that value selected by Marcus, Zwolinski and Eyring[5a] to reconcile the experimental data on the Fe(II)–Fe(III) exchange with their theoretical calculations. The 4 kcal. value represents our estimate based on the fact that a lower rearrangement energy should be required in the present case because of the symmetry of the ions.[7]

The following comments can be made about the results of these calculations. First, the lower rearrangement energy leads to a reasonable value of the tunneling distance if the electron transfer process occurs without interference of the primary hydration shells of the two ions. We would estimate that the radius of the activated complex must exceed 7.5 Å. if the water shells on the NpO_2^+ and NpO_2^{++} ions are to remain undisturbed. This is equivalent to assigning a radius of 1 Å. to both the Np(V) and Np(VI) ions plus two water molecule diameters. On the other hand the effective charges of +3 and +4, respectively, are probably too large since the Np–O bonds are presumably somewhere between single and double bonds.[7,10,11]

The most serious difficulties become apparent when calculations of the effect of variation of D on the rate are made. This is clearly shown in Fig. 1. The solid line represents the calculated values using $n_a = 1.59$, $n_b = 2.69$ and $r_{ab} = 5.04$ Å. The slope of the theoretical curve in the region of the dielectric constants used experimentally is -2.0. The experimental data shown in the figure can be represented by a least squares straight line with a slope of $+0.08 \pm 0.13$ standard deviation. For our experimental conditions the rate of the exchange is independent of the value of the gross dielectric constant of the solutions. The deviation of the experimental from the theoretical results is enhanced if larger n_a, n_b and r_{ab} values are used. An increase in magnitude of the numbers assigned to these parameters leads to an increase in the slope of the log k' *versus* $100/D$ plot.

It is obvious that the purported agreement between the calculated free energy of activation obtained from the equations for the electron tunneling hypothesis[5b] and the results of our experimental investigations[7] on the exchange in aqueous solution is fortuitous and occurs only because of the latitude possible in adjusting the parameters in the relevant equations.

The obvious explanation for the results of the present experiments is that non-electrostatic forces dominate the energetics. This suggests that the exchange may proceed by an atom transfer mechanism. The fact that the equations of Marcus, Zwolinski and Eyring do not apply is not, however, proof that direct electron transfer does not occur. As Platzman and Franck[12] have correctly pointed out, the Christiansen–Scatchard treatment is valid only for large distances. Polarization phenomena markedly alter the dielectric properties of the medium and at the distances involved in the formation of an activated complex the concept of the dielectric constant of the medium loses significance.[12,13] Weiss,[6] in his treatment of the electron transfer process has attempted to take this factor into account. If we accept his view that only the interaction energy in the final state (*i.e.*, in the activated complex) enters into the activation energy, then we are concerned with the optical dielectric constant of the medium and not the macroscopic value. Lack of detailed knowledge of the dielectric properties of the medium in high potential fields, however, makes calculations along these lines highly speculative at the present time.

[10] W. H. Zachariasen, "The Actinide Elements," McGraw-Hill Book Co., New York, N. Y., 1954, Chap. 18, pp. 784–785.

[11] J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **A229**, 20 (1955).

[12] R. Platzman and J. Franck, *Z. Physik*, **138**, 411 (1954).

[13] E. S. Amis and G. Jaffé, *J. Chem. Phys.*, **10**, 646 (1942).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MASSACHUSETTS AND THE DEPARTMENT OF CHEMISTRY OF OREGON STATE COLLEGE]

Solvent Extraction of Zirconium with Tributyl Phosphate[1]

BY ARNOLD E. LEVITT[2] AND HARRY FREUND

RECEIVED OCTOBER 19, 1955

A study of the effect of certain variables on the extraction of zirconium from hydrochloric acid solutions by tributyl phosphate (TBP) has been made. The variation in the zirconium distribution ratio D with TBP concentration in TBP–benzene solutions gives evidence of a 2:1 molar ratio of TBP to zirconium in the species extracted. Studies were made of the Cl:Zr molar ratio in the organic phase. An investigation of the variation of D with aqueous chloride concentration at constant acidity and constant ionic strength was made. The effect of aqueous acidity on D at constant chloride concentration and constant ionic strength was also investigated. The results of these studies offer evidence for $ZrCl_4(TBP)_2$ as the species present in the organic phase. A decrease in D with increasing initial zirconium concentration at constant aqueous hydrochloric acid concentration and constant organic TBP concentration indicates greater extent of zirconium polymerization in the aqueous phase than in the organic phase.

