[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY, TITANIUM DIVISION, RESEARCH LABORATORY, SAYREVILLE, N. J.]

Ion-Exchange Investigation of the Nature of Iron(II) in Sulfuric and Perchloric Acid

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The nature of complexing between Fe(II) and ligands derivable from H_2SO_4 has been studied by means of ion-exchange elution techniques. In dilute H_2SO_4 (2.2 *M* and less), $FeHSO_4^+$ and $FeSO_4$ presumably are formed. The association constants are 0.61 and 1.7, respectively. In $HClO_4$ the predominant ionic species is the free ferrous ion, Fe^{++}, but it is possible that the complex $FeClO_4^+$ also exists. The data are interpreted in such a manner as to exclude in solution such species as $FeOH^+$ and $Fe(OH)_2$ for both acid systems in a range of $[H^+]$ above 0.77 *M*. A simple experiment indicates that ferrous ion in very dilute (~0.03 *M*) H_2SO_4 is monomeric. An attempt was made to study the interaction between Ti(IV) and Fe(II) in H_2SO_4 solutions. Apparently, the tendency for complexing between Ti(IV) and Fe(II) in H_2SO_4 is too weak to be readily amenable to detection by these elution techniques.

There is very little information in the literature regarding the nature of complexing between ferrous ion and sulfate, bisulfate or perchlorate ligands. For example, only one reference is given in the comprehensive compilation by Bjerrum, *et al.*,[2] to this particular subject, the mention being to a paper[3] on the kinetics in sulfate systems of the oxidation of ferrous ion with oxygen. In that paper, the authors, with the aid of the assumption that only one ligand, $SO_4^=$, adds to Fe^{++}, deduce that $K = [FeSO_4]/[Fe^{++}][SO_4^=] = 1.1 \pm 0.2$.

Gayer and Wootner,[4] employing potentiometric techniques, have calculated, on the basis of certain reasonable assumptions, that, for the reaction: $Fe^{++} + HOH \rightleftarrows FeOH^+ + H^+$, $K = (FeOH^+)(H^+)/(Fe^{++}) = 1.2 \times 10^{-8}$, where parentheses refer to activities.

The purpose of the present investigation was to elucidate the nature of Fe(II) species in sulfuric and perchloric acid by means of ion-exchange elution techniques. It was hoped that this information, when compared with the results previously reported[5] for a similar study of Ti(IV) systems, could then be used to study the nature of interactions between Fe(II) and Ti(IV) in sulfuric acid.

Experimental

The techniques, eluents, pretreatment of the resin, apparatus, determination of column parameters and other pertinent details are given in a previous publication by the authors.[5] Samples of Fe(II) taken for elution were prepared by dissolving reagent grade $FeSO_4 \cdot 7H_2O$ in portions of the eluent to be used. The quantities of solute taken were such that a 5-ml. aliquot introduced into the column contained 0.05 mmole Fe(II). Fe(II) was determined in the eluted fractions colorimetrically with thiocyanate after oxidation with persulfate. Some oxidation to Fe(III) always occurred either previous to or during the elution step. The Fe was partitioned from the Fe(II) by colorimetric measurements of thiocyanate complexes before and after the addition of ammonium persulfate to the eluted fractions.

The column used for most of this work had an internal cross-sectional area of 4.52 cm.^{2} and a bed height (in water) of 16.3 cm. The capacity, *Q*, of this resin was found to be 4.99, the dry weight of resin, *W*, was 29.5 g., and the interstitial volume, *V*, was 29.4 ml., yielding a value for QW/V of 5.01. The resin was AG 50W × 8, 100–200 mesh, and was the same type described previously.[5]

Ligand and Hydrogen Ion Concentrations.—Throughout this work the concentrations of H^+, HSO_4^- and $SO_4^=$ in sulfuric acid were calculated from the Raman spectra data of Young.[6] The concentrations of these same ions in solutions of $NaHSO_4$ were calculated from the information given by Baes.[7] The concentration of hydrogen ion in perchloric acid was calculated from the proton magnetic resonance data of Hood, *et al.*[8]

