

Fig. 1.—Polarograms of titanium in 0.1 *M* HCl: curve I, residual current polarogram for 0.1 *M* HCl; curve II, polarogram of solution of titanium halides prepared after Forbes and Hall,² approximately two millimolar in titanium in 0.1 *M* HCl; curve III, polarogram of the same solution with Ti(III) partially oxidized.

tial and approximately twice the size of the first, indicating a one-electron reduction to Ti(II) followed by a two-electron reduction to Ti(0). Considering the dif-

ference in solvation energies of Ti(III) between water and acetonitrile to be expected by analogy with other tripositive transition metals,⁷ the aqueous potential corresponding to -1.3 v. *vs.* s.c.e. in acetonitrile would be at least -2 v. *vs.* n.h.e.

This estimate more nearly coincides with the theoretical work of George and McClure,⁸ who applied ligand field correction to the hydration energies of di- and tripositive ions of the first transition series in relating standard potentials of the metal ion couples to the third ionization potential of the free metals. Their calculations agreed with known standard potentials for the first transition series except in the case of the Ti(III)–Ti(II) couple. They estimated that the true E^0 of the Ti(III)–Ti(II) couple should be approximately -2.3 v. in aqueous solution. Such a potential would well explain the absence of Ti(II) in aqueous media.

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(8) P. George and D. S. McClure in "Progress in Inorganic Chemistry," F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

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The Effect of Specific Swamping Electrolytes upon the Formation Constant of the Monochloroiron(III) Complex¹

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The ultraviolet absorption spectrum of the monochloroiron(III) complex in perchloric acid and sodium perchlorate–perchloric acid mixtures was examined. The formation constant increased with increasing swamping electrolyte concentration but decreased when the ratio of sodium perchlorate to perchloric acid increased at constant total molarity. These results were correlated with the effect of the swamping electrolyte upon the activities of the species involved in the equilibria.

The chloro complexes formed by the hydrated iron(III) cation have been the subject of numerous spectrophotometric studies.^{4–9} Gamlen and Jordan⁹ reviewed this work in detail and concluded that 4 species, FeCl_2^+ , FeCl_2^+ , FeCl_3 , and FeCl_4^- , were formed in the system. Desesa and Rogers¹⁰ observed that the absorption spectra of iron(III) solutions containing chloride ion were greatly influenced by changes in hydrogen ion concentration. However, these investigators were interested in developing an analytical method for the determination of iron and did not examine the nature of the acid effect further. Subsequently, Coll, Nauman, and West¹¹ determined the

effect of perchloric acid concentration and mixtures of perchloric acid and perchlorates upon the absorption spectrum of the monochloroiron(III) complex. They found an enormous increase in the value of the formation constant with increasing perchlorate concentration and attributed this to the dehydration of the hydrated iron(III) cation by perchlorates. However, these authors felt that this was not the only factor responsible for the observed changes in the formation constant. The present study was undertaken to elucidate further the nature of the perchlorate ion effect upon the chloroiron(III) complexes.

Experimental

Reagents and Solutions.—Reagent grade iron(III) chloride was recrystallized from aqueous solution until free of metallic impurities. Iron(III) perchlorate was prepared from the chloride by the method of Mulay and Selwood.¹² The resulting violet crystals were dissolved in 0.1 *M* HClO_4 and diluted with the acid to a concentration 0.05 *M* total iron. The solution was analyzed for iron(III) and iron(II) by the Zimmerman–Reinhart method and for chloride ion by the Volhard method.¹³ There

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(12) L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2695 (1955).

(13) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Chemistry," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, pp. 545, 572–573.

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(4) A. VonKiss, J. Abraham, and I. Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

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(7) H. Olerup, *Svensk. Kem. Tidskr.*, **65**, 324 (1943).

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was less than 0.001% chloride and iron(II) present. Hydrochloric acid and perchloric acid solutions were standardized by titration against standard sodium hydroxide solution. Sodium perchlorate and lithium perchlorate solutions were prepared by carefully weighing out the required amount of recrystallized C.P. crystals (G. F. Smith Chem. Co.) and diluting to a specific volume. Double distilled water, free of carbon dioxide and chloride ion, was used in all the preparations.

