Solubilities of Benzoic Acid, *p*-Methylbenzoic Acid, *m*-Methylbenzoic Acid, *o*-Methylbenzoic Acid, *p*-Hydroxybenzoic Acid, and *o*-Nitrobenzoic Acid in 1-Octanol

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Using a laser monitoring observation technique, the solubilities of benzoic acid, *p*-methylbenzoic acid, *m*-methylbenzoic acid, *o*-methylbenzoic acid, *p*-hydroxybenzoic acid, and *o*-nitrobenzoic acid in 1-octanol were measured by the polythermal method in the temperature range of (293.15 to 323.15) K. The experimental data were regressed with the Wilson equation and the λH equation. The experimental results showed that the solubility of the six chemicals in 1-octanol increased significantly with temperature. The results indicate that the molecular structure and interactions affect the solubility significantly. Both the Wilson equation and the λH equation correlate the experimental data well.

Introduction

Benzoic acid derivatives are widely used reaction intermediates; hence, soil and groundwater body have been contaminated badly. The 1-octanol solubility, or the ratio of 1-octanol/water solubilities (which is different from the 1-octanol/water partition coefficient, log *P*), plays a prominent role in the prediction of the environmental fate of chemicals and can characterize transportation through membranes and the topical activity of drugs.[1–3] Several authors have made attempts to calculate the solubility from the available log *P* values and other parameters related to the structure.[4–7]

The solubilities in 1-octanol as a function of temperature *T* of benzoic acid derivatives have not been published before besides in our previous work.[8] 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.

Experimental

Materials. The benzoic acid derivatives tested included: 1-octanol (< 99 %), benzoic acid (< 99 %), *p*-methylbenzoic acid (< 99 %), *m*-methylbenzoic acid (< 99 %), *o*-methylbenzoic acid (< 99 %), *p*-hydroxybenzoic acid (< 99 %), and *o*-nitrobenzoic acid (< 99 %). The melting temperatures (T_m) and the enthalpies of fusion ($\Delta_{fus,m}H$) of the benzoic acid derivatives are listed in Table 1.[9] The compounds were purchased from commercial sources and the fine chemical industry graduate school of Tianjin guang-fu and used without any further purification.

Apparatus and Procedure. The apparatus has been described in detail previously,[8] and therefore, only a brief description is presented here. Preweighed amounts of the benzoic acid derivatives and 1-octanol were placed in an equilibrium vessel. The vessel was connected to a circulating water bath, and stirring was started. The temperature of the mixture was then increased in a stepwise fashion (0.5 K/20 min) until the temperature at which all the benzoic acid derivatives had dissolved was reached. Near the dissolution temperature (more than 1 K below), the temperature increase was typically kept at 0.2 K/20 min or slower.

Table 1. Melting Temperatures T_m and Enthalpies of Fusion $\Delta_{fus,m}H$ of the Benzoic Acid and Its Derivatives[a]

compounds	T_m / K	$\Delta_{fus,m}H$ / (kJ·mol^{-1})
benzoic acid	395.50	18.02
p-methylbenzoic acid	456.70	28.40
m-methylbenzoic acid	383.00	15.73
o-methylbenzoic acid	376.68	19.50
p-hydroxybenzoic acid	488.70	30.90
o-nitrobenzoic acid	418.95	27.99

[a] The data of T_m and $\Delta_{fus,m}H$ were taken from ref 9.

The laser monitoring equipment was used to monitor the dissolution condition of the solution. A steady laser beam passes through an aperture 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 light 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.

Uncertainty of the Results. The impurity of the compounds, weighing error, and temperature error might bring some errors in the final results. The weighing error can be neglected by mass preparation using an analytical balance with an accuracy of ± 0.0001 g. The purity of the chemicals tested is < 99 %, and impurity appears to be a homologue that does not affect the solubility data significantly. Therefore, the temperature error is the greatest uncertainty in the final results. Hence, to guarantee the accuracy of the results, the thermometer that was used in the experiments was calibrated with an accuracy of ± 0.05 K, and the temperature increase rate was controlled strictly at less than 0.2 K/20 min or even slower near the dissolution temperature.

