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Solid-Liquid Equilibria of Benzoic Acid Derivatives in 1-Octanol*

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Abstract The solid-liquid equilibrium of benzoic acid derivatives in 1-octanol was first determined in this article. Using a laser monitoring observation technique, the solubility data of *o*-amino-benzoic acid, *p*-amino-benzoic acid, *o*-chloro-benzoic acid, and *m*-nitro-benzoic acid in 1-octanol were measured by the polythermal method in the temperature range of 20—50℃. The experimental data were regressed with the Wilson equation and the λH equation. The experimental results showed that the solubility of the four chemicals in 1-octanol increased significantly with temperature. The results indicate that the molecular structure and interactions affect the solubility significantly. The solubility order of the benzoic acid derivatives is as follows: *m*-nitro-benzoic acid＞*o*-chloro-benzoic acid＞*o*-amino-benzoic acid＞*p*-amino-benzoic acid. Both the Wilson equation and λH equation are in good agreement with the experimental data.
Keywords solid-liquid equilibrium, polythermal method, *o*-amino-benzoic acid, *p*-amino-benzoic acid, *o*-chloro-benzoic acid, *m*-nitro-benzoic acid, 1-octanol

1 INTRODUCTION

Benzoic acid derivatives, which are considered as important priority contaminants, may affect the environment in a number of ways[1,2]. These are widely used reaction intermediates and may be discharged into the environment[3,4]. However, because of a host of products and the utilization of benzoic acid derivatives, soil and groundwater body have been badly contaminated. Also, the aqueous solubility governs the bioavailability of an agent through the influence of absorption, distribution, and elimination in the body [5—7]. The 1-octanol solubility, or the ratio of 1-octanol/water solubilities (which is different from the 1-octanol/water partition coefficient, lg*P*) can characterize transportation through membranes and the topical activity of drugs[8]. Several authors have made attempts to calculate the solubility from the available lg*P* values and other parameters related to the structure[7—11]. To evaluate the environmental contamination performance of benzoic acid derivatives in soil and groundwater, the basic physical-chemical parameters must be known.

The purpose of this study is to report the solubilities of benzoic acid derivatives in 1-octanol at several temperatures, and to test the capability of the selected equilibrium models to describe these data. The Wilson and λH models have been used to produce rapid and easy methods to provide acceptable values of solubility as a function of temperature.

2 EXPERIMENTAL

2.1 Materials

The benzoic acid derivatives tested included: 1-octanol(＞99%), benzoic acid(＞99%), *p*-amino-benzoic acid(＞ 99%), *o*-amino-benzoic acid (＞ 99%), *o*-chlor-benzoic acid(＞ 99%), and *m*-nitro-benzoic acid(＞99%). The melting temperatures (T_m) and the enthalpies of fusion ($\Delta_m H$) of the benzoic acid derivatives[12] are listed in Table 1. The organic acids were purchased from commercial sources, and used without any further purification.

Table 1 The melting temperatures (T_m) and the enthalpies of fusion ($\Delta_m H$) of the benzoic acid and its derivatives

Compounds	T_m, ℃	$\Delta_m H$, kJ·mol^{-1}
benzoic acid	122.35	18.02
p-amino-benzoic acid	188.25	20.92
o-amino-benzoic acid	144.10	20.38
o-chloro-benzoic acid	140.20	25.60
m-nitro-benzoic acid	141.15	28.20

2.2 Apparatus and procedure

The apparatus shown in Fig.1 has been described in detail previously[13,14], and therefore, only a brief description is presented here. The condensator was used specially to prevent the solvent volatilization.

