JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Thermodynamic Study on the Adduct Crystallization of Terephthalic Acid with Amides

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ABSTRACT: The thermodynamics of adduct crystallization of terephthalic acid (TA) in amide solvents, such as *N*,*N*-dimethylacetamide (DMAC) and *N*-methyl-2-pyrrolidone (NMP), was studied in this paper. The results showed that the molecule ratio of TA and solvent in the TA-DMAC and TA-NMP adduct crystals is about 1:2. With poor thermal stability, the dissociation temperatures of the TA-DMAC and TA-NMP adduct crystals are about (341 and 313) K, respectively. The adduct crystallization is an exothermic process; the crystallization enthalpy of the [TA·2DMAC] adduct is about −34.00 kJ·mol^{-1}, and that of the [TA·2NMP] adduct is about −31.12 kJ·mol^{-1}. Finally, analysis of the liquid−solid equilibrium indicated that the concentration difference between the solubility of adduct crystals and the notional TA solid may result in the automatic adduct crystallization process.

1. INTRODUCTION

As a crystallization separation method, there are many works reported on the research and application of the adduct crystallization process. With thiourea as an adduct solvent, the separation of aromatic or naphthenic isomers can be processed by adduct crystallization.[1−3] To separate the close boiling point mixtures such as 4-methylphenol/3-methylphenol, 2-methoxyphenol/alkylphenols, 3-methylpyridine/4-methylpyridine, or substituted anilines, Gaikar has developed an available adduct crystallization method.[4] Using isopropyl alcohol as an adduct solvent, the mixture of phenol can be separated by phenol solvent adduct isomers.[5,6] The use of urea as an adduct solvent can also increase the effective separation of esters.[7,8]

Recently, it was found that terephthalic acid (TA) could form new adducts with some amide solvents in the right conditions.[9−11] The previous results indicated that the formation of TA adducts crystallization with *N*,*N*-dimethylacetamide (DMAC) and *N*-methyl-2-pyrrolidone (NMP) processed spontaneously and rapidly, and the intermolecular hydrogen bonding between the TA and amide solvent molecules dominated in the adduct crystallization. During the TA purification process by TA-DMAC and TA-NMP adduct crystallization, the dissolution of TA solid and the precipitation of TA adduct crystals were carried out simultaneously. The high-purity TA (PTA) adduct crystals precipitated, and impurities were concentrated in the liquid solution phase. Then, the PTA products could be obtained by washing or heating the adduct crystals to remove the amide solvents.[9−11]

Therefore, the adduct crystallization process of TA with DMAC and NMP solvent can effectively remove the impurities in the TA residue and recover pure TA products from the TA residue[9,10] or crude TA products.[14,15] In this paper, the thermodynamic properties of the TA-DMAC and TA-NMP adduct crystallization process were investigated experimentally. These basic thermodynamic data and model will be necessary for the further development of the new crystallization separation method.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals. The chemicals used were as follows: PTA, weight percent of TA more than 99.95 (wt %), Xiamen Xianglu Chemical Fiber Company Limited; acetonitrile and methanol, HPLC pure, Tedia Co.; DMAC and NMP, analytical reagent, Hangzhou Green Chemical Limited. All reagents can be used directly, without pretreatment.

2.2. Analysis. The concentration of TA in the adduct crystal phase was achieved by high-performance liquid chromatography (HPLC) analysis, Agilent 1100 HPLC, which equipped with a vacuum degasser, quaternary pump, DAD UV detector (254 nm), Diamonsil C18 column (250 mm × 4.6 mm, Φ5 μm). About 0.200 g of adduct crystals of TA-DMAC or TA-NMP were weighed and dissolved in 10.0 mL of DMAC, and then 1.0 mL of solution was taken into 100 mL volumetric flask and diluted to the volume by methanol. TA concentration in the diluted methanol solutions were quantified by HPLC using the external reference method. The details were described by Cheng and Guo.[9,10] Five groups of TA-DMAC and TA-NMP adduct crystals were quantified, and the results are shown in Table 1.