Introduction

In recent years tributyl phosphate (TBP) has come into prominence as an extracting agent. It was first used to extract various organic acids from aqueous media.[3-5] Recently it has been found to be a useful solvent for extracting metal thio-

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the Minneapolis Meeting of the American Chemical Society, September, 1955.

[2] Department of Chemistry, University of Massachusetts, Amherst, Mass.

[3] H. A. Pagel, P. E. Toren and F. W. McLafferty, *Anal. Chem.*, **21**, 1150 (1949).

[4] H. A. Pagel and K. D. Schwab, *ibid.*, **22**, 1207 (1950).

[5] F. Fortress, A. J. Rosenthal and B. B. White, U. S. Patent 2,572,-128 (*C. A.*, **46**, 3557 (1952)).

cyanates,[6,7] polonium,[8] thorium,[9] uranium,[10] the rare earths[10–13] and zinc.[14] Scadden and Ballou[15] briefly studied the extraction of zirconium and niobium from hydrochloric and nitric acids with TBP.

Although it has been shown that zirconium can be extracted from hydrochloric acid with TBP[10,15] little information can be found in the literature concerning the mechanism of the extraction. The purpose of this investigation was to study the variables involved in the extraction of zirconium from hydrochloric acid solutions with TBP in order to obtain knowledge concerning the mechanism involved in the extraction.

Experimental

Materials.—Tri-*n*-butyl phosphate obtained from Commercial Solvents, Inc., was vacuum distilled. The fraction collected from 175–185° at 18–28 mm. was used in all work. Weighed amounts were dissolved in reagent grade thiophene-free benzene to give solutions of the desired concentrations.

Zirconium tetrachloride obtained from the U. S. Bureau of Mines, Albany, Oregon, was hydrolyzed to form zirconium oxychloride. $ZrOCl_2 \cdot 8H_2O$ was recrystallized several times from 8.2 *M* HCl and was used to prepare two stock solutions about 0.2 *M* in zirconium and 8 *M* in HCl. An aliquot of each stock solution was evaporated with sulfuric acid and ignited to the oxide. Spectrographic analysis of the oxide samples by the U. S. Bureau of Mines gave results of 240 and 290 parts per million HfO_2, respectively. Thus in all subsequent calculations this small amount of hafnium present was neglected.

Standard lithium chloride solutions were prepared by dissolving J. T. Baker reagent grade lithium chloride in distilled water and filtering. They were standardized by determining the chloride in suitable aliquots by the Volhard method.

Various standard zirconium–hydrochloric solutions were prepared by dilution of the stock solutions and hydrochloric acid and distilled water. The zirconium in these solutions was determined either by evaporation with sulfuric acid, precipitation with ammonium hydroxide, or precipitation with mandelic acid,[16] followed by ignition to the oxide, or by the quercetin colorimetric method of Grimaldi and White.[17] In these solutions chloride was determined by the Volhard method and the acidity was determined by titration with standard sodium hydroxide using phenolphthalein as the indicator.

A series of zirconium chloride–hydrochloric acid solutions of constant zirconium and chloride concentration, constant ionic strength, but varying acidity was prepared by addition from a buret of specified volumes of standard zirconium–hydrochloric acid, standard hydrochloric acid and standard lithium chloride solutions, followed by dilution with distilled water to a common volume.

