

512. Zinc Chloride and Zinc Bromide Complexes. Part II.¹ Solvent-extraction Studies with Zinc-65 as Tracer.

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The distribution of zinc at tracer concentration between tri-*n*-butyl phosphate (TBP) and aqueous solutions containing either chloride or bromide has been studied by using ⁶⁵Zn. Under the conditions of experiment, only mononuclear zinc complexes appear to exist in the two phases. In the systems Zn^{II}-TBP-HA-H₂O (A = Cl or Br), the complexes ZnA₂·2TBP, HZnA₃·3TBP, and H₂ZnA₄·2TBP may occur in the organic layer. Estimates have been made of relevant equilibrium constants. There is a marked parallelism between extraction with tributyl phosphate and anion-exchange sorption of zinc from aqueous HA solutions.

In the presence of NaA, salts or ion-pairs such as Na⁺[ZnA₃·2TBP]⁻ may be formed in the tributyl phosphate phase, in addition to the complexes ZnA₂·2TBP.

In the present work attempts have been made to ascertain the nature of zinc species extracted into tributyl phosphate (TBP)² from hydrochloric acid or hydrobromic acid, the distribution ratio being measured by means of ⁶⁵Zn as tracer. By using ⁶⁵Zn of high specific activity and γ -scintillation counting, the concentration of zinc has been kept very much smaller than that of hydrogen ion, halide ion, or tributyl phosphate and thus corrections for complex-formation need not be made.

The extraction of tracer zinc into tributyl phosphate from hydrochloric acid has been reported by Irving and Edgington³ and Ishimori *et al.*⁴ Relatively little has been published concerning the distribution of inorganic bromides between this phosphate and hydrobromic acid. The extraction of hydrobromic acid itself into the phosphate has been investigated by Kertes and Kertes.⁵ The acid is extracted by tributyl phosphate rather more readily than is hydrochloric acid,⁶ and the acid-solvent interaction appears to be similar in the two cases.

EXPERIMENTAL

Materials.—Zinc-65 (half-life 245 days) of high specific activity was supplied as the chloride by the Radiochemical Centre, Amersham. The radiochemical purity was checked by decay and γ -ray measurements. No radioactivity other than that due to ⁶⁵Zn could be detected. For the studies involving solutions containing bromide, the tracer was converted into bromide by passage through columns of the anion-exchange resin De-acidite-FF in (a) the ClO₄⁻ and (b) the Br⁻ form. There was no chloride in the solution after passage through the resin in the ClO₄⁻ form.

Tributyl phosphate was purified by the method of Alcock *et al.*⁷ Benzene from British Drug Houses Ltd., was material "for molecular weight determinations." Hydrobromic acid solutions were prepared from constant-boiling mixtures distilled immediately before use, thus eliminating contamination by free bromine. Other reagents were of "AnalaR" quality.

General Procedure.—The distribution ratio of zinc between tributyl phosphate and a series of hydrochloric or hydrobromic acid solutions was measured under a variety of conditions. Partition was obtained by mechanically stirring together 10 ml. each of the organic and the aqueous phase in 50-ml. glass centrifuge tubes. Agitation for 30 min. sufficed. After equilibration and centrifuging, the phases were separated by means of transfer pipettes for

¹ Part I, Short and Morris, *J. Inorg. Nuclear Chem.*, 1961, **18**, 192.

² Cf. McKay and Healy, *Progr. Nuclear Energy, Series III, Process Chem.*, 1958, **2**, 546.

³ Irving and Edgington, *J. Inorg. Nuclear Chem.*, 1959, **10**, 306.

⁴ Ishimori, Watanabe, and Nakamura, *Bull. Chem. Soc. Japan*, 1960, **33**, 636.

⁵ Kertes and Kertes, *Canad. J. Chem.*, 1960, **38**, 612.

⁶ Kertes, *J. Inorg. Nuclear Chem.*, 1960, **14**, 104; Baldwin, Higgins, and Soldano, *J. Phys. Chem.*, 1959, **63**, 118.

⁷ Alcock, Bedford, Hardwick, and McKay, *J. Inorg. Nuclear Chem.*, 1957, **4**, 100.

analysis. Aliquot parts were counted in Polythene counting cups under identical conditions with a NaI(Tl) γ -scintillation counter, of type 1186A. Values of the distribution ratio (organic/aqueous), D , were obtained from the ratio of the count rates (corrected for background) for the aliquot parts of the two phases. No corrections for the decay of the ^{65}Zn were necessary, since portions from any one experiment were assayed consecutively.

For each distribution measurement the initial halogen acid concentration $[\text{HA}]_i$ in the aqueous phase was known. Concentrations of halogen acid in the organic phase $[\text{HA}]_o$ and in the aqueous phase $[\text{HA}]_a$ after equilibration were determined by titration with alkali. (Here and below, A = Cl or Br.)

In most cases neither phase was pre-saturated with the other before equilibration in the extraction experiments. In the experiments with added sodium halide, however, the tributyl phosphate was adjusted to approximately the equilibrium acidity and halide concentration by agitation with four successive volumes of the aqueous phase in absence of the zinc tracer.

Distribution experiments were performed at $20^\circ \pm 1^\circ$. No adsorption of radiozinc was detected on the walls of the centrifuge tubes used for the equilibrations.