Thermal stabilities of the adduct crystallization of TA-DMAC and TA-NMP were determined with thermal gravimetric analysis (TGA) on NETZSCH (STA409PC). The 2.0 mg to 4.0 mg samples were placed in open ceramic pans and heated at a scan rate of 10 K·min^{-1}, while being purged with 100 mL·min^{-1} N_2, in the temperature range (308 to 523) K. The TG-DTG analysis diagrams of TA-DMAC and TA-NMP adduct crystals are given in Figures 1 and 2.

Special Issue: John M. Prausnitz Festschrift

Received: October 10, 2010
Accepted: January 18, 2011
Published: February 08, 2011

Table 1. TA Content in the Adduct Crystals of TA-DMAC and TA-NMP

run no.	TA content in TA-DMAC (mass fractions)	TA content in TA-NMP (mass fractions)
1	0.502	0.459
2	0.496	0.448
3	0.485	0.461
4	0.475	0.455
5	0.482	0.470

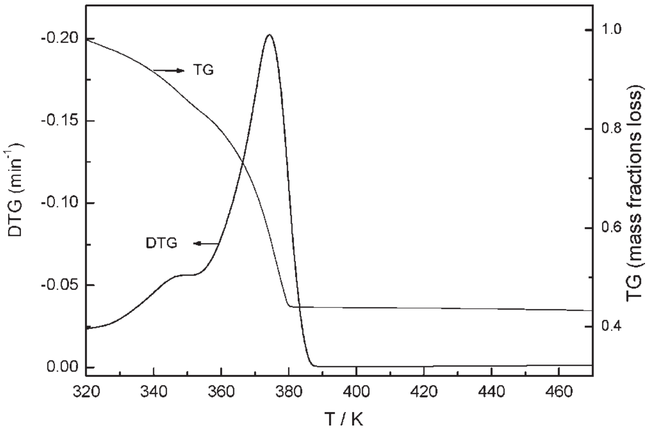

Figure 1. Thermal gravity analysis of TA-DMAC adduct crystals.

The crystallization enthalpy of TA-DMAC and TA-NMP adduct crystallization was analyzed by the differential scanning calorimeter (DSC), TA Instruments (Q200 DSC). To prevent the solvent evaporation of the adduct crystals, samples were sealed in aluminum plate with 100 mL/min nitrogen protection. Prepared experiments had been investigated at different temperature range and heating rates; then the right conditions were selected: the heating rate of 10 $\mathrm{K \cdot min^{-1}}$, the temperature range of (273 to 413) K. The DSC analysis diagrams of TA-DMAC and TA-NMP adduct crystals are shown in Figures 3 and 4.

2.3. Adduct Crystallization Experiments. A flask equipped with a certain amount (100 mL) of DMAC or NMP solvent was placed in a certain temperature water bath [(303 to 363) K], where the temperature control precision is about ± 0.1 K. While stirring, (20.0 to 50.0) g of TA solid was weighed and added into the flask equipped with DMAC or NMP solvent. It can be observed that, the semitransparent TA adduct crystal phase was forming simultaneously, while the suspending white TA powder dissolved. The TA adduct crystals of TA-DMAC and TA-NMP can be obtained after filtration and freeze-drying under 263 K. Then, these adduct crystals can be used for different analysis and characterization, such as HPLC, X-ray diffraction (XRD), TGA (TG-DTG), and DSC, and so forth.