Zirconium–perchloric acid solutions were prepared by precipitation of the zirconium in an aliquot of zirconium–hydrochloric acid stock solution with ammonium hydroxide, filtering and washing the zirconium hydroxide, and dissolving it in a certain volume of reagent grade perchloric acid of the requisite concentration. The acidity of these solutions was determined by titration with sodium hydroxide using phenolphthalein indicator.

Extraction Experiments.—Preliminary experiments showed that equilibrium was reached after 30 minutes shaking time, and also showed that the percentage of zirconium extracted increased with temperature. In all extraction experiments the TBP–benzene solution to be used was pre-equilibrated by mechanical shaking for one hour in a water-bath at 25 ± 0.02° with an equal volume of an aqueous solution of the same composition as that to be studied except for absence of zirconium. The zirconium extractions were made by shaking 25.00 ml. of the requisite zirconium solution for one hour at 25 ± 0.02° with 25.00 ml. of pre-equilibrated TBP–benzene of the desired concentration. After equilibration the phases were separated and reserved for analysis. Zirconium in the aqueous phase was determined either gravimetrically or colorimetrically. Gravimetric analyses were made on suitable aliquots by evaporation with sulfuric acid or precipitation with mandelic acid or ammonium hydroxide, followed by ignition to zirconium dioxide. The quercetin colorimetric method was used for analysis of micro amounts of zirconium. Chloride was determined in the aqueous phase by the Volhard method. The organic phase was centrifuged to remove droplets of the aqueous phase, and an aliquot was extracted with four portions of 2 *M* hydrochloric acid. These hydrochloric acid washings were analyzed for zirconium by one or more of the above methods. Chloride in the organic phase was determined by extracting an aliquot with four portions of 2 *M* nitric acid followed by determination of chloride in these washings by the Volhard method.

Discussion

Variation of Extraction with Equilibrium TBP Concentration.—The purpose of the following investigation was to study the variation in the extraction of zirconium with changing TBP concentration in the benzene phase and thus ascertain the molar ratio of TBP to zirconium in the extracted species.

In a concentrated hydrochloric acid solution of zirconium the presence of the following types of equilibria are assumed in the light of existing information.

$$Zr(OH)_3Cl + Cl^- \rightleftarrows Zr(OH)_2Cl_2 + OH^-$$

$$Zr(OH)_2Cl_2 + Cl^- \rightleftarrows Zr(OH)Cl_3 + OH^-$$

$$Zr(OH)Cl_3 + Cl^- \rightleftarrows ZrCl_4 + OH^-$$

Under conditions of constant high hydrochloric acid concentration the following assumptions are made. (1) All activity coefficients are constant at constant ionic strength. (2) Only one zirconium species is extractable into TBP. (3) The concentration of the extractable species is essentially equal to the total aqueous zirconium concentration since all other zirconium species are considered to be present in extremely small concentrations.

An equation for the reaction of TBP with the extractable species of zirconium can be written

$$Zr(OH)_x(Cl)_y(aq) + nTBP(b) \rightleftarrows Zr(OH)_x(Cl)_y(TBP)_n(b) \tag{1}$$

where (aq) designates a species present in the aqueous phase and (b) designates a species present in the benzene or organic phase.

Since the molar concentration of the extractable zirconium species, $[Zr(OH)_x(Cl)_y](aq)$, is essentially equal to the total aqueous zirconium molar concentration, $[Zr](aq)$, the following equation can be written

$$[Zn(OH)_x(Cl)_y](aq) = [Zr](aq) \tag{2}$$

---

[6] L. Melnick, H. Freiser and H. F. Beeghly, *Anal. Chem.*, **25**, 856 (1953).

[7] L. M. Melnick and H. Freiser, *ibid.*, **27**, 462 (1955).

[8] W. W. Meinke, Atomic Energy Commission Declassified Report, AECD-2738.

[9] D. F. Peppard, *et al.*, THIS JOURNAL, **75**, 4576 (1953).

