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ISOTOPES DEVELOPMENT CENTER

THE METHYL ISOBUTYL KETONE (4-METHYL-2-PENTANONE) EXTRACTION OF TRIVALENT IRON FROM HYDROCHLORIC ACID SOLUTIONS AND THE EFFECT OF AN INERT DILUENT ON THE DISTRIBUTION COEFFICIENT

J. J. Pinajian

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Isotopes Division

APRIL 1966

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ABSTRACT

The methyl isobutyl ketone extraction of iron (III) chloride from hydrochloric acid solutions was investigated as a function of the iron concentration and the hydrochloric acid concentration. Values of the K_D are given for 0.01-5 mM Fe^{3+} and 0.01-8 M HCl. The K_D increases with an increase in hydrochloric acid concentration and decreases only slightly with an increase in iron concentration.

In 6 M HCl there is little effect on the K_D from the addition of an inert diluent, up to a concentration of 2 M n-hexane, at which point the K_D rapidly decreases from 1.1×10^3 to 2.4×10^{-2} at 6 M n-hexane.

The distribution coefficients were determined for carrier-free ^{54}Mn and ^{55}Co for the 6 M HCl system and their factors for the separation from iron are estimated to be 10^7 and 10^6, respectively.

INTRODUCTION

There has been comparatively little work published on the use of the methyl isobutyl ketone/hydrochloric acid system in the extraction of iron. Kuznetsov[1] reported in 1947 on the extraction of iron chloride by organic solvents from hydrochloric acid solutions and compared the distribution coefficients obtained with simple ethers, alcohols, organic acids, complex ethers, ketones, and aldehydes. He found that for a concentration of trivalent iron of 3 g/liter (54 mM) the extractions with ketones are orders of magnitude better than with any of the other reagents. A more recent work, that of Bankmann and Specker,[2] covered a range of ~3.6 mM to ~716 mM.

Recent work involving the preparation of reactor-produced carrier-free ^{54}Mn[3,4] by the $^{54}Fe(n,p)^{54}Mn$ reaction involved solutions of iron in the range of 40 mM to less than 0.01 mM. It was convenient in these operations first, to use the solvent extraction techniques to separate the iron target and neutron-induced iron activities from the ^{54}Mn activity and, second, to use the precipitation of $Fe(OH)_3$ as a means of carrying or adsorbing the ^{54}Mn activity. The iron carrier for the latter operation was subsequently removed by solvent extraction. Methyl isobutyl ketone was used in preference to bis-(β-chloroethyl) ether because the

distribution coefficient of the methyl isobutyl ketone does not fall off as rapidly with an increase in the amount of iron. Of particular importance is the ability to back extract Fe^{3+} from methyl isobutyl ketone by contacting the organic phase with water or 0.1 M HCl. In addition, the use of methyl isobutyl ketone allows one to employ lower concentrations of hydrochloric acid (e.g., 6 M HCl) than those used with bis-(β-chloroethyl) ether (e.g., 10-12 M HCl). Hence one may have in solution relatively large amounts of alkali salts which would ordinarily precipitate in strong acids. The solvent extraction technique is used in preference to ion-exchange chromatography because it is less time consuming.

Solvent extraction with methyl isobutyl ketone was also used in the preparation of carrier-free ^{55}Fe[5] and ^{59}Fe[6] produced by the $^{55}Mn(p,n)^{55}Fe$ and $^{59}Co(n,p)^{59}Fe$ reactions, respectively.

PROCEDURE

The methyl isobutyl ketone (4-methyl-2-pentanone)* had a boiling range of 114-116°C. The reagent is normally available in sufficient purity that no purification is necessary for its use in these solvent extraction studies.

The stock ferric chloride solution was prepared from reagent grade $FeCl_3 \cdot 6H_2O$** and diluted to 5, 0.5, 0.05, and 0.01 mM with demineralized water (1.1×10^6-ohm resistance). A few drops of nitric acid per liter of ferric chloride solution insured the iron(III) state. The iron concentration was determined by a volumetric method involving reduction of $FeCl_3$ with $SnCl_2$ and the titration of $FeCl_2$ with a standard solution of K_2CrO_4. All hydrochloric acid solutions were made with the demineralized water. The ^{59}Fe activity*** used as the radioindicator was $FeCl_3$ in hydrochloric acid solution and was $\sim 8 \times 10^{-5}$ mM in iron. Approximately 200 μc ^{59}Fe was used in each experiment and the solutions, in each case adjusted to the desired molarity by adding Fe^{3+}, were of 20 ml volume.

