Solubility of Tripolycyanamide and Cyanuric Acid in Ethanediol, *N*,*N*-Dimethylformamide, and *N*,*N*-Dimethylacetamide from (301.07 to 363.35) K

Bao-zeng Ren,* Xiao-liang Yuan, Chen Li, and Hong-kun Zhao

Insititute of Chemical Engineering, Zhengzhou University, Zhengzhou, He'Nan 450002, People's Republic of China

By use of a laser-monitoring observation technique, the solubilities of tripolycyanamide and cyanuric acid in ethanediol, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide were measured at temperatures ranging from (301.07 to 363.35) K using a synthetic method at atmosphere pressure. All measurements were correlated with an empirical equation. Results indicated that the method was available and that the data measured were acceptable.

1. Introduction

Solid−liquid-phase equilibrium data is important in many chemical engineering processes such as extraction and crystallization. Many researchers have studied solid−liquid-phase equilibrium for a variety of chemicals in solvents, but the data of a lot of systems are insufficient. Solid waste effluents from chemical factories are large scaled and even have serious environmental impact. Crystal separation through dissolution in a solvent is an effective method, as the handling capacity is large. It can save energy, and the operational process is simple. However, solubility data are needed. As a significant organic chemical, tripolycyanamide is widely used in many applications; a large quantity of solid waste is discarded during its manufacturing. The main compositions of the waste are tripolycyanamide, cyanurodiamide, cyanuramide, cyanuric acid, etc.[1] To separate and reclaim valuable compounds in the solid waste, the solubility of the ingredients in certain solvents should be available.

There are no reports of the solubility of tripolycyanamide and cyanuric acid except that in some solvents, including tripolycyanamide in water,[2] in ethanol, in dimethyl sulfoxide,[3] and cyanuric acid in ethanol.[4] In this paper, the solubility of tripolycyanamide and cyanuric acid in ethanediol, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide at temperatures ranging from 301.07 K to 363.35 K at atmospheric pressure were systematically determined using a synthetic method.[3−6] The experimental values were correlated by an empirical equation[7]

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

2. Experimental Section

Chemicals. Melamine (tripolycyanamide), purchased from the Shanghai Chemical Reagent Co., and ethanediol, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide from the Beijing Chemical Reagent Co. were of AR grade and used without additional purification. Cyanuric acid, obtained from the Shanghai Chemical Reagent Co., was of

* To whom correspondence may be addressed. Tel.: +1-86-371-3887318. Fax: +1-86-371-3887318. E-mail: renbz@zzu.edu.cn.

Table 1. Mole Fraction Solubility *x* of Tripolycyanamide and Cyanuric Acid in Different Solvents

T/K	*x*	*T*/K	*x*
*x*Tripolycyanamide + (1 − *x*)Ethanediol			
311.23	0.01172	347.15	0.01372
319.30	0.01198	347.70	0.01376
326.30	0.01223	350.97	0.01403
339.65	0.01296	351.44	0.01440
341.75	0.01313	353.40	0.01459
346.53	0.01365		
*x*Cyanuric Acid + (1 − *x*)Ethanediol			
308.25	0.000400	336.15	0.000809
318.05	0.000516	338.85	0.000863
324.45	0.000608	345.55	0.001006
329.05	0.000682	348.24	0.001068
331.15	0.000717	351.45	0.001150
*x*Tripolycyanamide + (1 − *x*)*N*,*N*-Dimethylformamide			
303.25	0.000650	340.85	0.001551
320.60	0.001014	351.55	0.001972
324.86	0.001108	351.63	0.001981
325.25	0.001116	354.75	0.002113
332.40	0.001290	356.80	0.002214
335.25	0.001373	363.35	0.002567
338.13	0.001460		
*x*Cyanuric Acid + (1 − *x*)*N*,*N*-Dimethylformamide			
305.15	0.000528	319.70	0.001030
309.35	0.000648	321.15	0.001094
313.93	0.000800	325.10	0.001285
314.93	0.000838	328.97	0.001493
316.33	0.000891	334.30	0.001816
318.05	0.000960	337.46	0.002029
*x*Tripolycyanamide + (1 − *x*)*N*,*N*-Dimethylformamide			
322.75	0.000467	344.95	0.001336
325.25	0.000530	348.40	0.001563
329.45	0.000657	350.76	0.001739
333.77	0.000801	353.63	0.001979
337.45	0.000949	355.03	0.002108
340.55	0.001094	357.05	0.002308
342.39	0.001189	361.55	0.002823
343.80	0.001268		
*x*Cyanuric Acid + (1 − *x*)*N*,*N*-Dimethylacetamide			
301.07	0.001618	321.95	0.002845
304.98	0.001784	327.37	0.003232
308.20	0.001965	330.94	0.003498
311.00	0.002131	337.75	0.004022
314.13	0.002325	343.45	0.004475
317.30	0.002530		

