Thermodynamic equilibrium of hydroxyacetic acid in pure and binary solvent systems

Qiaoyin Huang^a, Chuang Xie^{a,b*}, Yang Li^a, Nannan Su^a, Yajing Lou^a, Xiaoxue Hu^a,
Yongli Wang^{a,b*}, Ying Bao^{a,b}, Baohong Hou^{a,b}

^aSchool of Chemical Engineering and Technology, Tianjin University, Tianjin
300072, China.

^bCollaborative Innovation Center of Chemical Science and Engineering (Tianjin),
Tianjin 300072, China.

*Corresponding author. Tel.: +86-22-27405754; Fax: +86-22-27374971.

E-mail address: acxie@tju.edu.cn, yliwang@tju.edu.cn

ABSTRACT: The solubility of hydroxyacetic acid in five pure organic solvents and two binary solvent mixtures were experimentally measured from 273.15 K to 313.15 K at atmospheric pressure ($p=0.1$ MPa) by using a dynamic method. The order of solubility in pure organic solvents is ethanol > isopropanol > n-butanol > acetonitrile > ethyl acetate within the investigated temperature range, except for temperature lower than 278 K where the solubility of HA in ethyl acetate is slightly larger than that in acetonitrile. Furthermore, the solubility data in pure solvents were correlated with the modified Apelblat model, NRTL model, and Wilson model and that in the binary solvents mixtures were fitted to the CNIBS/R-K model and Jouyban-Acree model. Finally, the mixing thermodynamic properties of hydroxyacetic acid in pure and binary solvent systems were calculated and discussed.

Keywords: Hydroxyacetic acid; Solubility; Correlation; Mixing properties

1. Introduction

Hydroxyacetic acid (HA, CAS: 79-14-1, Figure 1), the smallest and simplest compound of α -hydroxy acid family [1], is a fundamental organic compound and an important organic synthesis intermediate. HA is widely used in chemical cleaning and daily-used chemical industrial [2,3]. HA is also an important precursor to produce biodegradable materials such as polyglycolic acid and poly (lactic-co-glycolic) acid [4]. The purification of HA is usually achieved via extraction or crystallization [5]. Unfortunately, there is lack of the solubility data of HA except in water according to literatures. For aqueous solution, the extremely large aqueous solubility and gentle slope of HA solubility curve make it less efficient to produce via crystallization. So it is necessary to develop the crystallization process in other solvent systems.

In this work, the solubility of HA in five common pure solvents (ethanol, isopropanol, n-butanol, ethyl acetate, and acetonitrile) and two binary solvent mixtures (ethyl acetate + acetone and ethyl acetate + ethanol) were experimentally measured by a dynamic method from 273.15 K to 313.15 K under atmospheric pressure. The experimental data were then correlated with multiple models. Furthermore, the mixing thermodynamic properties were calculated and discussed. The results of this work would be helpful to develop and optimize a crystallization process of HA.

2. Experimental section

2.1. Materials

HA (≥ 99.9 wt%) used in this work was purchased from J&K Scientific Co., Ltd.

and dried before solubility measurement in a vacuum oven at 313.15 K for 48 h. All the organic solvents used in this work were purchased from Jiangtian Chemical Co., Ltd., Tianjin, and used without further treatment. The distilled water was prepared in laboratory. Table 1 provides the detailed information of all the materials used in this work.

2.2. Apparatus and methods

The solubility experiments were conducted by a dynamic method according to the literatures [6,7]. At the beginning of experiment, the weighed HA and solvent were mixed in a 50 ml double-jacketed glass vessel with continuous magnetic agitation at a preset temperature. The temperature was controlled by a thermostat (Xianou Laboratory Instrument Works Co., Ltd, Nanjing) with an accuracy of ± 0.1 K. A laser beam penetrating the vessel was used to monitor the dissolution process. When the solute dissolved completely, the solution became clear and the intensity of excident light reached the maximum. Afterward, small amount of solute with known weight was added into the vessel. The intensity of excident light rapidly dropped down due to the solute addition and then gradually increased to the maximum when the solute dissolved completely. Such addition of small amount of solute was repeated until the intensity of excident light could not return to the maximum in 4 h, indicating the solution was saturated. The mass of the added solute and solvent were weighed using an analytical balance (Mettler Toledo AB204-N, Switzerland) with an accuracy of ± 0.0001 g. Each experiment was repeated three times, and the average was used to calculate the mole fraction solubility.

The mole fraction solubility of HA was calculated by the following equation:

$$x_1 = \frac{m_1 / M_1}{(m_1 / M_1) + \sum m_i / M_i} \quad (1)$$

where x_1 represents the mole fraction solubility of HA; m_1 and m_i represent the mass of HA and the solvents respectively. M_1 , M_i are the molecular mass of HA and solvents, respectively.

2.3. Characterization of HA

The HA used in the experiment was verified by powder X-ray diffraction (PXRD), which was carried out on Rigaku D/max-2500 (Rigaku, Japan). Suspension experiments in the selected solvents were carried out to identify the HA phase transformation via determining the PXRD of suspended crystals.

The melting properties of HA were determined by DSC 1/500 (Mettler Toledo, Switzerland) under protection of nitrogen gas at a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$. The DSC instrument was calibrated by indium and zinc before determination. The standard uncertainty of temperature measurement and enthalpy of fusion measurement were 0.5 K and $0.5 \text{ kJ} \cdot \text{mol}^{-1}$ respectively.

3. Thermodynamic models

3.1. The Modified Apelblat equation

The Modified Apelblat equation in Eq. (2) is a semi-empirical model and widely used for accurate correlation of solid-liquid equilibrium data [8]:

$$\ln x_1 = A + B / (T / \text{K}) + C \ln(T / \text{K}) \quad (2)$$

where x_1 is the solubility of HA, T is the absolute temperature, and A , B , C are the empirical constants of this equation.

