Solubilities of 3-Pentadecylphenol in Ethanol, 1-Butanol, Toluene, Acetone, Tetrachloromethane, and Ethyl Acetate

Zhi-Bo Mao, Ting-Liang Luo, Tie-Bing Cui, Yu Wang, and Guo-Ji Liu*

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan 450001, People's Republic of China

Using a dynamic method, the solubilities of 3-pentadecylphenol in ethanol, 1-butanol, toluene, acetone, tetrachloromethane, and ethyl acetate have been determined experimentally from (291.47 to 312.87, 293.55 to 312.36, 295.25 to 317.38, 289.08 to 311.77, 288.46 to 312.23, and 290.83 to 313.35) K, respectively. The results are correlated with the λh equation, the Apelblat equation, and the Wilson equation. The calculated results show that the correlation of the Apelblat equation for six measured systems has less deviation than that of the λh equation and the Wilson model.

Introduction

3-Pentadecylphenol, $C_{21}H_{36}O$, is a valuable raw material derived from catalytic hydrogenation of cardanol, which is rich in resources, and used to produce various product required.[1−5] 3-Pentadecylphenol, which is similar to nonylphenol in structure, can be widely used in industry, agriculture, and other fields. The solventing-out crystallization method is used to separate 3-pentadecylphenol from the reaction product of the hydrogenation of cardanol, and the solubility data is essential to the engineering design. In this work, the solubilities of 3-pentadecylphenol in the solvents are determined over a range of temperatures, and the results are correlated with the simplified λh equation, Apelblat equation, and Wilson equation.

Experimental Section

Materials. 3-Pentadecylphenol, obtained from Tokyo Kasei Kogyo Co., Ltd., was recrystallized from alcohols for further purification. After filtration and drying, the purity analyzed by high-performance liquid chromatography (Daojin LC-A) was 99.1 % in mass fraction. Ethanol (99.7 %), 1-butanol (99.0 %), toluene (99.5 %), acetone (99.5 %), tetrachloromethane (99.5 %), and ethyl acetate (99.5 %) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China and used without farther purification.

Apparatus and Procedure. The normal melting temperature T_{fus} and enthalpy of fusion $\Delta_{\text{fus}}H$ of 3-pentadecylphenol were determined by differential scanning calorimetry (DSC, NETZSCH, type STA409PC-luxx) in the presence of nitrogen with the heating speed of 5 $\text{K}\cdot\text{min}^{-1}$. The normal melting temperature of 3-pentadecylphenol was (322.35 ± 0.5) K, and its enthalpy of fusion was (38092 ± 11) $\text{J}\cdot\text{mol}^{-1}$.

In this work, the solubilities of 3-pentadecylphenol in different solvents were determined by the dynamic method.[6] The experimental setup was a glass dissolution flask with a jacket, and the volume was about 50 cm^3. The water circulator ensured that the temperature of solution stably increased, and the use of a condenser to prevent the evaporation of the organic solvent is necessary. A magnetic stirring rotor was used for stirring. A thermometer was inserted into the solution to measure the temperature of the solution. The thermometer was checked at the Tianjin Metrology Institute (Tianjin, China), and its uncertainty was ± 0.01 K.

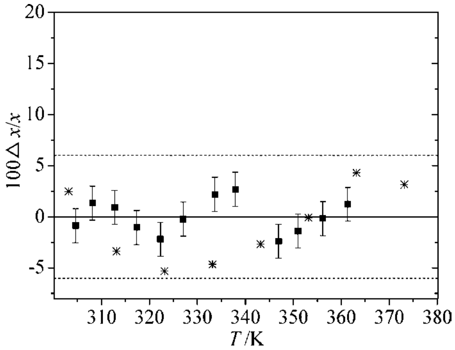

Figure 1. Fractional deviation $\Delta x = x(\text{expt}) - x(\text{calc})$ of the measured solubility and reported solubility for succinic acid in water. ■, this work; *, ref 7; dashed line, uncertainty of the correlation with Apelblat model.

