Thus divalent platinum is an example of the class of substrates which includes peroxide oxygen, divalent sulfur, monovalent halogen, and to a considerable extent, tetrahedral carbon.[11] These substrates respond chiefly to polarizability in the nucleophile and basicity is of little or no importance. It is expected that other metal complexes in which the metal atom is of low positive charge and surrounded by many *d*-orbital electrons, will fall into the same category.

In summary then, the rate data of Table IV show a nucleophilic series whose order can be interpreted according to well established principles. It seems quite reasonable to say that the values of k_X refer to S_N2 displacement processes, the first well established cases for an octahedral system. Other cationic octahedral complexes of high positive charge for the central atom and with few or no *d* electrons should show similar behavior.

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Ligand Exchange. I. Equilibria

BY F. HELFFERICH

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Sorption of complexing agents from solutions by ion exchangers containing a complexing metal ion as the counter ion ("ligand sorption") and exchange of complexing agents between solutions and such ion exchangers ("ligand exchange") are investigated. Equations for ligand-sorption and ligand-exchange equilibria are derived. The equations can be used for predicting equilibria from tabulated complex stability constants. Experimental results with Amberlite IRC-50 in Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^+ forms and ammonia and 1,3-diaminopropanol-2 as the ligands are in satisfactory agreement with the theory.

Introduction

"Ligand exchange"[1] is a novel application of ion exchangers and provides a useful technique for separating and isolating compounds which can form complexes or adducts with metal ions. An ion exchanger containing a complexing metal ion such as Cu^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Co^{3+}, Fe^{3+}, etc., as the counter ion is used as a solid sorbent. The potential ligands, for example ammonia, amines, polyhydric alcohols, olefins, amino acids, etc., are sorbed from solutions or gases and form complexes with the metal in the ion exchanger ("ligand sorption"), or displace other ligands that have previously complexed the metal ("ligand exchange"). By virtue of the strength and specificity of complex formation, high capacities and selectivities can be achieved. Ligand-exchange capacities and selectivities and their theoretical prediction are the subject of the present study.

Ligand sorption by cation exchangers containing complexing metal ions was observed as early as 1954 by Stokes and Walton.[2] Separations of ligands by virtue of differences in complexing strength occasionally have been achieved by other authors.[3-5] The idea of exploiting chemical interactions for separations by means of ion exchangers has also been applied in various other ways; for example, silica has been removed from water by anion exchange after addition of F^- ions which form $[SiF_6]^{2-}$,[6,7] and carbohydrates and other carbonyl compounds which form adducts with borate or bisulfite anions have been separated with anion exchangers in the borate[8] or bisulfite[9] forms. However, no systematic study of ligand exchange has so far been reported. In particular, the striking effect of the coördinative valences of the ligands[1] has apparently been overlooked in the past.

General Aspects

Ligand exchange resembles ion exchange in that molecular species are exchanged—usually in stoichiometrically equivalent amounts—between the solid ion exchanger and an external solution. The essential difference is that in conventional ion exchange, counter ions are exchanged, whereas in ligand exchange, ligands are exchanged while the counter ion remains in the solid. Typical ligand-sorption and ligand-exchange reactions are, for example (boxes indicate that the respective species is in the ion exchanger).

$$\boxed{Cu(H_2O)_4{}^{2+}} + 4NH_3 \longrightarrow \boxed{Cu(NH_3)_4{}^{2+}} + 4H_2O \quad (1)$$

$$\boxed{Cu(NH_3)_4{}^{2+}} + 2NH_2RNH_2 \longrightarrow \boxed{Cu(NH_2RNH_2)_2{}^{2+}} + 4NH_3 \quad (2)$$

Reaction 1 is sorption of ammonia by a cation exchanger in (aqueous) Cu^{2+} form; alternatively, this reaction can be viewed as a ligand exchange of ammonia for water of hydration. Reaction 2 is a ligand exchange of a (bidentate) diamine for ammonia on a resin in Cu^{2+} form.

Analogous to the ion-exchange capacity (number of fixed ionic groups per unit weight or unit volume of the resin) a "*ligand-exchange capacity*" of

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[1] F. Helfferich, *Nature* (London), **189**, 1001 (1961).

[2] R. H. Stokes and H. F. Walton, *J. Am. Chem. Soc.*, **76**, 3327 (1954).

[3] C. L. Thomas, U. S. Pat. 2,865,970 (1958).

[4] J. Giesen and F. Müller, U. S. Pat. 2,916,525 (1959).

[5] G. P. Cartoni, R. S. Lowrie, C. S. G. Phillips and L. M. Venanzi, in "Gas Chromatography 1960," editor R. P. W. Scott, Butterworths, London, 1960, p. 273.

