Measurement and Correlation for Solubilities of Naphthalene in Acetone, Toluene, Xylene, Ethanol, Heptane, and 1-Butanol

Tie-Bing Cui,[†] Ting-Liang Luo,[†] Chen Zhang,[†,‡] Zhi-Bo Mao,[†] and Guo-Ji Liu*[,†]

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan 450001, P. R. of China, and Henan Chemical Industry Research Institute Co., Ltd., Henan Academy of Sciences, Zhengzhou, Henan 450001, P. R. of China

Using a dynamic method, the solubilities of naphthalene in acetone, toluene, xylene, ethanol, heptane, and 1-butanol have been determined experimentally from (297.17 to 322.70, 291.35 to 334.65, 299.42 to 337.97, 304.26 to 339.76, 290.25 to 333.75, and 313.77 to 342.8) 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 Wilson model for six measured systems has less deviation than that of the Apelblat equation and the λ-h model.

Introduction

1,4-Naphthoquinone is an important raw material of fine chemicals which is widely used as an intermediate 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 in Japan,[1] and the solubilities of naphthalene present important evidence for the separation of 1,4-naphthoquinone from unreacted naphthalene. However, only a limited amount of solubility data for naphthalene have been reported. In this study, solubilities of naphthalene in acetone, toluene, xylene, ethanol, heptane, and 1-butanol have been measured. The experimental data were correlated with the Wilson model, the Apelblat equation, and the λ-h models.

Experimental Section

Materials. Naphthalene, obtained from Shanghai Chemical Reagent Purchase & Supply Station, was further purified by recrystallization from organic solutions (dissolved it in acetone, filtrated the solution to get rid of the indissolvable impurity, then recrystallized and dried; then the sample was recrystallized from methanol several times for further purification). Its purity was determined by UV spectrometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 0.998 in mass fraction. Acetone (99.5 %), toluene (99.5 %), xylene (in which the mole fractions of *ortho*-xylene, *meta*-xylene, and *para*-xylene are 13.3 %, 66.4 %, and 20.3 %, respectively), ethanol (99.7 %), heptane (99.7 %), and 1-butanol (99.0 %) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China.

Apparatus and Procedure. The normal melting temperature T_m and enthalpy of fusion $\Delta_{fus}H$ of naphthalene were determined by differential scanning calorimetry (DSC, NETZSCH, type STA409PC-luxx) in the presence of nitrogen with the heating speed of 8 K per minute. The normal melting temperature of naphthalene is (356.1 ± 0.5) K, and its enthalpy of fusion is (139.1 ± 0.1) $J \cdot g^{-1}$, that is (17 829 ± 13) $J \cdot mol^{-1}$.

The solubility was measured by a dynamic method.[2] A predetermined sample, after weighing with a precision balance (type AB204-N, produced by Mettler-Toledo Group) with the uncertainty of 0.0001 g, was heated very slowly [it was less than 0.1 $K \cdot h^{-1}$, 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.

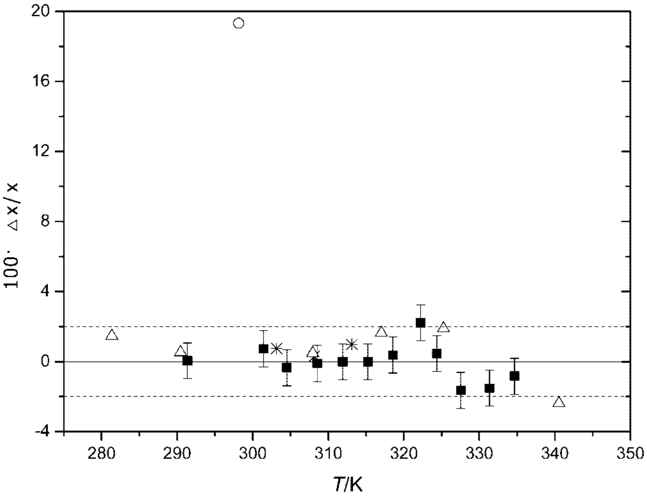

Figure 1. Fractional deviation $x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for naphthalene in toluene. ■, This work; *, ref 1; □, ref 2; ○, ref 3; ----, uncertainty of the correlation with the Wilson model.