To investigate the temperature effects on the adduct crystallization, several adduct crystallization experiments were carried out in different temperature conditions, including (303, 313, 323, 333, 343, 353, and 363) K. While stirring, about 20.0 g of TA solid was added into the flask equipped with 100.0 mL of DMAC or NMP solvent. After stirring (30 or 120) min, the solid−liquid mixtures were sampled and filtrated at the crystallization temperature. Then the solid samples were quantified by HPLC. If the TA content in the solid is about (45 to 55) wt % for TA-DMAC and (40 to 50) wt% for TA-NMP, "adduct crystals" formed. If the TA content in the solid is about (65 to 90) wt % for TA-DMAC and (60 to 90) wt % for TA-NMP, "some adduct crystals" formed. If the TA content in the solid is more than 90 wt %, "no adduct crystals" formed. The results are summarized in Table 3.

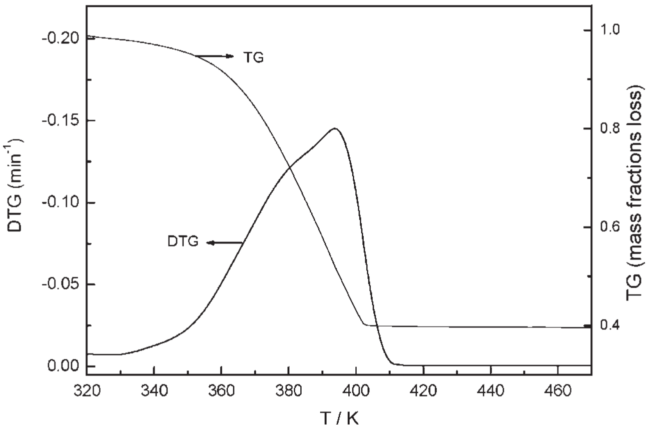

Figure 2. Thermal gravity analysis of TA-NMP adduct crystals.

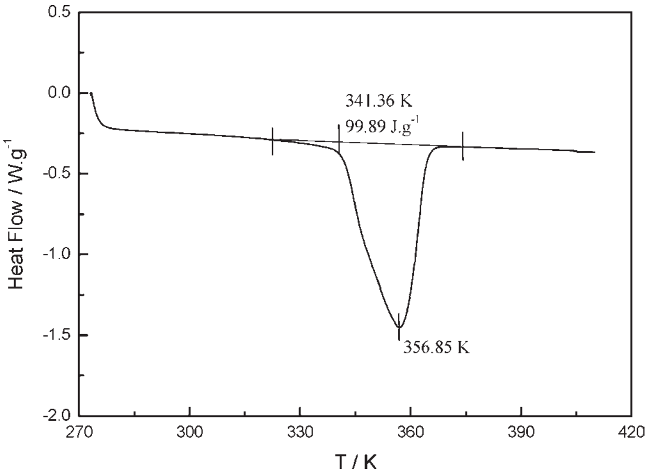

Figure 3. Differential scanning calorimetry (DSC) analysis of TA-DMAC adduct crystals.

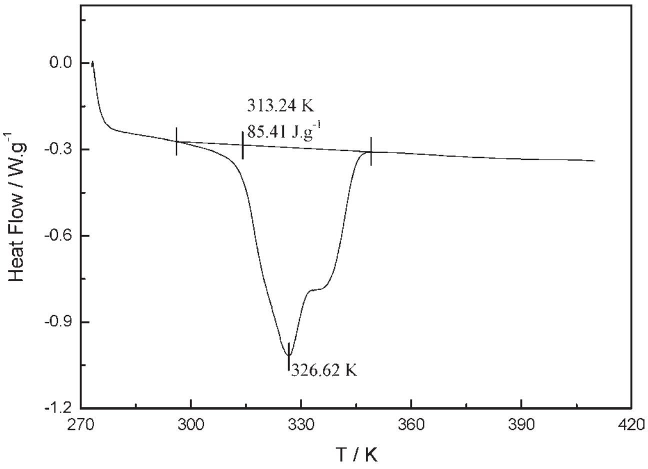

Figure 4. DSC analysis of TA-NMP adduct crystals.

