



Determination and modeling for solid–liquid phase equilibrium of ternary caprolactam + cyclohexanone oxime + methyl tert-butyl ether system



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ABSTRACT

The solid–liquid equilibrium (SLE) for ternary system of caprolactam + cyclohexanone oxime + methyl tert-butyl ether were determined at three temperatures of (278.15, 293.15 and 308.15) K under pressure of 101.2 kPa. Three isothermal phase diagrams of the system were constructed based on the measured mutual solubility data. There were two pure solids formed in the ternary phase diagram, including pure caprolactam and pure cyclohexanone oxime, which were identified by the method of Schreinemakers' wet residue. At each temperature, the phase diagram contained three crystallization regions (which corresponded to caprolactam, cyclohexanone oxime, and a mixture of caprolactam and cyclohexanone oxime), two crystallization curves, and one co-saturated point. The crystallization field of caprolactam was larger than that of cyclohexanone oxime. The NRTL model was employed to correlate and calculate the ternary phase diagram. The calculated ternary phase diagram with the NRTL model agreed well with the experimental ones. The solid–liquid phase equilibrium and phase diagram for the ternary system of caprolactam + cyclohexanone oxime + methyl tert-butyl ether could provide basis for the purification process of caprolactam.

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1. Introduction

Caprolactam is an important raw material for producing of Nylon 6 fiber and Nylon 6 resin [1,2]. Up to date, many methods have been developed for the manufacture of caprolactam [3–8]. Most of caprolactam is produced from cyclohexanone, which is first converted to its oxime, and then treated the oxime with acid to obtain caprolactam [5,6]. The other main production process of caprolactam in industrial scale involves formation of oxime from benzene, toluene and cyclohexane through the beckmann rearrangement [3,7,8]. During the production process, no matter which method is used, the impurity, cyclohexanone oxime, is brought to the product of caprolactam through the intermediate by-products [9–11]. The quality index for caprolactam is very rigorous because even a small amount of impurity significantly affects the physical–mechanical properties of Nylon 6 [12–14]. For example, the presence of 0.1% (mass fraction) cyclohexanone oxime will cause a considerable decrease in the relative viscosity of

polycaprolactam [14]. At present, the crude product of caprolactam is purified via multistage distillation and extraction in industrial process, which are highly energy-demanding separation operations to remove these impurities. Recently an adiabatic evaporative cooling crystallization procedure for the system of caprolactam–water was proposed by Diepen et al. [15]. Solvent crystallization is an attractive method for purifying the caprolactam from its crude product in industrial manufacturing process which leads to the product with high purity [16,17]. Some organic solvents have shown potential uses in purification of caprolactam, especially methyl tert-butyl ether [18,19].

In the design and optimization of solvent crystallization process, the solubility data and reliable phase diagrams of binary and multicomponent mixtures are of great importance. In the literatures, although the solubility of caprolactam and cyclohexanone oxime in several pure organic solvents including methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol, and 1-butanol are reported [18,19], no further study is made on solid–liquid equilibrium and phase diagrams for the ternary system of caprolactam + cyclohexanone oxime + methyl tert-butyl ether at different temperatures. In order to provide guidance and basic data

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for designing the crystallization process which is employed to develop the optimal crystallization process for caprolactam purification, the main object of this investigation is to study and generate the ternary phase diagrams for the ternary caprolactam + cyclohexanone oxime + methyl tert-butyl ether system at (278.15, 293.15 and 308.15) K by using the method of Schreinemakers' wet residue [20–22] and indicate the relation between temperature and the ternary phase diagrams.

2. Experimental section

2.1. Materials

Caprolactam and cyclohexanone oxime (0.98 and 0.975 in mass fraction, respectively) were supplied by Aladdin Chemical Reagent Co., Ltd., China. The crude materials were repeatedly purified by the method of recrystallization in ethanol. The mass fraction purity of caprolactam used in phase equilibrium determination is higher than 0.996, and of cyclohexanone oxime, 0.994. The compositions of the two compounds were confirmed by gas chromatography (GC) [18] with a type of Agilent 7890A Infinity GC provided by Agilent Technologies. The solvent methyl tert-butyl ether was purchased from Sinopharm Chemical Reagent Co., Ltd., China with the mass fraction purity of 0.995. No further purification was made before use. The detailed information of the materials is presented in Table 1.

