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Aqueous solubility calculation of aromatic acids within a wide temperature range using a modified regular solution model

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Abstract The modified RSFH model, based on the regular solution theory coupled with the Flory-Huggins entropy term, was extended to calculate the solubility of aromatic acids in water within wide temperature ranges. The aqueous solubility data on aromatic acids from the published literature were assembled and validated. A total of 1,009 aqueous solubility data points for 25 aromatic acids within the temperature range of 273–463 K were selected for modeling. The calculation results showed that the solubility of aromatic acids in water could be well represented by the proposed four-parameter solution model within a wide temperature range. The overall absolute average deviation (δ_{AAD}) is 6.76%. The estimated cohesive energies of the aromatic acids were found to be about 20–30 kJ mol^{-1}. For the majority of the aromatic acids investigated, the cohesive energy could be considered as a constant. Strong temperature dependency, however, was also observed for a few aromatic acids, and misleading results may be obtained if this dependency is neglected. The model also has a certain prediction ability and could be extrapolated to a high temperature range where no experimental solubility data are available.

Keywords Thermodynamics · Semiempirical calculations · Phase diagrams · Aromatic acid · Regular solution theory

Introduction

The solubility of a solid in liquid is of significant importance to many crystallization-related separation and purification processes. Reliable design, analysis, and operation of such processes could be achieved if the solubility data or an accurate estimation method were available [1]. Because of the widely recognized importance of solubility data in science and industry, vast numbers of quantitative studies on solubility phenomena have been made. Experimental observations are certainly the most reliable method to obtain the required solubility data [2, 3]. In many cases, however, the estimation of solubility by an appropriate thermodynamic model is preferred or the only choice when the expensive and time consuming solid-liquid equilibrium measurements at high temperature and pressure become impractical. Moreover, we can gain in-depth understanding of the interactions between the solute and solvent molecules via the solution model study from a molecular thermodynamics perspective.

For non-electrolyte systems, the basic expression for the solubility of solute in liquid is derived by setting up a virtual thermodynamic Hess cycle starting from the solid-liquid equilibrium criteria [4]. In this expression (Eq. 1), knowledge about the melting point, enthalpy of fusion, and activity coefficient of the solute at saturation in the solution is needed to estimate the solubility. The first two parameters are pure component properties of the solute that can be obtained by calorimetric measurements such as differential scanning calorimetry (DSC). Then the activity coefficient of the solute can be estimated from an appropriate excess Gibbs energy (G^{E}) solution model. Among numerous well-known activity coefficient models such as the van Laar, Wilson, NRTL, UNIQUAC, and UNIFAC equations, the regular solution model is widely employed to describe the

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solid-liquid equilibrium because of its simplicity and high accuracy for non-polar systems [4, 5]. The regular solution model, based on the solubility parameters theory, is the best expression for the activity coefficient of non-polar solute in non-polar solvents [6]. For polar systems, however, a poor result is always obtained because the assumptions for the regular solution theory are no more valid. Figure 1 shows a comparison between the experimental solubility of naphthalene in different solvents at 338.15 K [5] and that calculated with the regular solution model. Clearly, the regular solution model gives very poor predictions of the solubility except for the non-polar solvents *n*-hexane and chloroform.

Various improvements for the regular solution model have been proposed hoping to extend its application range while keeping the simple formulas. Some semi-quantitative success has been achieved [7–14]. Flory [10] and Huggins [11] each independently proposed the expression for the mixing entropy of athermal solution and added the expression into the regular solution model as a correction term accounting for the size differences among different molecules (modified RSFH model). Such correction has been proven to be successful for phase equilibrium of systems of large molecular size differences such as aqueous polymer solutions [4]. As can be seen from Fig. 1, however, the modified RSFH model provides very limited improvements for the solubility estimations.

Shin et al. [12] developed a simplified solution model based on the work of Flory and Huggins and validated it by correlating the solubility of organic salts in water vapor under high temperature and pressure. In the proposed RSFH model, Shin treated the cohesive energy and molar volume of the solute as adjustable parameters that were obtained by fitting the experimental solubility data. Higashi et al. [13] also applied that model to correlate their experimental solubility data on alkaline metal chlorides in water vapor at high temperature and pressure. In their model, the cohesive energy was treated as a temperature-independent constant, and the liquid solute molar volume was treated as a simple function of the solvent density. Though the solubility curves were reproduced rather well, the maximum average relative deviations of Shin and Higashi were up to 56.4 and 34.8%, respectively. Nevertheless, the correlation results of Shin et al. [12] showed that the cohesive energies of the solutes are slightly dependent on temperature, while the results of Higashi et al. [13] indicated that the cohesive energies of the solutes might be a linear function of temperature. Then they tried to utilize this relation for the model correlation, but worse calculation results were obtained, and no further discussion about this possible relation was made. Long et al. [14] applied the modified RSFH model to correlate the solubility of amino acids in water at different temperatures. They treated the solute cohesive energy as linearly dependent on temperature, and very good correlation results were observed. In this work, we extend the modified RSFH model to correlate the solubility of aromatic acids in water in a wide temperature range and investigate the temperature dependency of the cohesive energy of the aromatic acids.