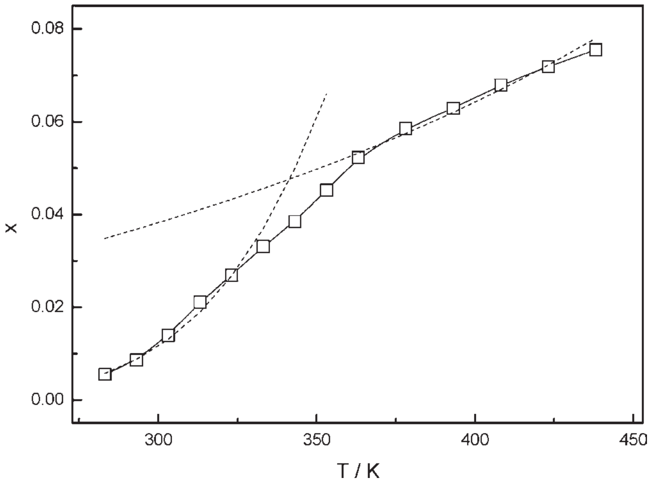

Figure 5. Solid−liquid equilibrium of TA-DMAC adduct crystallization; · · ·, solubility of TA and [TA·2DMAC] estimated by eq 4. −□−, experimental solubilities of TA in DMAC.

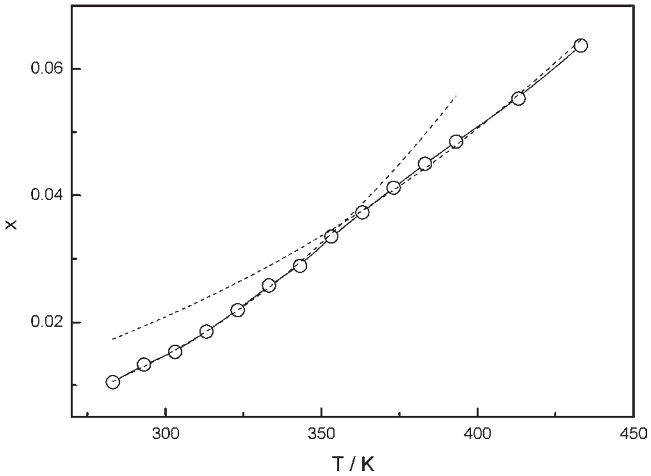

Figure 6. Solid−liquid equilibrium of TA-NMP adduct crystallization; · · ·, solubility of TA and [TA·2NMP] estimated by eq 4; −○−, experimental solubilities of TA in NMP.

2.4. Liquid−Solid Equilibrium Data. The solubility data are the most important thermodynamic data in the development of crystallization process. In this paper, the solubility data of TA in DMAC and NMP in the range of (283 to 443) K were obtained by the balance method, which had been described in detail in the previous papers.[10−13] The solubilities of TA in DMAC and NMP are shown in Figure 5 and 6. These results were in good agreement with the results reported in the previous literature.[10−15]

3. RESULTS AND DISCUSSION

3.1. Composition and Structure of the Adduct Crystals. Preparation experiments of the adduct crystals were repeated five times. The TA-DMAC adduct crystallized at 333 K and TA-NMP at 323 K. All the adduct crystals were filtrated at crystallization temperature and dried under 263 K. The results quantified by HPLC are summarized in Table 1 where the first column presents the experimental run number.

It is shown in Table 1 that the content of TA in TA-DMAC adduct crystals is about 48.8 ± 2.0 % (wt %) and 45.9 ± 2.0 % (wt %) TA in TA-NMP adducts. The molar ratio of TA molecule versus solvent molecule is about 1:2. Therefore, the adduct crystallization process can be described as:

$$\begin{aligned} &\mathrm{TA} + 2\mathrm{DMAC} \leftrightarrow [\mathrm{TA}\cdot 2\mathrm{DMAC}] \\ &\mathrm{TA} + 2\mathrm{NMP} \leftrightarrow [\mathrm{TA}\cdot 2\mathrm{NMP}] \end{aligned} \qquad (1)$$

where [TA·2DMAC] and [TA·2NMP] stand for the adduct crystals of TA-DMAC and TA-2NMP.