3.2. The NRTL model

According to the solid-liquid phase equilibrium theory, the fugacity of the compound in two phases should be equal when the system reaches phase equilibrium. Thus the relationship between equilibrium solubility and temperature can be expressed by Eq. (3) [9]:

$$\ln x_1 = \frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T_m / \text{K}} - \frac{1}{T / \text{K}} \right) - \ln \gamma_i - \frac{1}{(RT / \text{K})} \int_{T_m}^T \Delta C_p dT + \frac{1}{R} \int_{T_m}^T \frac{\Delta C_p}{T / \text{K}} dT \quad (3)$$

where $\Delta_{\text{fus}}H$, T_m and ΔC_p refer to the enthalpy of fusion, the melting temperature of solute, and the change of the heat capacity between the melting and solid state of pure solute, respectively. γ_i refers to the activity coefficient of solute. Considering the last two parts in the right hand side of Eq. (3) are less important than the first two parts due to the negligible value of ΔC_p , Eq. (3) can be simplified as [10]:

$$\ln x_1 = \frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T_m / \text{K}} - \frac{1}{T / \text{K}} \right) - \ln \gamma_i \quad (4)$$

To calculate Eq. (4), the activity coefficient γ_i should be obtained first. In this work, γ_i were calculated by using NRTL model and Wilson model.

NRTL model can be expressed as Eq. (5) for binary system (pure solvent) and as Eq. (6) for ternary system (binary solvent mixture) [11,12]:

$$\ln \gamma_i = x_j^2 \left[\frac{\tau_{ji} G_{ji}^2}{(x_i + G_{ji} x_j)^2} + \frac{\tau_{ij} G_{ij}^2}{(x_j + G_{ij} x_i)^2} \right] \quad (5)$$

$$\begin{aligned}
\ln \gamma_i = & \frac{(G_{ji}x_j + G_{kj}x_k)(\tau_{ji}G_{ji}x_j + \tau_{ki}G_{ki}x_k)}{(x_i + G_{ji}x_j + G_{ki}x_k)^2} \\
& + \frac{[\tau_{ij}G_{ij}x_j^2 + G_{ij}G_{kj}x_jx_k(\tau_{ij} - \tau_{kj})]}{(x_j + G_{ij}x_i + G_{kj}x_k)^2} \\
& + \frac{[\tau_{ik}G_{ik}x_k^2 + G_{ik}G_{jk}x_jx_k(\tau_{ik} - \tau_{jk})]}{(x_k + G_{ik}x_i + G_{jk}x_j)^2}
\end{aligned} \tag{6}$$

where i, j, k are the component of the solution system and G_{ij} , G_{ji} , G_{ik} , G_{jk} , G_{kj} , G_{ki} , τ_{ij} ,

τ_{ji} , τ_{ik} , τ_{jk} , τ_{kj} , τ_{ki} , are parameters of this model, which could be expressed as follows:

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{7}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT/K} = \frac{\Delta g_{ij}}{RT/K} \tag{8}$$

$$\alpha_{ij} = \alpha_{ji} \tag{9}$$

where Δg_{ij} is the parameter of this model and α is an adjustable constant between 0 and 1 [13,14].

3.3. Wilson model

Wilson model can be expressed as Eq. (10) for binary system (pure solvent) [15]:

$$\ln \gamma_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j \left(\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji}x_i} \right) \tag{10}$$

where,

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{jj}}{RT/K}\right) = \frac{V_j}{V_i} \exp\left(-\frac{\Delta \lambda_{ij}}{RT/K}\right) \tag{11}$$

In Eq. (11), V_i and V_j are the mole volume of solute and solvent, respectively. $\Delta \lambda_{ij}$ is the adjustable parameter of this model.

3.4. The CNIBS/R-K model

The CNIBS/R-K model, proposed by Acree and Zvaigzne [16,17], is suggested

to be the most appropriate model for binary solvent mixture system. The simplified equation is shown in Eq. (12):

$$\ln x_1 = B_0 + B_1 x_2^0 + \frac{1}{2} B_2 (x_2^0)^2 + B_3 (x_2^0)^3 + \frac{1}{2} B_4 (x_2^0)^4 \quad (12)$$

where x_1 is the solubility of HA, x_2^0 stands for the initial mole fraction composition of the binary solvent system, $B_0 - B_4$ are empirical model parameters.

3.5. The Jouyban-Acree model

The Jouyban–Acree model is also widely used to describe the solubility in binary solvent mixture system considering both composition of the solvent mixture and temperature. The model is shown as follows [18]:

$$\ln x_1 = A_0 + A_1 / (T / K) + A_2 \ln(T / K) + A_3 x_2^0 + \left[A_4 x_2^0 + A_5 (x_2^0)^2 + A_6 (x_2^0)^3 + A_7 (x_2^0)^4 \right] / (T / K) + A_8 x_2^0 \ln(T / K) \quad (13)$$

where $A_0 - A_8$ are empirical model parameters.

4. Results and discussion

4.1. Characterization and identification of materials

The PXRD pattern of HA used in this work is shown in Figure 2. Compared with the PXRD pattern of HA from Cambridge Crystallographic Data Centre (CCDC), the PXRD pattern of HA samples have the same peaks at 14°, 20°, 25°, 30°, 34°, 40° and so on, confirming high crystalline HA used in this work. In addition, the PXRD of solid HA obtained from suspension experiments kept unchanged, indicating that no polymorphic transformations occurred during the solid-liquid equilibrium in the selected systems.

The melting properties of HA were measured by DSC and given in Figure 3. The melting temperature (T_m) of HA is 350.75 K and the enthalpy of fusion ($\Delta_{fus}H$) is calculated as $19.9 \text{ kJ}\cdot\text{mol}^{-1}$, which are consistent with literature data ($T_m=351.3 \text{ K}$, $\Delta_{fus}H=19.3 \text{ kJ}\cdot\text{mol}^{-1}$) [19]. The density of HA obtained from literature is $1.49 \text{ g}\cdot\text{cm}^{-3}$ (293.15 K) [20]. Then the mole volume of HA could be calculated to be $51.04 \text{ cm}^3\cdot\text{mol}^{-1}$, which was used for Wilson model calculation. The mole volumes of the solvents used in this work were obtained from literature [21].

