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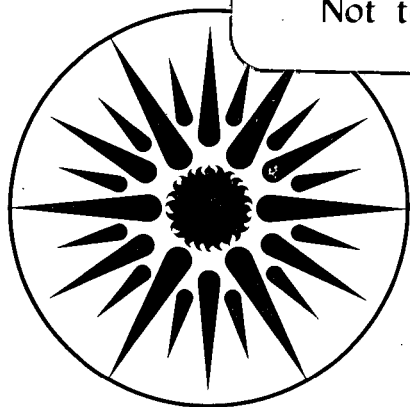
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The Solubility of the Potassium Salts of Nitrogen-Sulfur Compounds in Aqueous Solution

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Abstract

The aqueous solubility of the potassium salts of hydroxyimidodisulfate (HADS), hydroxysulfamic acid (HAMS), nitridotrisulfate (ATS), and imidodisulfate (ADS) have been determined by Raman spectrometry and ion chromatography over a temperature range of 0°C to 50°C. The compounds were synthesized and saturated solutions were prepared in a controlled-temperature bath. The solutions were diluted with either a reference solution, for Raman analysis, or with water, for ion chromatographic analysis. Equations for the solubilities were derived as a function of temperature. The effects of the solubilities of the nitrogen-sulfur compounds on the operation of wet flue gas scrubbing systems is discussed.

Introduction

The nitrogen-sulfur compounds hydroxyimidodisulfate (or hydroxylamine disulfonate, HADS), hydroxysulfamate (or hydroxylamine monosulfamate, HAMS), nitridotrisulfate (or amine trisulfonate, ATS), and imidodisulfate (or amine disulfonate, ADS) are formed by the reaction of nitrite ion with bisulfate ion in aqueous solution (Chang et al., 1982). Hydroxylamine and sulfamate are formed by hydrolysis of HAMS and ADS, respectively (Littlejohn et al., 1989; Doyle and Davidson, 1949). The reaction sequence for the nitrogen-sulfur compounds is shown in Fig. 1. These compounds are of considerable importance in wet flue gas scrubbing systems, since they build up in the scrubbing liquor. They are moderately stable in aqueous solution at conditions typically found in scrubbing liquors. While the nitrogen-sulfur materials are not believed to be hazardous (Felton, 1985), the solutions containing them generally will require treatment prior to disposal. Precipitation is probably one of the more cost-effective methods for removing the nitrogen-sulfur compounds from solution. There is little information in the literature on the solubilitiy of nitrogen-sulfur compounds, although potassium salts are the ones isolated when the compounds are prepared (Rollefson and Oldershaw, 1932; Sisler and Audrieth, 1948; Nast et al., 1952). The potassium salts of nitrogen-sulfur compounds are generally regarded as the least soluble of the common cations. We have undertaken a series of measurements of the potassium salts of nitrogen-sulfur compounds as a function of temperature.

Experimental

The salts of the nitrogen-sulfur compounds were prepared by the methods in the literature (Rollefson and Oldershaw, 1932; Sisler and Audrieth, 1948; Nast et al., 1952). Reagent grade materials were used in the preparation of the nitrogen-sulfur compounds. The 3-form of ADS was prepared by dissolving the ADS salt in warm water and raising the pH to about 11 with KOH. The solution was cooled in an ice bath to precipitate the potassium ADS^{3-} salt. The purity of the solids was checked by Raman spectroscopy. Compounds with impurity peaks were recrystallized.

Saturated solution of the nitrogen-sulfur compounds were prepared by adding excess solid to deionized water. The solutions were stirred continuously and kept in a controlled-temperature bath, where the temperature was maintained to within ±1°C of the desired temperature. The pH of the solutions were checked to insure that they were within the desired range. The pK_{a3} of ADS is 8.49 (Doyle and Davidson, 1949), and the ADS solubility measurements were made at pH 6-7 for ADS^{2-} and pH 10-11 for ADS^{3-}. HADS and ATS undergo noticeable hydrolysis at high temperatures, even in alkaline solutions. Consequently, there was a limited amount of time to saturate solutions of these compounds before impurities were formed at the higher temperatures studied.