[6] W. C. Bauman, J. Eichhorn and L. F. Wirth, *Ind. Eng. Chem.*, **39**, 1453 (1947).

[7] R. Wickbold, *Z. anal. Chem.*, **171**, 81 (1959).

[8] J. X. Khym, L. P. Zill and W. E. Cohn, in "Ion Exchangers in Organic and Biochemistry," editors C. Calmon and T. R. E. Kressman, Interscience Publ., New York, N. Y., 1957, p. 392, and earlier work quoted in this review.

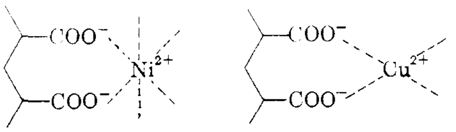
[9] O. Samuelson and E. Sjöström, *Svensk Kem. Tidskr.*, **64**, 305 (1952).

a resin in metal-ion form can be defined as the number of available coördinative sites per unit weight or unit volume of the resin. Since a metal ion with electrochemical valence z_M occupies z_M ionic groups of the resin, the relation between the ligand-exchange and ion-exchange capacities, X_{lig} and X_{ion}, is

$$X_{lig} = \frac{X_{ion} N_M}{z_M} \qquad (3)$$

where N_M is the number of available coördination sites of the metal ion. (Fixed ionic groups of the resin may block coördinative sites of the metal ion, so that N_M may be smaller than the maximum coördinative valence of the metal. This effect is discussed farther below.) For example, a resin such as Dowex 50 or Amberlite IR-120 (X_{ion} = 5 meq./g. dry resin) in the Ni^{2+} form ($z_{Ni} = 2$; $N_{Ni} = 6$) has a ligand-exchange capacity of about 15 meq./g. dry resin. As a sidelight, this example shows that the capacity of a cation exchanger for, say, ammonia can be tripled by using the resin as a "ligand exchanger" in the Ni^{2+} form rather than as an ion exchanger in the H^+ form. Of course, the ligand content of a resin can exceed the ligand-exchange capacity when "free" ligands in addition to the complexed ones are taken up and can fall short of the ligand-exchange capacity when complexing is incomplete. However, if the complexes formed are strong, the ligand content (in equivalents) approximately equals the ligand-exchange capacity over a wide range of concentrations and compositions of the external solution, and in this range ligands are accordingly exchanged in stoichiometric amounts. This analogy between ligand exchange and ion exchange warrants expressing ligand-exchange equilibria by the same means as ion-exchange equilibria, namely, in terms of exchange isotherms and separation factors.[10] This approach has been adopted in the present study.

The successful application of ligand exchange hinges on keeping the complexing metal ion in the resin. Displacement of the metal ion from the resin by ion exchange with other cations from the external solution would not only result in metal-ion losses but would also counteract ligand sorption and ligand-exchange selectivity since complex formation would then occur in the solution also. The most obvious remedy is to choose a resin with ionogenic groups which hold the metal ion tightly by partial complexing.[1] For example, Cu^{2+} and Ni^{2+} are eluted by concentrated ammonia or amine solutions from cation exchangers with sulfonic acid groups (Dowex 50, Amberlite IR-120, etc.), but not from resins with carboxylic acid groups (Amberlite IRC-50). However, such protection against ion exchange is achieved at a sacrifice in ligand-exchange capacity since the ionogenic groups of the resin block coördinative valences of the metal ion. In carboxylic-acid resins, for example, the number of operative coordination sites of Ni^{2+} is reduced from 6 to 4, that of Cu^{2+} from 4 to 2



Of course, this blocking of coördinative valences must be taken into account in eq. 3 and in the theoretical treatment of ligand-sorption and ligand-exchange equilibria.

Quantitative Theory

The most important qualitative features of ligand-sorption and ligand-exchange equilibria can be explained by applying the mass action law in its simplest form to equilibria such as (1) and (2), as was outlined in an earlier note.[1] For a quantitative treatment, however, this simple approach is inadequate. Factors that must be taken into account are, first, blocking of coördinative valences of the metal ion by ionogenic groups of the resin, second, formation of coördinatively unsaturated complexes, third, formation of "mixed" complexes (containing both competing ligand species), and fourth, sorption of "free" ligands in addition to the complexed ones. A theory which includes these effects is advanced in this section.

Ligand-sorption Equilibria.—First, consider sorption of a ligand A with coördinative valence a by a resin containing a metal ion M with N_M operative coördinative valences (valences blocked by resin groups not included). It is assumed that no polynuclear complexes (containing more than one metal ion) are formed and that the ligand A does not displace resin groups from coördinative sites they occupy.

