

Isothermal vapor–liquid equilibrium at 333.15 K and excess molar volumes and refractive indices at 298.15 K for the mixtures of *di*-methyl carbonate, ethanol and 2,2,4-trimethylpentane

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ABSTRACT

Isothermal vapor–liquid equilibrium data at 333.15 K are measured for the binary system ethanol + 2,2,4-trimethylpentane and for ternary system *di*-methyl carbonate (DMC) + ethanol + 2,2,4-trimethylpentane by using headspace gas chromatography. The experimental binary and ternary vapor–liquid equilibrium data were correlated with different activity coefficient models. Excess volume and deviations in molar refractivity data are also reported for the binary systems DMC + ethanol and DMC + 2,2,4-trimethylpentane and the ternary system DMC + ethanol + 2,2,4-trimethylpentane at 298.15 K. These data were correlated with the Redlich–Kister equation for the binary systems and the Cibulka equation for the ternary system, respectively. The ternary excess volume and deviations in molar refractivity data were also compared with estimated values from the binary contribution models of Tsao–Smith, Kohler, Rastogi and Radojkovič.

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1. Introduction

The addition of fuel oxygenates to gasoline raises combustion temperatures and improves engine efficiencies. The results are lower levels of carbon monoxide and unburned hydrocarbons in auto exhaust. Today, methyl *tert*-butyl ether (MTBE) dominates the market, but the insufficient supply of this ether and anxiety of contamination of ground water are the reason for the interest in heavier ethers and other substitutes [1,2]. Recently, environmentally friendly *di*-methyl carbonate (DMC) is considered as a suitable gasoline additive and ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and *di*-isopropyl ether (DIPE) are also considered as the most possible candidates among ether compounds. We have reported the phase equilibria and mixture properties systematically for several gasoline additive (octane booster) combinations, because the accurate data of such properties are needed for the processing of these compounds [3–5].

In this work, we report the vapor–liquid equilibrium (VLE) data at 333.15 K for the binary system ethanol (1) + 2,2,4-trimethylpentane (2) and for the ternary system DMC (1) + ethanol (2) + 2,2,4-trimethylpentane (3) by using headspace gas chromatography (HSGC). Densities (ρ) and refractive indices (n_D) at 298.15 K for the binary systems DMC (1) + ethanol (2), DMC (1) + 2,2,4-trimethylpentane (2) and the mentioned ternary system were also measured by using a digital vibrating tube densimeter and a precision digital refractometer. The ternary system DMC + ethanol + 2,2,4-trimethylpentane was chosen because DMC and ethanol are possible of green octane boosters and 2,2,4-trimethylpentane is a major component of gasoline. As far as we know, there are no ternary VLE data at 333.15 K and no excess property data at 298.15 K for DMC + ethanol + 2,2,4-trimethylpentane. We reported earlier VLE data at 333.15 K for the systems DMC (1) + ethanol (2), DMC (1) + 2,2,4-trimethylpentane (2) and ρ and n_D values at 298.15 K for ethanol (1) + 2,2,4-trimethylpentane (2) [6–8]. The binary VLE data and excess properties in this work are supplements of sub-binary data for ternary system DMC + ethanol + 2,2,4-trimethylpentane. The excess molar volumes (V^E) and deviations in molar refractivity (ΔR) were derived from measured densities and refractive indices.

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the predicted values by using the binary contribution models of Tsao–Smith [9], Kohler [10], Rastogi et al. [11] and Radojković et al. [12]. Among them, the Radojković model gave the best estimation results.

2. Experimental

2.1. Materials

Commercial grade DMC ($C_3H_6O_3$, $M=90.08 \text{ g mol}^{-1}$, CAS-RN 616-38-6) and 2,2,4-trimethylpentane (C_8H_{18} , $M=114.23 \text{ g mol}^{-1}$, CAS-RN 540-84-1) were obtained from Aldrich. Ethanol (C_2H_6O , $M=46.07 \text{ g mol}^{-1}$, CAS-RN 64-17-5) was obtained from J.T. Baker Chemical Co. All the chemicals were dried 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 values reported in the literature. All sample purities were better than 99.9 wt%, according to gas chromatographic analysis. The measured densities and refractive indices of the samples are summarized in Table 1, along with literature values and Antoine constants of the pure substances.

2.2. Apparatus and procedure

Isothermal VLE measurement has been carried out by head space gas chromatography (HSGC) for the binary and ternary systems. The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A), which has an electro-pneumatic sampling system and a precision thermostat, having an accuracy of $\pm 0.1 \text{ K}$. A HP-5 ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) capillary column and a thermal conductivity detector were used for the analysis. The experimental procedure is described in detail elsewhere [3,13]. Densities were measured by a digital vibrating glass tube density meter (Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of the density meter is stated as $5 \times 10^{-6} \text{ g cm}^{-3}$ in the range of 0–3. Temperature is controlled within $\pm 0.01 \text{ K}$ in the range from 273.15 K to 363.15 K. The details of operating procedures have been described elsewhere [3,14]. Refractive indices (n_D) of the pure components and mixture samples were measured by digital precision refractometer (KEM, model RA-520N, Kyoto, Japan). The uncertainty of this refractometer is stated as $\pm 5 \times 10^{-5}$ within range from 1.32 to 1.40 and $\pm 1 \times 10^{-4}$ within range from 1.40 to 1.58. The experimental procedure is described in detail elsewhere [15]. Calibration of density meter and refractometer were carried out periodically by using doubly distilled water and dried air. Mixture samples were prepared simultaneously for density and refractive indices measurements.

