

# Excess Molar Volumes of the Octane—1-Chlorobutane System at High Pressures and Elevated Temperatures\*

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The  $p$ - $V$ - $T$  behaviour of the octane—1-chlorobutane system was investigated at temperatures 298.15 K, 308.15 K, 318.15 K, and 328.15 K and in the pressure range of 0.1—40 MPa with an accuracy in density of  $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$ . An apparatus for  $p$ - $V$ - $T$  measurements of liquids and liquid mixtures the main part of which is a high-pressure vibrating-tube densimeter working in a static mode was used. Excess molar volume were calculated from the data and fitted using the Redlich—Kister equation.

$p$ - $V$ - $T$  Relations of liquids pertain to the fundamental physicochemical characteristics of liquid state. Density and excess volume 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 conversion of the thermodynamic functions of solutions. 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.

Excess molar volumes,  $V_m^E$ , for binary liquid mixtures of octane and 1-chlorobutane were determined by means of an apparatus [1] designed for measurements of the  $p$ - $V$ - $T$  behaviour of pure liquids and liquid mixtures at elevated temperatures 283 K to 333 K and high pressures (to 40 MPa). The measurements were carried out at the temperatures 298.15 K, 308.15 K, 318.15 K, and 328.15 K and in the pressure range of 0.1—40 MPa. The aim of the work was to establish a database [1—3] for testing of theories (equations of state) of liquid mixtures.

## EXPERIMENTAL

The octane and 1-chlorobutane used in the experiments were the best quality products from Fluka (octane, puriss. anal. grade, g.c. mass fraction  $> 0.995$ , 1-chlorobutane, puriss. anal. grade, g.c. mass fraction

$> 0.995$ ). 1-Chlorobutane was distilled in a packed column with 30 theoretical plates. Octane was used without further purification. In order to check the purity of the compounds, their densities and refractive indices were determined at 298.15 K and compared with literature values [4, 5]. The agreement was found, in general, to be good. The purity of the chemicals was checked by gas chromatography (HP Ser.II. model 5890 chromatograph with capillary column type 1909 1Z-413E and FID, column temperature 413.3 K, helium flow rate  $4.2 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1}$ ). Both substances were not degassed prior to weighing.

A schematic diagram and detailed description of the apparatus used for the measurement was given in one of our previous works [1]. It consists mainly of the measuring cell DMA 512P, supplied by Anton Paar, Graz, Austria. The temperature of the measuring cell was controlled by a thermostat LAUDA RC 20 CP (Lauda, Koenigshofen, Germany). The thermostat maintained the temperature in the measuring cell with the accuracy of  $\pm 0.01$  K. The pressure was measured with a pressure transducer LPN-N having a voltage output (ECOM, Prague, Czech Republic). The pressure gauge was calibrated with a Ruska pressure calibration system (Ruska Instruments Co., Houston, Texas, USA). The accuracy of the pressure measurement is better than 0.1 MPa. The pressure in the measuring cell can be set by means of the manual pressure controller accurate to 0.01 MPa. The DMA 512P measuring cell is connected to the DMA 58 densimeter which serves as a frequency counter and evaluates