4.2. Solubility of HA in pure solvents

The experimental solubility data of HA in pure solvents are listed in Table 2 and graphically plotted in Figure 4. It shows that the solubility in these pure solvents increases with rising temperature, indicating that the dissolution processes in all these solvents are endothermic. Within the temperature range of this work, the order of HA solubility in the tested solvents is: ethanol > isopropanol > n-butanol > acetonitrile > ethyl acetate, except for temperature lower than 278 K where the solubility of HA in ethyl acetate is slightly larger than that in acetonitrile. This order is consistent with the order of the polarity of the selected solvents which is ethanol > isopropanol > n-butanol > acetonitrile > ethyl acetate [16]. The solubility order of polar HA in these solvents can be explained by the principle of “like dissolve like”.

The experimental solubility data in pure solvents were correlated by the Modified Apelblat model, NRTL model and Wilson model. The calculated results and related parameters are listed in Table 2 and Table 3, respectively. The average relative deviation percentage (*ARDP*) and root-mean-square (*RMSE*), which are defined in Eq.

(14) and Eq. (15), were introduced to evaluate the precision of these models.

$$ARDP = \frac{1}{N} \sum_{i=1}^N \left| \frac{(x_i^{\text{cal}} - x_i^{\text{exp}})}{x_i^{\text{exp}}} \right| \quad (14)$$

$$RMSD = \left(\frac{\sum_{i=1}^N (x_i^{\text{cal}} - x_i^{\text{exp}})^2}{N} \right)^{1/2} \quad (15)$$

where N stands for the number of the experimental points, x_i^{exp} and x_i^{cal} refer to the experimental and calculated mole fraction solubility of HA, respectively. The values of $ARDP$ and $RMSD$ are also listed in Table 3.

According to Table 3, the $ARDP$ results of these three models are all less than 5%, and the 10^3RMSD results of these models are less than 10, which indicate that all these models can correlate the experimental data precisely.

4.3. Solubility of HA in binary solvent mixtures

The experimental solubilities of HA in two binary solvent mixtures (ethanol + ethyl acetate and acetone + ethyl acetate) at 273.15 K to 313.15 K are listed in Table 4 and Table 5 and plotted in Figure 5, Figure 6 and Figure 7. The solubility of HA in all the investigated solvent mixtures increases with rising temperature, and increases with decreasing mole fraction of ethyl acetate at a fixed temperature.

The CNIBS/R-K model and Jouyban-Acree model were used to correlate the experimental data in binary solvent mixture. The correlation results are also listed in Table 4 and Table 5. $ARDP$, R^2 , and related parameters of the two models are given in Table 6 and Table 7. According to the Table 6 and Table 7, the R^2 values for these two models are higher than 0.99, $ARDP$ are lower than 2% and 10^3RMSD are all lower than 5. These results reveal that both the CNIBS/R-K model and the Jouyban-Acree

model correlate the experimental data precisely.

4.4. The mixing thermodynamic properties

The mixing properties, such as mixing Gibbs energy ΔG_{mix} , mixing enthalpy ΔS_{mix} , and mixing entropy ΔH_{mix} , in pure solvents and binary solvent mixtures were calculated according to Eq. (16) - (18) [22]:

$$\Delta G_{\text{mix}} = G^{\text{E}} + \Delta G^{\text{id}} \quad (16)$$

$$\Delta S_{\text{mix}} = S^{\text{E}} + \Delta S^{\text{id}} \quad (17)$$

$$\Delta H_{\text{mix}} = H^{\text{E}} + \Delta H^{\text{id}} \quad (18)$$

where ΔG^{id} , ΔS^{id} and ΔH^{id} are the mixing properties of an ideal solution, and G^{E} , S^{E} and H^{E} refer to the excess properties of the real solution. For ideal solution,

$$\Delta G^{\text{id}} = R(T / \text{K}) \sum_i^n x_i \ln x_i \quad (19)$$

$$\Delta S^{\text{id}} = -\frac{\Delta G^{\text{id}}}{(T / \text{K})} \quad (20)$$

$$\Delta H^{\text{id}} = 0 \quad (21)$$

where x_i represents the mole fraction of each component in solution. n takes 2 for binary component (pure solvent), and takes 3 for ternary component (binary solvent system).

For non-ideal solution, the excess mixing properties could be first calculated by the following equations:

$$G^{\text{E}} = R(T / \text{K}) \sum_i^n x_i \ln \gamma_i \quad (22)$$

$$H^{\text{E}} = -R(T / \text{K})^2 \sum_i^n x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{p,x} \quad (23)$$

$$S^E = \frac{H^E - G^E}{(T / K)} \quad (24)$$

where γ_i refers to the activity coefficient of component i in non-ideal solution, which can be calculated by NRTL model (Eq. (5) and (6)).

Since the binary solvent systems are pre-mixed before the dissolution of HA, the mixing properties of solvent mixing process should be excluded first. The ideal and excess thermodynamic properties of pre-mixed solvents were calculated by using Eq. (19)-(24). Then the mixing properties of pre-mixed solvents were obtained and subtracted from the mixing properties of solute-solvent system. The calculated mixing thermodynamic properties in the five pure solvents are listed in Table 8 while the mixing thermodynamic properties excluding the pre-mixing in binary solvent mixtures are listed in Table 9 and Table 10. The mixing Gibbs energy ΔG_{mix} in both pure and binary solvent system are all negative, which also decrease with increasing temperature. It indicates that the dissolution processes of HA in all these solvent systems are spontaneous. The positive mixing enthalpy ΔS_{mix} in all the selected solvent systems indicates that the dissolution processes of HA in these solvent systems are entropy-driven [23].

5. Conclusions

In this work, the solubility of HA in five pure solvents and two binary solvent mixtures were experimentally measured from $T = (273.15 \text{ K to } 313.15) \text{ K}$ at atmospheric pressure by a dynamic method. The solubility of HA in the selected pure solvents increases with increasing temperature. Within the temperature range of this work, the solubility order of HA in the tested pure solvents is: ethanol > isopropanol >

n-butanol > acetonitrile > ethyl acetate, which is consistent with the polarity order of the selected solvents. The solubility data in the five pure solvents could be accurately correlated by the Modified Apelblat model, NRTL model, and Wilson model in the selected pure solvents, while the CNIBS/R-K model and the Jouyban-Acree model can fit the data in the tested two binary solvent mixtures with high accuracy. The calculation results of the mixing properties of HA in both pure and binary solvent mixtures revealed that the dissolution process of HA in all the selected solvent systems are spontaneous and entropy-driven.