The term "aromatic acid" includes a large class of industrially important solid organic acids that are commonly known as benzoic acid, phthalic acid isomers, and many other derivatives of them. In industry, they are widely used as stocks or intermediates for preparing polyester, resins, plastics, dyes, foods, and pharmaceuticals [15]. Generally, the final products of such aromatic acids are purified by crystallization or recrystallization from water [16, 17]. Thus, the aqueous solubility data are of great importance for their separation and purification

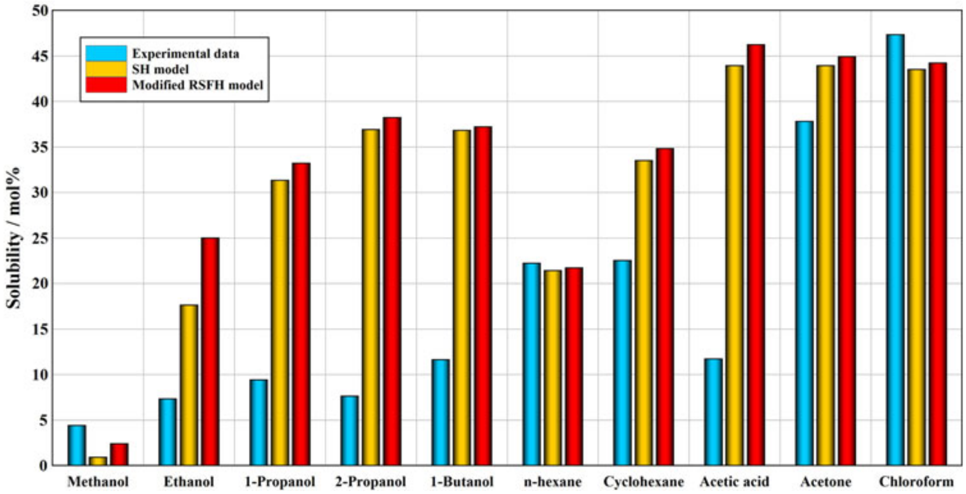

Fig. 1 Comparisons of the calculated and observed solubility of naphthalene in different solvents at 338.15 K

processes. Numerous measurement results for the aqueous solubility of aromatic acids have been reported from different sources, and some solubility data compilations with their data have been made available [18, 19].

Generally, the solubility of aromatic acids in water is very small at low temperature. Many aromatic acids are labeled as insoluble in water at room temperature. But the solubility of aromatic acids increases significantly as the temperature rises, which exhibits an exponential-like solubility curve. Moreover, because of the diversification of the positions of the carboxylic groups in the benzene ring, the possibilities to form hydrogen bonds with polar molecules of water and/or to form hydrogen-bonded polymers between carboxylic groups of the same acid are different for individual aromatic acids, which results in large solubility differences among the aromatic acids even for isomers of the same molecular group. These features make water a benign solvent for crystallization of aromatic acids from high-temperature aqueous solutions. The solubility of phthalic acid isomers is shown in Fig. 2. It can be seen that the solubility of the isomers at 440 K is over three magnitudes higher than that at 280 K, and the solubility among the isomers differs greatly at fixed temperature. Such strong temperature-dependent solubility cannot be adequately modeled by simple empirical models such as power or exponential functions. Therefore, a reliable model that can accurately estimate the temperature-dependent solubility will be very beneficial to the industry.

