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# Solubility of caprolactam in different organic solvents

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ABSTRACT

The solubility of caprolactam in methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol, and 1-butanol was measured at the temperature range from 278.15 K to 313.15 K under atmospheric pressure. The experimental data were correlated by the modified Apelblat equation which fits well with the experimental data. The dissolution enthalpy and entropy were predicted. Moreover, the solubility data were correlated using two local composition models: NRTL 1 and UNIQUAC.



## 1. Introduction

Caprolactam (CPL, CAS registry no. 105-60-2, Fig. 1) is the monomer of Nylon 6, which is an important industrial chemical used for the production of polyamidic synthetic fibers [1]. The specifications for caprolactam are extremely stringent because small amount of impurities greatly affect the physical–mechanical properties of the Nylon 6 [2,3]. Fisyuk and his co-workers found that the presence of only 0.1% cyclohexanone oxime (mass fraction) would cause an appreciable decrease in the relative viscosity of the polycaproamide [4]. Caprolactam is produced from the reaction of benzene, toluene and cyclohexane, mostly through the beckmann rearrangement, during the manufacture processes potential impurities are probably brought into the product of caprolactam through the intermediate byproducts in the reaction and/or the auxiliary operation units [5]. Current industrial processes adopt mainly multistage distillation and extraction, highly energy-demanding separation operations, to eliminate these impurities. Diepen et al. developed an adiabatic evaporative cooling crystallization process of the caprolactam-water system [6]. However, some organic solvents have shown promisingly potential applications in purification of caprolactam, which necessitates the solubility of caprolactam in organic solvents so as to develop optimal crystallization process for caprolactam refining. In this work, the solubility of caprolactam in methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol, and 1-butanol was measured, respectively using an Abbé refractometer in the temperature range of 278.15–313.15 K at atmospheric pressure. The results were fitted with the modified Apelblat equation. The dissolution enthalpy and entropy of caprolactam were predicted from the solubility data. Then the solubility data were correlated by two local composition models: NRTL 1 and UNIQUAC.

## 2. Experimental

### 2.1. Materials

Caprolactam with the purity higher than 99.9% (mass fraction) was supplied by Baling Branch, SINOPEC Co., Ltd. (Yueyang, China). Solid sample of caprolactam was desiccated at 333.15 K, a temperature lower than the melting point of caprolactam about 342 K for 24 h and assumed to be anhydrous and then stored in a desiccator. All the solvents used in this work were of analytical reagent grade, methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol, and 1-butanol with the purity higher than 99% (mass fraction), were purchased from the Tianjin Chemical Reagent Co., China. The physical properties of the pure solvents in this work are listed in Table 1 compared with the literature values. All the solvents were used without further purification.

### 2.2. Apparatus and procedures

The solubility of caprolactam was determined by the balance method. Dried samples were weighted using an analytical

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**Table 1**
Purity levels, densities ($\rho$) and refractive indexes of pure compounds at $T$ = 298.15 K.

| Solvents | Purity[a] | $\rho$ (g cm$^{-3}$) | | $n_D$ | |
|---|---|---|---|---|---|
| | | This work | Literature | This work | Literature |
| Methyl tert-butyl ether | >0.99 | 0.7368 | 0.73529[b] | 1.3664 | 1.3662[b] |
| Isopropyl ether | >0.99 | 0.7186 | 0.71854[c] | 1.3654 | 1.3655[c] |
| 1-Propanol | >0.99 | 0.7995 | 0.7996[e] | 1.3830 | 1.3832[d] |
| 2-Propanol | >0.99 | 0.7851 | 0.7809[e] | 1.3751 | 1.3750[f] |
| 1-Butanol | >0.99 | 0.8084 | 0.8058[e] | 1.3968 | 1.3967[d] |

[a] Purity in mass fraction.
[b] Ref. [21].
[c] Ref. [22].
[d] Ref. [23].
[e] Ref. [24].
[f] Ref. [25].

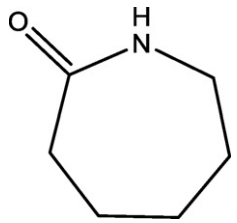


**Fig. 1.** Chemical structure of caprolactam.

balance (Sartorious CP224S, Germany) with an uncertainty of ±0.1 mg. Excess amount of solute was dissolved stirringly in certain solvent in a three necked bottle which was partly immersed in a constant-temperature bath (type GDH-3006, Ningbo Xinzhi Co. Ltd., China) to keep at the desired temperature. A thermometer (with the precision of ±0.02 K) was used to calibrate the inside temperature of the system. After the solid–liquid equilibrium reached, the supernatant was sampled and diluted appropriately to measure the concentration of the caprolactam via the refractive index recorded by an Abbé refractometer (type WAY-2W, Shanghai Precision & Scientific instrument Co. Ltd., China) at about 298.15 K. To make sure whether the method was suitable, we first made a curve of mole fraction $x_1$ (defined by Eq. (2)) of caprolactam vs. refractive index $n_D$ in methyl tert-butyl ether at 298.15 K, the results were shown in Table 2. The precision of the results showed that it was adequate to analyze the concentration of caprolactam in selected solvents. All of the measurements were repeated at least three times, and the mean value is considered as the solubility. The uncertainty of the experimental solubility values $x_1$ is $u_r(x_1) = 0.02$, which results from the uncertainties in temperature measurements, measuring the weight, and the instrumental error of the Abbé refractometer.