Determination of the Charge per Fe(II) Atom, and the Degree of Polymerization.—A 0.10 *M* solution of $FeSO_4$ in 0.036 *M* H_2SO_4 was prepared. Metallic zinc was introduced into this solution for 3–4 min. and then removed. This inhibited oxidation of the iron. This solution was immediately allowed to slowly flow through a small column containing 10.3 meq. of HR, the interstices of which were initially filled with water. Small uniform fractions of eluent were collected and titrated to the phenolphthalein end-point with standard NaOH. This was stopped when a fraction was obtained with which the end-point was no longer discernible due to precipitation of green ferrous hydroxide. At this point, 49.5 ml. of 0.10 *M* Fe(II) solution had entered the column. Also, the total meq. of H^+ liberated into the eluent by the resin was determined by totaling the meq. H^+ found in each titration up to this point. Corrections were made for the H_2SO_4 initially in the eluent.

Results

The elution data are summarized in Fig. 1 where it is shown that with H_2SO_4 elutions a log *C vs.* log $[H^+]$ plot yields a straight line of negative slope equal to two. With $HClO_4$ elutions the negative slope equals two only at lower concentrations of $HClO_4$. At higher acidities this slope approaches unity.

From the experiment designed to determine the charge per Fe(II) atom, it was found that 49.5 ml. of 0.10 *M* Fe(II) solution had entered the column before appreciable Fe(II) was detected in the effluent. Since the column contained 10.3 meq. of HR, the charge per atom[5] is $n = 10.3/4.95 = 2.08$. The total meq. of H^+ displaced from this column into the effluent (at the point where Fe(II) is first detected in the effluent) was 9.8, and the total mmoles Fe(II) subsequently removed from the resin was 4.9. These results correspond closely to the integer value of two which had been anticipated for the charge per atom.

The result that the charge per atom is two, when considered from the point of view that the charge per ionic species is also two (discussed subsequently), leads to the conclusion that the degree of

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[2] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances. Part II: Inorganic Ligands," The Chemical Society London, 1958.

[3] R. E. Huffman and N. Davidson, THIS JOURNAL, **78**, 4836 (1956).

[4] K. H. Gayer and L. Wootner, *ibid.*, **78**, 3944 (1956).

[5] J. Beukenkamp and K. D. Herrington, *ibid.*, **82**, 3025 (1960).

[6] T. F. Young, *Record Chem. Progress*, **12**, 81 (1951). See also C. H. Brubaker, Jr., *J. Chem. Ed.*, **34**, 325 (1957).

[7] C. F. Baes, Jr., THIS JOURNAL, **79**, 5611 (1957).

[8] G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **22**, 2067 (1954).

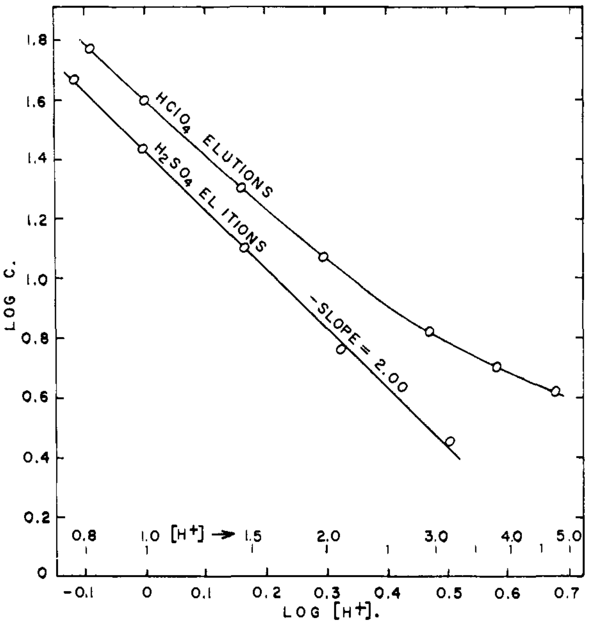

Fig. 1.—Summarized elution data for Fe(II) with sulfuric and perchloric acid.

