

Activity coefficient at infinite dilution, azeotropic data, excess enthalpies and solid–liquid-equilibria for binary systems of alkanes and aromatics with esters

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Abstract

Binary azeotropic data have been measured at different pressures for ethyl acetate + heptane, methyl acetate + heptane, isopropyl acetate + hexane and isopropyl acetate + heptane by means of a wire band column. Additionally activity coefficients at infinite dilution have been determined for ethyl acetate and isopropyl acetate in decane and dodecane in the temperature range between 303.15 and 333.15 K with the help of the dilutor technique. Furthermore excess enthalpies for the binary systems methyl acetate + hexane, methyl acetate + decane, ethyl acetate + hexane and ethyl acetate + decane at 363.15 and 413.15 K have been studied with the help of isothermal flow calorimetry. Finally solid–liquid equilibria for the systems ethyl myristate + benzene and ethyl myristate + *p*-xylene have been investigated by a visual technique. All these data have been used for the revision and extension of the group interaction parameters of the group contribution method modified UNIFAC (Dortmund) and the group contribution equation of state VTPR. The experimental data was compared with the results predicted using the group contribution method modified UNIFAC (Dortmund) and the group contribution equation of state VTPR.

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1. Introduction

Group contribution methods and group contribution equations of state are of great importance for the synthesis, design and optimization of thermal separation processes and a large number of other applications of industrial interest. The reliable knowledge of phase equilibria and excess properties is a prerequisite for the reliable synthesis and design of chemical processes. In particular the behavior of separation processes can be predicted with the help of group contribution methods and group contributions equations of state. Therefore they are especially important during the development of chemical processes.

To obtain the best representation of the real behavior of the systems across the whole composition and a large temperature range, the required group interaction parameters are fitted simultaneously to all available reliable experimental data (vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), azeotropic data (AZD), solid–liquid equilibria of eutectic systems (SLE), excess enthalpies (H^E), activity coefficients at infinite dilution (γ^∞), etc.) [1,2].

In this paper new experimental data for systems with esters are presented. The new experimental data have been used for the revision and extension of the group interaction parameters for the group contribution method modified UNIFAC (Dortmund) [3–6] and the group contribution equation of state called VTPR [7–12].

The knowledge of azeotropic points as a function of pressure (temperature) is of particular importance for the design and synthesis of distillation columns as well as for the selection of the most suitable solvent for azeotropic distillation. In

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this work azeotropic data for methyl acetate + heptane, ethyl acetate + heptane, isopropyl acetate + hexane and isopropyl acetate + heptane are presented from low to moderate pressures.

H^E data sets at higher temperatures are used as supporting data for fitting temperature-dependent group interaction parameters. Furthermore these data (measured at various temperatures) deliver the correct temperature dependence of the activity coefficients following the Gibbs–Helmholtz equation. In the present paper molar excess enthalpy data (H^E) are reported for the binary systems methyl acetate + hexane, methyl acetate + decane, ethyl acetate + hexane and ethyl acetate + decane at 363.15 and 413.15 K.

The activity coefficients at infinite dilution are very useful for the selection of selective solvents and for the reliable design of thermal separation processes. They deliver the required information for the very dilute region. In this work activity coefficients at infinite dilution for ethyl acetate and isopropyl acetate in decane and dodecane in the temperature range between 303.15 and 333.15 K are presented.

For the design and optimization of crystallization processes solid–liquid equilibria (SLE) are of great interest. At the same time SLE data deliver the supporting information for the group contribution model in the low temperature range. This paper presents new experimental SLE data for the binary systems ethyl myristate + benzene and ethyl myristate + *p*-xylene.

2. Experimental section

2.1. Materials

The chemicals used in this work were received from different commercial suppliers and distilled as described by Fischer and Gmehling [13]. The resulting purities were determined by gas chromatography and the water content was measured by Karl Fischer titration. In all cases the concentration of water was lower than 100 ppm. The chemicals used including their purity and supplier are summarized in Table 1.

Table 1
Supplier and purity of the chemicals

Compound	Supplier	Purity (%)	Water content (ppm)
Methyl acetate	Fluka	>99.9	84.9
Ethyl acetate	Aldrich	>99.9	75.4
Isopropyl acetate	Aldrich	>99.8	54.7
Ethyl myristate	Lancaster	>99.8	37.4
Hexane	Scharlau	>99.9	40.2
Heptane	Aldrich	>99.9	31.7
Decane	Aldrich	>99.9	69.2
Dodecane	Aldrich	>99.9	76.5
Benzene	Roth	>99.9	14.6
<i>p</i> -Xylene	Merck-Schuchardt	>99.9	83.5

2.2. Measurement of activity coefficients at infinite dilution

The principle of the measurement using the dilutor technique is that a highly diluted component is stripped from the solvent by a constant inert gas flow. The variation of the solute concentration in the vapor phase is recorded using gas chromatography (GC). The dilutor technique has already been described in detail by Krummen et al. [14]. Basically, the carrier gas (helium, Messer-Griesheim, purity: 99.996%) is brought to the desired temperature using a heating coil immersed in the thermostat (Lauda S) and the flow is controlled and measured using a digital mass flow controller (Bronkhorst Hi-TEC; F-201C-RA-33V). Before helium enters the measurement cell it is saturated with the solvent in a presaturation cell. The measurement cell contains a Pt-100 temperature sensor (Mesurix, model 2002A-RC), a septum, and a magnetic stirrer driven by a stirring motor to improve the mass transfer between the liquid and the gas bubbles. The pressure in the cell is measured via the septum using a home built mobile pressure sensor (Druck PDCR 911). After saturation with the solvent the carrier gas passes the measurement cell which is filled with approximately 80 cm³ of the same solvent and a highly diluted solute (mole fraction $x_i < 10^{-3}$), which is injected into the measurement cell via a septum. Finally, at different periods of time samples of carrier gas + solute + solvent are injected automatically via an electrical six-way valve (VICI, Valcon Instruments Co. Inc.) into the gas chromatograph (Hewlett Packard, model 6890) equipped with an FID detector and analyzed. During the measurement the logarithm of peak area for the solute is recorded as a function of time. It should be mentioned that for the measurements with the dilutor the quantitative peak areas are not required for the data evaluation, but only their variation with time.

At the beginning of the measurement, each cell (approximately 100 cm³) is filled with about 80 cm³ of solvent. The mass of the solvent in the measurement cell is determined by weighing. The constant level of the solvent in this cell is controlled in order to be sure that the carrier gas is saturated in the presaturation cell and no solvent is removed from the measurement cell. During the measurements the carrier gas removed more than 20% of the solute from the measurement cell. The accuracy of the temperature is determined to be ± 0.05 K. The relative error for the measurements carried out using the dilutor technique is approximately $\pm 2.5\%$ [14].

2.3. Measurement of azeotropic data

The measurement of azeotropic data was performed using a commercially available microspinning band column with an electronically controlled reflux ratio from NORMAG GmbH (Hofheim, Germany) to distill the mixtures. The reflux ratio is realized on the basis of vapor dividing principle. This apparatus allows measurements at low and moderate pressures

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