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- (7) High-resolution measurements were made on a Jena Zeiss 2-m grating spectrograph at the University of Copenhagen and on a modified McPherson RS-10 spectrometer at MIT. Other spectroscopic measurements (Figures 1 and 2) were made at Caltech on a Cary 17 spectrophotometer.
- (8) Mingardi and Porter^{6b} reported a very weak ($\epsilon \sim 0.01$) absorption band at $18\,500\text{ cm}^{-1}$. We have found this latter transition to be present in some, but not all, samples studied; it is likely associated with an impurity present in the lattice. For our experiments, large crystals of $\text{K}_3\text{Co}(\text{CN})_6$ were grown in darkness by slow evaporation of saturated, filtered aqueous solutions of commercial material. The resultant crystals were redissolved in water and the process was repeated; crystals from several different batches were used in our studies. Very large crystals were grown from seeds.
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Acidity of Zinc Chloride Solutions

Sir:

In a recent issue of *Inorganic Chemistry* the Hammett acidity function, H_0 , was reported for a series of zinc chloride solutions, and it was concluded that "highly concentrated solutions of certain metal salts must be regarded as strong protonic acids".¹ This conclusion was arrived at by comparing the H_0 of ZnCl_2 solutions with that of other acids at the same (high) molarities. It is the purpose of this correspondence to point out that comparisons of H_0 for the purpose of providing orders of acid strength should be made at the same water activity.²⁻⁴ Figure 1 displays the H_0 values as a function of water activity for the zinc chloride solutions, as well as for several strong acids and phosphoric acid ($\text{p}K_a = 2.15$). The

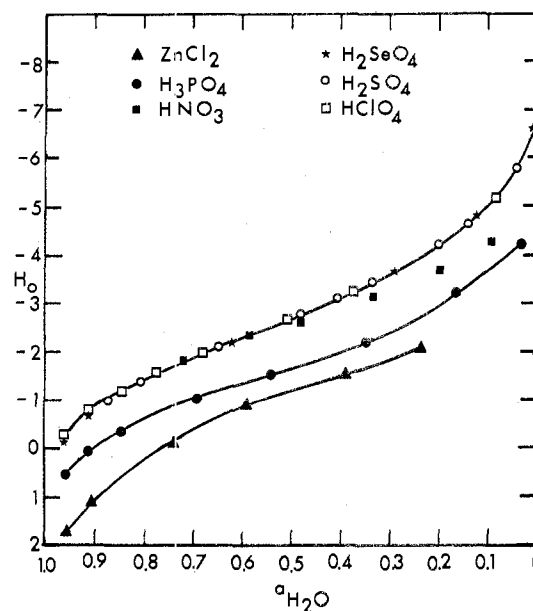


Figure 1. H_0 values of some mineral acid solutions and zinc chloride solutions vs. water activity of the solutions.⁸

curve for nitric acid⁵ is similar to that for the strong acids down to a water activity of 0.6.

From Figure 1 we may conclude that the acidity of the aquozinc ion is less than that of phosphoric acid even at high concentration. More quantitative treatments of acidity from H_0 and $a_{\text{H}_2\text{O}}$ data are available,⁶ but in view of the unknown salting-out effect⁷ of concentrated ZnCl_2 solutions on the neutral indicator, no attempt has been made to apply them.

Registry No. ZnCl_2 , 7646-85-7.

References and Notes

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