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Thermodynamic properties of melamine (2,4,6-triamino-1,3,5-triazine) in aqueous solution. Effect of ionic medium, ionic strength and temperature on the solubility and acid–base properties

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ABSTRACT

In this paper new solubility and potentiometric measurements are reported to model the behaviour of melamine in aqueous NaCl and $(CH_3)_4NCl$ ionic media at different ionic strengths ($0.1 \leq I/mol\,L^{-1} \leq 3.8$) and temperatures ($283.15 \leq T/K \leq 318.15$). For this purpose, some literature data were used together with experimental data. In NaCl solutions, the solubility of melamine decreases with increasing ionic strength and increases with increasing temperature ($\Delta H = 30.5\,kJ\,mol^{-1}$ at $I = 0\,mol\,L^{-1}$), whereas in $(CH_3)_4NCl$ solution increases with increasing both ionic strength and temperature. In NaCl, at $T = 298.15\,K$, the melamine solubility is 26.1 and 16.3 mmol L^{-1} at $I = 0.104$ and 2.304 mol L^{-1}, respectively; whereas in $(CH_3)_4NCl$ it is 29.9 and 33.6 at $I = 0.111$ and 1.058 mol L^{-1}, respectively, at $T = 298.15\,K$. Values at infinite dilution are provided together with solubility values of neutral species calculated at different temperatures and ionic strengths. As an example, the solubility of melamine is 0.0271 mmol L^{-1} in pure water. From solubility data, the Setschenow and the activity coefficients were also determined. The protonation constant are reported in condition similar to the solubility measurements, and their dependence on temperature shows that the proton binding is exothermic ($\Delta H = -26.6\,kJ\,mol^{-1}$ at $I = 0\,mol\,L^{-1}$). The entropic contribution is low ($T\Delta S = 2.4\,kJ\,mol^{-1}$ at $I = 0\,mol\,L^{-1}$) and increases with increasing ionic strength in NaCl, whereas in $(CH_3)_4NCl$ it remains almost constant. The ionic strength dependence was modelled by means of the extended Debye–Hückel and the Specific ion Interaction Theory (SIT) and data at infinite dilution are calculated. Finally, comparing the protonation constants in different ionic media, the formation of two weak complexes was noticed between the protonated melamine species, AH^+ and Cl^- and between the tetramethyammonium cation, $(CH_3)_4N^+$ and the deprotonated melamine species (A). At infinite diluition ($T = 298.15\,K$) it was found $K(AH^+ + Cl^-) = 0.45 \pm 0.05\,L\,mol^{-1}$ and $K(A + (CH_3)_4N^+) = 0.63 \pm 0.03\,L\,mol^{-1}$, in agreement with previous findings for amine ligands.

1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) (see Fig. 1) is a chemical intermediate that in its natural state is a white crystalline powder. It was commercially produced in the 1930s from the common substance urea, which is distilled to produce melamine. Melamine is used for a wide variety of applications, including plastics, adhesives, laminates, paints, permanent-press fabrics, flame retardants, textile finishes. In factories, it is mixed in large vats to produce a resin; which is commonly used in the manufacturing of particleboard [1]. Melamine is a monomer in the manufacturing of plastic materials (melamine–formaldehyde plastics) used to make tableware products, suitable for food contact applications because of its hardness, heat resistance and general stability. These superior characteristics enable the use of melamine-based tableware for this purpose; however, repeated use can increase the possibility of melamine migration into food [2]. Melamine is also added to plastic foams to increase density and durability. Melamine and other triazine compounds are used as a nitrogen source in slow release urea-based fertilizer mixtures. Their accumulation and persistence in the environment are well known [3]. Considering that melamine is almost tasteless and that it is very rich in nitrogen (67% by mass), it is added to foods to inflate the apparent protein levels; this adulteration caused the death of hundreds of pets and, more recently, in China the adulteration of milk for infant, caused renal failure because the formation of insoluble melamine–cyanurate crystals in the kidney [4,5]. According to the Environmental Protection Agency Toxic Chemical Release Inventory, until 1987 [6], 82 000 kg

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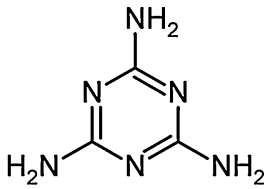

Fig. 1. Scheme of melamine.

melamine were released into the air, 240 000 kg were discharged into water, and the exposure to melamine in the environment was considered low, but few quantitative data were available. Following the incidents of China, the competent authorities (US-FDA, WHO, CONTAM and EFSA,) reevaluated health aspects of melamine, hence a number of risk assessments have been performed, and a recent review of Dorne et al. [7] provided an overview of these assessments. In the same paper, many toxicity data are reported for melamine in laboratory animals and in livestock, and a paragraph is devoted to the nephrotoxicity of melamine in humans. As already reported, all such uses may lead to a massive presence of melamine in food and environment, for this reason many studies on the hazard of melamine were found in the literature [8–10] (epidemiological and toxicological studies), whereas little attention has been focused on its acid–base properties. Among the available literature data, many studies regard analytical methods for the melamine trace determination, whilst few data are present for solution properties. Jang et al. [11] calculated the acid dissociation constants in water from density functional theory; Dudley [12] in the 1951 potentiometrically determined the dissociation constants of variously substituted melamines and related triazines, finding pK = 5 for melamine. Morales [13] in his paper described the potentiometric titration of melamine in dimethylsulfoxide.

