



Measurement and correlation of the solubility of urea L-tartaric acid in aqueous ethanol solution

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ABSTRACT

Date on the solubility of urea L-tartaric acid in aqueous ethanol solution are essential for industrial design and further theoretical studies. Using a laser monitoring system, the solubility of urea L-tartaric acid in aqueous ethanol solution at different temperatures was measured using the synthetic method. For the temperature range investigated, the solubilities of urea L-tartaric acid in the solvents increased with increasing temperature. The solubility data were correlated with Apelblat equation and Buchowski–Książczak λh equation. The Apelblat equation can regress the solubility data much better than Buchowski–Książczak λh equation. This study provides valuable data for the mechanism and preparation of the available crystal form of urea L-tartaric acid.

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1. Introduction

In recent years, nonlinear optical materials have gained attention due to their numerous applications in telecommunication activities, such as optical computing, optical information processing, optical disk data storage, laser remote sensing, laser driven fusion, color displays, and medical diagnostics [1]. As is well known, organic nonlinear optical materials are drawing attention as materials for achieving highly efficient wavelength conversion devices. Urea L-tartaric acid, which is combined with urea and L-tartaric acid, is known to be useful as a material for wavelength conversion devices because the compound possesses large second order nonlinear optical coefficient [2].

However, high quality of the crystal is an important factor for the performance of nonlinear optical materials. In the present work, we studied the possibility of applying the salting-out technique to obtain urea L-tartaric acid crystals from the aqueous ethanol solution. The salting-out technique has certain advantages over other methods of crystallization by cooling and evaporation because ambient temperature may be employed, producing crystals of high purity [3].

In this paper, the solubility of urea L-tartaric acid in aqueous ethanol solution at different temperatures was measured by a laser monitoring observation technique. The solubility data were

correlated with Apelblat equation and Buchowski–Książczak λh equation. The calculated values were in good agreement with the experimental values.

2. Experimental

2.1. Materials

High-grade L-tartaric acid from Sinopharm Chemical Reagent Co. was used directly without further purification. Its purity was greater than 99.5% by mass. Analytical grade urea obtained from Peking Biotech. Co. Ltd. was also used directly without further purification, and its purity was greatly than 99.8% by mass. Water used in the experiments was double-distilled water.

2.2. Apparatus and procedure

Urea L-tartaric acid was synthesized by dissolving urea and L-tartaric acid in a 1:1 ratio in double-distilled water [4,5]. The melting point of urea L-tartaric acid was determined by DSC (STA 449C, Germany NETZSCH Co.). The measured accuracy of the melting point was approximately ± 1 K. Elementary composition of urea L-tartaric acid was determined by an elemental analyser of Carlo Erba EA1110. Analysis is performed by heating the sample in either oxygen or an inert gas atmosphere and measuring the relative amounts of carbon, hydrogen, nitrogen produced by the flash combustion. The measured accuracy of Carlo Erba EA1110 was approximately 0.1%.

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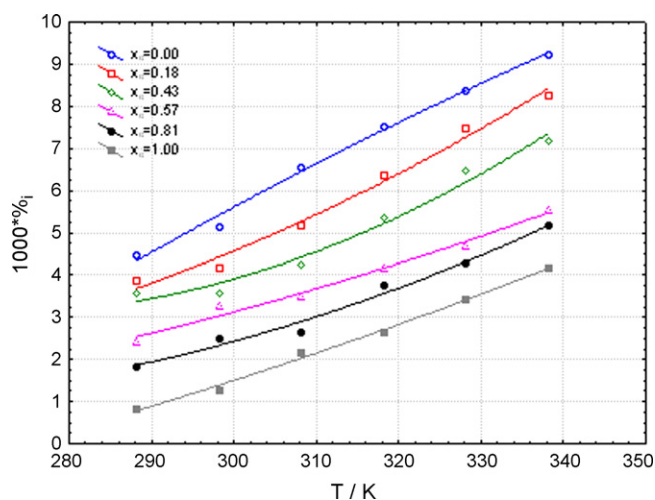


Fig. 1. Solubility of urea L-tartaric acid in aqueous ethanol solution.

Solid–liquid equilibrium data of urea L-tartaric acid in aqueous ethanol solution were measured by the synthetic method. Precalculated quantities of ethanol were weighed and mixed with water to create solutions of various mole fractions ethanol.

