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Solubility of Hydroquinone in Different Solvents from 276.65 K to 345.10 K

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Using a laser-monitoring observation technique, the solubility of hydroquinone in water, methanol, ethanol, 2-propanol, ethyl acetate, butyl acetate, and acetic acid were measured at temperatures ranging from 276.65 K to 345.10 K under the atmospheric pressure. The experimental solubility data was well-correlated with the data, calculated by means of a semiempirical equation.

Introduction

Hydroquinone (1,4-benzenediol, CAS Registry No. 123-31-9, a white or light gray crystal) is an important basic organic materials and has been extensively used in the fields of pharmaceutics, food, and chemical industry. Usually, the cooling crystallization process is used to purify hydroquinone. The crystal habit is an important factor needing to be considered in the crystallization process because it greatly affects the product's application and the subsequent processes, such as filtering, washing, drying, package, storage, and transportation.[1] It has been experimentally found that the crystal habit of hydroquinone is evidently influenced by the property of solvents used in the crystallization process.[2] To obtain the expected crystal habit, selecting the appropriate solvents is the first thing in designing the crystallization process. Therefore, the solubility values of hydroquinone in different solvents are required; however, the data availability in the literature is poor.[3−7] In this work, the solubility data of hydroquinone in water, methanol, ethanol, 2-propanol, ethyl acetate, butyl acetate, and acetic acid from 276.65 K to 345.10 K under atmospheric pressure were measured by use of the iso-composition method[8] and the laser-monitoring observation technique.[9−11]

Experimental Section

Materials. Hydroquinone crystals (mass fraction purity > 99.5 %) were obtained from Lianyungang Sanjili Chemical Co. of China and dried in vacuo at (323.15 ± 1) K for 48 h. The solvents used in the experiments (methanol, ethanol, 2-propanol, ethyl acetate, butyl acetate, and acetic acid) are of analytical reagent grade and were purchased from Tianjin University Kewei Co. of China. After being dehydrated with molecular sieves (4A-ZMS), their mass fraction purities were more than 99.5 %. Distilled deionized water was used.

Apparatus and Procedure. The solubility apparatus (Figure 1) is similar to that described in the literature.[9−11] A laser beam was used to observe the dissolution of the solid−liquid mixture with constant composition. The laser-monitoring system ($\lambda = 632.8$ nm, produced by Zhengzhou University, China) consisted of a laser generator, a photoelectric transformer, and a light intensity display. A jacketed vessel made of Pyrex glass having a working volume of 150 mL was used for the solubility measurement. The temperature in the vessel was maintained at the desired value by continuous forced water circulation from a thermostat (temperature uncertainty of ± 0.05 K). A mercury-in-glass thermometer (uncertainty of ± 0.05 K) was used for the measurement of the temperature in the vessel. To prevent the evaporation of the solvent, a condenser was positioned vertically on the jacketed vessel. A magnetic stirrer was used for the mixing of the solution.

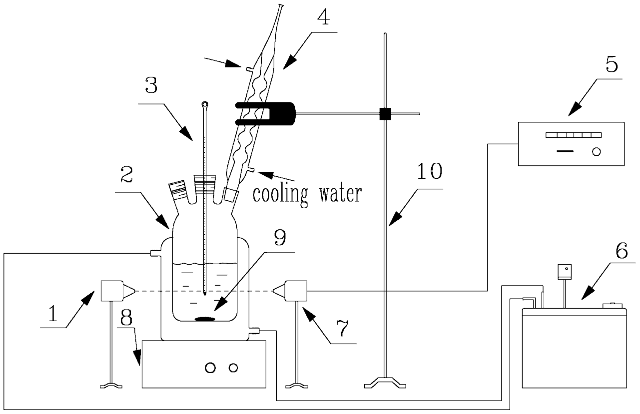

Figure 1. Schematic setup for the solubility measurement: 1, laser generator; 2, dissolution vessel; 3, thermometer; 4, condenser; 5, digital display; 6, thermostat; 7, photoelectric converter; 8, magnetic stirrer; 9, stir bar; and 10, a ring stand and clamp.

At the beginning of the experiment, 100 mL of solvent was loaded into the jacketed vessel, and the corresponding light intensity penetrated through the solution was recorded down and regarded as the maximum value. Then a quantificational solid hydroquinone was loaded into the vessel, and the intensity of the penetrated light would reduce to its minimum value. The weight of hydroquinone was determined using an analytical balance (Mettler Toledo AB204-N, Switzer-Land) with an uncertainty of ± 0.0001 g. The method for solubility measurement was based on the fact that the light intensity penetrated through the solution would increase with the dissolution of the solid hydroquinone when the temperature was gradually increased. The heating rate was controlled initially at 2 $K \cdot h^{-1}$ when the light intensity was at its lower level. When the light intensity increased to half the maximum value, the temperature was increased by 0.05 K in steps, and the light intensity was recorded every 10 min. When the light intensity was nearly constant between two readings, the heating-up was continued. When the light intensity nearly reached its maximum value and did not increase anymore, it was considered that the solid

