$S(= 6\alpha_{12} + 3\alpha_{21})$ according to equation 33 are recorded. It is to be observed that S at 1 μ is considerably larger than at the higher ionic strengths and that it is practically the same at 2 and 3 μ. Although the computation of α_{21} is quite sensitive, depending as it does on the accuracy of knowledge of ϕ_1 and ϕ_2, we have reason to believe that the variation in S is real and greater than can be accounted for by experimental error. If this is a true statement, then one would expect that equation 2 is not strictly valid at 1 μ but approaches an exact representation of the facts at the higher concentrations. A similar conclusion has been drawn by Harned[12] from results on HX–MX mixtures. Recent isopiestic vapor pressure measurements by Robinson[13] on the system sodium chloride–cesium chloride also substantiate the conclusion that the rule of linear variation of the logarithm of the activity coefficient becomes valid for both electrolytes in the more concentrated solutions.

TABLE IV

OSMOTIC COEFFICIENTS AND VAPOR PRESSURES AT 25° OF THE SYSTEM $HCl–BaCl_2–H_2O$ ACCORDING TO EQUATION 25

$\mu = 1$			$\mu = 2$			$\mu = 3$		
m_1	ϕ_x	ρ	m_1	ϕ_x	p	m_1	ϕ_x	p
1.0	1.039	22.88	2.0	1.188	21.75	3.0	1.348	20.53
0.9	1.026	22.94	1.7	1.156	21.99	2.7	1.319	20.75
.8	1.012	22.99	1.4	1.121	22.18	2.4	1.287	20.96
.7	0.977	23.04	1.1	1.083	22.36	2.1	1.255	21.17
.6	.981	23.09	0.8	1.040	22.54	1.8	1.220	21.38
.5	.964	23.14	.5	0.990	22.72	1.5	1.183	21.58
.4	.945	23.20	.2	.932	22.89	1.2	1.142	21.79
.3	.924	23.25	.0	.886	23.01	0.9	1.098	21.99
.2	.901	23.29				.6	1.050	22.19
.1	.896	23.35				.3	0.996	22.39
.0	.846	23.40				.0	0.934	22.61

We conclude these thermodynamical considerations by presenting in Table IV the osmotic coefficients, ϕ_x calculated by equation 25 and the water vapor pressures derived from these osmotic coefficients. It is to be noticed that if the logarithms of both activity coefficients in the mixtures obey equations 1 and 2, then ϕ_x must vary quadratically as evidenced by equation 25.

Conclusions

(1) The activity coefficients from electromotive force measurements confirm within narrow limits the validity of equation 1 for the logarithm of the activity coefficient of hydrochloric acid in barium chloride solutions at 1, 2 and 3 μ. The negative deviations at the higher and lower acid concentrations and the positive deviations between these concentrations for log γ_1 at 3 μ may indicate a slight bow convex upward from the linear relationship.

(2) The values of α_{12} are nearly the same at all three ionic strengths. That S is considerably higher at 1 μ than at the higher concentrations is evidence that equation 2 is not strictly valid for the variation of the activity coefficient of barium chloride in hydrochloric acid solutions at an ionic strength of unity.

(3) At the higher ionic strengths, these calculations indicate that both equations 1 and 2 are valid within narrow limits.

(4) In the investigations of these solutions, we believe that considerations of the deviations Δ_1 and Δ_2 in equations 1 and 2 should be explored experimentally for each system.

This contribution was supported in part by the Atomic Energy Commission under Contract AT(30-1)-1375.

NEW HAVEN, CONN.

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[12] H. S. Harned, Table I, *J. Phys. Chem.*, **58**, 683 (1954).

[13] R. A. Robinson, THIS JOURNAL, **74**, 6035 (1952); R. A. Robinson and C. K. Lim, *Trans. Faraday Soc.*, **49**, 1144 (1953); R. A. Robinson, *ibid.*, **49**, 1147, 1411 (1953).

[CONTRIBUTION NO. 1185 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Polarographic Characteristics of +3 and +5 Arsenic in Hydrochloric Acid Solutions

BY LOUIS MEITES

RECEIVED JUNE 16, 1954

Arsenic(V) has been found to be polarographically reducible from concentrated hydrochloric acid solutions, giving a double wave which corresponds to the scheme As(V) $\rightarrow$ As(0) $\rightarrow$ AsH_3. New data are presented on the polarographic characteristics of arsenic(III) in hydrochloric acid media.