Three methods were used to determine the concentration of the nitrogen-sulfur compounds in the saturated solution. Most of the measurements were done using Raman spectroscopy, which has been described previously (Littlejohn and Chang, 1984). Peak areas were found to be more accurate for concentration determination than peak heights, and were used in this study. Perchlorate ion was used as a reference for the Raman measurements, since sulfate is a hydrolysis product of the nitrogen-sulfur compounds. An aliquot of the saturated solution was mixed with an aliquot of .050 M ClO_4^- solution. In the case of the measurements at higher temperatures, the dilution prevented precipitation of the nitrogen-sulfur compounds. The concentrations were determined by comparing the area of the 934 cm^{-1} ClO_4^- peak with the peaks of the nitrogen-sulfur compounds. The peaks were assigned relative scattering efficiency (RSE) values using the equation

$$RSE = \frac{(\text{area of peak of X}) / [X]}{(\text{area of } ClO_4^- \text{ 934 } cm^{-1} \text{ peak}) / [ClO_4^-]} \qquad (1)$$

and measurements on solutions of known concentrations. The ClO_4^- 934 cm^{-1} peak was assigned a value of 1.00. The RSEs for the compounds under study are listed in Table I.

Ion chromatography (IC) was also used in measurement of the concentrations of HADS and ADS saturated solutions (Littlejohn and Chang, 1986). Aliquots of the saturated solutions were diluted to concentrations that were in the range of linear response of the ion chromato-

graph. The dilution factor was typically about 10^4. The IC peak height of the diluted solution under study was compared with the peak heights of injections of a standard solution made before and after the injection of the unknown.

HADS was also analyzed by oxidation to nitrosodisulfonate (NDS, also known as Fremy's salt) and colorimetric analysis of NDS at 545 nm (Oblath, 1981; Murib and Ritter, 1952). One ml of saturated HADS solution was mixed with 0.9 ml of 1 M silver nitrate solution, 0.1 M of 10 N sodium hydroxide, and 3 ml of water. It was then centrifuged to remove the silver oxide precipitate and the absorbance was measured at 545 nm. An extinction coefficient of 20 M^{-1} cm^{-1} was used to determine the NDS concentration and calculate the original HADS concentration. The results of the colorimetric measurements agreed well with those obtained by other methods.

The solubility of potassium sulfamate was previously measured by Ricci and Selikson (1949). We measured the densities of potassium sulfamate solutions at a range of concentrations at 25°C. Potassium sulfamate solutions were prepared by neutralizing a sulfamic acid solution with potassium hydroxide. Aliquots of the solutions were weighed on an electronic balance. The solution density can be expressed as

$$d = 0.9875 + 0.0578 \times [\text{sulfamate (m)}] \quad \text{for } 0.2 < m < 5.6 \qquad (2)$$

These measurements were then used to convert their values into units of molarity to make them compatible with our measurements.

Results and Discussion

The results of the solubility studies of the potassium salts of ATS and ADS^{2-} are shown in Fig. 2. Both of these salts have solubilities well below 1 M, even at high temperatures. The solubilities of HADS, ADS^{3-}, and HAMS are shown in Fig. 3. The solubilities of HADS and ADS^{3-} are fairly close. The solubility of potassium sulfamate is well in excess of all of these compounds. Least-squares fits to the data yield the following equations for the solubility in molar units (M).

$$[ATS] = 3.835e\text{-}3 + 4.13e\text{-}4 \times T \qquad\qquad T = 0\text{-}70°C \qquad (3)$$

$$[ADS^{2-}] = .0252 + 9.395e\text{-}4 \times T + 4.24e\text{-}5 \times T^2 \quad T = 0\text{-}50°C \qquad (4)$$

$$[ADS^{3-}] = .134 + 7.46e\text{-}3 \times T + 4.92e\text{-}5 \times T^2 \qquad T = 0\text{-}40°C \qquad (5)$$

$$[HADS] = .137 + 6.417e\text{-}4 \times T + 1.414e\text{-}4 \times T^2 \quad T = 0\text{-}50°C \qquad (6)$$

$$[HAMS] = .433 + .0454 \times T \qquad\qquad T = 0\text{-}40°C \qquad (7)$$

$$[sulfamate] = 2.023 + .09314 \times T \qquad\qquad T = 20\text{-}35°C \qquad (8)$$

The equation for the sulfamate solubility was adapted from the results of Ricci and Selikson (1947). Within the uncertainty of the data, the solubilities of ATS, HAMS and sulfamate had a linear dependence on temperature. The solubilities of the other compounds displayed significant non-linear temperature dependence.