TABLE 1.
Dependence of distribution on concentration (moles/l.) of hydrochloric acid:
extraction by tributyl phosphate from $\text{HCl} + \text{H}_2\text{O}$.

$[\text{Zn}]_i = 7.95 \times 10^{-5}\text{M}$.

$[\text{HCl}]_i$	D	$[\text{HCl}]_o$	$[\text{HCl}]_a$	$[\text{HCl}]_i$	D	$[\text{HCl}]_o$	$[\text{HCl}]_a$	$[\text{HCl}]_i$	D	$[\text{HCl}]_o$	$[\text{HCl}]_a$
0.0099	0.00211		0.02	1.50	14.5 ^a	0.13	1.48	3.462	29.5	0.62	3.24
0.049	0.0136		0.0525	1.978	23.8	0.17	2.00	3.50	29.2 ^c	0.63	3.25
0.099	0.0439		0.108	2.30	29.7	0.22	2.22	3.956	24.3	0.72	3.715
0.2473	0.247	0.005	0.285	2.473	34.6	0.31	2.385	4.945	17.8	1.065	4.5
0.4945	0.861	0.01	0.525	2.50	34.2 ^b	0.32	2.40	5.934	11.8	1.5	5.5
0.742	2.49	0.03	0.770	2.720	28.3	0.35	2.64	6.923	7.88	1.85	6.2
0.99	5.33	0.035	1.03	2.967	28.2	0.41	2.875	7.912	5.25	2.2	7.1
1.187	9.20	0.070	1.215	3.214	29.2	0.49	3.04	8.901	3.52	2.55	7.85
1.385	12.3	0.08	1.438								

Values for D are averages from duplicate measurements, except (a) (± 0.2), (b) (± 0.5), and (c) (± 0.3) which are averages of five measurements each.

TABLE 2.
Dependence of distribution on concentration (moles/l.) of hydrobromic acid: extraction by tributyl phosphate from $\text{HBr} + \text{H}_2\text{O}$. $[\text{Zn}]_i = 4.22 \times 10^{-5}\text{M}$. Max. value of D is accurate within ± 3 .

$[\text{HBr}]_i$	D	$[\text{HBr}]_o$	$[\text{HBr}]_a$	$[\text{HBr}]_i$	D	$[\text{HBr}]_o$	$[\text{HBr}]_a$	$[\text{HBr}]_i$	D	$[\text{HBr}]_o$	$[\text{HBr}]_a$
0.00975	0.0058		0.0095	2.3	186	0.51	2.01	3.77	226	0.94	3.25
0.05	0.0458		0.05	2.5	207	0.57	2.18	3.9	204	0.99	3.35
0.1	0.142	0.0005	0.10	2.6	226	0.60	2.28	4.0	195	1.01	3.45
0.2	0.485	0.005	0.20	2.8	259	0.66	2.43	4.1	185	1.04	3.53
0.4	1.96	0.025	0.45	2.9	267	0.69	2.53	4.3	158	1.11	3.69
0.6	5.80	0.07	0.625	3.0	273	0.71	2.60	4.6	124	1.20	3.95
0.8	11.3	0.091	0.74	3.1	267	0.75	2.69	5.0	96.8	1.32	4.30
1.0	21.9	0.138	0.92	3.2	250	0.78	2.78	5.5	69.2	1.49	4.71
1.2	28.1	0.185	1.08	3.3	213	0.81	2.85	6.0	60.2	1.66	5.13
1.4	52.2	0.24	1.27	3.4	228	0.84	2.93	6.5	42.8	1.88	5.55
1.6	71.1	0.30	1.43	3.5	233	0.87	3.03	7.0	33.3	2.01	5.97
1.8	105	0.36	1.59	3.6	240	0.90	3.10	8.0	18.6	2.28	6.85
2.0	139	0.42	1.76	3.7	233	0.93	3.18	8.5	14.9	2.45	7.30
2.2	165	0.48	1.93								

TABLE 3.
Dependence of the distribution ratio on concentration (mole/kg.) of sodium chloride:
extraction by tributyl phosphate from $\text{NaCl} + \text{HCl} + \text{H}_2\text{O}$. $[\text{HCl}]_a = 0.01\text{M}$.
 $[\text{Zn}]_i = 7.95 \times 10^{-5}\text{M}$.

D	0.00338	0.00601	0.0166	0.0417	0.115	0.461	1.497	4.14	4.61	4.15	4.26
$[\text{NaCl}]_a$...	0.01	0.02	0.05	0.10	0.20	0.50	1.0	2.0	3.0	3.25	3.5

TABLE 4.

Dependence of the distribution ratio on concentration (moles/kg.) of sodium bromide: extraction by tributyl phosphate from NaBr + HBr + H₂O. [HBr]_a = 0.01M. [Zn]_i = 4.22 × 10⁻⁵M.

<i>D</i>	0.011	0.0527	0.145	0.387	1.80	8.52	14.0	20.0	32.5	46.5	62.8	88.6	134	197	239
[NaBr] _a	0.01	0.05	0.1	0.2	0.5	1.0	1.2	1.4	1.72	2.0	2.1	2.46	3.0	4.0	5.0

TABLE 5.

Effect of varying the concentration of tributyl phosphate (TBP) in the organic phase on extraction from solutions containing chloride. [Zn]_i = 7.95 × 10⁻⁵M.

