[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Anion-Exchange Studies. X.[1,2]
Ion Exchange in Concentrated Electrolytes. Gold(III) in Hydrochloric Acid Solutions

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The anion-exchange behavior of Au(III) in hydrochloric acid solutions (0.1–12 *M*) was studied with tracer Au^{198} and a "strong-base" exchanger. Au(III) was found to be strongly adsorbed throughout the experimental range, and the distribution coefficients (amount per kg. resin/amount per liter solution) were found to decrease with increasing *M* HCl. The results are believed representative for the adsorption of the species MCl_4^-. A discussion is given of the thermodynamics of ion exchange in concentrated electrolyte solutions where equivalent exchange does not occur. The activity coefficient ratio $\Gamma_{HAuCl_4} = \gamma^r_{\pm HAuCl_4}/\gamma_{\pm HAuCl_4}$ has been computed as well as the proper activity coefficient quotient Γ for the ion-exchange equilibrium. Both log Γ_{HAuCl_4} and log Γ were found to vary linearly with molality of HCl.

The extent of adsorption of metals by anion-exchange resins may be expressed in terms of the fraction of the metal in the form of adsorbable species (negatively charged complexes) and by the intrinsic adsorbability of these species. This intrinsic adsorbability is probably primarily determined by the type and structure of the ion (or ions), by the charge of the ion, the medium from which adsorption is carried out, and by the resin used. Since most of the work on anion exchange of metal complexes has been carried out in concentrated electrolyte solutions, the effect of the medium on the adsorbability may be large and its evaluation, independent of possible changes in species, appears desirable. Gold(III) seems suited for this purpose since, according to Bjerrum,[3] the species $AuCl_4^-$ is very stable, exists even in relatively dilute HCl solutions, and does not tend to dissociate to $AuCl_3$ or positively charged ions. The assumption that Au(III) exists as the species $AuCl_4^-$ in concentrated HCl solutions, though apparently not proven, appears reasonable, since, *e.g.*, Au(III), like Fe(III) and Ga(III), can be extracted by ethers from relatively concentrated HCl solutions, a property which is probably characteristic for the complex MCl_4^-.[2]

Experimental

The adsorbability of Au(III) was studied by the equilibrium method at 25 ± 1°. Known volumes of solutions containing tracer Au^{198} were shaken for two to three days with known weights of resin. Gold concentrations before and after equilibration were determined by γ-counting with a sodium iodide scintillation counter, and distribution coefficients *D* (amount per kg. resin/amount per liter solution) were calculated from these data.

The tracer was obtained by neutron irradiation of gold in the ORNL graphite reactor. The purity of the tracer appeared satisfactory, since it followed a half life of 2.68 days through 7 half-lives without indications of a long-lived component. This half-life is in good agreement with the values reported in the literature.[4]

The tracer was of sufficiently high specific activity to permit the use of gold concentrations of the order of 3×10^{-8} *M*. These high dilutions in the aqueous phase yielded resin loadings with respect to gold of less than 1% of capacity throughout the experimental range. Considerable initial difficulties in obtaining reproducible distribution coefficients were overcome by addition of a small amount of chlorine to the solutions, suggesting that the lack of reproducibility resulted from reduction of Au(III) by the resin or impurities.

The resin (mesh size −200 +230, wet-screened) was from the same batch of quaternary amine polystyrene divinylbenzene resin (Dowex-1) which was used in the earlier work. It was washed with dilute HCl, concentrated HCl and water, air-dried, and the weight ratio of air-dried resin to that dried in a vacuum desiccator over "Anhydrone" at 60° determined.[2,5] Distribution coefficients were calculated on an "Anhydrone-dry" basis.

Results and Discussion

1. Adsorbability of Au(III), ($AuCl_4^-$).—Gold was found to be extremely strongly adsorbed at all hydrochloric acid concentrations studied (0.1 to 12 *M*), and the distribution coefficients were found to decrease with increasing hydrochloric acid concentration. Figure 1 summarizes the results from 2 to 12 *M* HCl. The data which were obtained at lower HCl concentrations exhibited the same trend. These data showed poor reproducibility, which resulted from the difficulties connected with measuring distribution coefficients larger than 10^6.

