[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1434]

The Distribution of Ferric Iron between Hydrochloric Acid and Isopropyl Ether Solutions. II. Polymerization of the Iron in the Ether Phase, the Effect of the Acid Concentration on the Distribution, and the Two-Ether-Phase Region

BY ROLLIE J. MYERS AND DAVID E. METZLER

Introduction

In the first paper[1] of this series data obtained from a study of the distribution of ferric iron between isopropyl ether and hydrochloric acid were presented which showed the nature of the iron compound in the ether phase and the dependence at constant acid concentration of the per cent. extraction on the quantity of iron present. In this paper certain considerations will be presented which indicate that this dependence is caused by polymerization of the iron in the ether phase, and the nature of this polymerization will be discussed. Consideration will also be given to the effect of the acid concentration on the distribution, and to the nature of the two-ether-phase system which can be produced under certain conditions.

In the following paper we show that isopiestic molecular weight determinations of the ethereal iron complex indicate polymerization. In the preceding paper we show also that a variation in the number of water molecules associated with the ethereal iron supports this assumption.

Nachtrieb and Fryxell[2] have explained the dependence of the distribution ratio on the iron concentration by assuming an activity effect in the acid layer. In this paper we are going to assume that at constant acid concentration the activity of aqueous iron is proportional to its formality. This assumption is certainly not valid in solutions sufficiently concentrated in ferric chloride. In the concentration range that we use, however, it would seem that such an assumption is justified.

Calculations Relating to the Polymerization Number.—In the subsequent discussion various symbols will be used:

Q = volume formality of the ethereal iron, fwts./l.
M = volume molality of the ethereal iron, moles/l. (as defined by Raoult's Law)
x = activity of the ethereal iron (as defined by Henry's law, and set equal in value to Q at infinite dilution)
n = Q/M = polymerization number
F = volume formality of the aqueous iron, fwts./l.

If it is assumed that at a constant acid concentration the activity of the aqueous iron in dilute ferric chloride solutions is proportional to its formality, a quantity called the distribution constant can be defined as

$$K_d = x/F \qquad (1)$$

This quantity should remain constant at a given acid concentration. From Fig. 4 of Part I of this series it is evident that the value of the distribution constant can be established by making use of the data in the dilute region of the curve, where the activity of the ethereal iron may also be assumed to be equal in value to its formality. Thereafter in the other region of the curve the value thus established for the distribution constant can be used to establish the ethereal iron activity.

By use of the data in Table V, Part I, the value of the ethereal iron molality can be established by integration. For solutions in which the mole fraction of the solute is small, the following approximate relation can be derived using the Gibbs–Duhem equation at constant temperature and pressure

$$\mathrm{d}M/\mathrm{d}x = Q/x \qquad (2)$$

and from Equation (1)

$$M_i = \int_0^{F_i} Q/F \, \mathrm{d}F \qquad (3)$$

A plot of a portion of the data in Table V, Part I, suitable for the integration of Equation (3) is shown in Fig. 1. By means of this integration the polymerization number was calculated, and the values obtained are plotted in Fig. 2.

If it is assumed that the only deviation from ideality is due to actual polymerization of the ethereal iron, x, the ethereal iron activity as defined above is equal to the monomer concentration in that layer. Taking K_r as the equilibrium constant for the formation of the r^{th} polymer from the monomer, the following general equations which give the molality and formality of the iron in the ether layer can be established

$$M = x + K_2x^2 + K_3x^3 + \ldots + K_rx^r \qquad (4)$$
$$Q = x + 2K_2x^2 + 3K_3x^3 + \ldots + rK_rx^r \qquad (5)$$

From these equations it is evident that Equation (2) is true.

Lassettre[3] has treated the problem of fitting functions to polymeric systems. However, it is evident from Fig. 2 that, in general, the functions he used cannot apply to our case. His curves for the polymerization of the aliphatic alcohols in benzene seem to be similar to ours, but the function that he used for these alcohols is difficult to apply and has little physical significance. If a general polymerization function must be used it is preferable that this function be based upon physical considerations applying to our system.