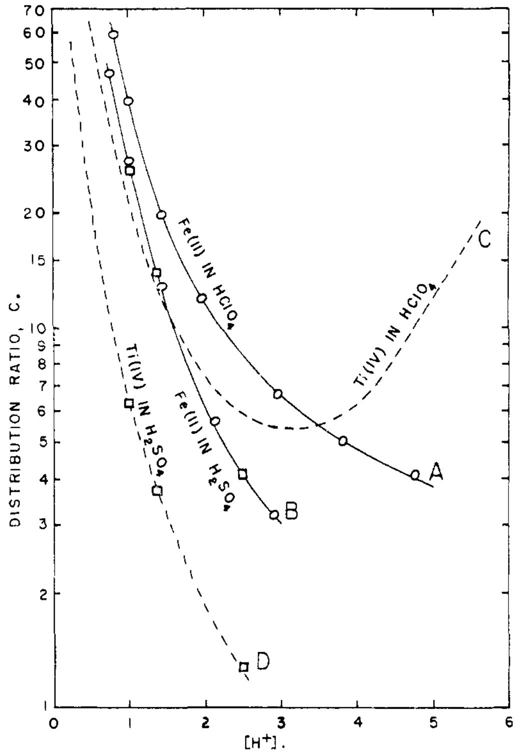

Fig. 2.—Comparison of distribution ratios of Ti(IV) and Fe(II) with sulfuric and perchloric acid. Circles indicate data obtained with the elution of Fe(II) in the absence of Ti(IV). Squares indicate elutions of mixtures of Ti(IV) and Fe(II) with sulfuric acid.

polymerization is one, *i.e.*, Fe(II) exists as monomers in the particular solution studied.

Several elutions with sulfuric acid eluents of samples containing both Ti(IV) and Fe(II) were carried out. Three sets of distribution ratios of these two elements when eluted from mixtures are shown with square points in Fig. 2. Curves C and D of Fig. 2 are taken from the previous publication[5] and show the variation of the distribution ratio of Ti(IV) in both H_2SO_4 and $HClO_4$. Curves A and B show the comparable behavior of Fe(II). In each case both Ti(IV) and Fe(II) displayed *C* values identical to that in the absence of the other element, *i.e.*, the points fall on the corresponding predicted curves for the individual components of the mixture.

Several elutions of similar mixtures were carried out with a cation exchanger of lower degree of cross-linking, AG 50WX2, 100–200 mesh, which is 2% cross-linked as compared with 8% for the other cation-exchanger. Similarly, no difference in *C* values could be detected when the behavior of these two elements in mixtures was compared with the individual behavior.

Several elutions of similar mixtures were carried out on a strong base anion exchanger, AG1X8, 100–120 mesh, employing sulfuric acid eluents of various concentrations. In each case, no adsorption of either element was detected.

Discussion

The Charge per Fe(II) Species in $HClO_4$.—That the negative slope of a log *C vs.* log $[H^+]$ plot can, under favorable circumstances, be identified with the charge per species has been discussed in our previous publication.[5] The upper curve of Fig. 1 points to a charge of two at lower concentrations of $HClO_4$. The approach to unity of the negative slope at higher concentrations could be attributed to any of a number of possible effects, as previously discussed.[5]

One of these possible effects is the formation of the complex ion $FeClO_4^+$. By considering that this ion is formed and that it will displace H^+ from HR (as does Fe^{++}), a distribution equation can be derived which contains three unknown parameters. One of these parameters corresponds to the concentration quotient, $[FeClO_4^+]/[Fe^{++}][ClO_4^-]$. Evaluation of the parameters by a curve-fitting technique yields a value of 0.12 for this concentration quotient. All other complexing reactions, considered either individually or in combinations, yielded distribution equations which in turn yielded negative values for the respective concentration quotients. It is the purpose here merely to point out the possibility of perchlorate complexing. Confirmatory evidence was not pursued.

A concentration quotient for the reaction of Fe^{++} with HR is defined as: $E_1 = [FeR_2][H^+]^2/[Fe^{++}][HR]^2$, where concentrations of resin species are in terms of mole fractions; others as molarities. Evaluation of the data shown in Fig. 1 at $HClO_4$ concentrations where the negative slope is two yields a value for E_1 of 7.9.

