Solubility of 2-(4-Ethylbenzoyl)benzoic Acid in Eleven Organic Solvents between 279.55 K and 343.15 K

Qun-Sheng Li, Ming-Gao Su, and Shui Wang*

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

The solubilities of 2-(4-ethylbenzoyl)benzoic acid in *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone, methanol, ethanol, 1-propanol, 2-propanol, tetrahydrofuran, benzene, 1,4-dioxane, acetone, and ethyl formate were measured using a synthetic method at temperatures in the range from (279.55 to 343.15) K under atmospheric pressure. The laser-monitoring observation technique was used to determine the dissolution of the solid phase in a solid + liquid mixture. The solubility of 2-(4-ethylbenzoyl)benzoic acid in different solvents increased as the temperature increased. Measured solubility values were well correlated as a function of temperature by the modified Apelblat equation.

Introduction

2-(4-Ethylbenzoyl)benzoic acid (EBA, CASRN 1151−14-0) is a pure white powdered crystal under standard conditions. It is a useful chemical for the preparation of 2-ethylanthraquinone, which is an important intermediate for the synthesis of hydrogen peroxide, pharmaceuticals, pesticides, and dyes.[1] In the industrial manufacture process of EBA, crystallization is the key operation unit to determine the quality of the final product. The selection and determination of solvent is the first task in the development and design of a crystallization process. One of the most important bases to determine the proper solvent is the solubility data of the material to be purified in different solvents.[2] Understanding and obtaining solubility data of EBA and other compounds will help the chemical industry with improvements in separation. However, from a review of the literature on EBA, it was found that no experimental solubility data in the organic solvents have been reported. The focus of this work is to determine the solubility of EBA in *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), methanol, ethanol, 1-propanol, 2-propanol, tetrahydrofuran (THF), benzene, 1,4-dioxane, acetone, and ethyl formate from (279.55 to 343.15) K under atmospheric pressure using a laser-monitoring observation technique.[3] The method employed in this work was classed as a synthetic method, which was much faster than the analytical method.[4]

Experimental Sections

Materials. A white crystalline powder of EBA ($C_{16}H_{14}O_3$, molecular weight 254.28) was supplied by Shanghai Jiachen Chemical Ltd. (China) and used without further purification. Its mass fraction purity, determined by HPLC, was higher than 99.0 %. All organic solvents were of analytical grade and purchased from Beijing Chemical Reagent Co. (China). The solvents were dehydrated with molecular sieves before use. The purities of solvents, determined by gas chromatography, were higher than 99.5 %.

Apparatus and Procedures. The experimental apparatus and procedures were stated in detail in the literature[5−8] and are described briefly here. The experiments were carried out in a 500 mL jacked glass vessel, which was magnetically agitated. The temperature in the vessel was controlled at the desired value by a continuous forced water circulation from a thermostat. A mercury-in-glass thermometer (uncertainty of ± 0.05 K) was used for the measurement of the temperature in the vessel. A condenser was connected vertically on the vessel to prevent the evaporation of the solvent. The masses of solid EBA and solvents were weighted using an analytical balance (Sartorius CP124S, Germany) with an uncertainty of ± 0.0001 g. The dissolution of the solute was examined by the laser beam penetrating the vessel.

In the experiments, the solubility of EBA was determined by the last crystal disappearance method using the laser-monitoring observation technique. The laser set consists of a laser generator, a photoelectric transformer, and a digital display. The method is based on sequentially adding known masses of a solid compound to a stirred solution kept at a predetermined temperature. The initial mass of solvent was known precisely. When an additional solid solute had completely dissolved, the next portion of solid was introduced. When the solute dissolved completely, the solution was clear, and the laser intensity penetrating through the vessel reached its maximum. If the solute could not dissolve completely, then the laser beam was scattered by the undissolved solute particles in the solution, and the penetrating laser intensity was below the maximum. All the experiments were conducted three times, and the mean values were used to calculate the mole fraction solubility of EBA in the solvent, x_1, based on the following equation:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1 and m_2 represent the mass of the solute and the solvent, respectively; M_1 and M_2 represent the molecular weight of the solute and the solvent, respectively. The uncertainty of the solubility values based on error analysis and repeated observations was estimated to be less than 1.0 %.

Results and Discussion

The solubility data of EBA in DMF, NMP, methanol, ethanol, 1-propanol, 2-propanol, THF, benzene, 1,4-dioxane, acetone,

* To whom correspondence should be addressed. E-mail: wangshui2000@sohu.com. Fax: +0086-10-64413151.

