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Solvent Extraction Systems. I. As(III) and Ge(IV) in Hydrochloric Acid and As(III) in Hydriodic Acid with Several Solvents[1]

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The extraction of As(III) and Ge(IV) from hydrochloric acid solutions by several solvents has been measured. The distribution ratios generally increase in a regular manner as the acid concentration is varied from 2 to 12 *F*. Differences in extractive power between the solvents carbon tetrachloride, chloroform, bis-(2-chloroethyl) ether and benzene are relatively small. Isopropyl ether shows a maximum in extraction between 7 and 8 *F* hydrochloric acid for As(III) accompanied by a sharp rise in the solubility of ether in the acid phase as has been observed in the extraction of other elements with this ether. As(III) in hydriodic acid shows a similar maximum with the solvents used but without the increased phase miscibility. This maximum appears to be related to a change in the nature of the aqueous phase species since the maximum corresponds to a minimum in the solubility of AsI_3 in hydriodic acid.

The solvent extraction method is potentially very useful for selective separations of various metals in aqueous solution. The method offers a particular advantage for isolating elements present in minute amounts since in uncomplicated cases the distribution of a species between two immiscible phases follows the Nernst distribution law and is independent of the concentration of the species extracted.

Analytical applications of extraction methods applied to inorganic ions have been reviewed by Irving.[2] Studies on the variation of extraction in halide systems as a function of metal concentration, acid concentration and solvent have been reported by Irving and Rossotti[3] for In(III)–HBr and by Nelidow and Diamond[4] for Mo(VI)–HCl and HBr.

Extraction of As(III), As(V) and Ge(IV) from 6 *N* hydrochloric acid by diethyl ether has been reported by Mylius and Hüttner[5] and by Swift.[6] Beamish, *et al.*,[7] report distribution ratios for Ge(IV) in the $HCl(aq)–CCl_4$ system but with very poor agreement with the data reported here. Prestwood has devised a separation of As(III) and Ge(IV) based on their extraction from hydriodic acid with chloroform.[8] Using the data obtained in this work, Green and Kafalas[9] devised a method of obtaining carrier-free arsenic from germanium. This paper reports the variation of the distribution ratio ($D_A = \Sigma[A]_{organic}/\Sigma[A]_{aqueous}$) with acid concentration for some As(III) and Ge(IV) halides using several solvents. Measurements of *D vs.* metal concentration show no variation over a concentration range of $\sim 10^6$.

Experimental

Radiotracer Preparation.—Radiochemical tracer techniques were used to determine the arsenic and germanium concentrations in both aqueous and organic phases. All samples were measured by γ-ray counting with a well-type NaI(Tl) scintillation counter.

As^{74} (17.5 day) tracer was prepared by bombarding metallic germanium with 15 Mev. deuterons. The reactions involved are $Ge^{73}(d,n)As^{74}$ and $Ge^{74}(d,2n)As^{74}$. Other radioisotopes of arsenic are formed simultaneously by similar reactions on the other isotopes of germanium. These products are either relatively short-lived or have radiations not detected with the counting arrangement used. The germanium target was burned in chlorine in a closed system, 10 ml. of 6 *F* HCl was added along with 0.5 ml. of 30% H_2O_2, and the $GeCl_4$ removed by distillation. The peroxide serves to keep the As(V) in the aqueous phase as H_3AsO_4. Following the distillation of $GeCl_4$, 1 ml. of 5 *F* HBr and 5 ml. of 6 *F* HCl were added and the carrier-free $AsCl_3$ distilled. The high purity germanium target contained less than 10^{-8} g. As^{75}/g. Ge.

Ge^{69} (40 hour) tracer was prepared by a deuteron bombardment of the gallium salt of 8-hydroxyquinoline. The reaction is $Ga^{69}(d,2n)Ge^{69}$. Ge^{71} which is formed at the same time was not detected in the counting arrangement used. Separation of carrier-free germanium from the gallium was effected by distillation of $GeCl_4$ from a 6 *F* HCl solution of the target material.

Other Reagents.—A stock solution of As(III) was prepared by dissolving a weighed amount of reagent grade arsenic trioxide in 12 *F* HCl or 6 *F* HI and diluted as needed. The Ge(IV) stock solution was prepared by dissolving germanium tetrachloride in 6 *F* HCl and analyzing for germanium.

