Solubility of Benzoic and Salicylic Acids in Subcritical Water at Temperatures Ranging from (298 to 473) K

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The solubility of benzoic acid and 2-hydroxybenzoic acid (salicylic acid) in water was determined at temperatures ranging from (298 to 473) K under a constant pressure of 5 MPa. The mole fraction solubility of these acids was enhanced by about two orders of magnitude when the water temperature was raised from (298 to 423) K. A new approximation model was developed to predict the solubility of solid organic acids in subcritical water at elevated temperatures. Our new model gives a better prediction for the solubility of the two acids than the approximation models reported in the literature.

Introduction

Water has a critical point of 647 K and 22 MPa. While supercritical water has been successfully used in the treatment of hazardous wastes, the extreme temperature and pressure conditions make it almost impossible for supercritical water application in analytical chemistry, primarily because of the degradation of organic analytes in supercritical water.

Compared to supercritical water, subcritical water requires much milder temperature and pressure conditions that may be suitable for extraction of organic analytes. A significant advantage of subcritical water is its widely tunable polarity, surface tension, and viscosity by simply varying the temperature of water at a mild pressure to keep water in the liquid state.[1] The decreased polarity of water with increasing temperature greatly enhances organic solubility in water at higher temperatures.[2] The enhanced organic solubility makes subcritical water an excellent extraction fluid for most organic compounds.[3]

Benzoic acid and its derivatives are widely used in preservation of foods, fats, and fruit juices as well as in the preparations of resins, plasticizers, dyes, inks, and pharmaceutical products.[4−7] These compounds were also found in medicinal herbs. The traditional preparation of herbal medicine is cooking the herb with boiling water. Recently, there are reports on subcritical water extraction of herbs at temperatures ranging from (393 to 473) K.[8] To optimize the subcritical extraction of benzoic acid and its derivatives, their solubility in water at elevated temperatures is of great importance. There are a number of papers on benzoic and salicylic acid solubility,[4−7,9−11,14−21] but none of them studied the solubility of these acids in water at high temperatures.

In this work, the solubility of benzoic acid and salicylic acid was determined at temperatures ranging from (298 to 473) K with a pressure of 5 MPa to keep water in the liquid state at all temperatures employed. A homemade system was used to obtain subcritical water aliquots saturated with benzoic or salicylic acid. The concentration of the acids in the collected aliquots was determined by high-performance liquid chromatography (HPLC).
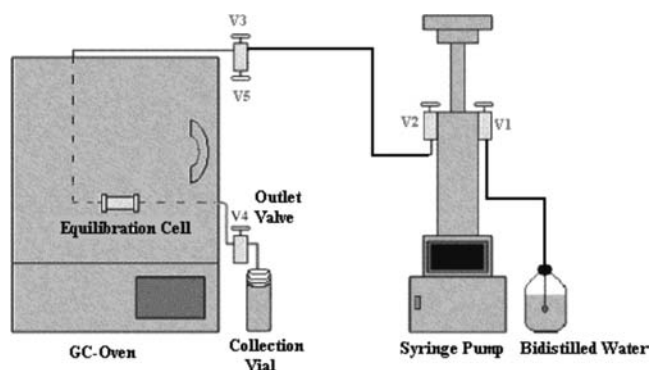

Figure 1. Schematic diagram of the solubility determination system.

An approximation model was developed to predict the solubility of solid organic acids in subcritical water. The predicated values are compared with the experimental ones in this paper.

Experimental Section

Chemicals. Benzoic acid (purity > 99 %), salicylic acid (purity > 99 %), HPLC grade methanol and acetonitrile, and potassium dihydrogen phosphate (purity > 99 %) were purchased from Merck (Darmstadt, Germany). HPLC grade trifluoroacetic acid was obtained from Acros (Geel, Belgium). Distilled water was prepared in our laboratory by using a GFL distillation system (Burgwedel, Germany).

Equipment and Procedures. Solubility experiments were carried out using a homemade system as shown in Figure 1. An empty HPLC column (300 × 7.8 mm i.d.) was used as the equilibration cell for solubility experiments. The equilibration cell was filled with 10 g of benzoic or salicylic acid. Both end-caps of the cell were tightened to prevent leakage. The loaded cell was placed in the oven of a Shimadzu model GC-9A gas chromatograph (Kyoto, Japan) to provide precise temperature control (± 0.1 K) for solubility determination. An ISCO model 260 D syringe pump (Lincoln, NE, USA) was used in the constant pressure mode to supply pressure at 5 ± 0.01 MPa. To ensure that the set temperature inside the equilibration cell was achieved, the counting of heating time before collection started 1 h after the oven reached the set temperature.