Introduction

Though the polarography of arsenic in hydrochloric acid solutions has been the subject of several studies, notably those by Kacirkova[1] and Lingane,[2] the published data are not in agreement on several important features.

Kacirkova[1] recorded polarograms of +3 arsenic in 1 N hydrochloric acid. These showed two waves, starting at about −0.3 and −0.6 v. *vs.* S.C.E., which she attributed to a stepwise reduction to elemental arsenic and arsine, respectively. At very low arsenic concentrations the two waves were of equal height, as one would expect, but when the arsenic concentration was increased above about 1mM the height of the well-defined first wave became substantially independent of the arsenic concentration. The height of the second wave, on the other hand, did continue to increase, but more rapidly than the arsenic concentration. Though the shape of the second wave was very poorly defined in the absence of a maximum suppressor, it was materially improved by the addition of, *e.g.*, 5×10^{-4} % methylene blue. Kacirkova explained the peculiar behavior of the first wave height by postulating the formation of a film of adsorbed ar-

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[1] K. Kacirkova, *Collection Czechoslov. Chem. Communs.*, **1**, 477 (1929).

[2] J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 583 (1943).

senious acid which prevented hydrogen ions from reaching the drop surface. But, as Kolthoff and Lingane[3] later pointed out, it is much more probable that the reduction gives a film of adsorbed elemental arsenic.

Lingane,[2] working with solutions containing 0.01% gelatin, also found a double wave, but its characteristics differed greatly from those reported by Kacirkova. His polarograms show waves starting at about −0.4 and −0.9 v. (incorrectly tabulated as half-wave potential values). The first wave showed only "some semblance of a plateau" between −0.8 and −0.9 v. Its diffusion current constant was 8.6, "which is large enough to correspond to a . . . 6-electron reduction to arsine,"[4] but the appearance of the later wave led to the conclusions that the first wave corresponded to only a 3-electron reduction (to elemental arsenic) and that the diffusion coefficient of the reducible species was abnormally high in comparison with those of +3 antimony and +3 bismuth in the same medium. Though the chemical interpretation attached to these waves was said to be in agreement with that of Kacirkova, both the positions and the shapes of the waves were considerably different. Moreover, Lingane's polarograms show that in the presence of 0.01% gelatin the height of the first wave is proportional to the concentration of +3 arsenic up to at least 1.5 mM, well above the point at which Kacirkova found i_d to become independent of C.

Neither Kolthoff and Lingane[3] nor Bambach[5] were able to find any supporting electrolyte in which +5 arsenic is reducible.

This paper describes what is therefore the first reported polarographic reduction of +5 arsenic, which, like +5 antimony,[6] is transformed into a reducible species in solutions containing sufficiently high concentrations of hydrogen and chloride ions. In order to interpret the double wave secured for +5 arsenic, it was necessary to re-examine the polarographic characteristics of +3 arsenic in hydrochloric acid media over a wide range of concentrations.

Experimental

Polarograms were recorded with a pen-and-ink recording polarograph, constructed by the author, which uses a 0–10 mv. d.c. recording potentiometer in a more or less conventional resistance–potentiometer circuit.

Solutions of +3 and +5 arsenic were prepared from accurately weighed amounts of the reagent grade oxides by solution in a minimal volume of 2 N sodium hydroxide followed by dilution to known volumes with hydrochloric acid of the appropriate concentration.

A modified H-cell having a sintered-glass gas-dispersion cylinder sealed into the solution compartment to facilitate rapid deaeration[7] was used throughout. Solutions were deaerated with tank hydrogen which had been passed through vanadium(II) perchlorate solutions to remove oxygen,[8] then, in the work with concentrated hydrochloric acid solutions, through concentrated hydrochloric acid at the temperature (25.00 ± 0.02°) of the solution in the cell.

All weights and volumetric apparatus had been calibrated by standard methods.

