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Measurement and correlation of liquid–liquid equilibrium for the ternary system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water at (298.15, 308.15, and 318.15) K

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ABSTRACT

Ternary liquid–liquid equilibrium (LLE) data of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water were measured at (298.15, 308.15, and 318.15) K under atmospheric pressure. Both the Bachman and the Hand equations were applied to check the reliability of the tie-line data, and their correlation coefficient (R^2) were all close to 1. Meanwhile, the nonrandom two-liquid (NRTL) activity coefficient model was applied to correlate the experimental data, which the results showed good agreement with the measured LLE data, and the binary interaction parameters were regressed. In addition, the distribution coefficients and separation factors were determined by using the experimental data and discussed in detail.

1. Introduction

Fluorinated alcohol is a kind of compound which hydrogen of carbon–hydrogen bond is partially replaced by fluorine. Due to the smaller radius and greater electronegativity of fluorine atoms, the energy of carbon–fluorine bond formation is greater than that of carbon–hydrogen bond. Therefore, fluorine atom added into such alcohol can improve the stability, biological activity and surface activity of the alcohol significantly. And it is also shown some different characteristics from the traditional fatty alcohols, which has extensive application in the synthesis of medicine, pesticide [1], dyestuff [2], variety of solvents and surfactant [3–5]. 2,2,3,3,4,4,5,5-Octafluoro-1-pentanol is one of an important aliphatic fluorine-containing intermediates.

Generally, the industrial production method of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol is telomerization with tetrafluoroethylene monomer and methanol [6–8]. After telomerization, a mixture contained 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, methanol, sodium fluoride, barium fluoride and a small amount of oligomer can be obtained. A large amount of organic compounds of the mixture such as methanol, 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol could be separated by distillation. After that, a residue mainly consists of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, oligomer and inorganic solid is left. Considering methanol is not only the synthesis material, but also has good dissolution ability for the fluorine alcohol-containing compounds, it is selected as an extractant to separate the residue [9,10], which can avoid introducing other material into the mixture. Up to now, few works of the VLE and LLE of systems that contained fluorinated alcohol have been reported in previous literature [11–13]. Only Dovyborov [13] investigated the ternary systems of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + acetic acid + water. Therefore, the liquid–liquid equilibrium data of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water and the parameters of the related thermodynamic model [14] are needed.

In this work, ternary liquid–liquid equilibrium data of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water was carried out at T = (298.15, 308.15, and 318.15) K under atmospheric pressure. And the phase diagram was classified as Treybal's type I phase diagram [15]. The reliability of the experimental data was confirmed by using the Bachman [16] and Hand [17] equations and the nonrandom two-liquid (NRTL) activity coefficient model [18] was selected to correlate the experimental data.

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2. Experimental section

2.1. Materials

The chemicals used in this experiment were 2,2,3,3,4,4,5,5-octafluoro-1-pentanol and methanol. Both of them were analytical pure reagents and their initial mass fraction were not less than 0.995. Deionized water was used throughout all the experiments. The purity of the reagents was checked and confirmed by gas chromatography. All reagents were used without further purification. The suppliers and mass fraction of the used chemical reagents and relevant detailed information are shown in Table 1. The 2AWJ refractometer (Shanghai experimental instrument Co., Ltd.) was used to measure the refractive index of all chemical reagents at 293.15 K and was calibrated by water, which the uncertainty of all chemicals was ±0.0002. All the measured and literature values are shown in Table 2.

2.2. Apparatus and procedures

Liquid–liquid equilibrium of the ternary system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water were determined by using tie-line method [19] at different temperatures. During the experiments, the ternary mixtures should be full of the equilibrium cell for the purpose of avoiding the volatilization of the mixtures. To cover the entire two-phase region as much as possible, usually the volume of water was fixed, and the other two components were increased and decreased correspondingly [20]. The change interval was 1–2 mL each time.

