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.

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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 (ρ) and refractive indexes of pure compounds at $T = 298.15$ K.

Solvents	Purity[a]	ρ (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].
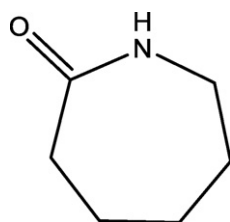[d] Ref. [23].
[e] Ref. [24].
[f] Ref. [25].

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, ΔH_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, γ_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:

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

where N is the number of experimental points, $x_{1,k}^{\text{exptl}}$ represents the experimental solubility value and $x_{1,k}^{\text{calcd}}$ 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

Table 3
Solubility of caprolactam in five selected solvents in the temperature range from $T = 278.15$ to 313.15 K at atmospheric pressure.[a]

T (K)	x^{exptl}	$10^2 (x^{exptl} - x^{calcd})$	T (K)	x^{exptl}	$10^2 (x^{exptl} - x^{calcd})$
Methyl tert-butyl ether					
278.15	0.0716	−0.0723	298.15	0.1253	−0.0836
283.15	0.0823	0.1173	303.15	0.1555	0.5171
288.15	0.0934	0.0801	308.15	0.1747	−0.6683
293.15	0.1053	−0.1985	313.15	0.2248	0.3239
Isopropyl ether					
278.15	0.0314	−0.0254	298.15	0.0656	−0.0204
283.15	0.0381	−0.0019	303.15	0.0758	−0.2950
288.15	0.0463	0.0535	308.15	0.0950	0.0821
293.15	0.0560	0.1115	313.15	0.1135	0.1135
1-Propanol					
278.15	0.2503	−0.1293	298.15	0.2940	−0.1682
283.15	0.2623	0.0582	303.15	0.3048	−0.3579
288.15	0.2739	0.1506	308.15	0.3217	0.0058
293.15	0.2863	0.2590	313.15	0.3376	0.1951
2-Propanol					
278.15	0.2041	−0.2776	298.15	0.2612	−0.3316
283.15	0.2209	0.2857	303.15	0.2829	−0.2287
288.15	0.2343	0.3134	308.15	0.3079	−0.1068
293.15	0.2474	0.0731	313.15	0.3394	0.3287
1-Butanol					
278.15	0.1881	0.2102	298.15	0.2572	0.5038
283.15	0.1977	−0.2053	303.15	0.2731	−0.0996
288.15	0.2125	−0.2704	308.15	0.3003	0.1494
293.15	0.2320	−0.0587	313.15	0.3243	−0.2202

[a] Standard uncertainties u are $u(T) = 0.02$ K, $u_r(p) = 0.05$, $u_r(x_1) = 0.02$.

Table 4
Parameters of Apelblat equation for caprolactam in five selected solvents.

	Solvents				
	Methyl tert-butyl ether	Isopropyl ether	1-Propanol	2-Propanol	1-Butanol
A	−449.361	−103.032	−43.8231	−176.045	−128.806
B	17357.4	1737.84	1267.836	6677.84	4428.37
C	68.2873	16.5829	6.73134	26.7337	19.7584
R^2	0.9968	0.9984	0.9952	0.9957	0.9968
10^3 rmsd	3.6176	1.3257	2.0850	2.7874	2.6656

hydrogen bond between the caprolactam molecule and the solvent molecule. For the solvent of two ethers, the solubility of caprolactam in methyl tert-butyl ether is higher than that in isopropyl ether, of which the viscosity (0.36 mPa s, 293.15 K) is higher than that of methyl tert-butyl ether (0.33 mPa s, 293.15 K). Intriguingly, there appears similar relationship between the solubility of caprolactam and the viscosity of the ethanol solvents. The solubility of caprolactam in the alcohol solvents decreases in the following order (278.15–308.15 K): 1-propanol > 2-propanol > 1-butanol, while the viscosity of the solvents increases in this temperature range, e.g., 1-propanol (2.26 mPa s) < 2-propanol (2.43 mPa s) < 1-butanol (2.95 mPa s) (293.15 K). As the temperature increases to 313.15 K, the viscosity of the solvents changes to be another order: 2-propanol (1.34 mPa s) < 1-proponal (1.39 mPa s) < 1-butanol (1.78 mPa s) (313.15 K), and the solubility of caprolactam turns to be a decreasing order: 2-propanol > 1-propanol > 1-butanol. Thus, it is illustrated that the solubility of caprolactam increases as the viscosity of the solvent decreases.