Within the resin, the following species can then exist

$$A, M, MA, MA_2, \ldots, MA_p$$

where p is the maximum ligand number. As a rule, $p = N_M/a$, or, if N_M/a is not an integer, p is the next smaller integer. The species are in equilibrium with one another

$$M + A \rightleftarrows MA, \qquad \bar{m}_{MA} = k_1 \bar{m}_M \bar{m}_A$$

$$M + 2A \rightleftarrows MA_2, \qquad \bar{m}_{MA_2} = K_2 \bar{m}_M \bar{m}_A^2$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$M + pA \rightleftarrows MA_p, \qquad \bar{m}_p = K_{MA_p} \bar{m}_M \bar{m}_A^A$$

or, generally

$$M + i\,A \rightleftarrows MA_i,$$

$$\bar{m}_{MA_i} = K_i \bar{m}_M \bar{m}_A^i \ (0 \leq i \leq p) \qquad (4)$$

Here, $\bar{m}_M$, $\bar{m}_A$, etc., are the molalities (moles per unit weight of solvent) of the respective species in the resin, and the K_i are the (molal cumulative) Bjerrum stability constants of the complexes with ligand numbers i,[11] and $K_0 = 1$. The over-all molality $\bar{M}_A$ of species A in the resin, including molecules complexed by the metal, then is, ac-

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(10) See, for example, F. Helfferich, "Ion-Exchange," McGraw-Hill Book Co., New York, N. Y., 1962, Sec. 5-4a.

(11) Instead of the molal "constants" which are not strictly constant, true equilibrium constants defined by $K_i = a_{MA}/a_M a_A^i$ (a = activity) can be used. The quantities K_i in the equations must then be replaced by $K_i \bar{\gamma}_M \bar{\gamma}_A^i / \bar{\gamma}_{MA}^i$ ($\bar{\gamma}$ = molal activity coefficient in the resin).

cording to eq. 4

$$\bar{M}_A = \bar{m}_A + \bar{m}_{MA} + 2\bar{m}_{MA_2} + \ldots i\bar{m}_{MA_i} + \ldots$$
$$= \bar{m}_A + \bar{m}_M \sum_{i \neq 0} (i\, K_i\, \bar{m}_A{}^i) \qquad (5)$$

Similarly, the over-all molality of the metal, including complexes, is

$$\bar{M}_M = \bar{m}_M + \bar{m}_{MA} + \bar{m}_{MA_2} \ldots + \bar{m}_{MA_i} + \ldots$$
$$= \bar{m}_M \sum_i (K_i\, \bar{m}_A{}^i) \qquad (6)$$

(note that $K_0 = 1$). The quantity $\bar{m}_A$ in eqs. 5 and 6 can be expressed in terms of m_A, which is the ligand molality in the external solution, by use of the molal distribution coefficient λ_A of the "free" ligand, defined by

$$\lambda_A \equiv \bar{m}_A / m_A \qquad (7)$$

From eqs. 5 through 7 one readily obtains the over-all distribution coefficient Λ_A of species A (including complexed molecules)

$$\Lambda_A \equiv \frac{\bar{M}_A}{m_A} = \left\{ 1 + \frac{\bar{M}_M \sum\limits_{i \neq 0} [i\, K_i\, (m_A\, \lambda_A)^{i-1}]}{\sum\limits_i \Sigma [K_i\, (m_A\, \lambda_A)^i]} \right\} \lambda_A \qquad (8)$$

If $\bar{m}_A$ is sufficiently high, then the coördinatively saturated complex MA_p predominates:

$$K_p\, \bar{m}_A{}^p \gg \sum_{i < p} K_i\, \bar{m}_A{}^i \qquad (9)$$

and eq. 5 reduces to

$$\bar{M}_A \cong \bar{m}_A + p\bar{M}_M \qquad (10)$$

Here, the second term stems from full utilization of the ligand-exchange capacity, and the first term from additional sorption of "free" ligands. If the complexes are strong as, for example, with Cu^{2+}, Ni^{2+}, Co^{3+}, Ag^+ and ammonia or amines, then the condition 9 is met at even rather low ligand concentrations in the external solution. Accordingly, practically the full ligand-exchange capacity is utilized for ligand uptake even when the external solution is rather dilute.

For practical purposes, ligand-sorption isotherms —giving $\bar{M}_A$ as a function of m_A— and distribution coefficients can be calculated from eq. 8 if $\bar{M}_M$, λ_A, and the K_i are known. The quantity $\bar{M}_M$, *i.e.*, the over-all molality of the metal in the resin, is readily obtained from the ion-exchange capacity and the solvent content of the resin. For the complex stability constants K_i in the resin, the corresponding values in solutions are likely to be reasonable approximations. These latter values are tabulated for a great number of complexes.[12,13]

The molal distribution coefficient, λ_A, of the "free" ligand must be determined independently. If the ligand is non-ionic, one may assume as a first and very crude approximation that the coefficient is unity.