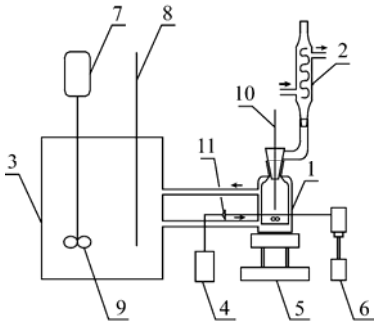

Figure 1 Equipment for the measurement of solubility of benzoic acid derivatives in 1-octanol
1—equilibrium vessel; 2—condensator; 3—thermostatic controller; 4—recorder; 5—electromagnetic stirrer; 6—laser; 7—whisk machine; 8—thermometer; 9—whisk rotor; 10—thermometer; 11—laser receiver

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Pre-weighed amounts of the benzoic acid derivatives and 1-octanol were placed in an equilibrium vessel. The vessel was then stoppered, connected to a circulating water bath, and stirring was started. The mixture was initially equilibrated at a temperature significantly below the dissolution temperature for at least 1h. The temperature of the mixture was then slowly increased in stepwise fashion until the temperature at which all the benzoic acid derivatives had dissolved was reached. Near the dissolution temperature, the temperature increase was typically kept at 0.2℃ per 20min or slower.

The laser monitoring equipment was used to observe and monitor the dissolution condition of the solution. A steady laser beam passes through an aperture and the adjustable lens and then through the solvent-solute mixture. If there are solids in the path of the beam, it will be scattered and the transmitted intensity will be reduced. The intensity of the transmitted laser is recorded by a computer in terms of the photovoltage. The corresponding temperature at a given composition is determined as the one at which the solid phase just disappears.

During the experimental procedure, errors in the final results may arise in three ways: impurity of the compounds, weighing error, and temperature error. The weighing error can be neglected by mass preparation using an analytical balance with an accuracy of ±0.0001g. The purity of the chemicals tested is >99% and impurity appears to be a homolog that does not affect the solubility data significantly. The temperature error is the greatest uncertainty in the final results. Therefore, the thermometer that was used in the experiments was calibrated with an accuracy of ±0.05℃ and the rate of temperature increase was controlled strictly at less than 0.2℃ per 20min or even slower near the dissolution temperature.

The experimental setup and its accuracy were validated by comparing the experimental solubility data of benzoic acid in water with those in Ref.[15]. As seen in Fig.2, the solubilities obtained in this study are in good agreement with the literature. The deviation of the measured solubilities from the literature values was <1%.

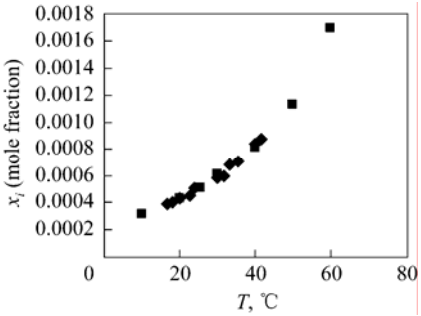

Figure 2 Experimental solubility of benzoic acid in water when compared with literatural data
◆ this work; ■ literatural data[15]

3 RESULTS AND DISCUSSION

3.1 Solubility data of benzoic acid derivatives in 1-octanol

The solubilities of benzoic acid derivatives in 1-octanol were measured and are listed in Tables 2—5, where, T is the temperature (℃), and x_{exp} represents the experimental solubility (in mole fractions of the solute). The experiments show that the solubilities of these compounds increase with temperature. Owing to the special molecular structure, there is a large difference between the solubilities of these chemicals. It is obvious that the solubility in 1-octanol of the measured are considerably better than those in water[13] as shown in Fig.3. The better solubility in 1-octanol can be explained by the non-polar character of the compounds and 1-octanol[16]. The solubility order of the benzoic acid derivatives in 1-octanol is as follows: *m*-nitro-benzoic acid > *o*-chloro-benzoic acid > *o*-amino-benzoic acid > *p*-amino-benzoic acid.