The apparatus were reported in the previous work [21], which mainly include a volume of 100 mL round-bottom flask (the equilibrium cell), a magnetic stirrer (JJ-1-40W, produced by Changzhou Danrui experimental instrument equipment Co., Ltd.), a super thermostatic water bath (SYC-15C, produced by Nanjing Huchuan electronic equipment Co., Ltd.) whose temperature measurement accuracy was 0.01 K and a gas chromatograph (Lunan GC SP-6890). After mix the ternary samples in the round-bottom flask, the ternary mixture was vigorously agitated by the magnetic stirrer for 2 h and then settled for about 14 h that make the system reach an equilibrium state. And all the procedures were operated in a constant temperature by using the super thermostatic water bath. Before the two phases reached the equilibrium state, any disturb from the outside should be avoided. At last, a syringe was used to take both the aqueous and the organic phase samples, respectively, and the samples were transferred into a 2 mL chromatograph vials immediately. Then the compositions of all samples were analyzed by a gas chromatography (Lunan GC SP-6890). The samples of both layers were analyzed three times, and average value was adopted. The descriptions of the gas chromatography analysis conditions are presented in details in Table 3.

The peak area of the sample was determined by gas chromatography with the N2000 chromatography workstation software which was developed by Zhejiang University. And it was calibrated by gravimetrical weighed mixtures, which the gravimetrical weighed standard uncertainty was 0.0001 g. The composition of three known ternary mixtures were prepared with mass and used to test and verify the reproducibility by the gas chromatography. The mole compositions were compared with those obtained by mass, and the uncertainty of measurement was 0.0006.

3. Results and discussion

3.1. LLE experimental data and reliability results

The tie-line data of the ternary system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, methanol and water were determined at T = (298.15, 308.15, and 318.15) K under atmospheric pressure. All compositions are expressed in mole fraction and listed in Table 4. In addition, the subscript 1, 2 and 3 represent 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, methanol and water and the superscript I and II refer to the aqueous phase and the organic phase, respectively. The corresponding equilibrium phase diagrams are shown in Figs. 1–3.

From the figures, it is shown that the ternary LLE phase diagrams of the system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, methanol and water belong to type I [15]. Compared with Figs. 1–3, the biphasic region for the ternary system was quite small, and the temperature had a slight effect on the immiscibility region. The biphasic region decreased slightly when the temperature increased from 298.15 K to 318.15 K. The phase diagrams also showed that the mutual solubility of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol and water increased with the increasing the fraction of methanol.

The reliability of the measured LLE experimental data at each temperature were confirmed by the Bachman [16] and Hand [17] equations, and the two equations are shown as the eqs (1) and (2):

$$x_1^{II} = a + b\left(\frac{x_1^{II}}{x_3^{I}}\right) \tag{1}$$

$$\ln\left(\frac{x_2^{I}}{x_3^{I}}\right) = a + bln\left(\frac{x_2^{II}}{x_1^{II}}\right) \tag{2}$$

where x_3^{I} is the mole fraction of water in the aqueous phase, x_1^{II} is the mole fraction of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol in organic phase and x_2^{I}, x_2^{II} are the mole fractions of methanol in aqueous phase and in organic phase, respectively, a and b are parameters to be regressed. All the experimental data were checked, and the correlation coefficients (R^2) were all closed to 1 that indicated the reliability of the tie-line data was good. The calculated results are listed in Table 5 and shown in Figs. 4 and 5.

Since distribution coefficient and separation factor are important for the liquid–liquid extraction, both of them were determined from the measured LLE data. Distribution coefficient (D) and separation factor (S) are presented as follows [22,23]:

$$D_i = \frac{x_i^{II}}{x_i^{I}} \tag{3}$$

$$S = \frac{D_1}{D_3} \tag{4}$$

where x_i^{I} and x_i^{II} are the mole fraction of component i in the

Table 1
Suppliers and mass fractions of the chemical reagent.

Component	CAS	Suppliers	Mass fraction	Purification method	Analysis method
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	>0.995	None	GC[a]

[a] Gas chromatograph.