Instrumentation.—All of the absorption spectra were recorded with the use of a Beckman DK-2 spectrophotometer. The reference spectrum was recorded with purified water in both cells. Samples were run at ambient temperatures which averaged $23 \pm 4^\circ$. Except for the initial experiments, the concentration of all solutions was such as to give absorbances in the range of 0.2–0.8. Several solutions were examined twice within a 24-hour period after preparation to determine their stability. The spectra of the pairs were identical within the experimental error of the instrument.

Results

In the first set of solutions the iron(III) chloride concentration was maintained constant at $5 \times 10^{-3} M$ while the hydrogen ion concentration was varied from 1 to 5 M with perchloric acid. The total electrolyte concentration was kept constant at 5 M with NaClO_4 . Thus, in all of these solutions the perchlorate ion concentration was also constant at 5 M . The spectra for a portion of the ultraviolet region in which the chloro complexes absorb strongly are shown in Fig. 1.

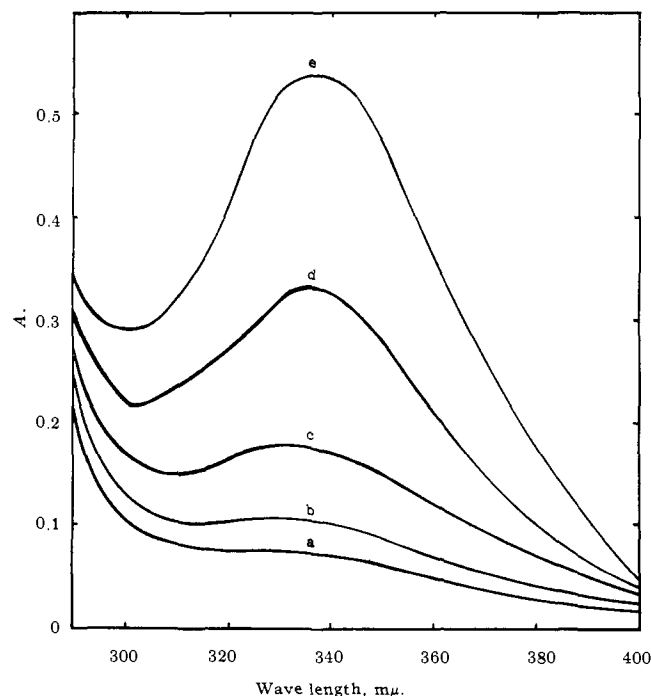


Fig. 1.—Ultraviolet absorption spectra of ferric chloride in $\text{NaClO}_4\text{-HClO}_4$ solutions, 0.1-cm. cell: $[\text{FeCl}_3] = 5 \times 10^{-3} M$; $[\text{ClO}_4^-] = 5 M$; $[\text{H}^+] =$ a, 1 M ; b, 2 M ; c, 3 M ; d, 4 M ; e, 5 M .

It is seen that the absorbance increased markedly with increasing hydrogen ion concentration. The increased absorbance could not be due to the dehydrating effect of perchlorate ion since the concentration of this ion was constant throughout.

In the next set of experiments, the chloride ion concentration was varied while the hydrogen ion and iron(III) concentrations were kept constant at 3 M and $1 \times 10^{-3} M$, respectively. The total electrolyte concentration was again maintained constant at 5 M . The absorbances of these solutions in the ultraviolet region of the spectrum are shown in Fig. 2. The appearance of the isosbestic points at 282 $m\mu$ and 238

$m\mu$ was taken as evidence that only two absorbing species, Fe^{3+} and FeCl^{2+} , were present. An isosbestic point was expected at λ 282 $m\mu$ from a consideration of the molar absorptivity coefficient curves of the species Fe^{3+} and FeCl^{2+} as given by Gamlen and Jordan.⁹ At high chloride ion concentrations the curves did not pass through the isosbestic points. When this occurred, it was assumed that higher chloro complexes were present. Thus, it was possible to define those conditions for which only the species Fe^{3+} and FeCl^{2+} were present in the solutions.