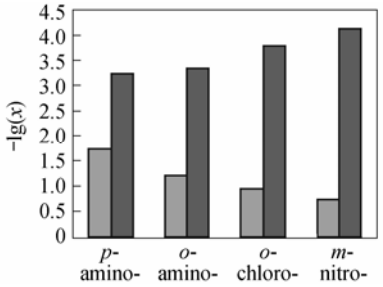

Figure 3 Comparison of the solubility in 1-octanol and in water
solubility in 1-octanol; solubility in water

3.2 Data correlation by Wilson and *λH* equations

Generally, solid-liquid equilibria (SLE) can be described by an equation containing pure solute properties such as enthalpy of fusion, melting temperature, and so on. If, as is the case in this work, a solid-solid transition does not occur, the equation for the description of SLE can be simplified to the form shown as Eq.(1):

$$\ln \gamma_i x_i = -\frac{\Delta_m H_i}{R}\left(\frac{1}{T}-\frac{1}{T_{mi}}\right) \tag{1}$$

where, $\Delta_m H_i$ is the enthalpy of fusion of the solute i, T_{mi} is the melting temperature, T is the absolute temperature, R is the universal gas constant, x_i indicates the real mole fraction, and γ_i represents the activity coefficient. Eq.(1) was used with the experimental data to determine the parameters in an activity coefficient model by regression.

According to Eq.(1), the activity coefficient γ_i is a key value in calculating the solubility, knowing T_{mi} and $\Delta_m H_i$. Among the several activity coefficient models that can be selected, in this study, the Wilson equation was chosen.

3.2.1 *Wilson equation*

For a binary system, the Wilson equation is as follows [17,18]:

$$\ln \gamma_1 = 1 - \ln\left(x_2 \Lambda_{12} + x_1\right) - \left(\frac{x_1}{x_1 + x_2 \Lambda_{12}} + \frac{x_2 \Lambda_{21}}{x_2 + x_1 \Lambda_{21}}\right) \tag{2}$$

In Eq.(2), Λ_{ij} represents the Wilson equation

Table 2 The solubility data of *p*-amino-benzoic acid and the regression results obtained using the Wilson equation and the *λH* equation

T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$		T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$	
		Wilson equation	*λH* equation			Wilson equation	*λH* equation
24.80	0.01849	0.0	−4.3	36.75	0.02605	0.8	0.5
27.70	0.02076	3.1	0.0	37.70	0.02659	0.3	0.2
30.40	0.02186	0.7	−1.6	38.60	0.02710	−0.1	0.0
30.30	0.02257	4.0	1.8	40.20	0.02814	−0.6	0.0
32.65	0.02307	0.0	−1.7	42.00	0.02926	−1.3	−0.3
34.50	0.02493	2.5	1.5	45.20	0.03165	−1.8	0.0
35.70	0.02550	1.5	0.9	46.90	0.03276	−2.7	−0.5

Table 3 The solubility data of *o*-amino-benzoic acid and the regression results obtained using the Wilson equation and the *λH* equation

T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$		T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$	
		Wilson equation	*λH* equation			Wilson equation	*λH* equation
22.15	0.05555	−3.1	−3.3	36.50	0.08392	0.6	0.7
25.30	0.06159	−1.2	−1.3	38.20	0.08761	0.7	0.8
26.80	0.06478	−0.2	−0.2	40.20	0.09187	0.5	0.6
28.65	0.06817	0.0	0.0	42.80	0.09735	0.0	0.0
30.00	0.07116	0.7	0.8	44.60	0.1013	−0.4	−0.4
31.90	0.07512	1.2	1.3	47.10	0.1076	−0.3	−0.3
33.90	0.07856	0.6	0.7	49.10	0.1109	−1.9	−2.1
35.40	0.08146	0.4	0.5				

Table 4 The solubility data of *o*-chloro-benzoic acid and the regression results obtained using the Wilson equation and the *λH* equation

T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$		T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$	
		Wilson equation	*λH* equation			Wilson equation	*λH* equation
24.50	0.1086	−1.5	−0.7	36.40	0.1620	1.7	3.2
25.40	0.1123	−1.1	0.0	38.00	0.1691	1.8	3.1
25.75	0.1136	−1.3	−0.2	39.90	0.1760	1.2	1.8
25.95	0.1144	−1.3	−0.2	41.95	0.1828	0.2	0.0
31.60	0.1398	0.7	2.6	43.55	0.1897	0.0	−0.6
33.25	0.1473	1.1	3.0	45.50	0.1965	−1.0	−2.3
34.85	0.1546	1.4	3.1	46.80	0.2006	−1.7	−3.7