At no HCl concentration are the distribution coefficients small enough to permit reasonably rapid elution. On the other hand, the distribution coefficients and the rates of adsorption are sufficiently high to permit batch extraction of gold from chloride solutions. Thus 99.9% of the gold could be extracted in less than 5 minutes from 10 ml. of a 1.4×10^{-3} *M* Au(III)–1.0 *M* HCl solution with *ca.* 100 mg. of resin.

The general decrease in adsorbability with M_{HCl} for Au(III) is qualitatively similar to the results with Tl(III), Pd(II) and Pt(IV).[2] The adsorbability of these elements, however, differs strikingly from that of most other elements studied which, in general, show initially an increase in *D* with M_{HCl} followed, in some cases, by a decrease. Since the fraction of gold as adsorbable species ($AuCl_4^-$) can safely be assumed to be unity throughout the whole experimental range, a decrease in *D* with M_{HCl} appears characteristic for adsorbable species, while increases in *D* with M_{HCl} are probably connected with increases in the fraction of the metal in the form of adsorbable complexes.

2. Adsorption Equilibria in Concentrated Electrolyte Solutions.—When ion-exchange resins are immersed in concentrated electrolyte solutions, a considerable amount of the electrolyte is taken up by the resin.[5] Under these conditions exact equivalent exchange cannot occur, and adsorption of one equivalent of ions by the resin is not accompanied

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

(3) N. Bjerrum, *Bull. soc. chim. Belg.*, **57**, 432 (1948).

(4) Nuclear data, NBS Circular 499 gives $T_{1/2}$ = 2.69 d, Suppl 2: 2.7 d. Suppl 3: 2.73 d, 2.66 d.

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

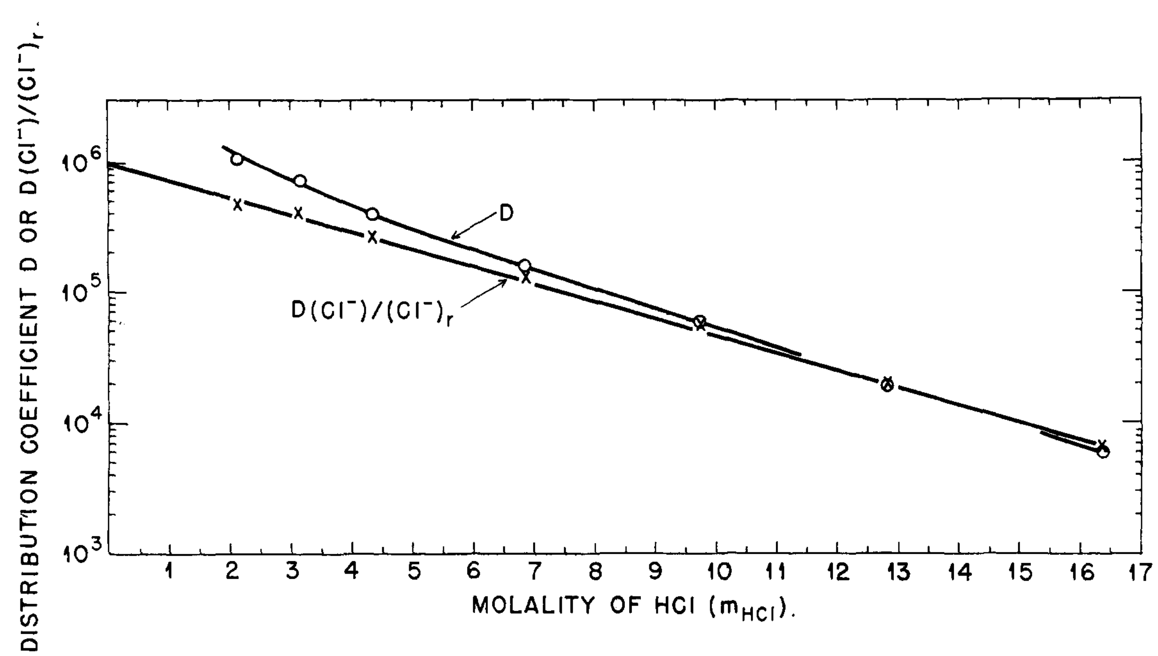

Fig. 1.—Adsorption of Au(III) by a strong base anion-exchange resin.

