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Measurements and correlations of density, viscosity, and vapour-liquid equilibrium for fluoro alcohols

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ABSTRACT

The measurements of density, viscosity for 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol are reported at different temperatures and pressure of 101.3 kPa. The experimental values of densities and viscosities of the above two fluoro alcohols were correlated successfully by a second-order polynomial and by a Vogel–Tammann–Fulcher equation, respectively. Meanwhile, isobaric vapour-liquid equilibrium results for two binary systems of (methanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol) and (2,2,3,3-tetrafluoro-1-propanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol were determined by a modified Rose type still. Both the Herington area method and the van Ness point to point test method were adopted to confirm the thermodynamic consistency of the experimental VLE findings, for which the test results showed good thermodynamic consistency. The Wilson and non-random two-liquid (NRTL) activity coefficient models were used to correlate the measured VLE values at different temperatures. The correlation results indicate good agreement with the experimental values. Also the binary interaction parameters of the two activity coefficients models were regressed. With the calculation of G^E, the negative deviation behaviour was observed for the two binary systems.

1. Introduction

Fluoro alcohol is a kind of compound in which the hydrogen of the carbon-hydrogen bond is partially substituted by fluorine atoms. Owing to its small radius and high electronegativity, the energy of the carbon-fluorine bond formation is greater than that of carbon-hydrogen bond [1]. Consequently, the fluorine atom added into traditional alcohols can make the hydrogen atom of hydroxylic more acidic than that in hydrocarbon alcohols [2] and provide a good surface activity and biological activity for the traditional alcohols. Because of its special structure, fluoro alcohols have extensive applications in the synthesis of medicine, pesticides [3], dyestuffs [4], variety of solvents and surfactant [5,6].

In a number of fluoro alcohols, 2,2,2-trifluoroethanol (TFE) is applied as a working fluid for energy transformation processes in many fields because of its suitable thermodynamic properties and thermal stability [7]. The 2,2,3,3-tetrafluoro-1-propanol (TFP) and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFP) have been applied widely as solvents due to their good solubility, volatility, non-toxicity, non-corrosiveness, excellent lubricity and surface activity. Particularly 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octa fluoro-1-pentanol are used as solvents in the production of CD-R and DVD-R discs since they can dissolve a variety of organic compounds [8].

Although the importance of fluoro alcohols for the industrial applications has been emphasized, very few experimental values for the physical chemistry properties are available. Up to now, a few experimental values of density, viscosity and vapour-liquid equilibrium or liquid-liquid equilibrium for fluoro alcohols are available in the literature [1,2,9,10,19–23]. And the measurement of density [11], viscosity [12], vapour pressure [7,13], vapour-liquid equilibrium [14], and excess thermodynamic properties [15–18] for pure 2,2,2-trifluoroethanol and its binary mixtures are reported.

In this work, the density and viscosity of 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol are reported over a wide temperature range at atmospheric pressure. The isobaric vapour-liquid equilibrium of (methanol + 2,2,3,3,4,4,5,5-octa fluoro-1-pentanol) and (2,2,3,3-tetrafluoro-1-propanol + 2,2,3, 3,4,4, 5,5-octafluoro-1-pentanol) have been determined. Based on the experimental results obtained, the density was correlated by using a second-order polynomial. The viscosity was correlated by the Vogel–Tammann–Fulcher (VTF) equation. The vapour-liquid equilibrium (VLE) of two binary systems of (methanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol) and (2,2,3,3-tetrafluoro-1-propanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol) was determined by a modified Rose type equilibrium still. Both binary

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systems were confirmed by the Herington [24] area method and the point to point van Ness method [25] for thermodynamics consistency test. Two activity coefficient models by Wilson [26] and the non-random two-liquid (NRTL) [27] were used to correlated the measured values. Meanwhile, the binary interaction parameters were obtained that can be used in the optimization and design of the separation process.

2. Experimental

2.1. Materials

The chemicals used in this work were 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol and methanol, all were analytical pure reagents. The 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol were supplied by Shandong Zhongfu Chemical Technology Co., Ltd., and methanol was from Tianjin Fuyu Fine Chemical Co., Ltd., for which the initial mass fractions were 0.999, 0.995, and 0.997, respectively. The purities of those reagents were checked and confirmed by gas chromatography. All reagents were used without further purification. Table 1 shows some relevant detailed information on those chemicals.

2.2. Apparatus and measurements

2.2.1. Density measurements

The measurement of density (ρ) was carried out by an Anton Paar DMA 5000 M densimeter at atmospheric pressure (P) of 101.3 kPa with temperature range from 293.15 K to 342.25 K. The densimeter was calibrated with dried air and ultrapure water before the test of samples. The automatic control equipment maintained the temperature fluctuation of the tested systems within ±0.01 K. The uncertainty for density in this work was within ±0.001 g·cm^{-3}.

