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Solubility of 1,3,5,7-tetra azatricyclo[3.3.1.1^{3,7}]decane (HMT) in water from 275.15 K to 313.15 K

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Abstract

The water solubility of 1,3,5,7-tetra azatricyclo[3.3.1.1^{3,7}]decane, hexamethylenetetramine (HMT) or urotropine was determined at temperatures between 275.15 K and 313.15 K. Van’t Hoff graphs of $\ln m_{\text{sat}}$ versus $1/T$ gave three different straight lines, suggesting the existence of three different forms of the substance in the temperature region studied.

Previous work reported both increasing and decreasing solubility with temperature. This work found the solubility does not have a simple behavior.

Keywords: Aqueous solubility; 1,3,5,7-tetra azatricyclo[3.3.1.1^{3,7}]decane; Hexamethylenetetramine (HMT); Urotropine

1. Introduction

1,3,5,7-tetra azatricyclo[3.3.1.1^{3,7}]decane, also known as urotropine, formamine, formine and hexamethylenetetramine (HMT), is an important product obtained from formaldehyde and ammonia. HMT is a tertiary amine, solid, colorless that regularly crystallizes into rhombic dodecahedrons, which exhibit piezoelectric properties. HMT hydrate $(CH_2)_6N_4{\cdot}6H_2O$ is obtained in the form of crystalline prisms when the saturated aqueous solution is cooled down to a temperature near 273.15 K [1].

An unusual property reported for HMT is that its solubility in water decreases while temperature increases, a remark made by Grützner in 1898 and later corroborated by Walker [1]. Later, Ütz determined the solubility of hexamethylenetetramine in water and other solvents (trichloroethylene, benzene, xylene, acetone, *n*-amyl alcohol, chloroform, etc.) at room temperature, finding that 1.67 g of hexamethylenetetramine dissolves in 1 mL of water and that bigger quantities can be dissolved in hot water and separated by cooling the solution [2]. Quadrifoglio et al. determined the solubility of hexamethylenetetramine in water between 298.15 K and 308.15 K, finding an increase in solubility while temperature decreases [3]. This last fact has been explained by HMT ability to bond water at low temperatures, forming a structure intermediate between a clathrate and a hydrate, called hexamethylenetetraminhexahydrate $(CH_2)_6N_4{\cdot}6H_2O$, in which the organic molecule is surrounded by water molecules and these form three bonds with three of the four nitrogens [1,3].

The physicochemical properties of 1,3,5,7-tetra azatricyclo [3.3.1.1^{3,7}]decane aqueous solutions suggests that this aminal exerts an important influence in the structural organization of water [4]. The properties studied for the HMT–water system have been: density, viscosity and activity coefficients [5], heat capacity [6], solubility of gaseous hydrocarbons and hydrophobic effect on hexamethylenetetramine aqueous solutions [7], integral heats of solution [8] and enthalpy composition diagram [9]. Nevertheless, a fairly complete study of this aminal solubility with temperature was not available in the usual literature.

2. Experimental

2.1. Chemicals

The 1,3,5,7-tetra azatricyclo[3.3.1.1^{3,7}]decane was reagent grade obtained from Sigma Co® with purity higher than 99.4%. The potassium chloride (KCl) was reagent grade from Riedel-de Haën Co® with purity higher than 99.5%. The water used was doubly distilled and deionized.

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2.2. *Experimental equipment and procedures*

The experimental equipment is similar to that used by Lee and Huang [10]. Ours has a unit containing four glass cells placed on a turbine stirrer, which works with water from the circulating thermostat. The volume of each glass cell is 10 mL. The Lauda® circulating thermostat controls to 0.1 K in the temperature range between 275.15 K and 373.15 K. The temperature of the glass cell was measured with a Boeco® thermometer, with an uncertainty of 0.1 K. An electronic balance Ohauss Analytical Plus Co® with an detection limit of 0.1 mg was used for determining the mass of the compounds.

To test the experimental technique, measurements on potassium chloride solubility in water were done between 275.15 K and 313.15 K and the data obtained compared with the available literature [10,11].

KCl was added, as calibration substance, to a cell containing a volume of 5 mL of water so that the solute was in excess. Samples of the saturated solution at different times were taken (60, 90 and 120 min), in order to determine the best time to get equilibrium. The samples from the saturated solution were taken at 0.5 cm above the undissolved solute by means of a glass syringe with a needle that had a filter attached to its end. The saturated solution was transferred to 5 mL glass flasks, which were left in the drier for 48 h and finally in a furnace at 318.15 K until constant weight. Experimental and literature solubility data for KCl are shown in Table 1. Each solubility determination is presented as the average result of three measurements.