Table 2. Thermodynamic Properties of the TA-DMAC and TA-NMP Adducts

thermodynamic parameters	TA-DMAC	TA-NMP
T_i/K	341.36	313.24
T_p/K	356.85	326.62
ΔH_c/kJ·mol^{-1}	−34.00	−31.12

According to the adduct crystallization data by XRD analysis, DMAC or NMP molecules are linked to one TA molecule by strong O−H· · ·O hydrogen bonds; every three crystal units get together to form a trimerical layer, and cross-stacking exists between the layers.[10,11]

3.2. Thermodynamic Properties of the Adducts. The NETZSCH (STA409PC) instrument was used to characterize the thermal stabilities of the adduct crystals of TA-DMAC and TA-NMP. The 2.0 to 4.0 mg of adduct samples were placed in open ceramic pans and heated at a scan rate of 10 K·min^{-1} from (308 to 523) K, while being purged with 100 mL·min^{-1} N_2. The TGA (TG-DTG) analysis diagrams of the adduct crystals of TA-DMAC and TA-NMP are shown in Figures 1 and 2.

Figures 1 and 2 indicated the poor thermal stability of the TA-DMAC and TA-NMP adduct crystals. As the temperature increasing, the decomposition of adduct crystals began from 330 K. the adduct crystals decomposed into free TA and solvent molecules gradually, and the solvent molecules evaporated and TA solid remained. TGA results also indicated that the content of the volatile solvents (DMAC and NMP) TA accounted for about (40 to 45) % (wt %) in these adduct crystals, which is consistent with the results in Table 1.

The enthalpy of the adduct crystallization of TA-DMAC and TA-NMP was quantitated by TA Instruments (Q200 DSC), (temperature accuracy: ± 0.01 K, dynamic range: more than ± 500 mW, calorimeter accuracy: ± 0.1 %, sensitivity: 0.2 μW) with aluminum plate sealed, nitrogen protection, 10 K·min^{-1} from (273 to 413) K. The DSC results of the adduct crystals are shown in Figure 3 and 4.

It is obvious that the dissociation of TA-DMAC and TA-NMP adducts is an endothermic process, which indicated that the adduct crystallization process of TA-DMAC and TA-NMP is an exothermic process. Figure 3 show that the initial temperature (T_i) of the dissociation of the TA-DMAC adducts crystal is about 341.36 K, and the peak temperature (T_p) of the crystal dissociation is about 356.85 K. The endothermic dissociation rate of the TA-DMAC adducts reaches the maximum at 356.85 K. The enthalpy of the TA-DMAC adduct crystallization (ΔH_c) is about −99.89 J·g^{-1}, that is, −34.00 kJ·mol^{-1}. Figure 4 show that the TA-NMP adducts are more unstable than the TA-DMAC adduct crystals; the initial temperature (T_i) of the dissociation of the TA-NMP adducts is about 313.24 K; the peak temperature (T_p) is about 326.62 K; the enthalpy of the TA-NMP adduct crystallization (ΔH_c) is about −85.41 J·g^{-1}, that is, −31.12 kJ·mol^{-1}.

Table 3. Effect of Temperature on the Adduct Crystallization of TA-DMAC and TA-NMP

T/K	TA-DMAC		TA-NMP	
	crystals	t/s	crystals	t/s
303	adduct crystals	2000−7000	adduct crystals	2000−7000
313	adduct crystals	2000−7000	adduct crystals	2000−7000
323	adduct crystals	2000−7000	adduct crystals	< 2000
333	adduct crystals	< 2000	some adduct crystals	< 2000
343	adduct crystals	< 2000	no adduct crystals	
353	some adduct crystals	< 2000	no adduct crystals	
363	no adduct crystals		no adduct crystals	

All of the above thermodynamic properties of the TA-DMAC and TA-NMP adduct are summarized in Table 2.

