Solubilities of 1,4-Naphthoquinone in Acetone, Toluene, Xylene, Ethanol, and *n*-Butyl Alcohol

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Using a dynamic method, the solubilities of 1,4-naphthoquinone in acetone, toluene, xylene, ethanol, and *n*-butyl alcohol have been determined experimentally from (293.27 to 319.63, 294.10 to 331.95, 289.63 to 323.07, 279.80 to 335.43, and 295.44 to 355.07) K, respectively. The experimental data were correlated with the Wilson model, Apelblat equation, and λ-h model. The calculated results show that the correlation of the Apelblat equation and λ-h model for five measured systems has less deviation than that of the Wilson model.

Introduction

1,4-Naphthoquinone is an important raw material of fine chemicals which is widely used as the middle product of medicine, dye, spices, pesticide, and plasticizing agents. At present, the process of making 1,4-naphthoquinone from naphthalene by air-catalytic oxidation has been industrialized somewhere, and the solubilities of 1,4-naphthoquinone present important evidence for its separation from phthalic anhydride and maleic anhydride, the byproducts. However, only a limited amount of solubility data for 1,4-naphthoquinone have been reported, In this study, solubilities of 1,4-naphthoquinone in acetone, toluene, xylene, ethanol, and *n*-butyl alcohol have been measured. The experimental data were correlated with the Wilson model, the Apelblat equation, and the λ-h model.

Experimental Section

Materials. 1,4-Naphthoquinones, obtained from Shanghai Haiqu Chemical Co. Ltd., were further purified by recrystallization from organic solutions. After filtration and drying, their purities were determined by UV spectrometry (type UV-2401PC, ShimadzuCo. Ltd.) to be 0.996 in mass fraction. Acetone, toluene, xylene (in which the mole fraction of *ortho*-xylene, *meta*-xylene, and *para*-xylene are 13.3 %, 66.4 %, and 20.3 %, respectively), ethanol, and *n*-butyl alcohol were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China.

Apparatus and Procedure. The thermodynamic properties normal melting temperature T_m and enthalpy of fusion ΔH_{fus} of 1,4-naphthoquinone were determined by differential scanning calorimetry (DSC, NETZSCH, type STA409PC-luxx).

The solubility was measured by a dynamic method.[1] A predetermined sample was heated very slowly [it was less than 0.1 K per hour, close *to* the solid−liquid equilibrium temperature]. The solid in the solution (sample) dissolved with an increase in temperature, and the temperature at which the last piece of the solid dissolved was the solid−liquid equilibrium temperature of the sample.

The experimental apparatus includes a dissolving flask, a laser detecting system (made by the College of Physical Science and Engineering, Zhengzhou University), a temperature-controlling and measurement system, and a magnetic stirring system (type 79-1, Shanghai Laboratory Instrument Works Co., Ltd.). A laser generator was installed at one side of the dissolving flask to generate the laser beam through the dissolving flask, and a laser electrical signal transducer was installed at the opposite side to detect the laser beam and then converted into an electrical signal, which increases as the solid dissolves. When the last piece of solid dissolves, the laser power reaches the greatest value, and the temperature corresponding to the greatest value of the galvanometer is the solid−liquid equilibrium temperature of the sample. The thermocouple used in the experiment was calibrated in the Tianjin Metrology Institute (Tianjin, China), and the accuracy of the thermocouple was ± 0.01 K.

The solubility of benzoic acid in water has been reported in the literature,[2] and it is also measured with the equipment in this article (Figures 1 and 2). By comparing the results, it is shown that the deviations of the measured solubility from the literature values were less than 2 %. Therefore, the reliability of the experimental apparatus was verified.

Results and Discussion

Experimental Results. With 1,4-naphthoquinone as the solute and acetone, toluene, xylene, ethanol, and *n*-butyl alcohol as solvents, the solubilities of five binary systems were determined in this study and are listed in Tables 1, 2, and 3, in which x_1 is the mole fraction of the solute in the solution.