3.2. Prediction of dissolution enthalpy, entropy and the molar Gibbs energy

On the other hand, the results obtained here indicated that the solubility of caprolactam in five selected solvents increases as rising the temperature. The dissolution enthalpy ΔH_d ($J \, mol^{-1}$), dissolution entropy ΔS_d ($J \, mol^{-1} \, K^{-1}$) and molar Gibbs energy ΔG_d ($J \, mol^{-1}$) are calculated by the following equations [10]:

$$\Delta H_d = RT \left[\frac{\partial \ln x_1}{\partial \ln T} \right] = R(-B + CT) \tag{7}$$
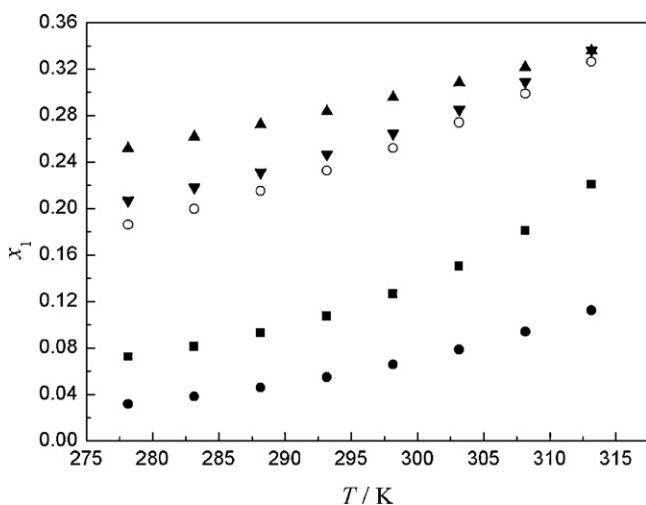

Fig. 2. Mole fraction solubility of caprolactam in five solvents from 278.15 K to 313.15 K: ■, methyl tert-butyl ether; ●, isopropyl ether; ▲, 1-propanol; ▼, 2-propanol; ○, 1-butanol.

Table 5
Dissolution enthalpy and entropy of caprolactam in five selected solvents from $T = 278.15$ to 313.15 K.

T (K)	ΔH_d	ΔS_d	T (K)	ΔH_d	ΔS_d
Methyl tert-butyl ether					
278.15	13607.63	27.09	298.15	24962.44	66.51
283.15	16446.33	37.20	303.15	27801.14	75.95
288.15	19285.03	47.14	308.15	30639.85	85.24
293.15	22123.74	56.91	313.15	33478.55	94.38
Isopropyl ether					
278.15	23900.20	57.22	298.15	26657.61	66.79
283.15	24589.55	59.67	303.15	27346.96	69.08
288.15	25278.91	62.09	308.15	28036.31	71.34
293.15	25968.26	64.46	313.15	28725.66	73.56
1-Propanol					
278.15	5025.67	6.60	298.15	6144.95	10.48
283.15	5305.49	7.59	303.15	6424.77	11.41
288.15	5585.31	8.57	308.15	6704.60	12.33
293.15	5865.13	9.53	313.15	6984.42	13.23
2-Propanol					
278.15	6303.17	9.56	298.15	10748.44	25.00
283.15	7414.49	13.52	303.15	11859.76	28.69
288.15	8525.81	17.41	308.15	12971.08	32.33
293.15	9637.13	21.24	313.15	14082.40	35.91
1-Butanol					
278.15	8874.60	17.92	298.15	12160.03	29.33
283.15	9695.96	20.85	303.15	12981.39	32.06
288.15	10517.32	23.73	308.15	13802.74	34.75
293.15	11338.67	26.55	313.15	14624.10	37.39