(a) *Extractions from HCl + H₂O.*

[HCl] _a = 0.4725M		[HCl] _a = 2.21M		[HCl] _a = 2.87M	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.00018	5	0.000105	2	0.00208	4
0.00064	9	0.00086	3	0.00616	7
0.00144	11	0.00148	3.5	0.0096	9
0.00183	13	0.00209	4	0.0164	11
0.00227	15	0.00367	5	0.0228	13
0.00328	17	0.0106	7	0.0299	15
0.00502	20				
0.0154	30				

[HCl] _a = 3.24M		[HCl] _a = 3.73M		[HCl] _a = 8.0M	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.00219	4	0.00229	4	0.00046	1
0.00666	7	0.00498	7	0.00184	2
0.0104	9	0.00836	9	0.00514	3
0.0171	11	0.0151	11	0.00804	4
0.0243	13	0.0229	13	0.0247	7
0.0306	15	0.0300	15	0.0486	9

(b) *Extractions from 0.01M-HCl + NaCl + H₂O.*

[NaCl] _a = 1.042m		[NaCl] _a = 2.289m		[NaCl] _a = 3.092m	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.00151	4	0.00188	4	0.00174	4
0.00381	7	0.00460	7	0.00482	7
0.00650	9	0.00785	9	0.00695	9
0.0129	13	0.0115	11	0.0101	11
0.0169	15	0.0156	13	0.0120	13
		0.0185	15	0.0198	15

RESULTS

The effect of the concentration of zinc on the distribution ratio *D* was studied, in the range [Zn]_i 2.1 × 10⁻⁵ to 1.99 × 10⁻⁴M. Values of *D* at given values of [HA]_a were found to be independent of the metal concentration, indicating that zinc complexes in both the organic and the aqueous phase are mononuclear.

In all further experiments with chloride solutions the initial zinc concentration in the aqueous phase was 7.95 × 10⁻⁵M and for measurements with bromide solutions 4.22 × 10⁻⁵M.

Tables 1 and 2 illustrate the dependence of the distribution ratio on the concentration of halogen acid. The results for the distribution of the halogen acids themselves correspond closely with those of Kertes and Kertes.^{5,6}

Measurements on the partition of zinc between the phosphate and a series of solutions 0.01M in HA and containing sodium halide are recorded in Tables 3 and 4.

In addition to studies with pure tributyl phosphate, experiments were made with an organic phase with varying amounts of it in benzene. The results are recorded in Tables 5 and 6.

TABLE 6.

 Effect of varying the concentration of tributyl phosphate (TBP) in the organic phase on extraction from solutions containing bromide. $[Zn]_i = 4.22 \times 10^{-5}M$.

 (a) Extraction from HBr + H₂O.

$[HBr]_a = 0.25M$		$[HBr]_a = 1.65M$		$[HBr]_a = 2.5M$	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.0004 ₅	4	0.0174	4	0.0505	4
0.0011	7	0.0605	7	0.175	7
0.0016	9	0.115	9	0.323	9
0.0025	11	0.166	11	0.522	11
0.0034	13	0.257	13	0.801	13
0.0040	15	0.354	15	1.195	15

$[HBr]_a = 3.05M$		$[HBr]_a = 5.8M$	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.0589	4	0.112	4
0.222	7	0.559	7
0.401	9	1.266	9
0.674	11	2.211	11
1.078	13	3.45	13
1.584	15	5.02	15

 (b) Extraction from 0.01M-HBr + NaBr + H₂O.

$[NaBr]_a = 1.4m$		$[NaBr]_a = 2.1m$		$[NaBr]_a = 3.0m$	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.0052	4	0.0178	4	0.0458	4
0.0177	7	0.0518	7	0.141	7
0.0313	9	0.0932	9	0.237	9
0.0520	11	0.156	11	0.366	11
0.0731	13	0.221	13	0.515	13
0.0973	15	0.314	15	0.768	15

$[NaBr]_a = 3.7m$		$[NaBr]_a = 5.0m$	
<i>D</i>	TBP (% v/v) in benzene	<i>D</i>	TBP (% v/v) in benzene
0.0545	4	0.0675	4
0.185	7	0.235	7
0.334	9	0.416	9
0.504	11	0.632	11
0.773	13	0.911	13
1.054	15	1.209	15

DISCUSSION

Extraction from Solutions containing Sodium Chloride.—Fig. 1 shows a log-log plot of *D* against chloride ion activity of the aqueous phase $\{Cl^-\}_a$, for distribution between tributyl phosphate and solutions 0.01M in hydrochloric acid containing sodium chloride.* If invasion of the phosphate phase by water and chloride is ignored, the slope of the plot in Fig. 1 may be identified with the derivative $(\partial \log D / \partial \log \{Cl^-\}_a)$ at constant concentrations of zinc, organic phosphate, hydrogen ion, and water; and it may be shown that under those conditions

$$\partial \log D / \partial \log \{Cl^-\}_a \approx \bar{n}_o - \bar{n}_a, \quad (1)$$

where \bar{n} indicates the average number of chloride ligands in zinc complexes in a given phase. At low $\{Cl^-\}_a$ the slope of the curve is 1.9, and it may be inferred from a knowledge of stability constants that \bar{n}_a , the ligand number in the aqueous phase, is not very much larger than zero at this region of the plot. It appears, therefore, that under these conditions the extracted zinc species has a molar ratio Zn:Cl of 1:2. Moreover, the maximum value of *D* occurs at $\{Cl^-\}_a \sim 1.5$ and from the stability constants of Part I¹ and