10.1021/je700426k CCC: $37.00
Published on Web 10/09/2007

Table 1. Mole Fraction Solubility x_1 of 2-(4-Ethylbenzoyl)benzoic Acid in Different Solvents

T/K	$10x_1$	δ^a	T/K	$10x_1$	δ	T/K	$10x_1$	δ
			N,*N*-dimethylformamide					
281.20	3.433	−0.2	286.49	3.674	−0.4	290.63	3.822	−1.4
296.42	4.200	1.8	305.65	4.513	0.5	314.34	4.704	−1.7
325.55	5.073	−0.4	335.75	5.318	0.3			
			N-methyl-2-pyrrolidone					
280.10	1.626	0.2	284.15	1.755	−0.2	293.44	2.095	−1.2
303.76	2.604	−0.5	313.15	3.147	−0.8	322.85	3.958	2.1
334.30	4.843	−1.4						
			methanol					
279.90	0.627	−1.4	285.60	0.827	1.6	290.81	1.014	1.4
295.45	1.184	0.2	305.56	1.644	1.2	314.40	2.016	−1.4
323.80	2.482	−0.7	328.69	2.727	−0.2	333.53	3.005	1.8
			ethanol					
282.29	0.733	−1.4	289.68	1.001	1.1	294.91	1.227	2.9
304.60	1.644	1.3	314.30	2.141	1.1	322.91	2.556	−1.8
328.65	2.895	−1.5	338.19	3.539	0.8	342.82	3.876	2.2
			1-propanol					
279.55	0.499	−0.8	288.67	0.777	0.3	299.23	1.208	1.3
308.86	1.677	0.7	318.93	2.230	−0.4	328.62	2.791	−2.0
338.45	3.443	−1.4	343.15	3.867	2.1			
			2-propanol					
279.79	0.023	0.4	284.74	0.037	−0.3	294.05	0.085	−1.2
303.99	0.174	−1.1	313.25	0.305	2.0	323.37	0.464	0.2
334.05	0.631	−1.1						
			tetrahydrofuran					
281.20	0.064	−2.3	286.49	0.085	2.6	296.42	0.125	0.9
305.65	0.178	−0.8	314.34	0.246	−1.3	325.55	0.377	0.4
330.34	0.442	−0.7	335.75	0.541	0.8			
			benzene					
283.05	0.023	−0.4	288.68	0.037	0.8	293.52	0.052	−2.3
302.78	0.109	1.2	313.15	0.228	1.8	322.65	0.408	−2.7
328.38	0.598	−0.5	332.70	0.793	1.3			
			1,4-dioxane					
288.88	0.042	−2.1	293.97	0.066	3.3	298.46	0.091	3.6
303.53	0.121	0.5	308.09	0.153	0.1	313.40	0.195	−0.6
319.15	0.240	−1.2	322.54	0.278	2.6	333.97	0.353	1.3
			acetone					
280.25	0.015	−1.3	284.85	0.022	2.3	290.87	0.032	0.6
299.83	0.054	2.0	310.39	0.087	−1.9	314.89	0.107	−1.5
319.60	0.132	1.4	324.16	0.156	1.6			
			ethyl formate					
280.60	0.014	−0.7	289.68	0.027	−1.1	294.91	0.038	0.5
299.65	0.050	2.6	304.60	0.060	−1.8	309.59	0.075	0.1
314.30	0.087	−1.8	318.67	0.100	−0.7	322.91	0.113	1.2

[a] $\delta = 100(x_1 - x_1^{\text{cal}})/x_1$

and ethyl formate at different temperatures are summarized in Table 1.

On the basis of the experimental results, the solubility of EBA also depends on the polarity of the solvent to some degree. From Table 1, it could be seen that the polar solvents such as DMF, NMP, methanol, ethanol, 1-propanol, and 2-propanol display good solvency for EBA except acetone. The acetone is also a polar solvent, but no intermolecular hydrogen-bonding exists in the solvent. In the other solvents, such as THF, benzene, 1,4-dioxane, and ethyl formate whose polarity is relatively lower, the solute is slightly soluble. The solid−liquid equilibrium behavior may be explained by the empirical rule that "like dissolves like". Further discussion of the dissolution of an organic solute in an organic solvent is complicated and beyond the scope of this article.

The experimental data reported in Table 1 show the solubilities of EBA in different solvents are temperature dependent. For the practical application, it is common to fit the experimental data with a theoretical semiempirical expression. Thus. the temperature dependence of the solubility of EBA in pure solvents is correlated by the modified Apelblat equation:[10−12]

Table 2. Parameters of Equation 2 for 2-(4-ethylbenzoyl)benzoic Acid in Different Solvents

solvent	A	B	C	10^3rmsd
N,*N*-dimethylformamide	93.075	−4919.9	−13.592	4.875
N-methyl-2-pyrrolidone	−88.572	2337.6	13.914	4.659
methanol	254.16	−13895	−36.787	2.468
ethanol	163.09	−9811.4	−23.203	4.277
1-propanol	218.23	−12694	−31.210	4.091
2-propanol	739.71	−38693	−107.83	0.404
tetrahydrofuran	−47.160	−1125.9	8.1819	0.264
benzene	25.073	−7030.7	−1.1173	0.599
1,4-dioxane	804.07	−41040	−117.80	0.356
acetone	333.98	−19287	−48.200	0.155
ethyl formate	604.33	−31061	−88.731	0.100

$$\ln x_1 = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) \tag{2}$$

where A, B, and C are parameters.

