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Vapor–liquid equilibrium in the ternary system isobutyl alcohol + isobutyl acetate + N, N-dimethyl acetamide and the binary systems isobutyl alcohol + N, N-dimethyl acetamide, isobutyl acetate + N, N-dimethyl acetamide at 101.3 kPa

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ABSTRACT

The isobaric Vapor-Liquid Equilibrium (VLE) data at 101.3 kPa were measured for the binary systems isobutyl alcohol + N, N-dimethyl acetamide (DMAC), isobutyl acetate + N, N-dimethyl acetamide and the ternary system isobutyl alcohol + isobutyl acetate + N, N-dimethyl acetamide using an all glass dynamics recirculating still. The isobutyl alcohol + DMAC system exhibits negative deviation from Raoult's law and isobutyl acetate + DMAC system deviates positively from ideal solution. The thermodynamic consistency of the binary VLE data was checked by Herington method and Wisniak point-to-point method. The NRTL, UNIQUAC and Wilson activity coefficient models were used to correlate the binary VLE data in order to obtain the binary interaction parameters which were used to predict ternary VLE data. The predicted results agree well with the experimental data. The results indicate that the solvent DMAC can greatly enhance the relative volatility of isobutyl acetate to isobutyl alcohol, and azeotrope of isobutyl acetate and isobutyl alcohol will be broken if the mole fraction of DMAC is greater than 0.361. The effects of the solvents 1-hexanol, butyl propionate (BUP), N, N-dimethyl formamide (DMF) and N, N-dimethyl acetamide (DMAC) were compared, and the selectivity of DMAC was the largest. The solvent DMAC is a promising extractive agent for the separation of mixtures of isobutyl alcohol and isobutyl acetate by extractive distillation.

1. Introduction

To separate the azeotrope, many strategies have been adopted, such as azeotropic distillation [1], extractive distillation [2–6], pressure-swing distillation [7–9] and membrane separation. Among them extractive distillation is widely used in industry. In extractive distillation process, a third component (called an entrainer or a solvent) is utilized to change the relative volatility of the components to be separated. Solvent selection is the key point of the extractive distillation process.

Isobutyl acetate, belonging to the family of carboxylic acid esters, is a clear colorless liquid with a fruity odor and is found in alcoholic beverages, fruits, brandies and fortified wines. Isobutyl acetate is widely used in pharmaceutical [10] and chemical industries [11] such as inks, industrial cleaners, coatings, degreasers and adhesives. Isobutyl acetate forms a minimum boiling point azeotrope with isobutyl alcohol (isobutyl alcohol 0.884, mole fraction) at 101.3 kPa [12], so it cannot be separated by conventional distillation. Extractive distillation is a good choice to achieve this. Several solvents have been chosen to separate the azeotropic system in the open litearatures [13–15], but the increase of relative volatility was not obvious. The computer-aided molecular design was applied to selecte solvents for extractive distillation and N, N-dimethyl acetamide (DMAC) was chosen as a more effective solvent as the result.

N, N-dimethyl acetamide (DMAC; CAS: 127-19-5) is a potent

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industrial solvent and also an intermediate for many organic reactions in the synthesis of agrochemicals, pharmaceuticals, and fine chemicals [16,17]. DMAC is highly soluble in a lot of chemicals such as water, aromatic compounds, esters, ketones, alcohols, ethers, benzene and trichloromethane etc. DMAC has high boiling point, high flash point, high thermal stability and chemical stability. Because of these merits, it is widely used as solvent in the open literature [18–20]. It is reported that DMAC is a promising solvent for separating the azeotropeic mixtures of alcohol and acetate [18], which presents high selectivity and fine solubility with alcohols and esters, good thermal stability, low toxicity and low corrosiveness. Because of the properties above, DMAC was selected as the solvent to separate isobutyl alcohol and isobutyl acetate here.

In this paper, the isobaric VLE data for isobutyl alcohol + DMAC, isobutyl acetate + DMAC and isobutyl alcohol + isobutyl acetate + DMAC have been measured. Thermodynamic consistency tests for all of the binary VLE data were carried out by Herington area method [21,22] and Wisniak point-to-point method [23], and ternary VLE data was carried out by Wisniak point-to-point method. The binary system VLE data were correlated with NRTL [24], UNIQUAC [25] and Wilson [26] models. The correlated binary parameters were used to predict the ternary VLE behavior and compared with the measured data.

