Effect of temperature on the density and surface tension of aqueous solutions of HMT

L. H. Blanco · O. M. Vargas · A. F. Suárez

Abstract In this study, a systematic study of the effect of the temperature on the density and surface tension of HMT (hexamethylentetramine) in water was developed. The density and surface tension were determined at temperatures of 288.15, 293.15, 298.15, 303.15, and 308.15 K. Precise data of surface tension have not been reported previously in literature. From the density measurements, the apparent molar and partial molar volumes were calculated. The apparent molar volume decreases with concentration, the molar partial volume increases with temperature. The surface tension of the aqueous solutions of HMT decreases with concentration. The excess surface concentration was calculated, the values increase with concentration, indicating that the amount of HMT that goes to the interface gas liquid increases at higher concentrations of HMT.

Keywords Hexamethylenetetramine · HMT · Surface tension · Densities · Aqueous solutions

Introduction

The determination of the thermodynamic properties of solutions is of great importance to understand the physicochemical phenomena involved in the solution process. The aminal used is 1,3,5 7-tetraazatricyclo [3.3. 1.13, 7]

decane better known as HMT is a solute of interest because it is a globular molecule, it is apolar and has a high solubility in water, also it is used in several processes like rubber production, pharmaceutical industry, photographic industry, organic synthesis, in other fields.[1–3]

Some physical properties of the aqueous solutions of HMT have been determined for instance viscosity, diffusion coefficient, solubility, heat of dilution, and molar volume [4–15]. However, some of the data lacks reproducibility and has large uncertainty.

A systematic study of the density and of the surface tension of aqueous solutions of HMT at several compositions and temperatures was made. Apparent molar volume and excess surface concentration were calculated and the behavior of these properties with temperature was determined.

Experimental section

The HMT analytic reagent was used (FISHER, 99.9%), it was dried for 48 h before the preparation of the solutions. The water was double distilled, degasified, and deionized with conductivity less than 2 μS/cm.

All solutions were prepared by weight, using a Mettler balance AT-261 dual range with sensitivity of 10^{-5} g in the lower range. The concentrations used were determined according with the solubility reported in a previous study [4].

The densities of the solutions of HMT were determined using an Anton Paar DMA 5000 densitometer. The temperatures were 288.15, 293.15, 298.15, 303.15, and 308.15 K. The repeatability of the instrument was 5×10^{-6} g/cm^3 and the uncertainty in the measurements was 1×10^{-5} g/cm^3. The temperature control was better than 0.01 K.

Surface tension measurements were made with LAUDA TVT2 drop volume tensiometer, based on the principle of

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the pending drop volume. The working temperatures were 288.15, 293.15, 298.15, 303.15, and 308.15 K, the temperature control was better than 0.01 K and a repeatability of $\pm 10^{-2}$ mNm^{-1} in the surface tension measurements. The syringe used had a capacity of 1.0 mL. Reported values are the average of 18–24 measurements with an uncertainty of 0.1 mNm^{-1}. This technique measures the volume of a drop detaching from a capillar with circular cross-section.

Results and discussion

The density values of the aqueous solutions of HMT as function of concentration and temperature are shown in Table 1. Some density values for HMT–water system were reported in previous studies. The techniques used were magnetic floating and pycnometry [8, 9].

The molar partial volume was calculated using the equation

$$\phi_V = M_2/\rho + (1000(\rho_0 - \rho)/m\rho\rho_0), \tag{1}$$

where M_2 is the molecular weight of the solute, m is the molality of the solute, ρ density of HMT solution, and ρ_0 is the density of the water for each temperature.

The molar apparent volume and the molar partial volume are related by the equation.

$$\phi_V = (\partial V/\partial n_2)_{T,P,n_1} = \overline{V}_2^0 + n_2(\partial \phi_V/\partial n_2)_{T,P,n_1}, \tag{2}$$

At infinite dilution, the molar apparent volume and the molar partial volume are equal to the molar partial volume at infinite dilution $\overline{V}_2^0 = \phi_V^0$ can be calculated by extrapolation of the molar apparent volumes to zero concentration using a polynomic fit of the data.