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Figure captions:

Figure 1. The chemical structure of HA.

Figure 2. The PXRD pattern of HA crystals.

Figure 3. Thermal analysis (DSC) of HA.

Figure 4. Experimental and calculated solubility of HA in different pure solvents

from 273.15 K to 313.15 K ($p=0.1$ MPa): ■, ethyl acetate; ▲, n-butanol; ▼, isopropanol; ◆, ethanol; ●, acetonitrile. Solid lines are correlated by the Modified Apelblat model.

Figure 5. Mole fraction solubility (x_1) of HA in binary {ethanol + ethyl acetate}

solvent mixtures at different mole fraction of ethanol: ■, 273.15 K; ◆, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ►, 298.15 K; ◄, 303.15 K; ◆, 308.15 K; ★, 313.15 K. The solid lines are correlated data from CNIBS/R-K model.

Figure 6. Mole fraction solubility (x_1) of HA in binary {acetone + ethyl acetate}

solvent mixture at different mole fraction of acetone: ■, 273.15 K; ◆, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ►, 298.15 K; ◄, 303.15 K; ★, 308.15 K; ◆, 313.15 K. The solid line are correlated data from CNIBS/R-K model.

Figure 7. 3-dimension plot of solubility in two binary solvent mixtures: (a), ethanol + ethyl acetate; (b), acetone + ethyl acetate.

Table Headings:

TABLE 1. Description of chemicals used in this work.

TABLE 2. Experimental mole solubility, x_1^{exp} , and calculated mole solubility, x_1^{cal} , of HA in pure solvents from 273.15 K to 313.15 K ($p=0.1$ MPa).

TABLE 3. Parameters of Modified Apeblat, NRTL model and Wilson models in pure solvents.

TABLE 4. Experimental mole fraction solubility, x_1^{exp} , and calculated mole fraction solubility, x_1^{cal} , of crystalline HA in binary solvent mixture {ethanol (2) + ethyl acetate (3)} from 273.15 K to 313.15 K ($p=0.1$ MPa).

TABLE 5. Experimental mole fraction solubility, x_1^{exp} , and calculated mole fraction solubility, x_1^{cal} , of crystalline HA in binary solvent mixture {acetone (2) + ethyl acetate (3)} from 273.15 K to 313.15 K ($p=0.1$ MPa).

TABLE 6. Parameters of the CNIBS/R-K model for the solubility of HA in binary solvent mixture.

TABLE 7. Parameters of the Jouyban-Acree model for the solubility of HA in binary solvent mixture.

TABLE 8. The mixing thermodynamic properties of HA in pure solvents.

TABLE 9. The mixing thermodynamic properties of HA in binary solvent mixture {ethanol (2) + ethyl acetate (3)}.

TABLE 10. The mixing thermodynamic properties of HA in binary solvent mixture {acetone (2) + ethyl acetate (3)}.

Figure 1. The chemical structure of HA.

Figure 2. The PXRD pattern of HA crystals.

Figure 3. Thermal analysis (DSC) of HA.

Figure 4. Experimental and calculated solubility of HA in different pure solvents from 273.15 K to 313.15 K ($p=0.1$ MPa): ■, ethyl acetate; ▲, n-butanol; ▼, isopropanol; ◆, ethanol; ●, acetonitrile. Solid lines are correlated by the Modified Apelblat model.

Figure 5. Mole fraction solubility (x_1) of HA in binary {ethanol + ethyl acetate} solvent mixtures at different mole fraction of ethanol: ■, 273.15 K; ◆, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ►, 298.15 K; ◄, 303.15 K; ⬠, 308.15 K; ★, 313.15 K. The solid lines are correlated data from CNIBS/R-K model.

Figure 6. Mole fraction solubility (x_1) of HA in binary {acetone + ethyl acetate} solvent mixtures at different mole fraction of acetone: ■, 273.15 K; ◆, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ►, 298.15 K; ◄, 303.15 K; ★, 308.15 K; ◆, 313.15 K. The solid line are correlated data from CNIBS/R-K model.

(a). ethanol + ethyl acetate

(b). acetone + ethyl acetate

Figure 7. 3-dimension plot of solubility in two binary solvent mixtures: (a), ethanol + ethyl acetate; (b), acetone + ethyl acetate.

TABLE 1

Description of chemicals used in this work

Material	Mass fraction Purity ^a	Water content ^b
hydroxyacetic acid	≥99.9%	No measured
acetonitrile	≥99.5%	≤0.05%
ethanol	≥99.7%	≤0.3%
ethyl acetate	≥99.5%	≤0.1%
n-butanol	≥99.5%	≤0.2%
isopropanol	≥99.7%	≤0.2%
acetone	≥99.5%	≤0.3%

^a The mass fraction purity of HA and all solvents are provided by the suppliers.^b Water content is the water mass fraction of the solvent, and is provided by the suppliers.

TABLE 2

Experimental mole fraction solubility, x_1^{exp} , and calculated mole fraction solubility,

x_1^{cal} , of crystalline HA in pure solvents from 273.15 K to 313.15 K ($p=0.1$ MPa).^{a,b}

T/K	$10^2 x_1^{\text{exp}}$	$10^2 x_1^{\text{cal,A}}$	$10^2 x_1^{\text{cal,N}}$	$10^2 x_1^{\text{cal,W}}$
ethyl acetate				
273.15	2.56	2.49	2.14	2.28
278.15	2.89	2.90	2.61	2.76
283.15	3.43	3.40	3.19	3.37
288.15	3.95	4.03	3.87	4.05
293.15	4.72	4.83	4.73	4.90
298.15	5.80	5.82	5.82	5.93
303.15	7.18	7.08	7.19	7.20
308.15	8.77	8.67	8.89	8.72
313.15	10.6	10.7	11.0	10.5
ethanol				
273.15	17.9	17.9	16.9	17.2
278.15	19.7	19.9	19.5	19.7
283.15	22.4	22.3	22.3	22.5
288.15	25.4	25.1	25.5	25.5
293.15	28.6	28.3	28.9	28.9
298.15	31.9	32.1	32.8	32.7
303.15	36.3	36.4	36.9	36.7
308.15	41.3	41.4	41.4	41.2
313.15	47.4	47.2	46.2	46.0
n-butanol				
273.15	10.8	10.7	10.7	10.4
278.15	12.0	12.4	12.4	12.3
283.15	14.5	14.4	14.4	14.3
288.15	16.8	16.7	16.7	16.7
293.15	19.5	19.3	19.3	19.4
298.15	22.4	22.3	22.3	22.4
303.15	25.4	25.7	25.6	25.8
308.15	29.6	29.7	29.6	29.7
313.15	34.4	34.2	34.3	34.1
isopropanol				
273.15	14.2	14.4	14.8	14.5
278.15	16.8	16.7	16.9	16.7
283.15	19.3	19.1	19.2	19.1