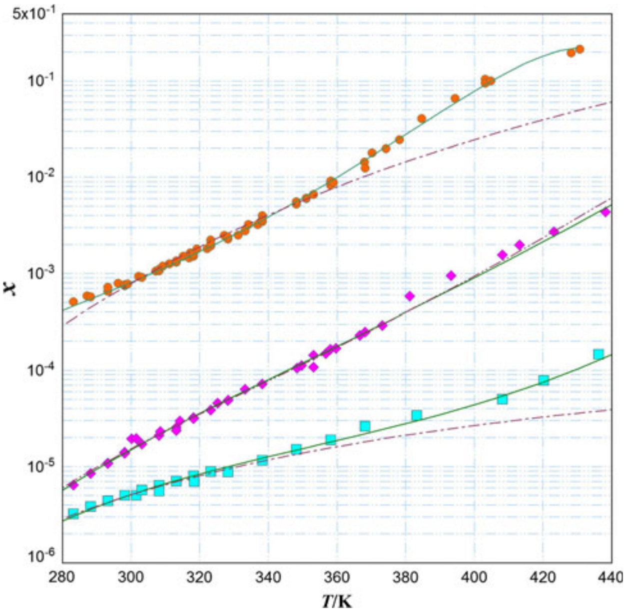

Fig. 2 Solubility of phthalic acid isomers in water: (*filled circles*) ortho; (*filled diamonds*) meta; (*filled squares*) para; (*dashed line*) extrapolation of the correlated results from the data below 373 K; (*solid line*) correlated from all the data

Results and discussion

Solubility data preparation

Organic acids whose basic molecular structures are a benzene ring and a carboxyl group are referred to as aromatic acids. Because of the possibilities of different numbers and positions of the carboxyl in the benzene ring together with other substituting groups such as methyl, hydroxyl, nitro, etc., the aromatic acids actually include many different compounds. The aqueous solubility of aromatic acids has long been studied and numerous experimental results have been published. However, the accuracies and agreements among different data sources are not always good [18–20]. Thus, it is necessary to assemble and choose appropriate values for each aromatic acid before the model analysis. Since the solution model proposed in this work (Eq. 4) has four adjustable parameters, only the sets reported with more than ten data points at different temperatures were chosen for modeling. Apelblat et al. [20] made a detailed review and discussion on the validity of the available solubility data for many benzene polycarboxylic acids in water, so their recommended values were adopted. Some data compilations [18, 19] also presented their assessment on the quality of data; thus, those with low grade were eliminated when large inconsistencies arose. When the data from different sources were combined, those differing considerably with most data trends were excluded. In addition, when different sources were still inconsistent, the reported data without clear descriptions of the experimental procedure and/or the uncertainties were excluded or given low weight when the modeling work was performed. If the data trend could not be determined, as in the case of the solubility data of *p*-phthalic acid below 298.15 K [20], only the data in the region where the data trend is clear were chosen. With the above-mentioned criteria, 1,009 aqueous solubility data points for 25 aromatic acids were selected for the model regression analysis. The information on selected aromatic acids including names, physical properties, data numbers, maximum solubility available, and the corresponding data sources are listed in Table 1.

General regression results

The regressed model parameters together with the calculated average deviations for each aromatic acid are tabulated in Table 2. The overall average deviation (δ_{AAD}) is 6.76%. For individual set data, the maximum deviation is 15.12%, while the minimum is 0.81%; that with the widest temperature range is 190 K, while the smallest is 50 K; that with the most data points is 215, while the least is 10.

Among all the aromatic acids, benzoic acid is the simplest one, and its aqueous solubility at different temperatures was

Table 1 Physical properties and solubility data source for different aromatic acids

Aromatic acids	T_m (K)	$\Delta_{fus}H$ (J mol^{-1})	T range (K)	x_{max}[d]	N_p	Data source
Benzoic acid	395.52[a]	18,006[a]	282–382	3.70×10^{-2}	215	[18, 19, 26, 28–30]
o-Phthalic acid	480.00[a]	52,264[a]	273–435	0.245	136	[18, 28, 31–33]
m-Phthalic acid	621.15[b]	48,194.3[b]	283–463	2.10×10^{-2}	47	[18, 28, 32–34]
p-Phthalic acid	452.75[b]	63,428.4[b]	273–463	3.42×10^{-4}	26	[28, 32, 33]
Trimellitic acid	511.15[a]	46,483[c]	273–473	0.214	34	[18, 20, 28, 35]
Trimesic acid	653.15[a]	44,455[c]	273–330	6.65×10^{-4}	34	[18, 20]
Hemimellitic acid	465.15[a]	47,458[c]	273–323	8.52×10^{-5}	13	[19, 28]
Pyromellitic acid	544.15[a]	67,720[c]	273–330	3.90×10^{-3}	28	[18, 20]
Mellophanic acid	584.48[c]	57,950[c]	273–323	4.25×10^{-2}	12	[20]
Prehnitic acid	580.74[c]	57,440[c]	273–323	1.30×10^{-2}	11	[20]
Pentacarboxylic acid	610.28[c]	72,387[c]	273–323	3.41×10^{-2}	13	[20]
Mellitic acid	635.78[c]	85,088[c]	273–369	5.50×10^{-2}	13	[18]
o-Toluic acid	376.68[a]	19,500[a]	298–423	1.33×10^{-2}	10	[19, 30, 33]
m-Toluic acid	383.00[a]	15,730[a]	298–413	8.04×10^{-3}	29	[19, 30, 33]
p-Toluic acid	452.75[a]	28,400[a]	278–413	5.91×10^{-3}	79	[30, 33, 36, 37, 39]
o-Nitrobenzoic acid	418.95[a]	27,990[a]	291–351	2.50×10^{-2}	23	[18, 19]
m-Nitrobenzoic acid	414.3[a]	20,200[a]	299–343	1.80×10^{-2}	61	[30, 38, 39]
o-Aminobenzoic acid	417.75[a]	20,380[a]	283–373	2.89×10^{-3}	12	[18, 19]
m-Aminobenzoic acid	452.9[a]	21,840[a]	273–351	6.29×10^{-3}	11	[15, 16]
p-Aminobenzoic acid	461.4[a]	20,920[a]	285–383	5.90×10^{-2}	14	[18, 19]
o-Hydroxybenzoic acid	432.1[a]	14,200[a]	273–373	1.01×10^{-2}	113	[18, 40]
m-Hydroxybenzoic acid	472.7[a]	55,400[a]	273–323	2.94×10^{-3}	10	[19, 41]
p-Hydroxybenzoic acid	488.7[a]	30,900[a]	273–372	4.34×10^{-2}	43	[19, 30]
3-Nitrophthalic Acid	489.15[c]	27,649[c]	285–348	9.55×10^{-3}	11	[35]
4-Nitrophthalic Acid	437.15[a]	24,709.7[c]	285–348	0.222	11	[35]
Total					1,009	