by the release of one equivalent of ions[6] as implied in the usual ion-exchange equation which, for anion exchange of the ions A^- and B^-, is written as

$$A^- + (B^-)_r \rightleftharpoons (A^-)_r + B^- \qquad (1)$$

Nevertheless, it can readily be shown that even under these conditions mass action constants of the type

$$K = \frac{(A^-)_r(B^-)}{(A^-)(B^-)_r} \times \frac{g^r{}_{A^-}\, g_{B^-}}{g_{A^-}\, g^r{}_{B^-}} = K_m G \qquad (2)$$

are applicable. In equation 2 parentheses and g indicate concentrations and activity coefficients of the species, sub- and superscript r the resin phase, no subscript the aqueous phase, and K_m and G the concentration quotient and the appropriate activity coefficient quotient, respectively.

Equation 2 can be derived from the conditions of equilibrium for the distribution of two components between two phases

$$\mu^r{}_{MA} = \mu_{MA} \text{ and } \mu^r{}_{MB} = \mu_{MB} \qquad (3)$$

where μ is the chemical potential of the component indicated as subscript and where M is the common positive ion of the two components. If the same standard states are assigned to the aqueous and resin phases for each component, equation 3 yields

$$a^r{}_{MA} = a_{MA} \text{ and } a^r{}_{MB} = a_{MB} \qquad (4)$$

where a is the activity. Equations 4 hold independently of each other for any two-phase equilibrium and hence for all equilibria involving ion exchangers whether equivalent exchange is involved or not.

Dividing equations 4 by each other, after raising one of these equations to an arbitrary power p yields $a^r{}_{MA}/(a^r{}_{MB})^p = a_{MA}/(a_{MB})^p$. If a mass action expression is desired in ionic form (as implied by the word "ion exchange") the activities of the common ions must be cancelled, and hence for 1–1 electrolytes setting $p = 1$ becomes a mathematical necessity. This yields

$$\frac{a^r{}_{MA}\, a_{MB}}{a_{MA}\, a^r{}_{MB}} = \frac{m^r{}_{M^+}\, m^r{}_{A^-}\, m_{M^+}\, m_{B^-}}{m_{M^+}\, m_{A^-}\, m^r{}_{M^+}\, m^r{}_{B^-}} \times \frac{(\gamma^r{}_{\pm MA})^2\, \gamma^2{}_{\pm MB}}{\gamma^2{}_{\pm MA}\, (\gamma^r{}_{\pm MB})^2} =$$
$$\frac{m^r{}_{A^-}\, m_{B^-}}{m_{A^-}\, m^r{}_{B^-}} \times \frac{\gamma^r{}_{A^-}\, \gamma_{B^-}}{\gamma_{A^-}\, \gamma^r{}_{B^-}} = 1 \qquad (5)$$

where m and γ are the stoichiometric concentrations and activity coefficients, respectively. Equations 2 and 5 are formally similar since the assignment $K = 1$ is required by the choice of the standard states. They differ, however, in that equation 2 involves concentrations and activity coefficients of species while equation 5 involves stoichiometric concentrations and stoichiometric activity coefficients. While the stoichiometric equation 5 is generally applicable, it is not very revealing. If interpretations are desired, the equation must involve concentrations and activity coefficients of species, *i.e.*, be of the form of equation 2. If the standard free energies to which the activities of the species refer are the same as those used in the computations of the stoichiometric activity coefficients, the relationships

$$m_{M^+}\, m_{A^-}\, \gamma^2{}_{\pm MA} = (M^+)(A^-) g_{M^+}\, g_{A^-}, \text{ etc.} \qquad (6)$$

hold for both phases. To use these relationships, estimates of the activity coefficients of the species must be available. Precedents exist for their estimation for certain aqueous solutions but not for the resin phase.