Reagent grade hydrochloric acid was diluted and titrated against sodium carbonate.

Hydriodic acid was prepared by the reduction of iodine by hydrogen sulfide and also by treating reagent grade acid with mercury to remove free iodine. The spontaneous decomposition of hydriodic acid caused a continuous change of titer but contamination of the acid with free iodine was prevented by storing the acid over mercury.

The bis-(2-chloroethyl) ether was a commercial grade purified by treatment with concentrated sulfuric acid, washing with sodium carbonate solution, drying with anhydrous sodium carbonate, and finally passing the ether through a 50-cm. column of activated alumina.

The other solvents were reagent grade and used without further purification.

Procedure.—Ten ml. of an aqueous phase containing the desired concentration of acid and metal were added to a small separatory funnel. Less than 0.1 ml. of the tracer solution with an activity of approximately 10^4 c./sec. was added. Ten ml. of solvent was added and separatory funnel shaken vigorously for several seconds after which it was placed on a rotating drum in a water-bath at 30° for 30 minutes or longer. Tests showed that distribution equilibrium was reached in less than 2 minutes. After equilibrating the phases the funnels were allowed to stand quietly in the bath until phase separation occurred. The lower phase was run into a small flask and 5-ml. aliquots of each phase were pipetted into small screw cap vials for activity measurements.

Since interchange between radiotracer and carrier should be rapid under all conditions of these experiments, the

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[2] H. M. Irving, *Quart. Rev.*, **V**, 200 (1951).

[3] H. M. Irving and F. J. C. Rossotti in a series of five papers, *J. Chem. Soc.*, 1906 (1955).

[4] I. Nelidow and R. M. Diamond, *J. Phys. Chem.*, **59**, 710 (1955).

[5] F. Mylius and C. Hüttner, *Ber.*, **44**, 1315 (1911).

[6] E. H. Swift, THIS JOURNAL, **46**, 2375 (1924).

[7] H. Newcombe, W. A. E. McBryde, J. Bartlett and F. E. Beamish, *Anal. Chem.*, **23**, 1023 (1951).

[8] R. J. Prestwood, A.E.C.-LA-1721 (December 1954).

[9] M. Green and J. A. Kafalas, *J. Chem. Phys.*, **22**, 760 (1954).

measured activity was directly proportional to the amount of tagged element present. Distribution ratios are calculated directly from counting data. Tests showed that differences in self-absorption of γ-rays were negligible in the samples compared. In some measurements, a material balance provided a check of technique. An estimated overall accuracy of 10% was achieved in the extraction experiments.

Radioactive arsenic triiodide was synthesized using Bailar's procedure.[10] Samples of this preparation were agitated with various concentrations of hydriodic acid in the water-bath and then allowed to settle. Five-ml. aliquots were withdrawn and their activity compared to a weighed sample of the radioactive arsenic triiodide dissolved in 5 ml. of hydrochloric acid.

Changes in phase volume were measured after shaking equal volumes of hydrochloric acid and solvent in a 50-ml. buret at room temperature.

Results and Discussion

D vs. [**M**].—The distribution ratio was found to be independent of the concentration of Ge(IV) and As(III) in all of the systems tested. For Ge(IV), extractions were made with bis-(2-chloroethyl) ether from 6.2 and 12 *F* HCl and with carbon tetrachloride from 6.0 *F* HCl. These extractions were made at several initial concentrations of Ge(IV) covering the range 10^{-2} *F* to C.F. (carrier free, $\sim 10^{-8}$ *F*). Extractions of As(III) were made at 10^{-1} *F*, 10^{-4} *F* and C.F. from 11.9 *F* HCl with bis-(2-chloroethyl) ether, carbon tetrachloride, chloroform and benzene and from 8.3 *F* HCl with isopropyl ether. From 2.2 *F* HI As(III) was extracted at 10^{-3} *F*, 10^{-5} *F*, 10^{-6} *F* and C.F. into carbon tetrachloride.