[a] Data from Landolf database [21]

[b] Data from Li et al. [27]

[c] Calculated by the group contribution method proposed by Marrero et al. [22]

[d] Maximum mole fraction solubility used for parameter fitting

better studied and documented in comparison with other aromatic acids. Therefore, as Apelblat et al. [20] did, only the results from systematic determinations at various temperatures were adopted in this work [18–20, 28–30]. Figure 3 shows the comparison between the calculated values and the literature data for benzoic acid. Though the data points are up to 215 and from 6 different sources, a reasonable agreement could be observed in the temperature range of 282–382 K and the solubility data were well reproduced by the modified RSFH model.

Effect of temperature on cohesive energy

As can be seen from Table 2, the cohesive energy parameter A (in Eq. 6) for the majority of aromatic acids investigated is reported as 0, which indicates that the cohesive energy for them is a temperature-independent constant. Regarding these aromatic acids, the cohesive energies are about 20–30 kJ mol^{-1}, which are lower than the obtained cohesive energies (50–120 kJ mol^{-1}) of the inorganic salts from Shin et al. [12] and Higashi et al. [13]. This difference may reasonably be attributed to the connecting ways of the molecular internal bonds. On the other hand, there are a few aromatic acids whose cohesive energies are of positive dependence on temperature. This indicates that the cohesive energies of the solutes are no longer a constant, but increase with the increase of temperature. In Fig. 4, we present the comparisons of regression results for *p*-phthalic acid and pyromellitic acid by two methods: with the cohesive energy as a constant ($A = 0$) and as a linear function of temperature ($A \neq 0$), respectively. As for the case of pyromellitic acid, the calculation results using two methods are very close, but treating cohesive energy as a constant tends to underestimate the solubility at higher temperature. In the case of

Table 2 Results of the regressed parameters for different aromatic acids and the calculated δ_{AAD}

Aromatic acids	$10^{-3}A$	$10^{-4}B$	α	β	δ_{AAD}
Benzoic acid	0.0000	3.113	26.36	−197.5	5.00
o-Phthalic acid	2.010	69.93	−2.490	9.433	5.87
m-Phthalic acid	0.0000	2.334	16.67	−128.2	9.78
p-Phthalic acid	2.149	25.46	−2.676	10.40	6.54
Trimellitic acid	0.0000	0.04109	−8.059	43.25	11.76
Trimesic acid	0.0000	23.94	0.06430	−10.10	11.41
Hemimellitic acid	0.0000	23.90	0.07961	−9.090	9.44
Pyromellitic acid	3.477	3.670	−3.854	18.77	5.04
Mellophanic acid	0.0000	3.321	−88.93	583.9	1.72
Prehnitic acid	0.2609	−3.943	−4.902	0.1265	1.18
Pentacarboxylic acid	0.2042	−4.120	−4.553	0.9442	4.96
Mellitic acid	0.3255	−8.047	−4.270	12.02	0.88
o-Toluic acid	0.0000	3.831	−2.492	3.279	15.12
m-Toluic acid	0.0000	8.783	−56.28	351.8	13.64
p-Toluic acid	0.0000	3.459	20.32	−154.8	4.34
o-Nitrobenzoic acid	0.0000	2.567	54.69	−393.9	11.26
m-Nitrobenzoic acid	0.0000	3.053	43.32	−315.4	12.19
o-Aminobenzoic acid	0.0000	2.780	43.15	−314.4	3.33
m-Aminobenzoic acid	0.0000	2.642	26.83	−201.0	3.30
p-Aminobenzoic acid	0.0000	2.676	36.08	−264.8	10.76
o-Hydroxybenzoic acid	0.0000	3.195	29.18	−217.4	6.05
m-Hydroxybenzoic acid	0.1600	−2.101	−3.602	0.9303	2.32
p-Hydroxybenzoic acid	0.0000	2.025	26.75	−200.2	6.89
3-Nitrophthalic acid	0.0000	2.266	2.672	−32.15	2.16
4-Nitrophthalic acid	0.0000	0.4129	−13.62	81.57	0.81
Overall					6.76

