

Phase diagram of the hexamethylenetetramine: water system

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Abstract Phase diagram of the hexamethylenetetramine–water system was studied with use of differential thermal analysis and powder X-ray diffraction methods. The only polyhydrate, with the composition $(\text{CH}_2)_6\text{N}_4 \cdot 6\text{H}_2\text{O}$ (m.p. = 12.9 °C), was found. New experimental data on the solubility of $(\text{CH}_2)_6\text{N}_4$ in water were obtained by different methods that show decreasing the $(\text{CH}_2)_6\text{N}_4$ solubility with increasing temperature.

Keywords Hexamethylenetetramine hydrate · Phase diagram · Binary system · X-ray powder diffraction

Introduction

Hexamethylenetetramine (HMTA) forms a hexahydrate with reported decomposition temperatures 13.5 °C [1] or 15.0 °C [2, 3]. X-ray diffraction study of HMTA·6H₂O was performed [4] and its clathrate-like nature was demonstrated (Fig. 1). In fact, the compound is intermediate between nonclathrate and semi-clathrate hydrates representing one of the most elegant among known hydrate structures. To the best of our knowledge, this structure is unique and cannot be assigned to any of the known hydrate types. Since no data on the HMTA–water phase diagram have been available so far, the existence of other HMTA

hydrates (possibly, also having unusual structures) could not be ruled out. The authors of articles [1, 5] also mentioned quite an unusual observation that the solubility of HMTA in water decreases with increasing temperature. However, the temperature dependence of the solubility of HMTA in water has not been studied and only few data are available. The above circumstances stimulated our interest in investigating the phase diagram of the binary HMTA–water system.

Experimental

“Pure” grade HMTA was additionally purified by double recrystallization using its decreasing solubility with increasing temperature. The quality of obtained product was controlled by NMR method. The phase diagram was studied by differential thermal analysis (DTA). The precision of temperature determination was $\pm 0.2^\circ$ as it was determined with use of standard reference samples. The heating rate was 1–2 °C/min. The samples for powder X-ray diffraction measurements were prepared from components by weighing. In order to establish equilibrium the samples were held for 1 month at the temperature near –5 °C. All samples were 2–3 times pounded in a cold mortar during this period. In order to determine the solubility of HMTA, a solid sample was equilibrated with aqueous solution at a certain temperature and after this a weighted portion of the solution saturated at this temperature was placed in a desiccator with P₂O₅ until a constant weight was established (4–6 days). The composition of the solution was then calculated from the weight loss resulted from the dehydration. X-ray diffraction studies were performed with use of synchrotron radiation at the 4th beamline of the VEPP-3 storage ring (Budker Institute of

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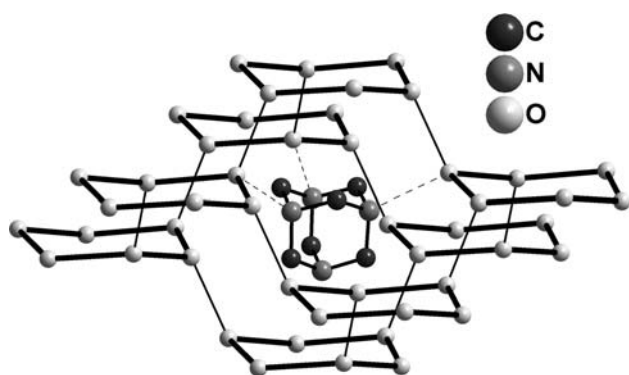


Fig 1 Structure of the $(\text{CH}_2)_6\text{N}_4$ hydrate [4]. The edges connecting oxygen atoms are hydrogen bonds. The host–guest hydrogen bonds are shown by dashed lines

Nuclear Physics SB RAS), at fixed wavelength of 0.3675 \AA [6]. Home-made cell was used to record powder diffraction patterns in the temperature interval $0\text{--}20 \text{ }^\circ\text{C}$; the diffraction patterns were recorded with the step of $2 \text{ }^\circ\text{C}$.

Results and discussion

Our data concerning phase diagram of the HMTA–water system are presented in Fig 2. The DTA results show that HMTA forms the only hydrate $\text{HMTA} \times 6\text{H}_2\text{O}$ which melts incongruently at $12.9 \text{ }^\circ\text{C}$. X-ray diffraction revealed only two solid phases in this system at temperatures above $0 \text{ }^\circ\text{C}$, namely solid HMTA and HMTA hexahydrate (Fig. 3). No polymorph transformation of HMTA or

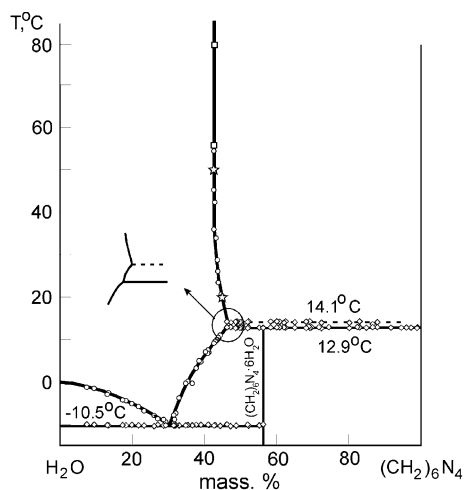


Fig 2 Phase diagram of the binary $(\text{CH}_2)_6\text{N}_4\text{--H}_2\text{O}$ system. Circles and rhombs—lines of liquidus and peritectic obtained by DTA method, respectively; asterisks - points obtained by solubility method; rectangles—visually observed points obtained at heating of HMTA solutions (see text). Probable view of the phase diagram in the indicated region is shown in the insert picture

