Notes

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Hydrolysis of Iron(2+) in Dilute Chloride at 25°[1]

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The hydrolysis behavior of Fe(II) was recently examined between 50 and 300° in acidic and basic media by Sweeton and Baes.[2] In that study the solubility of Fe_3O_4 was measured and stabilities were derived for the species $Fe(OH)_b^{(2-b)+}$ for $b = 1$–4. The value for log K of the equilibrium

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+ \qquad (1)$$

obtained by extrapolation to 25° is -9.3 ± 0.5. That result is consistent with the earlier work of Hedstrom[3] in 1 M $NaClO_4$ (-9.5 ± 0.2). Hedstrom employed a glass electrode in the conventional titration procedure for hydrolysis behavior. The wide range of literature values given for the logarithm of the hydrolysis constant for eq 1 which extends from -6.8 to -9.5 is reviewed by Sweeton and Baes. Because of the relatively large uncertainties given these measurements of the hydrolyses behavior and the susceptibility of such measurements to low levels of impurities where only a small amount of hydrolysis occurs, we have undertaken the present work which was designed to minimize contamination with protolytic impurities. The usual high concentration of electrolyte was omitted while using the very high-purity iron now available in a potentiometric cell with a hydrogen electrode for measuring acidity and controlling the oxidation state of the Fe.

Experimental Section

The $FeCl_2$ solution was made by dissolution of zone-refined Fe rod from Battelle Memorial Institute which contained less than 35 ppm of metallic impurities and 5 ppm of nonmetallic impurities. The dissolution was carried out in the absence of air with Ultra High Purity hydrochloric acid from J. T. Baker. The ferrous concentration was obtained by titration with dichromate to the diphenylaminesulfonate end point.

Oxygen-free water was prepared by the method described in ref 1. The high-purity hydrogen was obtained by passing commercial hydrogen through heated palladium alloy in a Serfass hydrogen purifier manufactured by the Milton Roy Co.

The NaOH used in the titrations was analyzed for protolytic impurities by titration between pH 5 and 9 and the upper limit for the mole ratio of impurities to hydroxide was found to be 10^{-3}. The base was stored in paraffin-lined vessels in an atmosphere of hydrogen. During titrations it was injected from a plastic syringe into a titration vessel and cell assembly of the type described previously.[4]

The cell consisted of a hydrogen electrode and an Ag–AgCl electrode separated by a liquid junction as

$$\text{Ag–AgCl}\left|0.0069\ m\ \text{KCl}\right\|\begin{matrix}0.0032\ m\ \text{FeCl}_2\\0.00047\ m\ \text{HCl}\end{matrix}\left|\text{Pt–H}_2\right. \qquad (2)$$

The composition of the solutions was as indicated above at the beginning of the experiment and the free acid was neutralized before hydrolysis commenced. During the titration of the last 20% of the free acid where the reference acidity was established and during the formation of $Fe(OH)^+$ the solution composition on the right of the cell (2) remained essentially unchanged since a concentrated titrant was used and the hydrolysis proceeded to less than 1% of the iron before precipitation commenced. Therefore although there is a liquid junction potential in the cell (2) it should remain approximately constant during the experiment. The free acid concentration was determined by the method of Baes[5] and was used as the acidity reference for the cell.

Results and Discussion

This approach, sometimes called the self-medium method, permits one to control the ionic strength through the ions involved in the hydrolysis equilibria when only a small amount of the metal ion present hydrolyzes. However, it is not possible to determine the dependence of hydrolysis behavior on metal ion concentration with this approach. The assumption was made in the analysis of the present data that only the $Fe(OH)^+$ species is formed. For a weakly hydrolyzing metal ion such as Fe^{2+} and the low concentrations of iron in the experiment this assumption is justified.

The results of titration experiments with 0.0031 m $FeCl_2$ solution are summarized in Table I. The ligand number, $\bar{n}_o$, was calculated from the relationship $\bar{n}_o = (h - m_H)/m_{Fe}$, where h is the free acidity as determined with the hydrogen electrode, m_H is the stoichiometric acidity in the absence of hydrolysis, and m_{Fe} is the total iron concentration. The ligand number, $\bar{n}_c$, was calculated by least squares assuming

Table I

Hydrolysis of Fe^{2+} at 25° in Dilute Solutions

$10^3\bar{n}_o$	$10^3\bar{n}_c$	$10^3(Fe^{2+})_T$, m	$10^7(H^+)$, m
0.31	0.25	3.078	10.30
1.25	0.91	3.077	2.83
2.15	1.89	3.076	1.37
3.07	3.14	3.075	0.822
4.00	4.79	3.075	0.538
0.22	0.23	3.079	11.34
1.40	0.87	3.078	2.96
2.80	1.96	3.077	1.31
4.23	3.73	3.076	0.692
5.66	5.79	3.075	0.442

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(2) F. H. Sweeton and C. F. Baes, Jr., *J. Chem. Thermodyn.*, **2**, 479 (1970).

(3) B. O. Hedstrom, *Ark. Kemi*, **5**, 457 (1953).

(4) R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **6**, 1951 (1967).

(5) C. F. Baes, Jr., *ibid.*, **4**, 588 (1965).

the formation of $Fe(OH)^+$ by the close approximation $\bar{n}_o = Q/h$, where Q is the equilibrium quotient for reaction 1 and unit weights were employed. In Table I the maximum $\bar{n}_o$ attained was 0.006 which is in good agreement with the observation of Hedstrom[3] but somewhat less than the value reported by Bolzan and Arvia[6] (0.012).

