

Excess Molar Volumes of the Heptane—1-Chloropentane System at High Pressures and Elevated Temperatures*

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The apparatus for p - V - T measurements of liquids and liquid mixtures was designed and tested. It works in the temperature range of 283 to 333 K and pressure range of 0.1 to 40 MPa with an overall accuracy of density measurement $1 \times 10^{-4} \text{ g cm}^{-3}$. Its main part is a high-pressure vibrating tube densimeter working in a static mode. The apparatus was used for measuring the p - V - T relations of the heptane—1-chloropentane system. Excess molar volumes were calculated from the data and fitted to the Redlich—Kister equation.

p - V - T Relations of liquids pertain to the fundamental physicochemical characteristics of liquid state. Density and excess volumes are important quantities, which together with excess Gibbs energy and excess enthalpy, quantitatively and widely enough describe the behaviour of real liquids. The knowledge of p - V - T behaviour of liquids and their mixtures is indispensable when we need to carry out the converting of the thermodynamic functions of solutions. Last but not least, these values are also used for testing the theories of liquid mixtures. From the practical point of view, these quantities are necessary for the rational design and functioning of the reservoirs and transport equipment of liquids.

An apparatus was designed and constructed based on the vibrating-tube densimeter for the measurement of p - V - T behaviour of pure liquids and binary liquid mixtures of alkanes and 1-chloroalkanes. This apparatus works in the temperature range of 283 to 333 K and the pressure range of 0.1 to 40 MPa.

Excess molar volumes, V^E , for liquid binary mixtures of heptane with 1-chloropentane were measured by means of the apparatus described at 298.15 K, 308.15 K, 318.15 K, and 328.15 K and within the pressure range of 0–40 MPa. The aim of the work is to form a database for testing modern theories (equations of state) of liquid mixtures.

EXPERIMENTAL

Heptane and 1-chloropentane used for experiments

were the best quality products from Fluka (Fluka Chemie, Buchs, Switzerland) 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 [1, 2], the agreement being, in general, good. The purity of all the chemicals was checked by gas chromatography (HP Ser.II. model 5890 chromatograph with capillary column and FID, column temperature 413.3 K, helium flow rate $0.025 \text{ dm}^3 \text{ min}^{-1}$). The found contents of the substances are: heptane 99.96 mass % and 1-chloropentane 99.85 mass %. The chemicals were dried over molecular sieves 4 Å. All these substances were not degassed prior to weighing.

The main part of the apparatus used for the measurement of p - V - T relations of liquid and liquid mixtures was the measuring cell DMA 512P, a product of Anton Paar, Graz, Austria. The measuring cell consisted of a U-shaped tube of stainless steel (inner volume about 1 cm^3 occupied by the sample). The measuring cell can be used in the temperature range of 283 to 333 K in a room without tempering, the temperature range is wider in a thermostated room (from 263 to 423 K). The maximum pressure, at which densities can be measured with the cell, is 70 MPa. The temperature of the measuring cell was controlled by the thermostat LAUDA RC 20 CP (Lauda, Koenigshofen, Germany). Water was used as the circulating liquid for the given temperature range. The temperature of the water bath was measured by platinum resistance thermometer Pt 100. The thermostat maintained the

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temperature of the measuring cell with the accuracy better than 0.01 K. The pressure was measured by the pressure transducer LPN-N with voltage output (Ecom, Prague, Czech Republic). The class of accuracy of the pressure transducer is 0.3. The density meter DMA 58 was used as a device evaluating the oscillating periods of vibrating tube of the measuring cell DMA 512P filled with sample. The sensitivity of density measurement was $1 \times 10^{-5} \text{ g cm}^{-3}$. The sample was transported from the closed glass vessel with liquid chromatography pump LCP 4000.1 (Ecom, Prague, Czech Republic). The chromatographic pump served both for pumping and pressurizing the liquids to the maximum pressure of 40 MPa. Valves, pres-

sure transducer, and manual pressure controller were placed in the air thermostat LCO 101 (Ecom, Prague, Czech Republic) at the temperature 303 K. The pressure could be changed with the manual pressure controller with an accuracy of 0.01 MPa. The overall accuracy of density measurements with this apparatus in the given temperature and pressure range was $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$.