Activity coefficients of the species can be evaluated, according to equation 6, either by estimating with a non-thermodynamic technique the concentrations of the species M^+ and A^-, as well as the stoichiometric activity, or by finding electrolytes for which one can be reasonably confident that the concentrations of the species are equal to the stoichiometric concentrations and that hence a simi-

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(6) Actually it has been shown in experiments with iron (K. A. Kraus and G. E. Moore, unpublished results) that the hydrochloric acid content of the resin decreases essentially to zero when the resin becomes heavily loaded with respect to $FeCl_4^-$.

lar equality exists for the activity coefficients, *i.e.*

$$m^r_{M^+} = (M^+)_r;\ m^r_{A^-} = (A^-)_r \cdot (\gamma^r_{\pm MA})^2 = g^r_{M^+}\, g^r_{A^-} = (g^r_{\pm MA})^2 \quad (7)$$

Hydrochloric acid, in this sense, probably could be considered essentially completely dissociated in the resin phase. Its activity coefficients in the resin phase, $\gamma^r_{\pm HCl}$ were shown[5] to be approximately equal to those in the aqueous phase. Furthermore, it was found that $d \log \gamma^r_{\pm HCl}/dm^r_{HCl} \cong d \log \gamma_{\pm HCl}/dm_{HCl}$. Since hydrochloric acid in the aqueous phase is usually considered a nearly completely dissociated electrolyte, one might conclude from the similarity of the activity coefficients in the resin and aqueous phases and particularly from the similarity of their derivatives, with respect to concentration, that HCl is also a highly dissociated electrolyte in the resin phase. It should be noted that in this treatment the resin is considered the solvent and that even if essentially complete dissociation of a component MA to M^+ and A^- should occur in the resin phase these ions should be considered solvated. In some cases this interaction of ions with the solvent resin may be considerably larger than their interaction with the solvent water in the aqueous phase causing, for example, the high selectivities which are characteristic for certain complex ions.

In most work with ion-exchange resins the implicit assumption was made that electrolytes in the resin phase are completely dissociated and stoichiometric concentrations and concentrations of species were used interchangeably. Such assumptions, however, do not appear safe, particularly with acids or ions of high charge. For ion exchange in concentrated electrolyte solutions, the concentrations of positive and negative ions in the resin phase are of the same order of magnitude because of the large electrolyte uptake. Under these conditions, association could occur with a resultant decrease in $\gamma^r_\pm$. However, even in dilute electrolyte solutions where the concentrations of positive and negative ions differ widely, possible association could seriously affect the mean stoichiometric activity coefficients of the components in the resin phase.

3. Adsorption Equilibrium of $AuCl_4^-$.—A discussion of the adsorption equilibrium of gold can be made either on the basis of equation 4 or on the basis of equation 5. In general, a decision as to which of these equations should be used for describing selectivity experiments depends largely on convenience. In dilute electrolyte solutions where, for anion exchangers, the concentration of M^+ in the resin phase may be very small, equation 5 may be preferred since it involves the more readily measurable anion concentrations instead of the more difficultly measurable cation concentrations. For concentrated electrolyte solutions where $m^r_{M^+}$ is large and readily measurable, equation 4 appears preferable because of its inherent simplicity and because it yields a simpler activity coefficient ratio. Expanding equation 4 yields

$$m_{M^+}\, m_{A^-}\, \gamma^2_{\pm MA} = m^r_{M^+}\, m^r_{A^-}\, (\gamma^r_{\pm MA})^2 \quad (8)$$

which, combined with the equation for the distribution coefficient

$$D = m^r_{A^-}/m_{A^-} \quad (9)$$

yields

$$D(m^r_{M^+}/m_{M^+}) = \gamma^2_{\pm MA}/(\gamma^r_{\pm MA})^2 \quad (10)$$

Thus, equation 4 yields the activity coefficient ratio $\gamma^r_{\pm MA}/\gamma_{\pm MA}$ while equation 5 would yield initially the activity coefficient ratio $\gamma^r_{\pm MA}\gamma_{\pm MB}/\gamma_{\pm MA}\gamma^r_{\pm MB}$ which would yield $\gamma^r_{\pm MA}/\gamma_{\pm MA}$ only by a circuitous route.