The solutions were placed in separate flasks. The flasks were covered by a 2 cm thick sand layer, topped by a layer of cotton tow that was kept moist by periodical addition of sterile water. This cover was meant to prevent the evaporation of ethanol. These flasks, fitted with submersible magnetic stirrer, were placed in the thermostatic bath at the desired temperature. The laser monitoring observation technique was used to determine the dissolution temperature of the solid–liquid mixture of a known composition. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The experiments were carried out in a 50 ml jacketed glass vessel with a magnetic stirrer; a constant temperature (± 0.02 K) was maintained at the required temperature by circulating water through the outer jacket from a thermoelectric controller. A glass bushing with a mercury glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The experimental temperature was measured using a digital thermometer with 0.05 K uncertainties. To improve the accuracy of the experimental results, three times of experiments were performed for each data point.

3. Results and discussion

Urea L-tartaric acid was grown from aqueous solution by the temperature lowering method. The determined melting point (T_m) of urea L-tartaric acid was 424 K, which shows good agreement with values from literature [6]. The elemental analysis results show that mass fraction of carbon, hydrogen and nitrogen in urea L-tartaric acid ($C_4H_6O_6-CH_4N_2O$) is 28.86, 4.72 and 13.30%, and the experimental results agree with the theoretical analysis.

The solubility data of urea L-tartaric acid in aqueous ethanol solution at $T = (288.2, 298.2, 318.2, 318.2, 328.2, 338.2)$ K were determined using the laser detection system. The solubility data of urea L-tartaric acid in aqueous ethanol solution are given in Fig. 1.

The same experimental results were obtained in both directions of increasing or decreasing temperature. The mole fraction data of urea L-tartaric acid in aqueous ethanol solution are given in Table 1. x_e is volume fraction of ethanol in the ethanol + water mixture, x_i is the mole fraction of urea L-tartaric acid in liquid phase.

From Fig. 1, it is clear that the solubility of urea L-tartaric acid increases with increasing temperature and decreases with increasing the concentration of ethanol in the solution.

Table 1

Solubilities of urea L-tartaric acid (x_i) in different compositions of ethanol–water mixtures at $T = (288.2, 298.2, 308.2, 318.2, 328.2$ and $338.2)$ K.

$x_e = 0.00$		$x_e = 0.18$	
T (K)	$x_i \times 10^3$	T (K)	$x_i \times 10^3$
288.2	4.463	288.2	3.856
298.2	5.142	298.2	4.172
308.2	6.546	308.2	5.153
318.2	7.528	318.2	6.346
328.2	8.377	328.2	7.483
338.2	9.234	338.2	8.261
$x_e = 0.43$		$x_e = 0.57$	
T (K)	$x_i \times 10^3$	T (K)	$x_i \times 10^3$
288.2	3.562	288.2	2.432
298.2	3.579	298.2	3.258
308.2	4.248	308.2	3.482
318.2	5.352	318.2	4.174
328.2	6.483	328.2	4.695
338.2	7.165	338.2	5.543
$x_e = 0.81$		$x_e = 1.00$	
T (K)	$x_i \times 10^3$	T (K)	$x_i \times 10^3$
288.2	1.836	288.2	0.825
298.2	2.475	298.2	1.253
308.2	2.654	308.2	2.175
318.2	3.754	318.2	2.643
328.2	4.262	328.2	3.432
338.2	5.167	338.2	4.152

To describe solid–liquid equilibrium, the relationship between solubility and temperature can be described as [7]:

$$\ln\left(\frac{1}{\gamma_x x}\right) = \frac{\Delta_{fus}H}{RT_t} \left(\frac{T_t}{T} - 1\right) - \frac{\Delta C_p}{R} \ln\left(\frac{T_t}{T} - 1\right) + \frac{\Delta C_p}{R} \ln\frac{T_t}{T} \quad (1)$$

where γ_x is the activity coefficient on a mole fraction basis, x the mole fraction solubility, $\Delta_{fus}H$ is the fusion enthalpy, ΔC_p is the heat capacity difference between the solid and the liquid, T is the equilibrium temperature (K), T_t is the triple point temperature, and R is the gas constant. The value of ΔC_p is so small in compared to $\Delta_{fus}H$ that the second and third terms can be neglected. The normal melting temperature T_m can be substituted for the triple point temperature T_t . Eq. (1) can be rewritten as [8]:

$$\ln(\gamma_x x) = \frac{\Delta_{fus}H}{RT_m} \left(1 - \frac{T_m}{T}\right) \quad (2)$$

