Solubility of Hexamethylenetetramine in a Pure Water, Methanol, Acetic Acid, and Ethanol + Water Mixture from (299.38 to 340.35) K

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The solubility of hexamethylenetetramine in pure water, methanol, acetic acid, and ethanol + water was measured by a synthetic method with temperature ranging from (299.38 to 340.35) K at atmospheric pressure. The laser monitoring observation technique was used to determine the disappearance of the solid phase in a solid + liquid mixture. The results were correlated by a semiempirical Apelblat equation.

Introduction

Hexamethylenetetramine (HMTA) (1,3,5,7-tetraazatricyclo-[3.3.1.1^{3,7}]decane, molecular weight 140.19, CAS Registry No.100-97-0) is widely used in the chemical industry, medicine, analytical chemistry, and many other fields.[1−3] The solubility of HMTA in pure solvent and solvent mixtures plays a crucial role in the development and operation of the crystallization process properly. As an important raw material, it is necessary to know the solubility of HMTA in different solvents.

Because of its importance, many works have been devoted to the experimental determination of the solubility of HMTA in different solvents. For example, the solubility of HMTA in pure water has been determined at temperatures from (293.15 to 329.15) K by Blanco et al.[4] and Aladko et al.[5] The solubility of HMTA in pure methanol was determined at room temperature,[6,7] and the solubility of HMTA in pure ethanol was also measured by Bourne.[8] However, the solubility of HMTA in these solvents was determined only at one temperature[6,7] or at a narrow temperature range.[8] No experimental solubility data of HMTA in pure acetic acid and ethanol + water are reported.

To verify the uncertainty of the measurement, the solubility of HMTA in pure water was determined from (303.21 to 340.35) K. In this work, the solubility of HMTA in pure water, acetic acid, methanol, and ethanol + water at a wide temperature range from (299.38 to 340.35) K was determined by a synthetic method, which was much faster and readily available than the analytical method.[9−11] The experimental data were correlated with the Apelblat equation.[12]

Experimental Section

Materials. Hexamethylenetetramine was supplied by Zhejiang Sanying Co. Its mass fraction purity is higher than 0.99. It was dried in a vacuum at 40 °C for 24 h and stored in a desiccatior. The solvents used for experiment were of analytical reagent grade. Distilled deionized water of HPLC grade was used.

Apparatus and Procedure. The solubility of HMTA was measured by a synthetic method with an apparatus similar to that described in the literature.[9−11] The system consisted of a laser generator, a photoelectric transformer, and a light-intensity display. The equilibrium cell is a cylindrical double-jacketed glass vessel (80 mL). A constant desired temperature was maintained by circulating water through the outer jacket from a thermostat (fluctuates with 0.05 K). A condenser was fitted to reduce the solvent evaporation. A mercury-in-glass ther-

Table 1. Mole Fraction Solubility x of HMTA in Water

exptl data				lit. data[5]			
T/K	x	x(calc)	100ADD	T/K	x	x(calc)	100ADD
303.21	0.0980	0.0987	0.75	293.15	0.0951	0.0938	1.39
307.40	0.0959	0.0963	0.39	296.65	0.0911	0.0927	1.80
312.18	0.0948	0.0940	0.80	299.75	0.0913	0.0919	0.68
317.05	0.0931	0.0923	0.82	301.85	0.0902	0.0914	1.35
321.86	0.0914	0.0912	0.27	307.05	0.0915	0.0903	1.26
326.15	0.0894	0.0905	1.21	315.35	0.0896	0.0894	0.28
330.45	0.0891	0.0901	1.17	321.85	0.0887	0.0885	0.25
335.42	0.0895	0.0901	0.72	323.15	0.0875	0.0884	1.01
340.35	0.0914	0.0905	0.94	329.15	0.0879	0.0881	0.23

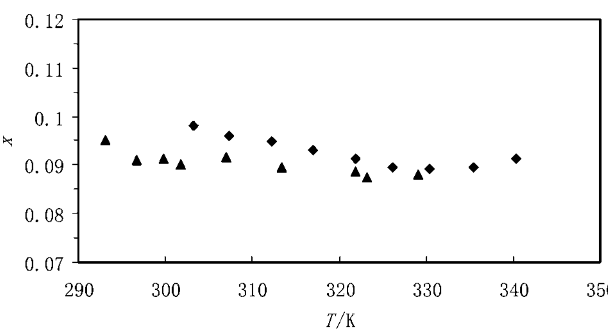

Figure 1. Solubility of HMTA in pure water: ♦, solubility of HMTA in water of this work; ▲, solubility of HMTA in water of the literature.