[10] J. C. Warf, *ibid.*, **71**, 3257 (1949).

[11] D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, **57**, 294 (1953).

[12] B. Weaver, F. A. Kappelmann and A. C. Topp, THIS JOURNAL, **75**, 3943 (1953).

[13] J. Bochinski, M. Smutz and F. H. Spedding, Atomic Energy Commission Declassified Report, ISC-348.

[14] D. F. Peppard, M. M. Markus and P. R. Gray, Abstracts of Papers, 124th Meeting American Chemical Society, Chicago, 1953, P. 56R.

[15] E. N. Scadden and N. E. Ballou, *Anal. Chem.*, **25**, 1602 (1953).

[16] R. E. Oesper and J. J. Klingenberg, *ibid.*, **21**, 1509 (1949).

[17] F. S. Grimaldi and C. E. White, *ibid.*, **25**, 1886 (1953).

If D is defined as the distribution ratio or the ratio of total organic zirconium molarity to total aqueous zirconium molarity, it can be shown that

$$\log D = \log K_1 + n \log [\text{TBP}](\text{b}) \qquad (3)$$

where K_1 is the equilibrium constant for equation 1, and [TBP](b) is the equilibrium organic TBP molarity. A plot of log D *versus* log [TBP](b) should then give a straight line with a slope equal to n.

The data for this study are shown in Table I. The equilibrium TBP concentration was calculated by assuming a 2:1 molar ratio of TBP to Zr in the complex extracted. The equilibrium TBP concentration was thus deduced by subtracting twice the organic zirconium molarity from the original TBP molarity. Since this correction is quite small compared to the total initial TBP concentration, this original assumption of a 2:1 complex did not appreciably affect the results. A plot of log D *versus* log [TBP](b) gave a slope of 1.97, indicating a 2:1 molar ratio of TBP to zirconium in the species extracted. Equation 2 can thus be rewritten as

$$\text{Zr(OH)}_x(\text{Cl})_y(\text{aq}) + 2\text{TBP(b)} \rightleftarrows \text{Zr(OH)}_x(\text{Cl})_y(\text{TBP})_2(\text{b}) \qquad (4)$$

TABLE I

VARIATION OF EXTRACTION OF ZIRCONIUM WITH EQUILIBRIUM TBP CONCENTRATION IN BENZENE

Initial Zr concentration, 0.00405 M in 6.667 M HCl.

Initial [TBP](b)	Final [TBP](b)	D	Initial [TBP](b)	Final [TBP](b)	D
0.2196	0.2123	7.60	0.06816	0.06452	0.775
.1757	.1688	4.89	.05790	.05480	.581
.1318	.1258	2.84	.05112	.04857	.446
.1098	.1044	1.876	.04090	.03910	.284
.08784	.08320	1.251	.03408	.03277	.192

The Role of the Chloride in the Extraction.—The object of the following investigations was to study the role of chloride in the extraction by analyzing the organic extracts for chloride and zirconium and by studying the change in distribution ratio of zirconium with varying chloride concentrations in the aqueous phase at equilibrium.

Table II shows the results of zirconium and chloride analyses in the organic phase after various zirconium–hydrochloric acid solutions were shaken with a pre-equilibrated solution of TBP in benzene containing 0.19 M TBP. The concentration of chloride associated with the zirconium was computed by subtracting the initial chloride concentration from the final chloride concentration in the organic phase.

The results of the above experiments show a trend of decreasing Cl:Zr ratio with increasing initial hydrochloric acid concentration in the aqueous phase. At the higher acid concentrations (above 7.7 M) greater corrections had to be applied for the solubility of free hydrochloric acid in the TBP–benzene. Possible errors may have been caused by incorrect estimations of these corrections or by volatility of the hydrogen chloride in the organic extracts containing zirconium. However, the results indicate a Cl:Zr ratio of 4:1 in the range, 6.4–7.7 M hydrochloric acid.