288.15	22.0	21.9	21.7	21.7
293.15	24.8	24.8	24.6	24.7
298.15	28.0	28.0	27.7	27.9
303.15	31.3	31.4	31.2	31.3
308.15	34.8	35.1	35.1	35.2
313.15	39.1	39.0	39.4	39.3
acetonitrile				
273.15	2.26	2.01	2.56	2.22
278.15	2.82	2.64	3.11	2.83
283.15	3.51	3.49	3.78	3.58
288.15	4.57	4.62	4.71	4.61
293.15	5.54	6.13	5.77	5.81
298.15	7.81	8.14	7.65	7.83
303.15	11.3	10.8	10.7	10.9
308.15	14.7	14.4	14.4	14.5
313.15	18.9	19.2	19.4	19.2

^a x_1^{exp} represent the experimental solubility of HA, $x_1^{\text{cal,A}}$, $x_1^{\text{cal,N}}$, $x_1^{\text{cal,W}}$ represent the calculated solubility by the Modified Apelblat equation, the NRTL model and the Wilson model, respectively.

^b The standard uncertainty are $u(T) = 0.06$ K, $u(p) = 6$ kPa. The relative standard uncertainties u is $u_r(x_1) = 0.05$.

TABLE 3

Parameters of Modified Apelblat, NRTL model and Wilson models in pure solvents

Models	Parameters	EA ^a	Ethanol	n-butanol	Isopropanol	acetonitrile
Modified Apelblat	A^b	-324.1	-162.0	-81.01	40.80	-241.1
	$10^{-2}B^b$	114.0	52.68	13.54	-36.57	63.21
	C^b	49.67	25.14	13.16	-5.231	38.15
	$ARDP\%^c$	1.268	0.6363	1.071	0.6088	4.696
	10^3RMSD^d	0.7474	1.996	2.195	1.503	3.368
NRTL	$10^{-3}\Delta g_{12}^e$	5.617	-3.091	16.40	6.288	-16.86
	$10^{-3}\Delta g_{21}^e$	3.495	3.891	-12.772	-3.400	26.26
	$ARDP\%^c$	4.512	1.708	0.957	1.146	5.687
	10^3RMSD^d	2.269	6.512	1.942	2.977	3.513
	$10^{-3}\Delta\lambda_{12}^f$	3.660	6.048	0.023	-1.442	4.533
Wilson	$10^{-3}\Delta\lambda_{21}^f$	12.97	-2.882	4.375	39.69	0.321
	$ARDP\%^c$	3.022	1.497	1.164	0.851	1.914
	10^3RMSD^d	1.353	6.401	2.457	2.072	2.181

^a EA represents ethyl acetate.^b A , B and C are the parameters of the Modified Apelblat equation.^c $ARDP\%$ is the average relative deviation percentage calculated by Eq (14).^d $RMSD$ is the the root-mean-square deviation calculated by Eq (15).^e Δg_{12} and Δg_{21} are the parameters of the NRTL model.^f $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are the parameters of the Wilson model.

TABLE 4

Experimental mole fraction solubility, x_1^{exp} , and calculated mole fraction solubility, x_1^{cal} , of crystalline HA in binary solvent mixture {ethanol (2) + ethyl acetate (3)} from 273.15 K to 313.15 K ($p=0.1$ MPa). ^{a,b}

T/K	x_2^0	$10^2 x_1^{\text{exp}}$	$10^2 x_1^{\text{cal,R}}$	$10^2 x_1^{\text{cal,J}}$
273.15	0.099	5.20	5.11	5.72
273.15	0.201	7.25	7.48	7.88
273.15	0.299	10.3	10.2	10.3
273.15	0.399	12.8	12.8	12.7
273.15	0.499	14.7	14.9	14.7
273.15	0.610	16.5	16.4	16.4
273.15	0.700	17.4	17.4	18.1
278.15	0.099	6.29	6.18	6.55
278.15	0.201	8.36	8.69	8.93
278.15	0.299	12.1	11.7	11.6
278.15	0.399	14.5	14.6	14.1
278.15	0.499	16.5	16.7	16.2
278.15	0.610	18.1	18.0	18.0
278.15	0.700	19.5	19.5	19.7
283.15	0.099	7.11	7.02	7.50
283.15	0.201	9.61	9.91	10.1
283.15	0.299	13.5	13.1	13.0
283.15	0.399	16.0	16.1	15.8
283.15	0.499	18.1	18.2	18.0
283.15	0.610	19.8	19.7	19.8
283.15	0.700	21.4	21.5	21.6
288.15	0.099	8.41	8.33	8.60
288.15	0.201	11.1	11.4	11.5
288.15	0.299	15.0	14.8	14.6
288.15	0.399	17.9	17.9	17.6
288.15	0.499	20.2	20.3	19.9
288.15	0.610	22.1	22.0	21.9
288.15	0.700	23.7	23.7	23.7
293.15	0.099	9.99	9.88	9.86
293.15	0.201	12.6	13.0	13.1
293.15	0.299	17.0	16.5	16.5
293.15	0.399	19.8	19.9	19.7
293.15	0.499	22.3	22.5	22.2
293.15	0.610	24.6	24.4	24.2

