[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anion-exchange Studies. III. Ni(II) in Aqueous Hydrochloric Acid and Lithium Chloride[1a]

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Ion-exchange studies on the system Ni(II)–HCl–Dowex-1 indicate the absence of anionic species $NiCl_3^-$, $NiCl_4^=$, etc., in the resin phase, and theory suggests the concomitant absence of these species in the aqueous phase. Optical measurements on aqueous solutions of $NiCl_2$ in HCl, $HClO_4$ and LiCl indicate the presence of only Ni^{++} and $NiCl^+$ up to chloride ion concentrations of ~11 M, with no evidence being observed for the presence of $NiCl_2$ in these solutions.

Unlike the other elements of the first transition group, nickel does not share in the general property of adsorption from hydrochloric acid solution by anion exchangers such as Dowex-1. In their systematic survey of the absorption of most of the elements which are expected to form anion complexes, Kraus[2a,b] and his co-workers have shown that Ni(II) is not appreciably absorbed even from 12 M HCl. Similarly Herber and Irvine[3] found negligible adsorption from aqueous HBr up to a concentration of ~7 M.

Two recent investigations have suggested conditions under which the anion-exchange adsorption of a given ion from aqueous solutions may be considerably increased. Kraus,[4] *et al.*, have shown that Mn(II), Sc(III), Fe(III), Co(II), Zn(II), Ga(III) and Au(III) are adsorbed ~200-fold better from 12 M LiCl than from 12 M HCl. Herber and Irvine[5] have reported a general increase in the retention of Mn(II), Zn(II), Co(II) and Cu(II) with an increase in the cross-linkage (DVB content) of Dowex-1. The earlier studies of the adsorption of Ni(II) on Dowex-1 have been extended in the present investigation to take advantage of these conditions for greater metal adsorption of the exchanger.

Experimental

The resin employed in this study was the strongly basic quaternary ammonium anion exchanger, Dowex-1. The resin of 16% nominal DVB content was found[5] to have a water content of 0.281 ± 0.002 g./g. of dry resin; the sample of 24% nominal DVB content was found to have a water content of 0.271 ± 0.010 g./g. of dry resin. These resins, both obtained in +200–400 mesh size, were treated with 12 M HCl and slurried into columns 5–10 cm. long and 0.4–0.7 cm. i.d. which had been provided with a stopcock at the bottom to control the flow of effluent, and plugged with glass wool. The resin bed so formed was subjected to alternate washings with 12 M HCl and deionized water.

Reagent grade concentrated hydrochloric acid was standardized against Na_2CO_3. Fisher Certified Reagent LiCl was used without further purification. Solutions of the salt in deionized water were standardized by titrating the chloride, using the Fajans adsorption indicator method.

As in the previous work[3,5] Na^{22} was used as a reference non-adsorbed cation. 2.6h Ni^{65} was prepared either by the Cu^{65}(d,2p) or the Ni^{64}(d,p) reaction in the MIT cyclotron, and the desired nickel activity isolated by anion-exchange techniques.

In each elution run, the column was pretreated with ~10 column volumes of the elutriant to be used, the nickel activity introduced as a few drops of solution at the top of the column, and elution continued in the standard manner. The volume of eluate passing through the column was determined by photoelectric drop-counting. The eluate flowing at a rate of ~0.03 cc./min. was collected in 4-cc. screw cap vials, which were subsequently radio-assayed using a NaI(Tl) scintillation counter.

Visible spectra of a number of solutions of $NiCl_2$ in HCl, LiCl and $HClO_4$ were taken using a Cary model 11MS Recording Double Beam Spectrophotometer in the range 400 to 750 mμ. Transmission measurements at 425 mμ were made using a Beckman Model DU Spectrophotometer.

Results and Discussion

The elution experiments are most conveniently summarized in terms of the ratio of the volume of reagent necessary to elute the maximum Ni^{65} activity from the column, to the volume required to elute Na^{22} under the same conditions. For the 16% DVB resin this ratio is 1.12 ± 0.07 with 7.75 M LiCl as elutriant and 0.87 ± 0.06 with 12 M HCl as elutriant. The respective values when the 24% DVB resin was employed were 0.49 ± 0.09 and 1.32 ± 0.12. It will be noted that no significant retention of nickel activity is obtained; even in 12 M HCl the maximum nickel activity is eluted within $^1/_3$ column volume of the elution maximum observed for the Na^{22} ion used as a reference non-adsorbed tracer. With the 24% DVB resin and 7.75 M LiCl as elutriant, one notes, indeed, that the nickel passes through the column more readily than the sodium ion employed as a reference non-adsorbed tracer. This effect is probably due to the more pronounced Donnan adsorption of the Na^+ as compared to the nickel under conditions where significant resin invasion occurs.[6]