TABLE II

DETERMINATION OF THE Cl/Zr RATIO IN THE COMPLEX EXTRACTED BY TBP–BENZENE

Initial TBP concentration in benzene, 0.1627–0.1946 M.

Initial [HCl] (aq)	Initial [Zr] (aq)	[Zr](b)	Final [Cl⁻] (b)	Initial [Cl⁻] (b)	[Cl⁻] in complex	Cl/Zr in complex
6.396	0.0289	0.0147[a]	0.0608	0.0033	0.0575	3.91
6.396	.0289	.0148[a]	.0596	.0033	.0563	3.81
6.735	.0431	.0294[b]	.1270	.0055	.1215	4.13
6.735	.0431	.0302[b]	.1283	.0048	.1235	4.09
6.735	.0431	.0318[a]	.1315	.0055	.1260	3.96
6.735	.0431	.0317[a]	.1315	.0053	.1262	3.98
7.736	.0276	.0274[b]	.1252	.0169	.1083	3.95
7.736	.0276	.0274[b]	.1248	.0165	.1083	3.95
8.285	.0506	.0499[b]	.2085	.0289	.1796	3.60
8.285	.0506	.0499[b]	.2090	.0289	.1801	3.61
8.806	.0289	.0288[a]	.1393	.0411	.0982	3.40
8.806	.0289	.0288[a]	.1393	.0406	.0987	3.43
11.32	.0276	.0269[b]	.1970	.1252	.0718	2.68

[a] Mandelic acid method. [b] Quercetin method.

Although data by other workers have shown that zirconium is chiefly present as the Zr^{+4} ion in concentrated perchloric acid solutions,[18,19] little is known about the chemistry of zirconium in chloride solutions. Evidence has been given[20,21] for a chloro complex of zirconium containing one atom of chlorine per atom of zirconium.

A study of the variation of the extraction of zirconium by TBP with changing chloride concentration at constant acidity and constant ionic strength was made to obtain more information on the contribution of chloride to the species extracted. Because of lack of knowledge of activity coefficients under these conditions concentrations are set equal to activities in this discussion. In addition, only one species of zirconium is assumed to be extracted into the organic phase, and the concentrations of intermediate chloro complexes of zirconium are assumed to be negligible.

For this study the initial ionic strength and acidity were held constant and the initial chloride concentration varied by the addition from a buret of the correct volume of zirconium–perchloric acid, standard perchloric acid, standard hydrochloric acid, and dilution to the mark with distilled water.

The following equations can be written to describe the equilibria involved in the TBP extraction of zirconium from hydrochloric–perchloric acid solutions.

$$\text{ZrCl}_n^m + x\text{Cl}^-(\text{aq}) \rightleftarrows \text{ZrCl}_{(n+x)}^{(m-x)}(\text{aq}) \qquad (5)$$

$$\text{ZrCl}_{(n+x)}^{(m-x)} + 2\text{TBP(b)} \rightleftarrows \text{ZrCl}_{(n+x)}^{(m-x)}[\text{TBP}]_2 \qquad (6)$$

If the original TBP concentration in the organic phase is held constant

$$[\text{ZrCl}_{(n+x)}^{(m-x)}(\text{TBP})_2](\text{b}) = K[\text{ZrCl}_{(n+x)}^{(m-x)}](\text{aq}) \qquad (7)$$

Hence

$$D = \frac{K[\text{ZrCl}_{(n+x)}^{(m-x)}](\text{aq})}{[\text{ZrCl}_n^m](\text{aq})} \qquad (8)$$

---

(18) A. J. Zielen, U. S. Atomic Energy Commission Declassified Report, UCRL-2268.

(19) E. M. Larsen and P. Wang, THIS JOURNAL, **76**, 6223 (1954).

