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Liquid–liquid equilibrium for the ternary system of isopropyl acetate + 2-propanol + glycerol at different temperatures under atmospheric pressure

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A B S T R A C T

The aim of this work is to analyze the possibility of separating isopropyl acetate and 2-propanol, an azeotropic system, by using glycerol. Thus, liquid–liquid equilibrium (LLE) data for the ternary system of isopropyl acetate + 2-propanol + glycerin have been determined at various temperatures $T = (298.15, 308.15, 318.15)$ K under atmospheric pressure. The consistency of the experimental data was verified by the mass balance. The extraction capacity was evaluated throughout the distribution coefficient and selectivity parameters. Phase diagrams have been obtained at each temperature. To facilitate the manipulation of the obtained data for industrial applications, the NRTL and the UNIQUAC models have been applied to correlate the experimental data and low deviations were obtained.

1. Introduction

Isopropyl acetate is an important material with a wide variety of manufacturing uses in the chemical industry. It has really good miscibility with other solvents like alcohol, ether and ketone, and is also described as an effective solvent for many synthetic and natural resins [1]. As a result, isopropyl acetate has been widely used in the fields of coating, printing ink, adhesive agents, etc. [2].

Generally, isopropyl acetate was produced from the esterification of acetic acid and 2-propanol [3]. Isopropyl acetate and the residual 2-propanol form an azeotropic mixture in this process, which is difficult to be separated by the traditional distillation. Several methods, including reactive distillation, extractive distillation, azeotropic distillation, liquid–liquid extraction and membrane separation, have been proposed to separate the azeotrope or close boiling mixtures [4–7]. As for the azeotropic mixtures containing isopropyl acetate and 2-propanol, Hong et al. [8] separate the ternary mixtures water + isopropyl acetate + 2-propanol through reactive distillation. Teodorescu et al. [9] studied the phase equilibrium of the quaternary system water + 2-propanol + acetic acid + isopropyl acetate. Andreatta and coworkers [10,11] used the ionic liquid as an azeotrope breaker in extractive distillation. In comparison to other separation processes, liquid–liquid extraction shows the advantage of being less energy intensive. Moreover, high separation efficiency can be reached with a suitable solvent [12]. However, no report about the extraction separation of isopropyl acetate and 2-propanol can be found so far. Selecting a suitable and applicable extractive solvent is of great importance for a cost-effective separation process. Preliminary studies showed that glycerol could be a potential solvent because it was completely miscible with 2-propanol but almost immiscible with the other one. This feature is mainly due to the strong polarity and the ability to act as a proton receptor that can form hydrogen bonds with 2-propanol.

To evaluate the feasibility of glycerol as an extractive solvent, the liquid–liquid equilibrium (LLE) data for isopropyl acetate + 2-propanol + glycerol were measured at various temperatures $T = (298.2, 308.15, \text{and } 318.15)$ K under atmospheric pressure. The mass balance was applied to ascertain the consistency of the experiment. The NRTL and the UNIQUAC models were used to correlate the experimental data for the studied ternary system.

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Additionally, the capacity of glycerol as an extractive solvent was analyzed by the solute distribution coefficient and the selectivity.

2. Experimental

2.1. Materials

In this work, isopropyl acetate, 2-propanol and glycerol were used. The source, CASRN, mass fraction purity and analysis method of all chemicals are listed in Table 1. Purities of the materials were determined by a gas chromatography (GC) equipped with a flame ionization detector. In addition, the water contents were measured by Karl Fischer titration and no appreciable water was detected. All the materials were used without further purification.

2.2. Apparatus and procedure

The LLE experiment was carried out in a 30 mL glass cell with a magnetic stirrer in it. The experimental method was described in literature [13–15]. In this study it was specified as follows: The temperature of the system was controlled by a refrigerated heating circulator (Julabo FP45-HF, German, temperature stability ±0.01 K) and measured by a platinum resistance thermometer Pt-100 (calibrated with an accuracy of 0.01 K). In each measurement of the LLE data, 10 ml mixture of isopropyl acetate and 2-propanol plus 10 ml glycerol were added into the glass cell and then stirred vigorously by the magnetic stirrer. Through a series of comparative tests, the stirring time was chosen to be 2 h to get a sufficient mixing for the extraction equilibrium. The mixture was settled for 5 h to ensure a complete separation of the two phases. Then the samples of the upper and lower phase (isopropyl acetate-rich and glycerol-rich phase) were carefully collected by syringes at least three times for the composition analysis.