Ligand-exchange Equilibria

Consider exchange of two ligands A and B with coördinative valences *a* and *b* between a solution and a resin containing a metal ion *M* with N_M coördinative valences. The same assumptions as before are made. These species can then exist in the resin

$$\begin{array}{cccccc}
 & & A & & & \\
 & M & MA & MA_2 & \ldots. & MA_p \\
B & MB & MAB & NA_2B & \ldots. & \\
 & MB_2 & MAB_2 & \ldots. & & \\
 & \ldots. & & & & \\
 & MB_q & & & &
\end{array}$$

where *q* is the maximum ligand number of the complexes with B. As a rule, $q = N_M/b$, or, if N_M/b is not an integer, *q* is the next smaller integer. The species are in equilibrium with one another, generally expressed

$$M + iA + jB \rightleftharpoons MA_iB_j \begin{pmatrix} i, j \geq 0 \\ ai + bj \leq N_M \end{pmatrix}^{14}$$
$$\bar{m}_{MA_iB_j} = K_{ij}\, \bar{m}_M\, \bar{m}_A{}^i\, \bar{m}_B{}^j \qquad (11)$$

(by definition, $K_{00} = 1$). The over-all molalities of the species A, B and M then are

$$\bar{M}_A = \bar{m}_A + \sum_{i \neq o,\, j} (i\bar{m}_{MA_iB_j}) =$$
$$\bar{m}_A + \bar{m}_M \sum_{i \neq o,\, j} (iK_{ij}\, \bar{m}_A{}^i\, \bar{m}_B{}^j) \qquad (12)$$

$$\bar{M}_B = \bar{m}_B + \sum_{j \neq o,\, i} (j\bar{m}_{MA_iB_j}) =$$
$$\bar{m}_B + \bar{m}_M \sum_{j \neq o,\, i} (jK_{ij}\bar{m}_A{}^i\, \bar{m}_B{}^j) \qquad (13)$$

$$\bar{M}_M = \sum_{i,j} \bar{m}_{MA_iB_j} = \bar{m}_M \sum_{i,j} (K_{ij}\, \bar{m}_A{}^i\, \bar{m}_B{}^j) \qquad (14)$$

From eqs. 7 and 12 through 14, one obtains the "ligand separation factor" (defined in analogy to the ion-exchange separation factor)

$$\alpha_A{}^B \equiv \frac{\bar{M}_B\, m_A}{\bar{M}_A\, m_B} = \frac{\lambda_B \left\{ 1 + \bar{M}_M \sum\limits_{j \neq o,\, i} [jK_{ij}(m_A\lambda_A)^i(m_B\lambda_B)^{j-1}] / \sum\limits_{i,j} [K_{ij}(m_A\lambda_A)^i(m_B\lambda_B)]^j \right\}}{\lambda_A \left\{ 1 + \bar{M}_M \sum\limits_{i \neq o,\, j} [iK_{ij}(m_A\lambda_A)^{i-1}(m_B\lambda_B)^j] / \sum\limits_{i,j} [K_{ij}(m_A\lambda_A)^i(m_B\lambda_B)^j] \right\}} \qquad (15)$$

Ligand-exchange isotherms and separation factors can now be calculated for given conditions from the constants K_{ij} and the distribution coefficients λ_A and λ_B. Here, however, the difficulty arises that the stability constants of the mixed complexes (containing both A and B) are usually not known. In several fortunate cases, formation of mixed complexes is unlikely. Consider, for example, a monodentate–bidentate ligand exchange ($a = 1$, $b = 2$) with a metal ion with only two operative coördination sites ($N_M = 2$). Here, the complex species MA, MA_2 and MB can exist, but MAB is unlikely to be stable since the bidentate ligand would be attached by only one valence bond. A practical example is ligand exchange of ammonia for a bidentate diamine with a resin in Ag^+ form. In other systems, the stability constants of the

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(12) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1957.

(13) Note, however, that a correction must be applied if a solvent other than water is used since the tabulated values are for aqueous systems, *i.e.*, apply to equilibria of the type $M(H_2O)_q + pA \rightarrow MA_p + qH_2O$. An alternative treatment of ligand sorption in non-aqueous systems is to consider the process as a ligand exchange of solvent for ligand molecules.

(14) Of course, if any of the mixed complexes cannot exist for steric or other reasons, they must be omitted here and in the subsequent summations.

mixed complexes must be determined by independent measurements.

A practical example illustrating the evaluation of the equations and involving stability constants of mixed complexes is given in the following.

