tions. The dependence of $G(H_2)$ on a function of the ceric concentration indicates that the presently accepted theoretical yield of cerous ion [$G(Ce^{III}) = 2.34$] may be obtained only in an infinitely dilute ceric solution.

Acknowledgment.—The author gratefully acknowledges the help of the discussions with C. J. Hochanadel, J. W. Boyle and P. S. Rudolph.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Adsorption of Negatively Charged Complexes by Cation Exchangers[1]

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Strong adsorption of some negatively charged complexes by cation-exchange resins is demonstrated. This adsorbability, which is negligible at low ionic strength, increases rapidly with ionic strength, is much greater from salt than from acid solutions and is strongly dependent on the type of the metal complex. With concentrated chloride salt solutions, distribution coefficients larger than 10^5 were found for trace amounts of the anionic complexes (MCl_4^-) of Fe(III), Ga(III) and Au(III). Under these conditions adsorbability of the anionic complexes of Sb(V) and Tl(III) is considerably less and that of the complexes of Mn(II), Co(II), Zn(II), Bi(III) and Sn(IV) is essentially negligible. Use of the adsorption of anionic complexes for separations by cation exchangers is illustrated with several examples.

One usually assumes in the ion-exchange field that cation exchangers adsorb only positively charged ions and anion exchangers only negatively charged ions. These restrictions are tempered by the recognition that, particularly at high ionic strength, substantial electrolyte invasion of the resin may occur and that uncharged species (*e.g.*, organic molecules, bromine, iodine) may be adsorbed; strong adsorption of anions by cation exchangers (or cations by anion exchangers) seems not to have been seriously considered.

Since adsorbability of some negatively charged complexes by anion exchangers is extremely high,[2] the question arose whether part of this high selectivity of the anion exchangers results from interactions of the complexes with the organic network. One might then expect that at least those negatively charged complexes which are very strongly adsorbed by anion exchangers could also be adsorbed by cation-exchange resins. This prediction was verified in a series of adsorption studies with the strongly acidic exchanger Dowex-50. This resin was chosen since it has the same organic network (polystyrene–divinylbenzene) as the Dowex-1 resin used for the earlier anion-exchange studies.

Characteristic features of anion-exchange adsorption of many metal complexes are a rapid rise of adsorbability with increasing salt concentration and a rapid divergence of adsorbabilities between those found in acids and their corresponding salts.[2,3] In the search for adsorption of anions by cation exchangers, media of very high ionic strength were therefore selected and data in acid and salt media compared.

Experimental

Adsorbabilities were determined at room temperature (25 ± 1°) by batch equilibration and column methods. In the equilibration method aliquots of the solutions were shaken for several days with weighed amounts of resin. From analyses of the solution phase before and after equilibration, distribution coefficients D (amount per kg. resin/amount per liter of solution) were computed.

In the determination of large distribution coefficients ($D > 500$), a modified column technique (pre-loaded column method) was used.[4] In this method the material is first adsorbed uniformly on a weighed amount of resin, preferably under conditions where the distribution coefficients are only moderately high. The pre-loaded resin is then transferred to a column, and the solution of interest is passed through the bed. Equilibrium between solution and resin bed normally is rapidly attained, and distribution coefficients may be computed from the known initial concentration of the material in the resin and from analyses of the effluent solutions. One may assume that equilibrium has been reached, when, after a change in eluent, the concentration of the material is the same in successive samples, provided, of course, one operates under conditions where the effluent composition is independent of flow rate. This technique is particularly convenient for comparative measurements at constant loading. When the distribution coefficients are high, a large number of column volumes of solution may be passed through the bed before the composition at its exit end, where final equilibration occurs, has changed significantly.