3. Results and discussion

In our VLE measuring method, the equilibrium pressure and liquid phase mole fractions are not directly measured, but they are calculated from the experimental vapor phase composition and thermodynamic equations [13]. The experimental VLE compositions and calculated pressures for the binary system ethanol (1)+2,2,4-trimethylpentane (2) at 333.15 K are listed in Table 2 and plotted in Fig. 1. A minimum boiling azeotrope was observed in this system. The other constituent binary systems of the ternary system DMC (1)+ethanol (2)+2,2,4-trimethylpentane (3), DMC (1)+ethanol (2), DMC (1)+2,2,4-trimethylpentane (2) have also minimum boiling azeotropes which was reported in our previous work [6,7]. They are also represented in Fig. 1 for better understanding. The coordinates of the azeotrope of the system ethanol (1)+2,2,4-trimethylpentane (2) is $x_1^{az} = 0.6110$ and $P^{az} = 63.89 \text{ kPa}$

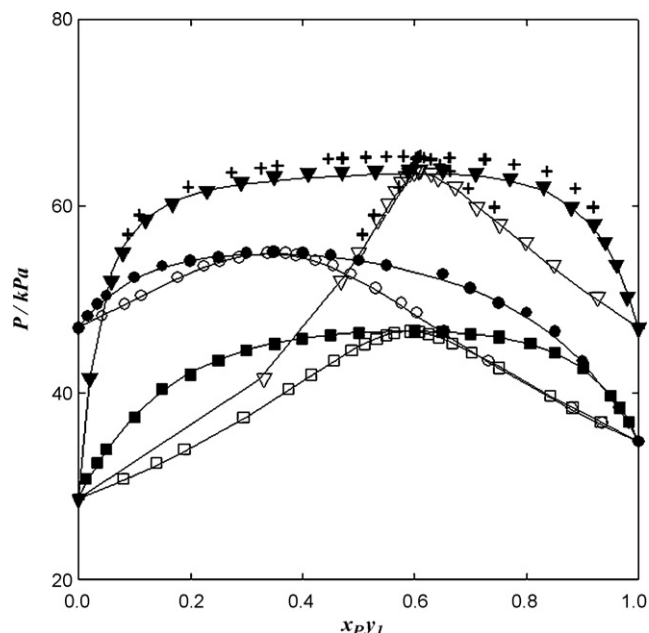


Fig. 1. P - x - y for the three binary systems at 333.15 K. Filled symbols, liquid phase; open symbols, vapor phase; (●), DMC (1)+ethanol (2) from previous work [6]; (■), DMC (1)+2,2,4-trimethylpentane (2) from previous work [7]; (▼), ethanol (1)+2,2,4-trimethylpentane (2); (+), ethanol (1)+2,2,4-trimethylpentane (2) by Hiaki et al. [16]. Solid curves were calculated from best fitted G^E model parameters.

as found by interpolation. The measured binary VLE for ethanol (1)+2,2,4-trimethylpentane (2) was compared with the reported data of Hiaki et al. [16] as shown in Fig. 1. The data of Hiaki et al. show a somewhat higher equilibrium pressure compared to our data at the same concentration. The difference in equilibrium pressure of both data sets is $\Delta P = 1.41 \text{ kPa}$. The difference of the azeotropic point of both data sets was $\Delta x_1^{az} = 0.0010$ and $\Delta P^{az} = 1.47 \text{ kPa}$, respectively.

The experimental binary VLE data for ethanol (1)+2,2,4-trimethylpentane (2) were correlated with Margules, van Laar, Wilson, NRTL and UNIQUAC equations and the adjustable binary parameters are listed in Table 3 along with the mean deviations between experimental and calculated data. The mean deviation of vapor-phase mole fraction (Δy_1) was calculated from Eq. (1).

$$\Delta y_1 = \frac{|\Delta y_{1,\text{exp}} - \Delta y_{1,\text{cal}}|}{N} \quad (1)$$

where N is the number of experimental data points. The binary parameters (A_{ij}) for the calculation of $\ln \gamma$ (activity coefficient) in case of the Wilson, NRTL and UNIQUAC models are defined as

$$A_{ij} = (\lambda_{ij} - \lambda_{ii}) (\text{J mol}^{-1}) \quad (\text{Wilson})$$

$$A_{ij} = (g_{ij} - g_{ii}) (\text{J mol}^{-1}) \quad (\text{NRTL})$$

$$A_{ij} = (u_{ij} - u_{ii}) (\text{J mol}^{-1}) \quad (\text{UNIQUAC})$$

The ternary VLE data of the system DMC (1)+ethanol (2)+2,2,4-trimethylpentane (3) at 333.15 K are listed in Table 4 and illustrated in Fig. 2. A minimum boiling azeotrope was observed in this ternary system and the interpolated azeotropic point coordinates are $x_1^{az} = 0.0959$, $x_2^{az} = 0.5983$ and $P^{az} = 60.79 \text{ kPa}$. The ternary VLE data were correlated with the Wilson, NRTL and UNIQUAC models. The NRTL model provided the best correlation result. Dashed lines in Fig. 2

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