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Surface Tensions and Densities of Sulfuric Acid + Dimethylamine + Water Solutions

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The surface tensions and densities of aqueous solutions of dimethylamine, $(CH_3)_2NH$, and sulfuric acid, H_2SO_4 , were measured at 24.2 °C. Mol fractions of dimethylamine were varied between 0 and 0.21 and of sulfuric acid between 0 and 0.48. The surface tension of the binary dimethylamine + water solution decreased exponentially as dimethylamine was added, from the surface tension of water $(72 \text{ mN} \cdot \text{m}^{-1} \text{ at } 25 \text{ °C})$ to the value of $34 \text{ mN} \cdot \text{m}^{-1}$ at the maximum dimethylamine mol fraction of 0.21. The surface tension of the ternary system did not change from that of water + sulfuric acid until a sufficient amount of dimethylamine was added to turn the solution alkaline. When the mol fraction of dimethylamine was more than double the mol fraction of sulfuric acid, the surface tension of the solution started to approach that of water + dimethylamine. Polynomial fits were applied to measured data sets of both surface tension and density. Results and fitting parameters are presented.

Introduction

Aerosols in the atmosphere can originate from many sources. A source that has received a lot of scientific attention lately is vapor to liquid nucleation, which is the formation of small droplets from condensable gases. Whereas nucleation from only one compound is unlikely to happen in atmospheric conditions, there can be conditions that favor particle formation from binary and/or ternary nucleation. New particle formation events in the atmosphere have been observed in various places around the world. 1-3 The most popular candidate to explain atmospheric nucleation events is the ternary nucleation of sulfuric acid + ammonia + water. 4,5 Preliminary laboratory experiments 6 show that ammonia is able to promote large enhancements in particle nucleation rates and decrease the number of sulfuric acid molecules in the critical cluster. It is unclear which species are able to influence atmospheric nucleation processes. Also, the lack of thermophysical properties (such as surface tension and density) makes it difficult to theoretically predict nucleation rates and critical cluster sizes and composition.

Surface tension has an important role in vapor—liquid nucleation and growth processes. Surface tension is a key parameter in the Kelvin equation, which describes the vapor pressure over a curved surface. Substances with low surface tensions are more likely to be found in the liquid phase, and they also nucleate more easily than substances with high surface tension. Therefore, surface-active organic substances, which in general lower the surface tension, can boost nucleation and reduce the number of sulfuric acid molecules in atmospheric critical clusters. §

Dimethylamine, (CH₃)₂NH, has been found in a particulate phase in a boreal forest area during nucleation events and in the gas phase during other times.⁵ Dimethylamine

has many similar properties to ammonia, NH_3 . For example, the proton affinity⁹ of dimethylamine is 929.5 kJ·mol⁻¹ and for ammonia is 853.6 kJ·mol⁻¹, and they both have a Henry's law constant^{10,11} of about 56 mol·kg⁻¹·bar⁻¹. Therefore, dimethylamine is able to replace ammonia in the ternary nucleation scheme. The equilibrium surface tensions of dimethylamine + water have been measured before by Mmereki et al.¹² The surface tensions and densities of sulfuric acid + water have been measured by Myhre et al.¹³ However, no surface tension or density measurements of the corresponding ternary compound have been made.

The reactions occurring in an aqueous sulfuric acid \pm dimethylamine \pm water solution can be expressed by parts a-c of eq 1

$$H_2SO_4 + H_2O \leftrightarrow HSO_4^- + H_3O^+$$
 (1a)

$$HSO_4^- + H_2O \leftrightarrow SO_4^{2-} + H_3O^+$$
 (1b)

$$(CH_3)_2NH + H_2O \leftrightarrow (CH_3)_2NH_2^+ + OH^-$$
 (1c)