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10.1021/je700677d CCC: $40.75
Published on Web 05/10/2008

Table 2. Solubility Data of Benzoic Acid Derivatives in 1-Octanol and the Regression Results Obtained Using the Wilson Equation and the λH Equation[a]

T/K	x^{exptl}	Wilson equation-RD^b	λH equation-RD^b	H^E/(J·mol^{-1})	T/K	x^{exptl}	Wilson equation-RD^b	λH equation-RD^b	H^E/(J·mol^{-1})
				benzoic acid					
295.30	0.1665	−3.1	−0.3	−105	309.35	0.2350	−0.2	0.0	−149
297.65	0.1801	−0.6	−0.8	−114	312.3	0.2499	−0.3	−0.1	−158
300.15	0.1922	0.1	0.0	−122	313.95	0.2655	2.4	2.5	−168
301.85	0.2033	1.8	1.8	−129	317.15	0.2793	0.8	1.0	−177
304.25	0.2114	0.4	0.4	−134	320.85	0.2897	−3.2	−2.7	−184
305.25	0.2194	1.9	1.9	−139	322.15	0.3000	−2.2	−1.8	−190
307.75	0.2274	0.0	0.1	−144					
				p-methylbenzoic acid					
297.35	0.0595	−0.5	−0.4	−236	314.35	0.0896	0.3	0.3	−355
298.05	0.0608	0.0	0.0	−241	315.8	0.0925	0.2	0.2	−366
298.95	0.0618	−0.9	−0.7	−244	317.65	0.0962	0.0	0.0	−381
301.65	0.0663	−0.4	−0.2	−262	319.65	0.0997	−1.1	−0.8	−394
307.25	0.0767	1.2	1.0	−303	320.40	0.1010	−1.6	−1.2	−399
308.65	0.0789	0.6	0.5	−312	321.55	0.1029	−2.3	−1.8	−407
309.65	0.0816	1.9	1.5	−323	322.15	0.1040	−2.6	−2.0	−411
312.95	0.0871	0.6	0.5	−344					
				m-methylbenzoic acid					
296.25	0.1741	−0.3	0.0	1060	308.45	0.2313	0.0	0.0	1409
297.25	0.1788	0.0	0.2	1089	311.75	0.2470	−0.7	−0.8	1504
299.15	0.1856	−0.6	−0.6	1131	313.80	0.2621	0.5	0.6	1597
300.25	0.1937	0.9	1.1	1180	316.25	0.2749	0.0	0.0	1674
302.90	0.1989	−2.3	−2.5	1211	317.65	0.2867	1.0	1.2	1746
303.80	0.2094	0.6	0.6	1276	322.15	0.3055	−1.9	−2.1	1861
305.85	0.2194	0.6	0.6	1337					
				o-methylbenzoic acid					
297.15	0.1548	−1.3	−1.8	416	310.65	0.2296	0.3	0.1	617
299.65	0.1646	−2.3	−2.8	443	312.25	0.2394	0.2	0.0	644
301.15	0.1805	2.3	2.1	485	314.05	0.2499	−0.3	−0.4	672
302.65	0.1895	2.8	2.7	510	315.75	0.2601	−0.7	−0.8	699
304.75	0.1956	0.4	0.0	526	316.95	0.2705	0.0	0.0	727
305.35	0.1967	0.6	−1.0	529	318.75	0.2807	0.9	−0.9	755
306.25	0.2002	−1.3	−1.7	538	320.35	0.2940	−0.4	−0.3	790
306.95	0.2076	0.3	0.0	558	321.55	0.3046	0.0	0.2	819
308.95	0.2194	0.3	0.1	590					
				p-hydroxybenzoic acid					
297.65	0.1053	−1.1	−0.1	1878	309.85	0.1172	0.7	0.2	2090
299.95	0.1072	−1.4	−0.3	1911	311.25	0.1188	1.2	0.4	2118
301.45	0.1089	−0.3	0.0	1941	313.15	0.1206	0.7	0.3	2150
302.85	0.1103	0.2	0.1	1967	315.45	0.1224	−0.7	−0.1	2183
304.25	0.1115	0.0	0.0	1988	317.25	0.1243	−1.0	−0.2	2216
305.85	0.1131	0.2	0.0	2016	318.65	0.1260	−0.7	0.0	2246
306.95	0.1146	1.3	0.4	2043	320.55	0.1279	−1.3	−0.1	2280
308.15	0.1159	1.6	0.5	2066	322.25	0.1299	−1.2	0.0	2317
				o-nitrobenzoic acid					
297.15	0.0761	−1.8	0.4	−2525	310.15	0.1172	1.5	1.0	−3893
299.65	0.0806	−4.4	−2.4	−2678	311.75	0.1219	0.8	0.1	−4049
300.15	0.0840	−1.6	0.1	−2791	313.15	0.1290	2.7	1.5	−4284
302.05	0.0895	−1.3	0.0	−2972	314.85	0.1351	2.6	1.1	−4487
303.15	0.0928	−1.1	0.0	−3082	317.15	0.1415	0.7	0.9	−4699
306.15	0.1011	−1.9	−1.2	−3356	318.65	0.1475	0.9	−1.0	−4899
307.15	0.1045	−1.5	−1.1	−3470	319.85	0.1541	2.4	0.0	−5118
308.35	0.1079	−1.9	−1.6	−3584	321.15	0.1607	3.4	0.6	−5338
309.25	0.1127	0.0	−1.3	−3742					

