tainly its activity changes as well. In the original mixture of TIBA and $TiCl_4$ there are probably present more than one species of alkyl. Thus it is only by holding the Al/Ti ratio constant that one can obtain a consistent solid surface and soluble fraction and thereby determine the over-all propagation rate. Even though our mechanism predicts a maximum in the rate, we cannot exclude that the changes in the solid surface also play an important role in determining the shape and location of the maximum.

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[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anion-exchange Studies. IV. Nature of the Adsorbed Species in the System Co(II)-HCl[1]

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The spectra of Co(II) solutions in the presence of LiCl, HCl and $HClO_4$ have been re-examined in the region from 325 to 650 mμ. The optical absorbancy data have been correlated with the known adsorption behavior of Co(II) on strong-base (quaternary ammonium) anion-exchange resins, and the principal species adsorbed on the resin is shown to be the neutral complex $CoCl_2 \cdot aq$. The equilibrium constant for the reaction $Co^{++} \cdot aq + 2Cl^- \rightleftarrows CoCl_2 \cdot aq$ is calculated to be $5.3 \times 10^{-2}\ F^{-2}$. These data appear to support the suggestion that at least two distinct anion adsorption processes may occur in transition metal ion retentions.

In the preceding paper[3] of this series, it was suggested that a necessary condition for adsorption of the metal by an anion exchanger is that *an anion complex of single or higher negative charge be formed or be present within the resin,* without implying a concomitant presence of anionic complexes in the aqueous phase. Two processes by which this condition can be met are

$$MA_\nu + RA \rightleftarrows RMA_{\nu+1} \qquad (1)$$

$$MA^-_{\nu+1} + RA \rightleftarrows RMA_{\nu+1} + A^- \qquad (2)$$

where MA_ν represents the ν^{th} complex of the metal ion $M^{+\nu}$ with anion A^- and RA represents the resin in the A^- form. In the case of the systems Ni(II)-HCl and Ni(II)-LiCl, a distinction between these two possibilities could not be made due to the absence of chloro-complexes higher than $NiCl^+$, even in concentrated chloride media. The system Co(II)-HCl offers the possibility of yielding data, on the basis of which a choice can be made between these adsorption processes. The ion-exchange behavior of Co(II) has been investigated with HCl,[4] LiCl[5] and HBr[6] present as additional electrolytes, and the adsorption spectra of Co(II) solutions in chloride media are known to undergo marked changes as the anion concentration increases.[7,8] With a view to correlating the spectral absorbancy of a particular complex with the ion exchange behavior of Co(II) in HCl, the spectra of these solutions have been reexamined in the present investigation.

Experimental

The cobalt chloride salt employed was J. T. Baker A.R. grade containing 0.001% copper, 0.001% iron and 0.06% nickel as the only possibly interfering impurities, and was used without further purification. The $CoCl_2$ stock solutions were made up to a concentration of 4.22×10^{-2} *F*. Reagent grade hydrochloric acid was standardized against Na_2CO_3 within 4 hours prior to use. All titrations were carried out at 25° to a replicate error of less than ±0.4%. J. T. Baker A.R. grade lithium chloride and G. F. Smith perchloric acid were used without further purification. The solutions examined spectrophotometrically were prepared from the Co(II) stock solution and appropriate amounts of hydrochloric acid, perchloric acid or lithium chloride solutions in demineralized water to give a final metal concentration of 3.4×10^{-3} *F*. The final solutions were stored in subdued light until just prior to spectrophotometric analysis.

Spectrophotometric measurements were made in the region from 325 to 650 mμ with a Cary recording double beam spectrophotometer, Model 14M, using as a blank a solution of Co(II) in water at the same concentration as the test solutions.

Results and Discussion

Inasmuch as all of the spectra of the present work were measured against a blank containing Co(aq)$^{++}$ and an equivalent amount of chloride ion, any absorption observed can be ascribed to species other than the hydrated Co(II) ion.

The Co(II) spectrum in 10.7 *F* $HClO_4$ showed an optical absorption identical to that of the blank and no evidence for the existence of species with a hydration number differing from that of Co(II) in water was found, although the absence of such species is not necessarily implied by these data. Three spectra of Co(II) in lithium chloride solution (0.05 *F* in HCl to avoid possible hydrolysis effects) were obtained. At 3.86 *F* LiCl, no absorption peaks were noted, while at concentrations of 7.95 and 10.8 *F* a strong absorption at 624 mμ and very much weaker absorptions at 530 and 350 mμ were observed. The weak absorption at 530 mμ, which is not sensitive to changes in the chloride ion concentration, corresponds to only 2% of the absorption at the 624 mμ peak. For the 7.95 and 10.8 *F* LiCl solutions, the absorption curve at 530 mμ

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[1] This work supported in part by the U. S. Atomic Energy Commission.

[2] To whom correspondence should be addressed.

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is no longer noted as a peak but rather as part of a slow rise in absorbancy toward longer wave lengths. The absorption at 530 mμ noted in the present work is probably identical with the 525 mμ peak reported by Robinson and Brown[9] in their study of $CoCl_2$ in chloride solutions.

