Solubilities of Vitamin K_3 in Benzene, Toluene, Ethylbenzene, *o*-Xylene, *m*-Xylene, and *p*-Xylene between (299.44 and 344.24) K

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The solubilities of vitamin K_3 in benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene have been measured using a static equilibrium method from (299.44 to 344.24) K. The experimental data were correlated against temperature with the absolute average deviations less than 1.0 %.

Introduction

Vitamin K_3 (2-methyl-1,4-naphthoquinone, MNQ) is widely used as a blood coagulating agent and is a key intermediate in the preparation of the other vitamins of group K (such as vitamin K_1, K_2, and K_4).[1] It is manufactured through several chemical methods.[2–5] An alternative method is the electrochemical synthesis.[6–8] The advantage in safety is particularly evident because the reaction is carried out in mild conditions, giving high product purity and reduced waste. In the synthesis and purification process of MNQ, it is necessary to know the solubility data of MNQ in organic solvents (such as ethanol, acetone, acetic acid, hexane, benzene, toluene, xylene, etc.), but the solubility data which have been reported are only in some alcohols + water.[9,10] In this study, the solubilities of vitamin K_3 in benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene have been measured from (299.44 to 344.24) K at atmospheric pressure.

Experimental Section

Materials. Analytical reagent MNQ obtained from Peking Biotech. Co. Ltd. was further purified by recrystallizations, and its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 0.997 in mass fraction. Benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene which were obtained from Shanghai Chemical Reagent Co. were purified by distillation. The mass fractions were determined by gas chromatography (type GC2010 Shimadzu Co. Ltd.) using a DB-1 capillary column with a FID detector, and they were 0.995, 0.995, 0.997, 0.997, 0.994, and 0.997, respectively. All the solvents were stored over molecular sieves before use.

Apparatus and Procedure. The solubilities were measured by a static equilibrium method[10,11] at atmospheric pressure. The experiments were carried out in a magnetically stirred, jacketed glass vessel (60 cm^3). A constant temperature (± 0.01 K) was maintained by circulating water through the outer jacket from a thermostatically controlled water bath at the required temperature. A condenser was connected with the vessels to prevent the solvents from evaporating.

MNQ-saturated solutions were prepared with benzene, toluene, ethylbenzene, and xylenes, respectively. These solutions were allowed to reach equilibrium with excess MNQ in a jacketed glass vessel at the corresponding temperature. After 36 h equilibration, samples were analyzed by gas chromatography (type GC2010 Shimadzu Co. Ltd.) using a DB-1 capillary column with an FID detector, column temperature of 473.15 K, detector temperature of 553.15 K, vaporization temperature of 553.15 K, and high purity of nitrogen as the carrier gas. From each equilibration cell, after the first 36 h, samples were analyzed once each 6 h until the analyzing results were replicated three consecutive times to confirm that the equilibration had been reached. In the processes of solubility measurement, the high purity nitrogen flowing at 1.5 $mL \cdot min^{-1}$ was maintained to prevent air from entering the vessel. All the solubility experiments were conducted three times to check the reproducibility, and the deviation of yielded solubility data is less than 1.0 %. The uncertainty of temperature measurements was ± 0.01 K. The reproducibility of the measurements was 0.1 K, which corresponds to a relative deviation in composition smaller than 1.0 %.

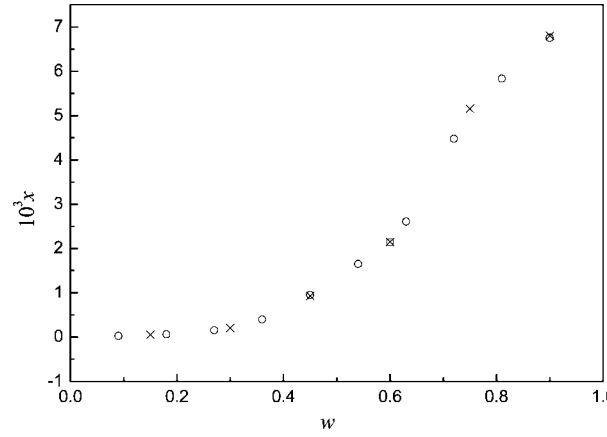

Figure 1. Mole fraction of vitamin K_3 in ethanol + water at 306.15 K: ×, this work; ○, literature data from ref 9; ■, literature data from ref 10. *w* is the mass fraction of ethanol in the mixed solvents, and *x* is the experimental solubility in mole fraction.