The dissolving of 3-pentadecylphenol was observed by a laser detecting system (made by College of Physical Science and Engineering, Zhengzhou University). The predetermined 3-pentadecylphenol and the solvent amounts were weighed with a precision balance (type AB204-N, Mettler-Toledo Group) with the uncertainty of 0.0001 g, placed into the flask, and heated very slowly. The rate of temperature increase was controlled and was less than 0.1 $\text{K}\cdot\text{h}^{-1}$, especially near the solid−liquid equilibrium temperature. A laser was installed at one side of the flask, and a laser electrical signal transducer was installed at the opposite side. The laser electric power signal was detected, and it was found that it increased as the solid amount decreased. When the last piece of solid disappeared, the laser power reached its maximum value, and the corresponding temperature was assumed as the solid−liquid equilibrium temperature of the sample.

No solubility data of 3-pentadecylphenol has been published yet, and the reliability of the above method was tested measuring the solubility of succinic acid in water. Figure 1 shows that our experimental data of succinic acid in water are in good agreement with the literature data,[7] so the method used in this study is accurate and reliable.

---

* Corresponding author. E-mail: guojiliu@zzu.edu.cn. Tel.: +86 37167781101.

10.1021/je900346t CCC: $40.75

Table 1. Solubilities of 3-Pentadecylphenol, $\Delta_{sol}H$, and Correlation Results of the Apelbalt Model

T/K	x	$\Delta_{sol}H$/kJ·mol^{-1}	dev/%	T/K	x	$\Delta_{sol}H$/kJ·mol^{-1}	dev^{a}/%
3-Pentadecylphenol + Ethanol							
291.47	0.158	45.96	−0.845	302.96	0.304	37.52	−0.495
293.83	0.181	44.23	0.650	304.83	0.332	36.15	−0.347
295.56	0.199	42.95	1.71	306.96	0.360	34.58	1.21
297.55	0.228	41.49	−0.182	309.16	0.398	32.97	0.440
299.15	0.252	40.32	−1.48	311.13	0.435	31.52	−0.445
301.28	0.278	38.75	−0.045	312.87	0.463	30.24	−0.130
3-Pentadecylphenol + 1-Butanol							
293.55	0.239	18.71	2.78	304.95	0.382	42.06	2.38
295.36	0.263	22.41	−1.47	306.72	0.422	45.68	2.38
297.33	0.282	26.45	−1.95	308.18	0.476	48.67	−0.943
299.16	0.302	30.20	−1.74	309.86	0.527	52.11	−0.545
300.86	0.321	33.68	−0.477	311.04	0.576	54.53	−1.56
302.94	0.349	37.94	0.889	312.36	0.619	57.23	0.392
3-Pentadecylphenol + Toluene							
295.25	0.122	59.41	−2.21	307.55	0.302	52.37	−1.87
297.45	0.140	58.15	1.48	309.86	0.344	51.05	−0.0495
299.20	0.160	57.15	1.84	311.75	0.383	49.96	1.33
301.23	0.186	55.99	1.79	313.86	0.438	48.76	0.640
303.66	0.228	54.60	−0.875	315.75	0.490	47.67	0.474
305.47	0.262	53.56	−1.77	317.38	0.543	46.74	−0.668
3-Pentadecylphenol + Acetone							
289.08	0.253	27.23	0.307	301.63	0.412	28.18	−0.614
291.32	0.272	27.40	1.81	303.86	0.436	28.34	2.13
293.55	0.309	27.57	−2.36	305.65	0.478	28.48	−0.496
295.54	0.330	27.72	−1.19	307.87	0.512	28.65	0.718
297.54	0.351	27.87	0.0703	309.65	0.554	28.78	−0.751
299.33	0.373	28.00	0.766	311.77	0.596	28.94	−0.329
3-Pentadecylphenol + Tetrachloromethane							
288.46	0.0912	67.00	−4.24	302.20	0.278	53.90	−1.03
290.45	0.101	65.10	4.08	304.07	0.312	52.11	0.447
292.51	0.124	63.14	2.94	306.05	0.356	50.23	0.231
294.42	0.150	61.32	0.322	308.17	0.402	48.20	1.46
296.55	0.180	59.29	−0.406	310.13	0.461	46.33	−0.475
298.36	0.210	57.56	−1.65	312.23	0.556	44.33	−7.16
300.24	0.242	55.77	−1.46				
3-Pentadecylphenol + Ethyl Acetate							
290.83	0.236	31.37	1.10	303.90	0.413	30.09	−0.251
295.86	0.299	30.87	−0.848	306.25	0.447	29.86	0.890
297.30	0.323	30.73	−2.32	308.58	0.490	29.63	0.630
300.12	0.352	30.46	0.714	310.96	0.541	29.40	−0.442
302.14	0.380	30.26	1.13	313.35	0.590	29.16	−0.552