Evaluation of the Species and Equilibria in H_2SO_4.—Distribution equations were derived and tested for agreement with the data for ten different possible equilibrium systems. All but one of these were rejected from consideration for one reason or another. For example, if a stepwise addition of either two HSO_4^- or two $SO_4^=$ ligands to Fe^{++} was assumed, negative values for concentration quotients were obtained. The same result was ob-

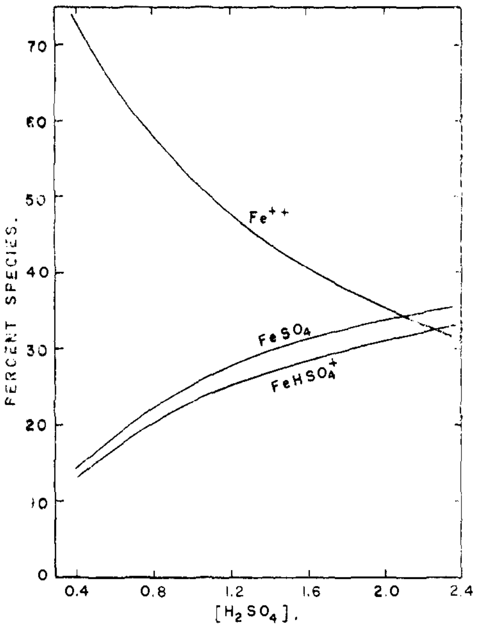

Fig. 3.—Relative concentrations of various Fe(II) species in sulfuric acid.

tained when a HSO_4^- ligand was assumed to add to $Fe(OH)^+$. When $Fe(OH)^+$ was assumed to be present in appreciable amounts with other systems where negative values for concentration quotients were not encountered, then a value for E_1 was derived which was quite different from that obtained with the perchloric acid data. When assuming that only one $SO_4^=$ ligand was involved, the same difficulty was encountered. Actually, the contribution of $FeOH^+$ could not be expected to be significant in view of the magnitude of the concentration quotient for the reaction $Fe^{++} + HOH \rightleftarrows FeOH^+ + H^+$. The concentration quotient, as evaluated by Gayer and Wootner,[4] predicts that at hydrogen ion concentrations of the range 0.5 to 2 M, the concentration of $FeOH^+$ would be of the order of 10^{-6}% of the total Fe(II).

When it was assumed that only one HSO_4^- ligand added to Fe^{++} to yield $FeHSO_4^+$, a distribution equation could be derived which yielded both positive parameters and a value for E_1 which was consistent with that from perchloric acid data. This system was rejected because elutions carried out with eluents in which the relative quantities of hydrogen ion and bisulfate ion were different from that with sulfuric acid demonstrated that this particular system could not adequately explain the observed elution behavior of Fe(II).

These trial-and-error methods eventually led to only one system which was satisfactory. This system, which is proposed here, considers Fe^{++} to be in equilibrium with both HSO_4^- and $SO_4^=$ as $Fe^{++} + HSO_4^- \rightleftarrows FeHSO_4^+$, and $Fe^{++} + SO_4^= \rightleftarrows FeSO_4$, for which the respective concentration quotients are defined as $K_1 = [FeHSO_4^+]/[Fe^{++}][HSO_4^-]$ and $K_2 = [FeSO_4]/[Fe^{++}][SO_4^=]$. Both Fe^{++} and $FeHSO_4^+$ undergo exchange with HR, and the respective concentration quotients are E_1 (defined before) and $E_2 = [FeHSO_4R][H^+]/[FeHSO_4^+]$. The data of Young[6] show that, for sulfuric acid solutions of the concentration range studied here, $[HSO_4^-] = 0.556\,[H^+]$ and $[SO_4^=] = 0.211\,[H^+]$. By appropriately combining the above definitions and relationships with a fundamental definition of C, equation 1 can be obtained which adequately describes the elution behavior of Fe(II) with sulfuric acid eluents.

$$C = \frac{QW}{V} \cdot \frac{E_1 + 0.556 E_2 K_1 [H^+]^2}{[H^+]^2 + (0.556\,K_1 + 0.211\,K_2)[H^+]^3} \quad (1)$$

Evaluation of the parameters in equation 1 from the data with sulfuric acid elutions reveals that K_1 and K_2 cannot be partitioned but that $(0.556\,K_1 + 0.211\,K_2) = 0.704$, $E_2K_1 = 1.8$, and $E_1 = 7.9$. Substitution of these values, along with $QW/V = 5.01$, yields an equation which is plotted as curve B in Fig. 2, and which is compared there with the data.