D vs. [**HCl**].—As(III) and Ge(IV) are qualitatively similar in their extractive behavior from HCl solutions and follow the pattern of other chlorides extracted into solvents which are essentially immiscible with HCl solutions. The extraction increases with HCl concentration and the curves tend to flatten out above 10 *F* HCl. Ge(IV) with isopropyl ether shows a maximum at about 7.5 *F* HCl which is related to the increased solubility of the ether in the aqueous phase at high acid concentrations (see Table I). This behavior has been described before.[11]

TABLE I

RATIO OF VOLUME OF ORGANIC PHASE TO VOLUME OF AQUEOUS PHASE FOR SEVERAL SOLVENTS EQUILIBRATED WITH HYDROCHLORIC ACID

Hydrochloric acid (form. wt./l.)	0.0	2.1	4.1	6.2	8.3	10.2	12.1
Bis-(2-chloroethyl) ether	0.98			0.98	0.98	0.97	0.96
Isopropyl ether		0.98	0.97	0.93	0.80	0.29	∞

At 0.0 and 12.1 *F* HCl, CCl_4 = 1.04, $CHCl_3$ = 1.00, C_6H_6 = 1.00

The mutual solubility of the same solvents (except isopropyl ether, not tested) was slightly greater with hydriodic acid. However, except for bis-(2-chloroethyl) ether (0.87 at 8.8 *F* HI) the differences were negligible. Quantitative comparisons of As(III) and Ge(IV) show the Ge(IV) to have about 20× larger distribution ratios at high acid concentration. The results of these measurements are summarized in Tables II and III.

TABLE II

DISTRIBUTION RATIO *vs.* HYDROCHLORIC ACID CONCENTRATION FOR As(III) (10^{-4} *F*) IN SEVERAL SOLVENTS AT 30°

Hydrochloric acid (form. wt./l.)	Bis-(2-chloroethyl) ether	Benzene	Chloroform	Carbon tetrachloride	Isopropyl ether
2.2	0.012	0.001	0.001	0.001	0.005
4.2	.017	.006	.010	.003	.078
6.2	.027	.17	.35	.076	.75
8.4	2.9	4.5	3.3	1.59	1.32
10.3	12.5	17.7	6.9	3.7	0.30
11.9	13.0	18.3	7.3	4.1	..

TABLE III

DISTRIBUTION RATIO *vs.* HYDROCHLORIC ACID CONCENTRATION FOR Ge(IV) (C.F.) IN SEVERAL SOLVENTS AT 30°

HCl acid (form. wt./l.)	Bis-(2-chloroethyl) ether	Benzene	Chloroform	Carbon tetrachloride	Tris-(*n*-butyl) phosphate
1.1	0.0015				
2.1	.020	0.0013	0.0010	0.0006	0.13
3.1	.013				
4.2	.034	0.025	.023	0.015	1.3
5.2	.088				
6.3	.63	0.23	.26	0.24	17
7.3	7.0				
8.3	98	64	125	125	120
9.4	237				
10.3	330	292	583	597	152
11.3	298				
12.1	309	434	630	594	221

The outstanding difference in the extractability of these two chlorides when compared with the chlorides of Fe(III) and Ga(III) is their relative indifference to the solvent used. Trivalent iron, and gallium, extract from HCl solution with oxygen containing solvents such as ethers, esters or ketones[12] and not with benzene, chloroform or carbon tetrachloride. It is known that for these elements the species extracted approximates the formula $HMCl_4$[13] and the extraction presumably involves hydrogen bonding with the oxygen of the extractant. Since As(III) and Ge(IV) show no pronounced differences in extractability with solvents of greatly differing basic and polar properties, there is an implication that the species extracted is not a complex halo-acid.

Attempts were made to characterize the species extracted by analyzing the organic phase for arsenic or germanium and chloride. After correcting for the free HCl extracted, the values of the Cl/M ratio were always low in both cases. The arsenic values ranged from 2.7 to 2.9, and the germanium values from 3.0 to 3.9. This evidence also tends to rule out a complex chloro-acid as the species extracted and may indicate that a partially hydrolyzed species such as an oxychloride is involved, with the major species extracted being the neutral molecules $AsCl_3$ and $GeCl_4$.

A material balance on extractions of Ge(IV) showed an increasing loss of Ge(IV) with increasing HCl concentration above 6 *F*. Qualitative measurements demonstrated the presence of germa-

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(10) J. C. Bailar, Jr., "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 103.

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

(12) B. Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 175 (1947).