In view of the apparent stability of the ion $AuCl_4^-$, the distributing component will be considered to be $HAuCl_4$. The activity coefficient ratios $\gamma^r_{\pm HAuCl_4}/\gamma_{\pm HAuCl_4}$ were computed by the equation

$$\frac{m^r_{H^+}\, m^r_{AuCl_4^-}}{m_{H^+}\, m_{AuCl_4^-}} = D\,\frac{m^r_{H^+}}{m_{H^+}} = \frac{\gamma^2_{\pm HAuCl_4}}{(\gamma^r_{\pm HAuCl_4})^2} = \frac{1}{\Gamma^2_{HAuCl_4}} \quad (10a)$$

Concentrations were expressed in molalities which for the resin phase are moles per 1000 g. of resin-water. Since the concentration of gold was very small in both phases it was assumed that $m^r_{H^+} = m_{HCl}$, and that $m^r_{H^+}$ is equal to its value for pure HCl solutions.[5]

A plot of $\log \Gamma_{HAuCl_4}$ *vs.* m_{HCl} was found to be strictly linear throughout the experimental range and to follow the equation

$$\log \Gamma_{HAuCl_4} = -3.24 + 0.075 m_{HCl} \quad (11)$$

Equation 11 may be contrasted with the equation for a similar linear plot of $\log \Gamma_{HCl}$ (where $\Gamma_{HCl} = \gamma^r_{\pm HCl}/\gamma_{\pm HCl}$) *vs.* m_{HCl} which, on the basis of the earlier data,[5] was found to be

$$\log \Gamma_{HCl} = -0.26 + 0.01 m_{HCl} \quad (12)$$

As discussed earlier, equation 12 does not apply at very low HCl concentrations. For this reason one also cannot expect equation 11 to hold at very low m_{HCl}. Nevertheless, the empirical extrapolations to $m_{HCl} = 0$ are of interest. The extrapolated value $\Gamma^0_{HAuCl_4}$ was found to be approximately a factor of 1000 smaller than the extrapolated value Γ^0_{HCl}. This large ratio indicates very strong interaction between the component $HAuCl_4$ and the resin phase. One is tempted to consider this interaction to be primarily between the complex ion $AuCl_4^-$ and the quaternary amine group of the anion-exchange resin.

The slopes $d \log \Gamma_{HAuCl_4}/d\, m_{HCl}$ and $d \log \Gamma_{HCl}/d\, m_{HCl}$ are both positive. The slope for gold is considerably larger than for HCl. If the ions H^+ and $AuCl_4^-$ were more associated in the resin phase than in the aqueous phase, a decrease in Γ_{HAuCl_4} with m_{HCl} might have been expected. Hence, assuming $HAuCl_4$ to be essentially completely dissociated to H^+ and $AuCl_4^-$ in the aqueous phase, one might also assume that it is also similarly essentially completely dissociated in the resin phase.

Since the mass-action (exchange) equations 2 and 5 were almost exclusively used in the past to represent ion exchange equilibria, computations according to these equations were also carried out. The units were molality for the aqueous phase and moles/kg. dry resin for the resin phase. Combining equations 5 and 9 yields

$$D(m_{B^-}/m^r_{B^-}) = \gamma^2_{\pm MA}(\gamma^r_{\pm MB})^2/(\gamma^r_{\pm MA})^2\gamma^2_{MB} = \Gamma^2_{MB}/\Gamma^2_{MA} = 1/\Gamma \quad (13)$$

which permits evaluation of the double ratios of the activity coefficients from the observed distribution coefficients and the concentrations of the other ions of the same charge. In the case of gold a plot of log $(D(m_{\text{Cl}^-}/m^{\text{r}}_{\text{Cl}^-}))$ *vs.* m_{HCl} (Fig. 1) yields a straight line, *i.e.*

$$\log (D(m_{\text{Cl}^-}/m^{\text{r}}_{\text{Cl}^-})) = \log 1/\Gamma = a + bm_{\text{HCl}} \quad (14)$$

with $a = 6.0$ and $d \log \Gamma/d\, m_{\text{HCl}} = -b = 0.13$.

Although this treatment is general, since it involves only stoichiometric quantities, the assumption might be made that $HAuCl_4$ and HCl are essentially completely dissociated to H^+, Cl^- and $AuCl_4^-$ in both phases and that dissociation of $AuCl_4^-$ does not occur. If the same standard states are retained, equation 2 can then be written as $K = D((Cl^-)/(Cl^-)_r) = 1/G$. Since G contains the ratio of activity coefficients $(G = G^2_{\text{HAuCl}_4}/G^2_{\text{HCl}})$ of 1–1 electrolytes, the difficulties mentioned earlier regarding extrapolation to $m_{\text{HCl}} = 0$ may not occur and the Debye–Hückel term of the quotient should vanish at low m_{HCl}. Hence, as a good approximation