All analyses were carried out radiometrically. Liquid samples, in small test-tubes, were counted in a well-type scintillation counter (sodium iodide crystal, thallium activated). The following tracers were used: Mn^{54} ($T_{1/2}$ = 300 d.), Co^{60} ($T_{1/2}$ = 5.24 y.), Zn^{65} ($T_{1/2}$ = 245 d.), Ga^{67} 77.9 h.), Sn^{113}–In^{113} ($T_{1/2}$ = 119 d. and 1.74 h.), Sb^{124} ($T_{1/2}$ = 60 d.), Au^{198} ($T_{1/2}$ = 2.7 d.), Tl^{204} ($T_{1/2}$ = 3.5 y.), and Bi^{210} ($T_{1/2}$ = 5 d.).

The tracers, except Ga^{67}, were obtained from and analyzed for purity by the Radioisotopes Division of ORNL. $Gallium^{67}$ was prepared by proton bombardment of zinc and separated from the target material by ether extraction. The purity of the tracer was checked by following its half-life.

A strongly acidic cation exchanger of the polystyrene–

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[1] This paper is based on work done for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. It is based on work summarized in the Chemistry Division Semiannual Progress Report, ORNL 2046, July to December 1955.

[2] See *e.g.*, K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products," Vol. VII, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, United Nations, New York, N. Y., 1956, pp. **113**, 131.

[3] (a) K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlston, THIS JOURNAL, **77**, 1391 (1955); (b) K. A. Kraus, "Ion Exchange," in "Trace Analysis," Symposium at the New York Academy of Medicine, November 1955, edited by J. H. Yoe and H. J. Koch, Jr., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 34. (c) K. A. Kraus and F. Nelson in Symposium on Ion Exchange and Chromatography in Analytical Chemistry (1956), Am. Soc. for Testing Materials, Special Technical Publication No. 195, 1958, p. 27; (d) F. Nelson and K. A. Kraus, THIS JOURNAL, **76**, 5916 (1954); (e) Y. Marcus and F. Nelson *J. Phys. Chem.*, **63**, 440 (1959).

[4] See also ref. 3c, p. 35.

divinylbenzene type (Dowex-50, mesh size 170 to 200) with relatively high cross-linkage (12% DVB) was used. Initially in the hydrogen form, it was purified by treatment with concentrated HCl, 4 *M* HCl and distilled water and air dried. Water content was determined by drying samples of the resin over the dehydrating agent "Anhydrone" at 60° in a vacuum desiccator. All resin weights and distribution coefficients have been converted to this "Anhydrone-dry" basis.

All reagents were C.P. or reagent grade. Concentrated HCl and LiCl "stock" solutions were, in addition, purified by passing them through anion-exchange beds to remove strongly adsorbable impurities.

Results and Discussion

1. **Au(III) in Cl^- Solutions.**—This element was selected for study since it exists even in dilute HCl solutions as negatively charged species. The complex $AuCl_4^-$ is extremely stable, with a reported[5] stability constant $k_{04} = 10^{22}$ for the reaction $Au^{+++} + 4Cl^- \rightarrow AuCl_4^-$. In addition, Bjerrum[6] reported that the first step in the dissociation of the complex, which occurs in dilute HCl solutions, leads to the anion $AuCl_3OH^-$ rather than to neutral or positively charged species. Thus, positive results with this element should unambiguously establish if anionic complexes can be adsorbed by cation exchangers.

Adsorption of Au(III) was studied from HCl, LiCl and a few other chloride solutions (NaCl, KCl, $CaCl_2$). The salt solutions contained *ca.* 0.1 *M* HCl to preclude possible hydrolytic reactions. To avoid errors from reduction of gold, small amounts of chlorine were added to the solutions, and the resin was pretreated with chlorine.

As shown in Fig. 1 Au(III) is adsorbed by Dowex-50 from HCl solutions with distribution coefficients of the order of 100 at high HCl concentrations. Very much higher distribution coefficients were found for LiCl solutions (D = *ca.* 10^5 in 12 molal (*m*)LiCl). Even higher distribution coefficients presumably occur in more concentrated LiCl solutions. These, however, were not established with sufficient precision, since equilibration rates were extremely slow in the most concentrated LiCl solutions and the results tended to be erratic.