(13) J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

nium in the vapor phase in the separatory funnels thus accounting for the losses. Since the distribution ratio is independent of Ge(IV) concentration, this vapor phase loss has no effect on the observed values of the distribution ratios. An attempt was made to study the extraction of As(V) from HCl solutions. However, above HCl concentrations of about 4 *F* and at high arsenic concentrations[14] chlorine was evolved with the reduction of As(V) to As(III), so these experiments were not continued. The distribution ratio for As(V) tracer from 11 *F* HCl (with a small amount of HNO_3) into benzene has been reported as $\leqslant$ 0.003.[9]

D vs. [HI].—The extraction of As(III) from HI solutions is a much more sensitive function of acid concentration than from HCl solutions. The extraction curves rise steeply between 2 and 3 *F* HI, go through maxima at about 3.3 *F* HI and then decrease up to 6.6 *F* HI as is shown in Fig. 1. The decrease in distribution ratio was unexpected. There was no large increase in solubility of solvent in the aqueous phase which produces a similar maximum in isopropyl ether–HCl systems.

Iodine-free solutions of concentrated hydriodic acid cannot be maintained because of spontaneous decomposition and air oxidation. Extractions were carried out with freshly prepared solutions and solutions which were 0.05 *F* in iodine. The presence of free iodine did not measurably affect the distribution ratio. Iodine titrations showed that none of the solutions exceeded 0.05 *F* so the presence of iodine in varying amounts should not have any effect on the distribution data reported.

Solubility measurements of AsI_3 in HI solutions show a minimum at the same HI concentration as the maximum in the extraction curves. In these solubility determinations no effort was made to characterize the solid phase in equilibrium with the acid. At low HI concentrations (<2 *F*) hydrolysis was evident from the change in color of the solid but above that concentration of acid the solid did not change visibly upon equilibration with the acid. Equilibrium was approached from both sides. Figure 1 gives the data on solubility.

The maximum in the extraction curve and the minimum in the solubility curve for arsenic at the same concentrations of hydriodic acid are undoubtedly related. However, our lack of knowledge of the species existing in these concentrated acid solutions make it difficult to formulate a consistent explanation. The formation of a complex iodoarsenious acid which might explain the solubility minimum is contra-indicated by the lack of differentiation between the ethers and the other solvents. With other HMX_4 species the differentiation is very marked.

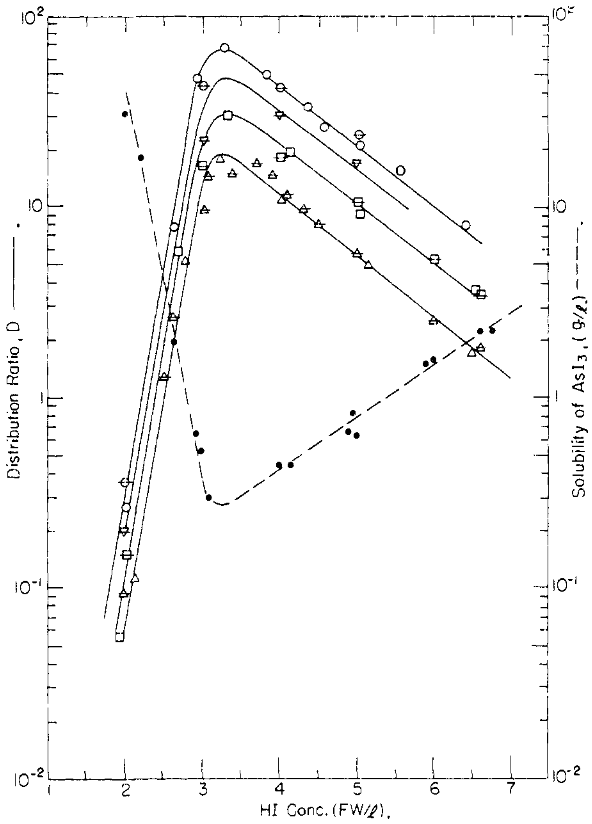

Fig. 1.—Distribution ratios of As(III) for HI and several solvents and the solubility of AsI_3 in HI at 30.0°. Open points O,□,Δ, 8.6×10^{-6} *F* initial As(III) concentration; barred points, ⊖, ⊽, ⊟, ⍙, 10^{-3} *F* initial As(III) concentration; O, benzene; ∇, bis-(2-chloroethyl) ether; □, chloroform, Δ, carbon tetrachloride.

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[14] J. A. N. Friend, *J. Chem. Soc.*, **87**, 1373 (1905).