The value of log Q obtained from the data of Table I is −9.58 with an estimated error of 0.08. This estimate includes random scatter of the least-squares fit and estimated systematic error due to errors in the original acidity. A small correction for activity coefficients was made using the Debye–Hückel expression to obtain the infinite dilution value or log K of −9.49 ± 0.08. This is in agreement with the relatively uncertain value of Sweeton and Baes (−9.3 ± 0.5). We would expect the value of log Q in 1 M $NaClO_4$ to be somewhat lower than log K.

The log Q for $Fe^{III}(OH)^{2+}$ (0.01 M $NaClO_4$)[7] is −2.4 or 7 log units more stable than $Fe^{II}(OH)^+$. This relatively low stability for $Fe^{II}(OH)^+$ compared with $Fe^{III}(OH)^{2+}$ must be attributed chiefly to the charge and radius of the cation since ligand field effects are small, particularly for ligands like OH^- displacing H_2O.

Also, the difference in stabilities predicted for the 1:1 fluoride complexes for Fe^{2+} and Fe^{3+} is only 4 log units based on the relationship between $(Z_+{}^2/r_+)$ for the cation and the stability of fluoride complexes.[8] Not only are the hydroxide complexes several orders of magnitude more stable than the corresponding fluoride complexes but the difference between ferric and ferrous complexes are greater for the hydroxides.

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[6] J. A. Bolzan and A. J. Arvia, *Electrochim. Acta*, **8**, 375 (1963).

[7] R. M. Milburn, *J. Amer. Chem. Soc.*, **79**, 537 (1957).

[8] R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 618 (1969).

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An Ion-Exchange Study of the Ethylenediamine-*N*,*N'*-diacetatodiaquochromium(III) System

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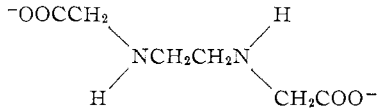
Studies concerning the geometry of coordinated ethylenediamine-*N*,*N'*-diacetate ion (EDDA)



have recently been reported in the literature for the metal ions Co(III),[1] Pt(II),[2] Pt(IV),[2] Ni(II),[3] and Cr(III).[4,5] In these studies it has been found that EDDA is capable of functioning as a bidentate, tridentate, or tetradentate ligand. This note is concerned with those cases where EDDA functions as a tetradentate ligand. For the octahedral cases the diaquo parent complexes have been reported for Co(III) and Ni(II). Although a number of mixed ligand–EDDA complexes with chromium(III) have been reported, studies pertaining to the parent diaquo complexes have not yet appeared in the literature. We wish to report here the results of our studies on the parent 1:1 (metal ion: ligand) complexes formed between Cr(III) and EDDA.

Experimental Section

Chemicals.—Reagent grade $CrCl_3 \cdot 6H_2O$ or $Cr(NO_3)_3 \cdot 9H_2O$ was used as the source of Cr(III) ion. Ethylenediamine-*N*,*N'*-diacetic acid, obtained from Pfaltz and Bauer, Inc., was recrystallized once from hot water before being used. All other chemicals were reagent grade. Deionized, distilled water was used in all experiments.

Preparation of the $Cr(EDDA)(OH_2)_2^+$ Reaction Mixture.—To 25 ml of an aqueous solution containing 1.36 g (7.7 mmol) of H_2EDDA and 0.52 g (3.8 mmol) of K_2CO_3 was added 10 ml of an aqueous solution containing 1.86 g (7.0 mmol) of $CrCl_3 . 6H_2O$. The resulting solution was heated on a steam bath for 1.5 hr with the final volume being approximately 25 ml. Preparation of the mixture using KOH instead of K_2CO_3 and/or $Cr(NO_3)_3 \cdot 9H_2O$ instead of $CrCl_3 \cdot 6H_2O$ gave identical results in terms of ratios of the desired products. The complexes could not be obtained in solid form; hence separation and characterization studies were carried out in solution.

Separation of the $Cr(EDDA)(OH_2)_2^+$ Isomers Using Cation-Exchange Chromatography.—The reaction mixture was introduced into a 3.5 × 30 cm jacketed column containing Dowex 50W-X8 (100–200 mesh) cation-exchange resin in the H^+ form. The column was cooled to 2° during the charging and elution procedures. After washing the column with H_2O, elution of the positively charged complexes was begun with 0.20 F HNO_3. Upon elution two red bands with 1+ charge characteristics were obtained with a dark blue band of $Cr(OH_2)_6^{3+}$ remaining unmoved at the top of the resin. The relative sizes of the two red bands were quite different, the first (eluted) or less polar red band being present to a much greater extent than the second or more polar red band. Upon elution from the column each band was collected in a container cooled to 0° and immediately thereafter the visible spectrum of each species was recorded. When using $CrCl_3 \cdot 6H_2O$ as starting material a small band of a residual chloro-containing complex was noted upon elution. The red complexes were analyzed in solution for chromium and nitrogen in order to obtain Cr:EDDA ratios.

Spectral Measurements.—All visible absorption spectral measurements were made on a Coleman 46 uv–visible spectrophotometer with the cell compartment cooled to approximately 8°. During the time (approximately 15 min) required to define the visible spectrum, no decomposition of the desired species was observed.

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[1] P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem.*, **9**, 937 (1970), and references therein.

[2] C. F. Liu, *ibid.*, **3**, 680 (1964).

[3] F. F. L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *ibid.*, **9**, 1139 (1970).

[4] Y. Fujii, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, **42**, 1569 (1969).

[5] Y. Fujii and K. Yamamoto, *ibid.*, **42**, 3451 (1969).