(20) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

(21) B. A. J. Lister and L. A. MacDonald, *J. Chem. Soc.*, 4315 (1952).

where D is defined as before.

$$\log D = \log K + \log \frac{[\mathrm{ZrCl}_{(n+x)}^{(m-x)}](\mathrm{aq})}{[\mathrm{ZrCl}_n^m](\mathrm{aq})} \qquad (9)$$

$$\log D = \log K + \log k_1 + x \log [\mathrm{Cl}^-](\mathrm{aq}) \qquad (10)$$

where k_1 is the equilibrium constant for reaction (4).

$$\log D = C + X \log [\mathrm{Cl}^-](\mathrm{aq}) \qquad (11)$$

Thus a plot of log D *versus* log $[\mathrm{Cl}^-]$(aq) should give a straight line with a slope equal to x.

The data in Table III give the results of the study of the effect of aqueous chloride on the extraction of zirconium by TBP. A plot of log D *versus* log $[\mathrm{Cl}^-]$(aq) gave a straight line with a slope of 2.94.

TABLE III

VARIATION IN EXTRACTION OF ZIRCONIUM BY TBP–BENZENE WITH CHANGING AQUEOUS CHLORIDE CONCENTRATION

Initial concentrations: TBP(b), 0.1946 *M;* Zr(aq), 0.00108 *M;* ionic strength, 6.54.

Final $[\mathrm{Cl}^-]$(aq)	D	Final $[\mathrm{Cl}^-]$(aq)	D
0.00000	0.000	0.3020	0.890
.00668	.000	.3397	1.06
.1353	.092	.4021	2.22
.2019	.271	.4712	3.29
.2687	.667	.5336	4.64

If a value of 3 is assigned to x, the equilibria may be written as

$$\mathrm{ZrCl}_n^m(\mathrm{aq}) + 3\mathrm{Cl}^-(\mathrm{aq}) \rightleftarrows \mathrm{ZrCl}_{(n+3)}^{(m-3)}(\mathrm{aq}) \qquad (12)$$

$$\mathrm{ZrCl}_{(n+3)}^{(m-3)}(\mathrm{aq}) + 2\mathrm{TBP(b)} \rightleftarrows \mathrm{ZrCl}_{(n+3)}^{(m-3)}(\mathrm{TBP})_2(\mathrm{b}) \qquad (13)$$

The Effect of Aqueous Acidity on the Extraction.—An investigation was carried out in order to determine the role of hydrogen ion in the extraction of zirconium by TBP. This was done by keeping the chloride concentration and ionic strength constant and determining the change in the distribution ratio for zirconium, D, with changing acidity. The results of this study are summarized in Fig. 1, which shows a plot of log D *versus* log $[\mathrm{H}^+]$(aq) where $[\mathrm{H}^+]$(aq) is the equilibrium aqueous hydrochloric acid molarity.

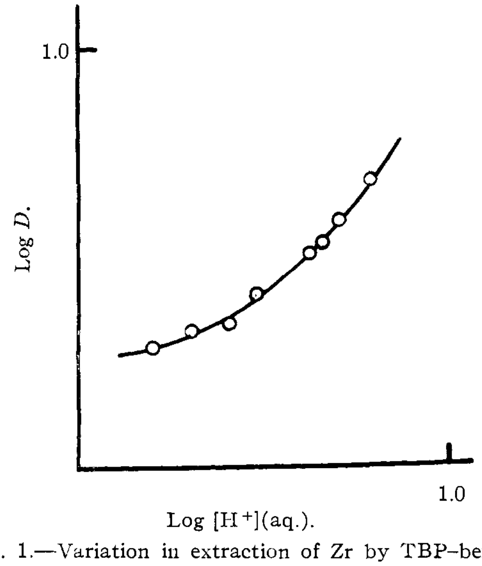

Fig. 1.—Variation in extraction of Zr by TBP–benzene with changing aqueous acidity; initial TBP concentration, 0.1946 *M;* initial aqueous Zr concentration, 0.00108 *M;* initial ionic strength, 6.54.

