
C_4H_9Cl	1.3427	−0.0637	0.0231	0.15
$C_5H_{11}Cl$	0.8899	−0.1393	0.0006	0.10
$C_6H_{13}Cl$	0.4700	−0.1858	0.0244	0.13

Table 2. Extremes on the Curves $V^E = V^E(x)$

	Pentane	Hexane	Heptane	Octane
1-Chloropropane	0.2207	0.3453	0.4302	0.4530
1-Chlorobutane	S-shaped	0.1536	0.2793	0.3359
1-Chloropentane	−0.3041	S-shaped	0.1406	0.2238
1-Chlorohexane	−0.4987	−0.1796	S-shaped	0.1220

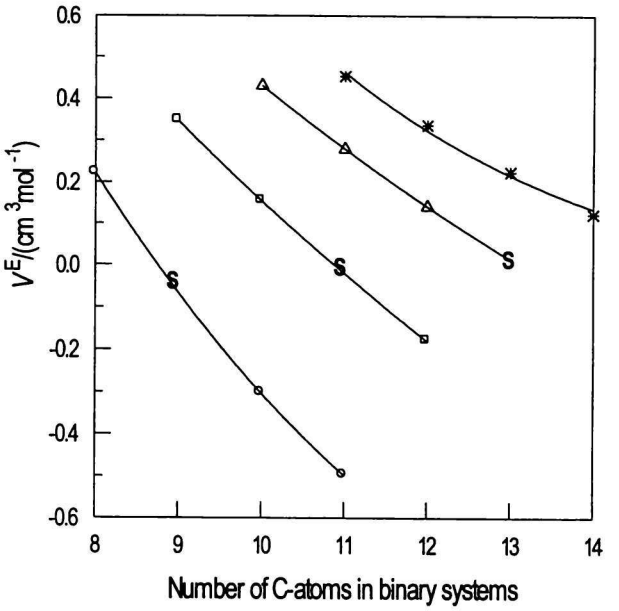

Fig. 5. Extremes on the curves V^E. Experimental results: ○ pentane, □ hexane, △ heptane, ∗ octane. S denotes an inflexion point of S-shaped course of the V^E curve.

DISCUSSION

It can be observed from the experimental results that V^E are negative for the pentane—1-chloropentane, pentane—1-chlorohexane, and hexane—1-chlorohexane systems over the entire range of composition. Pentane—1-chlorobutane, hexane—1-chloropentane, and heptane—1-chlorohexane systems exhibit an S-shaped V^E dependence. For all the other systems, V^E are positive.

Generally, V^E values of the alkane—1-chloroalkane systems increase in the series from pentane to octane for the same 1-chloroalkane (Table 2) with increasing the number of C-atoms of the alkanes (Fig. 5). On the contrary, for the same alkane, V^E values decrease from 1-chloropropane to 1-chlorohexane. These dependences may be explained by packing effects of the molecules considered.

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SYMBOLS

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

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