The sample density ρ measured by vibrating tube densimeter was deduced from the measurement of period of vibration τ in terms of the equation

$$\rho(T, p) = a(T, p)\tau^2 + b(T, p) \quad (1)$$

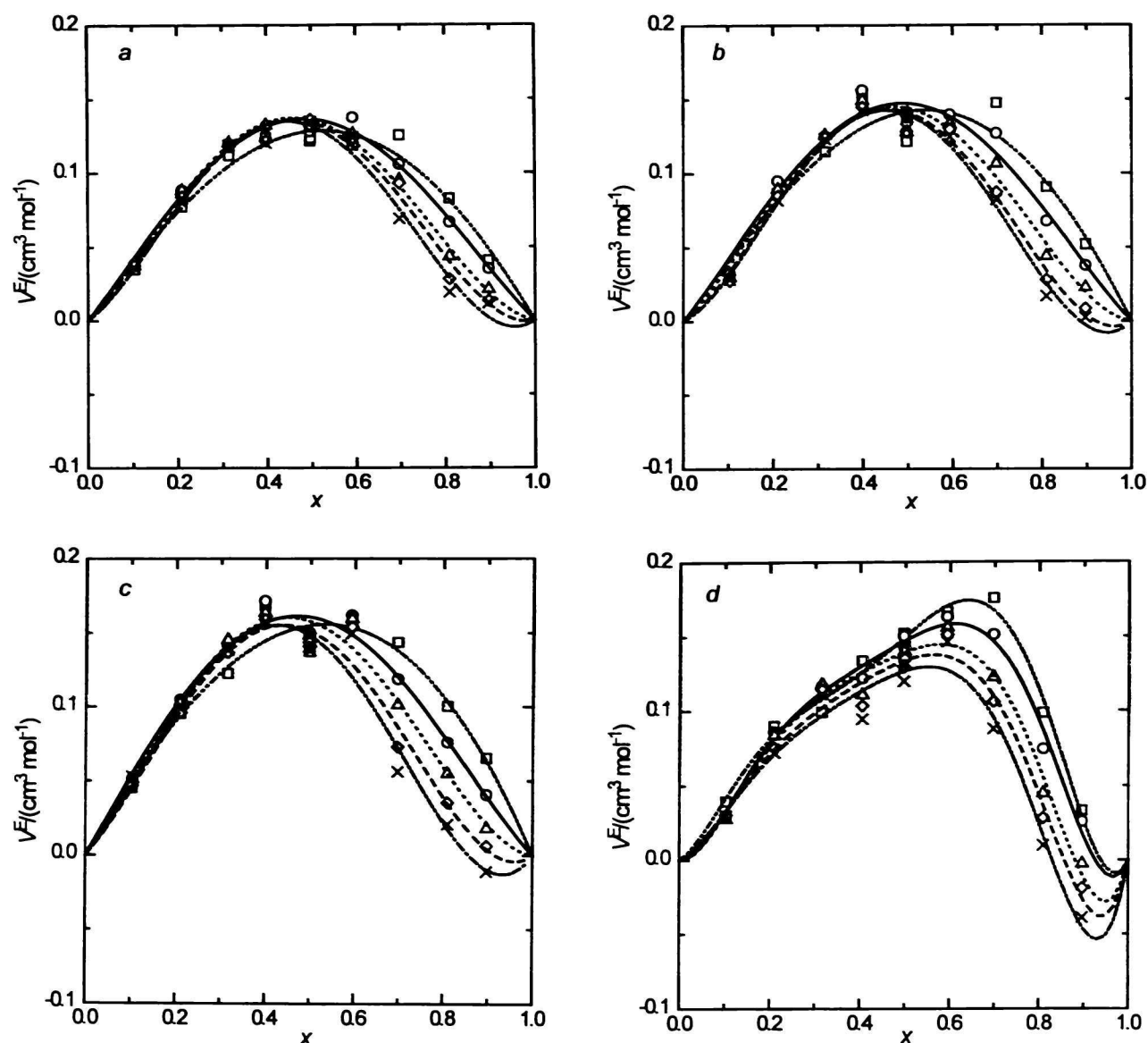


Fig. 1. Excess molar volumes, V^E , for the heptane—1-chloropentane system at a) 298.15 K, b) 308.15 K, c) 318.15 K, d) 328.15 K. Pressures: 2.13 MPa, \square experimental points, — — — calculated from eqn (3); 10.23 MPa, \circ experimental points, — calculated from eqn (3); 20.37 MPa, Δ experimental points, — — — calculated from eqn (3); 30.50 MPa, \diamond experimental points, — — — calculated from eqn (3); 38.60 MPa, \times experimental points, — — — calculated from eqn (3).

$a(T, p)$ and $b(T, p)$ are two characteristic temperature- and pressure-dependent parameters of the apparatus, which have to be determined by measuring the periods τ_1 and τ_2 for two substances of known density for the T, p set considered. For the calibration (at the given temperature and pressure), water and air are usually used as standards. For very accurate measurements, especially at higher temperatures and pressures, a pair of fluids with precisely determined densities is recommended. The density of a sample is then calculated in terms of the above relation (1).

The choice of the standards with known density at higher pressures and temperatures is rather limited. The manufacturer of the densimeter DMA 512P recommends the following substances: nitrogen, benzene, pentane, dichloromethane, and water [3]. In our case, the designed apparatus was calibrated with three pure substances (water, benzene, and heptane). It was proved that the equipment makes it possible to measure reliably the p - V - T behaviour of liquids and liquid mixtures in the given temperature and pressure range.