The distribution data were obtained by contacting equal volumes of the organic phase (methyl isobutyl ketone) with the hydrochloric acid solutions containing the ^{59}Fe-labeled iron. The methyl isobutyl ketone was equilibrated prior to use, with the same concentration of hydrochloric acid used in the study. Extractions were made at room temperature. Preliminary experiments with carrier-free iron in 6 M HCl established that equilibrium time was <30 sec. After contacting the two phases for 0.5-1 min, the phases were separated and centrifuged and 1.00-ml aliquots were taken for analysis. The analysis was made by counting the 1.097-Mev and 1.289-Mev photopeaks using a 3- by 3-in. NaI(Tl) gamma spectrometer.

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*Obtained from Matheson, Coleman, and Bell, Division of Matheson Company, Inc.

**Obtained from J. T. Baker Chemical Company.

***Obtained from Isotope Sales Department, Oak Ridge National Laboratory.

The effect of an inert diluent (n-hexane) on the distribution coefficient was studied in the same fashion; equal volumes of aqueous phase (carrier-free ^{59}Fe in 6 M HCl) and the organic phase (methyl isobutyl ketone or methyl isobutyl ketone diluted with n-hexane) were contacted.

Distribution data were also obtained on carrier-free ^{54}Mn and ^{55}Co in the same fashion.

RESULTS

The results of the distribution study are compiled in Table 1 and the results of the effect of an inert diluent (n-hexane) are compiled in Table 2.

Table 1. The Distribution Coefficient of Iron in Methyl Isobutyl Ketone as a Function of the Concentration of Iron and the Concentration of the Hydrochloric Acid

Iron concentration, mM	Distribution coefficient					
	Hydrochloric acid concentration					
	0.01 M	1 M	2 M	4 M	6 M	8 M[a]
0.01	0.00012	0.163	7.25	408	1559	1166
0.05	0.00011	0.206	7.75	1017	2486	1785
0.5	0.00016	0.097	3.81	439	1600	2646
5.0	0.00035	0.063	1.18	220	1458	6304

[a]Organic solvent appears to dissolve in the aqueous phase at this concentration of acid.

Table 2. The Effect of an Inert Diluent (n-hexane) on the Distribution Coefficient of Carrier-Free Iron-59 in the Methyl Isobutyl Ketone/6 M HCl System

Concentration		Distribution coefficient
methyl isobutyl ketone, %	n-hexane, M	
100	0	1559
87	1	1033
74	2	1076
61	3	471
48	4	23.3
22	6	0.0236

Figure 1 shows the distribution coefficient* of iron in methyl isobutyl ketone as a function of the concentration of hydrochloric acid as well as a function of the concentration of iron, and Figure 2 shows the effect of the inert diluent (n-hexane) on the distribution coefficient.

Using the standard deviation of the ratios of the respective counting rates (with their respective standard deviations) as an index of the reliability of the distribution data, then the following generalizations can be made regarding the accuracy of the K_D:

Range of K_D	Estimated Limit of Error in Data, %
10^3 - 10^4	+ 50, - 30
10^2 - 10^3	+ 50, - 30
10^1 - 10^2	+ 20, - 10
1 - 10	+ 10, - 5
10^{-1} - 1	+ 10, - 5
10^{-2} - 10^{-1}	+ 20, - 10
10^{-3} - 10^{-2}	+ 50, - 30

The results agree well with the data of Beckmann and Specker[2] for 3.5 mM Fe^{3+} at 4 M HCl and deviate only within the experimental error at 6 M HCl. The recommended acid concentration for the extraction of trivalent iron with methyl isobutyl ketone is 6 M HCl. The addition of an inert diluent (n-hexane) appears to have little effect on the distribution coefficient up to 2 M n-hexane, at which point the distribution coefficient falls off rapidly from 1.1×10^3 to 2.4×10^{-2} at 6 M HCl.