Data and Discussion

+3 Arsenic.—Typical polarograms of +3 arsenic in 1 M hydrochloric acid containing no maximum suppressor are shown in Fig. 1. Though both waves are fairly well defined at very low concentrations of arsenic, the second wave remains so up to only about 0.05 mM; concentrations of +3 arsenic higher than this give rise to a curious double maximum in the second wave. The diffusion current constant of the first wave is independent of the arsenic concentration between 0.018 and 0.9 mM (it will be apparent from the subsequent discussion that this limiting concentration is dependent on the characteristics of the capillary used) and, from the mean of 17 individual values, is equal to 6.04 ± 0.03 microamp./mmole/l./mg.$^{2/3}$ sec.$^{-1/2}$, which is considerably smaller than the value found by Lingane[2] for the distorted wave observed with gelatin present. The diffusion current constant for the three-electron reduction of +3 arsenic is, therefore, not importantly different from those for +3 antimony and +3 bismuth in hydrochloric acid media.

The half-wave potential of the first wave is −0.428 ± 0.005 v. *vs.* S.C.E. in 1 M hydrochloric acid. At acid concentrations between 0.1 and 2 M the half-wave potential is given with a mean error of ±2 mv. by the equation $E_{1/2} = -0.427 + 0.135 \log [\text{HCl}]$. Bambach[5] found −0.5 v. in 0.5 M, and −0.35 v. in 1.5 M, acid: these values agree reasonably well with those calculated from this equation. Because of the irreversibility of the wave ($E_{3/4} - E_{1/4}$ is equal to −35 ± 5 mv. in 0.05 − 3.5 M acid, whereas the expected value for a thermodynamically reversible three-electron reduction is −18.8 mv.), no conclusions can be drawn from the value of $\Delta E_{1/2}/\Delta \log [\text{HCl}]$. However, the fact that $E_{1/2}$ becomes more positive with increasing concentration of acid would be predicted from any hypothesis about the nature of the reducible species.

At arsenic concentrations above 0.9 mM the height of the first wave becomes constant, as shown by Fig. 1, and independent of changes in temperature (between 18 and 32°), in hydrochloric acid concentration (between 0.5 and 2.0 M) and in arsenic concentration (between 2 and 4 mM), where the limits quoted represent in each instance the extremes studied. Data on the diffusion current of this wave in 1 M hydrochloric acid containing 3 mM +3 arsenic secured with varying pressures of mercury above a capillary giving 9.02 ± 0.02 mg. drops show that the product $i_d t$ remains constant and equal to 58.5 ± 2.0 microcoulombs as the drop time is varied from 1.7 to 5.1 sec.

These facts cannot be explained on the basis of the adsorption of arsenious acid hypothesis advanced by Kacirkova, but only by the formation of a film of adsorbed elemental arsenic on the surface of the drop. Since elemental arsenic is a very poor conductor of electricity, it seems reasonable to assume that any portion of the drop covered by even a monatomic film of arsenic will be effectively insulated from the solution, so that further reduction can only occur at a potential on the plateau of the first wave as the drop area increases and fresh mercury is exposed.

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(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 261–262.

(4) Reference 3, 2nd edition, 1952, p. 543.

(5) K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **14**, 265 (1942).

(6) J. J. Lingane and F. Nishida, THIS JOURNAL, **69**, 530 (1947).

(7) L. Meites and T. Meites, *Anal. Chem.*, **23**, 1194 (1951).

(8) L. Meites and T. Meites, *ibid.*, **20**, 984 (1948).

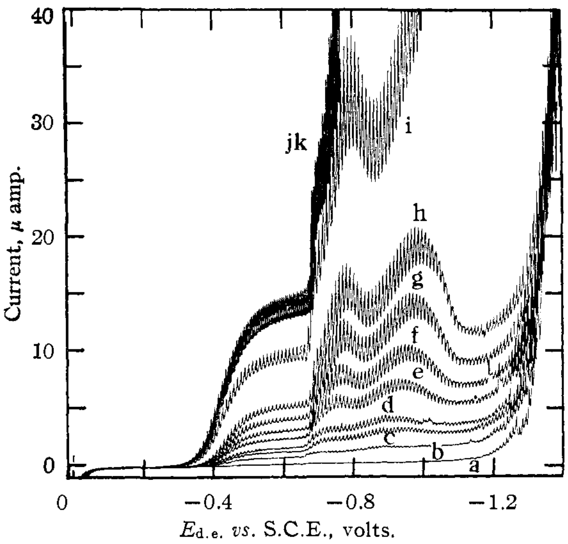

Fig. 1.—Polarograms of (a) 0, (b) 0.033, (c) 0.064 (d) 0.094, (e) 0.149, (f) 0.200, (g) 0.268, (h) 0.348, (i) 0.646, (j) 0.934 and (k) 1.499 mM + 3 arsenic in 1.00 M hydrochloric acid, secured with a capillary for which mt = 9.02 mg. Curves j and k are superimposed.