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[1] R. J. Myers, D. E. Metzler and E. H. Swift, THIS JOURNAL, **72**, 3767 (1950).

[2] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948).

[3] E. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

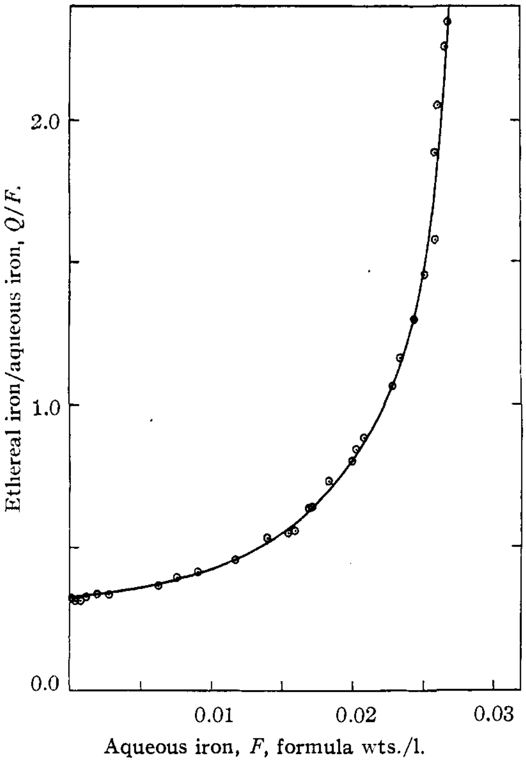

Fig. 1.—The distribution with a fixed acid concentration: a portion of the data of Table V, part I, is plotted in a manner suitable for integration in order to obtain the molality.

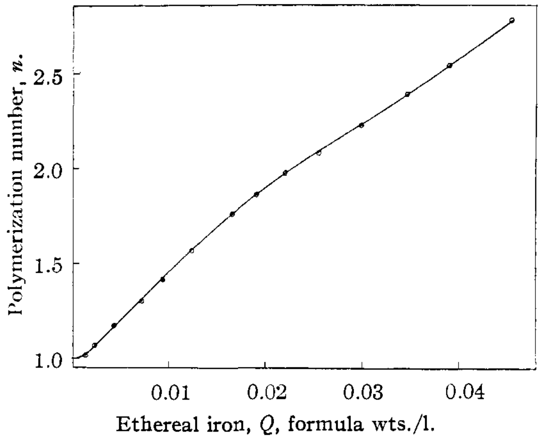

Fig. 2.—The apparent polymerization of the iron: the polymerization number was obtained by the integration of Fig. 1.

In this direction, the data contained in Fig. 2 can be fitted satisfactorily by using a continuous polymerization function in which the dimer term is omitted. For this case the polymerization constants, omitting the dimer constant, were connected in a geometrical manner, a device used by Lassettre based upon the inference of an equal free energy decrease for the formation of each polymerization bond. When the function which is obtained on the basis of the above restrictions is applied to the data in Fig. 2, a constant corresponding to the formation of each successive polymerization bond from the monomer of 70 l. moles^{-1} is obtained. However, when this constant is used to calculate distribution ratio values and these are compared with the data in Table V, Part I, the results are disappointing. It is to be emphasized then that this function at best gives only a rough picture of the actual situation.

It was pointed out to one of the authors by Dr. Verner Schomaker that the most general method for solving for the polymerization constants in our case is that of applying the method of least squares directly to the distribution data. This was not done by the authors because of the many difficult problems that this method presents, if the solution were to be carried out adequately.

Variation of the Distribution Constant with Acid Concentration.—In order to test the effect of variation of acid concentration upon the dependence of the distribution ratio upon the ethereal iron concentration, the variation of the distribution constant with acid concentration must be established. By the use mainly of spectrophotometric analyses of both layers, this was accomplished. In some cases the ethereal iron concentration was sufficiently high so that the directly obtained distribution ratio would not be expected to be the distribution constant for that acid concentration. In these cases the values were extrapolated to infinite dilution by using the data obtained in Part I for the extraction from 5.6 WF. acid. In the worst case such an extrapolation reduced the value of the distribution ratio by 7%. The values obtained for the distribution ratio are plotted in Fig. 3 and the averaged values are listed in Table I.