293.15	0.700	26.1	26.2	26.0
298.15	0.099	11.5	11.4	11.3
298.15	0.201	14.3	14.8	14.8
298.15	0.299	19.1	18.6	18.6
298.15	0.399	22.0	22.1	22.1
298.15	0.499	24.6	24.8	24.7
298.15	0.610	27.1	26.9	26.8
298.15	0.700	28.6	28.6	28.7
303.15	0.099	13.2	13.0	12.9
303.15	0.201	16.5	16.9	16.9
303.15	0.299	21.4	20.9	21.0
303.15	0.399	24.5	24.6	24.8
303.15	0.499	27.2	27.4	27.6
303.15	0.610	29.7	29.6	29.7
303.15	0.700	31.4	31.5	31.7
308.15	0.099	15.1	15.0	14.8
308.15	0.201	18.9	19.3	19.2
308.15	0.299	24.1	23.6	23.7
308.15	0.399	27.2	27.4	27.8
308.15	0.499	30.2	30.3	30.8
308.15	0.610	33.0	32.8	33.1
308.15	0.700	35.1	35.1	35.1
313.15	0.099	17.6	17.4	17.0
313.15	0.201	21.8	22.3	21.8
313.15	0.299	27.5	26.8	26.8
313.15	0.399	30.4	30.8	31.3
313.15	0.499	34.1	34.1	34.5
313.15	0.610	37.2	37.1	36.8
313.15	0.700	39.6	39.6	39.0

^a $x_1^{\text{cal,R}}$, $x_1^{\text{cal,J}}$ represent the calculated solubility of HA by the CNIBS/R-K and the Jouban-Acree models, respectively. And x_2^0 is the initial mole fraction composition of ethanol in the binary solvent mixture.

^b The standard uncertainty are $u(T) = 0.06$ K, $u(p) = 6$ kPa, the relative standard uncertainties is $u_r(x_1) = 0.05$, $u_r(x_2^0) = 0.02$.

TABLE 5

Experimental mole fraction solubility, x_1^{exp} , and calculated mole fraction solubility, x_1^{cal} , of crystalline HA in binary solvent mixture {acetone (2) + ethyl acetate (3)} from 273.15 K to 313.15 K ($p=0.1$ MPa). ^{a,b}

T/K	x_2^0	$10^2 x_1^{\text{exp}}$	$10^2 x_1^{\text{cal,R}}$	$10^2 x_1^{\text{cal,J}}$
273.15	0.100	3.29	3.29	3.43
273.15	0.166	3.59	3.61	3.67
273.15	0.230	3.89	3.87	3.98
273.15	0.299	4.18	4.19	4.35
273.15	0.400	4.82	4.82	4.92
273.15	0.499	5.34	5.34	5.56
278.15	0.100	4.14	4.14	4.05
278.15	0.166	4.38	4.39	4.33
278.15	0.230	4.69	4.68	4.69
278.15	0.299	5.11	5.12	5.13
278.15	0.400	5.94	5.94	5.80
278.15	0.499	6.51	6.51	6.56
283.15	0.100	4.82	4.82	4.78
283.15	0.166	5.13	5.12	5.12
283.15	0.230	5.54	5.55	5.55
283.15	0.299	6.12	6.11	6.06
283.15	0.400	7.00	7.00	6.86
283.15	0.499	7.77	7.77	7.76
288.15	0.100	5.68	5.68	5.66
288.15	0.166	6.13	6.13	6.07
288.15	0.230	6.65	6.65	6.58
288.15	0.299	7.28	7.28	7.19
288.15	0.400	8.29	8.29	8.14
288.15	0.499	9.32	9.32	9.21
293.15	0.100	6.67	6.67	6.72
293.15	0.166	7.28	7.28	7.21
293.15	0.230	7.93	7.93	7.82
293.15	0.299	8.67	8.67	8.54
293.15	0.400	9.81	9.81	9.69
293.15	0.499	11.1	11.1	11.0
298.15	0.100	7.94	7.94	7.99
298.15	0.166	8.62	8.62	8.58
298.15	0.230	9.33	9.33	9.30
298.15	0.299	10.2	10.2	10.2

298.15	0.400	11.5	11.5	11.5
298.15	0.499	13.2	13.2	13.1
303.15	0.100	9.41	9.41	9.51
303.15	0.166	10.2	10.2	10.2
303.15	0.230	11.0	11.1	11.1
303.15	0.299	12.1	12.1	12.1
303.15	0.400	13.6	13.6	13.8
303.15	0.499	15.5	15.5	15.7
308.15	0.100	11.3	11.3	11.3
308.15	0.166	12.1	12.1	12.2
308.15	0.230	13.0	13.1	13.2
308.15	0.299	14.5	14.4	14.5
308.15	0.400	16.2	16.3	16.5
308.15	0.499	18.4	18.4	18.8
313.15	0.100	13.6	13.6	13.5
313.15	0.166	14.7	14.6	14.6
313.15	0.230	15.8	15.9	15.8
313.15	0.299	17.5	17.4	17.4
313.15	0.400	20.0	20.0	19.8
313.15	0.499	22.8	22.8	22.5

^a $x_1^{\text{cal,R}}$, $x_1^{\text{cal,J}}$ represent the calculated solubility of HA by the CNIBS/R-K and the Jouban-Acree models, respectively. And x_2^0 is the initial mole fraction composition of acetone in the binary solvent mixture.

^b The standard uncertainty are $u(T) = 0.06$ K, $u(p) = 6$ kPa, the relative standard uncertainties is $u_r(x_1) = 0.05$, $u_r(x_2^0) = 0.02$.

TABLE 6

Parameters of the CNIBS/R-K model for the solubility of HA in binary solvent mixture.