If this is correct, it follows that the arsenic atoms produced by the flow of 58.5 microcoulombs just suffice to cover the exposed area of the drop at the instant of maturity. This area is given by mt, the density of mercury, and the assumption that the drop is practically spherical by the equation $A_{\max} = 4\pi(3\ m\ t/4000\pi d)^{2/3}$, whence $A_{\max}$ for a 9.02-mg. drop is 3.69 × 10^{-2} cm.^{2} or 3.69 × 10^{-14} Å.^{2} Since 58.5 microcoulombs suffice for the 3-electron reduction of 1.22 × 10^{14} atoms of arsenic, the calculated radius of the arsenic atom becomes 0.98 Å. Goldschmidt reported 1.16 Å., but this value relates to the spherical atom in a symmetrical electric field, whereas the polarographic value is for an atom polarized in a direction normal to the plane of the calculated radius by the electric potential gradient around the drop. Though the extent of the deformation thus imposed on the atom cannot readily be calculated, the fact that the difference between the two values is at least in the expected direction lends very strong support to the interpretation outlined.

The very sharp rise in current at the end of this plateau apparently corresponds to a potential at which the activation energy of the next reduction step just becomes available, so that the film of adsorbed arsenic is no longer stable.

Because of the large double maximum, the height of the second wave cannot be measured accurately in the absence of a maximum suppressor except in extremely dilute solutions. Gelatin is unsuitable for this purpose: as shown by Lingane's polarograms,[2] it not only does not give a well-defined plateau for the second wave, but it shifts the first wave to potentials so much more negative that the two waves nearly coalesce, and furthermore it decreases the total diffusion current constant by nearly 30%. Methylene blue, first suggested by Kacirkova,[1] is much more suitable. Figure 2 shows that the plateau of the second wave is quite well-defined in the presence of even 1.5 × 10^{-4}% methylene blue. In 1 M hydrochloric acid containing 1.5 × 10^{-4}% methylene blue the total diffusion current constant is 12.00 ± 0.04. This is almost exactly twice the value (6.04 ± 0.03) for the first wave alone, and constitutes conclusive proof that the reduction of +3 arsenic from hydrochloric acid solutions proceeds in two successive three-electron steps.

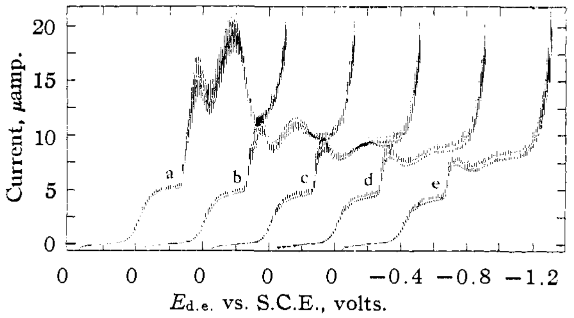

Fig. 2.—Polarograms of 0.3 mM +3 arsenic in 1.00 M hydrochloric acid containing (a) 0, (b) 0.43, (c) 0.83, (d) 1.61 and (e) 3.00 × 10^{-4}% methylene blue.

As was mentioned above, increasing the concentration of hydrochloric acid causes the first wave to move to more positive potentials, and it also causes the potential at which the dropping electrode is depolarized by chloride ion to become more negative. Accordingly, the zero-current portion of the polarogram becomes narrower and narrower as the acid concentration is increased, and above 4 M acid an inflection at zero current is no longer observed. This indicates that mercury is spontaneously oxidized (to mercurous chloride) by +3 arsenic in > 4 M hydrochloric acid, and indeed this reaction can be observed visually by virtue of the rapid blackening of a clean mercury surface in contact with such a solution.

The acid concentration at which this reaction becomes spontaneous appears to coincide with the concentration at which the height of the first wave ceases to be limited by the formation of the adsorbed film of arsenic. Presumably chloride ion is too strongly adsorbed on the drop surface from these concentrated solutions to permit the film to form. (Gelatin, of course, has the same effect in less strongly acid solutions.) In 11.5 M acid the height of the first wave is directly proportional to the concentration of +3 arsenic up to at least 4 mM. The diffusion current constant of the wave of this medium is 3.94 ± 0.07, only 65% of its value in 1 M acid. Though the half-wave potential of the second wave in concentrated acid is close to −0.55 v. vs. S.C.E., it is so poorly defined that a precise value for either its half-wave potential or its diffusion current constant is impossible to secure.

