

The overall formation constant K_f



is equal to the ratio K_0/K_1K_2 where the product K_1K_2 refers to the $\text{PH}_2/\text{P}^{2-}$ equilibria. The widely quoted¹⁰ $\log K_f = +29$ for zinc mesoporphyrin in detergent solutions is based on the assumption^{1,11} that $K_1K_2 \approx 10^{-32}$. Although tetra(2-*N*-methylpyridyl)porphine decomposes in base, most other natural porphyrins are in the PH_2 form at pH 14. Clarke, Dawson, Grigg, and Rochester¹² have solubilized various porphyrins in toluene and by titrations with NaOH in Me_2SO demonstrated that only the free base dianion (P^{2-}) equilibria occurs, with no evidence for the monoanion PH^- . Since diphenylamine ($\text{p}K_A$ in water = +22.49) was completely ionized in their solvent system under the reaction conditions, K_1K_2 in water for hematoporphyrin IX is probably at least 10^{23} , giving $\log K_f \geq +16$.

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Registry No. PH_2 , 59728-89-1; Zn^{2+} , 23713-49-7; ZnP , 59729-18-9.

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Metal Aquo Ions in Molten Salt Hydrates. A New Class of Mineral Acid?

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Sir:

Hydrolytic dissociation is an important feature in the chemistry of metal aquo ions in aqueous solution and has been the subject of a recent book.¹ Compared with conventional mineral acids the $\text{p}K_a$ values of metal aquo ions are usually greater by several orders of magnitude. At first sight this may seem surprising since one might have expected a *positively* charged acid species, e.g., $\text{Al}^{3+}(\text{aq})$ to be more liable to release protons than would a neutral oxy acid such as HNO_3 ($\text{p}K_a$ values respectively are 4.97 and -1.27). The feeble acidity of the metal aquo ion can plausibly be attributed to the attenuating effects of water molecules outside the coordination sphere. Thus it might be expected that concentrated solutions of metal salts, having an H_2O :metal ion ratio sufficiently low to minimize outer-sphere hydration, would show a marked degree of acidity. Indeed, such behavior has been indicated in a dramatic way by the work of Angell et al. in a proton magnetic resonance study of concentrated aqueous solutions of metal salts.² Furthermore, the application of the optical basicity concept³ (which allows the $\text{p}K_a$ values of oxy acids to be successfully correlated with the Lewis basicities of their oxy anions⁴) also suggests that metal aquo ions should have very high acidities.

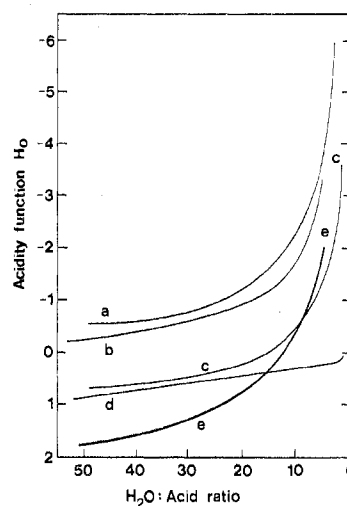


Figure 1. Variation in acidity function H_0 as the H_2O :acid ratio is decreased for the following acids: (a) H_2SO_4 , (b) HCl , (c) H_3PO_4 , (d) $\text{CH}_3\text{CO}_2\text{H}$, (e) ZnCl_2 . (Plots for (a)–(d) are based upon data taken from C. H. Rochester, "Acidity Functions", Academic Press, London and New York, Chapter 2; the ZnCl_2 plot is from results obtained in this study.)

Many molten salt hydrates are liquid at low temperatures (below 400 K say) and in effect are very concentrated solutions with a low H_2O :metal ion ratio. However, their acidic properties, apart from the report of their ability to dissolve noble metals,² have largely been ignored. The most obvious way of measuring their acidity is through the Hammett acidity function,^{5,6} but surprisingly such determinations have never been made for molten salt hydrates. We wish to report that such determinations are feasible, provided that certain practical requirements are fulfilled (e.g., not too high a melting point, good ultraviolet transparency). The best system for initial study was found to be $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$, particularly since this is a liquid at ambient temperature. Figure 1 shows how the acidity function of aqueous solutions of ZnCl_2 varies as the water content is progressively reduced. It is apparent that in dilute solution the $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ (or similar aquo ion) acts as a very weak acid. As the water content decreases, its protonating power increases rapidly, and when the H_2O :acid ratio is less than 9:1 it is stronger than phosphoric acid. The trend in acidity, in the region of composition $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$, is indeed similar to those of the strongest mineral acids.

An investigation into the acidity of molten salt hydrates generally would thus seem worthwhile. As well as being of interest in the field of acidity function studies, with possible applications to organic chemistry, the acidity of unsolvated aquo metal ions is of great importance in understanding the role of trace quantities of water in molten salt chemistry. The relationship between the Lewis (optical) basicities of metal aquo ions and the proton magnetic resonance shifts observed by Angell et al. will be discussed in a future publication.

Registry No. ZnCl_2 , 7646-85-7.

References and Notes

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