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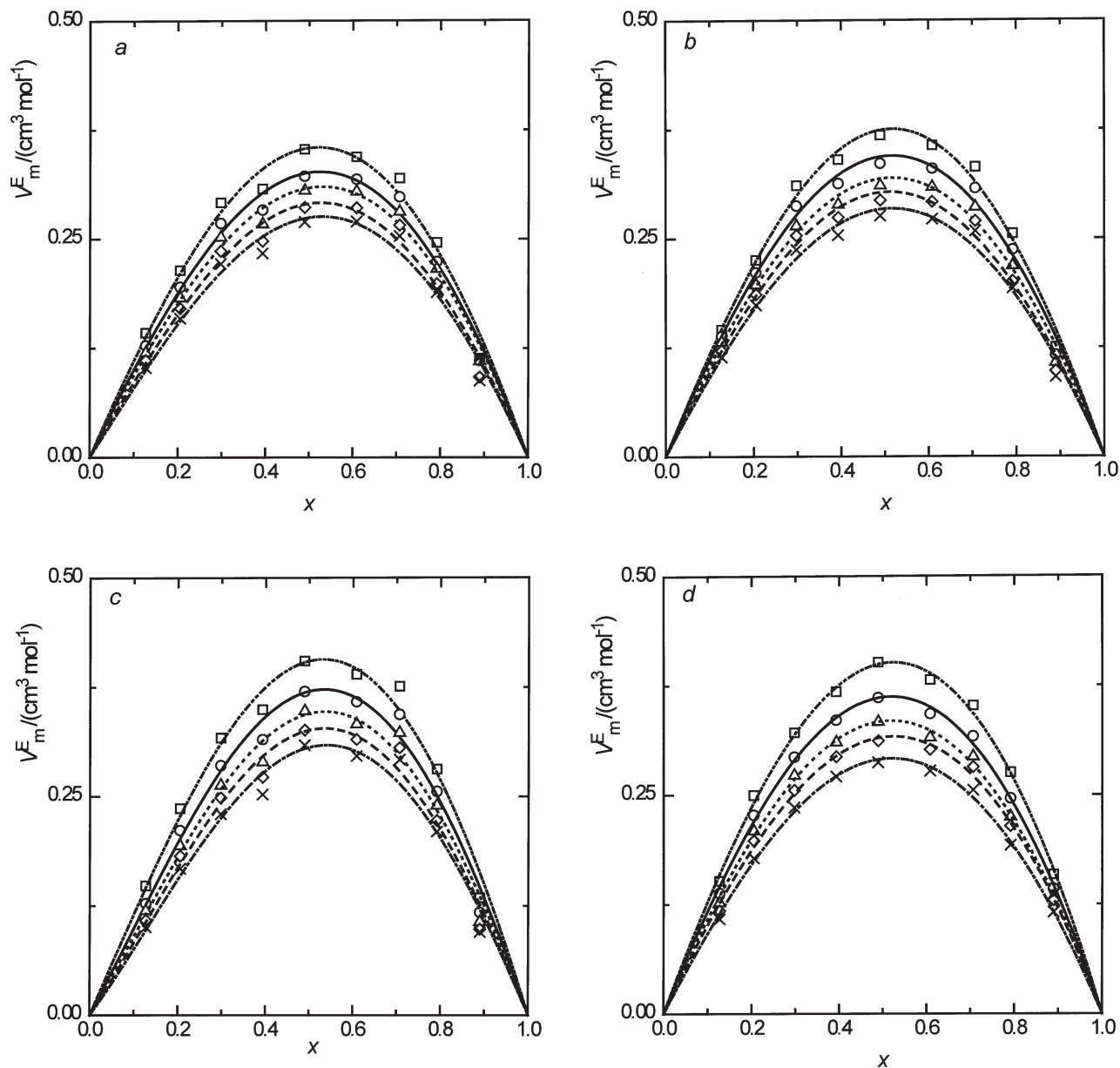
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the oscillating period from the signals of the measuring cell filled with sample. The samples of measured liquid mixtures prepared by weight in special vessels [3] are moved into the measuring cell with a liquid chromatography pump LCP 4000.1 (ECOM, Prague, Czech Republic). The overall accuracy in the density measurements within the given temperature and pressure ranges was  $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$ .

The sample density  $\rho$  was determined from the period of vibration  $\tau$  of the vibrating-tube densimeter as follows

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

The coefficients  $a(T, p)$  and  $b(T, p)$  are two characteristic temperature- and pressure-dependent parameters of the apparatus, which have to be determined by measuring the periods  $\tau_1$  and  $\tau_2$  for two substances of known density. For the calibration (at ambient 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 accurately determined densities is recom-



**Fig. 1.** Excess molar volumes,  $V_m^E$ , for the octane—1-chlorobutane system at *a*) 298.15 K, *b*) 308.15 K, *c*) 318.15 K, *d*) 328.15 K as a function of the mole fraction  $x$  of octane. Pressures: 2.13 MPa,  $\square$  experimental points,  $\cdots\cdots$  calculated from eqn (3); 11.25 MPa,  $\circ$  experimental points,  $\text{—}$  calculated from eqn (3); 20.37 MPa,  $\triangle$  experimental points,  $\cdots$  calculated from eqn (3); 29.50 MPa,  $\diamond$  experimental points,  $\text{---}$  calculated from eqn (3); 38.60 MPa,  $\times$  experimental points,  $\text{---}$  calculated from eqn (3).

mended. The density of a sample is then calculated from eqn (1) with the parameters determined by calibration.

The choice of standards of known density at high pressures and temperatures is rather limited. The manufacturer of the densimeter DMA 512P recommends the following substances: nitrogen, benzene, pentane, dichloromethane, and water. In our case, the apparatus was calibrated [1] with bi-distilled water and heptane.

The samples for the density measurements were prepared by weighing the mixture components (SCALTEC SBC 21 balance with an accuracy of  $\pm 1 \times 10^{-5}$  g) for the whole mole fraction range and then partially degassed in tightly closed special vessels [3] at the maximum measurement temperature for 3 h by means of an ultrasonic thermostated bath (Bandelin RK 100H, Berlin, Germany) prior to determining their density in order to prevent the formation of bubbles in the densimeter.

The values of  $V_m^E$  were calculated from the mixture densities,  $\rho$ , and the densities,  $\rho_i$ , and molar masses,  $M_i$ , of pure components  $i$  ( $i = 1, 2$ ) using the relation

$$V_m^E = \{xM_1 + (1-x)M_2\} / \rho - \{xM_1/\rho_1 + (1-x)M_2/\rho_2\} \quad (2)$$

where subscript 1 refers to octane and 2 to 1-chlorobutane and  $x$  stands for the mole fraction of octane.

