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Isothermal vapour–liquid equilibria and excess enthalpies for the binary mixtures containing an isomeric chlorobutane and diisopropyl ether

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ABSTRACT

Isothermal vapour–liquid equilibria for the four binary mixtures formed by an isomer of chlorobutane (1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, or 2-methyl-2-chloropropane) and diisopropyl ether has been studied at $T = 288.15$ K, 298.15 K, and 308.15 K. The experimental data have been satisfactorily checked for thermodynamic consistency using the method of van Ness. The isothermal vapour–liquid equilibrium data have been correlated using the Wilson equation and excess Gibbs energies have been calculated. Moreover, we have measured excess enthalpies at $T = 298.15$ K using an isothermal flow calorimeter; combining these excess enthalpies with excess Gibbs energies the corresponding entropic contributions to excess Gibbs energy have been obtained. The group contribution method UNIFAC has been used to predict the phase equilibrium behaviour of the mixtures at isothermal conditions.

1. Introduction

The study of vapour–liquid equilibria (VLE) at isothermal conditions provides experimental data of great interest in thermodynamics and chemical engineering and contributes decisively for the development of accurate methods to predict and correlate phase equilibria.

In the past years our research group has been involved in a systematic and comprehensive study about phase equilibria and thermodynamic properties of mixtures formed by a cyclic ether and a halogenated compound [1–4]. From a theoretical point of view, binary mixtures of ethers and chloroalkanes are particularly interesting due to their complexity, a consequence of the presence of specific Cl–O interactions. Moreover, the study of ether mixtures is very important since oxygenated compounds are added to improve the octane rating and the pollution-reducing capability of gasoline. Between these compounds, diisopropyl ether could be a suitable and alternative candidate as gasoline additive [5,6].

Recently we have reported densities, speeds of sound, refractive indices, and viscosities of binary mixtures formed by isomeric chlorobutanes (1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, or 2-methyl-2-chloropropane) and diisopropyl ether in the temperature range 283.15–313.15 K [7,8]. In this work, the isothermal vapour–liquid equilibria for the same mixtures has been studied at the temperatures of 288.15 K, 298.15 K and 308.15 K. Thermodynamic consistency of the experimental VLE data has been satisfactorily checked by the method of van Ness. We have also correlated activity coefficients of the components of the mixtures using the Wilson equation [9], from these activity coefficients the corresponding excess Gibbs energies have been calculated. The results presented here have been used to test the reliability of the UNIFAC predictions [10,11]. Moreover, excess enthalpies have been determined at the temperature 298.15 K using an isothermal flow calorimeter and finally from excess enthalpies and excess Gibbs energies we have estimated the corresponding entropic contributions to excess Gibbs energy.

2. Experimental

The liquids used were 1-chlorobutane, 2-chlorobutane, 2-methyl-2-chloropropane, and diisopropyl ether (better than 99% mass) obtained from Aldrich and 2-methyl-1-chloropropane (better than 99% mass) provided by Fluka. No additional purification has been carried out.

The vapour–liquid equilibrium was studied using an all-glass dynamic recirculating type still that was equipped with a Cottrell pump. It is a commercial unit (Labodest model) built in Germany by Fischer. The equilibrium temperature was measured with an uncertainty of ±0.01 K by means of a thermometer (model F25 with a PT100 probe) from Automatic Systems Laboratories, and the

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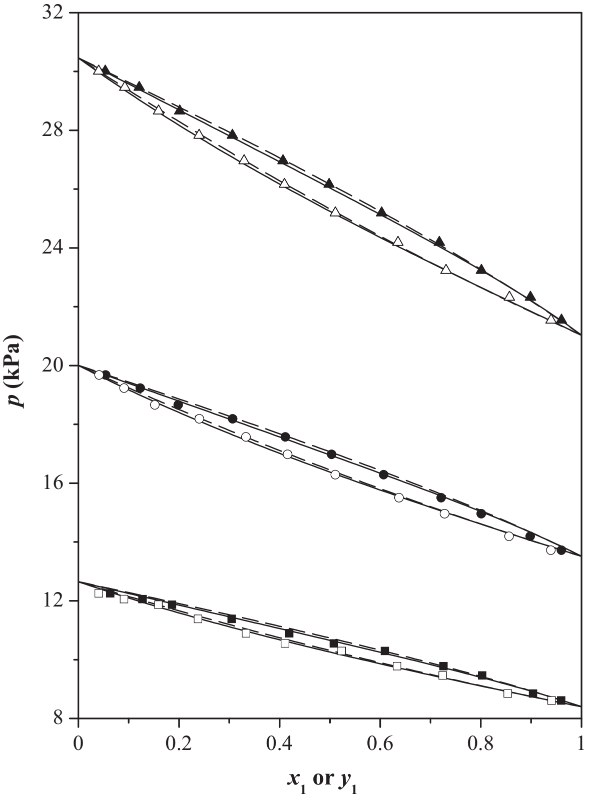

Fig. 1. p–x_1–y_1 diagrams for the binary mixture 1-chlorobutane (1) + diisopropyl ether (2): (□, ■) experimental data at T = 288.15 K; (○, ●) data at T = 298.15 K; (△, ▲) data at T = 308.15 K; (—) Wilson correlation; (– – –) UNIFAC prediction.