The interpretation of these data cannot be unambiguously made in the absence of a specific ion exchange–absorption mechanism. Using the symbolism of Bjerrum,[7] it is possible to write,[8] for example, as the main reaction in anion absorption of a metal M of charge $+\nu$ by an exchanger R^+ in the presence of anion A^-

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

with a thermodynamic equilibrium constant

$$K = \frac{(RMA_{\nu+1})}{(MA_\nu)(RA)}\,G \qquad (2)$$

where G is the pertinent activity quotient.

If the assumption is made that only one complex

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[2a] G. E. Moore and K. A. Kraus, THIS JOURNAL, **74**, 843 (1952).

[2b] K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1460 (1953).

(3) R. H. Herber and J. W. Irvine, Jr., *ibid.*, **76**, 987 (1954).

(4) K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlston, *ibid.*, **77**, 1391 (1955).

(5) R. H. Herber and J. W. Irvine, Jr., *ibid.*, **77**, 5840 (1955).

(6) K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1457 (1953).

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

(8) S. Fronaeus, *Svensk Kemisk Tidskr.*, **65**, 1 (1953); C. D. Coryell and Y. Marcus, *Bull. Res. Council Israel*, **4**, 90 (1954).

TABLE I

OPTICAL DENSITY OF 0.033 *M* $NiCl_2$ AT 400 mμ IN HCl, $HClO_4$ AND LiCl SOLUTIONS

HCl, *M*	$d_{400\ m\mu}$	$HClO_4$, *M*	$d_{400\ m\mu}$	LiCl, *M*	$d_{400\ m\mu}$
$1.185^a(1.012)^{b,c}$	0.16	$1.170(0.959)^d$	0.16	$0.775(0.581)^e$	0.165
3.555 (5.70)	.18	3.510(5.93)	.16	2.325(2.33)	.175
5.925(20.10)	.21	5.850(23.40)	.16	3.875(5.43)	.185
8.295 (58.07)	.25	8.190(102.4)	.16	5.425(12.22)	.197
10.665 (117.4)	.25	10.530(~380)	.16	6.975(25.48)	.22

[a] The first figure gives the molarity of the electrolyte. [b] The parenthetical number indicates the electrolyte activity. [c] Calculated from data in Gmelin, *Handbuch anorg. Chem.*, **5**, 165 (1926). [d] Calculated from data in "Landolt Börnstein, Physik. Chem. Tabellen" Erg. Bd. III, 2144 (1936). [e] Calculated from data of R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

of M and A contributes significantly to the absorption by the exchanger, the distribution constant for the partition of the metal M between aqueous phase and resin can be represented by

$$D = \frac{(RMA_{\nu+1})}{\sum\limits_{n=0}^{n=N} \beta_n(M^{+\nu})(A^-)^n} \tag{3}$$

where the denominator represents the sum of the concentrations of all of the metal complexes in the aqueous phase. From (2) and (3) it is then seen that

$$D = \left\{\frac{K(RA)}{G}\right\} \frac{(MA_\nu)}{\sum\limits_{n=0}^{n=N} \beta_n(M^{+\nu})(A^-)^n} \tag{4}$$

and that *D* is a function of the fraction of the metal which is in the form of the ν^{th} complex. If instead of reaction (1), the main process leading to resin adsorption is represented by

$$MA_{\nu-1}^{-} + RA \rightleftarrows RMA_{\nu+1} + A^- \tag{5}$$

a similar derivation leads to the distribution constant

$$D = \left\{\frac{K'(RA)}{(A^-)G'}\right\} \frac{(MA_{\nu+1}^{-})}{\sum\limits_{n=0}^{n=N} \beta_n(M^{+\nu})(A^-)^n} \tag{6}$$

and here, *D* is a function of the fraction of the metal which is present as the $(\nu + 1)$th complex.

The expressions (4) and (6) are related to each other by the stepwise formation constant of the $(\nu + 1)$th complex, $K_{\nu+1}$, *i.e.*

$$\frac{K}{G} = \frac{K'}{G'} K_{\nu+1} \tag{7}$$

From the above it will be seen that the only necessary condition for absorption of a metal by an anion exchanger is that an anion complex of single or higher negative charge be formed *within the resin*, this step being implied in both (1) and (5).

