before $P_3O_{10}^{5-}$ hydrolyzes. Possibly, V(V) bound to all three P's does not enhance hydrolysis while V(V) bound to only two P's frees the third or terminal PO_3^- to depart, dramatically accelerating the hydrolysis.

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Registry No. $(VOATP)^{2-}$, 63956-78-5; $(VOPPP_i)^{3-}$, 63956-79-6; $(VOATP)^-$, 63956-80-9; $(VOPPP_i)^{2-}$, 63956-81-0; MnO_4^-, 14333-13-2.

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(10) Recent observations by Charles Huber suggest that H_2O_2 is catalytically decomposed by VO^{2+} which is stabilized with respect to VO_2^+ by polyphosphate complexes.
(11) Postulated monovanadium complexes are tentative. Complexes of more than one V(V) per polyphosphate are readily conceivable.

Correspondence

Equilibrium Constants for the Metalation of Zinc Porphyrins

AIC701813

Sir:

The equilibrium between divalent metal ions and free base (PH_2) porphyrins to form metalloporphyrins (MP) is usually represented by the equation

$$M^{2+} + PH_2 = MP + 2H^+ \quad K_e \tag{1}$$

It is thus surprising to note that few mass law studies on this process have been reported. Dempsey, Lowe, and Phillips[1] investigated eq 1 with zinc sulfate and mesoporphyrin IX dimethyl ester solubilized in the detergent cetyltrimethylammonium bromide (CTAB) and found apparent equilibrium constants K_e* of 6 × 10^{-3} M (80 °C), 2.5 × 10^{-3} M (60 °C), and 1 × 10^{-3} M (20 °C). No experimental details were published. The K_e value in water differs from K_e* in detergents by the factor $(1 + K_S^{MP})/(1 + K_S^{PH_2})$ where it is assumed that there is an equilibrium between porphyrin species in the water and detergent phases, characterized by an unknown K_S value.

Table I. Equilibrium Data for the Zinc(II) Tetra(2-*N*-methylpyridyl)porphine Reaction 25.5 °C

$(ZnP)/(PH_2)$	(H^+),[a] M	$10^3(Zn^{2+})$, M	K_e,[b] M
0.195	0.99	1.0	191
0.410	0.99	2.0	191
0.746	0.99	4.0	183
1.39	0.99	8.0	172
1.97	0.99	10.0	193
1.56	0.89	6.4	193
1.82	0.79	6.4	177
2.40	0.70	6.4	183
3.29	0.60	6.4	185
4.41	0.50	6.4	172
8.24	0.40	6.4	206
35.5	0.19	6.4	200
			Av 188 ± 11

[a] $\mu = 1.0$ $(LiNO_3/HNO_3)$. [b] $K_e = (ZnP)(H^+)^2/(PH_2)(Zn^{2+})$.

Detergents also modify the behavior of the porphyrins that they solubilize. For example, acid–base titrations in CTAB show only the PH_2 and diacid PH_4^{2+} forms, while PH_2, PH_4^{2+}, and the monocation PH_3^+ are stabilized in cationic detergents. The cationic p*K* behavior approximates that found in water for similar prophyrins.

The only other K_e value that we can find was reported by Brisbin and Balahura[2] using zinc acetate and hematoporphyrin IX in 0.1 M $NaClO_4$ at 25 °C. At pH 7.0 and by assuming eq 1, the ratio $K_e/(H^+)^2$ was experimentally determined to be 1.3 × 10^7, giving $K_e = 1.3 \times 10^{-7}$ M. The equilibrium was studied at only this one pH. In general, the elucidation of eq 1 is somewhat difficult; the porphyrin should be monomeric and soluble in the acid range, the equilibrium constants between PH_2, PH_3^+, and PH_4^{2+} should be known, and the molar extinction coefficients of the various porphyrin forms are required.