The samples for the density measurement were prepared by weighing (SCALTEC SBC 21 balance with accuracy of 0.00001 g) covering the whole interval of mole fractions and then partially degassed at the respective measuring temperature for 3 h by means of an ultrasonic heated bath (Bandelin RK 100H, Berlin, Germany) prior to determining their density to prevent formation of bubbles during the measurement in the densimeter.

Values of V^E were calculated from the mixture densities, ρ , and the densities, ρ_i , and molar masses, M_i , of pure components i ($i = 1, 2$) on using the relation

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

Subscript 1 refers to heptane and 2 to 1-chloropentane and x stands for the mole fraction of heptane.

The experimental uncertainty of composition is less than $\pm 5 \times 10^{-5}$ in mole fraction, of the density measurement approximately $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$, and of V^E it is estimated to be about $\pm 8 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, which is about five times worse compared to measurements at 298.15 K and atmospheric pressure. As it has been stated [4], even the measurements at elevated temperatures and normal pressure showed approximately double inaccuracy in V^E , brought about probably by problems with degassing the mixture samples. The measurement at high pressures naturally worsens the experimental errors taking into account especially the hysteresis of the measuring capillary and the error in the pressure measurement.

RESULTS AND DISCUSSION

The results of the measurements are illustrated in Figs. 1a–d for four isotherms measured (298.15 K, 308.15 K, 318.15 K, and 328.15 K). Densities of 9 weighed mixtures on 20 pressure levels within 0.1–40 MPa were measured. The pressure levels chosen