$$\Delta S_d = R \left[\frac{\partial \ln x_1}{\partial \ln T} + \ln x_1 \right] = R[(A + C(1 + \ln T))] \tag{8}$$

$$\Delta G_d = \Delta H_d - T\Delta S_d \tag{9}$$

The estimated dissolution enthalpy and entropy of caprolactam are listed in Table 5. It is shown that the dissolving process of caprolactam in each solvent is endothermic ($\Delta H_d > 0$) within the experimental temperature range, and the entropy increases during the dissolving process, which is the reason that results in larger solubility at higher temperature. It is worthwhile to note that the absolute value of ΔH_d and ΔS_d in the two ethers are much higher than that corresponding value in three ethanol solvents. It is due to the interactions between caprolactam and the alcohol solvent molecules, which tends to form hydrogen bonds and consequently results in a lower endothermic value of ΔH_d and the suppression of the entropy increase to some extent; while in the ether solvents no hydrogen bonds exist between caprolactam and the solvent, much more energy is needed to break the original associated bonds among either solute or solvent molecules. The molar Gibbs energy of caprolactam at 298.15 in five solvents calculated by Eq. (9) is plotted with the solubility data in Fig. 3. ΔG_d at 308.15 K was compared with that at 298.15 K in five selected solvents, as listed in Table 6, suggesting that the higher temperature, the lower value of ΔG_d. It is indicated that a linear correlation exists between the molar Gibbs energy of solution and $\ln x_1$, i.e., the lower value of

Table 6
Molar Gibbs energy of solution ΔG_d (J mol^{-1}) at 298.15 K and 308.15 K in five selected solvents.

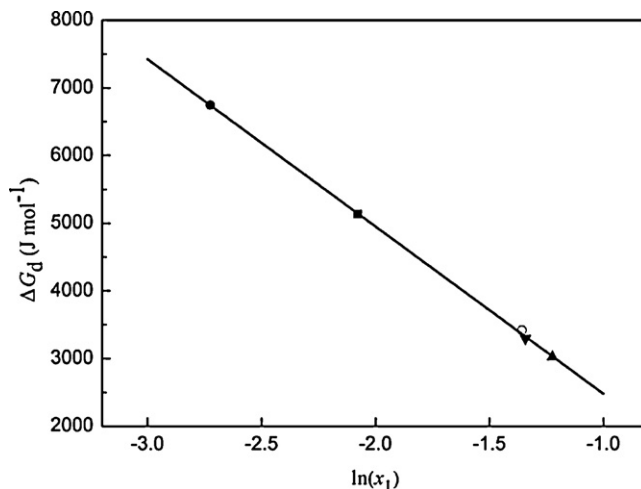| Solvents	Molar Gibbs energy of solution ΔG_d (J mol^{-1})	
	298.15 K	308.15 K
Methyl tert-butyl ether	5132.48	4373.14
Isopropyl ether	6744.17	6052.89
1-Propanol	3020.34	2905.11
2-Propanol	3294.69	3008.59
1-Butanol	3415.29	3094.53

Fig. 3. Molar Gibbs energy of solution at 298.15 K as function of the solubility values: ■, methyl tert-butyl ether; ●, isopropyl ether; ▲, 1-propanol; ▼, 2-propanol; ○, 1-butanol.

ΔG_d the higher solubility. The trend of ΔG_d with the solubility is similar to the previous literature [10].

3.3. Correlation of experimental solubility data

In this study, the experimental solubility data were correlated by two local composition models: the NRTL 1 model [11] and the UNIQUAC model [12]. The NRTL 1 model proposed by Nagata and Nakajima [11] has been applied for the correlation of experimental binary solid–liquid equilibrium data of imidazole and its derivatives by Domańsk et al. [7,13–15]. Therefore, the model was adopted here to correlate the solubility of caprolactam in the selected organic solvents. This model is shown in the following Eqs. (10)–(14):