TABLE I

THE VARIATION OF THE DISTRIBUTION CONSTANT WITH ACID CONCENTRATION

Hydrochloric acid Wt. formal	Hydrochloric acid Vol. formal	Distribution constant, K_d
4.368	4.01	0.0284
4.943	4.48	.0964
5.602	5.01	.320
6.116	5.41	.839
6.772	5.91	2.63
7.315	6.32	6.28
7.933	6.76	16.9

By use of the slope of the curve at 5.6 WF. acid, the original values obtained for the aqueous iron concentration were changed to the "adjusted" values listed in Table V, Part I. This adjustment was made in order to correct for the deviations of the actual acid concentrations of the distributions from the mean value of 5.602 WF. The aqueous iron formality was adjusted to values which would have the same ethereal iron activity at the mean acid concentration as the actual

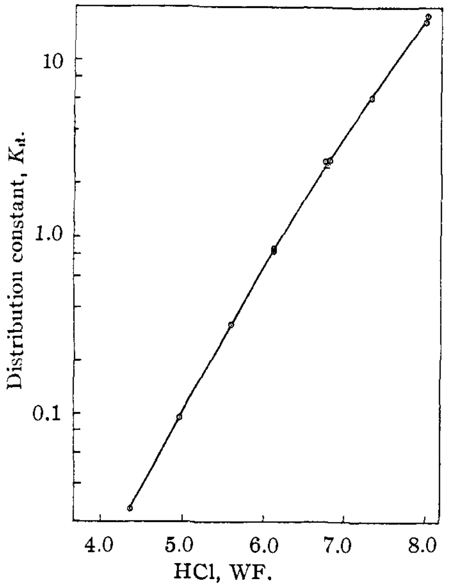

Fig. 3.—The variation of the distribution constant with acid concentration.

distributions had at their equilibrium acid concentrations.

Extraction at Several Acid Concentrations.—A series of extractions was made with sufficient iron present to cause a marked deviation from ideality. If this anomaly in the distribution were due to deviation from ideality in the ether layer, to a first approximation one would expect that at constant ethereal iron activity the effect should be independent of the acid concentration. Using the values of the distribution constant previously obtained to compute the iron activities, the effect of the acid concentration upon the distribution is shown in Fig. 4.

Considering the range over which the aqueous iron concentration was varied, the agreement between the curves in Fig. 4 is satisfactory. The manner in which the deviation varies with acid concentration is difficult to understand. It must be remembered, however, that as the acid concentration varies the nature of the ether layer varies also because of the dissolved acid and water. In the case of the highest point on the 4.9 WF. curve it is possible that some of the deviation may be due to the high aqueous iron concentration (about 0.05 VF.). In fact, there may be some error in the 5.6 WF. curve for this same reason. Any small error due to a lack of strict proportionality between the aqueous iron activity and its formality should, to a first approximation, affect only the value of any derived polymerization constants, and not the validity of any arguments used to establish a polymerization function.

The Two-Ether-Phase Region.—It was observed by Dodson, Forney and Swift[4] that at the