+5 Arsenic.—Typical polarograms of dilute solutions of +5 arsenic in 11.5 M hydrochloric acid are shown in Fig. 3. They consist of two waves: the first merges with the anodic wave due to dissolution of the electrode mercury (like +3 arsenic, +5 arsenic in concentrated hydrochloric acid oxidizes mercury spontaneously to mercurous chloride),

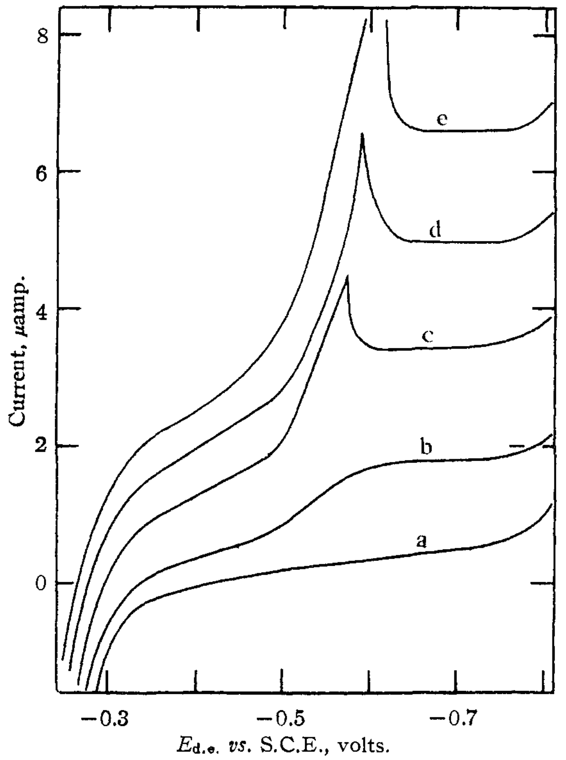

Fig. 3.—Polarograms of (a) 0, (b) 0.0585, (c) 0.1165, (d) 0.1742 and (e) 0.2315 m*M* +5 arsenic in 11.5 *M* hydrochloric acid. The drop time was 3.2 sec. at −0.75 v.

while the second, which is very irreversible, has a half-wave potential of −0.52 ± 0.02 v. The diffusion current constant of the total double wave is 10.7 ± 0.2, almost exactly 8/3 that for the three-electron reduction of +3 arsenic in this medium, and therefore must represent reduction all the way to arsine. The first wave cannot represent reduction to +3 arsenic, because +3 arsenic is reduced to the element at these potentials, and consequently the first wave must also correspond to reduction to elemental arsenic. The height of this wave is, however, somewhat less than the expected $^5/_8$ of the total wave height, but this merely shows that the true diffusion current of the first wave could only be measured at a potential so negative that the second wave has already begun. (The same phenomenon is encountered in polarograms of stannic tin in hydrochloric acid media.[9]) The half-wave potential of the second wave is in as good agreement as can be expected with the considerably less precise value for the second wave of +3 arsenic.

With concentrations of +5 arsenic above about 0.4 m*M*, especially at low drop times, the relative height of the second wave increases rapidly; with 2.5 m*M* +5 arsenic the total wave height is several times the expected value. At the same time the polarograms become much more complex as additional waves appear (Fig. 4). These are probably due to the formation of one or more polyarsenate species in sluggish equilibrium with the more simple species which predominates in the dilute solutions.