Let us examine the problem of predicting approximate ligand-exchange isotherms and separation factors from tabulated data and a minimum of experiments for the exchange of ammonia (A) for a bidentate diamine (B) between aqueous solutions and a carboxylic acid resin (Amberlite IRC-50) in Ni^{2+} form. Two of the six coördination sites of Ni^{2+} are blocked by carboxylic acid groups of the resin; hence, $N_M = 4$. The following species can exist in the resin

		A			
	M	MA	MA_2	MA_3	MA_4
B	MB	MAB	MA_2B		
	MB_2				

In the absence of detailed experimental data, it is assumed that the tabulated aqueous-phase stability constants of the complexes[12] MA_i and MB_j can be used, and that $\lambda_A \cong 1$, $\lambda_B \cong 1$, *i.e.*, $\bar{m}_A = m_A$, $\bar{m}_B = m_B$. The following relations then hold

$$\bar{M}_A = m_A + \bar{m}_M\,(K_{10}m_A + 2K_{20}m_A^2 + 3K_{30}m_A^3 + 4k_{40}m_A^4 + K_{11}m_Am_B + 2K_{21}m_A^2m_B) \quad (16)$$

$$\bar{M}_B = m_B + \bar{m}_M\,(K_{01}m_B + 2K_{02}m_B^2 + K_{11}m_Am_B + K_{21}m_A^2m_B) \quad (17)$$

$$\alpha_A{}^B = \frac{1 + \bar{m}_M(K_{01} + 2K_{01}m_A + K_{11}m_A + K_{21}m_A^2)}{1 + \bar{m}_M(K_{10} + 2K_{20}m_A + 3K_{30}m_A^2 + 4K_{40}m_A^3 + K_{11}m_B + 2K_{21}m_Am_B} \quad (18)$$

where

$$\bar{m}_M = \frac{M_M}{1 + K_{10}m_A + K_{20}m_A^2 + K_{30}m_A^3 + K_{40}m_A^4 + K_{01}m_B + K_{02}m_B^2 + K_{11}m_Am_B + K_{21}m_A^2m_B} \quad (19)$$

To determine $\bar{M}_M$, the water content of the resin in complexed form must be measured. The relation between $\bar{M}_M$, the ion-exchange capacity X_{ion} (in meq./g. dry resin in H^+ form), and the water content W (in weight per cent.) of the complexed resin in, say, $Ni(NH_3)_4{}^{2+}$ form is

$$\bar{M}_M = \frac{(100 - W)X_{ion}}{W[1 - (M_c - 1)10^{-3}X_{ion}]}{}^{15} \quad (20)$$

(M_c = equivalent weight of the complex, = 63.5 for $Ni(NH_3)_4{}^{2+}$). Actually, the water content of the resin and thus $\bar{M}_M$ depend somewhat on the composition of the external solution. For crude approximations, however, one may assume $\bar{M}_M$ to be constant and thus determine its value with only one measurement.

Equations 16 through 18 further contain the unknown stability constants K_{11} and K_{21} of the mixed complexes. These constants can be estimated as follows. The over-all distribution coefficient, Λ_A, of species A (in the presence of B) is, according to eq. 16

$$\Lambda_A \equiv \frac{\bar{M}_A}{m_A} = 1 + \frac{\bar{M}_M(K_{10} + 2K_{20}m_A + 3K_{30}m_A^2 + 4K_{40}m_A^3 + K_{11}m_B + 2K_{21}m_Am_B)}{1 + K_{10}m_A + K_{20}m_A^2 + K_{30}m_A^3 + K_{40}m_A^4 + K_{01}m_B + K_{02}m_B^2 + K_{11}m_Am_B + K_{21}m_A^2m_B} \quad (21)$$

For $m_A \to 0$, eq. 21 reduces to

$$\Lambda_A = 1 + \frac{\bar{M}_M(K_{10} + K_{11}m_B)}{1 + K_{01}m_B + K_{02}m_B^2} \quad (22)$$

Since $\bar{M}_M$ and the constants K_{10}, K_{01} and K_{02} are known, K_{11} can be calculated by use of eq. 22 from one experimental determination of Λ_A carried out in the presence of B in great excess over A or, preferably, from a series of such determinations and extrapolations of Λ_A to $m_A = 0$. Similarly, the over-all distribution coefficient of B is

$$\Lambda_B \equiv \frac{\bar{M}_B}{m_B} = 1 + \frac{\bar{M}_M(K_{01} + 2K_{02}m_B + K_{11}m_A + K_{21}m_A^2)}{1 + K_{10}m_A + K_{20}m_A^2 + K_{30}m_A^3 + K_{40}m_A^4 + K_{01}m_B + K_{02}m_B^2 + K_{11}m_Am_B + K_{21}m_A^2m_B} \quad (23)$$

for $m_B \to 0$, eq. 23 reduces to

$$\Lambda_B = 1 + \frac{\bar{M}_M(K_{01} + K_{11}m_A + K_{21}m_A^2)}{1 + K_{10}m_A + K_{20}m_A^2 + K_{30}m_A^3 + K_{40}m_A^4} \quad (24)$$

After K_{11} has been determined, K_{21} can now be calculated by use of eq. 24 from one determination, or a series of determinations, of Λ_B in the presence of A in great excess over B.