The 3- form of ADS is the dominant form of ADS only above pH 8.5, and is unlikely to be present in significant quantities in most limestone-based scrubbing liquors. From Fig. 1 and the equations above, it is observed that the nitrogen-sulfur compounds formed first, HADS and ATS, are less soluble than their respective hydrolysis products. They are more susceptible to hydrolysis than their hydrolysis products, HAMS and ADS. These factors indicate that, to most efficiently remove nitrogen-sulfur compounds from flue gas scrubbing liquor, prompt precipitation of HADS and ATS is desirable. Operation at relatively high pH conditions would be helpful to slow hydrolysis to HAMS and ADS, which are more difficult to remove. However, this would tend to increase the concentration of NO_2^- in solution, which is also difficult to remove. Since ATS is less soluble than HADS, it would be beneficial to operate the scrubber at high bisulfite concentrations, to aid in the conversion of HADS to ATS and ADS. Lowering the temperature of the scrubbing liquor would also assist in the removal of the nitrogen-sulfur compounds. Optimal conditions for removal of the nitrogen-sulfur compounds could be determined by modeling the chemistry of the scrubbing liquor (Littlejohn and Chang, 1991). After separation from the scrubbing liquor, the precipitated nitrogen-sulfur compounds could be given thermal treatment to generate potassium sulfate. This could then be used to

increase the potassium concentration of the scrubbing liquor rich in nitrogen-sulfur compounds to precipitate their potassium salts.

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Table I

Relative Scattering Efficiencies of Compounds Used in this Study

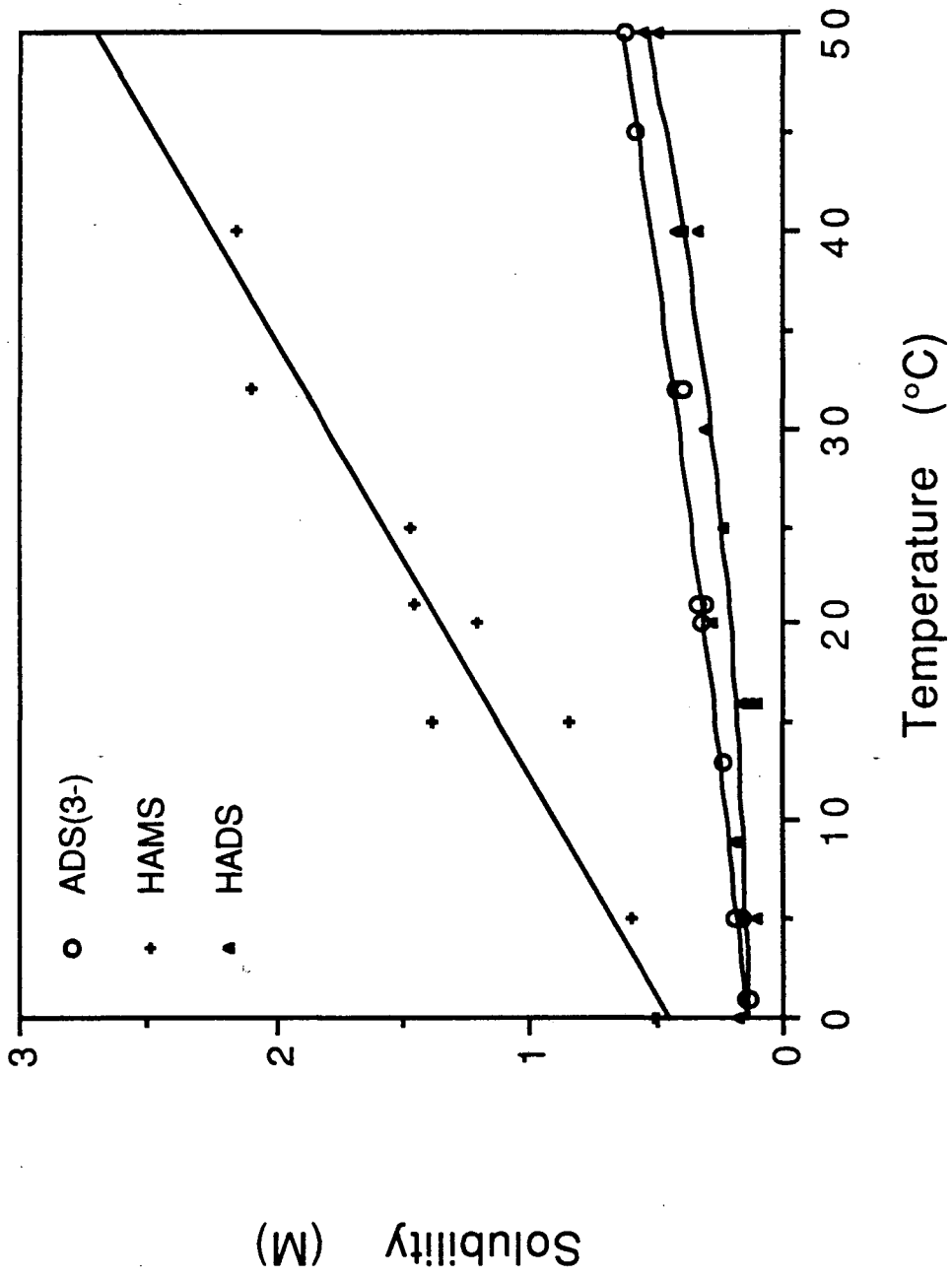| Compound	Raman Shift	Area RSE
ClO_4^-	934 cm^{-1}	1.00
SO_4^{2-}	981 cm^{-1}	0.72
HADS	1083 cm^{-1}	1.00
HAMS	1058 cm^{-1}	0.55
ATS	1097 cm^{-1}	1.20
ADS^{2-}	1085 cm^{-1}	1.00
ADS^{3-}	1063 cm^{-1}	0.65
sulfamate	1050 cm^{-1}	0.50

