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Extraction of Vanadium from Aqueous Acid Solutions by Isopropyl Ether

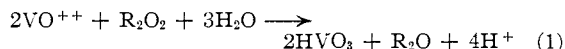
BY JAMES J. LINGANE AND LOUIS MEITES, JR.

Although ether extraction has been recommended for separating iron from vanadium, quantitative data on the behavior of vanadium in this separation are fragmentary and the optimum conditions for the separation have not been defined. Hillebrand and Lundell,¹ and Lundell, Hoffman and Bright,² state that only a trace of vanadium accompanies iron in the extraction by ethyl ether of a 6 *M* hydrochloric acid solution containing +4 vanadium, but they give data from one experiment which indicates that a considerable fraction of the vanadium is extracted when the element is present in the +5 state. Using isopropyl instead of ethyl ether, Dodson, Forney and Swift³ found that less than 0.08% of vanadium was extracted from a solution of +4 vanadium in 7.75 *M* hydrochloric acid by an equal volume of ether, but that 22% was extracted from a +5 vanadium solution under the same conditions. In acid solutions +4 vanadium exists chiefly as vanadyl ion, VO⁺⁺, which would not be expected to be soluble in ether, whereas +5 vanadium may be present ether as pervanadyl ion, VO₂⁺, or as an uncharged polyvanadic acid such as H₄V₆O₁₇, depending on the acid concentration, and it is not surprising that the latter is soluble in ether.

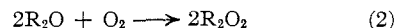
The purpose of the present study was to investigate systematically the various factors which influence the extractability of +4 and +5 vanadium in order to establish optimum conditions for the separation of iron from vanadium. We confirmed the fact that the extractability of vanadium is dependent on its oxidation state, but also found that it is greatly influenced by the

kind and concentration of acid present, the temperature, the time of contact between the ethereal and aqueous phases, and, in prolonged experiments, on whether or not the mixture is exposed to light.

No detectable amount of vanadium is extracted from hydrochloric acid solutions of +4 vanadium when *peroxide-free* isopropyl ether is used, and when the usual extraction technique is employed in which the phases are in contact for only a few minutes. When the ether contains peroxide, the latter rapidly oxidizes +4 vanadium

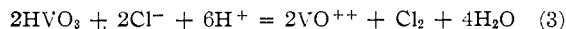


(metavanadic acid is indicated merely for simplicity), and the vanadic acid passes into the ether layer. If the ether is originally peroxide-free, but the extraction of a +4 vanadium solution is prolonged for a matter of hours *in the presence of light*, peroxide is formed by the familiar reaction



and since this reaction is rapidly followed by reaction 1, the net result is a photocatalyzed air-oxidation of the +4 vanadium. Consequently the amount of vanadium extracted from an illuminated solution of vanadyl ion increases with time.

Since reaction 1 is much more rapid than reaction 2, the rate of accumulation of vanadic acid in the ether layer would be a measure of the rate of reaction 2, were it not for the fact that vanadic acid is slowly reduced by chloride ion



Because this reaction opposes reactions 1 and 2, a steady state is finally established in which the concentration of vanadic acid in the ether phase becomes constant (see curve a in Fig. 1.)

(1) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929.

(2) G. E. F. Lundell, J. I. Hoffman and H. A. Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, N. Y., 1931.

(3) R. W. Dodson, G. J. Forney and E. H. Swift, *THIS JOURNAL*, **58**, 2573 (1936).

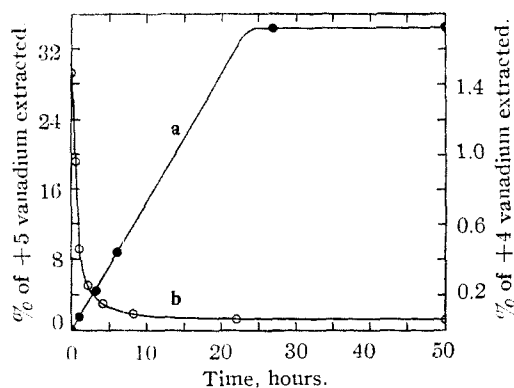


Fig. 1.—Influence of time on the extractability of vanadium from 8.0 *M* hydrochloric acid in diffuse daylight: (a) vanadium originally present entirely in the +4 state (right ordinate); (b) vanadium originally present in the +5 state (left ordinate).

