



Vapor–liquid equilibria at 333.15 K and excess molar volumes and deviations in molar refractivity at 298.15 K for mixtures of diisopropyl ether, ethanol and ionic liquids

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ABSTRACT

In this work, we have studied influence of ionic liquids (ILs) on the azeotrope composition for the system {diisopropyl ether (DIPE)+ethanol} using trihexyltetradecylphosphonium chloride ($[P_{666,14}][Cl]$) and trihexyltetradecylphosphonium bis(2,2,4-trimethylpentyl) phosphinate ($[P_{666,14}][TMPP]$). Isothermal vapor–liquid equilibrium data at 333.15 K are reported for the ternary systems {DIPE + ethanol + $[P_{666,14}][Cl]$ } and {DIPE + ethanol + $[P_{666,14}][TMPP]$ } with varying the mole fraction of ILs from 0.05 to 0.10. The experimental ternary VLE data were correlated using the Wilson equation. In addition, excess molar volumes (V^E) and deviations in molar refractivity (ΔR) data at 298.15 K are reported for the binary systems {DIPE + $[P_{666,14}][Cl]$ } and {ethanol + $[P_{666,14}][Cl]$ } by a digital vibrating tube densimeter and a precision digital refractometer. The V^E and ΔR were correlated by the Redlich–Kister equation.

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1. Introduction

Distillation is by far the most extensively used and common industrial separation process in the petroleum, natural gas and petrochemical industries. It is also common in many other industries including air fractionation, solvent recovery and recycling processes. However, distillation is highly restricted when azeotropes appear. Azeotropes can be separated using a pressure swing method or by distillation with an entrainer (liquid additive or solid salt) that modifies the relative volatility of the distilled components. The use of salts has problems associated with the causticity and the limited solubility in organic compounds, whereas volatile organic solvents may contaminate the environment and the product streams [1].

Recently, ionic liquids (ILs) have become useful in industrial separation methods because of their extremely low vapor pressures and thermal stabilities. Additionally, ILs have a highly polar character caused by Coulomb forces acting between the ions in the liquid state, and because they are exceedingly good solvents for a wide range of materials [2,3]. Many applications of ILs as “green solvents”, replacing volatile organic compounds, have been

reported [3]. Imidazolium-, pyridinium- and pyrrolidinium-based ILs are usually of interest in laboratories as extractive solvents.

Diisopropyl ether (DIPE) is considered one of the most attractive economical gasoline octane boosters as a substitute for methyl tert-butyl ether (MTBE), which was phased out in California, USA. Some primary alcohols have also been considered as candidates for new additives of gasoline. We have studied the phase equilibria and mixture properties systematically for several mixtures with ether compounds and alcohols, due to the presence of an azeotrope and the lack of equilibrium, and the thermophysical properties for ether compounds [4–6].

In this work, we report the influence of ILs on the shift of the azeotrope for the system {DIPE + ethanol} using phosphonium-based ILs, tri-hexyltetradecylphosphonium chloride ($[P_{666,14}][Cl]$) and tri-hexyltetradecylphosphonium bis(2,2,4-trimethylpentyl) phosphinate ($[P_{666,14}][TMPP]$). Because imidazolium-, pyridinium- and pyrrolidinium-based ILs are barely soluble in DIPE, whereas $[P_{666,14}][Cl]$ and $[P_{666,14}][TMPP]$ are soluble in DIPE, the isothermal vapor–liquid equilibrium (VLE) data at 333.15 K for the systems {DIPE + ethanol} with different concentrations of $[P_{666,14}][Cl]$ and $[P_{666,14}][TMPP]$ were measured using headspace gas chromatography (HSGC). The experimental ternary VLE data were correlated with the Wilson equation [7]. In addition, we report the mixture properties, excess molar volumes (V^E) and deviations in molar refractivity (ΔR) at 298.15 K for the binary systems {DIPE + $[P_{666,14}][Cl]$ } and {ethanol + $[P_{666,14}][Cl]$ } by a digital vibrat-

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Nomenclature

List of symbols

A, B, C	Antoine constant values
A_i	adjustable parameter for the Redlich–Kister equation
A_{ij}, A_{ji}	parameters used in the Wilson equation
M_i	molar mass of the pure component, i (g mol^{-1})
n	number of parameters, A_i
n_D	refractive index
N	number of experimental data points
ΔR	deviations in molar refractivity ($\text{cm}^3 \text{mol}^{-1}$)
V^E	excess molar volume ($\text{cm}^3 \text{mol}^{-1}$)
V_i	molar volume of a pure component, i
x_i	liquid-phase mole fraction of the component, i
y_i	vapor-phase mole fraction of the component, i

Greek letters

ρ_i	density of the component, i (g cm^{-3})
ρ_m	density of the mixture (g cm^{-3})
σ_{st}	standard deviation
ϕ_i	volume fraction of the pure components

Subscripts

i	component, i
exp.	experimental value
cal.	calculated value

ing tube densimeter and a precision digital refractometer. These binary data were correlated with the Redlich–Kister polynomial [8].