Sulfuric acid is a strong acid with an acid constant \$^{14}\$ of \$10^3\$ mol·dm $^{-3}$ at $25\ ^{\circ}\text{C}$ for its first dissociation step. Dimethylamine has an acid constant 14 of $2\times 10^{-11}\ \text{mol·dm}^{-3}$, which makes it a weak base. In an acidic solution, there will be a mixture of H_3O^+ , HSO_4^- , SO_4^{2-} , and $(CH_3)_2NH_2^+$ ions. When the mol fraction ratio is 2, there is an equivalent amount of acid and base, although the solution is slightly acidic due to sulfuric acid being a strong acid and dimethylamine being a weak base. As enough dimethylamine is added to make the mol fraction ratio between dimethylamine and sulfuric acid greater than 2, the excess dimethylamine makes the solution slightly alkaline (pH \approx 12.5). Most of the dimethylamine will remain in its neutral form in alkaline conditions

Experimental Methods

The surface tensions were measured with a thermostated tensiometer (Digital Tensiometer K 10ST, Krüss Gmbh,

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Table 1. Surface Tensions, σ , of Sulfuric Acid (i = 3) + Dimethylamine (i = 1) + Water as a Function of Mol Fractions, x_b of Sulfuric Acid and Dimethylamine^a

- Sunt	iric Acid ai	id Difficulty	ammile								
	σ	$\Delta \sigma$		σ	$\Delta \sigma$		σ	$\Delta \sigma$		σ	$\Delta \sigma$
<i>X</i> ₁	$\overline{\text{mN}\cdot\text{m}^{-1}}$	$\overline{\text{mN}\cdot\text{m}^{-1}}$	<i>X</i> ₁	$mN \cdot m^{-1}$	$\overline{\text{mN}\cdot\text{m}^{-1}}$	X_1	$\overline{\text{mN}\cdot\text{m}^{-1}}$	$mN \cdot m^{-1}$	X_1	$\overline{\text{mN}\cdot\text{m}^{-1}}$	$\overline{\text{mN}\cdot\text{m}^{-1}}$
					$x_3 =$	0.000					
0.000	70.4	+1.1	0.010	61.8	$+0.8^{\circ}$	0.052	49.1	-1.4	0.158	36.8	+0.2
0.002	68.4	+1.2	0.013	60.4	0.0	0.061	48.1	-2.0	0.184	35.3	+0.1
0.003	65.7	+2.5	0.016	58.4	+0.1	0.071	47.8	-3.0	0.210	33.7	+0.2
0.004	65.8	+1.6	0.025	56.1	-1.4	0.091	42.4	0.0			
0.006	64.7	+0.4	0.034	53.2	-1.3	0.112	40.4	0.0			
0.008	62.8	+1.0	0.043	51.0	-1.4	0.135	38.9	-0.3			
					$x_3 =$	0.001					
0.000	71.6	+0.5	0.007	64.5	+0.4	0.030	52.8	0.0	0.132	39.9	-1.1
0.002	71.9	-0.1	0.015	59.5	-0.1	0.038	51.2	-0.7	0.182	34.8	+0.7
0.004	69.0	+0.1	0.022	56.6	-0.9	0.082	45.5	-2.2			
					$\chi_3 =$	0.003					
0.000	71.4	+0.8	0.007	69.2	$+0.1^{\circ}$	0.030	53.9	-0.6	0.132	38.7	0.0
0.002	71.6	+0.6	0.015	61.3	0.0	0.038	51.7	-1.0	0.183	34.2	+1.1
0.004	71.3	+1.0	0.022	56.3	+0.2	0.082	44.1	-0.9	0.132	38.7	0.0
	$x_3 = 0.006$										
0.000	71.2	+1.1	0.007	71.6	+0.8	0.030	55.8	-0.2	0.189	34.6	+0.4
0.002	71.4	+0.8	0.015	67.3	0.0	0.038	52.9	-0.6	0.131	38.7	+0.1
0.004	71.6	+0.7	0.022	60.0	+0.5	0.082	44.6	-1.1	0.189	34.6	+0.4
	$x_3 = 0.008$										
0.000	71.9	+0.4	0.007	71.9	+0.7	0.038	54.7	-0.5	0.131	38.7	+0.2
0.002	71.7	+0.5	0.015	72.1	-1.9	0.046	50.4	+0.7	0.189	34.6	$+0.2 \\ +0.4$
0.002	71.7	+0.5	0.013	58.1	+0.2	0.040	45.5	-1.5	0.103	34.0	10.4
0.001	71.7	10.0	0.000	00.1		0.026	10.0	1.0			
0.000	72.4	+0.2	0.002	72.3	0.0^{-3}	0.020	70.4	+1.5	0.037	71.2	0.0
0.000	70.9	+1.6	0.002	71.2	+0.9	0.007	70.4	+0.2	0.037	46.8	+8.0
0.001	70.5	11.0	0.003	71.2			12.2	10.2	0.000	40.0	10.0
0.000	73.1	-0.1	0.003	72.2		0.052	72.0	-0.4			
0.000					+0.3	0.018	72.9				
$0.001 \\ 0.002$	73.0 72.7	$^{+0.4}_{+0.5}$	$0.004 \\ 0.007$	72.9 73.0	$0.0 \\ -0.4$	$0.038 \\ 0.089$	70.3 71.5	$^{+2.8}_{-3.8}$			
0.002	12.1	±0.5	0.007	73.0			71.3	-3.6			
0.000	740		0.000	740	$x_3 =$	0.090	~ 4 ~	0.0	0.000	~4.4	0.4
0.000	74.0	+0.8	0.002	74.9	-0.4	0.007	74.7	-0.9	0.038	74.1	-0.4
0.001	73.8	+0.9	0.003	73.7	+0.5	0.018	74.4	-1.0	0.088	72.4	0.0
						0.125					
0.000	74.7	+0.5	0.002	75.0	0.0	0.007	74.2	+0.1	0.038	74.6	-0.7
0.001	74.7	+0.4	0.004	74.7	0.0	0.018	75.0	-1.2	0.089	69.1	+4.0
						0.180					
0.000	75.2	-0.1	0.002	75.2	-0.4	0.007	74.9	-0.8	0.036	74.0	-0.5
0.001	75.2	-0.2	0.003	75.5	-1.0	0.017	74.7	-1.1	0.084	72.4	+0.8
						0.250					
0.000	73.6	+0.9	0.002	73.9	+0.3	0.007	72.9	+0.6	0.037	70.6	+2.3
0.001	73.5	+0.8	0.003	72.3	+1.6	0.017	70.9	+2.0			
					$x_3 =$	0.350	_				
0.000	72.3	+0.7	0.002	71.8	+0.8	0.007	71.9	0.0	0.038	72.2	-0.9
0.001	72.0	+0.8	0.003	72.1	+0.2	0.018	72.0	-0.6	0.087	71.1	0.0
					$\chi_3 =$	0.480					
0.000	69.4	+0.4	0.002	68.3	$+1.1^{\circ}$	0.007	68.2	+0.4	0.037	66.8	+1.1
0.001	68.5	+1.0	0.004	68.8	+0.2	0.017	68.3	-0.3	0.087	67.5	+0.2