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Table 1. Comparison of Experimental Mole Fraction Solubility x_2 for Benzoic Acid (2) in Water (1) with Values Predicated by Using Equations 1 to 4

							$10^3 x_2$				
T/K	expt $(x_2 \pm sd)^a$ (30 min)	expt^a (5 min)	ref 14	ref 15	ref 16	ref 17	ref 18	eq 1	eq 2	eq 3	eq 4
298	2.22 ± 0.24	0.483	0.501	0.503	n/a^b	0.504	0.612	2.22	2.22	0.30	5.55
323	4.87 ± 0.30	1.26	1.21	1.25	0.381	n/a	n/a	3.56	3.59	0.76	13.3
348	11.0 ± 2.6	3.50	3.35	n/a	n/a	n/a	n/a	5.34	5.73	1.68	28.2
373	40.4 ± 7.6	13.2	n/a	n/a	n/a	n/a	n/a	7.58	9.63	3.28	53.9
398	108 ± 10	103	n/a	n/a	n/a	n/a	n/a	10.3	18.2	5.73	95.1
423	131 ± 7.4	122	n/a	n/a	n/a	n/a	n/a	13.5	40.9	9.13	157
473	136 ± 9.7	124	n/a	n/a	n/a	n/a	n/a	21.3	444	18.5	364

^{a} Based on triplicate measurements. ^{b} n/a: not applicable.

Table 2. Comparison of Experimental Mole Fraction Solubility x_2 for Salicylic Acid (2) in Water (1) with Values Predicated by Using Equations 1 to 4

						$10^3 x_2$			
T/K	expt $(x_2 \pm sd)^a$ (30 min)	expt^a (5 min)	ref 19	ref 20	ref 21	eq 1	eq 2	eq 3	eq 4
298	0.469 ± 0.031	0.235	2.20	0.333	0.247	0.469	0.469	0.063	1.48
323	6.42 ± 0.85	1.60	6.27	0.743	0.682	0.849	0.856	0.182	4.43
348	13.3 ± 3.1	2.78	17.1	n/a^b	n/a	1.41	1.51	0.445	11.4
373	19.4 ± 4.3	8.18	n/a	n/a	n/a	2.19	2.78	0.947	25.6
398	83.1 ± 9.1	36.0	n/a	n/a	n/a	3.22	5.67	1.79	52.2
423	102 ± 7.9	86.9	n/a	n/a	n/a	4.52	13.7	3.05	97.8

^{a} Based on triplicate measurements. ^{b} n/a: not applicable.

Fractions (approximately 3 mL) of the heated water−acid mixture were collected at (5, 10, 15, or 30) min after the 1 h equilibration period at each temperature. Note that a new experiment was performed for each temperature and each heating time. The collected aqueous phase was mixed with 4.5 mL of either methanol (for benzoic acid experiments) or acetonitrile (for salicylic acid experiments) immediately after the collection. The mixtures were then analyzed by HPLC. To minimize the carryover effect, V4 was disconnected from the equilibration cell after each experiment. Both the connection tubing and the V4 were washed with either methanol for benzoic acid experiments or acetonitrile for salicylic acid experiments. Triplicate solubility experiments were performed to ensure the reliability of the experimental solubility data. Solubility experiments were carried out at seven different temperatures ranging from (298 to 473) K.

HPLC Analysis. All HPLC analyses were performed using a Perkin-Elmer Series 200 model liquid chromatography system (Norwalk, CT). A reversed-phase column LichroCART (RP-18 150 × 4.6 mm, 5 μm, Merck, Darmstadt, Germany) was employed. Benzoic acid standards were prepared in methanol + water (volume ratio = 3:2), while salicylic acid standards were prepared in acetonitrile + water (volume ratio = 3:2). Benzoic acid was eluted using a mixture of 0.05 M KH_2PO_4 (pH = 3.2) + methanol (volume ratio = 3:2) at a flow rate of 1.0 mL·min^{-1} and was detected at 254 nm with an UV-DAD detector. The salicylic acid samples were eluted by a mixture of (acetonitrile + 0.1 % trifluoroacetic acid by volume) + water (volume ratio = 3:2) at a flow rate of 0.7 mL·min^{-1}. Salicylic acid was detected at 235 nm with an UV-DAD detector. The HPLC separation and analysis were performed at ambient temperature. The error of HPLC analysis is typically less than 5 %.