2. Experimental

2.1. Chemicals

Commercial grade DIPE ($\text{C}_6\text{H}_{14}\text{O}$, $M = 102.18 \text{ g mol}^{-1}$, CAS-RN 108-20-3), $[\text{P}_{666,14}][\text{Cl}]$ ($\text{C}_{32}\text{H}_{68}\text{ClP}$, $M = 519.31 \text{ g mol}^{-1}$, CAS-RN 258864-54-9) and $[\text{P}_{666,14}][\text{TMPP}]$ ($\text{C}_{48}\text{H}_{102}\text{O}_2\text{P}_2$, $M = 773.27 \text{ g mol}^{-1}$, CAS-RN 465527-59-7) were obtained from Aldrich Chemical Company. Ethanol ($\text{C}_2\text{H}_6\text{O}$, $M = 46.07 \text{ g mol}^{-1}$, CAS-RN 64-17-5) was supplied from J.T. Baker Chemical Company. DIPE and ethanol have no impurities as determined by gas chromatography, and the purity of ILs, $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{TMPP}]$, was declared better than 99% by the supplier. The compounds were used without additional purification. The organic chemicals were used after water drying using molecular sieves with a pore diameter of 0.4 nm. The purity of the chemicals was examined by gas chromatography and by comparing the densities and refractive indices with the values reported in the literature [9,10]. The water content, determined by Karl–Fisher titration (Metrohm 684 KF coulometer), was less than 90 ppm for all the chemicals. The measured purities, densities, refractive indices and Antoine constants are summarized in Table 1.

2.2. Procedure

The isothermal VLE measurements were carried out using headspace gas chromatography (HSGC). The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A) with an electro-pneumatic sampling system and a precision thermostat with an accuracy of $\pm 0.1 \text{ K}$. An HP-5 (5%-diphenyl-95%-dimethylsiloxane, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) capillary column and a thermal conductivity detector were used for the analysis.

The uncertainty of the measured equilibrium mole fraction was estimated as $\pm 1 \times 10^{-4}$. According to the approximately calculated mole ratio, the heavier component was charged first in a vial and sealed with a Teflon/rubber septum and aluminum cap. Then, the volatile material was injected into the glass vial with a syringe to minimize experimental error. The prepared glass vials with the sample mixture were placed in the thermostat and equilibrated for more than 2 h. The equilibrium between the vapor and liquid phase is reached very quickly because of the total volume of the sample mixture is small at approximately 3 ml and because the equilibrium cell is small. When equilibrium was achieved between the two phases, a fixed amount of the vapor phase (headspace) was automatically sampled and transported to the gas chromatograph for analysis by the electropneumatic sampling system. The equilibrated liquid phase mole fraction can be calculated from the measured vapor phase mole fraction and mass balance.

The densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The densimeter was automatically calibrated with distilled water and dried air. The uncertainty of the densimeter is stated by the manufacturer as $5 \times 10^{-6} \text{ g cm}^{-3}$ in the density range of $0\text{--}3 \text{ g cm}^{-3}$. The temperature was controlled within $\pm 0.01 \text{ K}$. The details of the operating procedures have been described elsewhere [11,12]. The refractive indices (n_D) of the pure components and mixtures were measured by a digital precision refractometer (KEM, model RA-520N, Kyoto, Japan). The refractometer was calibrated with distilled water, and the uncertainty of this refractometer is stated as $\pm 5 \times 10^{-5}$ within the range from 1.32 to 1.40 and $\pm 1 \times 10^{-4}$ within the range from 1.40 to 1.58. The experimental procedure is described in detail elsewhere [13]. The accuracy of the densimeter and refractometer was tested periodically with doubly distilled water ($\rho_{298.15 \text{ K}} = 0.997047 \text{ g cm}^{-3}$) under atmospheric conditions. The uncertainty of ρ and n_D by this test was estimated to be less than $1 \times 10^{-5} \text{ g cm}^{-3}$ and 1×10^{-4} , respectively. Approximately 3 ml of the sample mixtures were prepared by mass using a microbalance (Ohaus DV215CD) with a precision of $1 \times 10^{-5} \text{ g}$, charging the heavier component first to minimize vaporization. The experimental systematic error was estimated to be less than 1×10^{-4} mole fraction. The time interval of the measurements was chosen as 15 min to attain a constant temperature and stability in oscillation.

3. Results and discussion

3.1. Isothermal VLE

The VLE data for the ternary systems {DIPE + ethanol + $[\text{P}_{666,14}][\text{Cl}]$ } and {DIPE + ethanol + $[\text{P}_{666,14}][\text{TMPP}]$ } at 333.15 K were measured and are listed in Tables 2 and 3, where x_3 is the mole fraction of $[\text{P}_{666,14}][\text{Cl}]$ or $[\text{P}_{666,14}][\text{TMPP}]$ in the liquid phase; x'_1 is the recalculated liquid phase mole fraction of DIPE as an IL-free basis; y_1 and y_2 are the mole fraction of DIPE and ethanol in the vapor phase, respectively; and P is the calculated equilibrium pressure. The activity coefficient of each component was calculated by the Wilson activity coefficient model, and then, the total pressure was calculated using the modified Raoult's law. The vapor pressures of each pure component at 333.15 K were calculated from the Antoine equation (1) using the Antoine constants:

$$\log p_i^{\text{sat}} (\text{kPa}) = A - \frac{B}{C + T(\text{K})} \quad (1)$$

The determined VLE data were correlated with the Wilson model [7]. The experimental x - y data of the ternary systems, {DIPE + ethanol + $[\text{P}_{666,14}][\text{Cl}]$ } and {DIPE + ethanol + $[\text{P}_{666,14}][\text{TMPP}]$ }, are plotted as the IL-free basis in Figs. 1 and 2 with the correlated VLE data from the Wilson

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