 $[^]a$ $\Delta\sigma$ is the difference of the value given by eq 5 compared to the measurement.

Germany) using the Wilhelmy plate method.¹⁵ Temperature was controlled with a circulation liquid path (Lauda RC6 CS). The temperature of the liquid bath was set at 25 °C. Temperature measurements of the sample liquids showed that all measurements were made at 24.2 °C. Dimethylamine was 40 mass % aqueous solution (Sigma-Aldrich), because of its low boiling point (7.4 °C). Sulfuric acid was a J. T. Baker product with a purity of 96 mass %. Water was purified to ultrapure quality (Milli-Q, 18 M).

The surface tensions of dimethylamine + sulfuric acid + water were measured with dimethylamine mol fraction ($x_{\rm DIMA}$) of 0–0.21 (0–40 mass %) and sulfuric acid mol fractions ($x_{\rm H_2SO_4}$) of 0–0.48 (0–80 mass %). In each measurement set, the mol fraction of sulfuric acid was constant and the mol fraction of dimethylamine was changed.

Measuring one set took about 8 h. The samples were prepared by mass so that the required amount of sulfuric acid was first diluted from the original 96% solution with water, after which dimethylamine was added to the solution. The sample had to be cooled as the reaction between dimethylamine and sulfuric acid is quite exothermic. In a typical surface-tension measurement, a sample with a volume of about 20 mL was inserted in the tensiometer in a glass container and mixed thoroughly with a magnetic stirrer. After mixing, the platinum plate was submerged in the sample and the measurement performed immediately. Time-dependent measurements were also performed, in which the platinum plate was left in the sample and the change in the surface tension was observed.