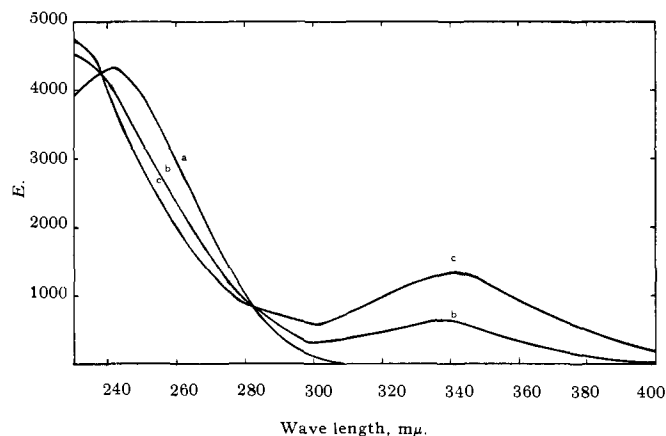


Fig. 2.—The effect of chloride ion concentration upon the ultraviolet absorption spectra of iron(III) perchlorate, 1.0-cm. cell: $[\text{Fe(III)}] = 1 \times 10^{-3} M$; $[\text{H}^+] = 3 M$; $[\text{ClO}_4^-] = 5 M$; $[\text{Cl}^-] =$ a, 0.00; b, $1 \times 10^{-2} M$; c, $4 \times 10^{-2} M$.

Similar sets of absorption curves were now obtained at three different iron(III) concentrations (2.5, 5, and $10 \times 10^{-4} M$) and at acidities of 1, 2, 3, 4, 5 M , all at 5 M total electrolyte concentration. The formation constants for the monochloro complex were then calculated from the relationships

$$A = E([\text{Fe}^{3+}] + [\text{FeCl}^{2+}]) = \epsilon_0[\text{Fe}^{3+}] + \epsilon_1[\text{FeCl}^{2+}] \quad (1)$$

$$K_1 = [\text{FeCl}^{2+}]/[\text{Fe}^{3+}][\text{Cl}^-] \quad (2)$$

where A = absorbance, E is the total absorptivity of the solutions and ϵ_0 , ϵ_1 , ϵ_2 are molar absorptivity coefficients of individual species. Applying the technique of Olsen and Simonsen¹⁴ to eq. 1 and 2 and assuming that the total chloride ion concentration, $[\text{Cl}^-]_0$, equals the free chloride ion concentration, $[\text{Cl}^-]$, gives

$$E[\text{Cl}^-]_0 + E/K_1 = \epsilon_0/K_1 + \epsilon_1[\text{Cl}^-]_0 \quad (3)$$

Equation 3 was solved for K_1 , ϵ_1 , and ϵ_0 from sets of simultaneous equations derived from the spectral data at about 25 different wave lengths. Only those curves which passed through the isosbestic points were used. The validity of the assumption that $[\text{Cl}^-]_0 = [\text{Cl}^-]$ was checked by calculation using the initially derived values of K_1 . The error was only appreciable when the chloride ion concentration approached the total iron(III) concentration and such values were not used for the final calculation of K_1 . The values of ϵ_0 and ϵ_1 are plotted in Fig. 3 and compared with the results of earlier studies.^{9,15} The agreement between our values of ϵ_0 and those obtained by Turner and Miles from hydrolysis studies of iron(III) perchlorate solutions is quite good. However, our ϵ_1 values are higher than those given by Gamlen and Jordan.

Absorption spectra were now obtained for solutions in which the total electrolyte concentration was 1, 2, 3,

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TABLE I

OBSERVED AND CALCULATED VALUES OF K_1 FOR PERCHLORIC ACID AND PERCHLORIC ACID-SODIUM PERCHLORATE SOLUTIONS

Molarity of HClO ₄	Total electrolyte molarity									
	5		4		3		2		1	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
5	48 ± 7	..								
4	42 ± 6	42	20 ± 4	22						
3	35 ± 5	37	18 ± 3	17.7	7.8 ± 2	11				
2	28 ± 5	32	15 ± 2	15.5	6.8 ± 1.6	6.9	5 ± 1	6.4		
1	20 ± 4	27	10 ± 2	13.5	5.2 ± 0.8	6.2	4.1 ± 1	4.5	3.9 ± 0.7	4.3

and 4 M and the acidity varied from 1 to $x M$, where x is the total electrolyte concentration for that particular set of solutions. Values of K_1 were calculated from these data using the values of ϵ_0 and ϵ_1 determined from the data at 5 M . The results are given in Table I in the columns marked obsd.

