(P, V_m, T) Measurements of (octane + 1-chlorohexane) at temperatures from 298.15 K to 328.15 K and at pressures up to 40 MPa

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Abstract

Densities were measured for the liquid octane and 1-chlorohexane, and for nine of their mixtures at four temperatures between 298.15 K and 328.15 K and at pressures up to 40 MPa. An apparatus for density measurements of liquids and liquid mixtures whose main part is a high-pressure vibrating-tube densimeter working in a static mode was used for the measurement. The density data were fitted to the Tait equation and the isothermal compressibilities were calculated with the aid of this equation. Excess molar volumes were also computed from the densities and fitted to the Redlich–Kister equation.
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1. Introduction

Research activities of our laboratory comprise, among others, the systematic measurement of volumetric properties of different groups of organic compounds. One of our current projects is devoted to the study of liquid systems containing alkanes with 1-chloroalkanes with the aim to establish a database [1–7] for testing theories (equations of state) of liquid mixtures.

To our knowledge, there exist no volumetric data for the liquid phase of the system (octane + 1-chlorohexane) at elevated pressures. Therefore, we have measured densities and calculated isothermal compressibilities and excess volumes of the system. The apparatus based on a high-pressure vibrating-tube densimeter working in a static mode [2] and designed for measuring the (p, V_m, T) behaviour of pure liquids and liquid mixtures at elevated temperatures (283 K to 333 K) and moderately high pressures (to 40 MPa) was used for the measurements. The measure-

ments were carried out at the temperatures 298.15 K, 308.15 K, 318.15 K, and 328.15 K and in the pressure range 0.1 MPa to 40 MPa.

The densities and excess volumes of the investigated liquids and their mixtures are required, for instance, for relating excess enthalpy and excess Gibbs free energy values. From a practical point of view, the data are useful for the design of mixing, storage, and process equipment. Last but not least, the data measured reflect interactions between the molecules of the mixtures studied and can serve for testing the theories of the liquid state.

2. Experimental

2.1. Materials

The octane and 1-chlorohexane used in the experiments were the products from Fluka (octane, puriss. p.a., g.c. mass fraction > 0.995, 1-chlorohexane, puriss., g.c. mass fraction > 0.99). The 1-chlorohexane 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

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determined at $T = 298.15$ K and compared with literature values [8–10]. The agreement was found, in general, to be good (table 1). The purity of the chemicals was checked by gas chromatography (HP Ser.II. model 5890 chromatograph with capillary column type 1909 1Z-413E and f.i.d., column temperature 413.3 K, helium flow rate $4.2 \cdot 10^{-4}$ cm$^3 \cdot$ s^{-1}).

2.2. Apparatus and procedure

A schematic diagram and detailed description of the apparatus used for the measurement was given in our previous work [2]. 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 under control within ±0.01 K. The pressure was measured with a pressure transducer LPN-N having a voltage output (ECOM, Praha, Czech Republic). The pressure gauge was calibrated with a Ruska pressure calibration system (Ruska Instruments Co., Houston, TX, 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 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 [11] are moved into the measuring cell with a liquid chromatography pump LCP 4000.1 (Ecom, Praha, Czech Republic).

The sample density ρ was deduced from the period of vibration τ of the vibrating-tube densimeter as follows:

$$\rho(T, p) = a(T, p)\tau^2 + b(T, p). \tag{1}$$

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 τ_1 and τ_2 for two substances of known density of the T, p set considered. For 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 recommended. The density of a sample is then calculated from equation (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 [2] with double-distilled water and heptane. The density data used for the calibration were taken from [12] for water and from [13] for heptane.

The samples for the density measurements were prepared by weight (SCALTEC SBC 21 balance with an accuracy of $\pm 1 \cdot 10^{-5}$ g) for the whole mole fraction range and then partially degassed in tightly closed special vessels of negligible vapour space [11] at the maximum measurement temperature for 3 h by means of an ultrasonic thermostatted bath (Bandelin RK 100H, Berlin, Germany) prior to determining their density in order to prevent the formation of bubbles in the densimeter. To estimate the effect of evaporation on the sample composition, the calculations were carried out taking into account the (vapour + liquid) equilibrium of the given system at the conditions applied. The concentration changes are proved to be well below the stated accuracy in composition.

The experimental uncertainty in the mole fraction composition is less than $\pm 5 \cdot 10^{-5}$, and that in the density is approximately $\pm 1 \cdot 10^{-4}$ g $\cdot$ cm^{-3}.

3. Results and discussion

3.1. Densities

The results of the density measurements are given in table 2. Densities of the pure substances and of nine weighed mixtures were measured at 23 pressures over the range 0.1 MPa to nearly 40 MPa.

The isothermal densities of pure substances and their mixtures at a given composition were fitted to the Tait equation

$$(\rho - \rho_0)/\rho = C \ln\{(D + p)/(D + p_0)\}, \tag{2}$$

where ρ_0 is the density at a reference pressure p_0 ($p_0 = 0.101325$ MPa in this work). The values of ρ_0 were those obtained by measuring the liquid samples with a low-pressure DMA 58 densimeter [5] because the high-pressure equipment cannot in principle provide sufficiently accurate data at atmospheric pressure. Since the procedure for determination of the parameters requires a special approach, it is described in detail in [14].

TABLE 1
Densities ρ and refractive index values n_D at $T = 298.15$ K of the pure components, and their comparison with literature; w is the mass fraction purity as determined by g.l.c.

Component	$\rho/(\text{g} \cdot \text{cm}^{-3})$			n_D			w
	Experimental	Literature	Reference	Experimental	Literature	Reference	
Octane	0.69864	0.69862	[8–10]	1.3950	1.39505	[8–10]	0.9991
1-Chlorohexane	0.87343	0.8745	[8]	1.4172			0.9953