With all the constants K_{ij} and $\bar{M}_M$ known, ligand uptake, over-all distribution coefficients, separation factors, and exchange isotherms can now be calculated by use of eq. 16 through 18, 21 and 23 for any given composition of the external solution. Note that only three experiments are required, namely, one water content determination and two distribution measurements, each with a trace of one ligand in the presence of a large excess of the other.

Ligand-exchange isotherms and separation factors for exchange of ammonia for 1,3-diamino-propanol-2 between aqueous solutions and Amberlite IRC-50 in Ni^{2+} form, calculated as described above, are shown as solid lines in Fig. 1. The data used were:

$K_{10} = 6.3\cdot10^2$, $K_{20} = 7.1\cdot10^4$, $K_{30} = 3.2\cdot10^6$, $K_{40} = 6.3\cdot10^7$, $K_{01} = 4.4\cdot10^5$, $K_{02} = 1\cdot10^{10}$, ion-exchange capacity 9.3 meq./g. dry H^+ form.

The water content was determined with the resin in $Ni(NH_3)_4{}^{2+}$ form in equilibrium with 0.01 *M* NH_3 and was 61% wt. The constant K_{11} was estimated from measurements with 0.1 *N* total concentration of the solution and extrapolation to $m_A = 0$; the value $K_{11} \cong 2\cdot10^9$ was obtained. The extrapolation leading to K_{21} was somewhat uncertain; however, even with a value as high as $4\cdot10^9$, which was used in the calculations, this constant has very little effect on the results.

Experimental Evidence and Discussion

The theory advanced in the previous section was tested by experimental determinations of ligand-

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(15) See, for example, ref. 10, eq. 4-2.

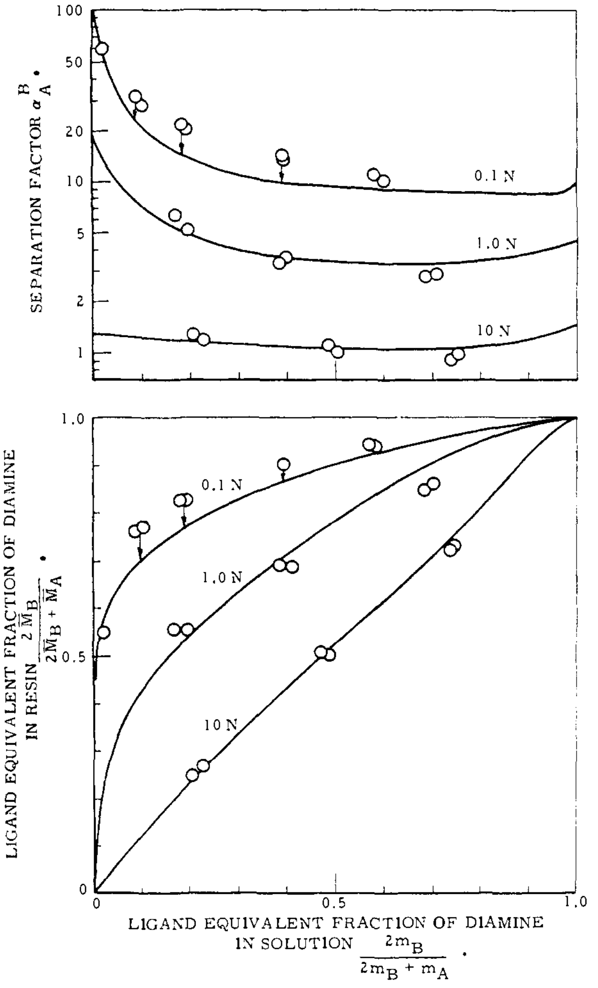
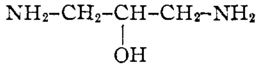


Fig. 1.—Ligand-exchange separation factors and isotherms for exchange of ammonia for 1,3-diaminopropanol-2 between aqueous solutions and Amberlite IRC-50 in Ni^{2+} form at 30°. Solid lines are calculated from eqs. 16 through 18, circles are experimental points.

exchange isotherms and separation factors for the exchange of ammonia for 1,3-diaminopropanol-2



$$NH_2\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2\text{-}NH_2$$

between aqueous solutions and Amberlite IRC-50 in Ni^{2+} form. Experimental results obtained at 30° with 0.1, 1.0 and 10 N total concentration of the external solution (in ligand equivalents) are shown as circles in Fig. 1. The same figure shows, for comparison, the theoretically predicted isotherms and separation factors as solid lines.