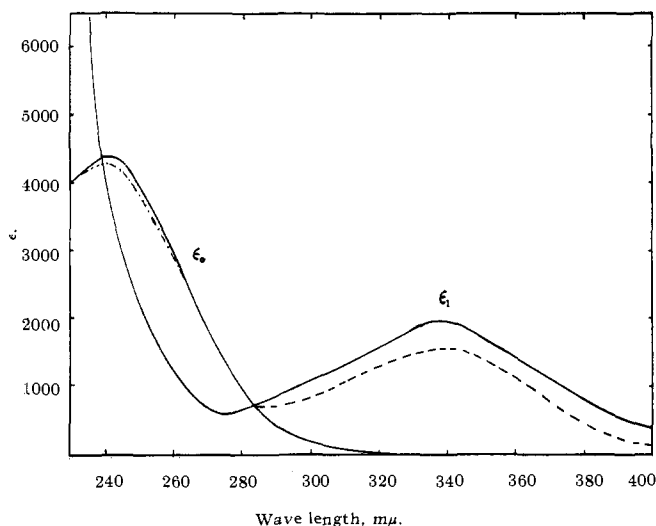


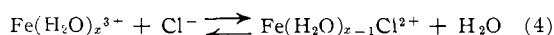
Fig. 3.—The ultraviolet absorption spectra of the iron(III) ion, ϵ_0 , and ϵ_1 , the monochloroiron(III) complex. Solid line represents data of this study, dashed line is data of Gamlen and Jordan, dot-dashed line is data of Turner and Miles.

The question now arises as to whether the observed changes in absorbance are due to some special hydrogen ion effect. If this were so, then similar results should be obtained with lithium perchlorate-perchloric acid mixtures. That this is not the case is shown in Fig. 4. The decrease in absorbance on substituting lithium perchlorate for perchloric acid is much smaller than was obtained with sodium perchlorate. This difference cannot be attributed to concentration differences of the swamping electrolyte since in all of these solutions the total electrolyte concentration was 6.48 formal to within 0.5%. Thus, the absorbance depends not only upon the total "inert" electrolyte concentration but also upon its composition.

Discussion

The possibility that the variations in K_1 result from changes in the activities of the species involved in the equilibrium with changing swamping electrolyte composition will now be explored.

For the reaction



we have

$$K_1 = \frac{(\text{FeCl}^{2+})(\text{H}_2\text{O})}{(\text{Fe}^{3+})(\text{Cl}^-)} = K_1 \frac{Y_{\text{FeCl}^{2+}}(\text{H}_2\text{O})}{Y_{\text{Fe}^{3+}}Y_{\text{Cl}^-}} \quad (5)$$

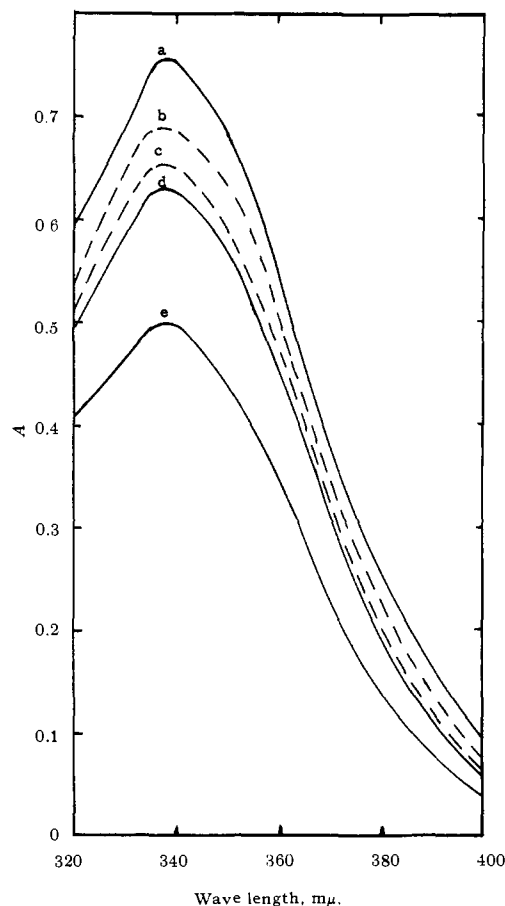


Fig. 4.—Comparison of ultraviolet absorption spectra of ferric chloride in several electrolyte mixtures, $[\text{FeCl}_3] = 1.8 \times 10^{-3} M$, $[\text{ClO}_4^-] = 5 M$: a, 5 M HClO₄; b, 4 M HClO₄-1 M LiClO₄; c, 3 M HClO₄-2 M LiClO₄; d, 4 M HClO₄-1 M NaClO₄; e, 3 M HClO₄-2 M NaClO₄.