* The chloride ion activities of the solutions were obtained from measurements of the E.M.F. of the cell Hg|Hg₂Cl₂(s), satd. KCl|(m)NaCl, 0.01M-HCl, AgCl(s)|Ag.

anion-exchange results of Horne⁸ this appears to correspond quite closely to the chloride ion activity at which $\bar{n}_a = 2$. It may be concluded, therefore, that in extractions from solutions of sodium chloride, 0.01M in hydrogen chloride, zinc is mainly present in the organic layer as a complex containing one atom of zinc and two atoms of chlorine.

The number of molecules of tributyl phosphate directly associated with the extracted zinc species may be deduced from the results in Table 5(b). For low concentrations of the phosphate in benzene, and constant concentrations of zinc, chloride, H⁺, and water, we have:

$$\partial \log D / \partial \log [\text{TBP}] = \bar{s}_o - \bar{s}_a, \quad (2)$$

where the symbol \bar{s} represents the average number of molecules of tributyl phosphate directly associated with zinc complexes in a given phase.^{3,9} Since the solubility of the

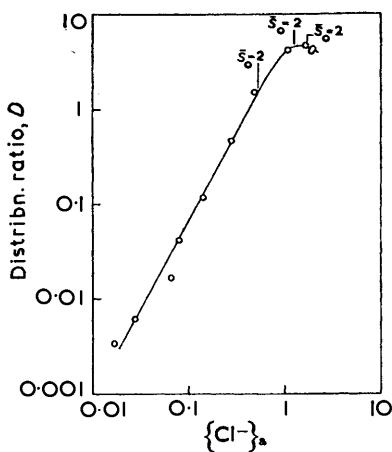


FIG. 1. Distribution of zinc tracer between tributyl phosphate and solutions 0.01M in hydrochloric acid containing sodium chloride. Variation of the distribution ratio with chloride ion activity of the aqueous phase at equilibrium.

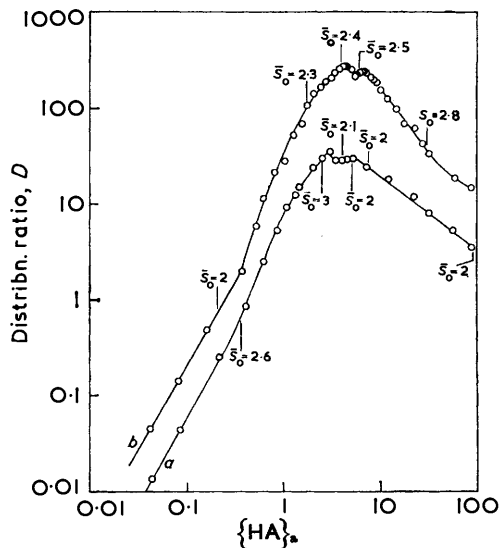


FIG. 2. Extraction of zinc tracer into tributyl phosphate from halogen acids. Variation of the distribution ratio with activity of (a) hydrochloric acid and (b) hydrobromic acid of the aqueous phase at equilibrium.

phosphate in the aqueous phase is small,¹⁰ \bar{s}_a may be taken as zero. Log-log plots of D against the amount (%) of tributyl phosphate in benzene for solutions containing fixed amounts of sodium chloride are all straight lines of slope 2: hence $\bar{s}_o = 2$.

It is concluded that for extraction from solutions 0.01M in hydrogen chloride containing varying amounts of sodium chloride, zinc occurs in the organic phase predominantly as the complex $\text{ZnCl}_2 \cdot 2\text{TBP}$ (probably $\text{ZnCl}_2 \cdot 2\text{TBP} \cdot 2\text{H}_2\text{O}$ ¹¹).

Extraction from Hydrochloric Acid.—The results of measurements of the extraction of zinc from hydrochloric acid into tributyl phosphate (see Table 1) are shown in Fig. 2(a), where the distribution ratio D is plotted against the acid activity of the aqueous phase

* A detailed analysis of the distribution data and Raman spectral studies¹¹ suggests that at the higher values of $\{\text{Cl}^-\}_a$ a proportion of the zinc extracted may be present in the organic layer as $\text{Na}^+[\text{ZnCl}_4 \cdot 2\text{TBP}]^-$ and $\text{Na}^+_2[\text{ZnCl}_6]^{2-}$.

⁸ Horne, *J. Phys. Chem.*, 1957, **61**, 1651; Marcus and Coryell, *Bull. Res. Council Israel*, 1959, **A**, 8, 1.

⁹ McKay, Proc. Internat. Conference Peaceful Uses of Atomic Energy, U.N., 1956, Vol. VII, p. 314.

¹⁰ Higgins, Baldwin, and Soldano, *J. Phys. Chem.*, 1959, **63**, 113.

¹¹ Morris, Short, and Waters, unpublished work.