[a] T is the absolute temperature; x^{exptl} represents the experimental solubility (in mole fraction of the solute); x_i^{calcd} stands for the calculated solubility of the compound i; and H^E is the molar mixing enthalpy of the solution. [b] $RD = x_i^{exptl} - x_i^{calcd}/x_i^{exptl} \cdot 100$.

The experimental setup and its accuracy were validated by comparing the experimental solubility data of benzoic acid in water (because there are no solubility data of the compound in 1-octanol) with those in the literature as shown in our previous work.[8] The solubilities of benzoic acid in water obtained in this study are in good agreement with the literature.[10] In this work, the estimated error of solubility in terms of mole fraction was < 0.0005.

Results and Discussion

Solubility Data of Benzoic Acid Derivatives in 1-Octanol. The solubilities of benzoic acid derivatives in 1-octanol were measured and are listed in Table 2. The experiments show that the solubilities of these compounds increase with temperature. It is obvious that the solubility in 1-octanol of the measured are considerably higher than those in water, which are shown in our previous work.[11] The higher solubility in 1-octanol can be explained by the nonpolar character of the compounds and 1-octanol.[12] Owing to the special molecular structure, there is a large difference between the solubilities of these chemicals.

Data Correlation by Different Equations. Generally, solid−liquid equilibria (SLE) can be described by an equation containing pure solute properties such as enthalpy of fusion and melting temperature. If, as is the case in this work, a solid−solid

Table 3. Regression Results with Equation 2[a]

systems	*A*	*B*	R^2	100AAD
benzoic acid + octanol	5.128	−2344	0.991	1.2
p-methylbenzoic acid + octanol	4.507	−2177	0.998	0.7
m-methylbenzoic acid + octanol	5.432	−2127	0.997	0.8
o-methylbenzoic acid + octanol	6.832	−2580	0.996	0.9
p-hydroxybenzoic acid + octanol	0.486	−815.0	0.999	0.1
o-nitrobenzoic acid + octanol	7.507	−2998	0.997	0.8

[a] AAD: Average absolute relative deviations, AAD = $1/N \sum_{i=1}^{N} |(x_i^{\text{exptl}} - x_i^{\text{calcd}})/x_i^{\text{exptl}}|$.

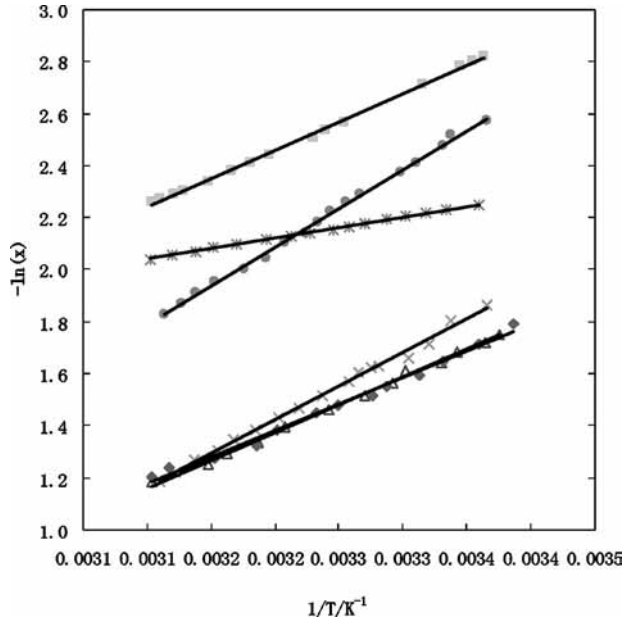

Figure 1. Relationship between $-\ln(x)$ and $1/T$. ♦,benzoic acid; ■, *p*-methylbenzoic acid; △,*m*-methylbenzoic acid; ×, *o*-methylbenzoic acid; *, *p*-hydroxybenzoic acid; ●, *o*-nitrobenzoic acid.

transition does not occur, the equation for the description of SLE can be simplified to the form shown as eq 1

$$\ln \gamma_i x_i = -\frac{\Delta_{\text{fus,m}} H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{mi}}}\right) \tag{1}$$

where $\Delta_{\text{fus,m}} H_i$ is the enthalpy of fusion of the solute *i*; $T_{\text{m}i}$ 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. Equation 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 $T_{\text{m}i}$ and $\Delta_{\text{fus,m}} H$. Among the several activity coefficient models that can be selected, in this study, the Wilson equation was chosen.