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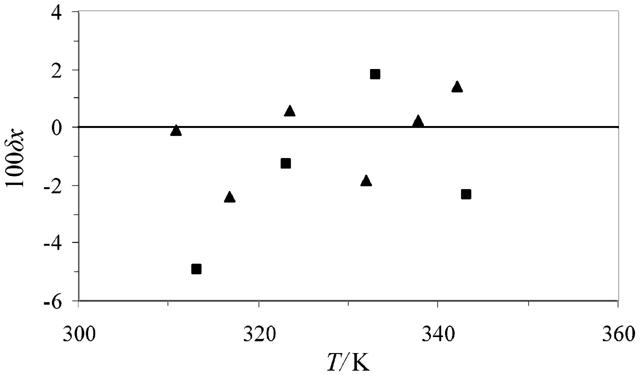

Figure 2. Comparison between the relative deviations of the solubility of hydroquinone in water from this work and literature[3] correlated with eq 4: ▲, this work; ■, Stephen and Stephen.[3]

hydroquinone had been completely dissolved. In the experiments, the dissolving equilibrium was believed to have been reached when the light intensity attained 92 % of its maximum value. The uncertainty of the mass fraction solubility values was estimated to be less than 1 %. All the measurements were repeated three times.

To testify the uncertainty of the measurement, a comparison with the literature values[3] for the solubility of hydroquinone in water was made. The results were correlated with eq 4, and the relative deviation of solubility values between literature[3] and this work was plotted in Figure 2. From Figure 2, it can be seen that the relative deviation in the mole fraction solubility was less than 3 %.

Results and Discussion

The solubility values of hydroquinone in different solvents were listed in Table 1 and visually shown by Figure 3, where T is the absolute temperature, δ_x is the relative deviation, and x_1^{exp} and x_1^{cal} are the experimental and calculation values of the solubility, respectively. The experimental solubility values were fitted with the following semiempirical equation by the least-squares method.

According to the solid−liquid phase equilibrium theory, the relationship between solubility and temperature is generally modeled by the following expression:

$$\ln x_1 = -\frac{\Delta_{\text{fus}}H}{RT_{\text{fus}}}\left(\frac{T_{\text{fus}}}{T}-1\right) - \frac{\Delta_{\text{fus}}C_{\text{p}}}{R}\left(\frac{T_{\text{fus}}}{T}-1\right) + \frac{\Delta_{\text{fus}}C_{\text{p}}}{R}\ln\frac{T_{\text{fus}}}{T} - \ln\gamma_1 \quad (1)$$

where x_1 is the experimental solute mole fraction solubility, $\Delta_{\text{fus}}H$ is the fusion enthalpy of the solute, T_{fus} is the melting temperature of the solute, and $\Delta_{\text{fus}}C_{\text{p}}$ is the difference of heat capacities of the solute between the liquid and solid phases. γ_1 is the activity coefficient of solute and can be written as

$$\ln\gamma_1 = a + \frac{b}{T/\text{K}} \quad (2)$$

where a and b are empirical constants. Combining eqs 1 and 2 gives eq 3:

$$\ln x_1 = \left[\frac{\Delta_{\text{fus}}H}{RT_{\text{fus}}} + \frac{\Delta_{\text{fus}}C_{\text{p}}}{R}(1+\ln T_{\text{fus}}) - a\right] - \left(b + \frac{\Delta_{\text{fus}}H}{R} + \frac{\Delta_{\text{fus}}C_{\text{p}}}{R}T_{\text{fus}}\right)\frac{1}{\text{T}} - \frac{\Delta_{\text{fus}}C_{\text{p}}}{R}\ln T \quad (3)$$

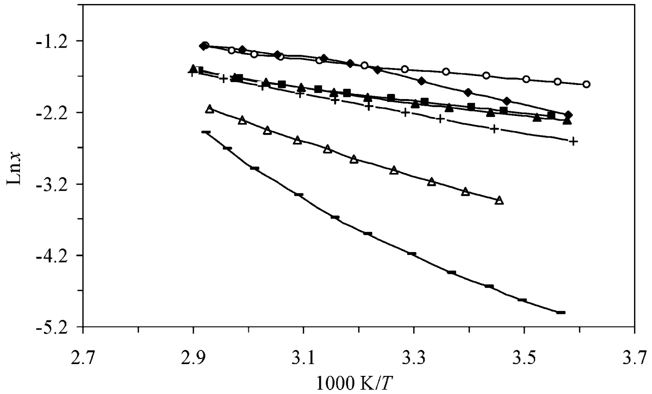

Figure 3. Solubility of hydroquinone in different solvents: —, water; △, acetic acid; +, ethyl acetate; ▲, butyl acetate; ■, methanol; ◆, 2-propanol; ○, ethanol.