Figure 3 shows the experimental results of the five binary systems. Five kinds of symbols were used to express these results. As shown in Figure 3, the solubility data of 1,4-naphthoquinone in acetone, toluene, xylene, ethanol, and *n*-butyl alcohol showed a flat uptrend when the temperature increased. When the temperature was higher than 325 K, the solubility of 1,4-naphthoquinone in *n*-butyl alcohol increased rapidly, but its solubility in the other four solvents still maintained a flat uptrend. Moreover, the solubilities of 1,4-naphthoquinone in acetone, toluene, and xylene are higher than those in ethanol and *n*-butyl alcohol overall. This made the solubility of 1,4-

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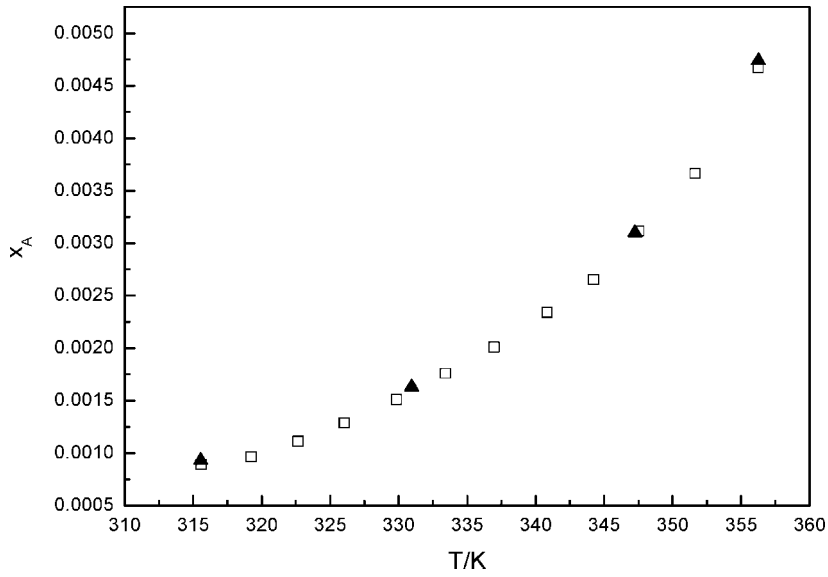

Figure 1. Mole fraction solubility of benzoic acid in water compared with the literature data. □, experimental value; ▲, literature value.[2]

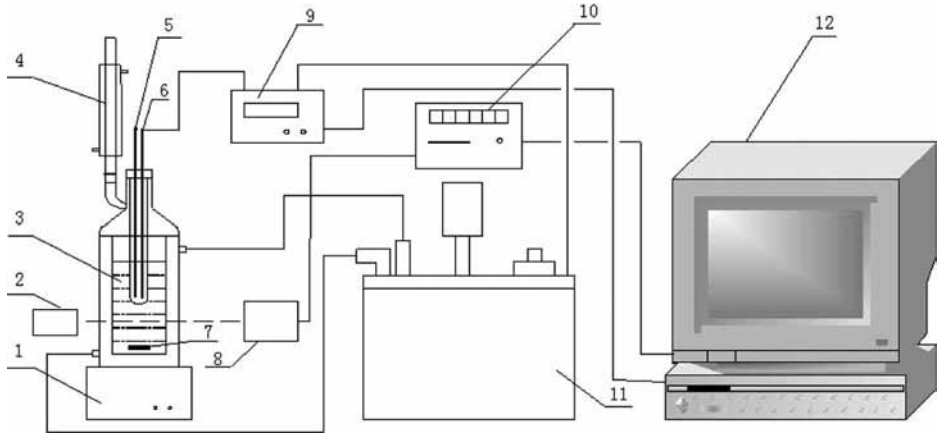

Figure 2. Sketch of the equipment of solubility measurement by the synthetic method. 1, magnetic stirring system; 2, laser generator; 3, dissolving flasks; 4, prolong; 5, thermometer; 6, thermocouple; 7, stirring rotor; 8, laser-electrical signal transducer; 9, controller; 10, digital monitor; 11, thermostatic bath; 12, workstation.