The adsorption functions in NaCl, KCl and $CaCl_2$ solutions were very similar to those in LiCl (Fig. 1), demonstrating that the difference in behavior in HCl and LiCl solutions is principally an acid effect. In this respect, the cation exchanger (Dowex-50) behaves similarly to the anion exchanger (Dowex-1), for which adsorbabilities from HCl solutions at high ionic strength are also substantially lower than from LiCl solutions.

For comparison, previously reported[5b,7] anion exchange data of Au(III) in HCl and LiCl solutions are included in Fig. 1. While the divergence of adsorbabilities in acid and salt solutions is similar for the two types of exchangers, the distribution coefficients for the cation exchanger are, throughout, less than for the anion exchanger. This is particularly marked at low ionic strength where adsorption by the cation exchanger tends to zero, while for the anion exchanger it remains very high.

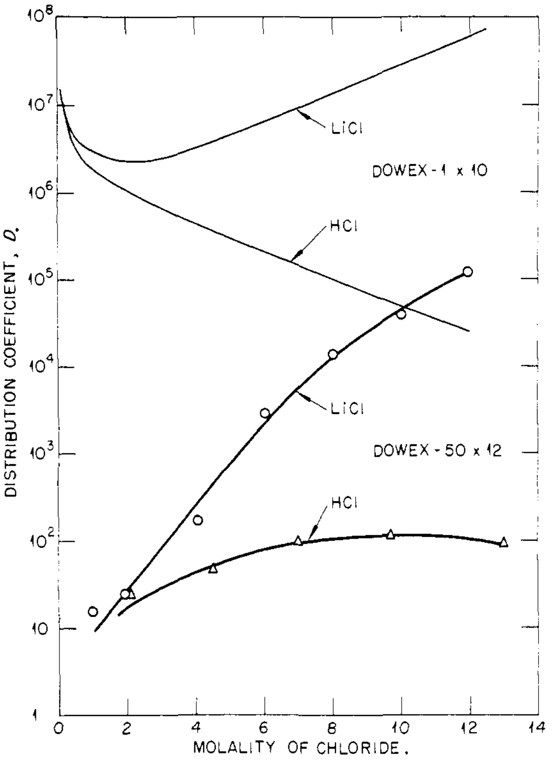

Fig. 1.—Adsorption of Au(III)($AuCl_4^-$) by cation- and anion-exchange resins.

One might wonder if adsorption of Au(III) by Dowex-50, which no doubt involves the anion $AuCl_4^-$, might be due to the presence of a small amount of anion exchanger as an impurity. This explanation, however, seems very unlikely.

The effect was found with various batches of Dowex-50, including the dark- and light-colored preparations. The ratio of adsorbabilities between Dowex-1 and Dowex-50 decreases from *ca.* 10^5 at m_{LiCl} = 2 to 700 at m_{LiCl} = 12; if the "impurities" would adsorb like the quaternary amine resin Dowex-1, this ratio should have remained constant and independent of ionic strength. Adsorbability of Au(III) by Dowex-50 rises with HCl concentration, with Dowex-1 it decreases. Most convincing that we are not dealing with an impurity problem is the observation that substantial loading of Dowex-50 with respect to Au(III) may be achieved. To be sure, the distribution coefficients rapidly decrease with loading, and it is difficult to load Dowex-50 to more than 0.55 mole of Au(III) per kg. of resin. However, for $m_{LiCl} > 12$, distribution coefficients larger than 1000 were observed at a loading of 0.11 mole of Au(III) per kg., and $D > 200$ was found at 0.5 mole of Au(III) per kg. The shape of the adsorption function at high loading is similar to that at low loading.

2. **Fe(III) and Ga(III).**—The adsorption functions of these elements (Fig. 2) have marked minima near m_{Cl} = 4, which should represent the optimum eluting medium for these elements. The rising adsorption branch at low chloride concentra-

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[5] See, *e.g.*, W. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

[6] N. Bjerrum, *Bull. soc. chim. Belg.*, **57**, 432 (1948).