where parentheses represent activities, Y_i is the molar activity coefficient of species i . The waters of hydration have been omitted from eq. 5 and subsequently for simplicity. Following the treatment given by Gamlen and Jordan⁹ for solutions at high ionic strength, *viz.*

$$Y_{\text{FeCl}^{2+}}/Y_{\text{Fe}^{3+}} = C_1 Y_{\text{Cl}^-} \cong Y_{\pm\text{HCl}}$$

eq. 5 becomes

$$K_1 = K_1 \frac{C(\text{H}_2\text{O})}{Y_{\pm\text{HCl}}} \quad (6)$$

for any two such solutions

$$K_1^{s2} \frac{(\text{H}_2\text{O})_2}{Y_{\pm\text{HCl}(2)}} = K_1^{s1} \frac{(\text{H}_2\text{O})_1}{Y_{\pm\text{HCl}(1)}} \text{ since } C_2 \cong C_1 \quad (7)$$

Equation 7 can be used to determine approximately how K_1 will vary with changes in the swamping electrolyte concentration or composition.

The first case to be considered is that in which the swamping electrolyte is perchloric acid only. The mean molal activity coefficients of HCl in perchloric acid have been determined¹⁶ up to $I = 1$. Although plots of $\log \gamma_{\pm\text{HCl}}$ vs. molality of HCl were only approximately linear, it was felt¹⁶ that the HCl-HClO₄ system obeyed Harned's rule.¹⁷ Therefore, we drew the best straight line through the data at $I = 1$ and its slope (-0.0147) was used to calculate values of $\gamma_{\pm\text{HCl}}$ at higher ionic strengths from the equation

$$\log \gamma_{\pm\text{HCl}} = \log \gamma_{\pm\text{HCl}(0)} + 0.147(m) \quad (8)$$

where m = total electrolyte molality and $\gamma_{\pm\text{HCl}(0)}$ is the mean molal activity coefficient of m molal hydrochloric acid.

As a check on the above procedure the experimentally determined¹⁶ activity coefficients were fitted to the equation

$$\log \gamma_{\pm\text{HCl}} = -\frac{a\sqrt{I}}{1 + \sqrt{I}} + bI \quad (9)$$

The constants obtained from this fit were $a = 0.460 \pm 0.011$ and $b = 0.156 \pm 0.007$. Equation 9 was then used to calculate activity coefficients at ionic strengths greater than 1. The two sets of activity coefficients differed by only 2-3%. Water activities for aqueous perchloric acid¹⁸ were used in place of the water activities of the actual solutions. This procedure is justified since the perchloric acid concentrations were very nearly equal to the total electrolyte concentrations.

The mean molal activity coefficients were converted to mean molar activity coefficients¹⁹ from the known densities of perchloric acid solutions.²⁰ Values of $K_1^{s_2}$ were now calculated for solutions 4, 3, 2, and 1 M in HClO₄ using $K_1^{s_1} = 48$ at 5 M perchloric acid. The results, shown in Table I, are in quite good agreement with the observed data considering the nature of the assumptions made in the calculations.

The second case to consider is that in which sodium perchlorate is partially substituted for perchloric acid at a constant total electrolyte concentration. The required water activities and activity coefficients have not been measured. Therefore, the following treatment was adopted. Harned's rule has been shown to apply precisely to the HCl-NaClO₄ system²¹ up to $I = 1$. We again assumed that the rule would apply at higher electrolyte concentrations since this is true for other similar systems.²² Thus, values of $\gamma_{\pm\text{HCl}}$ were calculated for concentrations greater than 1 molal by means of eq. 8 using the slope (0.0244) determined experimentally at $I = 0.1-1.0$. These values were converted to mean molar activity coefficients.²³ It was then assumed that, at constant total electrolyte concentration, the molar activity coefficient of HCl in HClO₄-NaClO₄ mixtures ($Y_{\pm\text{HCl}(as)}$), was given by the relationship

$$Y_{\pm\text{HCl}(as)} = Y_{\pm\text{HCl}(a)} - X(Y_{\pm\text{HCl}(n)} - Y_{\pm\text{HCl}(s)}) \quad (10)$$

where X is the mole fraction of NaClO₄ and $Y_{\pm\text{HCl}(a)}$,

(16) P. G. Murdock and R. C. Barton, *J. Am. Chem. Soc.*, **55**, 4074 (1933).

