Solubilities of 2-Methyl-1,4-naphthoquinone in Water + (Methanol, Ethanol, 1-Propanol, 2-Propanol, 1,2-Propanediol, and Glycerin, Respectively) from (293.15 to 337.92) K

Cheng-Ying Song,* Hong-Zhi Shen, Jian-Hong Zhao, Liu-Cheng Wang, and Fu-An Wang

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

The solubilities of 2-methyl-1,4-naphthoquinone in water + (methanol, ethanol, 1-propanol, 2-propanol, 1,2-propanediol, and glycerin, respectively) have been determined experimentally from (293.15 to 337.92) K by balanced method. The experimental data were correlated with the modified Apelblat equation.

Introduction

2-Methyl-1,4-naphthoquinone (menadione, vitamin K_3), which displays good antihemorrhagic activity, is an important compound in medical and dietary applications and a synthetic intermediate of vitamin K.[1,2] In the synthesis and purification process of menadione, it is necessary to know the solubility data of menadione in mixed solvents of water + alcohols (methanol, ethanol, 1-propanol, etc.). Dubbs and Gupta[1] have reported the solubility data in ethanol + water at 306.15 K. In this study, the solubilities of menadione in water + (methanol, ethanol, 1-propanol, 2-propanol, 1,2-propanediol, and glycerin, respectively) have been measured experimentally from (293.15 to 337.92) K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[3−5]

Experimental Section

Materials. Analytical grade menadione obtained from Peking Biotech. Co. Ltd. was further purified by recrystallizations from a solution of ethanol, and its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 0.997 in mass fraction. Methanol, ethanol, 1-propanol, 2-propanol, 1,2-propanediol, and glycerin of AR grade were obtained from Shanghai Chemical Reagent Co. and had purities of 0.995, 0.997, 0.995, 0.997, 0.990, and 0.990 in mass fraction, respectively. Water used in experiments was double-distilled.

Apparatus and Procedure. The solubilities were measured by a balanced method[1,6] at atmospheric pressure. The experiments were carried out in a magnetically stirred, jacketed glass vessel (60 cm^3). A constant temperature ($\pm$0.02 K) was maintained by circulating water through the outer jacket from a thermoelectric controller at the required temperature.

Solvents for the solubility measurement were prepared by mass using an electronic balance (type AW120, Shimadzu Co.) with an uncertainty of $\pm$0.0001 g. Menadione-saturated solutions were prepared with a mixed solvent of water + alcohols. These solutions were allowed to reach equilibrium with excess menadione at corresponding temperature. After the 24 h equilibration, samples were analyzed by UV spectrophotometry. From each equilibration cell, after the first 24 h, samples were taken at 4 h intervals to confirm that the equilibrium had been reached. Each experiment was repeated three times, and the deviation of yielded solubility data is less than 2.0 %.

* Corresponding author (e-mail songcy@zzu.edu.cn; fax +0086-371-67781027).

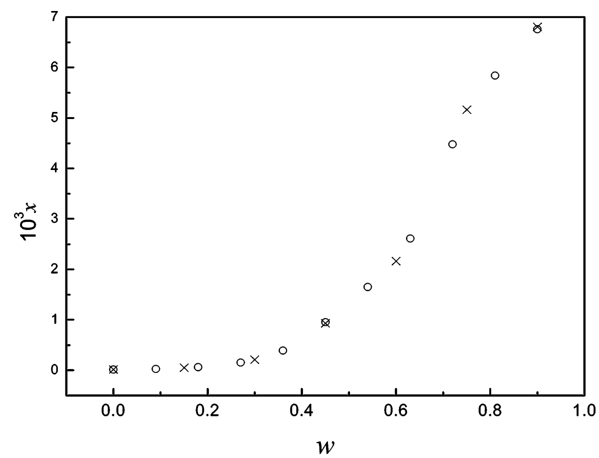

Figure 1. Solubility of menadione in ethanol + water at 306.15 K: ×, this work; ○, Dubbs and Gupta.[1] w is the mass fraction of ethanol in the mixed solvents, and x is the experimental solubility in mole fraction.