As already explained above, melamine is important in the environmental, industrial and biological fields, and therefore the study of a speciation model to better understand the interaction of this molecule in natural media is fundamental. In particular, in this paper the solubility and the acid–base properties of melamine in different media, NaCl and $(CH_3)_4NCl$, were studied at different temperatures (283.15–318.15 K) and ionic strengths.

2. Materials and methods

2.1. Chemicals

All chemicals were purchased from Sigma Aldrich or Fluka and used without further purification, except for the tetramethylammonium chloride ($(CH_3)_4NCl$), which was purified from methanol as described by Perrin et al. [14]. Sodium hydroxide, tetramethylammonium hydroxide and hydrochloric acid solutions were prepared from concentrated standard solution, and they were standardized against potassium hydrogen phthalate (for bases) and sodium carbonate (for acid), previously dried in oven at 383.15 K for 2 h. Sodium chloride (analytical grade) solutions were prepared weighing the solid previously dried in oven at 383.15 for 2 h. The solutions were freshly prepared, using grade A glassware and twice-distilled water ($R \geq 18\,M\Omega$).

2.2. Apparatus

To avoid systematic errors two different potentiometric apparatus were used to measure the free hydrogen ion concentration, (a) model 809 MetrohmTitrando, equipped with a combined pH glass electrode (from Methrom 6.032.100); (b) model 713 Metrohm potentiometer connected to a Metrohm 665 automatic burette and to a model 8101 Ross type Orion electrode, coupled with a standard calomel electrode. For both systems the estimated precision was ±0.20 mV and ±0.001 mL for e.m.f. and titrant volume readings, respectively. A PC was connected to the apparatus and automatic titrations were performed using the MetrohmTiAMO 1.0 software to control titrant delivery and data acquisition.

Table 1
Experimental conditions for the determination of protonation constants and solubility in NaCl and $(CH_3)_4NCl$ solutions.

c/mol L^{-1}	T/K	I/mol L^{-1} NaCl
0.003–0.005	283.15	0.10–3.37
0.003–0.005	291.15	0.10–3.35
0.004–0.010	298.15	0.09–2.92
0.005–0.010	310.15	0.10–3.00
0.004–0.015	318.15	0.09–3.16
		I/mol L^{-1} $(CH_3)_4NCl$
0.005–0.015	298.15	0.19–2.82
0.005–0.016	310.15	0.13–2.72
0.005–0.020	318.15	0.15–2.72
Solubility		I/mol L^{-1} NaCl
	298.15	0.10–3.45
	310.15	0.10–3.80
		I/mol L^{-1} $(CH_3)_4NCl$
	298.15	0.10–2.60
	318.15	0.10–2.70

2.3. Procedure for potentiometric and solubility measurements

The preparation of the solutions for the potentiometric measurements consisted in different amounts of melamine, dissolved in the desired ionic medium, sodium chloride or tetramethylammonium chloride. The melamine concentration in the experiments ranged between 3 and 15 mmol L^{-1} in NaCl and between 5 and 20 mmol L^{-1} in $(CH_3)_4NCl$ (see Table 1). During the titrations, the solutions were magnetically stirred and $N_{2(g)}$ was bubbled through the solution to debar $O_{2(g)}$and $CO_{2(g)}$ inside. A volume of 25 mL of aqueous solution, containing melamine and the ionic medium used (NaCl or $(CH_3)_4NCl$) at different ionic strengths, was titrated with sodium hydroxide or tetramethylammonium hydroxide up to pH ∼ 7.5. Before each experiment, independent titrations of HCl solutions with standard sodium hydroxide (or $(CH_3)_4NOH$) were performed to determine the formal electrode potential in the same experimental conditions (temperature and ionic strength) of the systems under investigation. The free hydrogen ion concentration scale was used (pH ≡ −log[H$^+$]).

Solubility measurements were performed as follows: saturated solutions were prepared in thermostatted vessels adding an excess of melamine to NaCl or $(CH_3)_4NCl$ aqueous solutions at fixed ionic strength values (0.1–3.0 mol L^{-1}) (see Table 1). The solutions were stirred at fixed temperatures (298.15 or 310.15 K) for 18–24 h. Preliminary conductivity tests showed that longer stirring times are unnecessary, and a time of 4–6 h is sufficient. After the stirring, the solutions were filtered with MFMillipore (MCEmembrane) filters 0.45 μm. To minimize the systematic errors, several independent experiments were carried out for each ionic strength. The titrations on the supernatant were carried out by potentiometry using NaOH or $(CH_3)_4NOH$ standard as titrant, as previously reported.

2.4. Calculations

All the computer programs used in this work were reviewed elsewhere [15].