In order to partition and evaluate K_1 and K_2 it became necessary to employ eluents in which the relative quantities of H^+, HSO_4^- and $SO_4^=$ were different from that in sulfuric acid. To do this required the presence of another cation, *e.g.*, Na^+, in addition to H^+. The presence of another cation in the eluent then required a knowledge of the ability, relative to H^+, of this other cation as an eluting agent for Fe(II). Eluents containing $NaHSO_4$ as the only solute were chosen for this purpose. The relative eluting ability of sodium ion was calculated from the data of Bonner and Vickers[9] who obtained equilibrium data at an ionic strength = 0.1 for the sodium-hydrogen exchange with a resin virtually identical to the one employed in this work. It was necessary to recognize that the concentration quotient for the sodium-hydrogen exchange varies with the mole fraction of NaR. The total concentrations of sodium ion in the eluents were converted to a basis equivalent to that of hydrogen ion. This concentration, which has been made equivalent to a corresponding amount of hydrogen ion, was then added to the actual hydrogen ion concentration in the eluent to give the total effective univalent cation concentration, $[M^+]$.

Then, equation 1 was rederived so as to be applicable to any mixture of HSO_4^- and $SO_4^=$ in which all cations are univalent and the term M^+ suitably expresses the relative eluting abilities of these cations. This yielded

$$C = \frac{QW}{V} \cdot \frac{E_1 + E_2K_1[HSO_4^-][M^+]}{[M^+]^2(1 + K_1[HSO_4^-] + K_2[SO_4^=])} \quad (2)$$

Knowing E_1 and E_2K_1 from data with sulfuric acid elutions, the partitioning and evaluation of K_1 and K_2 then was carried out with the data from sodium bisulfate elutions. This resulted in the values $K_1 = 0.61$, $K_2 = 1.7$ and $E_2 = 3.0$.

Analysis of the Slope of Fig. 1.—Recalling that the negative slope of a log C *vs.* log $[H^+]$ plot (lower curve of Fig. 1) is 2.0, and from an inspection of equation 1, it can be concluded that the ratio $(E_1 + 0.556E_2K_1[H^+]^2)/(1 + 0.556K_1[H^+] + 0.211 \cdot K_2[H^+])$ must be constant in order for this treatment to be correct. Insertion in this ratio of the appropriate values for the concentration quotients and hydrogen ion concentrations for the sulfuric acid concentration range studied reveals that this

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[9] O. D. Bonner and R. Vickers, *J. Phys. Chem.*, **57**, 254 (1953).

ratio is constant with a relative mean deviation of less than 2%. This accounts for the apparent linearity of the lower curve of Fig. 1.

From the concentration quotients evaluated, Fig. 3 was constructed to represent the relative quantities of Fe(II) species in sulfuric acid in the indicated concentration range. The assumption is made here that the concentration of Fe(II) is small enough not to alter the hydrogen ion concentration appreciably and that ionic strength effects need not be considered.

Complex Formation between Ti(IV) and Fe(II) in H_2SO_4.—Various investigators in the authors' laboratories have reported spectrophotometric evidence for complex formation between Ti(IV) and Fe(II) in sulfuric acid solutions. For example when a solution 1 *M* in H_2SO_4 and 0.2 *M* in Ti(IV) is mixed with an equal volume of a solution 1 *M* in H_2SO_4 and 0.2 *M* in Fe(II), both of which are colorless, a pale yellow color develops. Spectrophotometric analysis, using the method of continuous variations, indicates that this color is due to the formation of a complex in which the mole ratio of Fe(II) to Ti(IV) is 2.0. The possibility that this color arises from the products of an oxidation-reduction reaction has been eliminated. In the previous publication[5] the nature of Ti(IV) species in perchloric and sulfuric acids has been elucidated. The distribution ratios of Ti(IV) in perchloric and sulfuric acids have been reproduced here as curves C and D, respectively, in Fig. 2.