Table 1. Parameters A_i of Eqn (3) Evaluated by the Maximum Likelihood Method and Standard Deviations $\sigma(V^E)$ for the Heptane–1-Chloropentane System at High Pressures and Four Temperatures T Indicated

p/MPa	$A_0/(\text{cm}^3 \text{ mol}^{-1})$	$A_1/(\text{cm}^3 \text{ mol}^{-1})$	$A_2/(\text{cm}^3 \text{ mol}^{-1})$	$A_3/(\text{cm}^3 \text{ mol}^{-1})$	$A_4/(\text{cm}^3 \text{ mol}^{-1})$	$10^2 \sigma(V^E)/(\text{cm}^3 \text{ mol}^{-1})$
298.15 K						
2.13	0.51304	−0.0550	−0.05395	—	—	0.825
10.23	0.54546	0.0503	−0.18460	—	—	0.576
20.37	0.54276	0.1476	−0.34619	—	—	0.441
30.50	0.53620	0.1731	−0.44581	—	—	0.738
38.60	0.52706	0.2309	−0.51378	—	—	0.867
308.15 K						
2.13	0.56798	−0.0969	−0.05664	—	—	1.510
10.23	0.58947	0.0412	−0.23146	—	—	1.220
20.37	0.57617	0.1325	−0.41139	—	—	0.948
30.50	0.56460	0.2024	−0.56441	—	—	0.742
38.60	0.55873	0.2396	−0.63511	—	—	0.660
318.15 K						
2.13	0.62133	−0.0851	−0.00948	—	—	1.220
10.23	0.64358	0.1037	−0.21045	—	—	1.000
20.37	0.63162	0.2097	−0.37698	—	—	1.050
30.50	0.60497	0.2817	−0.53715	—	—	1.230
38.60	0.59192	0.3876	−0.61985	—	—	1.400
328.15 K						
2.13	0.60030	−0.5254	0.51343	0.9798	−1.35825	0.884
10.23	0.58982	−0.3291	0.31365	0.6945	−1.28125	0.905
20.37	0.55830	−0.2313	0.12146	0.8350	−1.30410	1.150
30.50	0.53627	−0.2161	−0.08980	0.9918	−1.10684	1.270
38.60	0.50815	−0.1853	−0.20335	1.1508	−1.12379	1.530

and depicted in the figures are approximately 2 MPa, 10 MPa, 20 MPa, 30 MPa, and 38 MPa.

The data were fitted to the Redlich—Kister equation

$$V^E = x(1-x) \left[\sum_n A_n (1-2x)^n \right] \quad (3)$$

$n = 0, 1, 2, 3, 4$

where A_n are parameters of the Redlich—Kister equation which were determined by the maximum likelihood method. Coefficients A_n and standard deviations $\sigma(V^E)$ of the fit are summarized in Table 1.

It can be observed from the experimental results in Figs. 1a—d that V^E curves are shifted in a regular way with increasing temperature and pressure. The increase in V^E values with increasing temperature is evident and corresponds to the findings when the temperature dependence of V^E was measured at ambient pressure [4]. The pressure dependence at constant temperature depends strongly on composition. Whereas the values at the 1-chloropentane concentration end seem to be nearly pressure-independent (at least within the experimental errors), at the heptane end, the V^E values decrease with increasing pressure resulting in an S-shaped dependence at the higher pressures. This effect is especially distinctive at the highest temperature (328.15 K, see Fig. 1d).

The correlation of such dependence with S-shape at the heptane concentration end appeared to be difficult. Three-constant Redlich—Kister equation was not able to describe the dependence with adequate deviations. As many as five parameters showed to suffice to get a satisfactory correlation.

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SYMBOLS

a	parameter of eqn (1)	$\text{g cm}^{-3} \text{ s}^{-2}$
A_0, A_1, A_2, A_3, A_4	parameters of the Redlich—Kister equation (eqn (3))	$\text{cm}^3 \text{ mol}^{-1}$
b	parameter of eqn (1)	g cm^{-3}
M_1, M_2	molar masses of pure compounds 1, 2	g mol^{-1}
p	pressure	MPa
T	thermodynamic temperature	K
V^E	excess molar volume	$\text{cm}^3 \text{ mol}^{-1}$
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}
$\sigma(V^E)$	standard deviation	$\text{cm}^3 \text{ mol}^{-1}$
τ	period of oscillation	s

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