The density shows a decrease with temperature and an increase with concentration, this is due to the nature of the

solvent. These observations are in agreement with previous results found in literature [9].

The molar apparent and molar partial volumes at infinite dilution are reported in the Table 2. The values of molar partial volumes increase with concentration and temperature.

The molar partial volumes at infinite dilution are shown in Table 3. The values increase with temperature. Some literature available data are also shown.

The expansibilities were evaluated for the solutions according with the equation.

$$\alpha = -1/\rho(\partial\rho/\partial T). \tag{3}$$

The expansibilities show a linear behavior as shown in the Fig. 1 for all cases when plotted as a function of concentration. The values increase with temperature and concentration [16–18].

The surface tension of the aqueous solutions of HMT is reported in Table 4. The surface tension of this system decreases with concentration and with temperature. At higher concentration of solute in the bulk of the solution, the HMT molecules tends to go to the surface of the air–solution interface, this decreases the surface tension.

The excess surface concentration can be found using the Gibbs equation [19] that gives a prediction of the number of molecules in the air–solution interface when the increase of the concentration of solute in the interface, decreases the surface tension.

$$\Gamma_2^1 = -a/RT(\mathrm{d}y/\mathrm{d}a). \tag{4}$$

Γ_2^1 is the excess of the component 2 in a section of 1 cm^2 of surface region that can be called also surface concentration, a represents the activity of the solute and γ is the surface tension of the solution Γ_2^1 is expressed in mol/cm^2.

Γ_2^1, was determined using Eq. 5, because activity coefficients are not reported.

Table 1 Densities of the aqueous solutions of HMT at several temperatures

m	ρ/g cm^{-3}				
	15 °C	20 °C	25 °C	30 °C	35 °C
2.80845	1.06613	1.06440	1.06253	1.06045	1.05836
2.49669	1.06003	1.05839	1.05660	1.05471	1.05256
1.99739	1.04987	1.04836	1.04669	1.04488	1.04286
1.79203	1.04546	1.04400	1.04238	1.04059	1.03863
1.49573	1.03878	1.03742	1.03587	1.03409	1.03225
1.19878	1.03152	1.03025	1.02875	1.02714	1.02528
0.99867	1.02678	1.02557	1.02415	1.02248	1.02072
0.79985	1.02167	1.02052	1.01916	1.01757	1.01581
0.49822	1.01355	1.01250	1.01121	1.00972	1.00799
0.10054	1.00214	1.00122	1.00003	0.99862	0.99698
0.00000	0.99912	0.99823	0.99707	0.99567	0.99406

Table 2 Molar apparent volume ϕ_v for aqueous solutions of HMT at several temperatures

m	ϕ_v/cm^3 mol^{-1}				
	15 °C	20 °C	25 °C	30 °C	35 °C
2.80845	109.10	109.53	109.94	110.33	110.70
2.49669	109.22	109.65	110.05	110.43	110.80
1.99739	109.29	109.73	110.13	110.50	110.85
1.79203	109.36	109.78	110.17	110.54	110.89
1.49573	109.41	109.83	110.22	110.58	110.93
1.19878	109.44	109.92	110.26	110.63	110.97
0.99867	109.54	109.95	110.33	110.69	111.03
0.79985	109.61	110.01	110.39	110.74	111.08
0.49822	109.70	110.10	110.47	110.82	111.15
0.10054	109.80	110.20	110.56	110.89	111.23

Table 3 Values of molar partial volume at infinite dilution $\overline{V}_2^0$ at several temperatures

T/°C	$\overline{V}_2^0$/cm^3 mol^{-1}	
15	109.80	110.5 [8]
20	110.21	–
25	110.56	111.4 [8]
30	110.90	–
35	111.23	112.3 [8]

