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The Effect of Pressure on the Dissociation of Iron(III) Monochloride Complex Ion in Aqueous Solution[1]

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The ionization of weak electrolytes in aqueous solution is known to increase with the application of hydrostatic pressure due to the effects of ionic solva-

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tion and the attendant decreases in solvent volume.[2] Correspondingly, the dissociation of complex ions might be expected to increase with increasing pressure. Such has been found to be the case. The dissociation constants of $CoCl_4^{-2}$ and of $CuCl_4^{-2}$ roughly double as the pressure is increased from 15 to 23,000 p.s.i.[3]

Our interest in the corrosion of devices and structures situated on the ocean bottom (the bottom of the deepest ocean trenches corresponds to pressures of about 15,000 p.s.i.) prompted us to examine the pressure dependence of the dissociation of the chloride complex of a common constructional metal such as iron.

Experimental

The apparatus and experimental techniques employed have been described elsewhere.[4] The aqueous electrolytic solutions of the desired concentration were prepared and analyzed by standard procedures. The light yellow $Fe(ClO_4)_3$–$HClO_4$ solution, comparable in color intensity to the $FeCl_3$–HCl and $Fe(NO_3)_3$–HNO_3 solutions, was prepared by dissolving G. Frederick Smith Chem. Co. "non-yellow" $Fe(ClO_4)_3$ salt in aqueous $HClO_4$. Attempts to prepare $Fe(ClO_4)_3$–$HClO_4$ solutions by other methods yielded dark, highly hydrolyzed solutions.

Results and Discussion

The variation at 25° of the specific conductance of aqueous HNO_3, $HClO_4$, HCl, $Fe(NO_3)_3$–HNO_3, $Fe(ClO_4)_3$–$HClO_4$, and $FeCl_3$–HCl solutions is summarized in Tables I and II.

TABLE I

PRESSURE DEPENDENCE OF THE SPECIFIC CONDUCTANCE OF AQUEOUS HCl, $HClO_4$, AND HNO_3 SOLUTIONS

Specific conductance in ohm^{-1} $cm.^{-1}$ at 25.03 ± 0.02°

Pressure, p.s.i.	0.0505 *M* HCl	0.0489 *M* $HClO_4$	0.0513 *M* HNO_3
15	0.02016	0.01918	0.02022
10,000	0.02145	0.02018	0.02143
20,000	0.02254	0.02096	0.02243
30,000	0.02338	0.02164	0.02324
40,000	0.02402	0.02222	0.02386
50,000	0.02447	0.02260	0.02435
60,000	0.02484	0.02280	0.02473
70,000	0.02514	0.02310	0.02500

TABLE II

PRESSURE DEPENDENCE OF THE SPECIFIC CONDUCTANCE OF AQUEOUS $FeCl_3$–HCl, $Fe(ClO_4)_3$–$HClO_4$, AND $Fe(NO_3)_3$–HNO_3 SOLUTIONS

Specific conductance in ohm^{-1} $cm.^{-1}$ at 25.03 ± 0.05°

Pressure, p.s.i.	0.05 *M* $FeCl_3$ 0.05 *M* HCl	0.05 *M* $Fe(ClO_4)_3$ 0.05 *M* $HClO_4$	0.05 *M* $Fe(NO_3)_3$ 0.05 *M* HNO_3
15	0.03040	0.03108	0.03071
10,000	0.03293	0.03215	0.03204
20,000	0.03462	0.03288	0.03305
30,000	0.03585	0.03322	0.03364
40,000	0.03671	0.03344	0.03401
50,000	0.03726	0.03352	0.03423
60,000	0.03761	0.03351	0.03427
70,000	0.03771	0.03338	0.03420
80,000	0.03773	...	...
90,000	0.03732	...	...

(2) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London, 1957, pp. 129–131, 149–156.

(3) A. H. Ewald and S. D. Hamann, *Australian J. Chem.*, **9**, 54 (1956).

(4) R. A. Horne and G. R. Frysinger, *J. Geophys. Res.*, **68**, 1967 (1963).

The conductive contribution of the salt, ΔK_a^-, may be estimated by subtracting the conductance of the acid alone (Table I) from that of the salt–acid solution (Table II), and values thus obtained are given in Table III.

