Isobaric vapor−liquid equilibrium of trifluoroacetic acid + water, trifluoroacetic acid + ethyl trifluoroacetate and ethyl trifluoroacetate + ethanol binary mixtures

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ABSTRACT

Vapor−liquid equilibrium data for ethyl trifluoroacetate + trifluoroacetic acid, ethyl tri-fluoroacetate + ethanol, and trifluoroacetic acid + water at the pressure 101.3 kPa were measured with a modified Rose still. The thermodynamic consistency of the VLE data was confirmed by Herrington's method. The VLE data were correlated by the NRTL and Wilson models with satisfactory results, and the interaction parameters of these mixtures were estimated.

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1. Introduction

Ethyl trifluoroacetate (ETFA) contains a trifluoroacetyl group, which can be used as an amines protecting group in organic synthesis [1]. So ETFA has been recognized as an important fine chemical intermediate and widely used for preparing a variety of pesticides, pharmaceuticals, dyes, and liquid crystal. ETFA can also be used as solvent in the manufacture of other fine chemicals [2]. There are several methods which can be used to produce ETFA. ETFA can be synthesized through the substitution reaction of tri-fluoroacetyl chloride with ethanol (EtOH), where a substantial stoichiometric excess of trifluoroacetyl chloride is used [3]. ETFA can also be prepared through the esterification reaction of tri-fluoroacetic acid (TFA) with EtOH by using a liquid hydrofluoric acid as a catalyst. Taking account of the toxicity and cost, however, the esterification reactions of TFA with EtOH using homogeneous cat-alysts has become the main method for producing ETFA nowadays.

Because the esterification reaction is a typical equilibrium-limited reaction, the conversion rate of TFA is strongly limited by thermodynamic equilibrium constrains. So the separation and pu-rification process (distillation was preferred) will be adopted in order to obtain ETFA with desired purity. As a common separating process, accurate vapor−liquid equilibrium (VLE) data are very important and necessary for the design and operation of the distillation [4−6]. Up to now, however, the VLE data for this system except EtOH−H₂O have never been reported in the literature.

Therefore, in this work isobaric VLE data for three binary mix-tures, including ETFA + TFA, ETFA + EtOH, and TFA + H₂O, were measured at 101.33 kPa with a modified Rose still. Then, both NRTL and Wilson models were used to correlate the experimental VLE data.

2. Experimental

2.1. Chemicals

Both trifluoroacetic acid (99.5%, mass%) and ethyl tri-fluoroacetate (99.0%, mass%) were provided by Aladdin Co., Ltd. Ethanol (99.7%, mass%) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. The purity of the chemicals was verified by gas chromatography and no appreciable peaks of impurities were detected. The water used was purified from an ultrafiltration sys-tem in our laboratory. The density, refractive index, and normal boiling point of the chemicals were determined by an density meter (Anton Paar DMA-58), an Abbe refractometer (Atago 3T), and

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the modified Rose still, respectively. The physical properties of the chemicals used in this work are listed in Table 1. It can be found that the measured physical property data of the chemical were basically consistent with literature values. So no further purification was performed for these chemicals.

2.2. Apparatus and procedure

Vapor—liquid equilibrium data were measured by the double circulating vapor—liquid equilibrium still (a modified Rose still) at atmospheric pressure. Details of this apparatus were given in our previous studies [5,22]. In a typical experiment, pure component 1 (light component) was introduced into the equilibrium cell firstly. Equilibrium between vapor and liquid phases was assumed when the equilibrium temperature remained constant for at least 30 min. Then, the readings of pressure and temperature of the equilibrium cell were recorded manually, and the vapor and liquid samples were withdrawn simultaneously for analysis. Next, a predetermined volume of liquid was withdrawn from the equilibrium cell and an equal volume of pure component 2 (heavy component) was added the cell. The vapor and the liquid phases were continuously circulating to provide intimate contact of the two phases and ensure that equilibrium can be established. The pressure and temperature of the equilibrium cell were read, and the vapor and liquid samples were withdrawn and analyzed during all runs. Repeating the above procedures, the additions of component 2 were continued until the target composition was reached. The concentration of ETFA and EtOH were analyzed by Gas Chromatography with dioxane as internal, while the TFA concentration was checked by titration with 0.1 N sodium hydroxide using phenolphthalein as indicator. Each measurement was repeated 3 times and averaged as the final result.

The equilibrium temperature was determined with a calibrated precision thermometer with maximum error of 0.1 K. The pressure in the apparatus was measured by means of a precision barometer with an uncertainty of 0.1 kPa (Jiangshan Glassware Instrument & Meter Factory, DYM3, China). Because the atmospheric pressure may change a little during the experiments, the equilibrium temperature was corrected to 101.3 kPa according to the method proposed by Hiaki and Kawai [23].

2.3. Reliability test of the experimental apparatus

To check the reliability of the experimental apparatus, the VLE data of methanol + isopropanol binary mixture at 101.3 kPa were determined. The experimental and literature data are presented in Fig. 1. The average relative deviations for equilibrium temperature and vapor molar fraction are 0.02% and 0.88%, respectively. The result shows that the validation data are in good agreement with the literature values [5], which illustrates that the data obtained by this method and the apparatus are repeatable and reliable.

3. Result and discussion

3.1. Vapor liquid equilibrium measurements

The VLE data for TFA—H$_2$O, ETFA—EtOH, and ETFA—TFA binary systems were measured at 101.3 kPa and presented in Tables 2–4, respectively. The T—x—y diagrams of three binary systems are showed in Figs. 2–4, respectively. Notice that there all have intercrossing points between the bubble point curve and the dew point curve over the entire composition range in three T—x—y diagrams, which demonstrates that all three binary systems exhibit deviations from Raoult's law and present azeotropic behaviors.

Table 1
Physical properties of pure compounds.

Compound	T_b (K) (101.3 kPa)		ρ (g/cm3) (293.15 K)		n_D (293.15 K)	
	This work	Literature	This work	Literature	This work	Literature
ETFA	335.65	335.15 [7] 334.85 [8]	1.1897	1.1900 [7] 1.1913 [9]	1.3086	1.3079 [10] 1.3077 [11]
EtOH	351.55	351.65 [12] 351.45 [13]	0.7891	0.7893 [14] 0.7898 [15]	1.3634	1.3618 [16]
TFA	344.91	344.93 [17]	1.4891	1.4890 [18]	1.2852	1.2850 [19]
H$_2$O	373.15	373.15 [20]	0.9981	0.9982 [21]	1.3332	1.3330 [19]

$u(T_b) = \pm 0.1$ K; $u(\rho) = \pm 0.0001$ g/cm^3 ; $u(n_D) = \pm 0.0001$.