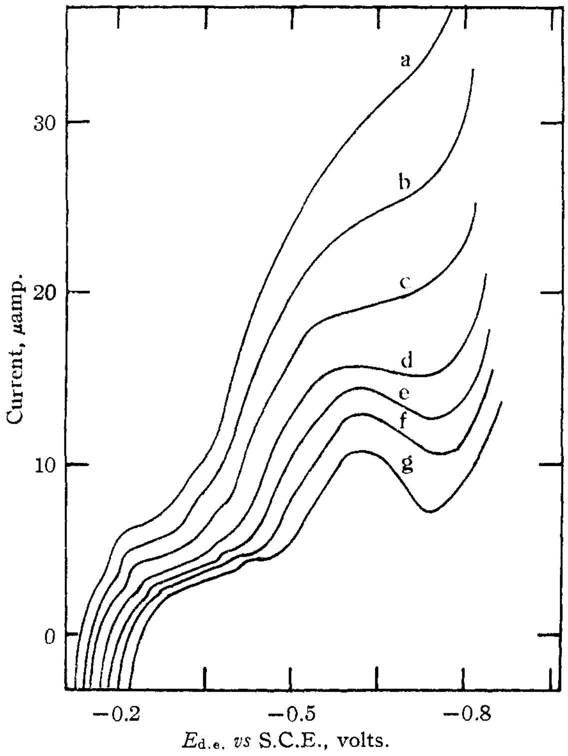

Fig. 4.—Polarograms of 0.431 m*M* +5 arsenic in 11.5 *M* hydrochloric acid, t at −0.75 v. = (a) 1.5, (b) 1.8, (c) 2.2, (d) 2.7, (e) 3.2, (f) 3.8 and (g) 4.8 sec.

A typical polarogram of a more concentrated solution of +5 arsenic is shown in Fig. 5a. Dilut-

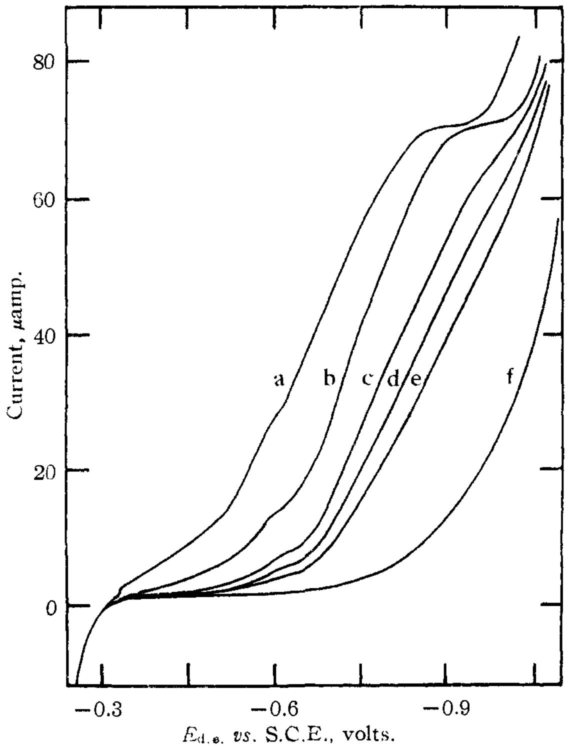

Fig. 5.—Polarograms of 0.884 m*M* +5 arsenic in (a) 11.5, (b) 10.9, (c) 10.6, (d) 10.4, (e) 10.2 and (f) 8.9 *M* hydrochloric acid. The drop time was 1.7 sec. at −0.9 v.

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(9) J. J. Lingane, THIS JOURNAL, **76**, 919 (1954).

ing such a solution with an equiconcentrated but nearly neutral solution of +5 arsenic, so that the concentration of +5 arsenic is kept constant while that of hydrochloric acid is varied, produces the effect shown by the succeeding curves of this figure. The waves are nearly completely suppressed even in 10.2 *M* acid (Fig. 5e), and absent altogether from 9 *M* acid (Fig. 5f). No reduction wave was found either in a hydrochloric acid–perchloric acid medium containing 10.7 *M* hydrogen ion and 7.7 *M* chloride ion, or in a hydrochloric acid–lithium chloride medium containing 8.2 *M* hydrogen ion and 11.2 *M* chloride ion. Evidently both hydrogen and chloride ions at very high activity are essential for the conversion of the +5 arsenic into the reducible species, which must be an ion in which some or all of the oxygen atoms of the arsenate ion have been replaced by chloride.