Empirical Formula. Since the solubility is the equilibrium concentration of a compound in solvent at certain temperature, the specified temperature is the most important and fundamental parameter. In this work, an empirical formula shown in eq 2 was used to correlate the solubilities of benzoic acid derivatives in 1-octanol. Where *x* is the aqueous solubility (as mole fraction of the solute) and *T* stands for the dissolving temperature, *A* and *B* are two parameters. The correlation results with the eq 2 are shown in Table 3 and Figure 1.

$$\ln x = A + \frac{B}{T/\text{K}} \tag{2}$$

All regressions produced high correlation coefficients ($R^2 > 0.991$), indicating satisfying descriptive capability of the models obtained. Also, using eq 2 yields a reasonable representation of our data to within the expected experimental error, which is shown in Figure 1. However, eq 2 could not embody the actual behavior of the temperature dependence of the solubility and could be used for interpolation but not extrapolation to other temperatures.

Wilson Equation. For a binary system, the Wilson equation is as follows[13]

$$\ln \gamma_1 = 1 - \ln(x_2\Lambda_{12} + x_1) - \left(\frac{x_1}{x_1 + x_2\Lambda_{12}} + \frac{x_2\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{3}$$

In eq 3, Λ_{ij} represents the Wilson equation parameters, which is a function of temperature.

$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left(-\frac{g_{ji} - g_{ii}}{RT}\right) \tag{4}$$

For our calculation system, x_1 indicates the mole fraction of the solute, and x_2 is the mole fraction of the solvent. V_i,V_j are the mole volume of solute or solvent *i*, *j*. 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 parameters remain in the Wilson equation for a binary system: $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$.

Equation 1 was combined with the Wilson equation to determine the Wilson parameters by regression of the measured aqueous solubilities. The results are shown in Table 2. The values of the objective function AAD and the parameters that were determined by regression are listed in Table 4. Also, to get an impression of the quality of the fits and the use of the Wilson equation, experimental data together with the calculated solubilities for *m*-methylbenzoic acid in 1-octanol are plotted in Figure 2.

To test the accuracy of the regressed parameters of the Wilson equation, the degree of confidence was calculated according to the *F*-function, the degree of confidence is calculated with the incomplete β function. The results show that all the degrees of confidence of the Wilson parameters $(g_{21} - g_{11})$ regressed for the different substances are >0.9925. For the Wilson parameters $(g_{12} - g_{22})$, the degree of confidence is > 0.9985.

λH Equation. The λH equation, eq 5, is another way to describe the solution behavior and was first suggested by Buchowski et al.,[14] which especially pointed to the solid−liquid equilibrium.

$$\ln[1 + \lambda(1 - x_i)/x_i] = \lambda\text{H}\left(\frac{1}{T} - \frac{1}{T_{\text{m}i}}\right) \tag{5}$$

In eq 5, λ and H are two equation parameters, and x_i represents the mole fraction of a solute in a binary, saturated solution. In the λH equation, the parameter λ is approximately identified as the mean association number of solute molecules in solution, and the parameter *H* is related to the enthalpy of solution per mole of solute. 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 Table 2 and Table 4. Also, experimental data together with the calculated solubilities for *o*-nitrobenzoic acid in 1-octanol are plotted in Figure 3, which demonstrated that the λH equation could correlate the experimental data very well.