Binary solvent mixture	<i>T</i> /K	B_0^a	B_1^a	B_2^a	B_3^a	B_4^a	R^2^b	<i>ARDP</i> % ^c	10^3RMSD^d
Ethanol + EA ^f	273.15	-3.367	3.914	1.691	-11.54	8.362	0.9968	1.257	1.394
	278.15	-3.050	1.939	10.11	-27.00	18.18	0.9942	1.530	2.013
	283.15	-2.982	2.936	5.236	-18.77	13.59	0.9959	1.230	1.821
	288.15	-2.770	2.519	5.141	-16.85	11.78	0.9971	0.965	1.627
	293.15	-2.549	1.929	5.929	-16.67	11.13	0.9944	1.255	2.412
	298.15	-2.405	2.022	4.629	-13.92	9.356	0.9922	1.397	3.027
	303.15	-2.303	2.591	1.719	-9.086	6.693	0.9944	1.109	2.716
	308.15	-2.172	2.802	0.227	-6.522	5.373	0.9944	1.038	2.929
	313.15	-2.044	3.288	-2.802	-0.688	1.768	0.9936	0.988	3.440
Acetone + EA ^f	273.15	-3.694	4.219	-18.48	46.01	-39.61	0.9982	0.271	0.135
	278.15	-3.300	1.669	-7.555	27.59	-29.22	1.0000	0.044	0.027
	283.15	-3.038	-0.623	8.132	-12.91	6.018	0.9999	0.068	0.049
	288.15	-2.954	0.592	3.111	-5.424	2.981	1.0000	0.007	0.006
	293.15	-2.809	0.686	4.278	-11.32	9.866	1.0000	0.020	0.020
	298.15	-2.654	1.177	0.382	-1.022	1.135	1.0000	0.008	0.010
	303.15	-2.418	-0.102	8.418	-21.06	18.19	0.9998	0.083	0.118
	308.15	-2.146	-1.522	15.200	-34.06	26.76	0.9978	0.307	0.517
	313.15	-2.030	-0.265	7.828	-16.13	11.92	0.9992	0.199	0.407

^a B_0 , B_1 , B_2 , B_3 and B_4 are the parameters of the CNIBS/R-K model.

^b R^2 is the determinate coefficient.

^c *ARDP* is the average relative deviation calculated by Eq (14).

^d *RMSD* is the the root-mean-square deviation calculated by Eq (15).

^f EA represents ethyl acetate.

TABLE 7

Parameters of the Jouyban-Acree model for the solubility of HA in binary solvent mixture

Parameters	Ethanol + EA ^b	Acetone + EA ^b
A_0^a	-99.23	-158.4
A_1^a	2123	4350
A_2^a	15.74	24.78
A_3^a	-39.41	-59.88
A_4^a	3049	2137
A_5^a	870.5	2188
A_6^a	-3455	-4708
A_7^a	2477	3581
A_8^a	5.560	9.226
R^2^c	0.9976	0.9992
$10^3 RMSD^d$	3.704	1.197

^a $A_0, A_1, A_2, A_3, A_4, A_5, A_6, A_7$ and A_8 are the parameters of the Jouyban-Acree model.

^b EA represents ethyl acetate.

^c R^2 is the determinate coefficient.

^d $RMSD$ is the the root-mean-square deviation calculated by Eq (15).

TABLE 8The mixing thermodynamic properties of HA in pure solvents.^{a,b}

T/K	γ_1	$H^E(\Delta H_{\text{mix}})$ $\text{J}\cdot\text{mol}^{-1}$	ΔG_{mix} $\text{kJ}\cdot\text{mol}^{-1}$	ΔS_{mix} $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Ethyl acetate				
273.15	6.743	-63.7	-0.154	0.331
278.15	6.481	-71.4	-0.171	0.358
283.15	6.162	-83.2	-0.196	0.397
288.15	5.878	-94.7	-0.219	0.433
293.15	5.547	-110	-0.250	0.477
298.15	5.166	-131	-0.289	0.532
303.15	4.767	-154	-0.334	0.594
308.15	4.389	-178	-0.381	0.657
313.15	4.028	-203	-0.429	0.722
Ethanol				
273.15	0.8531	285	-1.16	5.283
278.15	0.8658	296	-1.24	5.530
283.15	0.8797	316	-1.36	5.906
288.15	0.8932	335	-1.47	6.268
293.15	0.9057	351	-1.58	6.589
298.15	0.9174	362	-1.68	6.853
303.15	0.9300	375	-1.79	7.131
308.15	0.9422	382	-1.88	7.339
313.15	0.9549	385	-1.95	7.442
n-Butanol				
273.15	1.352	176	-0.700	3.206
278.15	1.362	184	-0.760	3.392
283.15	1.365	202	-0.860	3.751
288.15	1.365	215	-0.951	4.044
293.15	1.359	225	-1.04	4.320
298.15	1.350	227	-1.13	4.562
303.15	1.338	232	-1.21	4.759
308.15	1.315	237	-1.30	4.981
313.15	1.286	242	-1.39	5.143
Isopropanol				
273.15	0.975	300	-0.956	4.598
278.15	1.002	338	-1.07	5.077
283.15	1.026	366	-1.18	5.444
288.15	1.048	393	-1.28	5.791
293.15	1.068	415	-1.37	6.086
298.15	1.086	435	-1.46	6.370
303.15	1.100	447	-1.55	6.580

308.15	1.112	453	-1.62	6.732
313.15	1.120	456	-1.69	6.839
Acetonitrile				
273.15	5.628	34.8	-0.151	0.681
278.15	5.437	38.6	-0.178	0.780
283.15	5.198	43.0	-0.209	0.891
288.15	4.836	51.3	-0.252	1.053
293.15	4.549	56.1	-0.289	1.176
298.15	3.931	80.0	-0.361	1.479
303.15	3.208	127	-0.456	1.925
308.15	2.714	174	-0.538	2.309
313.15	2.279	236	-0.628	2.761

^a γ_1 is the activity coefficient of solute.

^b The combined expanded uncertainties are $Uc(\Delta G_{mix}) = 0.050\Delta G_{mix}$, $Uc(\Delta S_{mix}) = 0.055\Delta S_{mix}$ (0.95 level of confidence).