Table 1. Experimental Solubility Data and Correlation Result of the Wilson Model

solute, 1,4-naphthoquinone; solvent, acetone				solute, 1,4-naphthoquinone; solvent, xylene			
T/K	x_1^{exptl}	x_1^{calcd}	dev/%	T/K	x_1^{exptl}	x_1^{calcd}	dev/%
293.27	0.03619	0.03410	−5.77	289.63	0.03459	0.03365	2.71
295.46	0.03727	0.03682	−1.20	293.61	0.03917	0.03923	0.15
295.80	0.03765	0.03728	−0.99	297.43	0.04521	0.04531	0.21
298.25	0.03994	0.04065	1.78	298.06	0.04624	0.04638	0.30
298.51	0.04031	0.04103	1.79	298.70	0.04725	0.04749	0.51
299.07	0.04108	0.04187	1.91	303.53	0.05592	0.05661	1.24
300.66	0.04371	0.04435	1.45	305.33	0.06008	0.06038	0.50
302.06	0.04675	0.04670	−0.12	309.15	0.06833	0.06904	1.04
304.00	0.05027	0.05005	−0.44	311.02	0.07304	0.07365	0.84
305.30	0.05322	0.05247	−1.42	313.61	0.07992	0.08046	0.67
308.24	0.05839	0.05811	−0.48	316.46	0.08826	0.08856	0.34
311.24	0.06392	0.06440	0.75	319.43	0.09685	0.09768	0.86
312.91	0.06834	0.06830	−0.05	320.60	0.10151	0.10153	0.02
314.97	0.07265	0.07322	0.79	323.07	0.10953	0.10997	0.40
316.33	0.07670	0.07680	0.13				
318.06	0.08102	0.08142	0.50				
319.63	0.08555	0.08591	0.42				

naphthoquinone in toluene more than 10 times as much as that in ethanol, and it might be chosen as the solvent in the recrystallization purification process.

Solid−Liquid Equilibria Correlation Using the Wilson Model. The Wilson model was used early in vapor−liquid equilibrium studies. In 1967, Null[3] studied the solid−liquid equilibrium of melt salt using the Wilson model and got satisfying results.

Supposing as follows, when solid−liquid reaches equilibrium:

1. The solid phase is pure solute.

2. The liquid phase does not enter the solid phase during dissolving.

Table 2. Experimental Solubility Data and Correlation Result of the Wilson Model

solute, 1,4-naphthoquinone; solvent, ethanol			
T/K	x_1^{expyl}	x_1^{calcd}	dev/%
279.80	0.00145	0.00171	17.89
285.78	0.00221	0.00237	7.19
289.05	0.00277	0.00282	1.89
292.72	0.00335	0.00341	1.80
296.52	0.00412	0.00414	0.48
299.87	0.00487	0.00489	0.51
303.25	0.00596	0.00581	−2.45
305.99	0.00696	0.00668	−4.06
309.13	0.00825	0.00782	−5.22
311.85	0.00945	0.00895	−5.30
314.73	0.01085	0.01032	−4.93
316.84	0.01207	0.01147	−5.00
319.52	0.01340	0.01302	−2.85
321.15	0.01451	0.01413	−2.63
322.93	0.01567	0.01541	−1.67
328.25	0.01993	0.02010	0.86
329.13	0.02118	0.02119	0.04
331.34	0.02349	0.02377	11.19
333.04	0.02562	0.02608	1.79
334.13	0.02738	0.02784	1.67
335.43	0.02940	0.03001	2.08

solute, 1,4-naphthoquinone; solvent, toluene			
T/K	x_1^{exptl}	x_1^{calcd}	dev/%
294.10	0.047550	0.047087	−0.97
297.82	0.053700	0.053594	−0.20
300.35	0.058550	0.058401	−0.25
302.68	0.063110	0.063127	0.03
304.44	0.066810	0.066889	0.12
306.58	0.072350	0.071672	−0.94
310.16	0.080980	0.080309	−0.83
313.15	0.088990	0.088119	−0.98
315.25	0.094040	0.093981	−0.06
317.27	0.099450	0.099891	0.44
319.93	0.106990	0.10811	1.04
321.45	0.11324	0.11297	−0.24
322.53	0.11622	0.11659	0.32
322.93	0.11793	0.11793	−0.00
327.20	0.13293	0.13316	0.18
330.45	0.14503	0.14577	0.51
331.95	0.15332	0.15181	−0.99

Table 3. Experimental Solubility Data and Correlation Result of the Wilson Model

solute, 1,4-naphthoquinone; solvent, *n*-butyl alcohol			
T/K	x_1^{exptl}	x_1^{calcd}	dev/%[a]
302.10	0.006570	0.007021	6.87
307.20	0.009080	0.009191	1.22
312.32	0.01201	0.01196	−0.42
317.10	0.01515	0.01520	0.35
319.33	0.01697	0.01702	0.29
320.94	0.01834	0.01845	0.59
322.16	0.01991	0.01972	−0.95
325.85	0.02377	0.02375	−0.07
330.35	0.03074	0.03103	−6.17
334.33	0.03768	0.03741	−0.73
336.45	0.04340	0.04253	−2.00
339.23	0.05000	0.04962	−0.77
341.30	0.05600	0.05597	−0.05
343.26	0.06241	0.06290	0.79
344.60	0.06947	0.06948	0.02
346.03	0.07627	0.07656	0.38

[a] dev = $(x^{calcd} - x^{exptl})/x^{exptl} \cdot 100$ %.