The experimental apparatus includes a dissolving flask, a laser detecting system (made by 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 was installed at one side of the dissolving flask to provide the laser beam through the 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 the solid dissolves, the laser power reaches its greatest value and the temperature corresponding to the greatest value of the detector 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 uncertainty of the thermocouple was ± 0.1 K.

---

* Corresponding author. E-mail: guojiliu@zzu.edu.cn. Tel.: +86 37167781101.
[†] Zhengzhou University.
[‡] Henan Academy of Sciences.

10.1021/je800628a CCC: $40.75

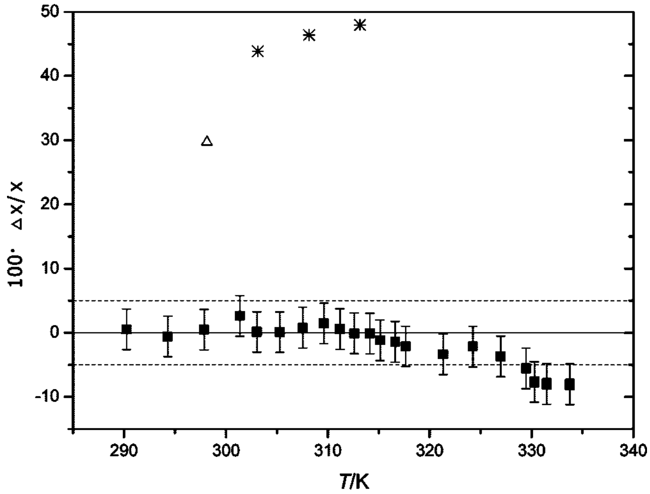

Figure 2. Fractional deviation $x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for naphthalene in heptane. ■, This work; *, ref 1; □, ref 5; ----, uncertainty of the correlation with the Wilson model.

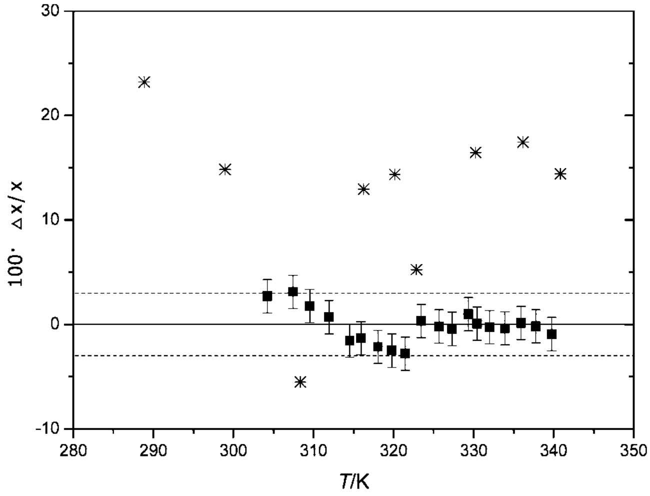

Figure 3. Fractional deviation $x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for naphthalene in ethanol. ■, This work; *, ref 4; ----, uncertainty of the correlation with the Wilson model.

The solubility of naphthlene in toluene has been reported in the literature,[3] and it is also measured with the equipment in this article. 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. The uncertainties of solubilities of naphthalene in acetone, toluene, xylene, ethanol, heptane, and 1-butanol are ± 0.7 %, ± 2 %, ± 1.0 %, ± 3 %, ± 5 %, and ± 2 %, respectively.