Table 1. Mole Fraction Solubility (x_1) of Hydroquinone in Different Solvents

T/K	$10x_1^{\text{exp}}$	$100\delta_x$	T/K	$10x_1^{\text{exp}}$	$100\delta_x$
Water					
280.50	0.0663	−1.4	316.85	0.2516	−2.4
286.00	0.0795	−0.38	323.50	0.3465	0.55
291.05	0.0965	2.2	332.00	0.4981	−1.9
296.95	0.1163	−0.086	337.70	0.6649	1.7
303.45	0.1515	1.7	342.10	0.8310	1.4
310.85	0.2000	−0.15			
Methanol					
281.65	1.047	−0.38	314.60	1.437	−0.14
288.70	1.121	0	319.85	1.521	0.26
293.80	1.177	0.17	326.65	1.608	−1.1
301.15	1.270	0.71	335.20	1.766	−0.51
306.85	1.335	0.15	343.40	1.949	0.82
Ethanol					
276.65	1.630	−0.74	311.50	2.123	0.14
280.85	1.685	−0.18	319.55	2.261	−0.13
285.30	1.748	0.46	326.95	2.392	−0.67
291.40	1.828	0.55	332.00	2.468	−1.9
297.65	1.914	0.57	336.75	2.610	−0.34
304.55	2.012	0.25	342.15	2.800	1.9
2-Propanol					
279.45	1.064	2.1	314.15	2.169	1.9
288.30	1.294	−1.4	318.75	2.325	2.7
294.35	1.469	−2.5	327.60	2.473	−0.89
301.75	1.712	−1.8	334.70	2.623	−1.3
309.10	1.998	1.2	342.55	2.803	−0.071
Ethyl Acetate					
278.70	0.7333	0.068	316.70	1.312	−0.23
290.15	0.8800	−0.38	323.25	1.444	0.14
298.80	1.017	0.59	330.60	1.595	0.13
304.60	1.103	0	338.35	1.770	0.28
310.80	1.205	−0.33	345.10	1.921	−0.21
Butyl Acetate					
279.55	0.9877	0.071	316.95	1.450	0.069
283.95	1.019	−0.79	323.05	1.555	0
290.85	1.100	0.36	329.95	1.677	−0.72
297.20	1.173	0.43	336.10	1.803	−1.0
302.85	1.247	0.64	344.7	2.049	1.1
311.00	1.352	−0.15			
Acetic Acid					
289.45	0.3210	0.12	318.15	0.6591	0.61
294.65	0.3645	0.19	323.75	0.7522	0.040
300.15	0.4193	0.072	329.65	0.8663	−0.30
306.35	0.4887	−0.061	334.70	0.9831	0.041
313.30	0.5791	−0.35	341.25	1.152	0

which can be written as

$$\ln x_1 = A + B/(T/\text{K}) + C\ln(T/\text{K}) \quad (4)$$

where A, B, and C are semiempirical constants. The experimental solubility data were fitted with eq 4 by the least-squares

Table 2. Parameters of Equation 4 for Hydroquinone in Different Solvents

solvent	*A*	*B*	*C*	$10^3\sigma_x$
water	−353.49	12735	53.771	0.53
methanol	−56.005	1676.8	8.4740	0.93
ethanol	−53.759	1749.0	8.1152	2.3
2-propanol	164.44	−8897.4	−23.943	3.5
ethyl acetate	−19.024	−414.84	3.1792	0.37
butyl acetate	−82.974	2817.7	12.529	1.1
acetic acid	−88.149	1891.1	13.792	0.17

method. The values of *A*, *B*, and *C* in eq 4 are obtained and listed in Table 2 together with the root mean square (σ_x), namely, standard deviation, which is defined as

$$\sigma_x = \left\{ \sum_{i=1}^{N} \frac{(x_i^{\mathrm{exp}} - x_i^{\mathrm{cal}})^2}{N - 1} \right\}^{1/2} \qquad (5)$$

where *N* is the number of experimental values.

From Table 1 and Table 2, the following conclusions can be drawn: (1) The solubility of hydroquinone in different solvents is in the following order: alcohol solvents > ester solvents > acetic acid > water. (2) All the solubility curves are similar except that of 2-propanol (Figure 3). The unique solubility behavior of hydroquinone in 2-propanol is perhaps due to the result of complex solute−solvent interaction. The mechanism needs to be further studied. (3) From Table 2, it can be seen that only for 2-propanol, the parameter *C* in eq 4 has a negative value. This indicates that the heat capacity of the hydroquinone solution in 2-propanol increases when hydroquinone transits from liquid to solid phase and is different from the others. (4) According to the values of the standard deviation (σ_x), it can be seen that the solubility of hydroquinone in the solvents under consideration can be fitted with eq 4 very well.

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