The expression due to Buchowski et al.[15] is given in eq 6, where H^{E} is the molar mixing enthalpy of the solution. Equation 6 can be used to estimate the values of H^{E} to get a better

Table 4. Regression Results of the Wilson Equation and the λH Equation

	Wilson equation			λH equation		
samples	$g_{21} - g_{11}$	$g_{12} - g_{22}$	100AAD	λ	H/K	100AAD
benzoic acid	−981.4	777.7	1.3	0.9650	2091.21	1.3
p-methylbenzoic acid	766.1	−2573.4	0.9	0.7326	2940.14	0.7
m-methylbenzoic acid	−686.4	2568.4	0.7	0.7617	2624.62	0.8
o-methylbenzoic acid	15.3	690.9	0.8	0.9531	2668.82	0.9
p-hydroxybenzoic acid	21062.6	−6052.3	0.8	0.0248	5861.21	0.2
o-nitrobenzoic acid	−10793.5	2608.5	1.8	8.5868	384.050	0.8

understanding of the solution characteristics. The H^E over the studied temperature range, shown in Table 2, was estimated for each system on the basis of the calculated parameter H and the enthalpy of fusion ($\Delta_{fus,m}H_i$).

$$HR = \Delta_{fus,m}H_i + \frac{H^E}{x_i} \quad (6)$$

From Table 4, it can be concluded that *o*-nitrobenzoic acid molecules tend to associate during the dissolution process, with an association number of 8.5868. In Table 2, the values of H^E are positive or negative, which indicates the existence of repulsive or attractive interactions between benzoic acid derivates and 1-octanol molecules. Also, if there are two polar groups in the benzene ring, like in nitrobenzoic acid and in hydrobenzoic acid, the values of H^E are much higher than those with only one polar group in the benzene ring. For the system *o*-nitrobenzoic acid, the absolute values of H^E are much higher than those of other systems and, therefore, a strong attractive interaction exists in this system.

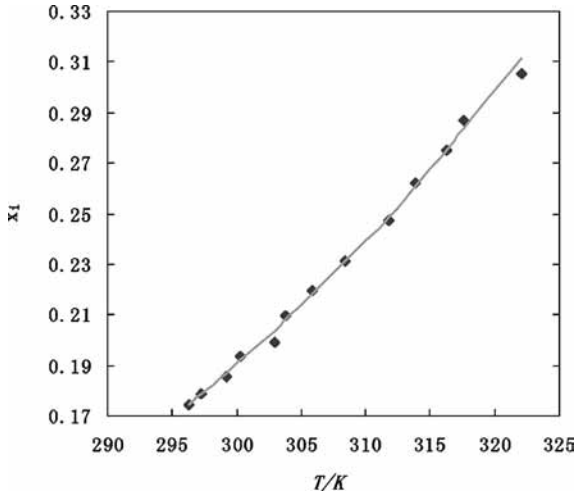

Figure 2. Solubility data of *m*-methylbenzoic acid in 1-octanol. ♦, experimental data; —, regression results obtained using the Wilson equation.

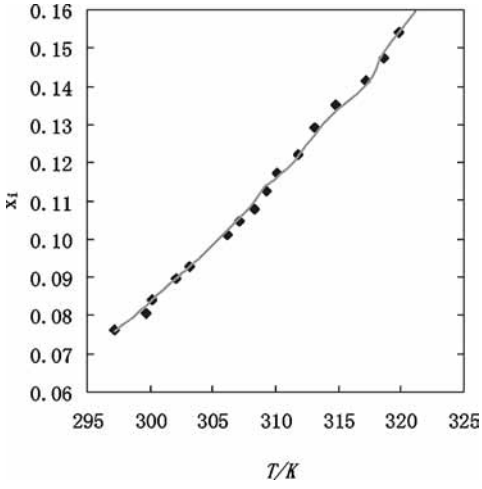

Figure 3. Solubility data of *o*-nitrobenzoic acid in 1-octanol. ♦,experimental data; —, regression results obtained using the λH equation.

Comparison between Models. From the results shown in Table 4, it can be observed that the goodness of fit for the Wilson equation and the λH equation are almost the same for benzoic acid and methylbenzoic acid. In the case of *p*-hydrobenzoic acid and *o*-nitrobenzoic acid, the λH equation is considerably better than the Wilson equation, which is in correspondence with the results obtained by Domanska and Mapeisheng et al.[16–18]

Conclusion

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. The mole fraction solubilities of benzoic acid, *p*-methylbenzoic acid, *m*-methylbenzoic acid, *o*-methylbenzoic acid, *p*-hydroxybenzoic acid, and *o*-nitrobenzoic acid in 1-octanol are usually of the order of 0.05 to 0.3 when temperature T = (293.15 to 323.15) K. 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. The experimental solubilities are well represented by the Wilson equation and especially by the λH equation.

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Received for review November 15, 2007. Accepted March 24, 2008. Thanks for the fund support of the National Natural Science (No. 20676101) and the Nature Science Foundation of Tianjin University of Science & Technology (No. 20070435).

JE700677D