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Table 2. Parameters in Equation 1 for Different Systems

systems	*A*	*B*	*C*	100σ
tripolycyanamide + ethanediol	−189.0	8.535×10^3	27.37	0.09274
cyanuric acid + ethanediol	−27.88	-1.264×10^3	4.214	0.02315
tripolycyanamide + *N*,*N*-dimethylformamide	−88.98	1.921×10^3	13.18	0.05366
cyanuric acid + *N*,*N*-dimethylformamide	315.1	-1.899×10^4	−45.53	0.04398
tripolycyanamide + *N*,*N*-dimethylacetamide	−134.1	1.784×10^3	20.94	0.06701
cyanuric acid + *N*,*N*-dimethylacetamide	113.3	-7.805×10^3	−16.44	0.08970

CR grade and was purified through dissolution in water and crystallizing. The final purity was analyzed with liquid chromatography. The final purities of the chemicals used were as follows: tripolycyanamide (99.5%), cyanuric acid (99.1%), ethanediol (99.5%), *N*,*N*-dimethylformamide (99.4%), and *N*,*N*-dimethylacetamide (99.5%).

Apparatus and Procedure. The solubility of tripolycyanamide and cyanuric acid in different solvents were measured with the synthetic method designed and installed with a computer monitor on line. The solubility apparatus consisted of a jacketed glass vessel maintained at the desired temperature through circulating water. The water temperature was controlled by a workstation with a temperature accuracy of ±0.1 K. Continuous stirring was achieved by a magnetic stirrer, and a condenser was fitted to reduce the solvent's evaporation. A thermometer with an uncertainty of ±0.01 K was used to determine the temperature of the system. A laser beam was used to observe the system dissolving. The signal transmitted through the vessel was collected by a detector that decided the rate of temperature rising and estimated the equilibrium point of the given system, based on the signal change.

The solute and the solvent were prepared using an electronic balance that had a range of measurement up to 120 g, with an uncertainty of ±0.0001 g. The estimated uncertainty in the mole fraction was less than 0.001.

The solubility of tripolycyanamide and cyanuric acid in solvents were measured as follows. Predetermined amounts of solute and solvents were placed into the jacketed vessel. The system was slowly heated with continuous stirring. While the particles disappeared thoroughly, the signal approached a maximum value. The workstation judged the signal difference at 10-min intervals; if less than the certain given value, the workstation then gave an order to stop heating and record the temperature. The temperature is just the corresponding liquidus temperature of a given composition.

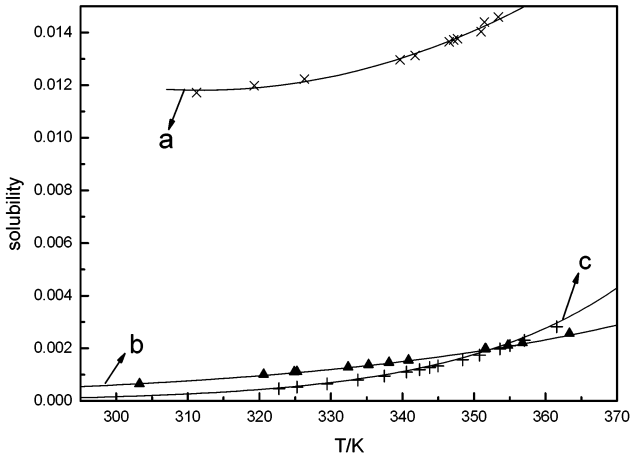

Figure 1. The solubility of tripolycyanamide in three solvents: (a) ethanediol; (b) *N*,*N*-dimethylformamide; (c) *N*,*N*-dimethylacetamide.