[7] K. A. Kraus and F. Nelson, "Anion Exchange Studies of Metal Complexes," Symposium on the Structure of Electrolytic Solutions (Electro-chemical Society, Spring 1957), John Wiley and Sons, Inc., New York, N. Y., 1959, p. 340.

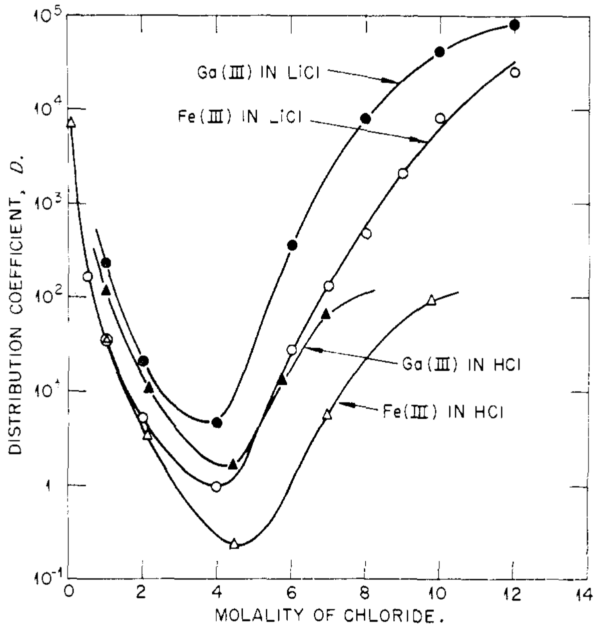


Fig. 2.—Adsorption of Fe(III) and Ga(III) by Dowex-50.

tions is typical for the adsorption of cations by cation exchangers. We would like to attribute the rising branch at high chloride concentration to adsorption of negatively charged complexes. To be sure, adsorption minima for cation exchange equilibria previously have been described[8] for alkali metals, alkaline earths and rare earths in HCl solutions for which formation of negatively charged complexes is highly unlikely.[2] For Fe(III) and Ga(III), however, formation of complexes of the type MCl_4^- seems well established. Further, the distribution coefficients of these elements at high chloride concentration, both in HCl and LiCl solutions, are very similar to those of Au(III) where adsorption of anionic complexes unquestionably occurs. The only difference seems to be that adsorption of Fe(III) and Ga(III) drops off more rapidly with decreasing chloride concentration than that of Au(III). This is not unexpected considering that simultaneously dissociation of the negatively charged complexes of Fe(III) and Ga(III) occurs.

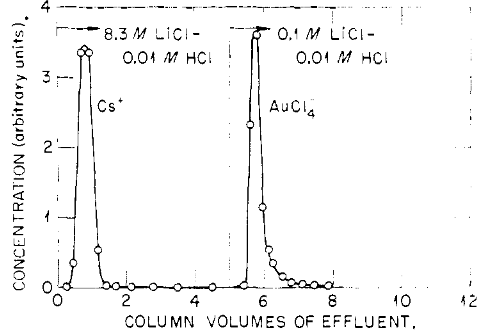
3. **Other Elements.**—The adsorption behavior in concentrated HCl and LiCl solutions of several other elements known to form anionic chloride complexes was examined to establish whether adsorption of negatively charged complexes by cation exchangers is a general phenomenon. Three typical divalent transition elements (Mn(II), Co(II) and Zn(II)) were found to have no significant adsorption from either concentrated HCl or LiCl solutions. These elements are considered to form complexes of the type MCl_4^{--} (and perhaps also MCl_3^-) and on the basis of anion-exchange data[2,7] their average charge becomes negative at different chloride concentrations (Zn(II) near 2 *M* Cl⁻, Co(II) near 9 *M* Cl⁻, Mn(II) in concentrated HCl).