Table 4. Mole Volume of Different Compounds

material	mol. wt	density/g·cm^{-3}	mole volume/cm^3·mol^{-1}
1,4-naphthoquinone	158.15	1.4220	111.22
ethanol	46.070	0.7890	58.390
toluene	92.140	0.8660	106.40
n-butyl alcohol	74.120	0.8109	91.405
acetone	58.080	0.7880	73.706
xylene	106.17	0.8600	123.45

Table 5. Data of Correlation Parameter for Different System

system	$g_{12} - g_{11}$	$g_{21} - g_{22}$
1,4-naphthoquinone + acetone	−463.90	−1214.5
1,4-naphthoquinone + xylene	−715.30	1084.9
1,4-naphthoquinone + toluene	1595.5	1824.7
1,4-naphthoquinone + ethanol	−2504.8	−4750.0
1,4-naphthoquinone + *n*-butyl alcohol	−3072.9	−1735.4

Then, the fugacity of pure solute is equal to that in liquid.

On the basis of the theory above, a thermodynamics equation of the liquid−solid equilibrium can be obtained as follows.

$$\ln x_2\gamma_2 = \frac{\Delta H_m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad (1)$$

In a binary system, Wilson equations are as follows.

Table 6. Correlation Results for Different Activity Coefficient Models

	F/%		
system	Wilson	Apelblat	λ-h
1,4-naphthoquinone + acetone	1.176	0.000537	0.000608
1,4-naphthoquinone + xylene	0.6985	0.01321	0.01326
1,4-naphthoquinone + toluene	0.4762	0.000472	0.000516
1,4-naphthoquinone + ethanol	3.404	0.000203	0.000255
1,4-naphthoquinone + *n*-butyl alcohol	1.354	0.000811	0.00124
total average deviation	1.422	0.003047	0.003175

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \quad (2a)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \quad (2b)$$

where x_2 is the mole fraction of the solute; x_1 is the mole fraction of solvent; and $\gamma_1$and γ_2 are the fugacity of solute and solvent, respectively.

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp[-(g_{12} - g_{11})/RT] \quad (3a)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp[-(g_{21} - g_{22})/RT] \quad (3b)$$

In which, $(g_{12} - g_{11})$ and $(g_{21} - g_{22})$ are dual correlation parameters and can be obtained by regression using MATLAB and V_1^L and V_2^L are mole volume of the solute and solvent, respectively. Results are listed in Tables 4 and 5.

Comparison with Other Models. The objective function in the simplex method was absolute average relative deviation between the experimental and calculated mole fraction of the solute

$$F = \frac{1}{n}\sum_n \left|\frac{x_i^{exptl} - x_i^{calcd}}{x_i^{exptl}}\right| \cdot 100\ \% \quad (4)$$

where x_i is the mole fraction of the solute and n is the number of the experimental data.

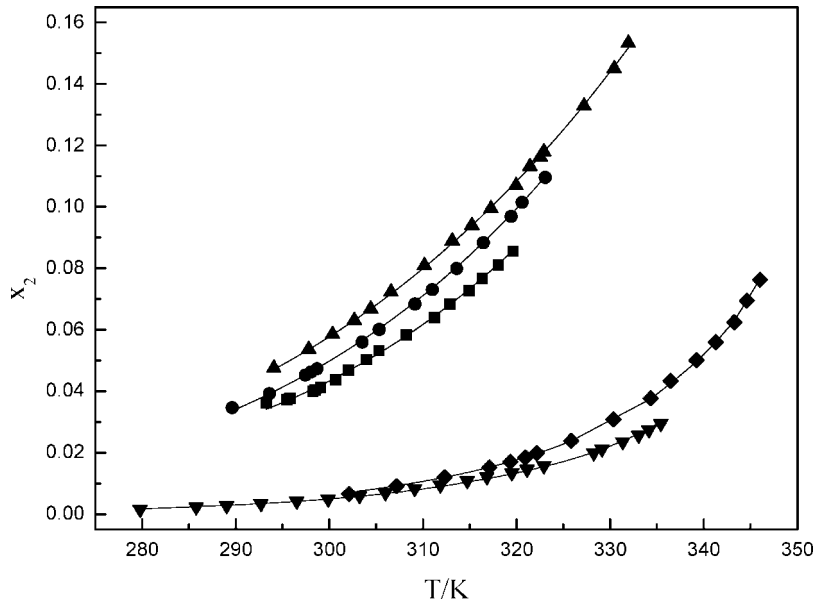

Figure 3. Solubilities of 1,4-naphthoquinone in acetone, toluene, xylene, ethanol, and *n*-butyl alcohol. ■, 1,4-naphthoquinone + acetone; ▲, 1,4-naphthoquinone + toluene; ▼, 1,4-naphthoquinone + ethanol; ●, 1,4-naphthoquinone + xylene; ◆, 1,4-naphthoquinone + *n*-butyl alcohol; —, Wilson model.