$\{\text{HCl}\}_a$, on logarithmic scales. Values of $\{\text{HCl}\}_a$ have been computed from activity coefficients listed by Harned and Owen.¹²

The average number of molecules of tributyl phosphate directly associated with zinc species in the organic phase may be obtained from log-log plots of D against amount (%) of tributyl phosphate in benzene, by using the results in Table 5(a). The values of \bar{s}_o obtained from such plots are shown in Fig. 2.

The slope of the curve in Fig. 2(a) may be taken as equal to the derivative $\partial \log D / \partial \log \{\text{HCl}\}_a$ for constant concentrations of zinc, organic phosphate, and water, except at higher acidities when miscibility of the two phases becomes marked. It can be shown readily³ that, under these conditions,

$$\partial \log D / \partial \log \{\text{HCl}\}_a \sim (\bar{h}_o - \bar{h}_a) + (\bar{n}_o - \bar{n}_a). \quad (3)$$

The symbol \bar{h} indicates the average number of (acidic) hydrogen atoms in zinc complexes in a given phase. If it is accepted that acido-complexes of zinc are strong acids in aqueous solution,^{1,13} \bar{h}_a may be taken as being essentially zero.

For low values of $\{\text{HCl}\}_a$ the curve Fig. 2(a) has slope 1.9 and closely follows the curve in Fig. 1. It may be concluded, therefore, that at low acidity the zinc is present in the organic layer as the complex $\text{ZnCl}_2 \cdot 2\text{TBP}$. However, at higher acidities it is clear that acido-complexes of zinc must be present in the phosphate phase.

At $\{\text{HCl}\}_a = 0.83$, the slope of the curve is 2.2, and application of equation (3) and stability-constant data¹ yields the value for $(\bar{h}_o + \bar{n}_o)$ of 3.9. This result, together with the information obtained in experiments with tributyl phosphate diluted with benzene, suggests that in addition to $\text{ZnCl}_2 \cdot 2\text{TBP}$, a zinc species of composition $\text{HZnCl}_3 \cdot 3\text{TBP}$ is present in the organic phase. As the acidity is increased further there is clearly another acido-complex of zinc in the organic layer, as the curve in Fig. 2(a) has two maxima. There is no evidence for chloride complexes of zinc with an atomic ratio (Cl : Zn) > 4 : 1,^{1,11} so it is concluded that this other acido-complex of zinc in the organic phase has the composition $\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}$. With $[\text{HCl}]_a > \sim 2.7\text{M}$, zinc appears to be extracted predominantly as this complex $\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}$.

The above conclusions are compatible with Raman spectra.¹¹ The zinc acido-complexes $\text{HZnCl}_3 \cdot 3\text{TBP}$ and $\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}$ appear to be ion pairs,¹¹ $[\text{H}, \text{TBP}]^+ [\text{ZnCl}_3 \cdot 2\text{TBP}]^-$ and $[\text{H}, \text{TBP}]_2^+ [\text{ZnCl}_4]^{2-}$, and are almost certainly hydrated.¹⁴

It follows that for extractions from hydrochloric acid solutions

$$D = ([\text{ZnCl}_2 \cdot 2\text{TBP}]_o + [\text{HZnCl}_3 \cdot 3\text{TBP}]_o + [\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}]_o) / [\text{Zn}]. \quad (4)$$

If the system is taken to be ideal, then

$$D = k_2 \alpha_2 [\text{TBP}]_o^2 + k_{13} K_{13} \alpha_3 [\text{H}^+]_a [\text{TBP}]_o^3 + k_{24} K_{24} \alpha_4 [\text{H}^+]_a^2 [\text{TBP}]_o^2, \quad (5)$$

where

$$\alpha_j = [\text{ZnCl}_j^{2-j}]_a / [\text{Zn}]_a,$$

$$k_2 = [\text{ZnCl}_2 \cdot 2\text{TBP}]_o / [\text{ZnCl}_2]_a [\text{TBP}]_o^2,$$

$$k_{13} = [\text{HZnCl}_3 \cdot 3\text{TBP}]_o / [\text{HZnCl}_3]_a [\text{TBP}]_o^3,$$

$$K_{13} = [\text{HZnCl}_3]_a / [\text{H}^+]_a [\text{ZnCl}_3^-]_a,$$

$$k_{24} = [\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}]_o / [\text{H}_2\text{ZnCl}_4]_a [\text{TBP}]_o^2,$$

and

$$K_{24} = [\text{H}_2\text{ZnCl}_4]_a / [\text{H}^+]_a^2 [\text{ZnCl}_4^{2-}]_a.$$

¹² Harned and Owen, "The Physical Chemistry of Electrolyte Solutions," 2nd edn., Reinhold Publ. Inc., New York, 1950.

¹³ Diamond, *J. Phys. Chem.*, 1957, **61**, 75; Rudzentsis, Irvine, and Mendez, *Ann. Progr. Report*, June 1957—May 1958, Lab. Nuclear Science, Massachusetts Institute of Technology; Chu and Diamond, *J. Phys. Chem.*, 1959, **63**, 2021.

¹⁴ Nekrassov and Ovsyankina, *J. Gen. Chem. (U.S.S.R.)*, 1941, **11**, 573; Hesford and McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 156; Hardy, A.E.R.E., Harwell, AERE-R3124, 1959; Diamond and Tuck, *Progr. Inorg. Chem.*, 1960, **2**, 109; Tuck and Diamond, *J. Phys. Chem.*, 1961, **65**, 193.