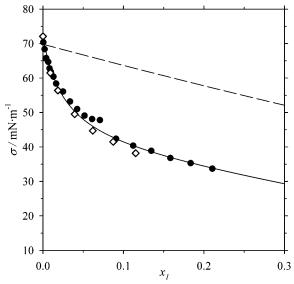


Figure 1. Surface tensions, σ , as a function of mol fraction of the base, x, of aqueous dimethylamine and ammonia solutions at 25 °C. ●, dimethylamine, this work; ♦, Mmereki et al.; 12 solid line, eq 5; dashed line, ammonia, ref 18.

The tensiometer was first tested by comparing measured surface tensions of *n*-alcohols to their literature values at 25 °C. All the measurements were found to be within 0.5% of the literature values. 16 Test results with distilled water were found to be within 1.0% of the literature value at 25 °C.14 Substances were weighted with a Precisa junior 310M balance (absolute accuracy 0.002 g) with an uncertainty of about 0.1%. This corresponds to an uncertainty of 0.1% in mol fractions. The biggest uncertainty arises from the low boiling point of dimethylamine (+7.4 °C). With large amounts of dimethylamine ($x_{DIMA} > 0.13$), there was an increase of surface tension with time. This happens when dimethylamine evaporates from the surface, thus changing the composition of the surface. A similar effect has been found also with surface-tension measurements of ammonia-water.¹⁷ The maximum deviation recorded in the time-dependent measurements was 4 mN·m⁻¹ in 40 min. This was the time after which the surface tension of the solution had stabilized. At lower mol fractions of dimethylamine, little or no change in the surface tension was observed and the maximum deviation was 1 mN·m⁻¹ in 10 min, after which the solution had stabilized. The total uncertainty of the surface tension measurements was estimated to be less than 2%.

The solutions for the density measurements were prepared in a manner similar to the surface tension measurements. A small sample volume of 10-15 mL was collected from a ready solution with a volumetric pipet and weighed. The accuracy of this method was tested with purified water at 25 °C. The test results were within 0.5% of the literature values. 14 The accuracy of the volumetric pipets was 0.02 mL for the 10-mL pipets and 0.03 mL for the 15-mL pipets. The same weighing balance was used as before (Precisa junior 310M). The accuracies of the pipet volumes and the balance cause an inaccuracy of about 0.3% to the density measurements. The error that constitutes of dimethylamine evaporation and other factors was estimated to be 0.5%. The total uncertainty of the density measurements was estimated to be less than 1.0%.

Results and Discussion

The measured surface tensions of sulfuric acid + dimethylamine + water with different mole fractions of

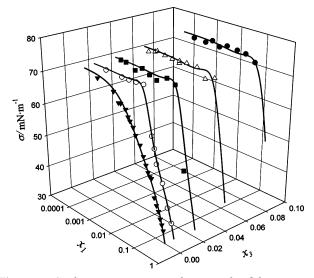


Figure 2. Surface tensions, σ , as a function of mol fractions, x_i , of sulfuric acid (i = 3) + dimethylamine (i = 1) + water. \bullet , x_3 = 0.090; \triangle , $x_3 = 0.052$; \blacksquare , $x_3 = 0.026$; \bigcirc , $x_3 = 0.008$; \blacktriangledown , $x_3 = 0.000$; solid line, eq 5.

Table 2. Parameters Used in Equation 5

parameter	value
С	$\frac{ax_3x_1 + bx_3^2x_1^2 + cx_1^2}{ax_3x_1 + bx_3^2x_1^2 + cx_1^2}$
D	$x_3^2 + dx_3x_1 + ex_3^2x_1^2 + fx_1^2$
a	4.10
b	476
c	-0.254
d	-2.12
e	109
f	1.08

sulfuric acid and dimethylamine are presented in Table 1. In the binary dimethylamine + water solution, the surface tension decreases fast as dimethylamine is added, see Figure 1. At the maximum dimethylamine mol fraction of 0.21, the surface tension is 34 mN·m⁻¹. This is less than half when compared to the surface tension of pure water $(72 \text{ mN} \cdot \text{m}^{-1}).$