The distribution coefficients of ^{54}Mn and ^{55}Co were found to be $\sim 10^{-4}$ and $\sim 10^{-3}$, respectively, for the methyl isobutyl ketone and 6 M hydrochloric acid system. Hence, in this system the factor for separation of ^{54}Mn from iron and ^{59}Fe from cobalt are of the order of 10^7 and 10^6, respectively.

ACKNOWLEDGMENTS

It is a genuine pleasure to acknowledge the help of A. P. Callahan in performing these analyses.

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*The distribution coefficient, K_D, is defined as

$$K_D = \frac{^{59}\text{Fe activity in the organic phase}}{^{59}\text{Fe activity in the aqueous phase}}$$

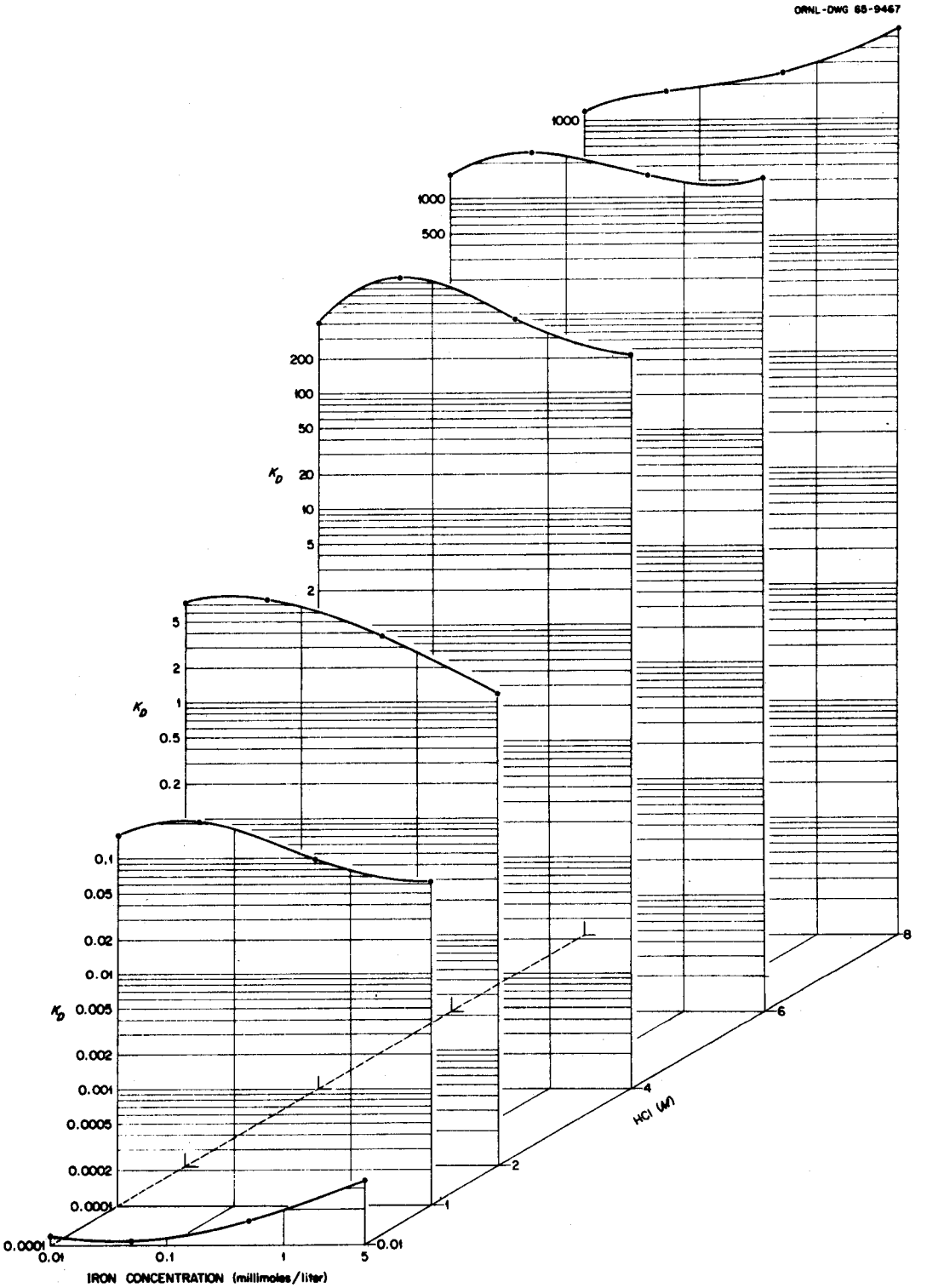

Fig. 1. The Distribution Coefficient of Trivalent Iron in Methyl Isobutyl Ketone (4-Methyl-2-Propanone) as a Function of Hydrochloric Acid Concentration.