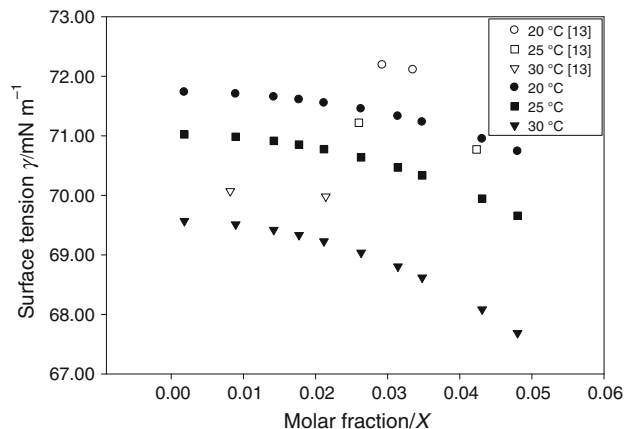**Table 4** Surface tension of HMT aqueous solutions at several temperatures

m	γ/mN m^{-1}				
	15 °C	20 °C	25 °C	30 °C	35 °C
2.80845	71.70	70.74	69.66	68.72	67.69
2.49669	71.82	70.95	69.94	69.02	68.08
1.99739	71.98	71.23	70.33	69.44	68.62
1.79203	72.04	71.33	70.47	69.59	68.80
1.49573	72.11	71.45	70.64	69.77	69.04
1.19878	72.17	71.55	70.78	69.92	69.23
0.99867	72.20	71.61	70.85	70.00	69.33
0.79985	72.22	71.65	70.91	70.07	69.42
0.49822	72.25	71.70	70.98	70.14	69.51
0.10054	72.27	71.73	71.02	70.18	69.57
0.00000	72.27	71.73	71.02	70.18	69.57
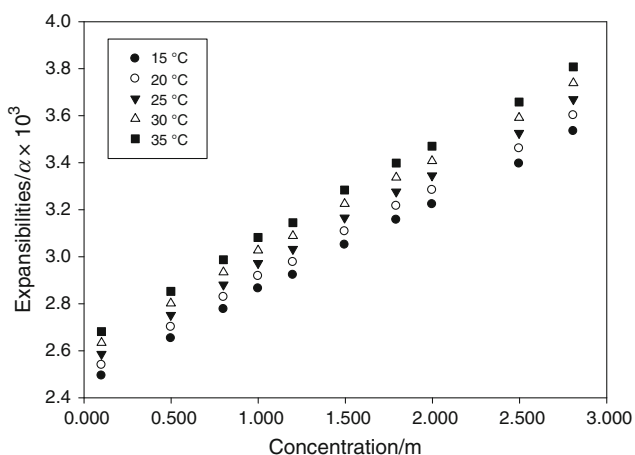
Fig. 1 Expansibilities of the aqueous solutions of HMT at several temperatures

$$\Gamma_2^1 = -1/RT(\mathrm{d}y/\mathrm{d}\ln X), \tag{5}$$

where X is the molar fraction of the component 2 in the solution.

The behavior of the surface tension with temperature is compared with previous results [13] in Fig. 2. The differences between the previous data and the study data may be

Fig. 2 Experimental surface tension measurements and comparison with literature
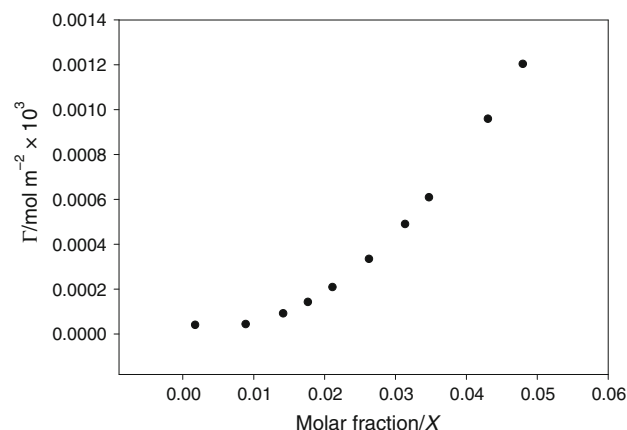
Fig. 3 Values of ESC/Γ/mol m^{-2} × 10^3 versus molar fraction/X, for the aqueous solutions of HMT at 25 °C

due to temperature control and the measurement technique used in the previous study.

The excess surface concentrations (ESC) were calculated with Eq. 5, and are shown in Fig. 3. For all the temperatures a similar behavior is observed, an increase of the ESC is shown with increase temperature. In the high concentration region an ESC increase is shown.

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