Results and Discussion

Effect of Temperature on Solubility. Literature data show that temperature has a significant effect on organic solubility in subcritical water.[12,13] In this work we determined the solubility of benzoic and salicylic acids in water at different temperatures as summarized in Tables 1 and 2. The solubility
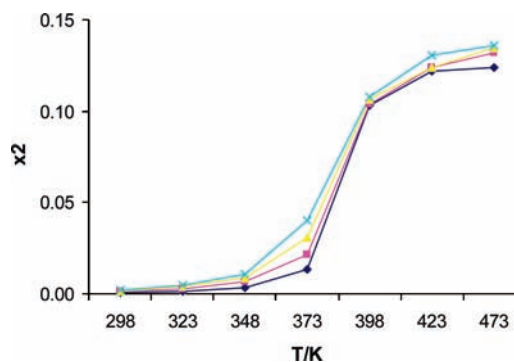

Figure 2. Temperature effect on mole fraction solubility x_2 of benzoic acid (2) in water (1). Heating time: ◆, 5 min; ■, 10 min; ▲, 15 min; ×, 30 min.

at low temperatures determined in this work was also compared with literature values in Tables 1 and 2.[14−21] As shown in Table 1, our benzoic acid solubility data obtained for experiments with 5 min of heating time compare very favorably with literature values. However, as the heating time increased, the solubility of benzoic acid was further enhanced as shown in Figure 2 and Table 1. The solubility of salicylic acid at 298 K determined in our work is similar as that reported in refs 20 and 21, while our data at (323 and 348) K with 30 min of heating time compare well with that reported in ref 19 as shown in Table 2. The experimental error of the overall solubility determination is around 20 % for experiments at (348 and 373) K and typically 10 % for experiments performed at other temperatures.

Figures 2 and 3 depict the profiles of mole fraction solubility versus varying temperature and heating time for benzoic acid and salicylic acid, respectively. As shown in Figures 2 and 3, the solubility reached the highest level with 30 min of heating time. The mole fraction solubility of benzoic acid approaches its maximum at 473 K as shown in Table 1 and Figure 2. However, Figure 3 demonstrates that the mole fraction solubility of salicylic acid dramatically decreases at 473 K because of severe degradation of this acid at the high temperature. This is supported by the result of an ongoing project in our laboratory at East Carolina University. In this ongoing project, we have been investigating the degradation of benzoic acid and salicylic
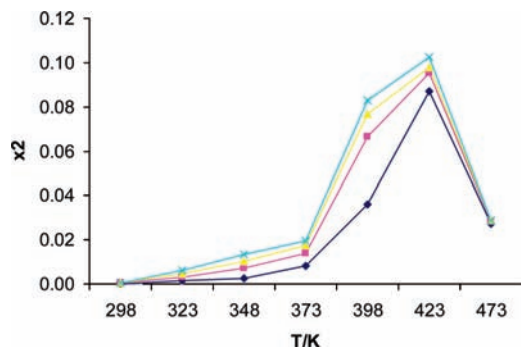
Figure 3. Temperature effect on mole fraction solubility x_2 of salicylic acid (2) in water (1). Heating time: ◆, 5 min; ■, 10 min; ▲, 15 min; ×, 30 min.
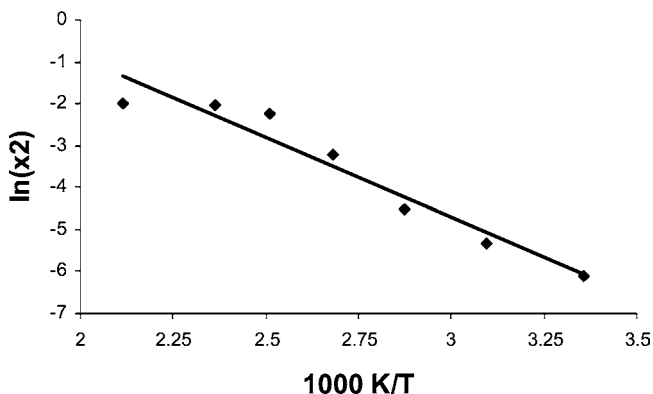