The higher valent elements Bi(III), In(III) and Sn(IV) which are believed to form complexes with charge more negative than −1 also showed no significant adsorption. Antimony(V) ($SbCl_6^-$?) and Tl(III) were slightly adsorbed with $D_{Sb(V)} = 10$, $D_{Tl(III)} = 3$ at $m_{HCl} = 16$ and $D_{Sb(V)} = 10$, $D_{Tl(III)} = 42$ at $m_{LiCl} = 10$.

On the basis of these results, it appears that strong adsorption of negative species by cation exchangers is confined to those complexes which are extremely strongly adsorbed by anion exchangers from concentrated chloride solutions (see chart of adsorption behavior of elements in HCl solutions in ref. 2). Interestingly, the same elements may also be extracted readily by ethers from HCl solutions, although the connection between these two types of extractions is not clear.

4. **Separations.**—The adsorption of complex anions by cation exchangers may be utilized in various separation procedures. A typical case, separation of cesium tracer from Au(III) in acidified LiCl solutions is illustrated in Fig. 3, Part A.

A. SEPARATION OF Cs^+ FROM $AuCl_4^-$.



B. SEPARATION OF Sn(IV) AND In(III) FROM Sb(V).

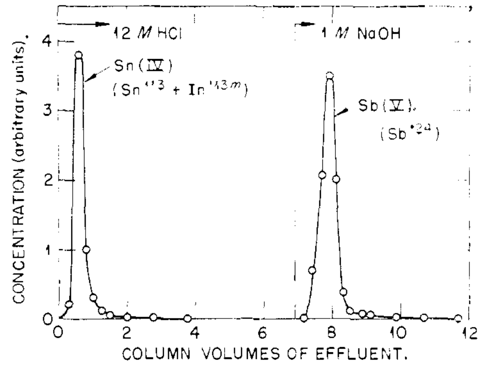


Fig. 3.—Separations with cation-exchange resin (Dowex 50, 12% D.V.B.).

Here Cs⁺ is not significantly adsorbed at high chloride concentrations and hence, paradoxically, in this cation-exchange separation, the cation may be flushed rapidly through the column while the anion is retained. A mixture of Cs and Au tracers in 8.3 *M* LiCl-0.01 *M* HCl was added to a small (0.28 cm.² × 3.5 cm.) column of Dowex-50 × 12 pretreated with the same supporting electrolyte solution. On elution with the slightly acidified LiCl solution, Cs⁺ appeared rapidly in the effluent in a symmetrical narrow band with elution maximum at less than one column volume. Gold(III) was held strongly. It was eluted at low chloride concentrations (0.1 *M* LiCl-0.01 *M* HCl).

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[8] (a) R. M. Diamond, K. Street, Jr., and G. T. Seaborg, This Journal, **76,** 1461 (1954); (b) R. M. Diamond, *ibid.*, **77**, 2978 (1955).

While the elution maximum appeared within less than a column volume after change of conditions, the Au(III) band tailed significantly, presumably a rate effect. Similar separations were carried out in HCl solutions where tailing of the Au(III) band seemed to be slightly greater than in LiCl solutions.

In part B of Fig. 3, separation of Sn(IV) and In(III) from Sb(V) is illustrated. A mixture of Sn(IV), In(III) and Sb(V) in 12 *M* HCl was added to a small column. Sn(IV) and In(III) were eluted within a few column volumes with 12 *M* HCl while Sb(V) remained adsorbed. It was removed with 1 *M* NaOH, presumably as the antimonate ion.

Since Fe(III) is strongly adsorbed by Dowex-50, the technique may be used for separation of traces of iron from various concentrated electrolyte solutions. A similar method previously has been described for anion exchangers.[9] The cation exchange method may be considered an adjunct to the anion exchange method since the supporting electrolyte may be chosen from a different group of metals. In the one case the metals should be nonadsorbable (or weakly adsorbable) by cation exchangers, in the other by anion exchangers.