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{n} x_j l_j + \sum_{j=1}^{n} \theta_{ji} \tau_{ji}$$
$$+ \sum_{j=1}^{n} \frac{x_j \theta_{ij}}{x_i} \left(\tau_{ij} - \sum_{k=1}^{n} \theta_{kj} \tau_{kj} \right) \tag{10}$$

$$\theta_{ij} = \frac{\theta_i \exp(-\tau_{ij} \alpha_{ij})}{\sum_{k=1}^{n} \theta_k \exp(-\tau_{kj} \alpha_{kj})} \tag{11}$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{n} r_j x_j} \tag{12}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{n} q_i x_i} \tag{13}$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \tag{14}$$

$$\tau_{ij} = \frac{a_{ij}}{T} \tag{15}$$

where r_i and q_i are the volume parameter and surface parameter of pure component i, respectively. These parameters can be calculated by the procedure described by Vear et al. [16,17]:

$$r_i = 0.029281 \, V_m \tag{16}$$

$$q_i = \frac{(Z - 2)r_i}{Z} + \frac{2(1 - b_i)}{Z} \tag{17}$$

where V_m is the molar volume of pure component i at 298 K, Z is the coordination number and was set as 10, b_i is the bulk factor of

Table 7
Molar volume of pure component at 298.15 K and molecular size parameter r_i and molecular area parameter q_i of the NRTL 1 model and the UNIQUAC model.

Component	V_m (cm^3 mol^{-1})	r_i	q_i
Caprolactam	106.1[a]	3.1067	2.4854
Methyl tert-butyl ether	119.9[b]	3.5108	2.8086
Isopropyl ether	142.1[a]	4.1608	3.3287
1-Propanol	72.7[c]	2.1287	1.7030
2-Propanol	77.0[c]	2.2546	1.8037
1-Butanol	92.0[c]	2.6939	2.1551

[a] Ref. [20].
[b] Ref. [7].
[c] Ref. [14].

component i and was taken as 1. The values of V_m, r_i as well as q_i of caprolactam and the selected solvents used in this study are listed in Table 7. It was reported that the value of α_{12} which is depending on the binary system can be set to a proper value in priori [18]. In this work, α_{12} was set to 0.2. a_{ij} is the fitting parameter in the NRTL 1 model.

Secondly, the UNIQUAC model is shown in Eqs. (18) and (19):

$$\ln \gamma_1 = \ln \frac{\Phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{n} x_j l_j + q_i \left[1 - \ln \left(\sum_{j=1}^{n} \theta_j \tau_{ji} \right) \right.$$

$$\left. - \sum_{j=1}^{n} \frac{x_j \theta_{ij}}{x_i} \left(\tau_{ij} - \sum_{k=1}^{n} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{n} \tau_{kj}} \right) \right] \tag{18}$$

$$\tau_{ij} = \exp\left(-\frac{A_{ij}}{T} \right) \tag{19}$$

where r_i, q_i, Z, Φ_i, θ_i and l_{ij} are the same parameters of the NRTL 1 model, A_{ij} is the fitting parameter of the UNIQUAC model.

In addition, the van't Hoff equation was used here to model the solid–liquid equilibria needed for the calculation of the two models:

$$\ln \gamma_i x_i = -\frac{\Delta H_f}{RT} \left(1 - \frac{T}{T_f} \right) \tag{20}$$

The values of ΔH_f and T_f were taken from Kabo et al. [19] and are 16096 J mol^{-1} and 342.305 K, respectively. The following objective function was applied in this work:

$$F_{obj} = \sum_{k=1}^{N} \left(\frac{(\gamma_{1,exptl} - \gamma_{1,calcd})}{\gamma_{1,exptl}} \right)_k^2 \tag{21}$$

The estimated parameters and absolute deviations of the solubilities of the two models are summarized in Tables 8 and 9. The correlated results were shown graphically in Figs. 4–8. It can be seen that for the five selected solvents in this work, either of the two models can provide accurate correlated results in the two ethers,

Table 8
Determined parameters and deviations between experimental and calculated solubilities of caprolactam (1) in selected solvents (2) by means of the NRTL 1 model.