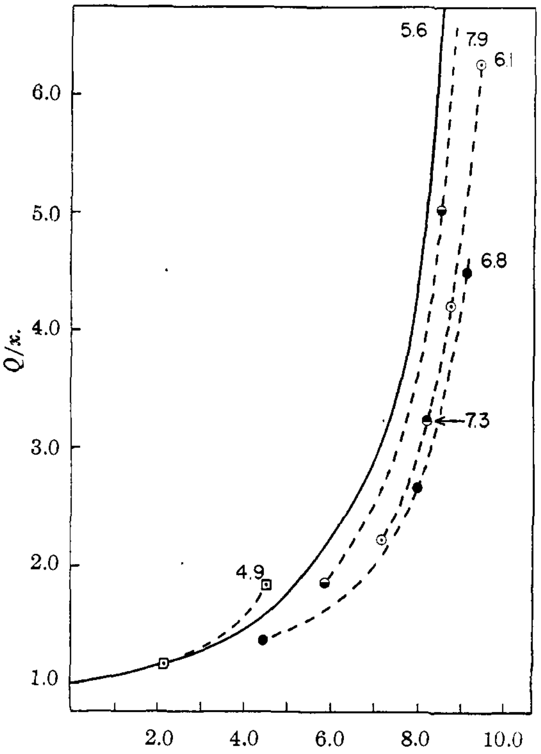

Fig. 4.—The effect of acid concentration upon the distribution of the iron; the equilibrium acid concentrations of the distributions in WF. were: ◻, 4.9; —, 5.6; ⊙, 6.1; ●, 6.8; ◓, 7.3; ◒, 7.9.

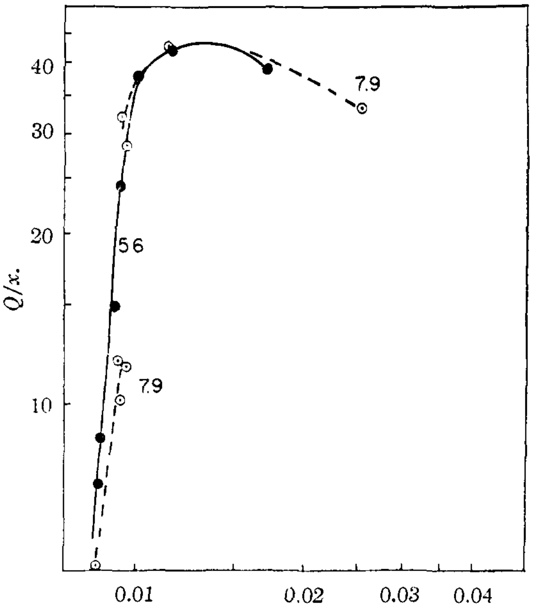

Fig. 5.—The distribution in the two-ether-phase region; the equilibrium acid concentrations of the distributions in WF. were: ●, 5.6; ⊙, 7.9.

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[4] R. H. Dodson, G. J. Forney and E. H. Swift, This Journal, **58**, 2573 (1936).

higher acid concentrations two ether phases would sometimes form. A brief study was made in order to examine the nature of the system when two ether phases are present.

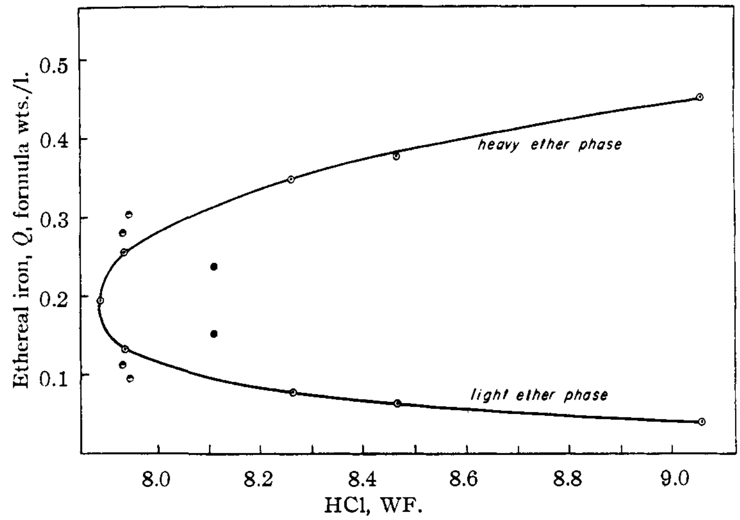

Fig. 6.—The effect of acid concentration upon the composition of the two ether phases: ○, 24-hr. equilibration; ◓, 2–6 hr.; ●, 24-hr. equilibration with concentrated acid added through the ether layer. The consolute point was obtained by adding water to the closest distribution.