TABLE III

CONDUCTIVE CONTRIBUTIONS OF THE SALTS

Pressure, p.s.i.	ΔK_{Cl^-}, ohm^{-1} $cm.^{-1}$	$\Delta K_{ClO_4^-}$, ohm^{-1} $cm.^{-1}$	$\Delta K_{NO_3^-}$, ohm^{-1} $cm.^{-1}$
15	0.00924	0.01190	0.01049
10,000	0.01148	0.01197	0.01061
20,000	0.01208	0.01192	0.01062
30,000	0.01247	0.01158	0.01040
40,000	0.01269	0.01122	0.01015
50,000	0.01279	0.01092	0.00988
60,000	0.01277	0.01071	0.00954
70,000	0.01261	0.01028	0.00920

The conductive contribution of $Fe(ClO_4)_3$ and $Fe(NO_3)_3$ both at first increase with increasing pressure, go through a maximum at about 10,000 to 15,000 p.s.i., the same pressure range in which the viscosity of water is a minimum,[5] and then decrease with roughly equal slopes. In contrast, the conductive contribution of $FeCl_3$, while starting below both of the former curves, increases rapidly with pressure and does not reach its maximum until about 53,000 p.s.i., behavior characteristic of a weak electrolyte. From these observations the qualitative conclusion may be drawn that the dissociation of iron(III) monochloride complex ion increases with increasing pressure.

Reliable association constants can be calculated from conductance data only in the case of relatively dilute solutions of 1:1 electrolytes. However, if we assume that ferric ion does not complex with perchlorate ion,[6] if we ignore the formation of higher complexes, polynuclear species, and hydrolysis products, and if we assume that the term $\Delta K/\Sigma\Lambda^0$, where $\Sigma\Lambda^0$ is the sum of the 1-atm. limiting conductances of all of the system's major ionic species, has the same value for all three salts and is independent of pressure, then a semiquantitative estimation of the pressure dependence of the equilibria constants can be made. Using the limiting equivalent conductivities of 67 (average value for trivalent cations) 76, 67, 71, and 53 (value for the larger divalent cations) for Fe^{+3}, Cl^- ClO_4^-, NO_3^-, and $FeCl^{+2}$, respectively,[7] one obtains 4.45×10^{-5} equiv./cm.^{3} for $\Delta K/\Sigma\Lambda^0$. If we let X be the fraction of Fe(III) in the form of the complex $FeCl^{+2}$, we can write

$$\frac{K_{Cl^-}}{(1 - X)67 + (3 - X)(76) + X53} = 4.45 \times 10^{-5} \text{ (at 1 atm.)} \quad (1)$$

from which it follows that the value of X is 0.97. Now

$$(Cl^-) = 3(FeCl_3)_i + (HCl)_i - (FeCl^{+2}) = 0.15 \quad (2)$$

(5) R. Cohen, *Ann. Phys.*, **45**, 666 (1892).

(6) M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Am. Chem. Soc.*, **83**, 2038 (1961); see also F. Klanberg, J. P. Hunt, and H. W. Dodgen, *Inorg. Chem.*, **2**, 139 (1963).

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths Scientific Publications, London, 1959, p. 463.

and at 1 atm. and 25° it follows that $K_{FeCl^{+2}}$ is 21 M^{-1}. This value is in agreement with Bray and Hershey[8] and Badoz-Lambling[9] but is higher than the values reported by other investigators. Similar analysis for the $Fe(NO_3)_3$–HNO_3 solutions using a value of 50 for $\Lambda^0_{FeNO_3^{+2}}$ yields a $K_{FeNO_3^{+2}}$ of 5.7 M^{-1}, which is in reasonable agreement with the results of Sykes[10] but again higher than the value reported by some other investigators. Repeating these calculations at the higher pressures we find that the formation constant of $FeCl^{+2}$ decreases 20-fold from 21 to 0.4 M^{-1} in going from 15 to 30,000 p.s.i., whereas the formation constant of $FeNO_3^{+2}$ decreases only from 5.7 to 4.6 M^{-1} in going from 15 to 70,000 p.s.i.

One might expect that the effect of pressure on ion-pair formation should be less than upon true complex ion formation inasmuch as the former requires fewer alterations in solvation and, hence, does not entail large volume changes. Such being the case, the present results suggest that $FeCl^{+2}$ is a complex ion, but that $FeNO_3^{+2}$ is an ion pair, that is to say, the composition of the innermost hydration spheres of the participants is unchanged.

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(8) W. C. Bray and A. V. Hershey, *J. Am. Chem. Soc.*, **56**, 1889 (1934).
(9) J. Badoz-Lambling, *Bull. Soc. Chim. France*, 552 (1950).
(10) K. W. Sykes, *J. Chem. Soc.*, 124 (1952).