Solvents	Parameters		Deviations	
	a_{12} (K)	a_{21} (K)	$|\Delta x_1|_{av.}$[a]	rmsd[b]
Methyl tert-butyl ether	756.2	−0.6	3.0×10^{-3}	3.7×10^{-3}
Isopropyl ether	425.0	381.9	1.1×10^{-3}	1.3×10^{-3}
1-Propanol	2686.7	−791.1	5.1×10^{-3}	5.7×10^{-3}
2-Propanol	1726.3	−724.6	5.3×10^{-3}	6.1×10^{-3}
1-Butanol	1629.7	−560.2	3.9×10^{-3}	4.7×10^{-3}

[a] $\left| \Delta x_1 \right|_{av.} = (\sum_{k=1}^{N} \left| x_{1,exptl} - x_{1,calcd} \right|_k)/N$, where N is the number of data points.
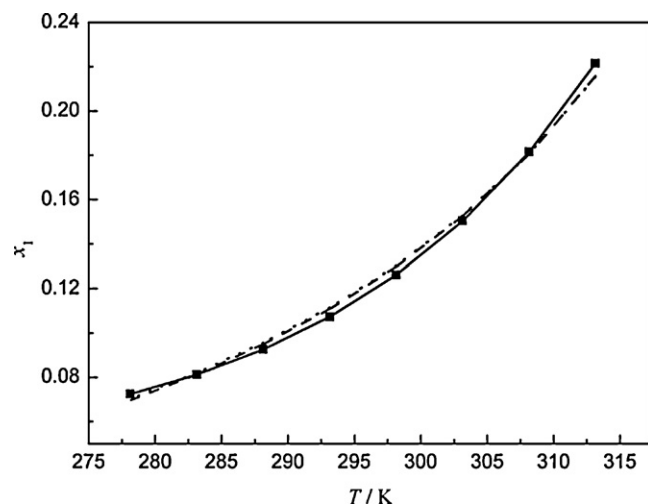[b] Calculated by Eq. (6).

Fig. 4. Experimental solubilities of caprolactam in methyl tert-butyl ether from 278.15 K to 313.15 K: –, this work; - - (dot), NRTL 1; – – (dash), UNIQUAC.
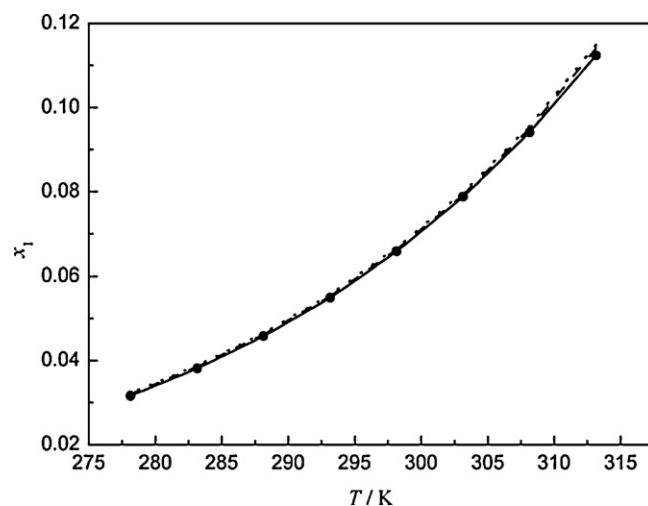

Fig. 5. Experimental solubilities of caprolactam in isopropyl ether from 278.15 K to 313.15 K: –, this work; - - (dot), NRTL 1; – – (dash), UNIQUAC.
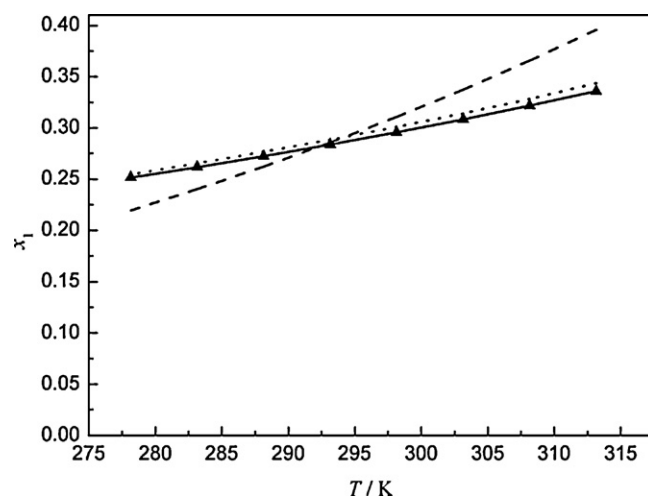