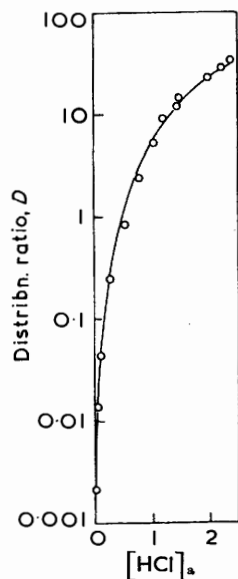


FIG. 3. Distribution of zinc tracer between tributyl phosphate and hydrochloric acid. The curve represents equation (5) with $k_2 = 0.16$, $k_{13}K_{13} = 2$, and $k_{24}K_{24} = 0.4$.

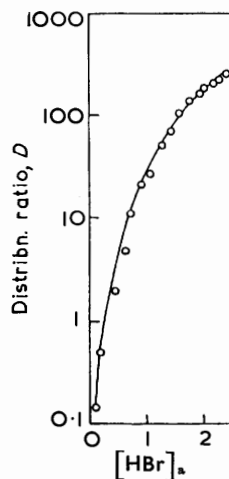


FIG. 4. Distribution of zinc tracer between tributyl phosphate and hydrobromic acid. The curve represents equation (8) with $k_2 = 1.7$, $k_{13}K_{13} = 12$, and $k_{24}K_{24} = 10$.

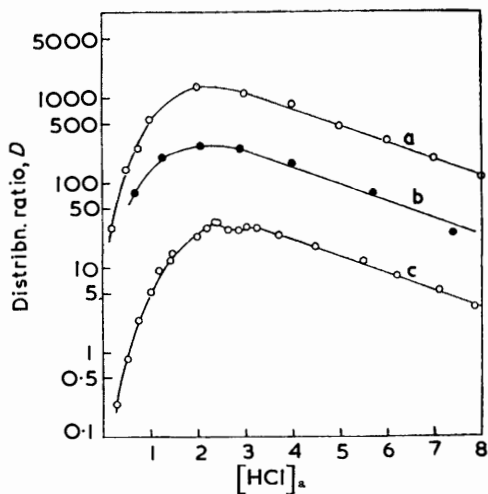


FIG. 5. Distribution of zinc tracer between (a) Dowex-1 anion-exchange resin, (b) 10% methyldioctylamine in trichloroethylene, (c) tributyl phosphate, and hydrochloric acid.

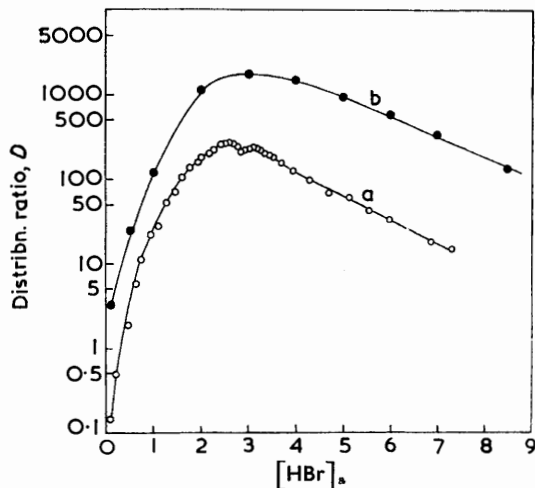


FIG. 6. Distribution of zinc tracer between (a) tributyl phosphate, (b) Dowex-1 anion-exchange resin, and hydrobromic acid.

By use of values of α_j , the degree of formation of the individual complexes, calculated from the stability constants of Part I, equation (5) yields values of D corresponding closely with the experimental results for values of $[\text{HCl}]_a$ up to $\sim 2.3\text{M}$ if $k_2 = 0.16$, $k_{13}K_{13} = 2$, and $k_{24}K_{24} = 0.4$ (Fig. 3). It should be noted that $[\text{TBP}]_o$ decreases as $[\text{HCl}]_a$ is increased, owing to transfer of water and hydrochloric acid into the organic phase.*

There is a marked similarity between extraction of zinc into the phosphate from aqueous hydrochloric acid and anion-exchange sorption of the element from corresponding solutions of the acid. Distribution behaviour for the anion-exchange resin Dowex-1¹⁵ and for the liquid anion-exchanger methyldioctylamine¹⁶ is shown in Fig. 5, in comparison with extraction by tributyl phosphate. [For anion-exchange sorption, $D = (\text{amount of zinc per g. of anion-exchanger})/(\text{amount of zinc per ml. of solution})$ at 25° .] The parallelism between anion-exchange sorption and solvent extraction of zinc is striking. In addition, a close correspondence between extraction by tributyl phosphate and anion-exchange sorption from hydrochloric acid occurs for various other elements.⁴

The formation of acido-complexes such as $\text{H}_2\text{ZnCl}_4 \cdot 2\text{TBP}$ in extraction by the phosphate could possibly be regarded as occurring through an anion-exchange mechanism, in which a complex anion exchanges with chloride from hydrochloric acid in the organic phase. This is illustrated schematically in Fig. 7. Such a mechanism could be correlated