The fast decrease of surface tension as a function of concentrations implies that dimethylamine partitions to the surface. As a comparison, ammonia—water surface tensions are also plotted in Figure 1. Surface tension of the ammonia + water solution is a fit18 to literature data.19 Dimethylamine lowers the surface tension as a function of mol fraction more efficiently than ammonia. At the mol fraction of 0.21, the ammonia−water surface tension is 57 mN·m⁻¹, which is 24 mN·m⁻¹ higher than the surface tension of dimethylamine. There is a slight scatter in our data around the dimethylamine mol fraction of 0.5-0.7. This is due to experimental errors. Our results were also compared to those measured by Mmereki et al.12 The results are in good agreement with each other, especially at lower dimethylamine mol fractions. At higher mol fractions ($x_{DIMA} > 0.1$), our results are about 2 mN·m⁻¹ higher than those by Mmereki et al.

Dimethylamine also decreases the surface tension of the ternary system, see Figure 2. For example, at the sulfuric acid mol fraction of 0.026 (~11 mass %) and the dimethylamine mol fraction of 0.086 (\sim 17 mass %), the surface tension experiences a sharp change. At the same time, there is a change in pH between acidic and alkaline. Twice as much dimethylamine is needed with respect to sulfuric acid to produce a neutral solution. It can be seen in Table 1 and Figure 2 that, if dimethylamine is added beyond this

Table 3. Measured Densities, ρ , of Sulfuric Acid (i = 3) + Dimethylamine (i = 1) + Water as a Function of Mol Fractions, x_b of Sulfuric Acid and Dimethylamine^a

			J								
	ρ	Δho		ρ	Δho		ρ	Δho		ρ	Δho
<i>X</i> ₁	kg⋅m ⁻³	kg∙m ⁻³	X_1	kg⋅m ⁻³	kg∙m ⁻³	x_1	kg⋅m ⁻³	kg⋅m ⁻³	X_1	kg⋅m ⁻³	kg⋅m ⁻³
					$\chi_3 =$	0.000					
0.001	998	-0.9	0.008	987	$+5.3^{\circ}$	0.034	969	+8.6	0.146	918	-0.3
0.002	994	+1.8	0.016	984	+3.5	0.043	967	+5.5	0.210	888	-0.5
0.004	988	+6.8	0.025	974	+8.5	0.091	941	+5.0			
					$\chi_3 =$	0.001					
0.000	998	+2.6	0.007	994	$+2.3^{\circ}$	0.030	980	+2.9	0.131	928	+1.3
0.002	997	+2.5	0.015	991	+0.9	0.038	974	+4.3	0.188	901	-0.5
0.004	994	+4.4	0.022	985	+2.4	0.082	950	+4.0			
					$\chi_3 =$	0.003					
0.000	1005	+2.4	0.007	1001	+2.2	0.030	988	+1.3	0.132	934	-0.2
0.002	1003	+3.3	0.015	998	+0.5	0.038	982	+2.3	0.190	905	+0.4
0.004	1007	-1.9	0.023	994	-0.1	0.082	957	+2.9			
					$\chi_3 =$	0.006					
0.000	1017	+0.4	0.007	1011	+1.9	0.031	999	-0.1	0.134	943	-1.1
0.002	1013	+3.3	0.015	1011	+5.5	0.039	993	+1.1	0.193	912	+0.7
0.004	1015	+0.2	0.023	1003	+0.6	0.083	968	+1.0			
					$x_2 =$	0.008					
0.000	1024	+0.1	0.007	1015	+4.5	0.031	1007	-1.8	0.135	948	-0.8
0.002	1018	+4.9	0.015	1016	-1.2	0.039	1003	-2.7	0.195	917	+0.5
0.004	1019	+2.8	0.023	1016	-6.0	0.084	974	+0.7	0.100	011	. 0.0
					v ₂ —	0.026					
0.000	1085	-3.7	0.002	1082	-1.6	0.007	1071	+6.0	0.037	1061	-3.8
0.001	1084	-3.1	0.003	1080	-0.8	0.017	1071	-1.1	0.086	1039	-11.9
						0.052					
0.000	1156	+0.5	0.002	1157	-1.5	0.002	1153	-1.2	0.038	1127	+2.1
0.001	1156	+0.2	0.002	1156	-1.7	0.018	1141	+2.7	0.089	1109	-14.3
					$x_3 =$						
0.000	1253	-0.4	0.002	1253	-1.5	0.090	1245	+2.1	0.038	1216	+5.5
0.000	1251	+1.3	0.002	1245	-0.1	0.014	1235	+6.1	0.038	1184	-1.1
3.001	1201	11.0	0.001	12.10		0.125	1200	1 0.1	0.000	1101	1.1
0.000	1328	+0.2	0.002	1329	$x_3 = -2.1$	0.125	1316	+6.2	0.038	1289	+5.0
0.000	1333	-5.0	0.002	1331	$-2.1 \\ -5.6$	0.007	1310	+3.5	0.038	1258	-6.8
0.001	1555	3.0	0.003	1331			1312	1 3.3	0.000	1230	0.6
0.000	1422	151	0.000	1425		0.180	1410	179	0.026	1070	1110
0.000	1422 1427	$^{+5.1}_{-0.8}$	$0.002 \\ 0.003$	1425 1421	$^{+0.4}_{+2.6}$	$0.007 \\ 0.017$	1413 1402	$^{+7.2}_{+7.5}$	$0.036 \\ 0.084$	1378 1337	$^{+11.9}_{+6.4}$
0.001	1427	-0.8	0.003	1421			1402	+7.5	0.084	1337	± 0.4
						0.250					
0.000	1528	-2.7	0.002	1527	-3.7	0.007	1513	+4.2	0.037	1478	+3.7
0.001	1525	-0.7	0.004	1516	+5.1	0.018	1498	+6.5	0.086	1428	-0.6
					$\chi_3 =$						
0.000	1622	+10.2	0.002	1636	-6.1	0.007	1625	-2.2	0.038	1591	-10.0
0.001	1632	-0.9	0.003	1625	+2.5	0.018	1608	-0.1	0.087	1532	-14.9
					<i>X</i> ₃ =	0.480					
0.000	1725	+19.3	0.002	1742	-0.5	0.007	1727	+6.0	0.037	1709	-24.3
0.001	1748	-4.8	0.003	1734	+5.1	0.017	1722	-5.9	0.086	1611	-0.2