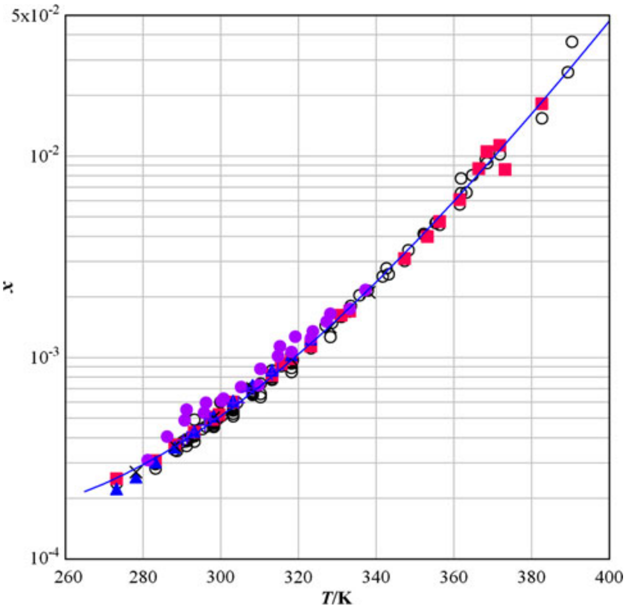

Fig. 3 Comparison of the reported solubility of benzoic acid in water and the calculated results by this work: (*filled squares*) Ref. [18]; (*open circles*) Ref. [19]; (*filled circles*) Ref. [20]; (*filled triangle*) Ref. [28]; (*times symbol*) Ref. [29]; (*plus symbol*) Ref. [30]; (*solid line*) calculated values

p-phthalic acid, very different results were obtained by the two methods. As can be seen in Fig. 4, if we forced the cohesive energy of *p*-phthalic acid as a temperature-independent constant ($A = 0$), misleading results would be obtained. It should be noted that the temperature range of *p*-phthalic acid is much wider than that of pyromellitic acid, which may indicate that when the solubility is over a wide temperature range, the cohesive energy of the solute should be treated with caution. Therefore, Eq. 6 is recommended to compute the cohesive energy of the aromatic acids. If the regression results show that A is extremely small, we may conclude that the cohesive energy is a constant and if it is not, it may indicate the cohesive energy has strong dependency on temperature.

Extrapolation of the regression results

Generally, the aqueous solubility under atmosphere (temperature below 373 K) is easy to measure; therefore, many reports with reliable and high quality data are only available in that region. In contrast, the solubility under high pressure and high temperature is expensive and difficult to

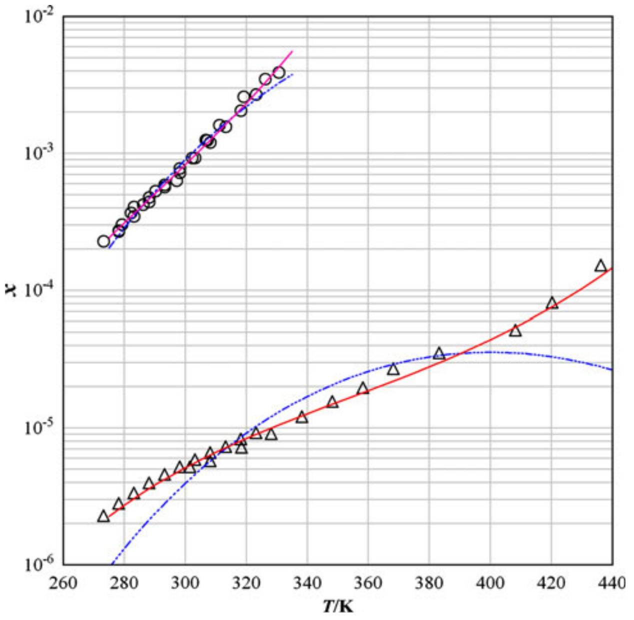

Fig. 4 Solubility of *p*-phthalic acid and pyromellitic acid in water: (*open circles*) pyromellitic acid; (*open triangles*) *p*-phthalic; (*dashed line*) correlated with $A = 0$; (*solid line*) correlated with $A \neq 0$