2.2.2. Viscosity measurements

The viscosity (η) for all samples was measured by an Anton Paar AMVn viscometer within the temperature ranging from 295.65 K to 333.15 K at 101.3 kPa. The viscometer maintained the efflux deflected time within ±0.001 s and the temperature fluctuation within ±0.05 K. The uncertainty of viscosity in the present work was ±0.07 mPa·s.

2.2.3. Vapour-liquid equilibrium measurements

The VLE measurement of two binary systems of (methanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol) and (2,2,3,3-tetrafluoro-1-propanol + 2,2,3,3,4,4,5,5-octafluoro-1-pentanol) was carried out in a modified Rose type still, which was described in detail in previous work [28,29]. During the measurement, both the condensed vapour phase and the liquid phase was recirculated consecutively to provide intimate contact of the phases so that the equilibrium state was achieved as soon as possible. The temperature was measured by using a precise mercury thermometer, Tianjin Glass Instrument Factory, and the pressure was kept by a U-shaped differential manometer, Nanjing Hengyuan Automatic Gauge Co., Ltd. With the two-step automatic control system, the fluctuation was controlled within 0.03 kPa. The uncertainties of temperature and pressure were ±0.3 K and ±0.05 kPa, respectively. In each measurement, the mixture was gradually heated until a condensation reflux rate of 2–3 drops per second was achieved. Then the temperature of the system was recorded every 5 min until there was no change of the temperature, the constant temperature was kept for at least 50 min to reach the equilibrium state. Meanwhile, the samples of the condensed vapour and liquid phases were withdrawn into a gas chromatograph vials immediately for analysis. The gas chromatograph vial was filled as much as possible to avoid any loss of the volatile component.

The gas chromatograph (SP 6890) was equipped with a capillary column (DB-WAX, 30 m × 0.53 mm × 1.00 μm, Agilent Technologies) and a thermal conductivity detector (TCD), Shandong Lunan Ruihong Chemical Instruments Co., Ltd. The carrier gas was high-purity hydrogen which the purity was 0.99999, and its flow rate was 12 mL·min^{-1}. For analysis, the initial oven temperature was kept 413.15 K. Both the injector and the detector were set at 443.15 K. All the samples of the two phases were analysed at least three times, then the average value was adopted. For each binary sample, the peak area of gas chromatography was calibrated through five standard mixtures of known composition which were prepared gravimetrically to cover the whole composition range. The gravimetric uncertainty was ±0.0001 g. In each experiment, the condensed vapour and liquid phases were tested more than three times to reduce the errors and ensure that a high accuracy of the VLE results could be attained. With the workstation software N2000 developed by Zhejiang University, the compositions of all the samples were determined. The mole compositions were checked by those obtained by mass. The uncertainty of mole fraction was ±0.001.

3. Results and discussion

3.1. Density

The experimental density for 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol were determined at pressure of 101.3 kPa which is shown in Table 2 and plotted in Fig. 1. Experimental values of density increase from 1.4010 to 1.4932 g·cm^{-3} for 2,2,3,3-tetrafluoro-1-propanol and from 1.5960 to 1.6742 g·cm^{-3} for 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, respectively, within the temperature range from 293.15 K to 342.25 K.

Meanwhile, the literature density values for 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol are compared in detail in Fig. 1. For 2,2,3,3-tetrafluoro-1-propanol, there are three points of density reported in the previous literature, which are 1.476 g·cm^{-3} [2], 1.45322 g·cm^{-3} [19] at 298 K, and 1.482 g·cm^{-3} [9] at 298.15 K, respectively. For 2,2,3,3,4,4,5,5-octa fluoro-1-pentanol, only one point of density was reported as 1.6583 g·cm^{-3} [30] at 298.15 K. Compared to the measured values in this work, the density, 1.482 g·cm^{-3} in Takagi's work shows a deviation of 0.0046 g·cm^{-3} for 2,2,3,3-tetrafluoro-1-propanol, and 1.6583 g·cm^{-3} in Terry's work with a deviation of 0.0113 g·cm^{-3} for 2,2,3,3,4,4,5,5-octafluoro-1-pentanol as shown in Fig. 1.

Table 1
Suppliers and Mass Fractions of the Chemical Reagent.

Component	CAS	Suppliers	Mass fraction	Purification method	Analysis method
2,2,3,3-Tetrafluoro-1-propanol	76-37-9	Shandong Zhongfu Chemical Technology Co., Ltd.	0.999	None	GC[a]
2,2,3,3,4,4,5,5-Octafluoro-1-pentanol	355-80-6	Shandong Zhongfu Chemical Technology Co., Ltd.	0.995	None	GC[a]
Methanol	67-56-1	Tianjin Fuyu Fine Chemical Co., Ltd.	0.997	None	GC[a]

[a] Gas chromatograph.