2.2. Apparatus and procedure

The ternary solid–liquid phase equilibrium was studied by employing the method of isothermal solution saturation [21,22]. The pure equilibrium solid phases were identified via the method of Schreinemakers' wet residue [20–22]. A jacketed dissolution vessel with a volume of 50 mL was used to dissolve the excess caprolactam and cyclohexanone oxime in methyl tert-butyl ether during the experiment. The original composition of system was approximately back-calculated based on the “lever rule” and “linking rule”. The components were taken in such ratios that the composition of the resulting saturated mixture fell in the desired portion of the solubility curve. A condenser was attached with the vessel to prevent the solvent from escaping. An isothermal water bath (Blon DCW 4600, Shanghai) was employed to maintain the experimental temperature constant. The real temperature of studied system was displayed by using a precision mercury thermometer inserted into solution of the vessel, and the standard uncertainty of which was 0.01 K. The solution procedure of the mixture was facilitated by stirring at a constant temperature. The system equilibrium was verified by testing repeatedly the composition of caprolactam and cyclohexanone oxime. The equilibration was considered to reach when the composition of solution didn't change. It showed that it would take about 22 h to reach equilibrium. After the ternary system arrived at equilibrium, the stirring was stopped. Thirty minutes later, the saturated liquid and

equilibrium solid adhering some saturated liquid were taken out respectively and analyzed by GC [18]. In order to acquire different compositions of the equilibrium solid phase and equilibrium liquid phase, the components of initial systems were taken by varying the ratio of caprolactam to cyclohexanone oxime. Generally, the selected temperature range should be as wide as possible. However, the boiling point of methyl tert-butyl ether is 328.4 K, the ternary solid–liquid phase equilibrium was studied at three temperatures of (278.15, 293.15 and 308.15) K.

2.3. Analytical method

The samples of wet solid phase and saturated liquid phase containing caprolactam and cyclohexanone oxime were dissolved in methanol, respectively. The mass fractions of caprolactam and cyclohexanone oxime in solution were quantitatively tested by GC [18]. The chromatographic column was a 122-1032G DB-1 capillary column (30 m × 0.320 mm; 0.25 μm film thickness). The temperature of injector was 520 K; and FID, 530 K. Pure nitrogen was used as carrier gas with a flow rate of 2.2 mL min⁻¹. Temperature program was from 323 K (10 min) to 530 K (20 min) at 12 K·min⁻¹. The injection mode was split with a split ration of 50:1. An analytical balance (Mettler Toledo ME) having a standard uncertainty of 0.0001 g was employed in the experiment to determine the mass of wet solid phase and saturated liquid phase. Each test was performed three times to ensure repeatability of the solubility determination, and the average value of corresponding experimental measurements was considered to be the solubility data. The relative stand uncertainty of the test was evaluated to be 0.020 in mass fraction.

3. Thermodynamic background

At a given temperature and pressure, if a solid–liquid system is in equilibrium, the fugacity of liquid equals to that of corresponding solid. For a component *i*, the equilibrium condition can be expressed as:

$$x_i^L \gamma_i^L f_i^L = x_i^S \gamma_i^S f_i^S \quad (1)$$

Here f_i is the fugacity of pure component *i*, and γ_i , the activity coefficient. *L* and *S* represent the liquid state and solid state, respectively.

The solid solubility in a liquid can be described in a very general form by equation (2), which is deduced in accordance with the classical theory of solid–liquid phase equilibrium [23].

$$\ln(x_i \cdot \gamma_i) = \frac{\Delta H_p}{R} \left(\frac{1}{T_p} - \frac{1}{T} \right) - \frac{\Delta C_p}{R} \left(\frac{1}{T_p} - \frac{1}{T} \right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_p}{T} \right) \quad (2)$$

Where ΔH_p is the molar fusing enthalpy at triple-point temperature T_p . ΔC_p is the difference of solute heat capacity between in the solid state and the liquid state. In general, the triple-point temperature is approximately equal to the normal melting point

Table 1

Sources, purity and properties of materials used in this work.

Materials	Molecular weight g mol ⁻¹	Mass fraction purity	Purification method	Sources	T_m	ΔH_m	Analytical method
					K	kJ mol ⁻¹	
Caprolactam	113.18	≥0.996	Recrystallization	Aladdin Chemical Reagent Co., Ltd. (China)	342.31 ^a	16.10 ^a	GC ^c
Cyclohexanone oxime	113.16	≥0.994	Recrystallization		362.2 ^b	12.45 ^b	GC
Methyl tert-butyl ether	88.15	≥0.995	–	Sinopharm Chemical Reagent Co.Ltd (China)	–	–	GC

^a Taken from literature [26].

^b Taken from literature [27].

^c Gas chromatography.

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