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

Results and Discussion

Experimental Results. The solubilities of 3-pentadecylphenol in ethanol, 1-butanol, toluene, acetone, tetrachloromethane, and ethyl acetate are shown in Table 1, in which T is the absolute temperature, x is the experimental mole fraction of 3-pentadecylphenol, its uncertainty was 0.001, and $\Delta_{fus}H$ is the molar enthalpies of dissolution which were calculated by eq 5.

λh Model. Buchowski et al.[8,9] studied the relations among activity, solubility, and temperature. They found that $\ln(1 - \alpha_2)$ is a linear function of the reciprocal of temperature and consequently deduced the solubility equation for the solid−liquid phase equilibrium of binary systems. It is named the λh equation because of the two parameters (λ and h) in the equation, and the equation is as follows:

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

where T_{fus} is the normal melting temperature of solute. The values of λ and h for different systems are presented in Table 2.

Table 2. Parameters in the λh Equation for Different Solvents

system	λ	h/K
3-pentadecylphenol + ethanol	0.37099	8711.4
3-pentadecylphenol + 1-butanol	0.57668	6056.7
3-pentadecylphenol + toluene	0.42406	11452
3-pentadecylphenol + acetone	0.39972	5398.2
3-pentadecylphenol + tetrachloromethane	1.3304	5513.4
3-pentadecylphenol + ethyl acetate	0.35332	6247.7

Apelblat Model. The Apelblat model, which assumes that the enthalpy of the solution is directly proportional to the temperature, gives the expression obtained from Clausius−Claperon equation:[10,11]

$$\ln x = A + \frac{B}{T} + C \ln T \tag{2}$$

where A, B, and C are the three parameters. The results of these parameters are listed in Table 3.

The relationship of solubility and temperature can be expressed as[12−14]

$$\frac{\partial(\ln x)}{\partial T} = \frac{\Delta_{sol}H}{RT^2} \tag{3}$$

where $\Delta_{sol}H$ is the molar enthalpy of dissolution and R is the molar gas constant.

Table 3. Parameters in the Apelblat Equation for Different Solvents

system	A	B/K	C
3-pentadecylphenol + ethanol	606.78	−31277	−88.341
3-pentadecylphenol + 1-butanol	−1639.7	70060	246.33
3-pentadecylphenol + toluene	482.73	−27483	−68.880
3-pentadecylphenol + acetone	−50.498	−653.62	9.0683
3-pentadecylphenol + tetrachloromethane	790.04	−41150	−114.72
3-pentadecylphenol + ethyl acetate	90.104	−7196.9	−11.774

Using eq 2 to the derivative of ln x to T, we obtain

$$\frac{\partial(\ln x)}{\partial T} = -\frac{B}{T^2} + \frac{C}{T} \tag{4}$$

Substituting eq 3 to eq 4, the equation for calculating the molar enthalpies of dissolution, $\Delta_{\text{sol}}H$, could be obtained accordingly, and the values calculated are represented in Table 1.

$$\Delta_{\text{sol}}H = -BR + CRT \tag{5}$$

Wilson Model. For the equilibrium system, there is an equation applied universally according to thermodynamic theory:[15]

$$\ln x\gamma = \frac{\Delta H_{\text{tp}}}{R}\left[\frac{1}{T_{\text{tp}}} - \frac{1}{T}\right] - \frac{\Delta C_{\text{p}}}{R}\left[\ln\frac{T_{\text{tp}}}{T} - \frac{T_{\text{tp}}}{T} + 1\right] - \frac{\Delta V}{RT}(P - P_{\text{tp}}) \tag{6}$$

The differences upon pressure and heat capacity terms were neglected for their small influence on the results. We replaced the triple point temperature by melting point temperature T_{fus} and simplified eq 6 as follows:

$$\ln x\gamma = \frac{\Delta_{\text{fus}}H}{R}\left[\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right] \tag{7}$$

where $\Delta_{\text{fus}}H$ is enthalpy of fusion of 3-pentadecylphenol.