When a fresh hydrochloric acid solution of +5 vanadium is extracted, the concentration of vanadic acid in the ether layer is initially relatively large, but it decreases more or less rapidly with time as reaction 3 proceeds and finally becomes constant (see curve b in Fig. 1).

Interpretation of the experimental data described below is further complicated by other side reactions, among which may be noted the reduction of the chlorine from reaction 3 by the peroxide formed in reaction 2, probably according to

$$\text{R}_2\text{O}_2 + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{R}_2\text{O} + \text{O}_2 + 2\text{Cl}^- + 2\text{H}^+ \quad (4)$$

Since this reaction competes with reaction 1, it influences the steady state concentration of vanadic acid in the ether layer.

Experimental Technique

Stock vanadium solutions were prepared from ammonium metavanadate which had been purified as follows. A hot saturated solution of the commercial salt, which contained about 5% silica as the chief impurity, was filtered and the salt was precipitated by cooling and saturating the solution with ammonium chloride.⁴ The product was dissolved in dilute sulfuric acid, filtered, and reprecipitated by saturating the solution with ammonium chloride. The salt was finally precipitated with ammonium chloride a third time from its saturated solution in water, washed with water, and dried in a vacuum desiccator over calcium chloride. The chloride content of the purified salt was determined by potentiometric titration with silver ion, and it corresponded to 0.33% ammonium chloride. Five samples of the salt ignited to vanadium oxide at 400° according to the method of Park⁵ showed a purity factor of $99.43 \pm 0.01\%$. Three samples assayed by reduction with sulfur dioxide in 2 *N* sulfuric acid and titration with permanganate showed a purity factor of $99.27 \pm 0.08\%$. The difference between these results probably represents silica. The sum of the ammonium vanadate and ammonium chloride percentages is 99.76, and the remaining 0.24% very probably represents water. Stock solutions of +5 vanadium were prepared by dissolving the purified ammonium vanadate in dilute sulfuric acid and standardizing by the usual sulfur dioxide-permanganate method.¹ Stock solutions of +4 vanadium were prepared by reducing ammonium vanadate solutions

with sulfur dioxide in dilute sulfuric acid, boiling out the excess sulfur dioxide, and finally standardizing by permanganate titration.

The *i*-propyl ether used was freed from peroxide by distillation from dilute aqueous potassium permanganate solution, the middle 0.1° fraction being collected. Since peroxide forms rather rapidly when *i*-propyl ether is exposed to air and light, the ether was used immediately after purification.

The general technique of the extraction experiments was as follows. A suitable volume of standard vanadium solution was pipetted into a 250-cc. volumetric flask, the required amount of acid was added, and the solution was diluted to about 200 cc. Redistilled *i*-propyl ether was added in small portions with thorough shaking until the solution was just saturated with ether, and it was then diluted to the mark. Exactly 200 cc. of the solution was placed in a 500-cc. glass-stoppered Erlenmeyer flask, and an equal volume of peroxide-free isopropyl ether, previously saturated with the appropriate acid solution, was added. The flask was placed in a water thermostat at $25.00 \pm 0.01^\circ$, and was shaken periodically by hand.