Figure 4. Solubility x_2 (30 min of heating time) of benzoic acid (2) in water (1) at different temperatures.
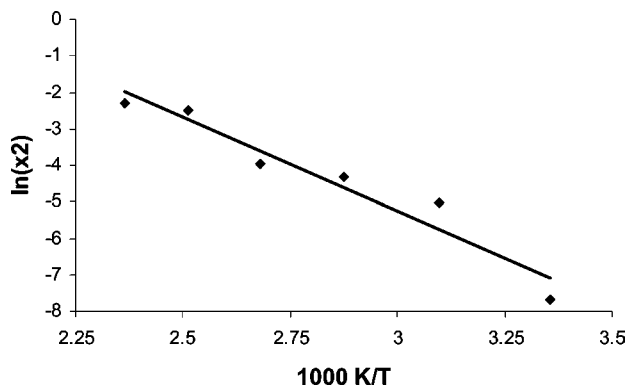

Figure 5. Solubility x_2 (30 min of heating time) of salicylic acid (2) in water (1) at different temperatures.

acid in subcritical water. Our results show that benzoic acid is stable in water at temperatures as high as 523 K, while salicylic acid is slightly degraded at 423 K but severely degraded at 473 K.[22]

The relationship between the reciprocal of Kelvin temperature and $\ln(x_2)$ for the two acids is shown in Figures 4 and 5. The data point of 473 K is excluded in Figure 5 because of the severe degradation of salicylic acid as discussed earlier. The relative linear relationship in Figures 4 and 5 is similar to what reported in the literature.[12,13]

Approximation Models. Miller et al. suggested an approximate model for the mole fraction solubility of polycyclic aromatic hydrocarbons in high-temperature water.[12] As shown in eq 1, the mole fraction solubility at higher temperatures can be predicted with the knowledge of the mole fraction solubility at ambient temperature (T_o).

$$\ln x_2(T) \approx \left(\frac{T_o}{T}\right)\ln x_2(T_o) \tag{1}$$

where the mole fraction solubility at any temperature T is $x_2(T)$ and the ambient mole fraction solubility is given by $x_2(T_o)$.

The authors then added a cubic equation to the base eq 1 yielding the first approximation for the mole fraction solubility at T as given by

$$\ln x_2(T) = \left(\frac{T_o}{T}\right)\ln x_2(T_o) + 15\left(\frac{T}{T_o} - 1\right)^3 \tag{2}$$

In a previous study,[13] we modified eq 1 to better predict the solubility of liquid nonpolar organic compounds in subcritical water by using the following equation:

$$\ln x_2(T) = \left(\frac{T_o}{T}\right)\ln x_2(T_o) + 2\left(\frac{T - T_o}{T_o} - 1\right)^3 \tag{3}$$

To examine the suitability of these models for the solubility prediction of the two acids investigated in this work, we summarized the experimental data in comparison with the predicted values obtained by eqs 1 to 3. As shown in Tables 1 and 2, all three equations failed to correctly predict the mole fraction solubility of both benzoic and salicylic acids. This is not surprising since these models were developed to predict the solubility of nonpolar organic compounds.[12,13] However, the two solutes studied in this work are polar compounds, and thus, a different model is needed to describe the solubility behavior. Therefore, eq 1 was modified to better predict the solubility of organic acids in subcritical water. The new approximation model is given by the following equation:

$$\ln x_2(T) = \left(1.85\frac{T_o}{T} - 1\right)\ln x_2(T_o) \tag{4}$$

The mole fraction solubility predicted by eq 4 is also included in Tables 1 and 2. As shown in these two tables, the new model yields a reasonable prediction for the solubility of both acids at most temperatures when compared with experimental values. Most importantly, the solubility data predicted by eq 4 are much closer to the experimental values than those predicted by eqs 1 to 3 as indicated in Tables 1 and 2.

Conclusions

Varying the temperature of water with enough pressure to preserve the liquid state has a remarkable effect on the solubility of benzoic and salicylic acids. When the water temperature was increased from (298 to 423) K, the solubility of benzoic and salicylic acids was enhanced by about two orders of magnitude. Our solubility data also show that benzoic acid was stable at temperatures up to 473 K. However, salicylic acid underwent severe degradation at 473 K. Our new model (eq 4) yields better prediction for the solubility of the two acids than the approximation models developed previously.

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