Results and Discussion

Experimental Results. With naphthalene as the solute and acetone, toluene, xylene, ethanol, heptane, and 1-butanol as solvents, the solubilities of six binary systems were determined in this study and are listed in Table 1, in which x_1 is the mole fraction of the solute in the solution. Each measurement was performed more than 5 times, and the data reported were the average value. The maximum deviations between the measurements were ± 0.18 K, ± 0.16 K, ± 0.11 K, ± 0.23 K, ± 0.10 K, ± 0.21 K, and ± 0.15 K for SLE temperature of naphthalene in acetone, toluene, xylene, ethanol, heptane, and 1-butanol, respectively.

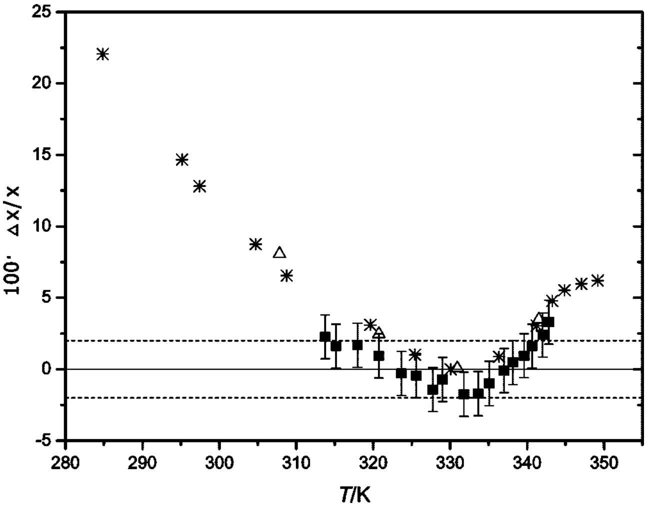

Figure 4. Fractional deviation $x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for naphthalene in 1-butanol. ■, This work; *, ref 2; □, ref 4; ----, uncertainty of the correlation with the Wilson model.

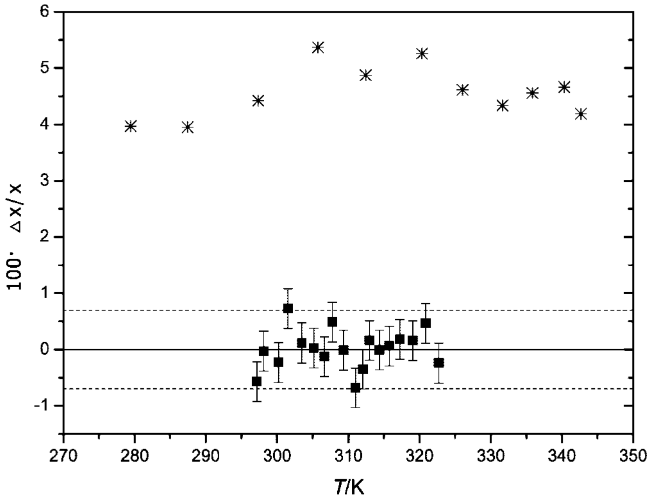

Figure 5. Fractional deviation $x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for naphthalene in acetone. ■, This work; *, ref 2; ----, uncertainty of the correlation with the Wilson model.

The results of these determinations were compared with the published results of earlier workers. The results are shown in Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5. H. Lee Ward's results on naphthalene solubilities in toluene, 1-butanol, and acetone have been found to be somewhat different from the present results, and further the differences are all positive. The procedure chosen for the solubility determinations leads to the conclusion that H. Lee Ward and this work used the same method for the solubility determination. However, H. Lee Ward used a sealed tube with definite quantities of solvent and solute for solubility determinations, while a flask with a condensing prolong was used in this work which kept the pressure of the flask at 1 atm throughout the procedure. Therefore, when the temperature rose, the pressure of the sealed tube used in H. Lee Ward's work might be a little bit higher than that of the flask used in this work. Subsequently, the solubilities of naphthalene in toluene, 1-butanol, and acetone reported in H. Lee Ward's work were slightly larger than that in this work according to Raoult's Law.