The vanadium in the ether phase was determined polarographically. A 100-cc. sample of the ether layer was withdrawn, transferred to a distilling flask containing about 5 cc. of water, and the ether was distilled off. The residual aqueous solution was treated with 20 cc. of concentrated nitric acid and evaporated to incipient dryness to ensure that all the vanadium was in the +5 state. Three cc. of concentrated sulfuric acid was added, the solution was boiled down to about 1 cc., cooled, diluted with water, transferred to a 100-cc. volumetric flask, and diluted to the mark. A suitable aliquot of this solution was analyzed polarographically in a supporting electrolyte containing 1 *M* ammonia, 1 *M* ammonium chloride, and 0.005% gelatin, as previously described.⁶ The ammoniacal solutions were allowed to stand for forty minutes before measurement to be certain that the vanadium had assumed a reproducible ionic state.⁶ Freshly prepared ammoniacal solutions of +5 vanadium are colored yellow, but decolorize after standing for about thirty minutes; during this period the diffusion current increases and finally attains a constant value approximately 4% greater than its initial value. The concentration of vanadium was computed from the measured diffusion current, using the previously determined experimental value, 4.72, for the diffusion current constant.⁶

Data and Discussion

The influence of time on the extractability of vanadium from 8 *M* hydrochloric acid is illustrated in Fig. 1. Curve a was obtained with a 38.8 millimolar solution of +4 vanadium, and curve b with a 21.1 millimolar solution of +5 vanadium. Note that a different ordinate scale is used for the two curves. In both experiments the extraction mixtures were exposed to diffuse daylight. The extraction of the +5 vanadium solution was started within a minute after the vanadate and acid solutions were combined. The steep negative slope of curve b shows that in the presence of ether reaction 3 proceeds fairly rapidly in 8 *M* hydrochloric acid at 25°.

It is evident that the steady state, in which reactions 1 and 2 are balanced by reaction 3, is reached much sooner in the extraction of the +5 vanadium solution than in the case of the vanadyl solution. This indicates that in 8 *M* hydrochloric acid the rate of reaction 3 is greater than the net rate of reactions 1 and 2. However, in the extraction of the +5 vanadium solution the concen-

(4) J. Meyer, *Z. Elektrochem.*, **15**, 266 (1909).

(5) B. Park, Dissertation, Columbia University, 1930.

(6) J. J. Lingane, *This Journal*, **67**, 182 (1945).

tration of chlorine produced is much greater than in the extraction of the vanadyl solution, and this may influence the time required to attain the steady state as well as the steady state concentration of vanadic acid in the ether.

The existence of a steady state involving reactions 1, 2 and 3 was further verified by the following experiments, which were all performed with a 38.8 millimolar solution of +4 vanadium in 8.0 *M* hydrochloric acid. After eight minutes of shaking less than 0.01% vanadium was found in the ether layer when the ether was peroxide-free, but when 0.55 millimolar hydrogen peroxide was added to the initial aqueous solution the concentration of vanadium in the ether layer was 0.16 millimolar after eight minutes of shaking, corresponding to 0.41% extraction. The fact that the concentration of vanadic acid in the ether layer in the latter experiment was much smaller than twice the concentration of added hydrogen peroxide, as expected from reaction 1, results from the fact that part of the +5 vanadium produced by reaction 1 is reduced according to reaction 3. (An alternative possibility that the distribution coefficient of vanadic acid is very small is ruled out by experiments described below, which indicate that the distribution coefficient actually is close to 1.)

Although the addition of hydrogen peroxide increases the amount of vanadium extracted during the first few minutes of shaking, the concentration of vanadic acid in the ether after fifty hours of extraction in diffuse light was found to be the same (0.665 millimolar) as when no hydrogen peroxide was initially added (0.667 millimolar), thus confirming the establishment of a steady state. The effect of light (reaction 2) was substantiated by extracting the +4 vanadium solution with peroxide-free ether for twenty-three hours in a brown glass bottle; only 0.02% vanadium was extracted, compared to 1.71% extraction in diffuse daylight during the same period.

Tables I and II present data on the extraction from hydrochloric acid solutions of +5 and +4 vanadium as a function of the acid concentration and the initial concentration of vanadium in the aqueous phase, and Table III contains data from the extraction of sulfuric acid solution of +5 vanadium. In all these experiments the extraction mixtures stood for thirty hours or longer in diffuse daylight to insure the attainment of the steady state. The data are presented graphically in Figs. 1 and 2.