2.3. Sample analysis

The collected samples were analyzed by gas chromatography (Agilent Technologies 6890N). The gas chromatography was equipped with a flame ionization detector and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The carrier gas was nitrogen with the purity of 0.99999 provided by Liufang industrial gases co., LTD, Tianjin. The operation condition was as follows: The injector temperature and detector temperature were 573 K and 583 K, respectively. The column temperature was programmed at 310 K for 3 min firstly, then increased to 563 K at a rate of 45 K min^{-1} and held for 1 min. The calibration factor was obtained to correct the measured values. The accuracy of the analytical method was tested by known samples of mixtures and the maximum relative error of the mass fraction did not exceed 0.003.

3. Results and discussion

3.1. Experimental data

The LLE data for isopropyl acetate (1) + 2-propanol (2) + glycerol (3) system at various temperatures T = (298.15, 308.15, and 318.15) K under atmospheric pressure are listed in Table 2. Triangular phase diagrams with tie-lines are shown in Fig. 1. The experimental data show that the ternary system is a type-I system. The large two-phase region in Fig. 1 enables a large operation range for the extraction process. The mutual solubility of isopropyl acetate and glycerol increases with the addition of 2-propanol. The increasing temperature from 298.15 K to 318.15 K does not show obvious effect on the equilibrium of the ternary system. But it is worthy of mention that increasing temperature will decrease the viscosity of glycerol significantly. According to the research of Secur et al. [16], the viscosity of glycerol decreases from 1005 mPa s to 550 mPa s as the temperature increasing from 293.15 K to 323.15 K, which provides convenience for operation.

The consistency of the LLE data was verified by the method proposed by Marcilla et al. [17]. According to the mass balance between the initial mixture and the two conjugated phases (extract phase and raffinate phase), three independent mass balance equations can be written as follows:

$$M'(x_1)' = M_{\mathrm{I}}(x_1)_{\mathrm{I}} + M_{\mathrm{II}}(x_1)_{\mathrm{II}} \tag{1}$$

$$M'(x_2)' = M_{\mathrm{I}}(x_2)_{\mathrm{I}} + M_{\mathrm{II}}(x_2)_{\mathrm{II}} \tag{2}$$

$$M'(x_3)' = M_{\mathrm{I}}(x_3)_{\mathrm{I}} + M_{\mathrm{II}}(x_3)_{\mathrm{II}} \tag{3}$$

where M' is the mole of initial mixture, M_{I} and M_{II} are the mole of the isopropyl acetate-rich phase and the glycerol-rich phase respectively. $(x_i)'$ is the mole fraction of component i in the initial mixture, while $(x_i)_{\mathrm{I}}$ and $(x_i)_{\mathrm{II}}$ are the mole fraction of component i in the isopropyl acetate-rich phase and the glycerol-rich phase respectively, i = 1, 2, 3.

The values of M_{I} and M_{II} were calculated by solving these overdetermined linear equations with least-squares method. The relative error RE of the mass balance was determined by the following equation:

$$RE = \frac{M_{\mathrm{I}} + M_{\mathrm{II}} - M'}{M'} \tag{4}$$

The maximal RE is less than 1%. From Fig. 1, one can also conclude that the experimental data is reliable because the points of the overall compositions agree the tie line with great accuracy.

3.2. Evaluation of the extractive solvent

The distribution coefficient (β) and the selectivity (S) are used to evaluate the extraction capacity of glycerol. These parameters are defined as follows:

$$\beta = \frac{x_2^{II}}{x_2^{I}} \tag{5}$$

Table 1
Experimental chemicals.

Chemical	Source	CASRN	W(Mass fraction)	Analysis method
Isopropyl Acetate	Yuanli, China	108-21-4	0.990	GC[a], KF[b]
2-Propanol	Yuanli, China	67-63-0	0.999	GC[a], KF[b]
Glycerol	Yuanli, China	56-81-5	0.995	GC[a], KF[b]

[a] Gas chromatography.
[b] Karl Fischer titration.