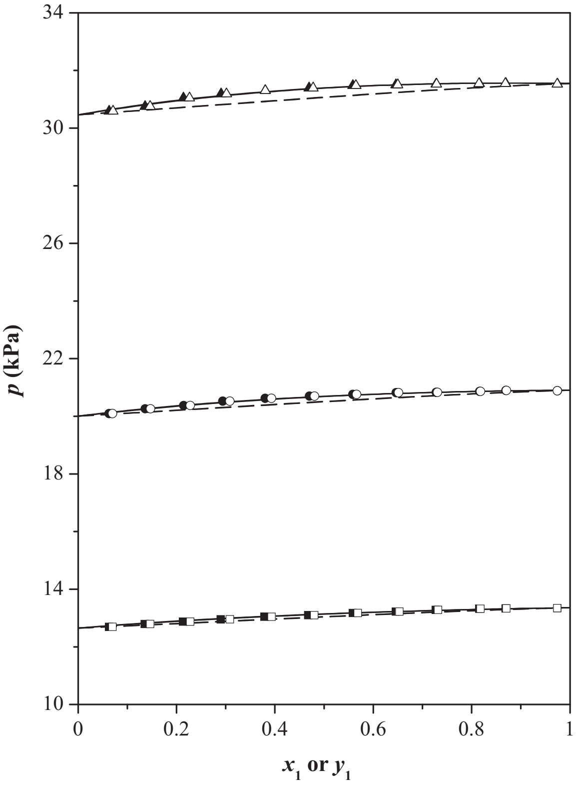

Fig. 2. p–x_1–y_1 diagrams for the binary mixture 2-chlorobutane (1) + diisopropyl ether (2): (□, ■) experimental data at T = 288.15 K; (○, ●) data at T = 298.15 K; (△, ▲) data at T = 308.15 K; (—) Wilson correlation; (– – –) UNIFAC prediction.

pressure in the still was measured with a Digiquartz 735-215A-102 pressure transducer from Paroscientific equipped with a Digiquartz 735 display unit, the uncertainty of the pressure measurements is ±0.01% of reading [1]. The composition of both phases (liquid and condensed vapour) has been determined by measuring their densities with an Anton Paar DMA-5000 vibrating tube densimeter. The uncertainty of the density measurements was $\pm 1 \times 10^{-3}$ kg m^{-3}. The error in the determination of liquid and vapour mole fractions is estimated to be ±0.0005.

Excess enthalpies, H^E, were determined using a commercial isothermal flow calorimeter from Hart Scientific (model 7501) previously described [12]. In this apparatus, two syringe pumps (model LC-2600, ISCO) provide a flow of constant composition through a thermostated calorimeter cell equipped with a pulsed heater and a Peltier cooler. The Peltier cooler is working at constant power, producing a constant heat loss from the calorimeter cell, which is compensated by the pulsed heater. The required frequency is influenced by endothermal or exothermal heat effects, so that the heats of mixing can be determined from the observed frequency change between the baseline and the actual measurement. A back-pressure regulator serves to keep the pressure at a level at which evaporation and degassing effects can be prevented. The experimental uncertainties of this device are as follows: ±0.005 K in temperature, ±0.0001 in mole fraction and less than 1% in H^E.

3. Results and discussion

The pressure–composition diagrams, p–x_1–y_1, are shown in Figs. 1–4. The Wilson equation has been used to correlate the activity coefficients of the components in the liquid phase. Estimation of the adjustable parameters of the equation was based on

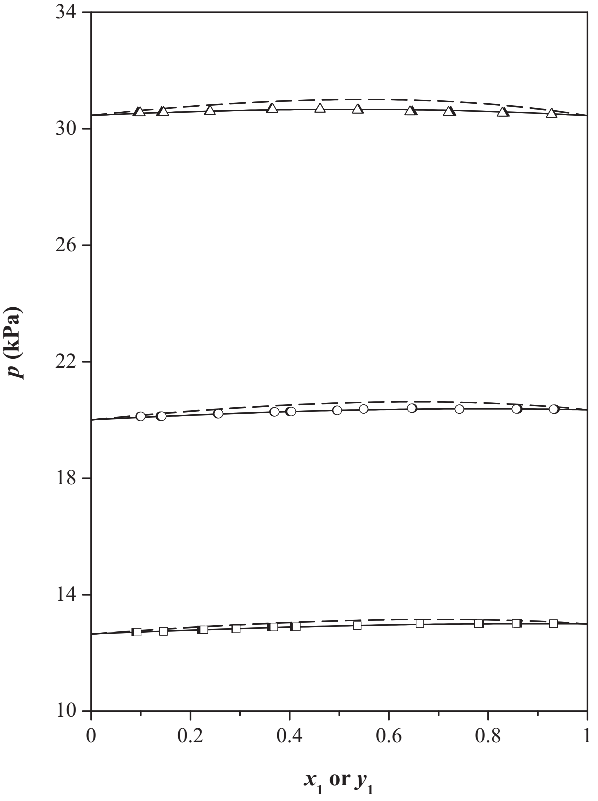

Fig. 3. p–x_1–y_1 diagrams for the binary mixture 1-chloro-2-methylpropane (1) + diisopropyl ether (2): (□, ■) experimental data at T = 288.15 K; (○, ●) data at T = 298.15 K; (△, ▲) data at T = 308.15 K; (—) Wilson correlation; (– – –) UNIFAC prediction.