Fig. 6. Experimental solubilities of caprolactam in 1-propanol from 278.15 K to 313.15 K: –, this work; - - (dot), NRTL 1; – – (dash), UNIQUAC.

Table 9
Determined parameters and deviations between experimental and calculated solubilities of caprolactam (1) in selected solvents (2) by means of the UNIQUAC model.

Solvents	Parameters		Deviations	
	A_{12} (K)	A_{21} (K)	$|\Delta x_1|_{av.}$[a]	rmsd[b]
Methyl tert-butyl ether	298.4	-24.7	2.7×10^{-3}	3.3×10^{-3}
Isopropyl ether	141.1	137.6	6.5×10^{-4}	8.2×10^{-4}
1-Propanol	2968.3	−280.3	2.7×10^{-2}	3.4×10^{-2}
2-Propanol	2014.1	−257.6	1.1×10^{-2}	1.4×10^{-2}
1-Butanol	1609.3	−247.7	2.2×10^{-3}	2.7×10^{-3}

[a] $\left|\Delta x_1\right|_{av.} = (\sum_{k=1}^{N}\left|x_{1,exptl} - x_{1,calcd}\right|_k /N)$, where N is the number of data points.
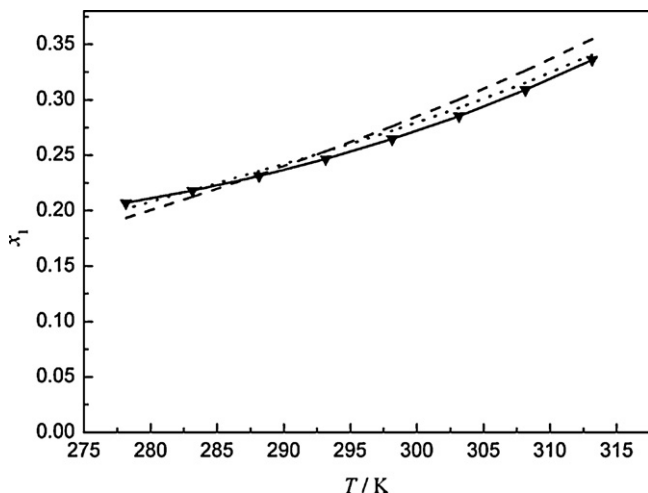[b] Calculated by Eq. (6).

Fig. 7. Experimental solubilities of caprolactam in 2-propanol from 278.15 K to 313.15 K: –, this work; - - (dot), NRTL 1; – – (dash), UNIQUAC.

with the rmsds of 3.7×10^{-3} (NRTL 1) and 3.3×10^{-3} (UNIQUAC) in methyl tert-butyl ether; 1.3×10^{-3} (NRTL 1) and 8.2×10^{-4} (UNIQUAC) in isopropyl ether, respectively. For the solvents of 1-propanol, 2-propanl and 1-butanol, the NRTL 1 model shows more accurate correlated results with the rmsds of 5.7×10^{-3}, 6.1×10^{-3} and 4.7×10^{-3}, which are smaller than those of the UNIQUAC model, i.e., 3.4×10^{-2}, 1.4×10^{-2} and 2.7×10^{-3}, respectively.
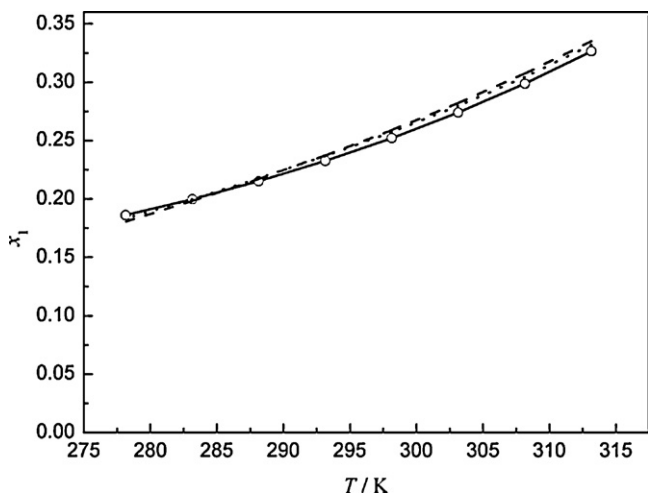