Table 5 The solubility data of *m*-nitro-benzoic acid and the regression results obtained using the Wilson equation and the *λH* equation

T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$		T, ℃	x_{exp}	$(x_{exp}-x_{cal})\times 100/x_{exp}$	
		Wilson equation	*λH* equation			Wilson equation	*λH* equation
23.10	0.1741	−3.0	−0.1	35.30	0.2312	0.8	−0.5
24.10	0.1787	−2.5	0.0	38.60	0.2470	1.0	−1.1
26.00	0.1856	−2.8	−0.8	40.65	0.2621	3.4	0.4
27.10	0.1937	−0.5	0.8	43.10	0.2749	3.7	0.0
29.75	0.1988	−3.8	−2.9	44.50	0.2867	5.6	1.32
30.65	0.2094	0.0	0.2	49.00	0.3055	3.8	−1.34
32.70	0.2194	0.6	0.1				

parameters, which is a function of temperature.

$$\Lambda_{ij}=\frac{V_j}{V_i}\exp\left(-\frac{g_{ji}-g_{ii}}{RT}\right) \quad (3)$$

Generally, the energy parameter $(g_{ji}-g_{ii})$ in the Wilson equation is thought to be independent of temperature. Therefore, if the difference in the molar volume between the constituents is ignored, two

Table 6 Regression results of the Wilson equation and the λH equation

Samples	Wilson equation			λH equation		
	$g_{21}-g_{11}$	$g_{12}-g_{22}$	AAD①	λ	H	AAD①
p-amino-benzoic acid	35.9315	37759.1	1.4	0.2257	9393.62	0.9
o-amino-benzoic acid	−1408.44	8633.32	0.8	0.4895	4520.42	0.9
o-chlor-benzoic acid	17641.0	−2543.04	1.1	1.885	1567.84	1.7
m-nitro-benzoic acid	−2782.06	1751.80	2.4	1.866	1274.18	0.7

① AAD: Average absolute relative deviations.

parameters remain in the Wilson equation for a binary system: $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$.

Eq.(1) was combined with the Wilson equation to determine the Wilson parameters by regression of the measured aqueous solubilities. The results are shown in Tables 2—5. The values of the objective function AAD and the parameters that were determined by regression are listed in Table 6.

3.2.2 *λH equation*

The λH equation, Eq.(4), is another way to describe the solution behavior and was first suggested by Buchowski *et al*.[19,20], which is specially pointed to the solid-liquid equilibrium. It is thermodynamically correct and it fits the experimental data well for several systems although only two parameters, λ and H, are involved.

$$\ln\left[1+\lambda\left(1-x_i\right)/x_i\right]=\lambda H\left(\frac{1}{T}-\frac{1}{T_{\mathrm{m}i}}\right) \tag{4}$$

In Eq.(4), λ and H are two equation parameters, and x_i represents the mole fraction of a solute in a binary, saturated solution. The regression results of the aqueous solubilities and the values of the parameters λ and H as well as AAD for the solubility calculations are shown in Tables 2—6.

3.2.3 *Comparison between models*

From the results shown in Table 6, it can be observed that the goodness of fit for the Wilson equation and the λH equation are almost the same for *o*-amino-benzoic acid. In the case of *m*-nitro-benzoic acid and *p*-amino-benzoic acid, the λH equation is considerably better than the Wilson equation, which is in correspondence with the results obtained by Domanska and Ma *et al*.[21—23].

4 CONCLUSIONS

Using a laser monitoring observation technique, the solubilities of the benzoic acid derivatives in 1-octanol as a function of temperature have been determined in this study. Based on all results, some conclusions can be drawn:

(1) The solubilities of *o*-amino-benzoic acid, *p*-amino-benzoic acid, *o*-chloro-benzoic acid, and *m*-nitro-benzoic acid in 1-octanol are usually in the range of 0.01—0.3 (mole fraction).

(2) The solubilities of the compounds increase with temperature. Owing to the special molecular structure, the solubilities of different benzoic acid derivatives in 1-octanol as a function of temperature vary significantly.

(3) The experimental solubilities are well represented by the Wilson equation and especially by the λH equation.

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