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

BY F. HELFFERICH

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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-

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

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

tivity in analytical separations is an obvious advantage which requires no further comment. In addition, the selectivity reversal can be exploited for efficient and economical separations of large quantities of ligands by a simple sorption-displacement cycle. This latter application is discussed in the following.

Sorption-displacement Cycles with Selectivity Reversal.—In the usual fixed-bed exchange-sorption or ion-exchange separations of two components A and B, one component (A) is selectively removed from the stream in exchange for the other one (B). This sorption step is followed by a regeneration step in which A is removed from the bed by elution with B. In the sorption step, a high selectivity of the sorbent for A is desired to attain a high operative capacity and a sharp breakthrough. In the regeneration step, however, selectivity for A is detrimental since it greatly increases the amount of regenerant required. Moreover, if A rather than the stream free of A is the desired product, recovery of A from the bed in high concentration necessitates displacement with a third species which is preferred to A, and an additional regeneration step involving an even larger amount of regenerant B must then follow.

The efficiency of any such cycles is greatly increased if the selectivity of the sorbent is reversed in such a way that preference for A in the sorption step gives selective uptake, and preference for B in the second step permits A to be recovered, and the bed to be regenerated, with little more than a stoichiometric amount of B.

One of the few cases in which such a selectivity reversal can be achieved is water softening by ion exchange. Here, the ion exchanger prefers the polyvalent cations in the softening step where the concentration is low, and prefers Na^+ in the regeneration step where concentrated brine is used as the regenerant. Much of the early success of ion exchange in water softening is due to this fortunate coincidence.

As pointed out before, an analogous selectivity reversal can be achieved in ligand exchange if the ligands differ in their coördinative valences. A suitable ligand exchanger prefers the ligands of higher valence when the solution is dilute, and those of lower valence when the solution is concentrated. The ligand or ligands with the higher valence can thus be selectively removed from *dilute* mixtures in exchange for a ligand of lower valence. The ligand or ligands with the higher valence can then be recovered in high concentration, and the bed be efficiently regenerated, by displacement with a *concentrated* solution of the ligand with the lower valence.[2] No additional regeneration step, except for washing with solvent, is required to restore the bed for the next cycle. Such exchange cycles with selectivity reversal are particularly useful for removing undesired polydentate ligands from dilute streams or for isolating them from dilute mixtures. Experiments to test the feasibility of such ligand-exchange operations are discussed in the following.

Experimental Results and Discussion.—Fixed-bed experiments were made with Amberlite IRC-50 in the Ni^{2+} form and with ammonia and 1,3-diaminopropanol-2 as the exchanging ligands. The particular resin was chosen because its carboxylic-acid groups hold the metal ion tightly by partial complexing and thus offer sufficient protection against metal-ion loss from the resin by ion exchange for ammonium or propanoldiammonium ions even at very high solution concentrations.[1] The ligands and Ni^{2+} as the complexing ion were chosen because this combination gives the desired selectivity reversal[3]; equilibrium measurements in Part I show that the bidentate diamine is strongly preferred when the solution concentration is low, and ammonia is slightly preferred when the solution concentration is higher than 10 N. Three experiments were made, namely, uptake of the diamine from a dilute solution in exchange for ammonia, uptake of the diamine from a dilute ammonia-diamine mixture and displacement of the diamine from the bed with concentrated ammonia.

The interpretation of the results is facilitated by the fact that the advancing bands and boundaries in the column are clearly visible. With increasing ammonia or diamine concentration of the solution, the color of the resin changes from blue green to turquoise, sky blue, violet blue, pale violet, and dark violet. This color sequence is the same for ammonia and 1,3-diaminopropanol-2, with the difference that the ammonia solutions must be about ten times as concentrated as the diamine solutions to produce the same color of the resin. For example, in the diamine uptake from dilute solutions the exhausted resin in the diamine form is violet blue while the still unexhausted resin in the (water-washed) ammonia form is blue green. Such ligand exchange thus is "chromatography" in the original and literal sense of the word.

Diamine Uptake from Dilute Solutions.—1,3-Diaminopropanol-2 was removed from a dilute aqueous solution (0.005 M) and from a dilute aqueous mixture containing a large excess of ammonia (0.1 M ammonia + 0.001 M diamine) by passing the solutions through a small laboratory column containing Amberlite IRC-50 in the $Ni(NH_3)_4^{2+}$ form. Operating conditions and results are given in Table I.

