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Anion-exchange Studies. XVIII. Germanium and Arsenic in HCl Solutions[1,2]

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The anion-exchange behavior of Ge(IV), As(III) and As(V) in hydrochloric acid solutions was studied with a strong base quaternary amine anion-exchange resin. Both Ge(IV) and As(III) show little adsorption at low *M* HCl and rapidly increasing adsorption with increasing *M* HCl above *ca.* 5 *M* HCl. Adsorption of As(V) was low throughout the HCl concentration range studied (0.1 to 12 *M*). Application of these data to separations is discussed.

It was demonstrated in previous papers that anion exchange is a powerful tool for the separation of many elements. A systematic study of essentially all metals has been carried out in hydrochloric acid solutions and the present paper summarizes the results for Ge(IV), As(III) and As(V). Distribution coefficients *D* have been measured in the range 0.1 to 12 *M* HCl. Considerable differences in adsorbability were found which may be used as the basis of a number of separations.

Experimental

Adsorbabilities were measured by the equilibrium or column techniques.[3] In the equilibrium technique measured amounts of solution and resin were agitated for at least one day, after which the solution phase was analyzed. From the change in concentration after equilibration, distribution coefficients *D* (amount per kg. dry resin/amount per liter solution) were calculated. All resin weights and distribution coefficients refer to resin dried over "Anhydrone" at 60° in a vacuum desiccator. The resin was from the same batch of relatively highly cross-linked polystyrene divinylbenzene quaternary amine resin (Dowex-1, 200–230 mesh) which was used in most of the earlier studies and which was characterized previously.[4]

Most concentrations were determined radiometrically with the tracers Ge^{77} ($T_{1/2}$ = 12 hr.); As^{77} ($T_{1/2}$ = 40 hr.) and the mixed tracer As^{73}–As^{74} ($T_{1/2}$ = 76 day and $T_{1/2}$ = 19 day). The Ge^{77}–As^{77} tracer was prepared by neutron irradiation of GeO_2 in the ORNL Low Intensity Training Reactor (LITR). Aliquots of a stock solution, prepared by dissolving the irradiated oxide in 0.5 *M* NaOH, were used after appropriate acidification. Half-life determinations indicated that the tracer was of satisfactory purity. All final counting in the Ge(IV) equilibration experiments was carried out after secular equilibrium with the daughter activity As^{77} had been reached. Since Ge(IV) is easily volatilized from strong HCl solutions, both the resin and solution phases were counted to ensure that no serious loss of Ge(IV) had occurred during sampling. For this purpose the shaking experiments were carried out in 2-ml. tubes. Samples of the solution (1 ml.) were counted, as well as the remaining liquid–resin mixture. The fraction of germanium in the resin could then be computed and "material balance" checked. No experiments are recorded where loss exceeded 20% of the activity.

The As^{73}–As^{74} tracer in HCl solution was obtained from the Radioisotopes Division of ORNL and analyzed by them for radiochemical purity. It contained 20% As^{74}, 80% As^{73} and negligible amounts of other activities.

The adsorbabilities of As(III) and As(V) were determined by the column method. In this method elution bands characteristic of only one oxidation state can be followed and errors from possible oxidation–reduction reactions and resulting cross-contamination by the various oxidation states can be avoided. The method is thus more reliable than the equilibrium method which in the absence of separate oxidation state analyses yields only average adsorbabilities.

Most experiments with As(III) were carried out with properly acidified aliquots of a stock solution prepared by dissolving C.P. As_2O_3 in 0.5 *M* NaOH. The elution maxima were located by spot testing successive aliquots of the effluent ($SnCl_2$ method[5]). The experiments with As(V) were carried out with the arsenic tracer. It originally contained both As(III) and As(V). To prepare essentially pure As(V) solutions the tracer was oxidized with chlorine and to avoid possible reduction, particularly at high hydrochloric acid concentrations,[6] chlorine was added to all the solutions as a "holding oxidant."

All experiments were carried out in an air-conditioned room at 25 ± 2°. Further experimental details will be given in connection with the discussion of the various systems.