The rather satisfactory agreement between calculated and observed values in Fig. 1 shows that, at least in the case studied, the theory is basically sound. In particular, the theory accounts correctly for the two most characteristic features of the system, namely, the increasing preference of the resin for the diamine with dilution of the external solution and with decreasing equivalent fraction of the diamine. The first effect results from the higher coördinative valence of the diamine and has been briefly discussed and qualitatively explained in an earlier note.[1] It is interesting that the effect of the coördinative valences of the ligands in ligand exchange is analogous to that of the counter-ion valences in ion exchange; indeed, the analogy between the isotherms in Fig. 1 and those of, say, the Cu^{2+}/Na^+ ion exchange[16] is striking. The second effect—increasing preference for the diamine with decreasing equivalent fraction of the diamine—can be traced to the formation of mixed and unsaturated complexes. In fact, a simpler treatment in which such complexes are disregarded would give the opposite effect.

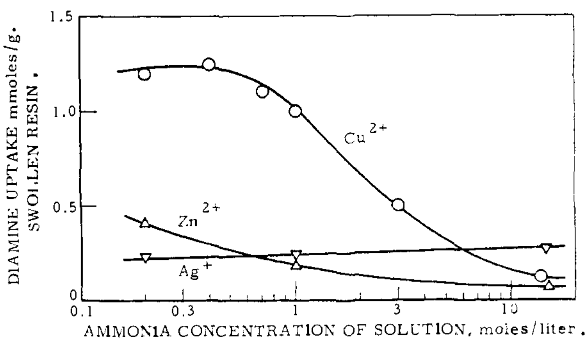


Fig. 2.—Uptake of 1,3-diaminopropanol-2 by Amberlite IRC-50 in Cu^{2+}, Zn^{2+} and Ag^+ form at 30° from solutions containing ammonia and diamine in the mole ratio 50:1.

The magnitude of the discrepancies between observed and calculated values in Fig. 1 is not surprising in view of the simplifying assumptions that were made in the calculations. The most serious deviation occurs with 0.1 N solutions and equivalent ligand fractions of the diamine in the solution of 0.1 to 0.5. In this range, the constant K_{11} is of considerable importance. Conceivably, this constant is smaller than estimated.

Additional experimental results with the same resin in the Cu^{2+}, Ag^+ and Zn^{2+} forms are shown in Fig. 2. In these experiments, the mole ratio ammonia/diamine in the external solution was kept constant at 50:1, and the solution concentration was varied. The following effects are apparent. The diamine uptake by the resin in the Cu^{2+} and Zn^{2+} forms increases with dilution of the solution; this reflects the above discussed increase in preference of the resin for the ligand having the higher coördinative valence. In the Cu^{2+} form, the resin prefers the diamine up to much higher solution concentrations than in the Zn^{2+} form; this is as expected since, relative to the ammonia complexes, the diamine complexes with Cu^{2+} are more stable than with Zn^{2+} (for Cu^{2+}: $K_{20} = 8{\cdot}10^7$, $K_{01} = 5{\cdot}10^9$; for Zn^{2+}: $K_{20} = 2.5{\cdot}10^4$, $K_{01} = 4{\cdot}10^4$). With the resin in the Ag^+ form, the diamine uptake is concentration-independent, *i.e.*, the preference for the ligand of high coördinative valence does *not* increase with dilution of the solution. Here, indeed, the theory predicts the absence of the ligand-valence effect because only one coördinative valence of Ag^+ is operative and, hence, both ammonia and the diamine can only form complexes containing one ligand molecule. The

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(16) See, for example, H. C. Subba Rao and M. M. David, *A.I.Ch.E. Journal*, **3**, 187 (1954).

experimental results thus are in qualitative agreement with the theory.

Experimental

Reagents.—Cation exchanger Amberlite IRC-50 as supplied by manufacturer, conditioned by alternate treatment with 1 *M* NaOH and 1 *M* HCl (10 cycles) and intermittent washing with deionized water. 1,3-Diaminopropanol-2 supplied by Shell Chemical Company, purified by shaking with activated charcoal after dissolution in equal amount of water and subsequent vacuum distillation at 0.1 mm., 68°. All other reagents: standard analytical-grade laboratory reagents.