3.3. Temperature Effects on the Adduct Crystallization. The experimental results of the temperature effects on the adduct crystallization process are shown in Table 3. Experimental results (Table 3) indicated the remarkable temperature effects on the adduct crystallization process of TA-DMAC and TA-NMP. At the temperature range conditions (303 to 343) K, the precipitation of the translucent adduct crystals occurs, while the suspended white TA solid dissolved gradually. Furthermore, the rate of adduct crystallization is accelerated at elevated temperatures, but too-high temperatures will hinder the formation of adduct crystals.

It was concluded that the right adduct crystallization temperature condition of TA-DMAC adducts is (333 to 343) K. Under this temperature range, with the suspended white solid TA powder dissolving and the translucent TA-DMAC adduct crystals generating, TA-DMAC adduct crystallization process is less than 30 min. However, when the temperature is higher than 353 K, it can be observed that some suspended solid TA gradually dissolved, but the TA-DMAC adduct crystallization did not occur. There was no TA-DMAC adduct formation, but there was white TA solid and TA solution in DMAC.

Similarly, the right adduct crystallization temperature condition of TA-NMP adducts is around 323 K. Under about 323 K, the TA-NMP adducts crystallization can process quickly. Once above the 343 K, TA can be dissolved in NMP, but not TA-NMP adduct crystallization.

The adduct crystallization temperature of TA-DMAC and TA-NMP can be illustrated by the DSC results of Figures 3 and 4. As the transitional temperature of the TA-DMAC adducts is (341 to 357) K, so the adduct crystallization temperature is about (333 to 343) K, closing to 341 K. The transitional temperature of the TA-NMP adducts is (313 to 327) K; the adduct crystallization temperature is about 323 K. Therefore, the temperature effect may be due to the poor thermal stability of the TA-DMAC and TA-NMP adduct crystals.

3.4. Liquid−Solid Equilibrium of the Adduct Crystallization. The measured mole fraction solubilities of TA in DMAC and NMP in the temperature range (283 to 483) K are shown in Figures 5 and 6.

All of the above results show that, in the DMAC or NMP solvent system, the solid-state TA exists in the form of the TA adduct crystallization with amides at low temperatures, but in the existence of only TA solid at high temperatures. Thus, there is a different liquid−solid equilibrium under the different temperature ranges. It can be considered that the dissolution and crystallization of TA in the DMAC or NMP solvents at high temperatures is the liquid−solid equilibrium between the TA solid and the TA solution but also is the liquid−solid equilibrium between the TA adduct crystals and the TA solution at the low temperature. These equilibria can be described as:

Table 4. Model Parameters in eq 4 and σ

adduct crystallization	temperature range	λ	h	σ
TA-DMAC	low, 283−341 K	$1.461 \cdot 10^{1}$	$2.450 \cdot 10^{2}$	0.0308
TA-DMAC	high, 357−483 K	$8.340 \cdot 10^{-4}$	$1.250 \cdot 10^{4}$	0.0254
TA-NMP	low, 283−313 K	$3.420 \cdot 10^{-1}$	$4.659 \cdot 10^{3}$	0.0041
TA-NMP	high, 327−483 K	$7.417 \cdot 10^{-2}$	$1.016 \cdot 10^{4}$	0.0150

Low temperature:

$$\begin{aligned}&[\mathrm{TA \cdot 2DMAC}](\mathrm{s}) \leftrightarrow \mathrm{TA}(\mathrm{l}) + \mathrm{DMAC}(\mathrm{l})\\&[\mathrm{TA \cdot 2NMP}](\mathrm{s}) \leftrightarrow \mathrm{TA}(\mathrm{l}) + \mathrm{NMP}(\mathrm{l})\end{aligned} \tag{2}$$