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

T/K	x	dev/%	T/K	x	dev/%[a]
		Naphthalene + Acetone			
297.17	0.2106	−0.570	311.03	0.3230	−0.684
298.11	0.2185	−0.0288	312.03	0.3346	−0.353
300.23	0.2329	−0.231	312.97	0.3468	0.163
301.55	0.2460	0.727	314.37	0.3608	−0.00541
303.47	0.2589	0.116	315.74	0.3762	0.0622
305.14	0.2724	0.0274	317.26	0.3942	0.180
306.63	0.2846	−0.126	319.06	0.4154	0.158
307.76	0.2972	0.487	320.87	0.4397	0.465
309.37	0.3101	−0.0122	322.70	0.4586	−0.240
		Naphthalene + Xylene			
299.42	0.2918	0.318	322.13	0.5083	0.132
302.70	0.3179	0.292	325.05	0.5446	0.463
306.14	0.3434	−0.695	328.66	0.5802	−1.03
309.84	0.3715	−2.00	330.46	0.6086	−0.170
311.96	0.3981	−0.369	333.53	0.6467	−0.558
315.52	0.4395	0.871	335.56	0.6850	0.889
319.25	0.4791	0.765	337.97	0.7196	0.906
		Naphthalene + Ethanol			
304.26	0.04640	2.7	325.68	0.1162	−0.200
307.44	0.05311	3.12	327.32	0.1285	−0.432
309.53	0.05656	1.75	329.34	0.1395	0.978
311.93	0.06141	0.713	330.43	0.1539	0.0767
314.52	0.06584	−1.57	332.00	0.1742	−0.269
315.93	0.07025	−1.33	333.90	0.2036	−0.374
318.07	0.07601	−2.15	335.90	0.2382	0.147
319.80	0.08161	−2.51	337.76	0.2935	−0.184
321.46	0.08761	−2.81	339.76	0.3815	−0.921
323.45	0.1035	0.335			
		Naphthalene + Toluene			
291.35	0.2395	−0.0508	318.55	0.4717	−0.371
301.45	0.3103	−0.732	322.23	0.5027	−2.21
304.54	0.3396	0.348	324.37	0.5371	−0.462
308.53	0.3739	0.101	327.55	0.5889	1.64
311.93	0.4055	0.00252	331.35	0.6374	1.51
315.25	0.4387	0.00168	334.65	0.6773	0.838
		Naphthalene + Heptane			
290.25	0.05948	−0.5402	315.15	0.1583	1.17
294.30	0.07054	0.595	316.63	0.16823	1.43
297.85	0.07982	−0.469	317.65	0.1770	2.12
301.37	0.08893	−2.60	321.33	0.2090	3.38
303.04	0.09778	−0.0987	324.25	0.2302	2.16
305.30	0.1066	−0.0831	326.98	0.2646	3.71
307.53	0.1150	−0.775	329.45	0.3044	5.57
309.63	0.1234	−1.45	330.26	0.3294	7.66
311.20	0.1326	−0.560	331.50	0.3505	7.96
312.60	0.1412	0.102	333.75	0.3890	8.04
314.13	0.1498	0.132			
		Naphthalene + 1-Butanol			
313.77	0.1127	2.26	333.65	0.3326	−1.73
315.17	0.1195	1.61	335.10	0.3749	−1.01
317.98	0.1388	1.67	337.00	0.4363	−0.0998
320.74	0.1590	0.920	338.15	0.4766	0.470
323.67	0.1828	−0.312	339.63	0.5265	0.933
325.60	0.2046	−0.439	340.65	0.5674	1.60
327.76	0.2279	−1.43	342.04	0.6197	2.24
329.03	0.2524	−0.721	342.80	0.6605	3.29
331.80	0.2937	−1.75			

[a] dev = $(x - x^{\text{calc}})/x$, where x^{calc} is the value correlated with the Wilson model.