Equilibration Procedure.—About 1 gram of the resin was converted to the metal–ammonia complex form by treatment with a large excess of *ca.* 2*M* aqueous $[Ni(NH_3)_6]Cl_2$, $[Ag(NH_3)_2]NO_3$, etc., was washed with 0.1% wt. NH_3, centrifuged to remove adherent liquid and weighed in a stoppered weighing bottle. The resin was then placed in a stoppered Pyrex glass bottle, and a solution made up from titrated stocks of aqueous ammonia and 1,3-diaminopropanol-2 was added (*ca.* 500 ml. with 0.1 to 0.5 *N* solutions, *ca.* 250 ml. with 0.7 to 1.0 *N*, *ca.* 100 ml. with 3 to 10 *N*). The bottle was kept in a thermostated water bath at 30.0 ± 0.1° and was shaken occasionally. The solution was renewed five times at 2 to 4 hour intervals. After final equilibration, both the resin and the solution were analyzed for ammonia and diamine.

Displacement of Ammonia and Diamine from the Resin for Analysis.—After equilibration as described above, the resin was centrifuged to remove adherent liquid, transferred to a 100 ml. Pyrex glass bottle and treated with five successive charges of *ca.* 40 ml. 2 *M* HCl, for 2 to 4 hr. each, with occasional shaking. The HCl was combined by decanting into a 250 ml. volumetric flask which was then filled to the mark with deionized water. The contents of the flask were analyzed for ammonia and diamine (hydrochlorides).

Analysis Methods. Determination of Ammonia and Diamine in Aqueous Solutions.—The total base concentration was determined by titration of an aliquot with 0.1 *M* HCl. Ammonia was determined by adding an aliquot containing about 1 meq. NH_3 to 100 ml. 5% wt. H_2SO_4, adding concentrated NaOH + $Na_2S_2O_3$ solution, distilling NH_3 into a receiver containing boric acid solution, and titrating NH_3 in the receiver with 0.1 *N* H_2SO_4. The diamine concentration was then calculated by difference.

Determination of Ammonia and Diamine in HCl Solutions.—The total base concentration was calculated from Kjeldahl determination of total nitrogen. Ammoniacal nitrogen was determined as described above. The diamine concentration was then calculated by difference.

Water Content of the Resin in Complexed Form.—The water content was determined by an indirect method. First, the water content of the water-swollen H^+ form was determined by drying a weighed amount of the resin in this form to constant weight (20 mm., 60°, 3 days). A weighed amount of the resin in the water-swollen H^+ form then was converted to the $Ni(NH_3)_4^{2+}$ form as described earlier and was weighed in this form, after centrifuging to remove adherent liquid, in a stoppered weighing bottle. The Ni and NH_3 content of the resin sample was then determined after displacement of these species with 2 *M* HCl as described earlier. The water content is then readily calculated by difference.

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Ligand Exchange. II.[1] Separation of Ligands Having Different Coördinative Valences

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"Ligand exchange" can be used for chromatographic separations of compounds that form complexes with metal ions. An ion exchanger containing the complexing metal ion is used as the solid sorbent. A particular advantage of ligand exchange for separating ligands which differ in their coördinative valences is that the selectivity of the sorbent can be reversed by changing the concentration of the external solution. Under suitable conditions the sorbent preferentially takes up the ligand with the higher valence from dilute solutions, and the ligand with the lower valence from concentrated solutions. Accordingly, the ligand with the higher valence is efficiently and selectively taken up from dilute solutions or mixtures in exchange for a ligand of lower valence and can be recovered from the column in high concentration by displacement with a concentrated solution of the ligand of the lower valence. The feasibility of such sorption-displacement cycles with selectivity reversal is demonstrated with Amberlite IRC-50 in Ni^{2+} form as the sorbent and ammonia and 1,3-diaminopropanol-2 as the exchanging ligands.

Introduction

Ion exchangers containing complexing metal ions can be used as solid sorbents for chromatographic and other separations of compounds which can form complexes with the metal in the resin. In such separations, an exchange of ligands for others or for solvent molecules takes place between the external solution and the coördination shells of the metal ion in the resin. The principles of such ligand-exchange separations have been outlined in an earlier note,[2] and ligand-sorption and ligand-exchange equilibria have been discussed in more detail in Part I.[1]

Separations of ligands by ligand exchange can be carried out by the usual chromatographic procedures (elution development, gradient elution, displacement development, frontal analysis). Except for the advantage of high selectivities, attained by virtue of the high specificity of complex formation, there is no essential difference between ligand-exchange chromatography and other chromatographic techniques. For separating compounds having different coördinative valences, however, ligand exchange offers the additional advantage that, within wide limits, the selectivity can be adjusted at will by varying the concentration of the external solution. Dilution of the solution increases the preference of the resin for the ligand having the higher coördinative valence, and *vice versa*.[1,2] If a suitable metal ion is chosen, the selectivity can even be reversed so that one ligand is preferentially taken up from dilute mixtures, and the other from concentrated mixtures. The possibility of adjusting, by simple means, the selec-

(1) For Paper I, see *J. Am. Chem. Soc.*, **84**, 3237 (1962).

(2) F. Helfferich, *Nature* (London), **189**, 1001 (1961).