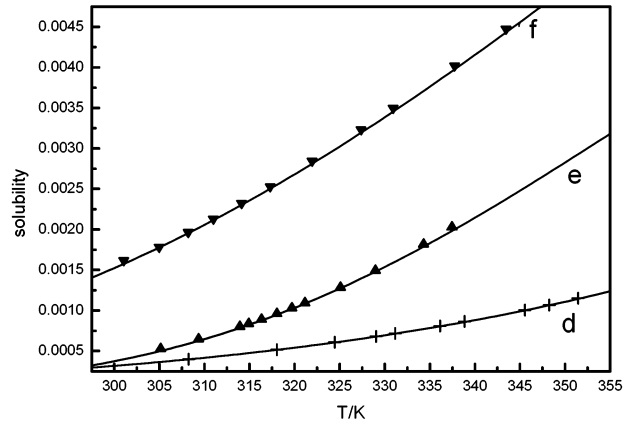

Figure 2. The solubility of cyanuric acid in three solvents: (d) ethanediol; (e) *N*,*N*-dimethylformamide; (f) *N*,*N*-dimethylacetamide.

3. Results and Discussion

The experimental solubility of tripolycyanamide and cyanuric acid in solvents are presented in Table 1, where *T* is the absolute temperature and *x* (mole fraction) is the experimental solubility. All these systems were correlated with eq 1, and the parameters *A*, *B*, and *C* were listed in Table 2. In Figures 1 and 2, curves *a*, *b*, *c*, *d*, *e*, and *f* represent the system of tripolycyanamide + ethanediol, tripolycyanamide + *N*,*N*-dimethylformamide, tripolycyanamide + *N*,*N*-dimethylacetamide, cyanuric acid + ethanediol, cyanuric acid + *N*,*N*-dimethylformamide, and cyanuric acid + *N*,*N*-dimethylacetamide, respectively.

Figures 1 and 2 show that the solubility of tripolycyanamide and cyanuric acid in the solvents studied is somewhat large, so these solvents can be good solvents for separating the solid waste effluents from the tripolycyanamide producing process.

Literature Cited

(1) Sergio, N. High Yields, High Purity Tripolycyanamide Manufacturing Process. W.O. Patent 0146159, 2001.
(2) Chapman, R. P.; Averell, P. R.; Harris, R. R. Solubility of Melamine in Water. *Ind. Eng. Chem.* **1943**, *35*, 137−138.
(3) Ren, B.-Z.; Li, C.; Yuan, X.-L.; Wang, F.-A. Determination and Correlation of Tripolycyanamide Solubility. *J. Chem. Ind. Eng.* **2003**, *54*, 1001−1003.
(4) Ren, B.-Z.; Li, C.; Li, Y.; Zhao, H.-K.; Wang, F.-A. Solubility of Cyanuric Acid, Cyanurodiamide and Cyanuramide in Ethanol. *J. Chem. Eng. Chin. Univ.* **2003**, *17*, 612−615.
(5) Jiang, Q.; Gao, G.-H.; Yu, Y.-X.; Qin, Y. Solubility of Sodium Dimethyl Isophthalate-5-Sulfonate in Water and in Water + Methanol Containing Sodium Sulfate. *J. Chem. Eng. Data.* **2000**, *45*, 292−294.
(6) Ma, P.-S.; Chen, M.-H.; Dong, Y. Solid−Liquid Equilibria of Several Binary and Ternary Systems Containing Maleic Anhydride. *Chin. J. Chem. Eng.* **2002**, *10*, 323−327.
(7) Apelblat, A.; Manzurola, E. Solubilities of *o*-Acetylsalicylic, 4-Aminosalic, 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.

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