Results and Discussion

1. Adsorbability of Ge(IV), As(III) and As(V).—The observed distribution coefficients *D* (amount per kg. dry resin/amount per liter of solution) are summarized in Fig. 1. The adsorbability of Ge(IV) is essentially negligible from 0.1 to *ca.* 4 *M* HCl and then rises sharply with increasing *M* HCl to *D* = 185 in 10 *M* HCl. There is indication that *D* continues to increase at higher HCl concentrations. However, the high volatility of Ge(IV) under these conditions precludes accurate measurements. The adsorbability of As(III) is essentially negligible in the region 0.1 to *ca.* 4 *M* HCl. There is indication that at lower HCl concentrations its adsorbability rises with decreasing *M* HCl, possibly due to adsorption of arsenite ions. At HCl concentrations larger than 4 *M*, adsorbability of As(III) increases with increasing *M* HCl (*D* = *ca.* 26 in 11 *M* HCl). The adsorbability of As(V) is low throughout the entire range of HCl concentrations studied. Distribution coefficients increase slightly with *M* HCl from *D* = *ca.* 1.8 in 0.1 *M* HCl to *D* = *ca.* 4 near 10 *M* HCl.

The strong adsorption of Ge(IV) and As(III) at high hydrochloric acid concentrations suggests that both elements form negatively charged complexes. In the case of Ge(IV) these negatively charged complexes are apparently not yet completely formed in 10 *M* HCl since adsorption appears to continue to increase with increasing *M* HCl in this region. For As(III), on the other hand, above 10 *M* HCl negatively charged complexes may become dominant since the distribution coefficients tend to level off. Qualitatively the adsorption behavior of As(III) and Ge(IV) is essentially in agreement with the known continued increase in the volatilities of both Ge(IV) and As(III) with *M* HCl, and one might further conclude by combination of the observations on volatility and anion exchange that formation of the negatively charged complexes for

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous communication: F. Nelson and K. A. Kraus, THIS JOURNAL, **77**, 3972 (1955).

[3] See *e.g.*, K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

[4] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1457 (1953).

[5] F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., New York, N. Y., 1946.

[6] J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., p. 144.

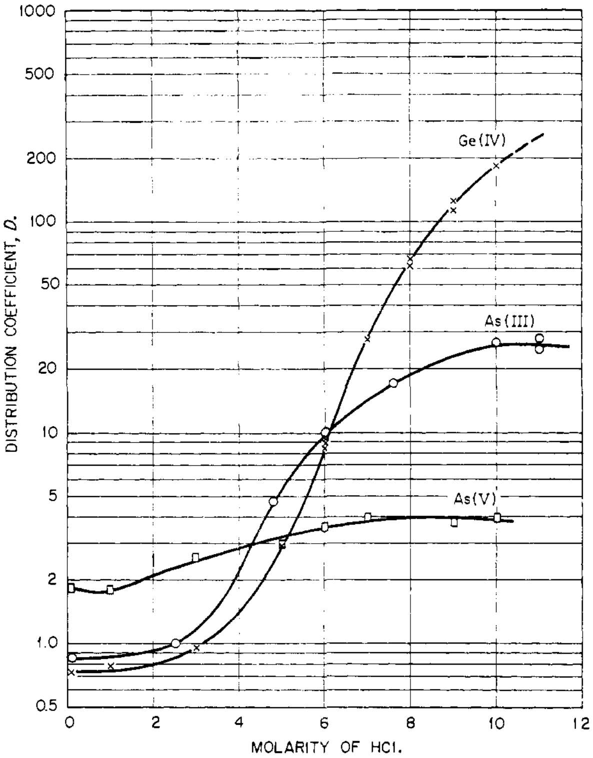

Fig. 1.—Adsorption of Ge(IV), As(III) and As(V).

these elements proceeds through the neutral species ($GeCl_4$ and $AsCl_3$).

It is interesting to note that both Ge(IV) and As(III) are extractable from strong hydrochloric acid solutions by organic solvents,[7] which is in accordance with these considerations, although it is felt that for these elements the fact that solvent extraction occurs cannot be taken as an indication that singly negatively charged complexes are formed.[3] It is likely that in these cases solvent extraction involves the neutral species $GeCl_4$ and $AsCl_3$.

One might be tempted to conclude that the adsorption of As(V), though small, indicates existence of negatively charged complexes. However, this is unlikely in view of the instability of $AsCl_5$ and the apparent non-existence of As(V)-chloride complexes.[8] More probably the slight adsorption is due to extraction of arsenic acid (H_3AsO_4) by the resin. The small increase in adsorption with *M* HCl probably reflects a relatively minor change in the ratio of the activity coefficients of the species H_3AsO_4 in the two phases.