The experimental solubility values have been correlated with eq 2 by the least-squares method. The regressed values of the parameters A, B, and C for the modified Apelblat equation are listed in Table 2 together with the root-mean-square deviation (rmsd), namely, standard deviation, which is defined as the following:[7−9]

$$\text{rmsd} = \left[\frac{\sum_{i=1}^{N}(x_{1,i} - x_{1,i}^{\text{cal}})^2}{N-1}\right]^{1/2} \tag{3}$$

where N is the number of the experiment points; $x_{1,i}$ and $x_{1,i}^{\text{cal}}$ denote the experimental and calculated values of the solubility, respectively.

From the data listed in Table 1, the experimental results state that the solubility of EBA in each solvent is a function of the temperature and increases at the range of temperature investigated. According to the values of δ in Table 1 and rmsd in Table 2, it can be observed that the modified Apelblat equation is suitable to correlate the solubility data of EBA in each solvent.

Conclusions

In this work, new data were measured for the solubility of EBA in DMF, NMP, methanol, 1-propanol, 2-propanol, THF, benzene, 1,4-dioxane, acetone, and ethyl formate at the temperature between (279.55 and 343.15) K using the laser-monitoring observation technique. On the basis of the results of the experiment, the following conclusions can be drawn: (i) The solubility of EBA in different solvents increases as the temperature increases. (ii) The solubility of EBA also depends on the polarity of the solvent to some degree. The title compound is soluble in polar solvents (DMF, NMP, methanol, ethanol, 1-propanol, 2-propanol) except acetone and is slightly soluble in nonpolar solvents such as THF, benzene, 1,4-dioxane, and ethyl formate. (iii) The modified Apelblat equation is appropriate to describe the temperature dependence of EBA in pure solvents, and its parameters are obtained by regression. Therefore, the experimental solubility and correlated equation in this work can be used as essential data and models for the purification process or crystallization of EBA.

Literature Cited

(1) Xu, R. S.; Guo, X. W.; Wang, G. R.; Zhang, Z. X. A green synthesis of 2-ethylanthraquinone by dehydration of 2-(4′-ethylbenzoyl)benzoic acid over solid acid catalysts. *Chin. Chem. Lett.* **2005**, *16*, 1587−1589.

(2) Mullin, J. W. *Crystallization*, 3rd ed.; Butterworth Heinemann: Oxford, 2000.

(3) Wang, S.; Wang, J. K.; Yin, Q. X.; Wang, Y. L. Light extinction method for solubility measurement. *Chin. Opt. Lett.* **2005**, *3*, 149−151.

(4) Heffter, G. T.; Tomkins, R. P. T. *The Experimental Determination of Solubilities*; John Wiley: Chichester, England, 2003.

(5) Wang, S.; Li, Q. S.; Li, Y. L. Solubility of D-p-hydroxyphenylglycine in water, methanol, ethanol, carbon tetrachloride, toluene, and *N*,*N*-dimethylformamide between 278 K and 323 K. *J. Chem. Eng. Data* **2006**, *51*, 2201−2202.

(6) Wang, S.; Wang, J. K.; Yin, Q. X. Measurement and correlation of solubility of 7-aminocephalosporanic acid in aqueous acetone mixtures. *Ind. Eng. Chem. Res.* **2005**, *44*, 3783−3787.

(7) Li, Q. S.; Liu, Y. M.; Wang, S.; Wu, H. L. Solubility of D(-)-*p*-hydroxyphenylglycine dane salt in mixtures of methanol and ethanol. *J. Chem. Eng. Data* **2006**, *51*, 2182−2184.

(8) Wang, S.; Li, Q. S.; Li, Z.; Su, M. G. Solubility of xylitol in ethanol, acetone, *N*,*N*-dimethylformamide, 1-butanol, 1-pentanol, toluene, 2-propanol, and water. *J. Chem. Eng. Data* **2007**, *52*, 186−188.

(9) Liu, B. S.; Gong, J. B.; Wang, J. K.; Jia, C. Y. Solubility of potassium clavulanate in ethanol, 1-propanol, 1-butanol, 2-propanol, and 2-methyl-1-propanol between 273 K and 305 K. *J. Chem. Eng. Data* **2005**, *50*, 1684−1686.

(10) Apelblat, A.; Manzurola, E. Solubilities of *o*-acetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and *p*-toluic acid, and magnesium-DL-aspartate in water from T = (278 to 348) K. *J. Chem. Thermodyn.* **1999**, *31*, 85−91.

(11) Li, X. N.; Yin, Q. X.; Chen, W.; Wang, J. K. Solubility of hydroquinone in different solvents from 276.65 K to 345.10 K. *J. Chem. Eng. Data* **2006**, *51*, 127−129.

(12) Wang, L. H.; Song, Y. T.; Chen, Y.; Cheng, Y. Y. Solubility of artemisinin in ethanol + water from (278.2 to 343.2) K. *J. Chem. Eng. Data* **2007**, *52*, 757−758.

Received for review July 27, 2007. Accepted September 9, 2007. We gratefully acknowledge financial support from The Young Scholars Fund of Beijing University of Chemical Technology (QN0710).

JE700426K