The spectra of the Co(II)-HCl solutions showed a single sharp peak at 624 mμ with the additional very weak absorption at 530 mμ noted above. The absorbancies at 624 mμ at various HCl and LiCl concentrations are summarized in Table I, together with the comparable data of the single spectrum obtained in $HClO_4$ solution. The activity data for HCl are calculated from values given by Harned and Owen.[10] Density data for the LiCl solutions are taken from standard tables[11] while the activity data for this salt are those reported by Robinson.[12]

TABLE I

SPECTRAL DATA AT 624 mμ

Soln.	[HCl], *F* wt./l.	$[HCl]\gamma_\pm^{25°}$	log A_{624}, mμ
1	6.010	19.5	0.062
2	6.480	24.0	.133
3	7.212	33.0	.348
4	7.693	40.5	.544
5	8.414	56	.847
6	8.895	67	.987
7	9.376	82	1.092
8	8.856	98	1.153
9	10.34	120	1.193
10	10.82	144	1.210
	[LiCl]	$[LiCl]\gamma_\pm^{25°}$	
12	3.86	5.55	0
13	7.95	39.6	1.127
14	10.83	129	1.266
	$[HClO_4]$	$[HClO_4]\gamma_\pm^{25°}$	
11	10.67	469	0

A plot of log absorbancy *vs.* log $[HCl]\gamma_\pm^{25°}$ is shown in Fig. 1. From this plot it is evident that up to HCl activities of about 60, the optical density is a linear function of $[HCl]\gamma_\pm^{24°}$ thus confirming the results of Kiss and Gerendas.[7] The slope of the plot in Fig. 1 over the linear portion is 1.95 indicating the participation of two chlorine atoms per complex giving rise to the 624 mμ absorption.

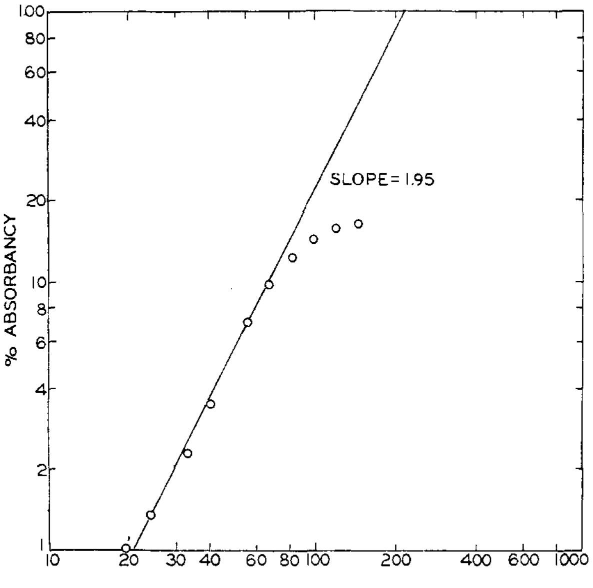

Fig. 1.—Optical density *vs.* HCl activity at 624 mμ for solution of Co(II) in HCl.

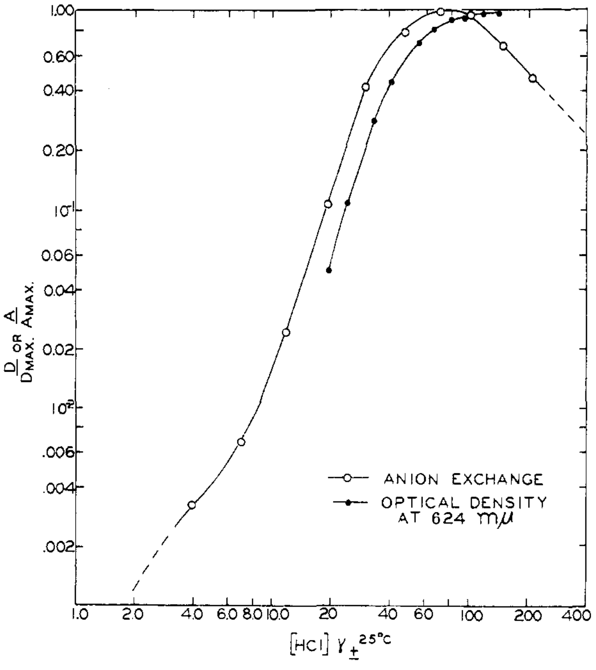

Fig. 2.—Comparison between the normalized anion exchange distribution constant and the normalized optical density at 624 mμ for solutions of Co(II) in HCl.