When the distribution curve for 7.9 WF. hydrochloric acid shown in Fig. 4 is extended to higher ethereal iron concentrations, two ether phases are formed. At 25° and 1 atm. pressure the system $HCl-FeCl_3-H_2O$-isopropyl ether should be invariant at a constant acid concentration if three liquid phases are present. A comparison of the distribution curve for 7.9 WF. acid with that obtained at 5.6 WF. is shown in Fig. 5. It can be seen from Fig. 5 that the appearance of the two curves is very nearly the same except for the discontinuity which is present in the two-ether-phase region.

As a further illustration of the two-ether-phase region, the effect of acid concentration upon the composition of the two ether phases is shown in Fig. 6. Some difficulty was experienced in obtaining consistent results in this acid range. This seemed to be due to a slow reaction between isopropyl ether and the acid. As an illustration, the difference between the results of a 2–6 hour equilibration period and a 24-hour period is shown in Fig. 6. Also, the effect of adding concentrated acid through the ether layer is illustrated in that figure.

The distributions used for the 24-hour equilibration period curve were allowed to stand outside of the thermostat for a period of several months. During this time they were shaken occasionally. Under these conditions the two-ether-phase systems gradually reverted to one-ether-phase systems. The times for this transition, in order of increasing acid concentration starting at 8.26 WF. acid, were 7 days, 11 days, and 5.5 months. The ultimate stability of the two-ether-phase region is not in question, for such a system has been kept for $1^1/_2$ years.

The ultraviolet and visible absorption of the lighter of the two ether phases has been examined and the positions of the maxima are found to be the same as in an ether layer from a 5.6 WF. acid distribution. The visible spectrum of the heavy phase has been found to have the same extinction within experimental error as a 5.6 WF. ether layer. The densities of the heavy and light ether phases are shown in Fig. 7. They compare very closely with those of a comparable 5.6 WF. ether layer.

From Fig. 3, Part I, it can be seen that there is an anomaly in the amount of water coördinated in the two phases. The heavier ether phase contains more water per iron than does the lighter phase. This does not follow the rule established for the 5.6 WF. distributions, in which the water coördination decreases with increasing iron concentration. The study of the chloride and hydrogen coördination has not been sufficiently systematic to make it possible to conclude whether these cases are anomalous also.

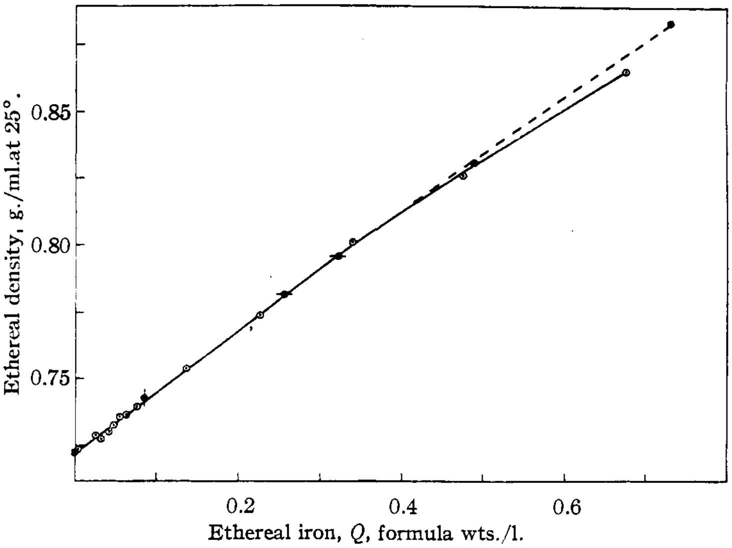

Fig. 7.—Ethereal layer density: ○, equilibrium acid concentration of 5.6 WF.; ●, same for 7.9 WF.; ⏀, light layer; -●-, heavy layer.

Another experiment was performed by bubbling anhydrous hydrogen chloride into an anhydrous solution of ferric chloride in isopropyl ether. A heavy liquid containing most of the iron separated out. It had a visible absorption spectrum containing all of the maxima found in the spectrum of an ether layer from a 5.6 WF. extraction. Such a two-phase anhydrous system is present in a simple phase rule diagram of the two-ether-phase system. In this diagram the two two-phase regions ($FeCl_3 \cdot nHCl$–isopropyl ether and HCl aq.–isopropyl ether) meet at certain acid concentrations to form a three-phase system.