 $^{^{}a}\Delta\rho$ is the difference of the value given by eq 6 compared to the measurement.

Table 4. Parameters Used in Equation 6

	-				
parameter	value				
a b c d e f	-4410 9090 -7230 3420 -600 220				
g h	$-800 \\ 180$				

point, surface tensions start to drop, approaching the values of pure dimethylamine—water solutions. It seems evident that, when the salt-forming process of dimethylamine + sulfuric acid has used up all the sulfuric acid, the excess dimethylamine partitions to the surface. The effect can be seen more clearly with lower sulfuric acid mol fractions. At the sulfuric acid mol fractions of 0.052 and above (20 mass %), the measured surface tensions remain

unaffected with the addition of dimethylamine. They are close to those of pure sulfuric acid + water, around $70\!-\!75$ mN·m $^{-1}$. The mol fraction of dimethylamine could be increased only up to a limited mol fraction because of the original 40 mass % aqueous dimethylamine solution. It is likely that when the solution turns alkaline as dimethylamine is added, its surface tension would decrease also with higher sulfuric acid concentrations.

The experimental binary water + dimethylamine surface tensions were fitted to an equation based the equation presented by Chunxi et al. 20

$$\sigma_{21}/\text{N}\cdot\text{m}^{-1} = x_2\sigma_2 - \frac{x_1x_2B}{1 + x_1A} = (1 - x_1)(\sigma_2/\text{N}\cdot\text{m}^{-1}) - \frac{x_1(1 - x_1)B}{1 + x_1A}$$
(2)

In eq 2, σ is the surface tension and x is the mol fraction.