Figure Captions

1. Reactions involved with the formation and interconversion of nitrogen-sulfur compounds used in this study.

2. Solubility of the potassium salts of ATS and ADS^{2-} as a function of temperature.

3. Solubility of the potassium salts of HADS, ADS^{3-} and HAMS as a function of temperature.

$$HONO + 2HSO_3^- \longrightarrow HON(SO_3^-)_2 \xrightarrow{\;HSO_3^-\;} N(SO_3^-)_3$$

$$\text{(HADS)} \qquad\qquad\qquad \text{(ATS)}$$

$$\downarrow H^+ \qquad \searrow HSO_3^- \qquad\qquad \downarrow H^+$$

$$NO_2^- + N_2O \xleftarrow{\;O_2\;} HONH(SO_3^-) \xrightarrow{\;HSO_3^-\;} HN(SO_3^-)_2$$
$$+\; SO_3^{2-} + SO_4^{2-}$$

$$N_2O + SO_3^{2-} \qquad\qquad \text{(HAMS)} \qquad\qquad \text{(ADS)}$$

$$\text{OH}^- \qquad\qquad \downarrow H^+ \qquad \searrow HSO_3^- \qquad \downarrow H^+$$

$$NH_2OH \xrightarrow{\;SO_2\;} H_2NSO_3^-$$

Temperature (°C)

Solubility (M)