2. Experimental section

2.1. Materials

The chemicals isobutyl alcohol, isobutyl acetate and DMAC used in this work were analytical reagents (AR). The corresponding information was listed in Table 1. They were analyzed by gas chromatography (GC) with a FID detector (Beifen Ruili SP-1000) and the mass fraction were greater than 0.995. The water content determined by Karl Fischer titration was below 500 ppm. The normal boiling point (T_b) at 101.3 kPa and density (ρ) at 298.15 K, 101.3 kPa of these components are given in Table 2. The density was measured by the Anton Paar DMA-58 density meter with a combined expanded uncertainty of 0.0008 g/cm^3 and the boiling point was measured by all glass dynamics recirculating still at 101.3 kPa using a calibrated thermometer with a standard uncertainty of 0.02 K.

2.2. Apparatus and procedure

An all glass dynamic recirculating still was used to measure the VLE for both binary and ternary systems, and the details of the apparatus and measurement procedure were described in our previous papers [27–29]. The pressure of the system was maintained 101.3 kPa by a gas buffer. The pressure was measured by a manometer with a standard uncertainty of 0.1 kPa. The temperature was determined with a standard and calibrated thermometer with a standard uncertainty of 0.02 K. When the temperature fluctuation of the still was within 0.1 K over 30 min, the vapor liquid equilibrium was reached and the vapor phase and liquid samples were taken respectively at the same time.

2.3. Sample analysis

The condensed vapor and liquid samples were analyzed by gas chromatograph (Beifen Ruili SP-1000) with a FID detector. The GC is equipped with a WEL-30 GC capillary column (50 m in length, 0.32 mm in diameter, and 5.0 μm in thickness, chromatographic support: 100% dimethyl polysiloxane, provided by Welch Materials, Inc, Shanghai China.). The temperature of column, injector and detector were 393.15 K, 473.15 K and 483.15 K respectively. The flow rate of carrier gas (nitrogen) was 30 mL/min, and the flow rates of hydrogen and air were 30 mL/min and 300 mL/min, respectively.

3. Result and discussion

3.1. Experimental data

The isobaric VLE data of the systems isobutyl alcohol (1) + DMAC (3), isobutyl acetate (2) + DMAC (3) and isobutyl alcohol (1) + isobutyl acetate (2) + DMAC (3) measured at 101.3 kPa and activity coefficients γ_1, γ_2, γ_3 calculated from the experimental VLE data are listed in Tables 3–5. The activity coefficients presented in Tables 3 and 4 demonstrate that the isobutyl alcohol (1) + DMAC (3) system has negative deviation from ideal solution and the isobutyl acetate (2) + DMAC (3) system shows positive deviation from ideal solution and no additional azeotropes present.

3.2. Thermodynamic consistency test of experimental data

The relationship of vapor and liquid equilibrium systems can be expressed as follows:

$$\widehat{\varphi}_i P y_i = P_i^s x_i \gamma_i \varphi_i^s exp\left[\frac{V_i^L(P-P_i^s)}{RT}\right] \quad (\mathrm{i}=1,2,\ \ldots\mathrm{n}) \tag{1}$$

Where x_i and y_i are the mole fractions of component i in the liquid and vapor phase, respectively; P is the equilibrium pressure; γ_i is the activity coefficient of component i in liquid phase; V_i^L is the pure liquid molar volume; R is the universal gas constant; $\hat{\varphi}_\mathrm{i}$ is the vapor-phase fugacity coefficient; φ_i^s is the pure component fugacity coefficient at saturated state; P_i^s is the saturation vapor pressure of component i at equilibrium temperature T, which was obtained by the extended Antoine equation

$$\ln(P_i^s) = C_{1,i} + C_{2,i}/(T + C_{3,i}) + C_{4,i}T + C_{5,i}\ln T + C_{6,i}T^{C_{7,i}} \tag{2}$$

The value of constants $C_{1,\ i}$-$C_{7,\ i}$ illustrated in Table 6 are taken from Aspen plus V8.6 physical properties databank and the units of P_i^s and T are kPa and K, respectively. Under atmospheric pressure, the poynting factor $exp\left[\frac{V_i^L(P-P_i^s)}{RT}\right]$ approximately equals to 1 and vapor phase is treated as ideal gas, so φ_i^s and $\widehat{\varphi}_i$ are assumed to be 1. Therefore, Eq. (1) can be simplified as:

Table 1
The Source, Purity, Water content and Analysis method for isobutyl alcohol, isobutyl acetate and DMAC.[a].

Components	Source	Purity(mass%)	Water content (mass%)	Analysis method
isobutyl alcohol	Gauangfu. China	99.8	0.02	GC[b] KF[c]
isobutyl acetate	Gauangfu. China	99.8	0.03	GC[b] KF[c]
DMAC	Gauangfu. China	99.9	0.01	GC[b] KF[c]

[a] DMAC = N, N-dimethyl acetamide.
[b] GC = gas chromatography, the standard uncertainty u is $u = 0.1$(mass%).
[c] KF = Karl Fischer titration, the standard uncertainty u is $u = 0.01$(mass%).