The dissociation of the singly charged anion complex in the two phases can be expressed as

$$(MA_{\nu+1}^{-})^R = K_{\nu+1}^R(MA_\nu)^R(A^-)^R \tag{8}$$

and

$$(MA_{\nu+1}^{-})^W = K_{\nu+1}^W(MA_\nu)^W(A^-)^W \tag{9}$$

where the superscripts R and W refer to the resin and aqueous phase, respectively. Inasmuch as $(A^-)^R > (A^-)^W$, and it is probable[8] that $(MA_\nu)^R$ is approximately the same as $(MA_\nu)^W$, it is reasonable to conclude that equation (9) is shifted to the right, relative to (8), and that the absence of $(MA_{\nu+1}^{-})^R$ implies the concomitant absence of $(MA_{\nu+1})^W$.

Kiss and Csokán[9] have investigated the spectra of Ni(II) in several different electrolytes, and find that $NiCl_2$ in 12.6 *M* has an absorption maximum at 425 mμ, whereas 2.0 *M* $NiCl_2$ in H_2O shows an absorption peak at ~390 mμ. This latter peak is also evident in aqueous solutions of nickel perchlorate[10] and is ascribed to the $Ni(H_2O)_6^{++}$ ion. These results are interpreted by Kiss, *et al.*, as being due to the presence, in concentrated HCl, of $NiCl_4^=$, this ionic species giving rise to the peak at 425 mμ.

In the present work, the spectra of $NiCl_2$ in HCl, $HClO_4$, and LiCl have been determined, using a double beam method with $NiCl_2$ in water as reference liquid, and the optical density at 400 mμ has been summarized in Table I. It will be noted that the optical density of $NiCl_2$ at 400 mμ does not vary with a perchloric acid activity change of ~380-fold. It has been inferred[11] from diffusion and dialysis experiments that Ni(II) has a hydration number greater than 8 in neutral and slightly acid solution. Since the nickel ion is normally 6-coördinated,[12] it may be concluded that at least six solvent molecules are associated with the metal ion which may be represented as $Ni(H_2O)_6^{++}$. Even though the activity of water in these solutions falls to ~0.5 in the more concentrated cases,[13] and a change in the hydration of the nickel ion may reasonably be expected, it is evident from the optical density measurements on the perchloric acid solutions that any such change is apparently not accompanied by a change in $d_{400\ m\mu}$.

The observed change in $d_{400\ m\mu}$ in the HCl and LiCl solutions must then be a result of the formation of $NiCl^+$ or $NiCl_2$ in these solutions, with possibly an additional effect due to the change in the number of molecules of water associated with these two species as the electrolyte activity is increased.

Examination of the spectra of nickel in solutions of high Cl^- concentration showed the presence of an absorption peak at 425 mμ in agreement with earlier work.[9,10] The optical density at 425 mμ of a series of solution 0.163 *f* in $NiCl_2$ was determined using a Beckman Spectrophotometer with $NiCl_2$ in H_2O as solvent blank. The results of this determination are represented in Fig. 1, in which log (% transmission) is plotted *vs.* log (HCl activity). The right-hand portion of this curve is seen to have a

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(9) A. V. Kiss and P. Csokán, *Z. anorg. allgem. Chem.*, **245**, 355 (1941).

(10) A. Kiss and R. Szabo, *ibid.*, **252**, 172 (1943).

(11) H. Spanday, *Z. physik. Chem.*, **192**, 211 (1942); G. Jander and H. Möhr, *ibid.*, **190**, 81 (1942).

(12) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1945, p. 520.

(13) R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

slope of unity, and even at an HCl activity of 365 (10.9 *N*) there is no evidence of a leveling off of % T. Optical density determinations on the same solutions at 400 mμ—the region of an absorption maximum for Ni^{++}—showed a much smaller decrease in % T as a function of concentration, while at 350 mμ the transmission of the solution 10.9 *M* in HCl had decreased only 18.5% with respect to the $NiCl_2$ in H_2O blank. Since log (extinction coefficient) for $NiCl_2$ in H_2O drops from 0.70 at 390 mμ to ~0 at 425 mμ,[9] the change in the contribution by the Ni^{++} ion to the adsorption peak at 425 mμ must be negligible. It is thus concluded that the unity slope of the log % T *vs.* log [HCl] plot at 425 mμ implies that the growth of this peak is dependent on the first power of the chloride ion activity. Since $NiCl_2$ in dilute solutions in the absence of other anions yields only $Ni(H_2O)_6^{++}$, the first order dependence of % T on [HCl] must be a consequence of the formation of $NiCl^+$ from Ni^{++}.