Figure 1 illustrates the relatively low effect of acidity on the extraction of zirconium at constant chloride concentration and ionic strength. Indeed at the lower hydrogen ion concentrations the change in extraction with hydrogen ion concentration is very slight. Thus it is believed that hydrogen is not present in the complex extracted into TBP.

The Effect of Zirconium Concentration on the Extraction.—In order to test the constancy of the distribution ratio D with changing initial aqueous zirconium concentration an investigation was conducted by observing the change in D with increasing initial aqueous zirconium concentration. The initial TBP concentration in the organic phase and the initial aqueous hydrochloric acid concentration was held constant while the initial zirconium concentration was increased a hundred-fold. The results showed a definite decrease in the distribution ratio of zirconium (*e.g.*, a decrease in per cent. extraction of zirconium) with increasing initial zirconium concentration. This could be resulting from polymerization of zirconium in the aqueous phase.

The possibility of the existence of zirconium polymers in hydrochloric acid solution is not unlikely as other workers[16,18,19,22,23] have observed polymer formation of zirconium in perchloric acid.

Connick and McVey[20] have shown that a decrease in per cent. extraction with increasing initial metal ion concentration indicates polymerization of the metal in the aqueous phase.

Myers, Metzler and Swift,[24] in studying the extraction of ferric iron with isopropyl ether, observed an increase in per cent. extraction with increasing initial ferric ion concentration. They plotted the logarithm of the organic metal ion molarity against the logarithm of the aqueous metal ion molarity over the range of ferric ion concentrations studied. A slope of more than one resulted, which indicated a greater degree of polymerization of ferric ion in the organic phase than in the aqueous phase.

A similar curve shown in Fig. 2 in this investigation was plotted except that conversely the logarithm of the aqueous zirconium molarity, log [Zr](aq) was used as the ordinate and the logarithm of the organic zirconium molarity, log [Zr](b), the abscissa. At the higher initial zirconium concentrations the slope of the curve is greater than one, indicating a greater degree of polymerization of zirconium in the aqueous phase. The slope of the curve increases with rising zirconium concentration, giving evidence of more than one polymer present.

In a recent paper Irving, Rossotti and Williams[25] demonstrated that at constant acidity (H) and ligand concentration (L) and at equal phase volume at equilibrium the distribution ratio D

---

(22) R. E. Connick and W. H. Reas, THIS JOURNAL, **73**, 1171 (1951).

(23) K. A. Kraus and J. H. Johnson, *ibid.*, **75**, 5769 (1953).

(24) R. J. Myers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3767 (1950).

(25) H. Irving, F. J. C. Rossotti and R. P. J. Williams, *J. Chem. Soc.*, 1906 (1955).

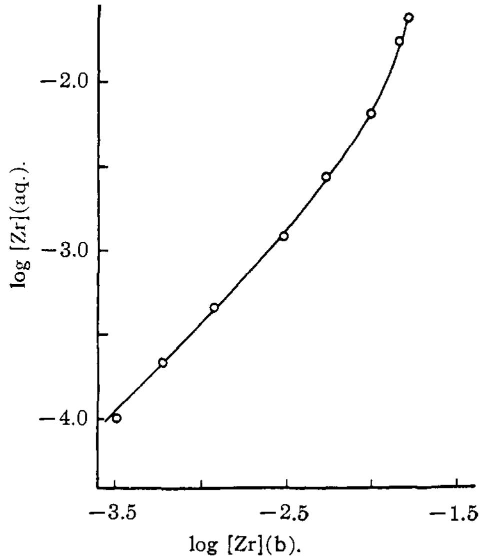

Fig. 2.—Change in equilibrium aqueous and organic Zr molarity with changing Zr concentration; initial TBP concentration in TBP–benzene, 0.131 *M*, initial aqueous HCl concentration, 6.628 *M*.

varies with initial metal concentration in the following manner

$$\left(\frac{\partial \log D}{\partial \log C_m}\right)_{[\mathrm{H}],\,[\mathrm{L}]} = \frac{(m - \overline{m})\,(1 + D)}{(m + \overline{m}D)} \qquad (14)$$

where C_m is the total metal ion concentration, m represents the "polymerization number, "*i.e.*, the average number of metal atoms per molecular species in the organic phase and $\overline{m}$ the "polymerization number" in the aqueous phase.