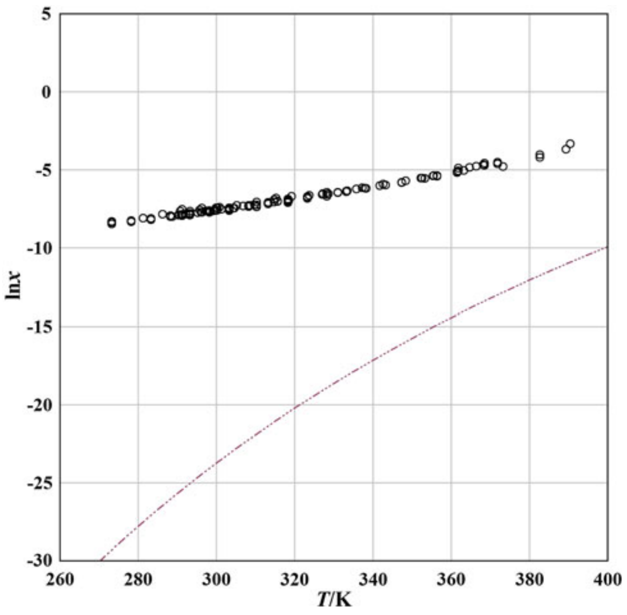

Fig. 5 Solubility of benzoic acid in water: (*open circles*) literature data; (*dashed line*): calculated with the Hansen solubility parameter at 298.15 K

measure, which means the needed data are not always readily available. Moreover, the data at high temperature from different sources are often inconsistent and even conflict with each other. Thus, it would be very helpful if we could predict the solubility data under high pressure and high temperature from the low temperature data together with reasonable models and parameters. We selected the case of phthalic acid isomers to investigate the prediction ability of the modified RSFH model because of the availability of the solubility data in a very wide temperature range. The phthalic acid isomers are the main intermediates for preparing polyesters, and their aqueous solubility is of great importance to their purification processes. In industry their final products were purified by recrystallization from water, which is often carried out at elevated temperature and pressure. For example, the crystallization of *p*-phthalic acid from water can be carried out at up to 533 K and 4.6 MPa. We used the reported solubility data below 373 K for the regression and then predicted the solubility at higher temperature up to 460 K with the optimized parameters. The calculation results are also shown in Fig. 2. It can be seen from the figure that the predicted solubility for *m*-phthalic acid agrees perfectly with those in the literature at high temperature. However, for *o*-phthalic acid and *p*-phthalic acid, the predicted values are lower than those in the literature. Such underestimation increases with the increase of temperature, but the data are still within the same order of magnitude and probably remain acceptable for engineering calculations as a preliminary estimation. Though the modified RSFH model is a correlation model in nature, it could be semi-quantitatively used as a prediction tool for the preliminary estimation of the solubility where only limited experimental data are available.

Solubility parameter of the aromatic acids

Clearly, the solubility parameter plays an essential role in our proposed model. The concept of the solubility parameter was first proposed by Hildebrand and Scott [6], and defined as the square root of the cohesive energy density (Eq. 5). The solubility parameter has been widely used to describe the solubility phenomenon as well as to select appropriate solvents. It is developed, however, on the liquid state basis, and using the vaporization enthalpy of a solid less the expansion work RT to estimate the solubility parameter ($[(\Delta H - \mathrm{RT})/V]^{1/2}$, Eq. 5) does not yield a reasonable result [42]. One direct way to obtain the solubility parameter of the solute with high melting temperature or decomposing before melting is by fitting the experimental solubility data with an appropriate model. Currently, there are two widely used solubility parameters, the Hildebrand solubility parameter [42] and the Hansen solubility parameter [43]. The Hildebrand solubility parameter has a sound theoretical basis and can be a good indication of solubility, but is limited to non-polar and non-hydrogen-bonding materials. The Hansen solubility parameter is a little more empirical in comparison with the Hildebrand, but allows wider applications [43]. For most material, however, these two parameters are only available at 298.15 K, and no report is found for most aromatic acids. Figure 5 shows the calculation results of benzoic acid solubility versus temperature by employing the Hansen solubility parameter at 298.15 K [43]. Clearly, the Hansen solubility parameter method may considerably underestimate the solubility if the temperature effect is not taken into account.