An attempt was made to study the nature of this complex by eluting samples containing both Ti(IV) and Fe(II) in H_2SO_4 with sulfuric acid eluents. Had these cations, when eluted from a mixture, displayed distribution ratios different from that obtained individually, this would have been evidence for complexing.

That the data for such elutions (square points in Fig. 1) coincide with the corresponding predicted curves for the individual elements, indicates that either no complex exists or, more likely, a complex exists but it is so highly dissociated as not to alter the normal elution behavior of its components. The lack of observable adsorption of either Ti(IV) or Fe(II) from mixtures in sulfuric acid by a strong-base anion exchanger is considered as indicative of the absence of negatively-charged complexes of any appreciable stability.

The difficulty here may lie with the fact that only small quantities of Fe(II) and Ti(IV), 0.05 to 2.0 mmole of each, were taken for elution. Greater quantities would have overloaded the column. Furthermore, most of these quantities existed in the resin phase rather than in solution, so that the net effect is a shift in equilibrium away from complex formation. This, of course, implies a complex with a relatively high dissociation constant.

Analytical Separations of Ti(IV) and Fe(II).—It is quite apparent from an inspection of Fig. 2 that ion-exchange chromatography can be used as the basis for a quantitative separation of iron and titanium provided that the iron is maintained in the oxidation state of two. With a proper choice of perchloric acid concentration, either cation can be made to precede the other. For example, an eluent of about 2.5 *M* $HClO_4$ will elute titanium first, whereas an eluent of about 5 *M* $HClO_4$ will elute ferrous ion first. The respective elution curves, obtained when 0.1 mmole of each were eluted, were sufficiently narrow that no overlapping of elution curves is anticipated. With the three sulfuric acid elutions of actual mixtures these two cations were quantitatively separated (no overlapping), in which case titanium was eluted first.

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Ion-Exchange Investigation of the Nature of Titanium(IV) in Sulfuric Acid and Perchloric Acid

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Ion-exchange elution techniques have been employed to elucidate the nature of Ti(IV) ions in $HClO_4$ and H_2SO_4 solutions. In $HClO_4$ up to about 1.5 *M*, Ti(IV) is shown to exist in two ionic forms as follows: $Ti(OH)_3^+ + H^+ \rightleftarrows Ti(OH)_2^{++}$ for which the concentration quotient is 2.0. In H_2SO_4 solutions up to about 2.0 *M* the same ions exist, but in addition each accepts a HSO_4^- ligand to form $Ti(OH)_3HSO_4$ and $Ti(OH)_2HSO_4^+$, respectively. The concentration quotients for these association reactions have been determined to be 11.3 and 0.64 respectively. The data point to monomeric titanium species in dilute acid. At high $HClO_4$ concentrations, the distribution ratio goes through a minimum. It is possible to interpret this behavior in terms of complexing of Ti(IV) with ClO_4^-.

There is very little information in the literature regarding the nature of titanium (IV) in solution and the extent and type of complexing encountered in sulfuric acid solutions. For example, in a rather comprehensive compilation of stability constants of metal-ion complexes by Bjerrum, *et al.*,[1] no mention is made of interaction between titanium(IV) and ligands derivable from sulfuric acid. With regard to equilibria with hydroxide, other than that involving a solid phase, Delafosse[2] claims the coexistence of $Ti(OH)^{+3}$ and TiO^{++}, the former existing at $pH < 0.3$ and the latter at $pH > 0.4$. The titanium(IV) species indicated by Barksdale[3] are speculative.

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(1) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances. Part II: Inorganic Ligands," The Chemical Society, London, 1958.

(2) D. Delafosse, *Compt. rend.*, **240**, 1991 (1955).

(3) J. Barksdale, "Titanium," Ronald Press Co., New York, N. Y., 1949.