$$a = \log \frac{1}{G^\circ} = \log \left(\frac{g_{\text{AuCl}_4^-}\, g^{\text{r}}_{\text{Cl}^-}}{g_{\text{Cl}^-}\, g^{\text{r}}_{\text{AuCl}_4^-}}\right)_{m_{\text{HCl}} = 0} = \log \left(\frac{g^{\text{r}}_{\text{Cl}^-}}{g^{\text{r}}_{\text{AuCl}_4^-}}\right)_{m_{\text{HCl}} = 0} = 6.0 \quad (15)$$

where G^0 is the activity coefficient quotient for the distribution equilibrium at $m_{\text{HCl}} = 0$.

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Anion-Exchange Studies. I. Bromide Complexes of Co(II), Cu(II), Zn(II) and Ga(III)*

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The anion-exchange behavior of Zn(II), Cu(II), Ga(III), Co(II) and Ni(II) was studied in hydrobromic acid solutions. On the basis of widely differing adsorbabilities, several separations of these ions from each other in HBr solutions are feasible. With the exception of Ga(III), the anion-exchange behavior of these divalent transition elements in HBr closely parallels their behavior in HCl solutions.

A recent study by Kraus and Moore[1] has demonstrated the feasibility of separating several divalent transition elements from each other by means of an ion-exchange technique. By use of the strongly basic resin Dowex-1, a quaternary amine polystyrene–divinylbenzene resin, they were able to separate Ni(II), Mn(II), Co(II), Cu(II), Fe(III) and Zn(II) by gradually decreasing the hydrochloric acid concentration from 12 to 0.005 *M* in the eluting solution. Kraus and Moore concluded from their study that one species primarily involved in the retention by the resin was the monovalent anion, and that the order of elution from the column with increasingly dilute solutions of HCl could be correlated to the association constant of this complex. The formation of the anion complex can then be expressed as

$$M^{+\nu} + (\nu + 1)X^- = MX^-_{\nu+1} \quad (1)$$

for which

$$K_1 = \frac{(MX^-_{\nu+1})}{(M^{+\nu})(X^-)^{\nu+1}} \quad (2)$$

where M^+ represents the ν-positively charged transition element ion. The adsorption of the anion complex is given by

$$RX + MX^-_{\nu+1} = RMX_{\nu+1} + X^- \quad (3)$$

with

$$K_2 = \frac{(RMX_{\nu+1})(X^-)}{(RX)(MX^-_{\nu+1})} \quad (4)$$

where R represents the organic portion of the polymer, and which is assumed to be inert with respect to the ionic equilibria established in the system.

Ion-exchange techniques, by virtue of their ability to handle carrier-free amounts of material, are ideally suited to separation problems where concentrations of less than 10^{-8} are involved. As part of an extensive study of the separation of carrier-free amounts of cyclotron produced radioactivities, it seemed of interest, on the basis of the work of Kraus and Moore,[1] to determine the behavior of the bromide anion complexes, to see whether significant differences in elution behavior between the bromide and chloride complexes existed, and in particular to check the order of complexing of the transition elements Zn(II), Cu(II), Co(II) and Ni(II), when the complexing anion was the bromide rather than the chloride.

Due to the similarity in the anion-exchange behavior of Ga(III) and Cu(II) in HCl solutions in the presence of Dowex-1, it was also deemed of interest to study the behavior of gallium in hydrobromic acid systems, to see whether or not a separation from copper was more feasible in the latter system than in the former.

Experimental

The anion exchanger used in this study was the strongly basic resin, Dowex-1.[2] This resin, received in the chloride form, was converted to the bromide form, dried at 105° for 4–6 hours, ground in a mortar, and screened through standard (Tyler Mesh) screens. The fraction −150 +200 was slurried with distilled water, and transferred to 7–8 mm. i.d. Pyrex glass columns to make a deep bed 20–30 cm. long. The bottoms of these columns were plugged with a small amount of glass wool, fitted with a stopcock, and connected to a plastic spiral flow cell,[3] housed in a lead shield by means of a standard ball-and-socket joint. The outflow of the

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[1] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1460 (1953).

[2] Marketed by the National Aluminate Corporation under the trade name Nalcite SBR, and generously supplied to us by Dr. J. I. Bregman.

[3] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).