Table 7. Parameters of the Apelblat Equation and λ-h Model for Five Systems

	Apelblat			λ-h	
system	*A*	*B*	*C*	λ	h
1,4-naphthoquinone + acetone	−137.17	3351.7	21.540	0.3041	11444
1,4-naphthoquinone + xylene	−71.648	346.30	11.833	0.3746	9513.8
1,4-naphthoquinone + toluene	−10.246	−2191.1	2.5777	0.3613	9231.2
1,4-naphthoquinone + ethanol	−122.56	1304.7	19.796	0.1263	40410
1,4-naphthoquinone + *n*-butyl alcohol	−142.11	1475.6	23.132	0.3638	17812

To examine the accuracy of the Wilson model, the correlation result of the Wilson model[4,5] was compared with that of Apelblat equation[6–8] and λ-h model.[9,10] The objective function *F* of the measured systems that were correlated using different models is listed in Table 6, and the parameters of the Apelblat equation and λ-h models for five measured systems are listed in Table 7. The results of calculation showed that the Wilson model had the largest average deviation of 1.4218 %, and the Apelblat equation and λ-h models have less average deviations of 0.003047 % and 0.003175 %, respectively.

Conclusion

Using a dynamic method, the solubilities of 1,4-naphthoquinone in acetone, toluene, xylene, ethanol, and *n*-butyl alcohol have been determined experimentally from (293.27 to 319.63, 294.10 to 331.95, 289.63 to 323.07, 279.80 to 335.43, and 295.44 to 355.07) K, respectively. The experimental data were correlated with the Wilson model, Apelblat equation, and λ-h model. The calculated results show that the correlation of the Apelblat equation and λ-h model for five measured systems has less deviation than that of the Wilson model.

Literature Cited

(1) Ma, P. S.; Xia, Q. Determination and correlation for solubility of aromatic acids in solvents. *Chin. J. Chem. Eng.* **2001**, *1*, 39–44.
(2) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, 1963.
(3) Morimi, J. K.; Nakanishi, K. Use of the Wilson equation to correlate solid-liquid phase equilibria in binary and ternary system. *Fluid Phase Equilib.* **1977**, *1*, 153–160.
(4) Domanska, U.; Hofman, T. Solubility correlation of monocarboxylic acids in one-component solvents. *Ind. Eng. Chem. Process* **1986**, *4*, 996–1008.
(5) Domanska, U.; Hofman, T. Correlations for the solubility of normal akanoic acids and o-toluic acid in binary solvent mixture. *J. Solution Chem.* **1985**, *7*, 531–547.
(6) Zhang, C. L.; Wang, F. A.; Wang, Y. Solubilities of sulfadiazine, sulfamethazine, sulfadimethoxine, sulfamethoxydiazine, sulfamonomethoxine, sulfamethoxazole, and sulfachloropyrazine in water from (298.15 to 333.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1563–1566.
(7) Apelblat, A.; Manzurola, E. Solubilities of manganese, cadmium, mercury and ead acetates in water from *T*= 278.15 to 340.15 K. *J. Chem. Thermodyn.* **2001**, *33*, 147–153.
(8) Apelblat, A.; Manzurola, E. Solubilities of L-glutamic acid, 3-nitrobenzoic acid, p-toluic acid, calcium-L-lactate, calcium gluconate, magnesium-DL-aspartate, and magnesium-L-lactate in water. *J. Chem. Thermodyn.* **2002**, *34*, 1127–1136.
(9) Song, W. W.; Ma, P. S.; Xiang, Z. L.; Fan, L. H. Solubility of glutaric acid in cyclohexanone, cyclohexanol, their five mixtures and acetic acid. *Chin. J. Chem. Eng.* **2007**, *2*, 228–232.
(10) Buchowski, H.; Kslazcak, A.; Pletrzyk, S. Solvent activity along a saturation line and solubility of hydrogen-bonding solids. *J. Phys. Chem.* **1980**, *84*, 975–979.

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