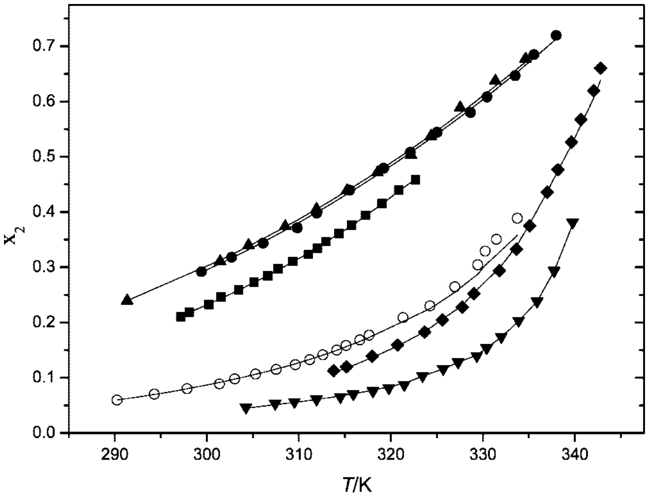

Figure 6. Solubilities of naphthalene in acetone, toluene, xylene, ethanol, 1-butanol, and heptane. ■, naphthalene + acetone; ▲, naphthalene + toluene; ▼, naphthalene + ethanol; ●, naphthalene + xylene; ◆, naphthalene + 1-butanol; ○, naphthalene + heptane; —, Wilson model.

Table 2. Data of Dual Correlation Parameters of the Wilson Model for Different Systems[a]

system	$(g_{12} - g_{11})$/J·mol^{-1}	$(g_{21} - g_{22})$/J·mol^{-1}
naphthalene + acetone	−361.20	−1090.2
naphthalene + xylene	−591.24	366.17
naphthalene + toluene	−318.37	−112.28
naphthalene + ethanol	−1328.4	−955.30
naphthalene + 1-butanol	−2153.8	147.70
naphthalene + heptane	100460	6810.0

[a] The mole volume of naphthalene is 110.3 mL·mol^{-1}. The mole volume was calculated with the data of mole quality and density of naphthalene, which were obtained from the producer of naphthalene.

Table 3. Parameters of the Apelblat Equation and λ-h Model for Five Systems

	Apelblat			λ-h	
system	A	B	C	λ	h
naphthalene + acetone	−55.641	19.068	9.4879	1.0642	4097.0
naphthalene + xylene	−11.758	−1499.4	2.7243	1.6190	2906.0
naphthalene + toluene	−69.291	1194.7	11.240	1.4722	2962.2
naphthalene + ethanol	−112.31	−1481.7	19.833	0.62042	15339.0
naphthalene + 1-butanol	−87.689	−2104.5	15.999	1.8991	6048.3
naphthalene + heptane	−127.81	1951.1	20.824	0.62352	9451.2

Table 4. Comparison of Absolute Average Relative Deviation for Different Models

	F/%		
system	Wilson	Apelblat	λ-h
naphthalene + acetone	0.273	0.352	1.31
naphthalene + xylene	0.557	0.677	2.94
naphthalene + toluene	0.487	0.992	3.45
naphthalene + ethanol	1.33	15.7	19.5
naphthalene + 1-butanol	1.32	5.42	12.3
naphthalene + heptane	2.98	4.66	8.98
total average deviation	1.16	4.63	8.09

Arthur A. Sunier used the same procedure with a sealed glass tube, so his results were a little bit larger than that in this work. Also, the different purity of the solvent leads to the same conclusion.

The present results of naphthalene's solubility in toluene and William E. Acree's results were in good agreement. However, the results of heptane were larger than this work, and further the deviation became larger with increasing temperature. Different volatility of heptane and toluene and the different determination method lead to this conclusion. William E. Acree measured the solubility with an analytical method, in which naphthalene concentration was determined with a gas chromatograph, which was not a very accurate instrument. For this work, when the solvent was heated to a relatively high temperature, a very small amount of solvent might be evaporated. It caused a negative difference of experimental data from the correlated value when the temperature got to 315 K. Also, the same factors made E.L. Herlc's results larger than that in this work.