The Wilson equation, which succeeds in calculating the gas−liquid and liquid−liquid phase equilibrium, is a local-composition activity coefficient equation that also has a good accuracy in the calculation of solid−liquid phase equilibrium.[16]

In a binary system, Wilson equations are as follows:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \tag{8}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \tag{9}$$

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 the activity coefficients of solute and solvent, respectively.

$$\Lambda_{12} = \frac{V_2^{\text{L}}}{V_1^{\text{L}}}\exp[-(g_{12}\text{-}g_{11})/RT] \tag{10}$$

$$\Lambda_{21} = \frac{V_1^{\text{L}}}{V_2^{\text{L}}}\exp[-(g_{21}\text{-}g_{22})/RT] \tag{11}$$

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

Table 4. Parameters of Wilson Equation for Different Solvents[a]

system	(g_{12}-g_{11}) J·mol^{-1}	(g_{21}-g_{22}) J·mol^{-1}	V_2^{L} cm^3·mol^{-1}
3-pentadecylphenol + ethanol	3461.0	−3750.7	58.39
3-pentadecylphenol + 1-butanol	2485.1	−3077.2	91.56
3-pentadecylphenol + toluene	1264.9	−2020.3	106.3
3-pentadecylphenol + acetone	6127.8	−2958.0	73.71
3-pentadecylphenol + tetrachloromethane	1021.9	−3241.1	96.44
3-pentadecylphenol + ethyl acetate	5514.9	−1806.6	99.00

[a] The mole volume of 3-pentadecylphenol is 310.8 cm^3·mol^{-1}. The mole volumes of the solute and solvents were calculated with the data of mole quality and density which were obtained from the producer.

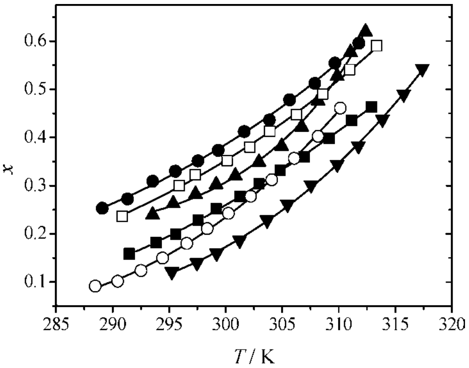

Figure 2. Comparison of experimental solubilities with calculated values by the Apelblat model for 3-pentadecylphenol in different solvents: ■, ethanol; ▲, 1-butanol; ▼, toluene; ●, acetone; ○, tetrachloromethane; □, ethyl acetate; solid line, Apelblat model.

Table 5. Comparison of Absolute Average Relative Deviation for Different Models

	σ/%		
system	λh	Apelblat	Wilson
3-pentadecylphenol + ethanol	3.59	0.660	2.75
3-pentadecylphenol + 1-butanol	3.35	1.35	3.06
3-pentadecylphenol + toluene	4.44	1.25	3.09
3-pentadecylphenol + acetone	1.43	0.960	1.19
3-pentadecylphenol + tetrachloromethane	2.43	1.56	3.31
3-pentadecylphenol + ethyl acetate	2.03	0.890	1.24
total average deviation	2.89	1.11	2.44

Comparison between Models. The average absolute deviations between calculated values and experimental data are presented in Table 5. The average absolute deviation is defined as:

$$\sigma = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_{ci} - x_i}{x_i}\right| \tag{12}$$

where x is the experimental solubility, x_{c} is the calculated value, and n is the number of experimental points.