**Table 2**
Refractive indexes for caprolactam solutions in methyl tert-butyl ether at $T$ = 298.15 K.[a]

| $x_1$, mole fraction (mol mol$^{-1}$) | $n_D$ | $\Delta x_1/\Delta n_D$ | $x$, mole fraction (mol mol$^{-1}$) | $n_D$ | $\Delta x_1/\Delta n_D$ |
|---|---|---|---|---|---|
| 0 | 1.3664 | | 0.0198 | 1.3700 | 5.6977 |
| 0.0050 | 1.3674 | 5.2083 | 0.0246 | 1.3709 | 5.1064 |
| 0.0100 | 1.3683 | 5.4348 | 0.0294 | 1.3718 | 5.3333 |
| 0.0149 | 1.3691 | 5.9756 | | | |

[a] Standard uncertainties $u$ are $u(T) = 0.02$ K, $u(n_D) = 0.0001$, $u_r(x_1) = 0.02$.

## 3. Results and discussion

### 3.1. Solubility in five selected solvents

The solubility data of caprolactam in an organic solvent can be expressed in a general manner by Eq. (1) [7]:

$$-\ln x_1 = \frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right) - \frac{\Delta C_{pf}}{R}\left(\ln\frac{T}{T_f} + \frac{T_f}{T} - 1\right) + \ln\gamma_1 \quad (1)$$

$$x_1 = \frac{m_A/M_A}{m_A/M_A + m_S/M_S} \quad (2)$$

where $x_1$ is the mole fraction of the solute, $T_f$ is the melting temperature of caprolactam, $T$ is the equilibrium temperature, $\Delta H_f$ is the enthalpy of fusion, $\Delta C_{p,f}$ is the difference in solute heat capacity between the solid and the liquid at the melting temperature, $\gamma_1$ is the activity coefficient, $m_A$, $m_S$, $M_A$ and $M_S$ stand for the mass of the solute, the mass of the solvent, the molecular weight of the solute and the molecular weight of the solvent, respectively. Generally, an empirical formula can be applied to calculate the activity coefficient within a small temperature range [8]:

$$\ln\gamma_1 = a + \frac{b}{T} \quad (3)$$

where $a$ and $b$ are empirical constants, introducing Eq. (3) to (2) results in Eq. (4):

$$\ln x_1 = \left[\frac{\Delta H_f}{RT_f} + \frac{\Delta C_{pf}}{R}(1 + \ln T_f) - a\right] - \left[b + \left(\frac{\Delta H_f}{RT_f} + \frac{\Delta C_{pf}}{r}\right)T_f\right]\frac{1}{T} - \frac{\Delta C_{pf}}{R}\ln T \quad (4)$$

Eq. (4) can be written as:

$$\ln x_1 = A + \frac{B}{T} + C\ln T \quad (5)$$

this is the modified Apelblat equation [9], where A, B and C are empirical constants.

The solubility of caprolactam in methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol, and 1-butanol at different temperatures are listed in Table 3. The experimental solubilities as a function of temperature were correlated with Eq. (5). Table 3 also lists the calculated solubility values of caprolactam using Eq. (5) and the relative deviation between the experimental solubility and the calculated value. The values of the model parameters A, B, and C together with the root-mean-square deviation (rmsd) are reported in Table 4. The root-mean-square deviation (rmsd) of mole fraction solubility $x_1$ is defined as:

$$\mathrm{rmsd} = \left\{\frac{1}{N-1}\sum_{k=1}^{N}\left(x_{1,k}^{\mathrm{calcd}} - x_{1,k}^{\mathrm{exptl}}\right)^2\right\}^2 \quad (6)$$

where $N$ is the number of experimental points, $x_{1,k}^{\mathrm{exptl}}$ represents the experimental solubility value and $x_{1,k}^{\mathrm{calcd}}$ represents the solubility calculated from Eq. (5).

Fig. 2 displays the solubility of caprolactam in methyl tert-butyl ether, isopropyl ether, 1-propanol, 2-propanol and 1-butanol in the temperature range of 278.15–313.15 K. In combination with the calculated solubilities in Table 3 and the model parameters of Apelblat equation in Table 4, it is illustrated that the solubility value calculated by the Apelblat equation shows a fine representation of the experimental data, the Apelblat equation can provide an accurate estimation for the solubility of caprolactam in these five solvents in the temperature range of 278.15–313.15 K.

According to the obtained solubility data, caprolactam is more soluble in the three alcohols than in the two ethers due to the