Figure 6 shows the experimental results of the six binary systems. The solubility data of naphthalene in acetone, toluene, xylene, ethanol, heptane and, 1-butanol showed a flat uptrend when the temperature increased. When the temperature was higher than 328 K, the solubilities of naphthalene in 1-butanol and ethanol increased rapidly, but its solubility in the other four solvents maintained a flat uptrend. Moreover, the solubilities of naphthalene in acetone, toluene, and xylene are higher than that in heptane and 1-butanol which are higher than that in ethanol. The solubilities of naphthalene in toluene and xylene are more than 6 times as much as that in ethanol below 320 K, 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[4] correlated the solid−liquid equilibrium of melt salt using the Wilson model.

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.

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.

$$\ln x_2\gamma_2 = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right) \tag{1}$$

In a binary system, Wilson equations are as follows.

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

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

where x_2 is the mole fraction of the solute; $x_1$is the mole fraction of solvent; and γ_1 and γ_2 are activity coefficients of solute and solvent, respectively.

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

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

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 molar volume of the solvent and solute, respectively. Results are listed in Table 2.

Apelblat Equation and λ-h Model. The temperature dependence of naphthalene solubility in six solvents has been described by the modified Apelblat equation[5−7]

$$\ln x = A + \frac{BK}{T} + C\ln(T/\mathrm{K}) \tag{4}$$

where x is the mole fraction of naphthalene; T is the absolute temperature; and A, B, and C are constants.

The λ-h model[8,9] can also be used to correlate the solubilities of naphthalene in six solvents. The λ-h model can be expressed as

$$\ln\left[1 + \frac{\lambda(1-x)}{x}\right] = \lambda\mathrm{h}\left(\frac{K}{T} - \frac{K}{T_{\mathrm{m}}}\right) \tag{5}$$

where x is the mole fraction of naphthalene; T is the absolute temperature; and T_{m} is normal melting temperature of naphthalene.

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

$$F = \frac{1}{n}\sum_n\left|\frac{x_i^{\mathrm{exp}} - x_i^{\mathrm{cal}}}{x_i^{\mathrm{exp}}}\right| \tag{6}$$

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

To examine the accuracy of the Wilson model, the correlation result of the Wilson model[10,11] was compared with that of the Apelblat equation and the λ-h model. The objective function F of the measured systems that were correlated using different models is listed in Table 4, and the parameters of the Apelblat equation and λ-h models for six measured systems are listed in Table 3. The results of calculation showed that the Wilson model had the lest average deviation of 1.2 %, and the Apelblat equation and λ-h models have larger average deviations of 4.6 % and 8.1 %, respectively.

Conclusion

The solubilities of naphthalene in six solvents have been measured with a dynamic method. The experimental data were correlated with the Wilson model, Apelblat equation, and λ-h model. The calculated results show that the correlation of the Wilson model for six measured systems has less deviation than that of the Apelblat equation and the λ-h model.

Literature Cited

(1) Liu, G. J.; Chen, J. Z.; Luo, T. L.; Niu, B. L.; Yang, J. Review of Methods of Preparation of 1,4-naphthoquinone by Air-catalytic Oxidation. *J. Zhengzhou Univ.* **2001**, *2*, 4–7.

(2) Ma, P. S.; Xia, Q. Determination and correlation for solubility of aromatic acids in solvents. *Chin. J. Chem. Eng.* **2001**, *1*, 39–44.

(3) William, E. A.; Nicholas, M. P.; Cheryl, L. J. Solubility in binary solvent systems. 6. Preabbreciationdiction of naphthalene and biphenyl solubilities based on the Wilson model. *Int. J. Pharm.* **1986**, *31*, 225–230.

(4) 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.

(5) 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.

(6) 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.

(7) 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.

(8) 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.

(9) 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.

(10) Domanska, U.; Hofman, T. Solubility correlation of monocarboxylic acids in one-component solvents. *Ind. Eng. Chem. Process* **1986**, *4*, 996–1008.

(11) 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.

Received for review August 11, 2008. Accepted January 4, 2009.

JE800628A