Since solid–liquid equilibrium data are not often available, especially in mixed solvents, correlation and prediction schemes are frequently employed. The Apelblat equation has already been used to correlate the solute concentration in saturated aqueous organic acids by Apelblat and Manzurola [9–11]:

$$\ln x = A + \frac{B}{T} + C \ln T \quad (3)$$

where x is the mole fraction of solute, T is the absolute temperature, and A , B and C are the model parameters. The correlated results show good agreement with the experimental results for many systems containing aqueous organic acids. Further, the equation is simple and easy to be applied to engineering. So we used the Apelblat equation to correlate the solubility data of urea L-tartaric acid in aqueous ethanol solution. The root mean square deviations (R.M.S.D.) of Apelblat equation can be described as follows:

$$\text{R.M.S.D.} = \left[\frac{1}{n} \sum_{i=1}^n (x_i^{\text{calc}} - x_i^{\text{exp}})^2 \right]^{1/2} \quad (4)$$

Table 2
Regression result of Apelblat equation.

x_e	A	B ($\times 10^{-3}$)	C	R.M.S.D. ($\times 10^5$)
0.00	143.55	-7.805	-14.07	0.38
0.18	24.12	-2421.22	-1.77	0.45
0.43	-103.61	-9.146	-15.6	0.36
0.57	-1.35	-1145.26	0.77	1.20
0.81	5.36	-1894.05	0.22	0.74
1.00	379.3	-20167.6	-37.9	0.61

Table 3
Regression result of Buchowski–Ksiazczak λh equation.

x_e	λ	h	R.M.S.D. ($\times 10^5$)
0.00	0.03	11708.58	3.56
0.18	0.03	13448.29	4.12
0.43	0.04	13331.85	4.25
0.57	0.05	12416.70	4.87
0.81	0.04	16599.35	5.25
1.00	0.02	23064.60	4.32

where x_i^{calc} is the solubility calculated by Eq. (3) using the parameters in Table 1, and x_i^{exp} is the experimental value of mole fraction solubility of urea L-tartaric acid, and n is the number of experiment points.

The values of the three parameters A, B and C together with the root mean square deviations (R.M.S.D.) of Apelblat equation are listed in Table 2.

As shown in Apelblat equation can well regress the solubility data of urea L-tartaric acid in aqueous ethanol solution.

The Buchowski–Ksiazczak λh equation, Eq. (5), is another way to describe the solution behavior and was suggested firstly by Buchowski et al. [12]. The Buchowski–Ksiazczak λh equation could fit the experimental data well for many systems with only two parameters, λ and h [13–16]. In this paper, the solubility data were also correlated with the Buchowski–Ksiazczak λh equation:

$$\ln \left[1 + \frac{\lambda(1-x)}{x} \right] = \lambda h \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (5)$$

where T is the absolute temperature and x is the mole fraction solubility of urea L-tartaric acid. The values of the two parameters λ and h together with the root mean square deviations (R.M.S.D.) are listed in Table 3.

It can be observed that the regression result of Buchowski–Ksiazczak λh equation was less remarkable than that of the Apelblat equation. It seems that the problem with the Buchowski–Ksiazczak λh equation is that its parameter

is temperature dependent. Compared with Apelblat equation, Buchowski–Ksiazczak λh equation is proposed for solid–liquid equilibrium directly, and it is widely accepted to be capable of dealing with strong polarity systems, which involve strong interaction between molecules. This will be investigated in future work.

4. Conclusion

Using the laser monitoring observation technique, the solubility of urea L-tartaric acid in aqueous ethanol solution as a function of temperature was determined in this study. It was found that the solubility of urea L-tartaric acid was very small in pure ethanol and in solvents with low water content.

For the temperature range investigated, the solubilities of urea L-tartaric acid in the solvents increased with increasing temperature. The solubility data were correlated with Apelblat equation and Buchowski–Ksiazczak λh equation. The Apelblat equation can regress the solubility data much better than λh equation. The solubility measured in this study can be used for the urea L-tartaric acid purification or its optical resolution by the preferential crystallization procedure.

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