(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1959, p. 483.

(18) R. A. Robinson and O. J. Baker, *Trans. Proc. Roy. Soc. New Zealand*, **76**, 250 (1946).

(19) Reference 17, pp. 30-33.

(20) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 54.

(21) S. J. Bates and J. W. Urston, *J. Am. Chem. Soc.*, **55**, 4068 (1933).

(22) J. E. Hawkins, *ibid.*, **54**, 4480 (1932).

(23) Densities of sodium perchlorate solutions determined at 18° (ref. 20, p. 84) were used for this calculation.

$Y_{\pm\text{HCl}(s)}$ are the mean molar activity coefficients of HCl in perchloric acid and sodium perchlorate, respectively. An analogous procedure was used to obtain approximate water activities of HClO₄-NaClO₄ mixtures using water activities of sodium chloride solutions in place of those for sodium perchlorate solutions. Values of K_1 were now calculated for each set of solutions at constant total electrolyte concentrations using as $K_1^{s_1}$ the experimentally determined formation constants for those solutions in which only perchloric acid was the swamping electrolyte. The results are shown in Table I. The agreement with the observed data is poorer than it was in the previous case but is still good in view of the very approximate nature of the calculations.

The activity coefficients required for eq. 5 are those based on standard states in which $Y_j = 1$ at infinite dilution of species j in each of the particular electrolyte solutions used to obtain the K_1 values. However, the activity coefficients actually used in the above calculations were based on a standard state in which $Y_{\pm\text{HCl}} = 1$ at infinite dilution in water. This was done because data based on the correct standard states were not available.

Some idea of the magnitude of the error incurred by the incorrect choice of standard states may be obtained from the following treatment. The activity coefficients of HCl in perchloric acid solutions and in sodium perchlorate solutions were determined from measurements^{16,21} of the e.m.f. of cells of the type H₂/HCl(M_1) + salt (M_2)/Ag Cl + Ag. For such cells

$$E_s = E_w^0 - 2k \log M_1 Y_w^s \quad (11)$$

where E_w^0 is the standard electrode potential, Y_w^s is the mean molar activity coefficient of HCl in a particular electrolyte solution, S , referred to a standard state in which $a = m$ in dilute solutions of HCl in water and $k = 2.303 RT/F$. The activity coefficients actually required are given by the equation

$$E_s = E_s^0 - 2k \log M_1 Y_s^s \quad (12)$$

where E_s^0 and Y_s^s are the standard electrode potential and activity coefficient, respectively, referred to a standard state in which $a = m$ in dilute solutions of the particular electrolyte medium S . Combining 11 and 12 we obtain

$$E_w^0 = E_s^0 - 2k \log (Y_s^s / Y_w^s) \quad (13)$$

For any two electrolyte solutions S_1 and S_2

$$E_{s_2}^0 - E_{s_1}^0 = +2k \log \frac{Y_{s_2}^{s_2} Y_w^{s_1}}{Y_{s_1}^{s_1} Y_w^{s_2}} \quad (14)$$

Rewriting eq. 7 in the same notation as above gives

$$K_1^{s_2} \frac{(\text{H}_2\text{O})_2}{Y_{s_2}^{s_2}} = K_1^{s_1} \frac{(\text{H}_2\text{O})_1}{Y_{s_1}^{s_1}} \quad (15)$$

In calculating $K_1^{s_2}$ we used the activity coefficients in the form Y_w^s so that

$$K_1^{s_2'} \frac{(\text{H}_2\text{O})_2}{Y_w^{s_2}} = K_1^{s_1} \frac{(\text{H}_2\text{O})_1}{Y_w^{s_1}} \quad (16)$$

where $K_1^{s_2'}$ is the calculated formation constant and $K_1^{s_1}$ the formation constant obtained from extinction data in the electrolyte solution s_1 . Dividing eq. 15 by 16 and substituting back into eq. 14 gives

$$E_{s_2}^0 - E_{s_1}^0 = 2k \log \frac{K_1^{s_2}}{K_1^{s_2'}} \quad (17)$$

Thus, the error incurred by using activity coefficients of the type Y_w^s in place of Y_s^s is a function of the difference in the standard potentials of the two electrolyte solutions. The difference will be small for solutions which do not differ greatly in electrolyte concentration and composition. This trend is generally observed by the data in Table I. The agreement between calculated and observed K 's becomes poorer as one proceeds down the columns of the table, *i.e.*, as the difference in composition of the two solutions S_1 and S_2 increases.