Curve a in Fig. 2 shows the influence of the hydrochloric acid concentration on the percentage of total vanadium extracted at equilibrium from a 21.1 millimolar vanadate solution by an equal volume of isopropyl ether when the solutions are exposed to diffuse daylight for more than thirty hours. The inflections at acid concentrations of about 4.5, 6.3 and 7 molar indicate that at these points more highly polymerized vanadic acids begin to replace the simpler and less readily ex-

TABLE I
ISOPROPYL ETHER EXTRACTION OF HYDROCHLORIC ACID SOLUTIONS OF +5 VANADIUM

Acid, <i>M</i>	Vanadium, millimolar Aqueous phase, initially	Vanadium, millimolar Ether phase, at equilibrium	% Extracted by equal vol. <i>i</i> -propyl ether
1.0	21.1	0.00	0.000
3.0	21.1	.00	.000
4.5	21.1	.00	.000
5.0	21.1	.102	.481
5.5	21.1	.226	1.07
6.0	21.1	.266	1.26
6.5	21.1	1.31	6.20
7.0	21.1	1.98	9.35
7.25	21.1	3.14	14.9
7.5	21.1	3.05	14.45
7.75	21.1	2.32	11.0
8.0	21.1	0.272	1.29
8.5	21.1	.126	0.598
9.0	21.1	.124	.587
6.0	5.29	.066	1.26
6.0	2.11	.026	1.26
8.0	5.29	.068	1.29
8.0	2.11	.027	1.29

TABLE II
ISOPROPYL ETHER EXTRACTION OF HYDROCHLORIC ACID SOLUTIONS OF +4 VANADIUM

Acid, <i>M</i>	Vanadium, millimolar Aqueous phase, initially	Vanadium, millimolar Ether phase, at equilibrium	% Extracted by equal volume <i>i</i> -propyl ether
1.0	38.8	0.00	0.000
4.0	38.8	.00	.000
5.0	38.8	.0586	.151
6.0	38.8	.352	.907
7.0	38.8	.410	1.055
8.0	38.8	.670	1.73
8.5	38.8	.684	1.76
9.0	38.8	.694	1.79
8.0	15.51	.665	4.23
8.0	7.75	.672	8.78

TABLE III
ISOPROPYL ETHER EXTRACTION OF +5 VANADIUM FROM SULFURIC ACID

Acid, <i>M</i>	Vanadium, millimolar Aqueous phase, initially	Vanadium, millimolar Ether phase, at equilibrium	% Extracted by equal volume <i>i</i> -propyl ether
1.0	77.0	0.00	0.000
4.0	77.0	.00	.000
6.0	77.0	.00	.000
7.0	77.0	.0158	.0205
7.5	77.0	.0539	.0700
8.0	77.0	1.21	1.58
8.5	77.0	1.89	2.45
9.0	77.0	4.08	5.03

tractable acids as the principal un-ionized compounds of +5 vanadium in the aqueous phase. The rapid decrease in extractability when the hydrochloric acid concentration is increased above 7.5 *M* is probably related to the fact that the equilibrium concentration of +5 vanadium from reaction 3 diminishes as the hydrochloric acid concentration is increased, and this decrease

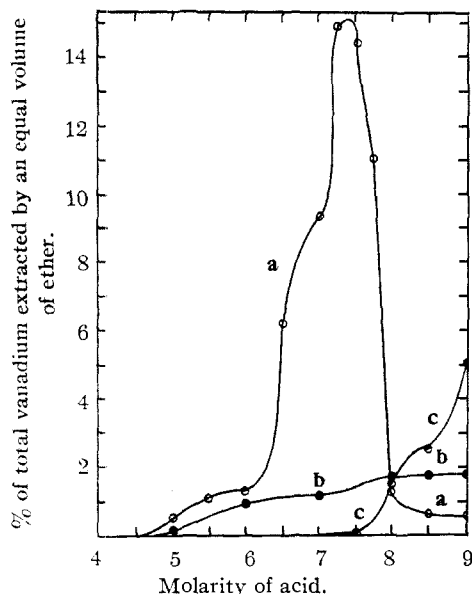


Fig. 2.—Influence of acid concentration on the extraction of vanadium: curve a from hydrochloric acid originally containing the vanadium in the +5 state; curve b from hydrochloric acid originally containing the vanadium in the +4 state; curve c from +5 vanadium solutions in sulfuric acid.

overbalances the increased extractability with increasing hydrogen ion concentration.