From the results shown in Table 5, it can be observed that the average absolute deviations obtained by the λh model, Apelblat model, and Wilson model are less than 4.5 %, 1.6 %, and 3.4 %, respectively. Figure 2 shows the experimental results and the comparisons between the experimental data and the calculated values by the Apelblat model since it is the most accurate. When correlation of the solubilities of 3-pentadecylphenol in pure solvents is required, the Apelblat model is preferred for the best correlation results obtained. The Wilson model is well-known in industrial applications, and the λh model is simple and the only model specifically proposed for solid−liquid equilibrium, so they are also valuable.

Conclusion

The solubilities of 3-pentadecylphenol in ethanol, 1-butanol, toluene, acetone, tetrachloromethane, and ethyl acetate were determined by a dynamic method and correlated with the λh equation, Apelblat equation, and Wilson equation. The parameters of these models were obtained, and the average absolute deviations between calculated values and experimental values were evaluated. The precisions of the λh, Apelblat, and Wilson models are satisfactory, and the results of those three models are very important for industrial design.

Literature Cited

(1) Liu, Y. R. Preparation of Cardanol Formaldehyde Resin Emulsions. *Chem. Ind. For. Prod.* **2006**, *4*, 51–53.

(2) Menomm, C. Coating composition from cashew nutshell liquid. *Paintindia* **1957**, *6*, 23–27.

(3) Wang, H. Y.; Wang, D. N. Poly urethane/linseed oil composite coating modified by cashew nut shell liquid. *Chem. Ind. For. Prod.* **2005**, *3*, 45–48.

(4) Dasare, B. D. Preparation and properties of an anion-exchangers based on cashew nutshell liquid and tetraethylene pentamine. *Indian J. Technol.* **1965**, *3*, 212–214.

(5) Dasare, B. D.; Krishuaswamy, N. Chelating properties of anion exchangers prepared from melamine and commercial cashew nutshell liquid. *Br. Polym. J.* **1969**, *1*, 41–47.

(6) Cui, T. B.; Luo, T. L.; Zhang, C.; Mao, Z. B.; Liu, G. J. Measurement and correlation for solubilities of naphthalene in acetone, toluene, xylene, ethanol, heptane and 1-butanol. *J. Chem. Eng. Data* **2009**, *54*, 1065–1068.

(7) Liu, G. Q.; Ma, L. X.; Liu, J. *Handbook of chemical property date (organic volume)*; Chemical Industry Press: Beijing, 2002; pp 60−61.

(8) 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.

(9) Buchowski, H. Solubility of solids in liquids one-parameter solubility equation. *Fluid Phase Equilib.* **1986**, *25*, 273–278.

(10) Apelblat, A.; Manzurala, E. Solubilities of o-acetylsalicylic, 3,5-dinitrosalicylic, and p-toluicacid, and magnesium-DL-aspartate in water from T = (278 to 348) K. *J. Chem. Thermodyn.* **1999**, *31*, 85–91.

(11) Apelblat, A.; Manzurola, E. Solubilities of manganese, cadmium, mercury and lead acetates in water from T = 278.15 to 340.15 K. *J. Chem. Thermodyn.* **2001**, *33*, 147–153.

(12) Lerchner, J.; Kirchner, R.; Seidel, J.; Wahlisch, D.; Wolf, G.; Konig, W. A.; Lucklum, R. Determination of molar heats of absorption of enantiomers into thin chiral coatings by combined IC-calorimetric and microgravimetric (QMB) measurements. 2. Thermodynamics of enantioselectivity in modified cyclodextrins. *Thermochim. Acta* **2006**, *445*, 98–103.

(13) Bourgois, D.; Thomas, D.; Fanlo, J. L.; Vanderschuren, J. Solubilities at high dilution of toluene, ethylbenzene, 1,2,4-trimethylbenzene, and hexane in di-2-ethylhexyl, diisoheptyl, and diisononyl phthalates. *J. Chem. Eng. Data* **2006**, *51*, 1212–1215.

(14) 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.

(15) Stanley, M. W. *Phase equilibria in chemical engineering*. Butterworth: New York, 1985; pp 397−400.

(16) De Fina, K. M.; Hernandez, C. E. Solubility of trans-stilbene in binary alkane +2-propanol solvent mixtures at 298.2 K. *Phys. Chem. Liq.* **2000**, *38* (1), 89–94.

Received for review April 10, 2009. Accepted July 3, 2009.

JE900346T