This result appears to support the conclusions of Moore, Gootman and Yates,[13] Robinson and Brown[9] and of Katzin and Gebert,[8] that the cobalt species responsible for the optical absorption is either $CoCl_2 \cdot 2H_2O$ or $CoCl_2 \cdot 4H_2O$, and that higher cobalt complexes (anionic) are not present in appreciable concentration. Since Robinson and Brown[9] have shown that high concentrations of dehydrating agents such as H_2SO_4 and $LiNO_3$ do not affect the optical absorption in the 624 mμ region, it can be concluded that the deviation from linearity noted in Fig. 1 probably is due to the conversion of essentially all of the cobalt to the neutral hydrated molecule. In Fig. 2, the anion exchange and optical absorption data are compared by normalizing the chemical and optical data at their maximum. The close parallelism of these two curves over a fairly wide range of aqueous hydrochloric acid activity indicates strongly that the species giving rise to the 624 mμ absorption is also the dominant complex responsible for the resin interaction. The displacement of the optical curve to

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the left can be explained qualitatively from the observation of Kraus and Moore[14] that the concentration of HCl in the resin phase is substantially higher than in the aqueous phase (*e.g.*, $m^r_{HCl}/m^a_{HCl} = 1.11$ at 10 *m*). The comparisons of the optical and ion-exchange data do not imply a constancy of the activity coefficient for $CoCl_2 \cdot aq$, although the former is a function of concentration while the latter is a function of activity. Indeed, from the data of ref. 13 it is clear that γ_{CoCl_2} changes markedly as a function of the HCl activity, being 1.8 at 4.84 *F* HCl, 4.45 at 4.97 *F* HCl and 6.55 at 8.86 *F* HCl. However, the activity coefficients in the resin cannot differ markedly from those in the ambient solution, and hence changes in γ_{CoCl_2} as a function of the chloride ion activity cancel almost completely from the pertinent equilibrium expression.

The anion-exchange data of Kraus, *et al.*[4,5] allow a calculation[15] of the magnitude of the equilibrium constant for the formation of the neutral cobalt complex to be made. The distribution constant maximum is 43.1 in 9 *F* HCl, so that for a cobalt concentration of 4.22×10^{-2} *F* the concentrations of $CoCl_2 \cdot aq$ and $Co^{++} \cdot aq$ are 4.12×10^{-2} and 1×10^{-3} *F*, respectively, if it is assumed that the concentration of the intermediate complex is negligibly small. Extrapolation of the activity coefficient data of Moore, *et al.*,[13] gives a value of $\gamma_{\pm}{}^3{}_{CoCl_2}$ in 9 *F* HCl of 6.5. From these values

$$K_{eq} = \frac{(CoCl_2 \cdot aq)}{(Co^{++} \cdot aq)(Cl^-)^2} \cdot \frac{\gamma_{\pm}{}^3 CoCl_2}{\gamma_{\pm Co^{++}} \gamma^2_{\pm HCl}} = 5.3 \times 10^{-2}\ F^{-2}$$

(if $\gamma_{\pm Co^{++}}$ is assumed equal to unity) which is of the same order of magnitude as the values previously reported.[13]

On the basis of the above observations it seems reasonable to conclude that the anion resin absorption of Co(II) is a function of the concentration of the neutral complex in the ambient solution. They further strongly suggest (although equilibrium data are not valid criteria for mechanisms) that resin retention occurs by migration into the exchanger of the neutral complex and the formation of the anionic species at the exchange site in the resin. This is in agreement with the postulate of Fronaeus[16] and of Coryell and Marcus[17] that the anion-exchange maximum (D_{max}) occurs when the average ligand number ($\bar{n}$) equals the oxidation state (γ) of the central metal atom of the adsorbed complex. These conclusions are also similar to those of Neuman and Cook[18] who report correlation of the anion exchange adsorption and optical density for the system Mo^{VI}–HCl, and ascribe the adsorption of molybdenum by anion exchangers as due to invasion by the neutral complex MoO_2Cl_2.

The conclusions reported here are not in agreement with those of Dawson and Chaudet[19] who ascribe the optical absorption at 630 mμ to the complex $CoCl_3^-$.

Our optical density measurements show greater absorption for Co(II) solutions of LiCl than for HCl at equal chloride activities, in contrast to the results of Robinson and Brown,[9] who report a higher concentration of the "blue complex" in HCl than in LiCl (*e.g.*, 60 and 30%, respectively, at 10 *M* chloride ion). However, the optical absorption data of the present work, and our interpretation of these data, are in agreement with the observed[5] greater Dowex-1 adsorption of Co(II) from lithium chloride than for HCl at equal concentrations.

The present results also appear to indicate that anion exchanger adsorption of metal complexes may occur by at least two distinct mechanisms. In the case of Co(II) in chloride media, a neutral species migrates into the resin phase, and forms the requisite anionic complex *in situ*, possibly only near the adsorption site. In other systems, notably Au(III), Bi(III), Hg(II) and Ag(I) in chloride media, in which the presence of high concentrations of well defined anionic species has been demonstrated, it is probable that the species migrating into the resin phase do so as an anionic complex in some form to satisfy the charge neutrality requirements. However, these solutions do not show adsorption maxima,[20] but have high values of *D* at low chloride concentrations, and *D* decreases as the aqueous chloride concentration increases, without going through a maximum. Elements showing intermediate behavior (Pd(II), Pt(IV), etc.) are probably adsorbed by both mechanisms.

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