We have simplified this problem by working with tetra(2-*N*-methylpyridyl)porphine,[3,4] which exists as only the PH_2 form from below pH 0 to above pH 7. At 25.5 °C, $\mu = 1.0$ $(LiNO_3/HNO_3)$, mixtures of PH_2, ZnP, HNO_3, and $Zn(NO_3)_2$ were equilibrated in the dark for periods of up to 3 weeks. At constant total porphyrin concentrations, isosbestic points were found in the visible region indicating that PH_2 and ZnP were the major species. The ratio $(ZnP)/(PH_2)$ was determined spectrophotometrically by standard methods. The total porphyrin concentrations were ca. 10^{-5} to 10^{-6} M, while (H^+) and (Zn^{2+}) values were greater than 10^{-3} M, so that $(H^+) = (H^+)_0$ and $(Zn^{2+}) = (Zn)_0$. The typical results shown in Table I indicate that eq 1 is followed with $K_e = 188 \pm 11$ M.

At constant ionic strength in water, the formation rates of zinc porphyrins usually follow the rate law $R_f = k_f(PH_2)\cdot(Zn^{2+})$, while the acid-catalyzed dissociation rates are of the form $R_d = k_d(ZnP)(H^+)^2$. Thus the ratio k_f/k_d should also equal K_e. Such results are shown in Table II. The overall trend is that K_e values decrease with an increase in porphyrin basicity, with the basicity measured by pK_3 (H_3P^+/H_2P). In other words, the less basic the porphyrin ligand, the more "stable" is the corresponding metal–porphyrin complex.

Table II. Equilibrium Constants for Zinc–Porphyrin Metalation Reactions

Reaction	pK_3[g]	k_f, M^{-1} s^{-1}	k_r, M^{-1} s^{-1}	K_e, M
Zinc hematoporphyrin IX[a]	6.1			1.3 × 10^{-7}
Zinc en-protoporphyrin IX[b]	5.0	2.4 × 10^{-1}	8.2 × 10^6	2.8 × 10^{-8}
Zinc tetra(4-sulfonatophenyl)porphine[c]	4.95[d]	4.8 × 10^{-1}	1.1 × 10^1	4.4 × 10^{-2}
Zinc tetra(4-*N*-methylpyridyl)porphine[e]	2.1	3.7 × 10^{-2}	8.5 × 10^{-3}	4.4
Zinc tetra(2-*N*-methylpyridyl)porphine[f]	<0	4.9 × 10^{-4}	2.4 × 10^{-6}	1.9 × 10^2

[a] Reference 2. [b] Reference 5. [c] Reference 6. [d] pK_3 and pK_4 (4.86) refer to the trisulfonated tetraphenylporphine. [e] k_f from ref 8, k_r from ref 9. [f] Present work. [g] pK_3 for the H_3P^+/H_2P reaction.

The overall formation constant K_f

$$Zn^{2+} + P^{2-} = ZnP \quad K_f \tag{2}$$

is equal to the ratio K_e/K_1K_2 where the product K_1K_2 refers to the PH_2/P^{2-} equilibria. The widely quoted[10] 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 Rochester[12] 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 (pK_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?

AIC70092Q

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 pK_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., $Al^{3+}(aq)$ to be more liable to release protons than would a neutral oxy acid such as HNO_3 (pK_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 concept[3] (which allows the pK_a values of oxy acids to be successfully correlated with the Lewis basicities of their oxy anions[4]) also suggests that metal aquo ions should have very high acidities.

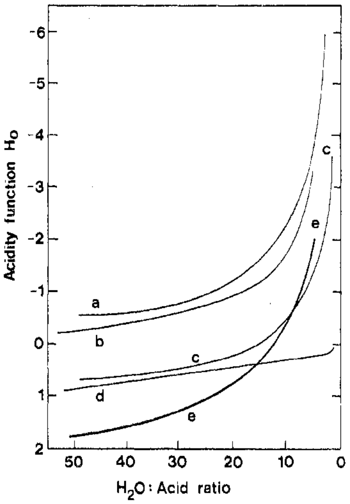

Figure 1. Variation in acidity function H_0 as the H_2O:acid ratio is decreased for the following acids: (a) H_2SO_4, (b) HCl, (c) H_3PO_4, (d) CH_3CO_2H, (e) $ZnCl_2$. (Plots for (a)–(d) are based upon data taken from C. H. Rochester, "Acidity Functions", Academic Press, London and New York, Chapter 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 $ZnCl_2{\cdot}4H_2O$, 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 $[Zn(H_2O)_4]^{2+}$ (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 $ZnCl_2{\cdot}4H_2O$, 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.

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