2. Separations Involving Arsenic and Germanium.—The differences in adsorbability between As(III) and Ge(IV) at low HCl concentrations are too small to permit separations with small columns. At high HCl concentrations where the differences between these two elements are considerable, adsorption of As(III) becomes sufficiently large to necessitate inconveniently large volumes for its elution, although separation is feasible. The separation of As(V) from Ge(IV), on the other hand, readily can be achieved at high HCl concentrations. Even at low HCl concentrations, where $D_{As(V)} > D_{Ge(IV)}$, this separation is still feasible. Under these conditions $D_{As(V)}$, though low, is high enough to delay appearance of the As(V) elution band until essentially all the Ge(IV) (or any other "non-adsorbable" element) has been removed.

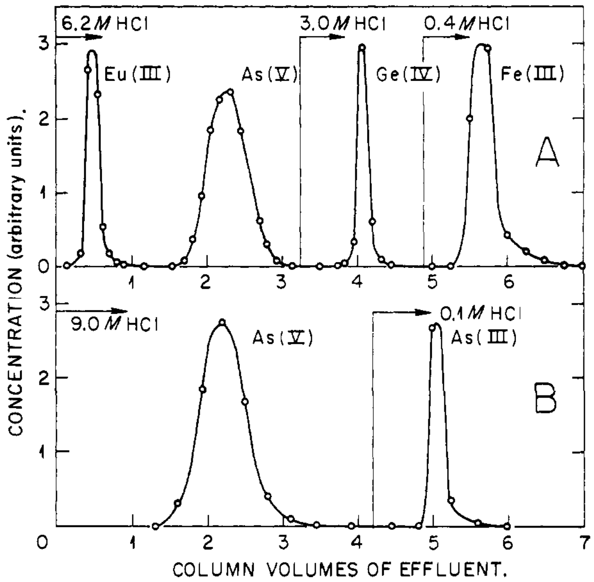

Fig. 2.—Separations involving germanium and arsenic.

A typical separation involving Ge(IV) and As(V) is illustrated in Fig. 2a. For this experiment, Fe(III) was added, as well as a typical non-adsorbable element. For the latter Eu(III) was chosen since its tracer (Eu^{155}) was conveniently available. An 0.5-ml. aliquot of a solution containing Eu(III)^{155}, As(V)^{77}, Ge(IV)^{77}, 0.01 *M* Fe(III), 6 *M* HCl and chlorine was added to an 0.45 cm.^{2} × 9.0 cm. column of resin pretreated with 6.2 *M* HCl and Cl_2. Elution was carried out with 6.2 *M* HCl(Cl_2). The non-adsorbable element, Eu(III), appeared in a sharp band with a maximum near 0.4 column volume and was separated from As(V), Ge(IV) and Fe(III). As(V) appeared in a reasonably sharp band with a maximum near 2.2 column volumes. Ge(IV) was removed with 3 *M* HCl and then Fe(III) with 0.4 *M* HCl.

The differences in the adsorbability of As(III) and As(V), particularly at high *M* HCl, permit separation of these oxidation states, as demonstrated in Fig. 2b. An 0.1-ml. aliquot of a solution containing As(III)$^{73-74}$-As(V)$^{73-74}$ tracer and 9 *M* HCl was added to an 0.24 cm.^{2} × 7.2 cm. column of resin which had been pretreated with 9 *M* HCl. Elution was carried out with 9 *M* HCl. As(V), as expected, appeared in the effluent in a reasonably sharp band near 2.2 column volumes of effluent, while As(III) remained adsorbed. Removal of the As(III) was accomplished with 0.1 *M* HCl.

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(7) (a) K. Rohre, *Z. anal. Chem.*, **65**, 109 (1924), (extractability of $AsCl_3$ by CCl_4 from HCl solutions); (b) H. M. Irving, *Quart. Revs.*, **5**, 200 (1951).

(8) See *e.g.*, (a) Gmelin's "Handbuch der anorganischen Chemie," Eighth Edition, System No. 17, Verlag Chemie, Weinheim, Germany, 1952, p. 391; (b) N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. 1, Clarendon Press, Oxford 1950, p. 791.