Once the equilibrating time was established for the KCl (>60 min), the solubility of HMT, following the same procedure as for KCl but with 2 h equilibrium times, was determined. The drying process of the HMT saturated solution required to discard part of the solvent in the dryer, so that there is crystal formation, before continuing with the drying process in the Abderhalden vacuum pistol [12]; otherwise, the HMT hydrate, $C_6H_{12}N_4 \cdot 6H_2O$, breaks down with efflorescence and quantification is more difficult [1]. To verify that the substance obtained after drying corresponds to the initially added, analysis by gas chromatography coupled to mass spectrometry (CG–EM) and by X-ray diffraction were performed.

Since HMT aqueous solutions exhibit a mild degree of hydrolysis, it was necessary to quantify the amount of formaldehyde in each solubility essay. The mercurometric method was used [1]. The aqueous solubility of HMT is lower when ammonium is present in the solution. The magnitude of this effect can be evidenced from the following data at room temperature: 52 g HMT are dissolved in 100 mL ammonia free water and 22.2 g of HMT are dissolved in 100 mL water containing 18.4 g of ammonia [5].

Table 1
Solubility of the KCl in water

Temperature (K)	Experimental KCl solubility in water (%, w/w)	Literature data of solubility (%, w/w) [10,11]
275.15	22.05	22.0
277.15	22.41	22.5
279.15	22.82	22.9
283.15	23.63	23.7
288.15	24.59	24.5
293.15	25.51	25.4
298.15	26.64	26.2
303.15	27.06	27.1
313.15	28.60	28.6

3. Results and discussion

Generally speaking, stirring times longer than 60 min at constant temperature guarantee solid–liquid equilibrium conditions for solutions of KCl, in all cases, the difference with literature was less than 0.5%. Given the high solubility of HMT in water, 2 h at constant temperature were used as the stirring time, in order to get saturation.

The discrepancy on the data for solubility of HMT in water can be associated with the method used for its measurement. Unfortunately, a method does not exist for the determination of HMT that is both specific and reproducible [1]. The United States Pharmacopeia recommends the hydrolytic method for the determination of HMT in small quantities. Solubility data obtained for HMT in water are shown in Table 2.

Experimental solubility of HMT in water showed significant variations with temperature, which were analyzed using van't Hoff graphs ($\ln m_{\text{sat}}$ versus $1/T$). Three straight lines with correlation coefficients higher than 0.98 (Fig. 1) are obtained, suggesting that the solute is present in three different forms. Solubility of HMT in water increased while temperature decreased between 275.15 K and 283.15 K. It had a

Table 2
Experimental solubility of HMT in water in function of temperature

Temperature (K)	Solubility (%, w/w)	Formaldehyde (%, w/w)
275.15	45.52	0.0360
277.15	44.65	0.0232
279.15	44.09	0.1417
283.15	43.11	0.1008
284.15	46.21	0.1125
285.15	46.08	0.0945
288.15	45.59	0.0479
293.15	44.34	0.0479
298.15	43.32	0.0412
303.15	44.38	0.0298
308.15	45.13	0.0352
313.15	45.58	0.0123

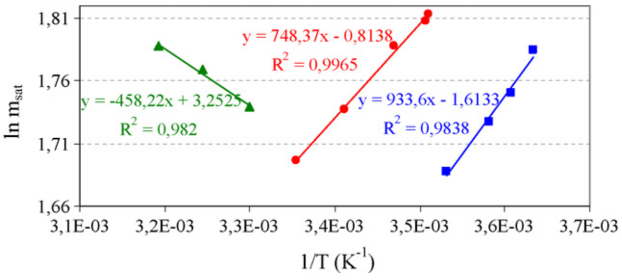

Fig. 1. van't Hoff graph for the HMT–water system.

sharp increase in the neighborhood of 284.15 K then continued decreasing until 298.15 K was reached, and from then on increased until the last temperature studied, 313.15 K was reached.

Fig. 1 shows similarities with the behavior of polymorphs as shown by Yalkowsky [13]. Then, we could say that different solids are in equilibrium with the solvent in the three regions found: below 283.15 K, from 284.15 K to 298.15 K and from this value up. The transitions should occur in the interval 283.15–284.15 K and 298.15–303.15 K.

Reagent grade HMT and two of the solids recovered from saturate solutions at 275.15 K and 293.15 K were analyzed by X-ray diffraction, having found the same signals with different intensity, which shows that after drying the saturated solution, the solid recovered is the same as the starting one. CG–EM analyses carried out on pure HMT and on the product obtained after vacuum drying of the saturated solutions showed that the same substance remained. In the gas chromatograms, a peak was observed, indicating the presence of a single compound, and in the mass spectra, the molecular ion coincided with the molecular mass of the compound, the division of ions being the same.

The differential heats of solution obtained from the van't Hoff graph's slope are negative for HMT between 275.15 K and 298.15 K (-7711 ± 1 J/mol and -6571 ± 1 J/mol).

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