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PHYSICAL-CHEMICAL EXAMINATION OF THE \( \text{N}_2\text{O}_3-\text{SO}_3-\text{H}_2\text{O} \) SYSTEM

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When (NO)HSO₄ is added to absolute H₂SO₄, specific conductivity rises sharply, possibly due to an increase in mutual interionic effects and viscosity as the (NO)HSO₄ concentration rises. The addition of SO₃ to the solution yields a precipitate; a combination of analysis, IR spectroscopy and x-ray diffraction techniques indicates that this precipitate is (NO)HS₂O₇.
Hantsch's determinations of the molar mass of (NO)HSO$_4$ in absolute sulfuric acid [1] yielded a mean value of 71.4 for four values varying from 70.8 to 72.5; whereas the calculated value was 127.076. Thus (NO)HSO$_4$ is highly dissociated in absolute H$_2$SO$_4$.

It was therefore of interest to investigate how the addition of (NO)HSO$_4$ to absolute H$_2$SO$_4$ affects the specific conductivity of anhydrous sulfuric acid. It develops that at first, specific conductivity rises sharply as the solution's (NO)HSO$_4$ content increases (Fig. 1). Each of the three isotherms demonstrates a maximum, the position of which is displaced as a function of temperature from $\kappa = 0.1100 \ \Omega^{-1} \text{cm}^{-1}$ at 25 °C and 21.8 Mol% (NO)HSO$_4$ to $\kappa = 0.340 \ \Omega^{-1} \text{cm}^{-1}$ at 75 °C and 25.5 Mol% (NO)HSO$_4$.

The initial rise in the isotherms corresponds to the conductivity isotherm curves obtained by Gillespie and Wasif [2] and Bass, Flowers et al. [3] for solutions of alkaline and alkaline earth hydrogen sulfates in absolute H$_2$SO$_4$. Gube [4], who examined the viscosity...
of solutions of (NO)HSO$_4$ in absolute H$_2$SO$_4$, found a sharp rise after 20 Mol% (NO)HSO$_4$ at 25 °C, the start of which shifted in the direction of higher concentrations of (NO)HSO$_4$ as the concentration rose. Thus, in addition to the increase in interionic mutual effects as the (NO)HSO$_4$ concentration increases, the sharp increase in viscosity may also be responsible for the decrease in specific conductivity.

The specific conductivity of solutions of (NO)HSO$_4$ in absolute H$_2$SO$_4$ is also decreased by the addition of SO$_3$. A subsequent paper will report on these results.

When SO$_3$ is introduced into a solution of (NO)HSO$_4$, a crystalline solid phase is precipitated. This precipitate was cleared of the mother liquor on clay over P$_4$O$_{10}$ in a desiccator, and then examined by element analysis, IR spectroscopy and x-rays.

The analysis yielded 0.0177 Mol sulfur and 0.0088 Mol nitrogen, or 0.0195 Mol sulfur and 0.0096 Mol nitrogen, respectively. This corresponds to a sulfur-nitrogen molar ratio of 2:1 or 2.05:1.

For IR spectroscopy, the substance was incorporated in Nujol and examined between Si plates in the wave number range 400-2500 cm$^{-1}$. Since Nujol demonstrates its own absorption in the range around 750 cm$^{-1}$, the substance was also incorporated in hexachlorobutadiene and examined in the same wave number range. The readings are given in Fig. 2. A comparison of our results
Fig. 3. X-ray interferences of: a. (NO)HSO₄ (after Stopperka); b. (NO)H₂S₂O₇.
Key: c. Intensity  d. θ in degrees

with data from other authors [5-9] for analogous substances suggests the following correlations for the characterization of this substance:

740 cm⁻¹: νₗₗ S-O-S; 793 cm⁻¹: νₛₛ S-O-S; 960 cm⁻¹: νS-OH;
2304 cm⁻¹: νNO⁺. The exact position of the absorption bands was determined by comparison with calibration spectra obtained for NH₃ and CO.

X-ray diffraction readings for the same substance, given in Fig. 3 together with Stopperka's data for (NO)HSO₄ [10], show differences in comparison with Stopperka's values; these differences, in connection with the analytical and IR-spectroscopic examinations, indicate that the substance examined, which was obtained by introducing SO₃ into solutions of (NO)HSO₄ in anhydrous H₂SO₄, is the (NO)H₂S₂O₇ described by Wartel and Heubei [11].
Further investigations of the system are currently in progress.
REFERENCES