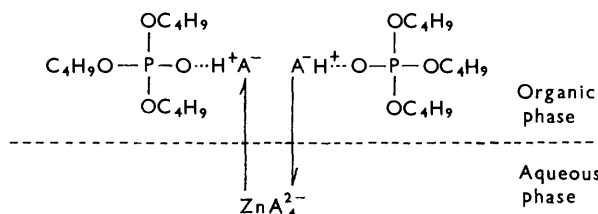


FIG. 7. A possible anion-exchange process in the extraction of zinc into tributyl phosphate from a solution of a halogen acid HA (schematic).

with the striking retrograde extraction of zinc observed at high hydrochloric acid concentrations.¹⁶

Formation of species such as $\text{ZnCl}_2 \cdot 2\text{TBP}$ appears to involve direct interaction of the phosphate molecules with the extracted zinc and cannot occur through a straightforward anion-exchange mechanism. For the sorption of zinc by the anion-exchange resin from chloride solutions, it is interesting that doubts have existed as to whether the sorption process may be regarded as just a simple anionic metathesis.¹⁵ Marcus and Coryell's theory,¹⁷ although applicable to systems incapable of forming neutral complexes, is based on the formulation that the principal adsorbing species is ZnCl_2 . This adsorbed neutral complex is then regarded as combining with further Cl^- ions within the resin to yield predominantly ZnCl_4^{2-} .

From the point of view of analytical separations, extraction by tributyl phosphate from hydrochloric acid solutions offers a number of useful possibilities. Results obtained in our laboratory for the percentage extraction of some elements at tracer concentration are illustrated in Fig. 8. [Percentage extraction E is related to the distribution ratio D by the expression $E = 100DR/(1 + DR)$, where R is the ratio of the volume of the organic phase to the volume of the aqueous phase after equilibration.] It can be seen from Fig. 8

* In the application of equation (5) values of $[\text{TBP}]_o$ have been computed from the relationship

$$[\text{TBP}]_o = (1000\bar{d}_o - 36.5[\text{HCl}]_o - 18.0[\text{H}_2\text{O}]_o)/266.3,$$

where \bar{d}_o is the density of the organic layer after equilibration.

¹⁵ Horne, Holm, and Meyers, *J. Phys. Chem.*, 1957, **61**, 1655.

¹⁶ Schindewolf, *Z. Electrochem.*, 1958, **62**, 335.

¹⁷ Marcus and Coryell, *Bull. Res. Council Israel*, 1959, **A**, **8**, 1.

that Hg^{II} , Zn , Co^{II} , and Mn^{II} may be separated easily from one another. The results of Irving and Edgington,³ Ishimori *et al.*,⁴ and Gal and Ruvarac¹⁸ indicate the possibility of many other separations by extraction with tributyl phosphate from hydrochloric acid solutions.

Extraction from Hydrobromic Acid.—Tables 1 and 2 show that zinc is extracted into tributyl phosphate more readily from aqueous hydrobromic acid than from corresponding solutions of hydrochloric acid.

In Fig. 2(b) the distribution ratio D for partition of zinc between the phosphate and hydrobromic acid is plotted against the acid activity of the aqueous phase $\{\text{HBr}\}_a$, on

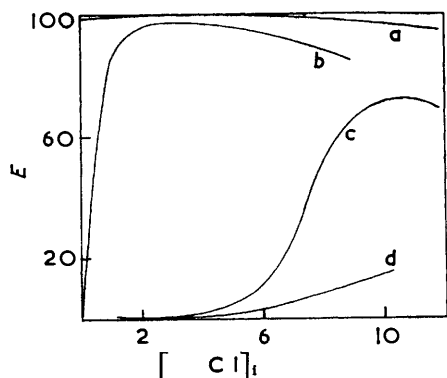


FIG. 8. Extraction of (a) Hg^{II} , (b) Zn^{II} , (c) Co^{II} , and (d) Mn^{II} at tracer concentration from aqueous hydrochloric acid into tributyl phosphate at 20°.

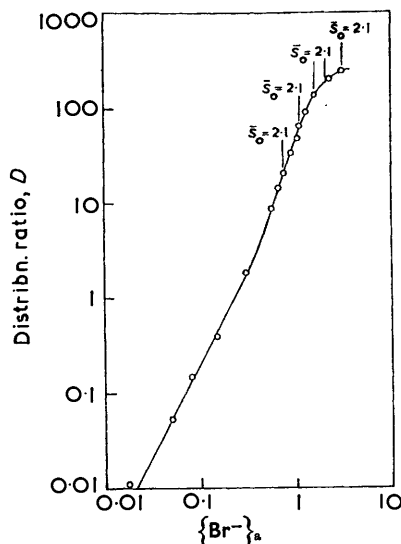


FIG. 9. Distribution of zinc tracer between tributyl phosphate and solutions 0.01M in hydrobromic acid containing sodium bromide. Variation of the distribution ratio with bromide ion activity of the aqueous phase at equilibrium.

logarithmic scales. Values of $\{\text{HBr}\}_a$ have been evaluated by using activity coefficient data from Harned and Owen,¹² Biermann and Yamasaki,¹⁹ and Vinnik *et al.*²⁰ The shapes of the two curves in Fig. 2 are similar, but the maxima occur at higher acid activities in the case of extraction from hydrobromic acid. This is to be expected if the extracted species are of similar formula type in the two systems, as Zn-Br complexes in aqueous solution are generally weaker than corresponding Zn-Cl complexes.¹

Values of \bar{s}_0 , the average number of molecules of tributyl phosphate associated with zinc bromide complexes in the organic phase, are included in Fig. 2(b). These have been obtained from the data in Table 6(a).