The group contribution method is another way to estimate the solubility parameter. One of the most commonly used group contribution methods for estimation of the solubility parameters is the one developed by Fedors [44]. By employing the group contribution method, we can theoretically estimate the solubility parameter for any compound as long as the solute molecule can be reasonably divided into several known groups with the necessary information available. It is a pure prediction method and very easy to use. Figure 6 shows the comparison between the solubility parameter optimized in this work and those estimated with the Fedor group contribution method at 298.15 K. It can be seen that the agreement in general is fairly good and the solubility parameters estimated from the Fedor group contribution method for the most aromatic acids are less than 30% higher than ours. This agreement may be reasonable because this group contribution method, like any other predictive group contribution method, strongly depends on how the molecule is divided into groups and the corresponding group parameter values. The former is more or less arbitrary, and the latter strongly depends on the experimental data with which the group parameters were fit. What is more important is that the aromatic acids contain lots of isomers whose properties cannot be distinguished by current group contribution methods. Although the model proposed in this work is correlative in nature, it provides a sound thermodynamic framework to quantitatively correlate solubility data for interpolation and limited extrapolation with rather high accuracy as shown above. It could be anticipated that the model could be further extended to calculate the solubility of other classes of non-electrolyte solutes in water and in other solvents.

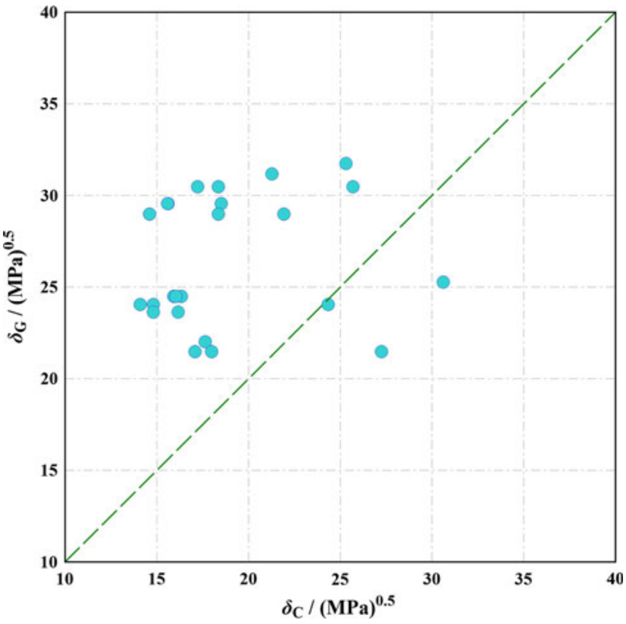

Fig. 6 Solubility parameters of the aromatic acids: (δ_C) this work; (δ_G) estimated by the Fedor group contribution method

Methods

Modified regular solution model

The equilibrium solubility for non-electrolyte solute is often described by the following rigorous thermodynamics equation [4]:

$$\ln x_2 = -\ln\gamma_2 + \frac{\Delta_{\text{fus}}H_2}{R}\left[\frac{1}{T_{2\text{m}}} - \frac{1}{T}\right] - \frac{1}{RT}\int_{T_{\text{m}}}^{T}\Delta C_{\text{p}}\,\mathrm{d}T + \frac{1}{R}\int_{T_{\text{m}}}^{T}\frac{\Delta C_{\text{p}}}{T}\,\mathrm{d}T \qquad (1)$$

where the subscript 2 stands for the solute, x is the mole fraction solubility, and γ is the activity coefficient in the solution at equilibrium. Here γ is on the mole fraction basis and references to Henry's law [45]. T_{m} and $\Delta_{\text{fus}}H$ are the melting point (K) and enthalpy of fusion (J mol^{-1}) of the solute, respectively. ΔC_{P} is the difference in the molar heat capacity between the melting and solid state of the solute.

In Eq. 1, the second term on the right-hand side is much more important than the remaining two terms containing ΔC_{P}, which almost cancel out each other [4]. Therefore, a reasonable simplification of Eq. 1 is commonly adopted:

$$\ln x_2 = -\ln\gamma_2 + \frac{\Delta_{\text{fus}}H_2}{R}\left[\frac{1}{T_{2\text{m}}} - \frac{1}{T}\right] \qquad (2)$$

By combining the regular solution theory [6] with the Flory-Huggins entropy expression [10, 11], we can express the activity coefficient γ_2 as [12–14]:

$$\ln\gamma_2 = \frac{v_2}{RT}(\delta_1 - \delta_2)^2 + 1 - \frac{v_2}{v_1} + \ln\frac{v_2}{v_1} \qquad (3)$$

where the subscript 1 stands for the solvent; v indicates molar volume (m^3 mol^{-1}), and δ is the solubility parameter, (J m^{-3})$^{0.5}$.