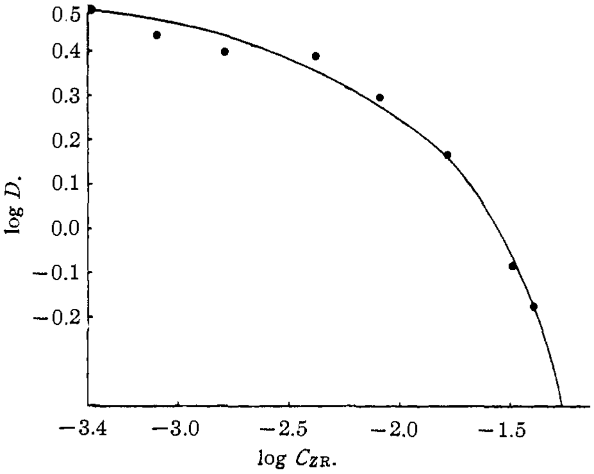

Fig. 3.—Change in distribution ratio *D* with changing initial Zr concentration; conditions as in Fig. 2.

In this study a plot of log *D versus* log C_{Zr} was constructed as shown in Fig. 3. In the lower zirconium concentrations the slope of the curve is very close to zero, indicating little difference in extent of polymerization between the two phases. At the higher zirconium concentrations the slope approaches a minus one value, again indicating a higher degree of polymerization in the aqueous phase than in the organic phase.

AMHERST, MASS.
CORVALLIS, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Diffusion Coefficients for Aqueous Solutions of Sodium Chloride and Barium Chloride

BY V. VITAGLIANO AND P. A. LYONS

RECEIVED SEPTEMBER 12, 1955

In this report are presented diffusion coefficients for aqueous solutions of sodium chloride and barium chloride obtained at 25 ± 0.01° using the Gouy interferometric technique. They supplement existing data, in each case confirm the electrometric results for dilute solutions and assist in the selection of consistent self-diffusion measurements in concentrated sodium chloride solutions.

Materials and Methods—Solutions of NaCl were prepared by weighing dried C.P. salt and transferring it into calibrated volumetric flasks. $BaCl_2$ solutions were prepared from an analyzed stock solution of the C.P. salt.

Diffusion measurements were made using the Gouy interferometric technique for which detailed descriptions are available.[1,2] At the lowest concentrations experiments were performed in a Tiselius cell with channel dimensions 92 × 50 × 5 mm. and the other data were obtained using a cell with 92 × 25 × 3 mm. channels.

A few viscosity measurements were made to supplement the information in the International Critical Tables. A Cannon–Fenske viscometer was used for this purpose.

Experimental Results

In Table I are listed diffusion coefficients measured in a Gouy diffusiometer, and related information obtained for NaCl solutions. Table II contains analogous data for $BaCl_2$ solutions.

The reported diffusion coefficients were estimated using the positions of the lowest six or seven fringe minima. No unusual drifts in C_t were observed for the data reported. In previous work it has been reported that for electrolytes downward drifts in C_t occur at low concentrations.[3] Similar results were obtained in the present work, the value of C_t at $J \cong {}^1/_2 J_m$ being about 0.3 or 0.4% lower than the average of C_t obtained from the lowest seven fringes. The earlier work[3] argues strongly for the possibility that the lowest concentration Gouy data for electrolytes might be 0.1–0.2% high when the conventional computation[2] is used. This method of computation was used here, and with the excep-

---

(1) L. G. Longsworth, THIS JOURNAL, **69**, 2510 (1947).

(2) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

(3) P. A. Lyons and J. F. Riley, *ibid.*, **76**, 5216 (1954).