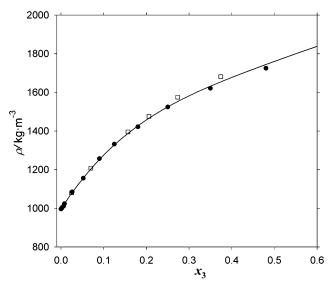


Figure 3. Density, ρ , as a function of mol fraction x_i of sulfuric acid (i = 3) + water. \bullet , this work; \square , Myhre et al.; ¹³ solid line, eq 6.

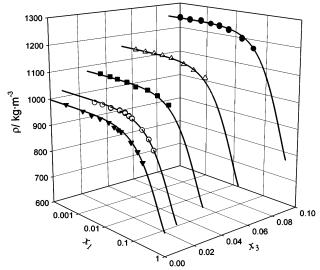


Figure 4. Densities, ρ , as a function of mol fractions, x_i , of sulfuric acid (i = 3) + dimethylamine (i = 1) + water. \bullet , $x_3 = 0.090$; \triangle , x_3 = 0.052; \blacksquare , $x_3 = 0.026$; \bigcirc , $x_3 = 0.008$; \blacktriangledown , $x_3 = 0.000$; solid line, eq 6.

Subscripts 1 and 2 denote pure dimethylamine and water, respectively. The fitting parameters A and B are

$$A = 37.9 \tag{3}$$

and

$$B = 1.241$$
 (4)

The experimental values of surface tensions of the ternary system are presented in Table 1. They were fitted to the equation

$$\sigma = \frac{Cx_3}{Cx_3 + Dx_1} \,\sigma_{23} + \frac{Dx_1}{Cx_3 + Dx_1} \,\sigma_{21} \tag{5}$$

In eq 5, x_3 is the mol fraction of sulfuric acid and σ_{23} is the surface tension of binary sulfuric acid + water. The fitting parameters C and D are polynomial functions listed in Table 2. For the surface tension of binary sulfuric acid + water solutions, an equation presented in Myhre et al. 13 was used. The difference between the measured surface tensions and those calculated with eq 5 are listed in Table 1. The fitted curves at constant mol fraction of sulfuric acid have a mean deviation ranging from 0.5 mN·m-1 to 1.5 mN·m⁻¹ from the measured values. The maximum deviation is 8.0 mN·m⁻¹ at the sulfuric acid mol fraction of 0.026 and the dimethylamine mol fraction of 0.086. An example of the measured surface tensions and the fitted curves is presented in Figure 2. Equation 5 is valid in the dimethylamine mol fraction range of 0.0-0.3, as it is fitted to the experimental points. Extrapolating the equation to higher mol fractions would not give meaningful results. At higher mol fractions of dimethylamine, the solution would boil unless the measurements were made at higher pressure than 1 bar or lower temperature than 25 °C. Thus, the measurement conditions would not be consistent with each other.

The measured densities of sulfuric acid + dimethylamine + water are presented in Table 3. The densities were fitted to the equation

$$\rho/\text{kg}\cdot\text{m}^{-3} = (ax_3^4 + bx_3^3 + cx_3^2 + dx_3 + (\rho_2/\text{kg}\cdot\text{m}^{-3})) \exp(ex_1 + fx_1^2 + gx_1x_3 + hx_1x_3^2)$$
 (6)

where ρ_2 is the density of water. Parameters *a* to *h* are listed in Table 4. The differences between the measured densities and those calculated from eq 6 are also listed in Table 3. The fitted curves at constant mol fractions of sulfuric acid have a mean deviation ranging from 2 kg·m⁻³ to 7 kg·m⁻³ from the measured values. The densities of binary sulfuric acid + water are compared to those measured by Myhre et al. 13 in Figure 3. The results are in fairly good agreement with each other, although our results are about 15 kg·m⁻³ lower than those by Myhre et al. at a sulfuric acid mol fraction of 0.27. An example of the measured densities of the sulfuric acid + dimethylamine + water system along with the fitted curves from eq 6 is presented in Figure 4.

Conclusions

Dimethylamine was found to lower the surface tension to a greater extent than ammonia in aqueous solutions. Our measurements also show that dimethylamine lowers the surface tension of sulfuric acid + water solutions when the mol fraction ratio between dimethylamine and sulfuric acid is greater than 2, i.e., when the pH of the bulk liquid turns alkaline.

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