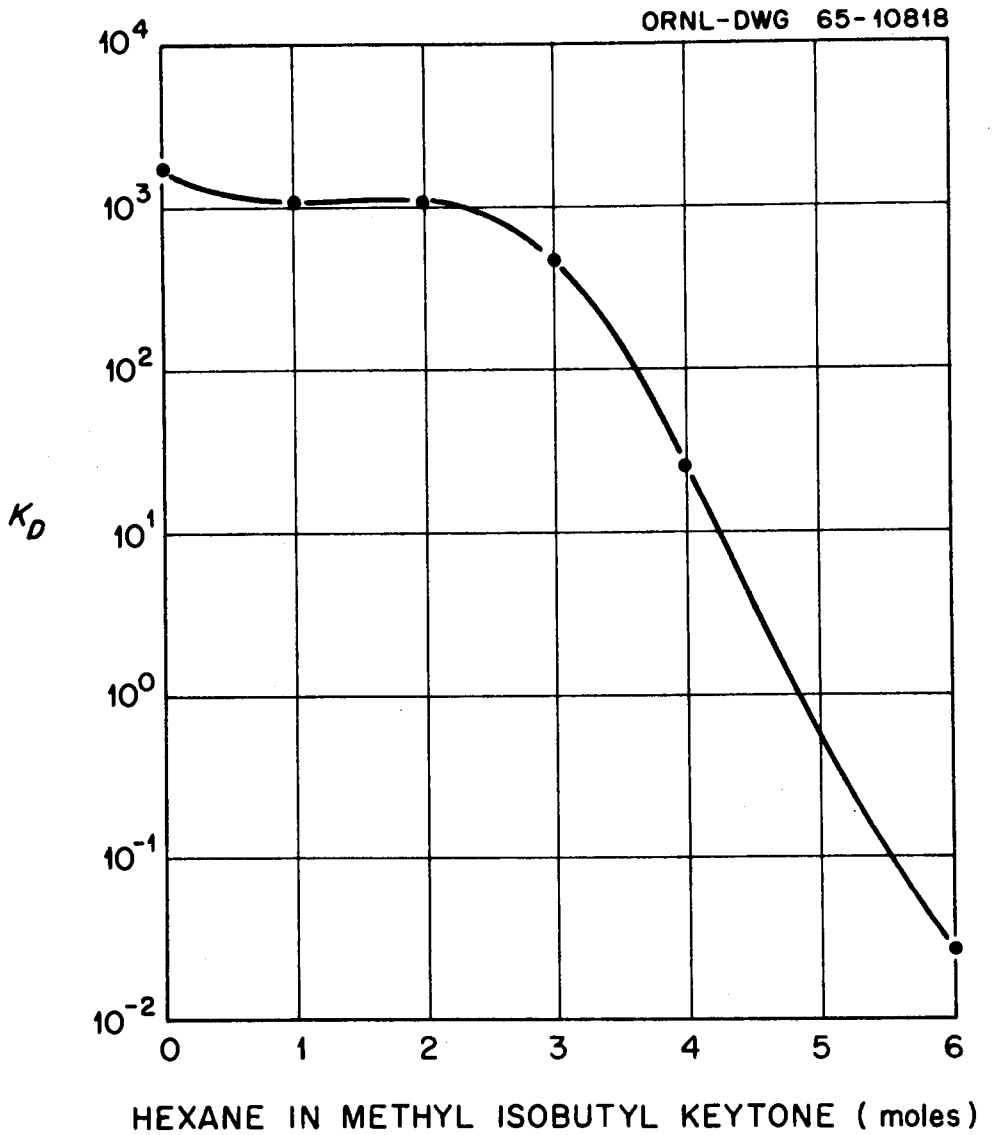

Fig. 2. The Effect of an Inert Diluent (n-Hexane) on the Distribution of Coefficient of Carrier-Free ^{59}Fe in Methyl Isobutyl Ketone/6 M HCl System.

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