The experimental uncertainty in the mole fraction composition is less than  $\pm 5 \times 10^{-5}$ , that in the density is approximately  $\pm 1 \times 10^{-4}$  g cm $^{-3}$ , and that in  $V_m^E$  is estimated to be about  $\pm 1 \times 10^{-2}$  cm $^3$  mol $^{-1}$ , which is about five times higher compared to measurements at 298.15 K and atmospheric pressure. As it has been stated [3], even the measurements at elevated temperatures and normal pressure had twice the uncertainty in  $V_m^E$  compared to the measurements at 298.15 K, because of incomplete degassing of the mixtures. The measurements at high pressures naturally worsen the uncertainty because of hysteresis of the densimeter vibrating tube and error in the pressure measurement.

## RESULTS AND DISCUSSION

The results of the measurements are illustrated in Figs. 1a–d along four isotherms, *i.e.* 298.15 K, 308.15 K, 318.15 K, and 328.15 K. Densities of 9 weighed mixtures were measured at 20 pressures over the range of 0.1 to nearly 40 MPa. The pressures depicted in the figures are chosen as about 2 MPa, 11 MPa, 20 MPa, 29 MPa, and 38 MPa.

The data were fitted to the Redlich–Kister equation

$$V_m^E = x(1-x) \left\{ \sum_{n=0}^2 A_n (1-2x)^n \right\} \quad (3)$$

The parameters  $A_n$  and standard deviations  $\sigma(V_m^E)$  of

**Table 1.** Parameters  $A_i$  of Eqn (3) Determined by Using the Maximum Likelihood Principle and Standard Deviations  $\sigma(V_m^E)$  for the Octane–1-Chlorobutane System at Selected Pressures  $p$  and Four Temperatures  $T$

$p/\text{MPa}$	$A_0/(\text{cm}^3 \text{ mol}^{-1})$	$A_1/(\text{cm}^3 \text{ mol}^{-1})$	$A_2/(\text{cm}^3 \text{ mol}^{-1})$	$10^2 \sigma(V_m^E)/(\text{cm}^3 \text{ mol}^{-1})$
$T = 298.15 \text{ K}$				
2.13	1.4178	−0.1279	0.1384	1.75
11.25	1.3039	−0.1416	−0.1172	1.50
20.37	1.2339	0.1593	−0.0952	1.29
29.50	1.1612	−0.1343	−0.1596	1.57
38.60	1.0975	−0.1463	−0.1570	1.49
$T = 308.15 \text{ K}$				
2.13	1.5005	−0.1095	−0.1710	1.33
11.25	1.3770	−0.0959	−0.0982	1.30
20.37	1.2753	−0.0859	−0.0776	1.22
29.50	1.2115	−0.0623	−0.1285	1.26
38.60	1.1350	−0.0795	−0.0975	1.36
$T = 318.15 \text{ K}$				
2.13	1.6202	−0.2365	−0.2371	1.96
11.25	1.4824	−0.2406	−0.2949	1.91
20.37	1.3797	−0.2398	−0.2920	1.98
29.50	1.3033	−0.2270	−0.3153	1.94
38.60	1.2246	−0.2442	−0.2997	1.90
$T = 328.15 \text{ K}$				
2.13	1.6020	−0.1579	−0.0846	0.76
11.25	1.4469	−0.1195	−0.0775	0.70
20.37	1.3363	−0.1080	−0.0735	0.69
29.50	1.2629	−0.1275	−0.0491	0.72
38.60	1.1636	−0.1021	−0.0983	0.57

the fit are summarized in Table 1.

It can be observed from the experimental results in Figs. 1a—d that the  $V_m^E$  curves are shifted in a regular way with increasing temperature and pressure. The increase in  $V_m^E$  values with increasing temperature is rather evident and follows the temperature dependence of  $V_m^E$  at atmospheric pressure [3]. The pressure dependence at constant temperature is also regular. The  $V_m^E$  values are apparently decreasing with increasing pressure for the same composition. The positions of maxima on the curves are not noticeably shifted with the pressure change.

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### SYMBOLS

$a$	parameter of eqn (1)	$\text{g cm}^{-3} \text{ s}^{-2}$
$A_n$	parameters of the Redlich—Kister equation (eqn (3))	$\text{cm}^3 \text{ mol}^{-1}$
$b$	parameter of eqn (1)	$\text{g cm}^{-3}$

$M_1, M_2$	molar masses of pure compounds	$\text{g mol}^{-1}$
1, 2		
$p$	pressure	MPa
$T$	thermodynamic temperature	K
$V_m^E$	excess molar volume	$\text{cm}^3 \text{ mol}^{-1}$
$x$	mole fraction of alkane	
$\rho$	density of binary mixture	$\text{g cm}^{-3}$
$\rho_1, \rho_2$	densities of pure components 1, 2	$\text{g cm}^{-3}$
$\sigma(V_m^E)$	standard deviation	$\text{cm}^3 \text{ mol}^{-1}$
$\tau$	period of oscillation	s

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