Though the increase of i_d/C with increasing concentration of +5 arsenic above about 0.4 m*M* is clearly disadvantageous in practical analytical work, no maximum suppressor has been found which eliminates this behavior without causing a severe distortion of the entire polarogram.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Thermodynamics of the Neptunium(IV) Sulfate Complex Ions

BY J. C. SULLIVAN AND J. C. HINDMAN

RECEIVED JUNE 9, 1954

The extraction of neptunium(IV) into benzene with the chelating agent, thenoyltrifluoroacetone, has been used to demonstrate the existence of the +4 ion of neptunium in acid perchlorate solution. This +4 ion of neptunium has been shown to associate with sulfate in perchloric acid solution at an ionic strength of 2.00 according to the reactions $Np^{+4}(aq.) + HSO_4^- = NpSO_4^{++} + H^+$. $NpSO_4^{++} + HSO_4^- = Np(SO_4)_2 + H^+$. The association constants for the stepwise reactions at 25° are $k_1 = 270 \pm 27$ and $k_2 = 11.0 \pm 2.2$. The partial molal heat changes for the reactions are, respectively, −1.17 ± 0.16 and +3.64 ± 1.02 kcal./mole. The corresponding partial molal entropy changes are 7.2 ± 0.6 and 18.7 ± 3.6 e.u.

Studies of the distribution of a metal cation between an aqueous and a benzene phase with the aid of the chelating agent, thenoyltrifluoroacetone, have proved extremely useful in determining both the charge on a metal ion in the absence of a complexing ligand and the association constants in complexing media.[1,2] This method has been used in the present paper to definitely establish the existence of the Np^{+4}(aq.) ion as the predominant species in perchloric acid solution.

The measurements have been extended to a study of the association behavior of Np^{+4} (aq.) in sulfate media. In order to determine the factors affecting the association with this ligand, calculations of the heat and entropy changes involved in the association process have been made from measurements of the temperature dependence of the equilibrium constants.

Experimental

A. Materials.—The perchloric acid was G. Frederick Smith, reagent grade double-vacuum distilled standardized against NaOH. The sodium perchlorate was prepared from perchloric acid and sodium carbonate and twice recrystallized from distilled water. Solutions were prepared on a weight basis. The sulfuric acid was reagent grade assayed both for total sulfate and for acidity. The thenoyl trifluoracetone (abbreviated TTA, hereafter) was a product of the Dow Chemical Co. The TTA solutions were made by weighing a given amount of the solid into a known volume of benzene. The Np(IV) was prepared by the method of Cohen and Hindman.[3]

B. Procedure.—The total ionic strength was kept constant at 2.00 by use of sodium perchlorate and perchloric acid. For the sulfate studies the acidity was kept constant at 2.00 *N*. Two ml. of aqueous and benzene solutions were pipetted into 10-ml. erlenmeyer flasks fitted with ground glass stoppers. The stoppers were waxed and the flasks were then covered with special rubber containers. The covered vessels were agitated in a constant temperature water-bath until equilibrium was reached. It was found that the same equilibrium was attained if a concentrated solution of the neptunium(IV) chelate in benzene was agitated with a perchloric acid solution as when a perchloric acid solution of neptunium(IV) was agitated with a benzene phase containing the chelating agent, thus demonstrating the reversibility of the system. Duplicate aliquots of each layer were mounted on Pt plates and radiochemically assayed using a methane proportional counter. These duplicate assays checked to within the statistical accuracy of the counting, ±0.5%. Duplicate samples checked to within ±1%. The isotope of neptunium was the long lived α-emitter, Np^{237}.

Results and Discussions

Formula of the TTA Complex of Neptunium Extracted into Benzene.—As Connick and McVey[1] have pointed out, the first step in the process of studying complex formation by the TTA method is the assignment of the formula of the metal ion complex extracted into the benzene layer and the determination of the degree of complex formation by the chelating species in the aqueous phase. A general equation for the reactions between Np(IV) and TTA may be written

$$(Np(OH)_iB_j)^{+4-i-j} + (p-j)HB = Np(OH)_{4-p}B_p + (4-i-j)H^+ + (i+p-4)H_2O \quad (1)$$

where HB is used to represent undissociated TTA. In the following equations, brackets are used to indicate concentrations of the enclosed species.

$[Np(OH)_iB_j{}^{+4-i-j}]$ = complexed species in aqueous phase
$[Np(OH)_{4-p}B_p]$ = complexed species in benzene phase[4]

The extraction coefficient may be defined as

$$E = \frac{\sum_p [Np(OH)_{4-p}B_p]}{\sum_i \sum_j [Np(OH)_iB_j{}^{+4-i-j}]} \quad (2)$$

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[1] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[2] R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

[3] D. Cohen and J. C. Hindman, *ibid.*, **74**, 4679 (1952).

[4] The possible species in the benzene layer are subject to the requirement that only neutral molecules be present and limited by the maximum coördination number of the neptunium(IV) which is considered to be 8 for oxygen.