With cation-exchange technique we have, as an example, separated Fe(III) from 2 *M* $ZnCl_2$ solutions containing excess HCl (Zn(II) is strongly adsorbed by anion exchangers). Unfortunately, if the Fe(III) concentration is substantially larger than 10^{-4} *M*, breakthrough of iron occurs after only a moderate number of column volumes of solution have been passed through, presumably because of the rapid decrease of adsorbabilities with loading. Better retention of Fe(III) would probably occur with less acidic supporting electrolyte solutions, *e.g.*, using LiCl rather than HCl.

The technique is of course also adaptable to the isolation of other adsorbable elements, *e.g.*, to the isolation of Ga(III) from concentrated Zn(II) solutions as one might encounter, for example, in the isolation of Ga^{67} tracer from zinc targets. In all these cases removal of the adsorbed material from the column (regeneration) may be achieved by washing with dilute chloride solutions.

OAK RIDGE, TENNESSEE

[9] K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 5792 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Equivalent and Ionic Conductances for Mixtures of Potassium and Lithium Chlorides in Aqueous Solution at 25°

BY G. S. KELL AND A. R. GORDON

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Conductances for KCl–LiCl mixtures at an ionic strength of 0.01 have been determined by the direct current method. Transference numbers for potassium and chloride ions were obtained by the electrometric method of following boundary movement and for lithium ion by the adjusted indicator technique. The deficit in the equivalent conductance of the mixture as compared with that calculated by the simple additivity rule was less than that predicted by the Onsager and Fuoss theory of the mixture effect, in agreement with other earlier results at higher concentrations. The cation conductances, while not of the highest precision, show a decrease in conductance for the potassium ion and an increase for the lithium in the mixture as compared with their values in binary solution, numerically greater than is predicted by the theory.

In 1911 Bray and Hunt[1] reported that the conductance of a mixture of HCl and NaCl (concentrations C_1 and C_2) was not additive in the contributions of the two electrolytes, *i.e.*, if Λ_1 and Λ_2 were the equivalent conductances of the single electrolytes in solution at the same ionic strength J as obtained in the mixture, the equivalent conductance Λ of the mixture was less than $(C_1\Lambda_1 + C_2\Lambda_2)/J$, where $\Lambda = 1000\kappa/J$, κ is the specific conductance of the mixture, and $J = C_1 + C_2$. Subsequently, Bennewitz, Wagner and Küchler[2] and Longsworth[3] measured transference numbers for HCl–KCl mixtures, the former by the Hittorf method and Longsworth by the moving boundary technique. It appeared that the conductance of the faster cation was decreased, and of the slower cation increased, the common anion being relatively unaffected—the increase (or decrease) being numerically the greater the less the particular ion fraction in the mixture. The net effect on the conductance of the mixture was that it was less than that predicted by the additivity rule in conformity with Bray and Hunt's findings.

In a classic paper,[4] Onsager and Fuoss gave a general treatment of the problem and for the three-ion case obtained a solution in closed form.[5] Their development, however, involves essentially the assumptions underlying the Debye–Onsager Limiting Law for single binary electrolytes, and it was therefore not to be expected at an ionic strength of 0.1 (as obtained in Longsworth's measurements) that more than qualitative agreement with theory could be obtained. Later, Krieger and Kilpatrick[6] studied KCl–LiCl mixtures over a range of ion fractions at varying ionic strengths and also found decreases in conductance in the mixtures as compared with the additivity rule; these were in general less numerically than those predicted by the Onsager–Fuoss theory, although the discrepancy tended to decrease with decreasing ionic strength. Since they made no transference measurements,

[1] W. C. Bray and F. L. Hunt, THIS JOURNAL, **33**, 781 (1911).

[2] K. Bennewitz, C. Wagner and K. Küchler, *Physik. Z.*, **30**, 623 (1929).

[3] I. G. Longsworth, THIS JOURNAL, **52**, 1897 (1930).

[4] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] For the polyion case, see L. Onsager and S. K. Kim, *ibid.*, **61**, 215 (1957).

[6] K. A. Krieger and M. Kilpatrick, THIS JOURNAL, **59**, 1878 (1937).