Table 2. Mole Fraction Solubility x of HMTA in Different Solvents

methanol				acetic acid			
T/K	x	x(calc)	100ADD	T/K	x	x(calc)	100ADD
299.91	0.0234	0.0235	0.48	304.52	0.2448	0.2450	0.06
304.45	0.0251	0.0251	0.05	310.83	0.2453	0.2455	0.10
307.85	0.0264	0.0263	0.37	317.35	0.2463	0.2469	0.24
311.90	0.0280	0.0278	0.78	321.91	0.2492	0.2482	0.39
315.95	0.0293	0.0293	0.00	327.65	0.2501	0.2503	0.12
319.63	0.0304	0.0307	1.02	332.65	0.2513	0.2526	0.55
323.65	0.0320	0.0322	0.90	337.15	0.2556	0.2550	0.22
326.25	0.0335	0.0332	0.52				
330.85	0.0353	0.0350	0.30				

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Table 3. Mole Fraction Solubility x of HMTA in Ethanol (1) + Water (2) Mixed Solvents[a]

T/K	x	x(calc)	100ADD	T/K	x	x(calc)	100ADD
	$w_1 = 0.20174$				$w_1 = 0.39639$		
299.38	0.0957	0.0959	0.19	300.26	0.0904	0.0902	0.24
304.13	0.0961	0.0962	0.05	303.98	0.0905	0.0906	0.16
309.00	0.0961	0.0963	0.16	308.74	0.0912	0.0913	0.08
312.40	0.0962	0.0962	0.03	312.40	0.0921	0.0918	0.32
316.86	0.0958	0.0961	0.30	316.23	0.0926	0.0924	0.23
321.55	0.0957	0.0958	0.11	320.63	0.0930	0.0931	0.11
326.18	0.0953	0.0954	0.11	325.24	0.0940	0.0939	0.10
				329.15	0.0947	0.0946	0.08
	$w_1 = 0.62731$				$w_1 = 0.79070$		
301.05	0.0761	0.0763	0.30	300.27	0.0566	0.0566	0.03
304.08	0.0768	0.0772	0.47	303.09	0.0573	0.0575	0.33
307.63	0.0781	0.0782	0.09	306.86	0.0585	0.0587	0.32
311.43	0.0792	0.0793	0.10	311.52	0.0602	0.0602	0.01
315.39	0.0800	0.0805	0.57	316.34	0.0616	0.0618	0.37
319.11	0.0812	0.0816	0.49	320.40	0.0633	0.0632	0.10
323.12	0.0828	0.0829	0.08	323.30	0.0641	0.0643	0.25
327.52	0.0840	0.0843	0.34	326.64	0.0653	0.0655	0.25
			$w_1 = 1.00000$[8]				
288.19	0.0085	0.0085	0.00	293.49	0.0096	0.0096	0.00
298.43	0.0107	0.0107	0.00	303.40	0.0120	0.0120	0.00
312.91	0.0148	0.0148	0.00				

[a] w_1 is the mass fraction of ethanol in the mixed solvents in the table.

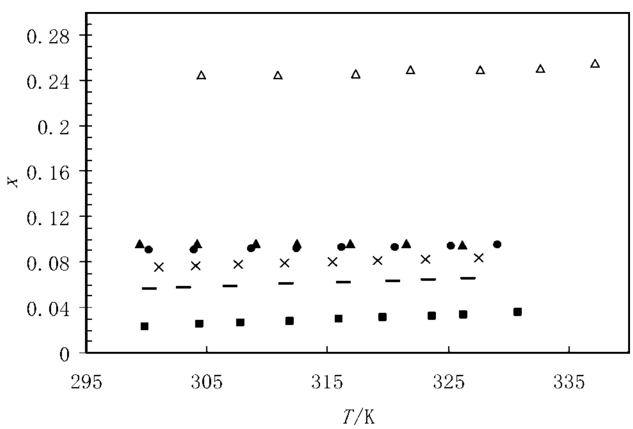

Figure 2. Solubility of HMTA in different solvents: Δ, acetic acid; ▲, water + ethanol (1): $w_1 = 0.20174$; ●, water + ethanol (1): $w_1 = 0.39639$; ×, water + ethanol (1): $w_1 = 0.62731$; −, water + ethanol (1): $w_1 = 0.79070$; ■, methanol.

mometer was inserted into the inner chambers of the vessel to determine the temperature. The temperature had an uncertainty of ± 0.05 K. The mass of the solute and solvents was weighed by an analytical balance with an accuracy of ± 0.0001 g.