Results and Discussion

To verify the reliability of the measurement, the solubility of MNQ in various mass fractions of ethanol + water was measured at (306.15 ± 0.1 K), using the same apparatus and procedure, and the results are shown in Figure 1. It is clear from Figure 1 that the experimental results show good agreement with the literature data, and the deviations of the measured

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10.1021/je7003885 CCC: $40.75
Published on Web 11/14/2007

Table 1. Mole Fraction of Vitamin K_3 in Benzene Systems

T/K	x	100·RD	T/K	x	100·RD
		Benzene			
299.44	0.1088	−1.0	321.86	0.2243	0.40
304.83	0.1302	−0.12	326.75	0.2616	0.32
309.71	0.1523	0.12	330.75	0.2966	0.23
313.92	0.1742	0.24	334.65	0.3343	−0.14
317.75	0.1970	0.43	338.96	0.3791	−1.2
		Toluene			
303.44	0.1194	−1.1	325.99	0.2463	1.2
308.84	0.1428	0.0046	330.04	0.2768	0.26
313.63	0.1655	−0.14	333.86	0.3114	0.16
317.65	0.1893	0.79	337.8	0.3507	−0.21
321.85	0.2157	0.78	342.59	0.4036	−1.1
		Ethylbenzene			
302.85	0.09763	0.12	327.93	0.2283	−0.68
309.44	0.1218	−0.29	331.75	0.2602	−0.66
314.77	0.1464	−0.12	335.44	0.2967	−0.15
319.53	0.1726	0.074	339.42	0.3423	0.54
323.75	0.1994	0.079	343.86	0.3957	−0.14
		o-Xylene			
302.95	0.1404	−0.27	326.77	0.2744	−0.60
309.24	0.1687	0.31	330.54	0.3050	−0.69
314.25	0.1935	−0.14	334.23	0.3396	−0.37
318.34	0.2186	0.49	338.32	0.3829	0.065
322.45	0.2453	0.40	342.43	0.4321	0.53
		m-Xylene			
301.65	0.1270	0.0080	325.94	0.2581	−0.27
307.74	0.1515	−0.20	329.73	0.2881	−0.38
312.76	0.1761	0.13	333.64	0.3230	−0.41
317.36	0.2021	0.42	337.61	0.3645	0.043
321.64	0.2295	0.59	341.55	0.4109	0.48
		p-Xylene			
302.5	0.1289	0.031	327.68	0.2687	−0.54
309.53	0.1579	−0.35	332.02	0.3039	−0.99
314.64	0.1841	−0.016	335.89	0.3445	0.17
318.96	0.2103	0.59	340.1	0.3899	0.17
323.35	0.2386	0.31	344.24	0.4403	0.16

Table 2. Parameters of Equation 1 and the Absolute Average Deviation (AAD) for the Vitamin K_3 + Benzene Systems

solvent	A	B	100·AAD
benzene	−11.6793	0.0316	0.42
toluene	−11.5513	0.0311	0.57
ethylbenzene	−12.6823	0.0342	0.29
o-xylene	−10.5249	0.0283	0.39
m-xylene	−10.9050	0.0293	0.29
p-xylene	−10.9425	0.0294	0.33

solubility from the literature values[9,10] are less than 2.0 %. In this work, the uncertainty for solubility measurement is estimated based on the principle of the error of propagation and is found to be within 1.0 %.

The measured mole fraction solubilities (x) of MNQ in benzene systems at different temperatures T are presented in Table 1, and experimental data were correlated as a function of temperature as follows[12]

$$\ln x = A + B(T/\mathrm{K}) \tag{1}$$

where x is the mole fraction solubility of MNQ; T is the absolute temperature; and A and B are the parameters in eq 1. The values of these parameters together with the absolute average deviations (AAD) are listed in Table 2. The AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \tag{2}$$

where N is the number of experimental points and x_c is the solubility calculated by eq 1. The relative deviations between the experimental value and calculated value are also listed in Table 1. Relative deviations are calculated according to

$$\mathrm{RD} = \left(\frac{x - x_c}{x}\right) \tag{3}$$

From Tables 1 and 2, it can be found that the calculated solubilities show good agreement with the experimental data. The overall absolute average deviation is 0.33 %, and the relative deviations among all these values do not exceed 2.0 %. The experimental solubility and correlation equation in this work can be used in the synthesis and purification process of MNQ.

It can be observed from Table 1 that the solubilities of MNQ in benzene, toluene, and ethylbenzene follow the order benzene > toluene > ethylbenzene, which agrees with the dipole moment order of the investigated aromatic hydrocarbons, benzene ($\mu = 0$) < toluene ($\mu = 0.375$) < ethylbenzene ($\mu = 0.59$),[13] and the solubilities of MNQ in xylene systems follow the order *o*-xylene > *m*-xylene > *p*-xylene, which is inconsistent with the order of dipole moments. However, according to Scatchard–Hildebrand's theory,[14] the solubility of the solute in the solvent is the largest when the solubility parameters of the solute and the solvent are the same, which means further that the smaller the difference of the solubility parameter value between the solute and the solvent, the larger the solubility of the solute in the solvent is. The values of the solubility parameter of MNQ, *o*-xylene, *m*-xylene, and *p*-xylene are 25.1 (calculated by the Fedors group contribution method), 18.4, 18.0, and 17.9,[15] respectively. The results of the experiment showed good agreement with Scatchard–Hildebrand's theory. The reason for this phenomenon needs to be studied further.

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Received for review July 10, 2007. Accepted October 16, 2007.

JE7003885