From a slope analysis of the curve (b) in Fig. 2, together with the results for \bar{s}_0 , it follows that the distribution of zinc between the phosphate and aqueous hydrobromic acid may be represented by:

$$D = \frac{([\text{ZnBr}_2, 2\text{TBP}]_o + [\text{HZnBr}_3, 3\text{TBP}]_o + [\text{H}_2\text{ZnBr}_4, 2\text{TBP}]_o)}{[\text{Zn}]_a} \quad (7)$$

¹⁸ Gal and Ruvarac, *Bull. Inst. Nuclear Sci., Boris Kidrich*, 1958, **8**, 67.

¹⁹ Biermann and Yamasaki, *J. Amer. Chem. Soc.*, 1955, **77**, 241.

²⁰ Vinnik, Kruglov, and Cherkov, *Zhur. fiz. Khim.*, 1956, **30**, 827.

Raman spectra support this conclusion¹¹ and it appears that the zinc acido-complexes in the organic phase are ion-pairs, $[\text{H,TBP}]^+[\text{ZnBr}_3,2\text{TBP}]^-$ and $[\text{H,TBP}]_2^+[\text{ZnBr}_4]^{2-}$.

Where the bromide system may be taken as behaving essentially ideally, the distribution ratio should be represented by:

$$D = k_2\alpha_2[\text{TBP}]_o^2 + k_{13}K_{13}\alpha_{13}[\text{H}^+]_a[\text{TBP}]_o^3 + k_{24}K_{24}\alpha_4[\text{H}^+]_a^2[\text{TBP}]_o^2, \quad (8)$$

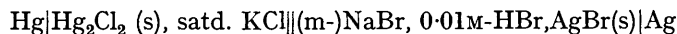
which is analogous to equation (5). In this case, however,

$$\begin{aligned} \alpha_j &= [\text{ZnBr}_j^{2-j}]_a/[\text{Zn}]_a, \\ k_2 &= [\text{ZnBr}_2,2\text{TBP}]_o/[\text{ZnBr}_2]_a[\text{TBP}]_o^2, \\ k_{13} &= [\text{HZnBr}_3,3\text{TBP}]_o/[\text{HZnBr}_3]_a[\text{TBP}]_o^3, \\ K_{13} &= [\text{HZnBr}_3]_a/[\text{H}^+]_a[\text{ZnBr}_3^-]_a, \\ k_{24} &= [\text{H}_2\text{ZnBr}_4,2\text{TBP}]_o/[\text{H}_2\text{ZnBr}_4]_a[\text{TBP}]_o^2, \\ \text{and} \quad K_{24} &= [\text{H}_2\text{ZnBr}_4]_a/[\text{H}^+]_a^2[\text{ZnBr}_4^{2-}]_a. \end{aligned}$$

By using values for α_j calculated from the stability constants of Part I, equation (8) yields values of D corresponding closely with experiment for values of $[\text{HBr}]_a$ from 0.1M to 2M if $k_2 = 1.7$, $k_{13}K_{13} = 12$, and $k_{14}K_{14} = 10$ (Fig. 4).

In Fig. 6 the distribution of zinc tracer between aqueous hydrobromic acid and (a) tributyl phosphate and (b) the anion-exchange resin Dowex-1²¹ is shown. For anion-exchange, $D = (\text{amount of zinc per g. of resin})/(\text{amount of zinc per ml. of solution})$ at 25°. The similarity between extraction by tributyl phosphate and anion-exchange is evident.

Extraction from Solutions containing Sodium Bromide.—A plot with logarithmic scales of D against bromide ion activity $\{\text{Br}^-\}$ is shown in Fig. 9, for distribution of zinc tracer between tributyl phosphate and aqueous solutions 0.01M in hydrogen bromide, containing sodium bromide. Results for D have been taken from Table 4, and values of $\{\text{Br}^-\}_a$ have been obtained from measurements of the E.M.F. of the cell



Results for \bar{s}_o obtained from the data of Table 6(b) are included in Fig. 9.

A comparison of Fig. 9 with Fig. 2(b) shows that at low values of $\{\text{Br}^-\}_a$ the zinc is present in the phosphate layer as the complex $\text{ZnBr}_2,2\text{TBP}$. With increase in $\{\text{Br}^-\}$ other species, such as $\text{Na}^+[\text{ZnBr}_3,2\text{TBP}]^-$, occur in the organic phase.

A Raman spectrum¹¹ of a tributyl phosphate extract from an aqueous solution M in zinc bromide and 4M in sodium bromide shows lines attributed to ZnBr_2 , ZnBr_3^- , and ZnBr_4^{2-} . In this case the organic solution probably contains the species $\text{ZnBr}_2,2\text{TBP}$, $\text{Na}^+[\text{ZnBr}_3,2\text{TBP}]^-$, and $\text{Na}^+_2[\text{ZnBr}_4]^{2-}$.

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²¹ Horne, Holm, and Meyers, *J. Phys. Chem.*, 1957, **61**, 1661.