TABLE 9

The mixing thermodynamic properties of HA in binary solvent mixture {ethanol (2) + ethyl acetate (3)}^a

x_2^0	ΔH_{mix} kJ·mol ⁻¹	ΔG_{mix} kJ·mol ⁻¹	ΔS_{mix} J·mol ⁻¹ ·K ⁻¹	x_2^0	ΔH_{mix} kJ·mol ⁻¹	ΔG_{mix} kJ·mol ⁻¹	ΔS_{mix} J·mol ⁻¹ ·K ⁻¹
<i>T</i> =273.15 K				<i>T</i> =278.15 K			
0.099	0.169	-0.330	1.68	0.099	0.167	-0.368	1.78
0.201	0.474	-0.459	3.42	0.201	0.481	-0.493	3.50
0.299	0.773	-0.610	5.06	0.299	0.782	-0.653	5.16
0.399	0.946	-0.730	6.24	0.399	0.934	-0.767	6.25
0.500	0.973	-0.826	6.15	0.500	0.971	-0.864	6.17
0.610	1.04	-0.919	6.57	0.610	1.02	-0.952	6.55
0.700	1.06	-0.982	6.87	0.700	1.05	-1.029	6.86
<i>T</i> =283.15 K				<i>T</i> =288.15 K			
0.099	0.166	-0.396	1.84	0.099	0.165	-0.435	2.08
0.201	0.485	-0.529	3.58	0.201	0.488	-0.566	3.66
0.299	0.777	-0.681	5.15	0.299	0.769	-0.710	5.13
0.399	0.915	-0.793	6.18	0.399	0.891	-0.821	6.12
0.500	0.958	-0.890	6.12	0.500	0.942	-0.917	6.07
0.610	1.00	-0.984	6.50	0.610	0.976	-1.016	6.45
0.700	1.03	-1.067	6.85	0.700	1.01	-1.101	6.80
<i>T</i> =293.15 K				<i>T</i> =298.15 K			
0.099	0.161	-0.476	2.17	0.099	0.153	-0.511	2.23
0.201	0.486	-0.599	3.70	0.201	0.479	-0.630	3.72
0.299	0.756	-0.738	5.09	0.299	0.736	-0.761	5.02
0.399	0.860	-0.843	6.01	0.399	0.824	-0.859	5.86
0.500	0.919	-0.938	5.97	0.500	0.888	-0.952	5.84
0.610	0.943	-1.041	6.36	0.610	0.902	-1.056	6.22
0.700	0.978	-1.130	6.71	0.700	0.940	-1.150	6.58
<i>T</i> =303.15 K				<i>T</i> =308.15 K			
0.099	0.140	-0.544	2.26	0.099	0.122	-0.577	2.27
0.201	0.466	-0.662	3.72	0.201	0.446	-0.687	3.68
0.299	0.707	-0.778	4.90	0.299	0.668	-0.787	4.72
0.399	0.782	-0.870	5.67	0.399	0.727	-0.871	5.42
0.500	0.849	-0.958	5.67	0.500	0.796	-0.954	5.40
0.610	0.855	-1.063	6.03	0.610	0.800	-1.057	5.78
0.700	0.893	-1.162	6.40	0.700	0.835	-1.160	6.16
<i>T</i> =313.15 K							
0.099	0.0965	-0.609	2.25				
0.201	0.413	-0.707	3.58				
0.299	0.612	-0.784	4.46				

0.399	0.659	-0.858	5.09
0.500	0.719	-0.929	5.01
0.610	0.735	-1.028	5.41
0.700	0.757	-1.133	5.79

^a The combined expanded uncertainties are $U_c(\Delta G_{\text{mix}}) = 0.050 \Delta G_{\text{mix}}$, $U_c(\Delta S_{\text{mix}}) = 0.055 \Delta S_{\text{mix}}$ (0.95 level of confidence).

TABLE 10

The mixing thermodynamic properties of HA in binary solvent mixture {acetone (2) + ethyl acetate (3)}^a

x_2^0	ΔH_{mix} J·mol ⁻¹	ΔG_{mix} kJ·mol ⁻¹	ΔS_{mix} J·mol ⁻¹ ·K ⁻¹	x_2^0	ΔH_{mix} J·mol ⁻¹	ΔG_{mix} kJ·mol ⁻¹	ΔS_{mix} J·mol ⁻¹ ·K ⁻¹
<i>T</i> =273.15 K				<i>T</i> =278.15 K			
0.100	92.7	-0.219	1.14	0.100	82.0	-0.251	1.20
0.166	147	-0.240	1.41	0.166	138	-0.267	1.46
0.230	181	-0.257	1.60	0.230	173	-0.283	1.64
0.299	202	-0.272	1.74	0.299	196	-0.300	1.78
0.400	216	-0.301	1.89	0.400	215	-0.331	1.96
0.499	220	-0.324	1.99	0.499	225	-0.354	2.08
<i>T</i> =283.15 K				<i>T</i> =288.15 K			
0.100	72.4	-0.276	1.23	0.100	60.1	-0.305	1.27
0.166	128	-0.292	1.48	0.166	115	-0.321	1.51
0.230	164	-0.308	1.67	0.230	152	-0.336	1.69
0.299	189	-0.327	1.82	0.299	179	-0.354	1.85
0.400	211	-0.357	2.01	0.400	206	-0.383	2.04
0.499	227	-0.383	2.16	0.499	229	-0.414	2.23
<i>T</i> =293.15 K				<i>T</i> =298.15 K			
0.100	45.3	-0.335	1.30	0.100	26.1	-0.369	1.33
0.166	100	-0.350	1.54	0.166	80.7	-0.381	1.55
0.230	137	-0.365	1.71	0.230	119	-0.393	1.72
0.299	166	-0.381	1.87	0.299	150	-0.407	1.87
0.400	198	-0.410	2.07	0.400	186	-0.434	2.08
0.499	228	-0.443	2.29	0.499	223	-0.468	2.32
<i>T</i> =303.15 K				<i>T</i> =308.15 K			
0.100	16.0	-0.403	1.34	0.100	13.2	-0.440	1.48
0.166	57.5	-0.411	1.54	0.166	27.6	-0.441	1.52
0.230	96.5	-0.420	1.70	0.230	68.3	-0.444	1.66
0.299	129	-0.432	1.85	0.299	100	-0.454	1.80
0.400	170	-0.456	2.06	0.400	147	-0.474	2.01
0.499	213	-0.490	2.32	0.499	197	-0.505	2.28
<i>T</i> =313.15 K							
0.100	5.12	-0.467	1.53				
0.166	13.0	-0.469	1.55				
0.230	27.7	-0.472	1.58				
0.299	60.7	-0.475	1.69				
0.400	111	-0.482	1.90				
0.499	170	-0.509	2.17				

^a The combined expanded uncertainties are $U_c(\Delta G_{\text{mix}})=0.050\Delta G_{\text{mix}}$,

$$U_c(\Delta S_{\text{mix}})=0.055\Delta S_{\text{mix}} \text{ (0.95 level of confidence).}$$