ADS(3-) ○

HAMS +

HADS ◄
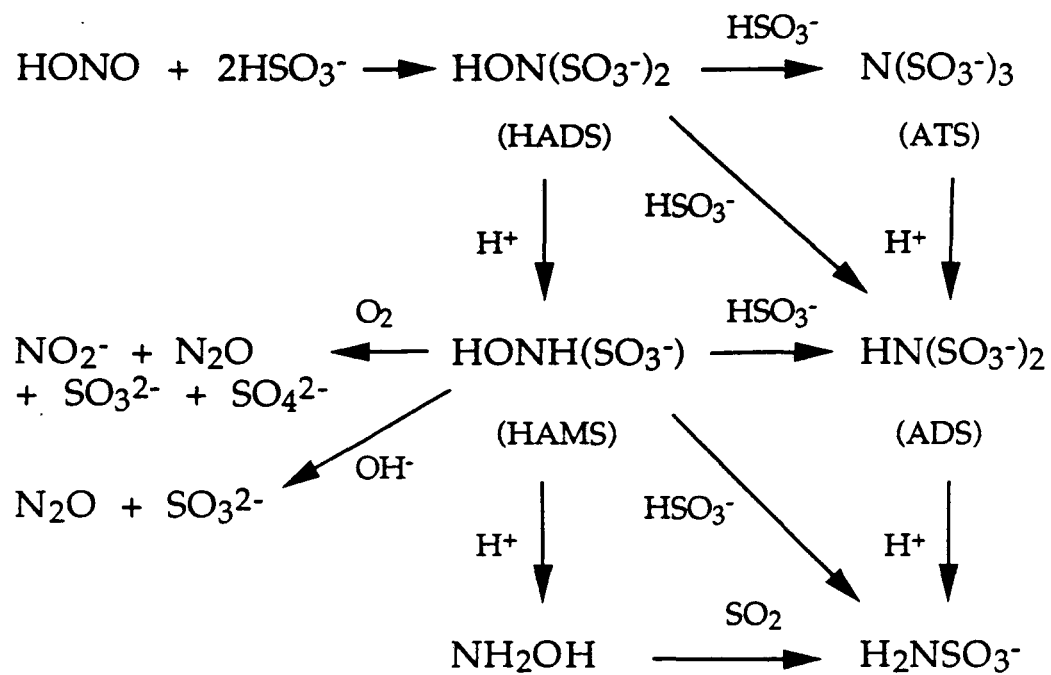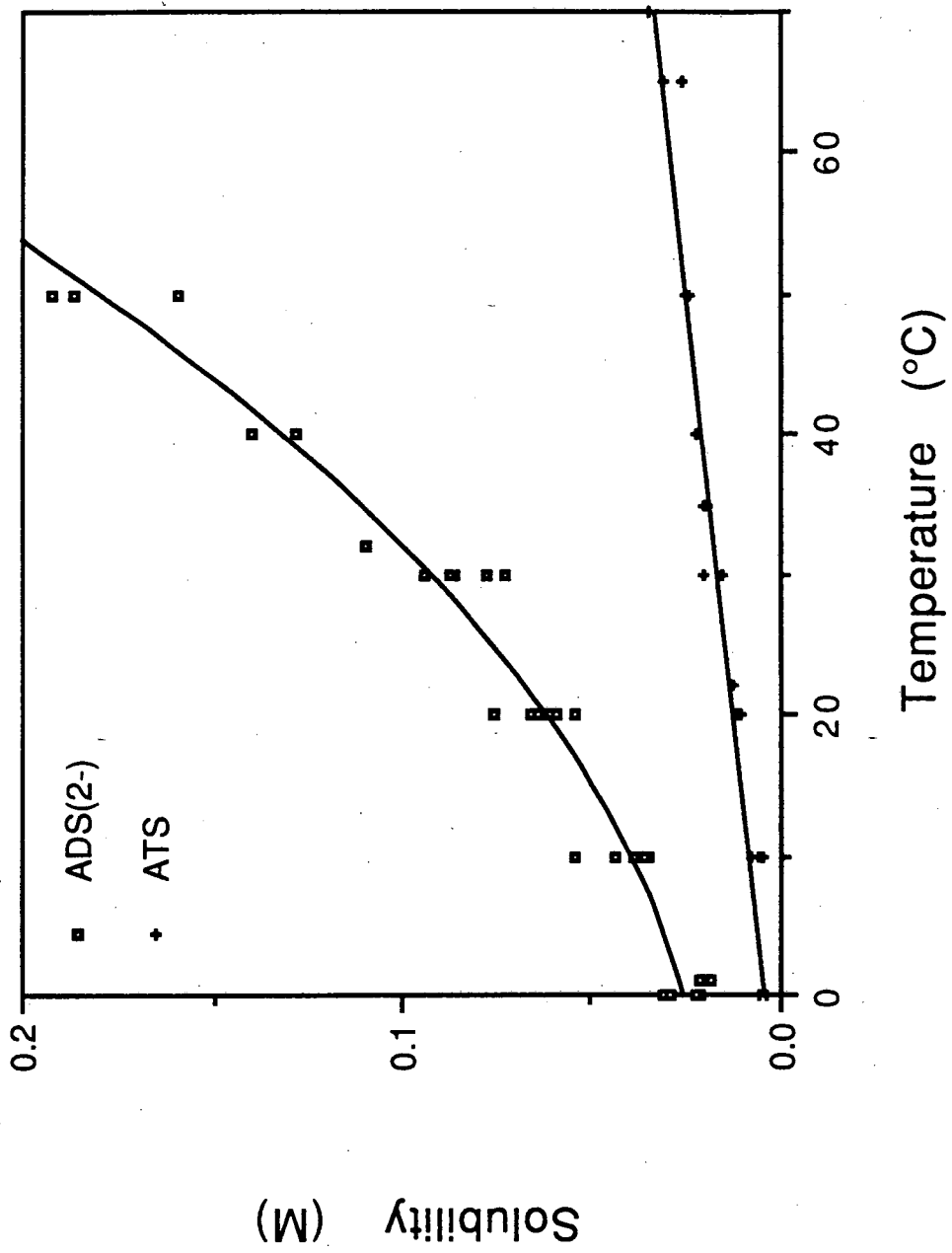
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