Combining Eqs. 2 and 3, we arrive at:

$$\ln x_2 = \frac{\Delta_{\text{fus}}H_2}{RT}\left(\frac{T}{T_{2\text{m}}} - 1\right) - \frac{v_2}{RT}(\delta_1 - \delta_2)^2 - 1 + \frac{v_2}{v_1} - \ln\frac{v_2}{v_1} \qquad (4)$$

Determination of the model parameters

In Eq. 4, the T_{m} and $\Delta_{\text{fus}}H$ data for the aromatic acids are taken from experimental reports [21] whenever possible.

For the solutes without reported values, the properties were estimated by a multilevel group contribution method proposed by Marrero and Gani [22], which allows the physical properties such as T_m and $\Delta_{fus}H$ of pure components to be estimated much more accurately than previous group contribution methods. More importantly, those of isomers can be well distinguished by a three-level estimation according to the specific molecular structure of the isomeric compounds. The uncertainties of T_m and $\Delta_{fus}H$ estimations by this method, as declared by the authors [22], are 7.6 and 15.7%, respectively. The values of T_m and $\Delta_{fus}H$ used for correlation are summarized in Table 1.

In Eq. 4, the solubility parameters of the solute and solvent are estimated by different methods. The Hildebrand solubility parameter δ_2 of the solute is defined as [4, 6]:

$$\delta_2 = \sqrt{\frac{\Delta U_2}{v_2}} \tag{5}$$

where ΔU_2 is the molecular cohesive energy (J mol^{-1}) of the solute, which is defined as the energy required to isothermally evaporate liquid from saturated liquid to ideal gas. As stated above, it is not reasonable to directly use the vaporization enthalpy to estimate the solubility parameter of a solid [42]. The alternative method to estimate the solubility parameter is by fitting it to the solubility data. Based on the results from Shin et al. [12], Higashi et al. [13], and Long et al. [14], ΔU_2 is empirically expressed as a linear function of temperature in this work:

$$\Delta U_2 = \mathrm{AT} + B \tag{6}$$

where A and B are two adjustable parameters to be regressed from the experimental solubility data.

To estimate the liquid molar volume v_2 in Eq. 5, we employed the empirical expression proposed by Iwai et al. [25], which is based on many experimental observations of the molar volume of solid solute in dense solvents:

$$\ln v_2 = \alpha \ln \rho_1 + \beta \tag{7}$$

where ρ_1 is the density of the solvent (kg m^{-3}), while α and β are two empirical parameters. Shin et al. [12] and Higashi et al. [13] both fixed α as a constant of -1 for inorganic salt solutes. In this work, both α and β are considered as adjustable parameters that are obtained by fitting the solubility data.

The solubility parameter δ_1 of liquid water at different temperatures can also be computed from Eq. 5 by utilizing the vaporization enthalpy and liquid molar volume data of water. However, a much simpler expression is used in this work, which has been proven by SaGara [23] to be mathematically equivalent to Eq. 5 based on the hole theory and random mixing assumption:

$$\delta_1 = \frac{\sqrt{6 v_1^{S} \varepsilon_{11} N_A}}{v_1} \tag{8}$$

where v_1^s is the molar volume of solid water, N_A is the Avogadro's constant, and v_1 is the molar volume of liquid water, which was calculated from the correlation formula recommended by Yaws et al. [24]. ε_{11} is the pair potential energy and determined by fitting Eq. 8 to the experimental solubility parameters [12]. The procedure was explained in detail by Sagara et al. [23] and Shin et al. [12].

Equations 2, 3, 4, 5, 6, 7, and 8 constitute the whole modified RSFH model for modeling the solubility of aromatic acids in water. In the proposed model, there are four adjustable parameters (A, B, α, and β) to be regressed from the experimental solubility data. To optimize the parameters, the following objective function was employed [26]:

$$\min f(A, B, \alpha, \beta) = \sum_{i=1}^{N_p} \left(\frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right)^2 \tag{9}$$

where Np is the number of data points for each system, and superscripts cal and exp stand for calculated values and the literature ones, respectively. The Levenberg-Marquardt method was adopted as the optimization algorithm. The goodness of the fit of the models to the experimental data can be expressed by the absolute average deviation (δ_{AAD}), which is calculated according to the following definition:

$$\delta_{AAD} = \frac{1}{N_p} \sum_{i=1}^{N_p} \left| \frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right| \tag{10}$$

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