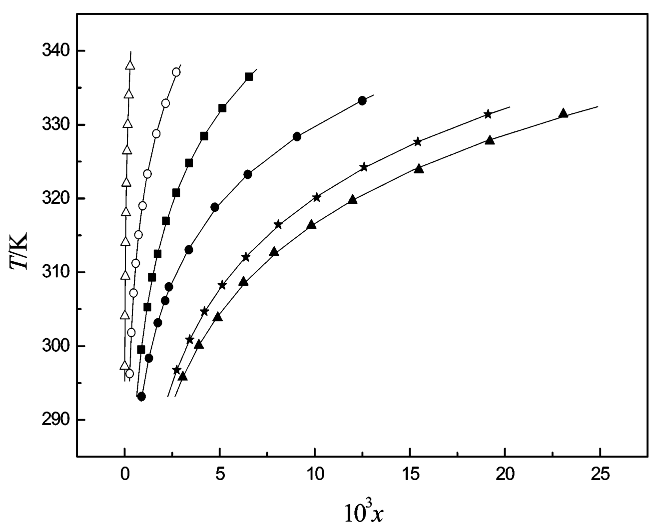

Figure 2. Solubilities of menadione in (w = 0.400) water + (w = 0.600) alcohols: △, water + glycerin; ○, water + 1,2-propanediol; ■, water + methanol; ●, water + ethanol; □, water + 2-propanol; ▲, water + 1-propanol; −, calculated from eq 1.

10.1021/je7002989 CCC: $37.00
Published on Web 07/27/2007

Table 1. Solubilities of Menadione in Water + (Methanol, Ethanol, 1-Propanol, 2-Propanol, 1,2-Propanediol, and Glycerin, Respectively)

T / K	10^3x	rel dev / %	T / K	10^3x	rel dev / %
Water + (w = 0.600) Methanol					
299.51	0.8721	−0.78	320.76	2.722	0.070
305.28	1.207	1.8	324.81	3.395	−0.17
309.30	1.453	−0.80	328.45	4.190	0.61
312.44	1.740	0.46	332.24	5.146	−0.089
316.94	2.184	−1.0	336.50	6.550	0.045
Water + (w = 0.600) Ethanol					
293.15	0.9017	−1.1	313.15	3.376	1.0
298.34	1.294	1.4	318.80	4.747	−1.7
303.15	1.747	0.33	323.25	6.477	0.14
306.15	2.143	1.2	328.37	9.068	−0.22
308.01	2.344	−1.8	333.24	12.49	0.29
Water + (w = 0.600) 1-Propanol					
295.76	3.064	−0.13	316.34	9.825	−0.24
300.07	3.914	0.16	319.73	11.99	0.22
303.83	4.900	1.4	323.89	15.48	1.8
308.64	6.265	−1.2	327.75	19.21	1.2
312.67	7.870	−1.4	331.44	23.08	−1.7
Water + (w = 0.600) 2-Propanol					
296.73	2.743	−0.010	316.44	8.078	−0.69
300.85	3.435	0.22	320.13	10.11	0.86
304.66	4.206	−0.34	324.24	12.60	−0.54
308.24	5.136	−0.12	327.65	15.43	0.15
312.03	6.381	0.49	331.40	19.12	−0.015
Water + (w = 0.600) 1,2-Propanediol					
296.24	0.2735	0.65	319.01	0.9493	1.8
301.83	0.3649	0.97	323.31	1.206	0.64
307.16	0.4709	−1.8	328.75	1.675	0.96
311.19	0.5869	−1.8	332.89	2.160	1.1
315.08	0.7397	−0.56	337.11	2.720	−1.9
Water + (w = 0.600) Glycerin					
297.24	0.01398	−0.030	322.05	0.1006	0.22
304.09	0.02515	−0.18	326.44	0.1367	0.31
309.45	0.03893	−0.084	330.03	0.1728	−0.40
314.04	0.05594	0.46	334.02	0.2210	−1.7
318.05	0.07524	0.083	337.92	0.2915	1.3

Results and Discussion

To verify the reliability of the measurement, the solubility of menadione in various mass fractions of ethanol + water were measured at (306.15 ± 0.1) K, and the results are shown in Figure 1 together with the measurements of Dubbs and Gupta.[1] It is clear from Figure 1 that the experimental results show good agreement with the literature data.