From these data it is concluded that in solutions up to ~11 *N* in HCl, only two nickel species—Ni^{++} and $NiCl^+$—are present in appreciable extent in the aqueous phase, and that no significant concentrations of negatively charged complexes such as $NiCl_3^-$ are formed in the Dowex-1 resin phase under the conditions of the present work.

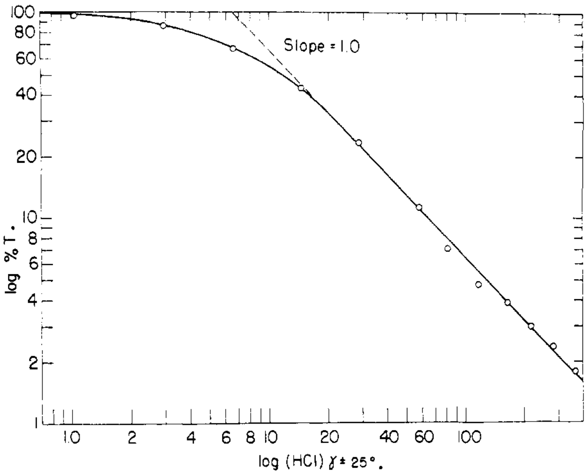

Fig. 1.—Transmission *vs.* HCl activity for Ni(II) at 425 mμ.

At the present time, it is not understood why Ni(II), which behaves as a Lewis acid toward nitrogen (54 ammine complexes are listed by Sidgwick[14]!) and which readily forms anionic cyanide complexes,[15,16] forms no anionic complexes with chloride and bromide ions, in contrast to the behavior of Co(II), Cu(II) and Zn(II). Manganese, the only other divalent element of the first transition period which also shows a small extent of adsorption from concentrated HCl by Dowex-1, is nevertheless sufficiently well held[5] by 16 and 24% DVB resin, that a ready separation from Ni(II) in 12 *M* HCl can be effected.

The authors wish to thank Mr. A. A. Fournier, Jr., for making a part of the optical density determination reported in this work, as well as Professor C. D. Coryell for a number of valuable discussions.

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[14] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1439.

[15] W. F. Pickering, *Anal. Chim. Acta*, **8**, 344 (1953).

[16] Indeed, the cyanide complex is so strong, that Ni(II) activity placed on a 24% DVB Dowex-1 column which had been pretreated with 1 *M* NaCN could not be eluted from the column within 15 column volumes even with 0.2 *M* HCl as the elutriant.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

Reactions of Ethylenimines. VII. Hammett ρ Constants for Ring Opening with Benzoic Acids

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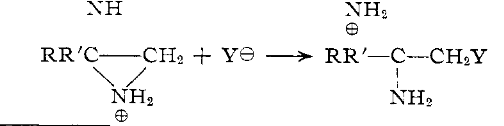
Hammett constants were determined for the ring opening of 2-ethylethylenimine ($\rho = +1.66$) and 2,2-dimethylethylenimine ($\rho = +1.50$) with five substituted benzoic acids in dioxane at 45°. Two alternative rationalizations are proposed to account for these high positive ρ-values.

The Hammett ρ constants for the ring opening of the ethylenimine ring by substituted benzoic acids were determined for 2-ethylethylenimine and 2,2-dimethylethylenimine in an endeavor to throw more light on the reactions of this small ring. Previous work on the ring opening of substituted ethylenimines indicated that the following steps are involved when the attack of a nucleophilic agent occurs at the unsubstituted carbon



(1)

(2)

Meguerian and Clapp[2] suggested that when HY was thiophenol the slow step was probably a proton transfer following hydrogen bridge formation. The results of the present work with substituted benzoic acids can also be interpreted as indicating that the rate-determining step is a proton transfer or dependent on a proton transfer.

The ρ-values found for the reactions of 2-ethylethylenimine and 2,2-dimethylethylenimine with five substituted benzoic acids in dioxane at 45° are $+1.66 \pm 0.17$ and $+1.50 \pm 0.17$, respectively (Fig. 1). The difference between the ρ-values for the two imines is within experimental error. The difference is probably real, however; the ratios of the rates of reaction of the two imines with the benzoic acids do not vary in a random manner but there

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[1] (a) Jesse Metcalf Fellow, 1953–1954; (b) Edwin P. Anthony Fellow, 1952–1954.

[2] G. H. Meguerian and L. B. Clapp, THIS JOURNAL, **73**, 2121 (1951).