The solubility of HMTA was measured by the last crystal disappearance method. The laser monitoring observation technique was used to determine the disappearance of the last crystal in the solid + liquid mixtures. Predetermined excess amounts of solute were transferred into the vessel, and the solvent of known mass was introduced slowly. Continuous stirring was achieved with a magnetic stir bar at a desired temperature for 30 min. At the early stages of the experiment, the laser beam was blocked by the undissolved particles of HMTA in the solution, so the intensity of the laser beam penetrating the vessel was lower. Along with the solute dissolved, the intensity of the laser beam penetrating the vessel increased gradually. When the equilibrium was reached, a drop solvent was introduced every 30 min to ensure that the solvent was not excessive. When the last particles of the solute disappeared completely, the intensity of the laser beam penetrating the vessel reached maximum. Then more drop solvent was added, and if the maximum value did not change between two readings, the equilibrium was believed to have been reached (the error of a drop solvent to the solubility value was estimated to be less than 0.5 %). The temperature was recorded, and the masses of solute and solvents were recorded. The solubility was obtained. The same experiment was performed three times. The uncertainty in the solubility values is estimated to be less than 1.0 %.

Results and Discussion

The mole fraction solubility data of HMTA in pure water of this experiment and the literature[5] are shown in Table 1 and Figure 1. The solubilities of HMTA in methanol and acetic acid are shown in Table 2. The solubilities of HMTA in ethanol + water mixed solvents and in pure ethanol of the literature[8] are presented in Table 3, where T (K) is the absolute temperature and x and x(calc) are the experimental and calculated mole fraction of the solubility, respectively. The solubilities of HMTA in acetic acid, methanol, and ethanol + water mixture solvents are plotted in Figure 2.

The temperature dependence of HMTA solubility in different solvents was correlated by the modified Apelblat equation[12]

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

where A, B, and C are the model parameters. The values of parameters A, B, and C together with the root-mean-square deviations (rmsd) are listed in Table 4. The rmsd is defined as the following

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N}(x_{1,j} - x_{1,j}^{\mathrm{calc}})^2}{N-1}\right]^{1/2} \tag{2}$$

N is the number of experimental points; $x_{1,j}^{\mathrm{calc}}$ is the solubility calculated from eq 1; and $x_{1,j}$ is the experimental value of solubility.

ADD is the relative error which is defined as follows

$$\mathrm{ADD} = \frac{|x - x(\mathrm{calc})|}{x} \tag{3}$$

From Table 1 and Figure 1, it can be seen that in this work from (303.21 to 330.45) K the solubility of HMTA in water decreases with increasing temperature. Then the solubility increases as the temperature increases. This trend is the same as what was reported in the literature.[5,7] From Figure 1, it can be seen that the relative deviation of solubility values between the literature and this work in the mole fraction was less than

Table 4. Parameters of Equation 3 for HMTA in Different Solvents

				ethanol (1) + water (2) mixed solvents			
	water	methanol	acetic acid acid	$w_1 = 0.20174$	$w_1 = 0.39639$	$w_1 = 0.62731$	$w_1 = 0.79070$
A	−140.855	6.763	−49.656	42.956	−24.368	−25.463	−27.927
B	6771.449	−1582.767	2175.195	−2082.669	896.169	752.076	705.906
C	20.341	−0.918	7.188	−6.725	3.374	3.573	3.980
10^3 rmsd	0.8146	0.1908	0.7803	0.1668	0.1818	0.3038	0.1610

2 %. In pure methanol and acetic acid, the solubility increases as the temperature increases. In ethanol + water mixed solvents, the solubility of HMTA in mixture solvents decreases when the mass fraction increases. From the mass fraction (w = 0.39639), the solubility of HMTA increases with the increase of temperature.

From Table 1 to Table 3, Figure 1, and Figure 2, it can be seen that HMTA dissolved much more in acetic acid than in other solvents. From Table 4, it is found that the calculated solubility of HMTA shows good agreement with the experimental values. This shows that eq 1 is appropriate to describe the temperature dependence of the solubility of HMTA.

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