Fig. 8. Experimental solubilities of caprolactam in 1-butanol from 278.15 K to 313.15 K: –, this work; - - (dot), NRTL 1; – – (dash), UNIQUAC.

4. Conclusion

The solubility of caprolactam was determined by the balanced method using an Abbé refractometer, the experimental data were correlated with the modified Apelblat equation, then the dissolution enthalpy and entropy and the molar Gibbs energy were predicted. The solubility in five selected solvents decreases with the viscosity of the solvent, whereas increases with the temperature. The formation of hydrogen bonds between caprolactam and the solvent molecules is attributed to the endothermic and entropy-increasing dissolving process of caprolactam. Finally, the experimental solubility data were correlated by two local composition models: the NRTL 1 and the UNIQUAC. Either of the two models can provide accurate correlated value in methyl tert-butyl ether and isopropyl ether with the more accurate results of the UNIQUAC model. While for the solvents of 1-propanol, 2-propanol and 1-butanol, the NRTL 1 model can provide accurate estimation of the solubility, compared to the UNIQUAC model.

List of symbols

a_{ij}	adjustable parameter in the NRTL 1 model (K)
A_{ij}	adjustable parameter in the UNIQUAC model (K)
b_i	bulk factor of component i in the NRTL 1 and UNIQUAC models
F_{obj}	objective function
ΔH_f	molar enthalpy of fusion (J mol^{-1})
ΔH_d	the dissolution enthalpy (J mol^{-1})
ΔG_d	the molar Gibbs energy of solution (J mol^{-1})
l_i	parameter in the NRTL 1 and UNIQUAC models
m_A	the mass of the solute (g)
m_S	the mass of the solvent (g)
M_A	the respective molecular mass of the solute (g mol^{-1})
M_S	the respective molecular mass of the solvent (g mol^{-1})
n_D	the refractive index of the solution
N	number of data points per system
q_i	surface parameter in the NRTL 1 and UNIQUAC models
r_i	volume parameter in the NRTL 1 and UNIQUAC models
r^2	coefficient of correlation
R	gas constant (J mol^{-1} K^{-1})
ΔS_d	the dissolution entropy (J mol^{-1} K^{-1})
T	absolutely temperature (K)
T_f	melting temperature (K)
V_m	molar volume of pure component i in the NRTL 1 and UNIQUAC models
x_1	solubility of the solute (mol mol^{-1})
$|\Delta x_1|_{av.}$	average absolute deviation between experimental and calculated x_1
x^{exptl}	experimental solubility of the solute (mol mol^{-1})
x^{calcd}	calculated solubility of the solute (mol mol^{-1})
Z	coordination number in the NRTL 1 and UNIQUAC models

Greek letters

α_{ij}	parameter in the NRTL 1 and UNIQUAC models
Φ_i	parameter in the NRTL 1 and UNIQUAC models
θ_i	parameter in the NRTL 1 and UNIQUAC models
θ_{ij}	parameter in the NRTL 1 model
τ_{ij}	parameter in the NRTL 1 and UNIQUAC models
γ_1	activity coefficient of the solute

Subscripts

1, 2, i, j	components 1, 2, i, and j
calcd	calculated
exptl	experimental

Acknowledgments

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