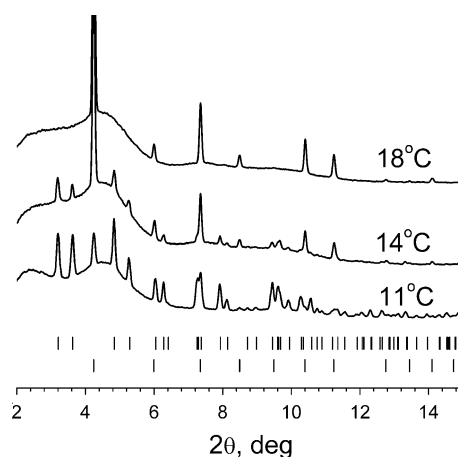


Fig 3 Typical diffraction patterns obtained for the samples in the HMTA–water system in the region of hexahydrate stability (bottom line), hexahydrate in the process of decomposition (middle line) and after decomposition (top line). Upper and lower rows of vertical sticks correspond to calculated positions of the HMTA hexahydrate and solid HMTA reflections, respectively

HMTA hexahydrate was revealed at temperatures above $-100 \text{ }^\circ\text{C}$. The decomposition temperature of the hexahydrate obtained in the present work differs from determined in [1–3]. Possibly, authors of these works determined the melting point visually that caused some inaccuracy due to incongruent mode of melting. Positions of the special points on the phase diagram are following: eutectic point 30.7 mass\% HMTA and $-10.5 \text{ }^\circ\text{C}$; peritectic point 45.6 mass\% HMTA and $12.9 \text{ }^\circ\text{C}$. Water-rich part of the liquidus curve may be calculated with equation $T(^\circ\text{C}) = -0.120X - 0.00695X^2$ (14 points, the value $\Sigma(T_{\text{experimental}} - T_{\text{calculated}})/14 = 0$ with standard deviation $0.2 \text{ }^\circ\text{C}$), HMTA hexahydrate-rich part of the liquidus line may be calculated with equation $T(^\circ\text{C}) = -371.41 + 25.241X - 0.5837X^2 + 0.004715X^3$ (27 points, the value $\Sigma(T_{\text{experimental}} - T_{\text{calculated}})/27 = 0$ with standard deviation $0.6 \text{ }^\circ\text{C}$); in both cases X —mass% of HMTA in solution.

Besides, it was noted that in many experiments a shoulder at $\sim 14 \text{ }^\circ\text{C}$ was observed on the differential peak corresponding to the hexahydrate decomposition. Area of this shoulder may be estimated as $\sim 10\%$ of the area of $12.9 \text{ }^\circ\text{C}$ DTA peak for the sample with composition close to HMTA hexahydrate. Control experiments indicated that this effect was reproducible at different experimental conditions. For example, the effect was reproducible in spite of considerable variations in sample quantity and time for equilibrating the system (to 4–6 h). At the same time this effect was not observed in some of our experiments especially with low water content samples (Fig. 2). It was evident from diffraction patterns that the hexahydrate decomposed to HMTA without formation of any intermediate compounds (Fig. 3). The most probable explanation

Table 1 Solubility of HMTA in water determined with different methods

Concentration of the solution, mass% HMTA	<i>t</i> , °C	Concentration of the solution, mass% HMTA	<i>t</i> , °C
45.00 ^a	20.0	43.40 ^b	42.2
45.00 ^b	20.4	43.10 ^b	48.7
43.83 ^b	23.5	42.73 ^a	50.0
43.90 ^b	26.6	42.87 ^c	56.0
43.57 ^b	28.7	42.05 ^c	80.0
43.94 ^b	33.9		

^a Composition of solution equilibrated with solid HMTA at given temperature was determined

^b DTA data

^c Observed precipitation of HMTA in the course of heating of the solution

of the observed feature is likely to be a change in the character of the solubility dependence on temperature that may be caused by temperature-induced drastic changes of hydration of HMTA molecules in liquid phase (see insert picture in Fig. 3).

As it was mentioned above, the solubility of HMTA in water decreases with increasing temperature at temperatures above HMTA hexahydrate melting point. We obtained experimental data on the HMTA solubility at different temperatures with use of several methods (see Table 1 and Fig. 2). First, a series of experimental points

was obtained with DTA method. Points at 20 and 50 °C were obtained by determination of HMTA content in the saturated solutions equilibrated with solid HMTA at these temperatures. Finally, a set of homogeneous transparent solutions with various compositions was prepared at room temperature and heated in thin-walled test-tubes in order to observe at what temperature solid HMTA will start to precipitate. The results obtained by different methods are in reasonable agreement (Fig. 2). No precipitate of HMTA was observed at the HMTA concentration less than 42.0 mass% even when the solution was heated up to the boiling point.

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