Houben and Fischer[5] have isolated the compound $FeCl_3 \cdot HCl \cdot 2Et_2O$ from a mixture of ferric chloride, hydrogen chloride, and ethyl ether. However, when the above experiment is performed with either ethyl or β,β′-dichloroethyl ether two phases do not form, while both isopropyl and *n*-butyl ether do form these two phases. In the extraction of iron with either ethyl or β,β′-dichloroethyl ether a two-ether-phase region has never been observed. The authors have also been unable to find the conditions for the extraction of iron whereby *n*-butyl ether forms two ether phases, although in this case it would be expected that such a region should exist.

Summary

From the distribution data of the first paper of this series, the effective polymerization of the ethereal iron has been evaluated. The variation of the distribution constant with the acid concentration and the effect of acid upon the apparent polymerization of the ethereal iron have been measured. Also, the formation of two ether phases and the effect of acid concentration upon the composition of the two phases were investigated.

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[5] J. Houben and W. Fischer, *J. prakt. Chem.*, **123**, 89 (1929).

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The Distribution of Ferric Iron between Hydrochloric Acid and Isopropyl Ether Solutions. III. Spectral, Isopiestic and Magnetic Susceptibility Studies

BY DAVID E. METZLER AND ROLLIE J. MYERS

This paper presents the results of spectral measurements made for the purpose of determining the various species present in the aqueous and ether layers, and of isopiestic and magnetic susceptibility studies of the iron in the ether layer.

Spectrophotometric Measurements.—A model DU Beckman spectrophotometer was used. The absorption cells were 1-cm. quartz cells, some use also being made of 0.9-cm. quartz spacers. As a blank the identical solvent without iron was used. It was not necessary to purify the "reagent grade" hydrochloric acid, but the isopropyl ether was purified as described in Part I.

The extinction coefficients (ε) were calculated by means of the formula

$$I = I_0 10^{-\epsilon c l}$$

where *c* is the concentration in formula weights/liter and *l* is the cell path in centimeters. The measurements were made at room temperatures of about 24° with an unthermostated instrument.

Absorption Spectra of the Ether Extracts.—The light absorption of the isopropyl ether layers was studied extensively both for analytical purposes and because of general interest. The ultraviolet absorption was studied with respect to dependence upon both the iron and acid concentrations. The relative values of the absorption at 364, 340, 316 and 287 mμ were found to be constant with initial acid concentrations ranging from 2–9 VF., and at 5 VF. the values of these extinction coefficients were constant in ether layers containing 8×10^{-5} to 10^{-3} fwts./l. of iron. Since this ethereal iron concentration range represents a region over which distribution studies have demonstrated near ideality for the extraction, the ordinate of the spectrum shown in Fig. 1 and the extinction values listed in Table I, Part I, may be called molal extinction.

The absorption spectrum from 420 to 460 mμ was studied very little, but because a small maximum is present the spectrum is shown in Fig. 2. Since the visible spectrum is most conveniently studied in a region where the distribution studies indicate polymerization of the ethereal iron, this spectrum was studied to check any possible effect of such polymerization. As shown in Table I the visible absorption shows no deviation from Beer's law over the concentration range studied. It was also found that for ether layers from extractions with acid concentrations of 5–7.3 VF. the extinction coefficients were constant within experimental error. The visible spectrum is shown in Fig. 3.

The visible spectrum given by Nachtrieb and Conway[1] qualitatively compares favorably with ours. The average values of the extinction coefficients given by them, however, are higher than ours by 10–30%. It is apparent from their data that some of their light density values for the dilute solutions are very high. We have recalculated new average extinction coefficient values from Nachtrieb and Conway's data, rejecting all

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[1] N. H. Nachtrieb and J. G. Conway, THIS JOURNAL, **70**, 3547 (1948).