It is seen that curve c, representing the extraction from sulfuric acid solutions of +5 vanadium under the same conditions, also shows an inflection similar to the first inflection in hydrochloric acid. Due to the greatly increasing solubility of the ether in the aqueous phase, it was impossible to obtain data for acid concentrations greater than 9 *M*. The displacement of curve c along the acid concentration abscissa may reflect a difference in the activities of the ions involved in the several reactions. However, replotting the curves on an acid activity abscissa, using the data of Shedlovsky and MacInnes⁷ on the activity coefficients of hydrochloric acid and those of Randall and Young⁸ for the activity coefficients of sulfuric acid, leads to a large overcorrection. This may perhaps be attributed to a difference in the activity coefficient of one or more of the vanadium ions, but data to check this possibility are not available.

Our conclusion that the extracted substance is the same irrespective of the initial state of the vanadium in the aqueous phase is strengthened by curve b of Fig. 2, which represents the extraction of vanadium from hydrochloric acid solutions of 38.8 millimolar vanadyl ion, and which exhibits the same inflections that are found in curve a.

It was thought that a peroxyvanadic acid might be the extractable species of +5 vanadium,

(7) T. Shedlovsky and D. A. MacInnes, *THIS JOURNAL*, **58**, 1970 (1936).

(8) M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928).

but experiments on extraction of sulfuric acid solutions of +5 vanadium to which had been added large concentrations of hydrogen peroxide indicated that the peroxyvanadic acid formed by the reaction



is not measurably extracted by isopropyl ether from any concentration of sulfuric acid up to 9 *M*.

The actual distribution coefficients of the +5 vanadium in 6, 7.5 and 8.5 *M* hydrochloric acid at 25° were determined as follows. Two hundred-cc. portions of each aqueous phase, containing 21.6 millimolar total vanadium originally added as vanadate, were equilibrated for thirty-eight hours with equal volumes of *i*-propyl ether saturated with the appropriate acid. Each aqueous phase and each ethereal phase was then analyzed for +5 vanadium. The ether phases were analyzed polarographically as described above. Two methods were used to determine +5 vanadium in the aqueous phases. In one of these a sample of the solution was added to a solution containing excess sodium acetate to remove free acid and excess phenol to remove chlorine, the solution was titrated with standard permanganate, and the vanadyl concentration so found was subtracted from the total concentration of vanadium (21.6 millimolar) to obtain the concentration of +5 vanadium. The reliability of this method was established with synthetic samples containing known amounts of +4 and +5 vanadium. The other method used was the familiar potentiometric titration with standard ferrous solution in strongly acid medium, and the results obtained checked those by the permanganate method. In 6 *M* hydrochloric acid the equilibrium concentration of +5 vanadium in the aqueous phase was 10.0 millimolar, the concentration in the ether phase was 0.28 millimolar, and hence the distribution coefficient is 0.028. In 7.5 *M* hydrochloric acid the aqueous phase contained 2.61 millimolar +5 vanadium, and the ether phase 3.13 millimolar, corresponding to a distribution coefficient of 1.20. In 8.5 *M* hydrochloric acid the equilibrium concentration of +5 vanadium in the aqueous phase was 0.060 millimolar, in the ether phase 0.062 millimolar, and the distribution coefficient is 1.03. The fact that the distribution coefficient is virtually the same in 7.5 and 8.5 *M* hydrochloric acid confirms the postulate made above that the decreased *percentage* extraction above 7.5 *M* acid based on the total amount of vanadium (curve a in Fig. 2) is due to a smaller equilibrium concentration of +5 vanadium in the aqueous phase. The small distribution coefficient in 6 *M* acid proves that the rapid increase in *percentage* extraction between 6 and 7.5 *M* acid is due to an increase in the distribution coefficient.