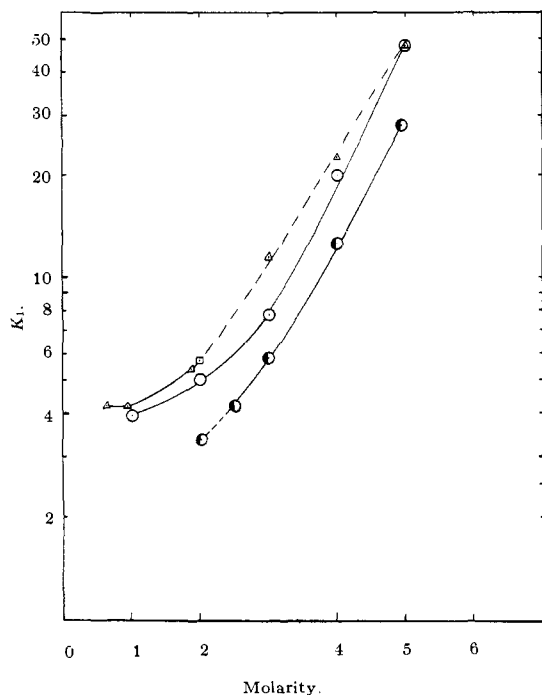


Fig. 5.—Plot of $\log K_1$ vs. molarity of perchloric acid. Dashed lines represent extrapolated values. Extrapolation of Rabinowitch and Stockmayer's data based on their eq. 13⁶: O, Clearfield and Heistand; Δ , Rabinowitch and Stockmayer; \square , Olerup; \bullet , Coll, Nauman, and West.

Data for the activity coefficients of HCl in the presence of lithium perchlorate are not available. However, since the activity coefficients of lithium perchlorate and perchloric acid do not differ greatly, lithium perchlorate would be expected to have much the same

effect on $Y_{\pm\text{HCl}}$ as does perchloric acid. The much smaller changes in absorbance which result when LiClO_4 rather than NaClO_4 is used to replace part of the HClO_4 as swamping electrolyte can be rationalized on this basis.

The formation constants determined in this work for solutions in which only perchloric acid was the swamping electrolyte are compared to those of other workers in Fig. 5. Our values are in good agreement with those of Rabinowitch and Stockmayer⁶ and Olerup,⁷ but are somewhat higher than those of Coll, Nauman, and West.¹¹ These latter workers measured the absorbance at λ_{max} for solutions in which $[\text{Fe(III)}]/[\text{Cl}^-] \cong 100$. They assumed that FeCl^{2+} would be the only chloro complex present under these conditions and that the limiting absorbance would be obtained at high (9 M) perchloric acid concentrations. These assumptions permitted them to calculate the concentration of FeCl^{2+} in solutions of lower acid concentrations from the measured absorbances. However, the value of E_{max} which they obtained in 9 M HClO_4 , 2910, is much higher than our value of E_1 , 1980, determined in 5 M HClO_4 . Furthermore, they observed a shift in λ_{max} from 336 to 352 m μ with increase in the acidity of the solutions from 2.5 to 9 M. We observed a similar shift in λ_{max} , but this was brought about by increasing the amounts of higher chloro complexes in solution, *i.e.*, by conditions which produced increased divergence of the absorption curves from the isosbestic point at $\lambda = 282 \text{ m}\mu$. Thus, either higher chloro complexes are present in the solutions 9 M in perchloric acid or the absorption curves are altered by medium effects. Either reason could account for the differences in K_1 as determined in this work and by Coll, Nauman, and West.

In conclusion, our results show that the ionic strength principle is not valid for dilute solutions of FeCl^{2+} in the presence of large concentrations of noncomplexing electrolytes. Instead the effect of the specific electrolyte medium upon the activity coefficients of the species involved in the equilibrium must be considered. Similar conclusions were reached by Zielen and Sullivan²⁴ from their study of the electrochemical potentials of several oxidation-reduction systems.

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(24) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962).