The measured solubilities of menadione in water + (methanol, ethanol, 1-propanol, 2-propanol, 1,2-propanediol, and glycerin, respectively) at different temperatures are presented in Table 1. For each mixed solvent system, the mass fraction of alcohol in the mixed solvents is 0.600. The temperature dependence of menadione solubility at fixed solvent composition is described by the modified Apelblat equation[3−5]

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

where x is the mole fraction solubility of menadione. T is the absolute temperature, and A, B, and C are the parameters in eq 1. The values of these parameters together with the root-mean-square deviations (rmsd values) are listed in Table 2. The rmsd is defined as

$$\mathrm{rmsd} = \left[\sum_{i=1}^{N} \frac{(x_{ci} - x_i)^2}{N}\right]^{1/2} \qquad (2)$$

where N is the number of experimental points and x_c is the solubility calculated by eq 1. The relative deviations between

Table 2. Parameters of Equation 1 and the Absolute Average Deviation (AAD) for the Menadione + Water + (Methanol, Ethanol, 1-Propanol, 2-Propanol, 1,2-Propanediol, and Glycerin, Respectively) Systems

solvent	A	B	C	10^4 rmsd	10^2 AAD
water + (w = 0.600) methanol	−323.745	10245.6	49.5428	0.59	0.58
water + (w = 0.600) ethanol	−281.305	7337.04	43.8815	0.37	0.92
water + (w = 0.600) 1-propanol	−278.05	7910.85	43.1523	1.8	0.95
water + (w = 0.600) 2-propanol	−302.612	9133.83	46.7135	0.41	0.34
water + (w = 0.600) 1,2-propanediol	−438.198	15314.3	66.4699	0.20	1.2
water + (w = 0.600) glycerin	141.827	−13456.5	−18.9186	0.018	0.48

the experimental value and calculated value are also listed in Table 1. Relative deviations are calculated according to

$$\text{relative deviations } (\%) = \left(\frac{x - x_c}{x}\right) \times 100 \qquad (3)$$

The absolute average deviations (AAD) are also listed in Table 2. The AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}^{N} \left|\frac{x_i - x_{ci}}{x_i}\right| \qquad (4)$$

From Tables 1 and 2, it can be found that the calculated solubilities show good agreement with the experimental data, the overall rmsd of 60 data points for the water + alcohols system being $0.78 \cdot 10^{-4}$. The relative deviations among all of these values do not exceed 2.0 %, which indicates that the modified Apelblat equation is fit to correlate the solubility data of menadione in six mixed solvent systems.

The graphical presentation of solubilities of menadione in water + alcohols is shown in Figure 2. It can be observed from Figure 2 that all of the solubilities follow the order water + glycerin < water + 1,2-propanediol < water + methanol < water + ethanol < water + 2-propanol < water + 1-propanol, which agrees with the dipole moment order of the investigated alcohols: glycerin (D = 2.68) > 1,2-propanediol (D = 2.27) > methanol (D = 1.70) > ethanol (D = 1.69) > 2-propanol (D = 1.58) > 1-propanol (D = 1.55).[7]

Literature Cited

(1) Dubbs, M. D.; Gupta, R. B. Solubility of vitamin E (α-tocopherol) and vitamin K_3 (menadione) in ethanol−water mixture. *J. Chem. Eng. Data* **1998**, *43*, 590−591.

(2) Shigekazu, Y. Chromium(VI) oxide-catalyzed oxidation of arenes with periodic acid. *Tetrahedron Lett.* **2001**, *42*, 3355−3357.

(3) Wang, L. C.; Wang, F. A. Solubility of niacin in 3-picoline + water from (287.65 to 359.15) K. *J. Chem. Eng. Data* **2004**, *49*, 155−156.

(4) Gao, J.; Wang, Z. W.; Xu, D. M.; Zhang, R. K. Solubilities of triphenylphosphine in ethanol, 2-propanol, acetone, benzene, and toluene. *J. Chem. Eng. Data* **2007**, *52*, 189−191.

(5) Zhao, J. H.; Wang, L. C.; Wang, F. A. Solubilities of *p*-aminophenol in sulfuric acid + water + (methanol, ethanol, 1-propanol, 2-propanol, 1,2-ppropanediol, and glycerin, respectively) from (292.35 to 348.10) K. *J. Chem. Eng. Data* **2006**, *51*, 376−381.

(6) Martinez, F.; Avila, C. M.; Gomez, A. Thermodynamic study of the solubility of some sulfonamides in cyclohexane. *J. Braz. Chem. Soc.* **2003**, *14*, 803−808.

(7) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill Book: New York, 1999; pp 5.115−5.125.

Received for review May 29, 2007. Accepted June 27, 2007.

JE7002989