It is apparent from the data in Table I that the *percentage* of vanadium extracted from a vanadate solution in 6 and 8 *M* hydrochloric acid by an equal volume of *i*-propyl ether is constant regard-

less of the vanadium concentration, thus showing that a true distribution equilibrium is attained. However, when the vanadium is originally present as vanadyl ion, it is the *amount*, rather than the percentage, of extraction which is constant (see Table II). The only difference in the conditions of extraction in the two cases is that a much larger concentration of chlorine is produced by reaction 3 during the extraction of a +5 vanadium solution than during the extraction of a vanadyl solution, and chlorine (or hypochlorous acid) may undergo a variety of reactions with both peroxide and isopropyl ether which might change the conditions in the steady state. For example, chlorine may oxidize the peroxide formed in reaction 2, probably according to reaction 4, and since such a reaction competes with reaction 1 and tends to aid reaction 3, the relative concentration of vanadic acid would be expected to decrease.

We found that the extraction from both +5 and +4 vanadium solutions increases rather markedly with decreasing temperature. For example with a 5.29 millimolar solution of +5 vanadium in 8 *M* hydrochloric acid the percentage extracted when the steady state was reached was 2.40 at 0°, 1.29 at 25°, and only 0.04% at 46.6°. With a 38.8 millimolar solution of +4 vanadium in 8 *M* hydrochloric acid the percentage extracted was 3.56 at 0°, 1.73 at 25° and 0.29 at 46.6°.

From the foregoing data the optimum conditions for the separation of ferric iron from vanadium are: (a) the vanadium must be present in the +4 state; (b) the *i*-propyl ether used must be peroxide-free; (c) the extraction must not be prolonged for more than about ten minutes in the presence of light; and (d) the concentration of hydrochloric acid should be between 7 and 8 *M* since, as shown by Dodson, Forney and Swift,³ the distribution coefficient of ferric iron is maximal at this acid concentration. If any doubt exists as to the oxidation state of the vanadium, the iron-vanadium solution should be evaporated to dryness with concentrated hydrochloric acid before extraction to convert all the vanadium to the +4 state.

These conditions were tested with synthetic mixtures with the results shown in Table IV. Two extractions were made with a volume of isopropyl ether equal to that of the aqueous phase, and the hydrochloric acid concentration was 7.8 *M*. It is evident that a very sharp separation of iron from vanadium is obtained when the foregoing conditions are fulfilled.

TABLE IV
SEPARATION OF IRON AND VANADIUM BY ISOPROPYL ETHER
EXTRACTION

Composition of sample	Fe in aqueous phase, mg.	V in combined ether phases, mg.
500 mg. Fe, 10 mg. V	0.00	0.00
1 g. Fe, 10 mg. V	.05	.00
1 g. Fe, 100 mg. V	.08	.01
1 g. Fe, 1 g. V	.10	.03

Summary

1. Vanadium is extracted by isopropyl ether from its solutions in hydrochloric and sulfuric acids in the form of a vanadic acid.
2. Extraction from solutions originally containing the vanadium in the +4 state is initially very small, but increases with time as the vanadium is oxidized by peroxide photolytically formed in the ether.
3. Extraction from hydrochloric acid solutions originally containing the vanadium in the +5 state is initially large, but decreases as the vanadate is reduced by chloride ion.
4. Peroxyvanadic acid is not extracted from sulfuric acid solutions by *i*-propyl ether.
5. The optimum conditions for the quantitative separation of ferric iron from vanadium by an *i*-propyl ether extraction have been defined as follows: the vanadium must be present in the +4 state, the isopropyl ether used must be peroxide-free, the extraction must be completed within about ten minutes, and the hydrochloric acid concentration should be between 7 and 8 *M*. Under these conditions a very complete separation is obtained.

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