High temperature:

$$\begin{aligned}&\mathrm{TA}(\mathrm{s}) \leftrightarrow \mathrm{TA}(\mathrm{l}) + \mathrm{DMAC}(\mathrm{l})\\&\mathrm{TA}(\mathrm{s}) \leftrightarrow \mathrm{TA}(\mathrm{l}) + \mathrm{NMP}(\mathrm{l})\end{aligned} \tag{3}$$

For TA in DMAC, the transitional temperature range is (341 to 357) K, the low temperature range is (283 to 341) K, and the high temperature range is (357 to 483) K. For TA in NMP, the transitional temperature range is (313 to 327) K, the low range is (283 to 313) K, and the high range is (327 to 483) K.

The Buchowski equation,[13,16] eq 4, is used to correlate solid−liquid equilibrium data. Although only two parameters (h and λ) are involved, this equation is thermodynamically correct and gives an excellent description of experimental data:

$$\ln\left(1 + \frac{\lambda(1-x)}{x}\right) = \lambda h\left(\frac{1}{T} - \frac{1}{T_\mathrm{m}}\right) \tag{4}$$

In eq 4, T is the absolute temperature of solid−liquid equilibrium; x is the mole fraction of a solute TA in the saturated solution, T_m is melting point of TA (T_m =745.93 K);[13] h and λ are two parameters. h stands for the enthalpy characteristic of the solid−liquid equilibrium, and λ stands for the ratio of the activity function of solvent versus the activity function of solute.[16] These two parameters can be regarded as implicit constants, which were regressed using a nonlinear optimization method.

For the different temperature ranges, the Buchowski equation was adopted to correlate the liquid−solid equilibrium data. With the solubility curves calculated from eq 4, the extrapolation curves of the TA solubility in low temperature and the solubility of the TA adducts in high temperature are drawn in Figures 5 and 6.

The values of the parameters h and λ are listed in Table 4, together with the average relative standard deviation between the experimental and the calculated values. The average relative standard deviation σ is defined as

$$\sigma = \left[\frac{i}{n}\sum_{i=1}^{n}\left(\frac{x - x_{(\mathrm{cal})}}{x}\right)^{2}\right]^{1/2} \tag{5}$$

where x is the experimental solubility of TA, n is the number of experimental points, and $x_{(\mathrm{cal})}$ is the solubility calculated from eq 4. The average relative standard deviation of the simulated value and the experimental data is less than 0.031. It can be seen that the obtained agreement is in general satisfactory.

The results in Table 4 showed that the values of the parameters h and λ varied greatly in different temperature ranges. This is due to the different liquid−solid equilibria under the different temperature ranges, that is, adduct-solution equilibrium at the low temperature but only TA-solid-solution equilibrium at high temperatures.

4. CONCLUSIONS

(1) The molar ratio of TA molecule versus amide solvent molecule in TA-DMAC and TA-NMP adducts is about 1:2. With poor thermal stability, the dissociation temperatures of [TA·2DMAC] and [TA·2NMP] adduct crystals are about (341 and 313) K.

(2) The adduct crystallization process of TA-DMAC and TA-NMP is an exothermic process. The enthalpy of the TA-DMAC adduct crystallization is about −34.00 kJ·mol^{-1}, and the enthalpy of the TA-NMP adduct crystallization is about −31.12 kJ·mol^{-1}.

(3) Due to the poor thermal stability of the TA-DMAC and TA-NMP adduct crystals, temperature is the most important factor in adduct crystallization, the process. The right adduct crystallization temperature of the TA-DMAC crystallization is about (333 to 343) K, and that of the TA-NMP is about 323 K.

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Funding Sources

Acknowledgment is expressed for the financial support from the National Science Foundation of China (No. 20806072) and the Research Fund for the Doctoral Program of Higher Education of China (No. 200803351111).

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