In both experiments, the advancing front boundary of the diamine zone was rather sharp and of the "self-sharpening" type, as one should expect in view of the favorable separation factors. The sharpness of the boundaries (observed visually) is evidence that ligand exchange is fast enough to keep pace with the motion of the boundaries. The sharpness of breakthrough was significantly affected by distortion of the boundary because of flow maldistribution in the column. This distortion thus accounts for a considerable part of the deviation of the degree of utilization (defined as the

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(3) The theory and experimental measurements of ligand-exchange equilibria with ammonia and 1,3-diaminopropanol-2 (see Part I) lead to the following picture for other potential complexing ions. Ag^+ and Cu^{2+} give no selectivity reversal, the former because it has only one operative coördinative valence in a carboxylic-acid resin, the latter because its complex-stability constants with the diamine are so much greater than those with ammonia that the diamine is preferred up to the highest solution concentrations. For Zn^{2+}, the complex-stability constants with the diamine are relatively small as compared to those with ammonia, so that the selectivity reversal occurs at an impractically low solution concentration (below 0.1 N).

TABLE I

OPERATING CONDITIONS AND RESULTS

	Sorption from dilute solution	Sorption from dilute mixture	Displacement
Bed height	18.0 cm.		65 cm.
Bed diameter	1.0 cm.		2.54 cm.
Amount of resin	10.0 g.		250 g.
Ligand-exchange capacity of bed	49 meq.		122 meq.
Initial form of bed	$Ni(NH_3)_4^{2+}$		$Ni(diamine)_2^{2+}$
Feed concentration	0.005 *M* diamine	0.1 *M* NH_3 + 0.001 *M* diamine	15.6 *M* NH_3
Flow rate	1 ml./min.	4 ml./min.	2.5 ml./min.
Temperature	20°	20°	20°
Breakthrough volume	3.88 liters	10.55 liters	See Fig. 1
Breakthrough capacity for diamine	19.4 mmoles	10.55 mmoles	
Equilibrium capacity for diamine	24.5 mmoles	12.9 mmoles	
Degree of column utilization	0.79	0.82	

ratio of the breakthrough and equilibrium capacities) from unity. The equilibrium capacity of the bed for diamine uptake from the diamine solution practically equals the ligand-exchange capacity since, in equilibrium with a 0.005 *M* diamine solution, the predominant species in the resin is $Ni(diamine)_2$ and sorption of "free" diamine and formation of the coördinatively unsaturated complex Ni(diamine) are negligible. This is in accordance with the equations in Part I. The equilibrium capacity for diamine uptake from the ammonia–diamine mixture is lower since the solution contains a 100-fold excess of ammonia (on a molar basis) and the resin thus is only partially converted to the diamine form. Nevertheless, because of the favorable separation factor about 45% of the ligand-exchange capacity is utilized for diamine uptake even from a solution which contains that large an excess of the competing ligand ammonia.

Diamine Displacement by Concentrated Ammonia.—1,3-Diaminopropanol-2 was recovered from a large laboratory column containing Amberlite IRC-50 in the $Ni(diamine)_2$ form by displacement with concentrated (15.6 *M*) aqueous ammonia. The operating conditions are given in Table I, and the effluent concentration history is shown in Fig. 1.

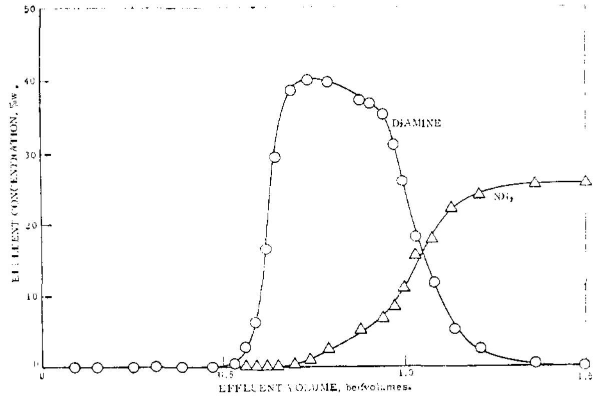

Fig. 1.—Effluent concentration history in displacement of 1,3-diaminopropanol-2 by concentrated ammonia from Amberlite IRC-50 (Ni^{2+}).

The qualitative aspects of this somewhat unusual displacement operation are the following. The bed initially contains water as the interstitial liquid. Upon displacement with ammonia, about one void volume of water thus emerges first. Concentrated ammonia, introduced at the top of the column, displaces the diamine from the resin and thus generates a highly concentrated diamine "sweep wave" which increases in width on its travel down the column as more and more diamine is displaced. One may compare the action of the ammonia to that of a broom which is pushed over a dusty floor and accumulates more and more dust on its front side. All the diamine that was initially in the resin thus emerges in a highly concentrated and rather small effluent fraction (about 0.85 bed volumes) which follows the interstitial water and is followed by the displacement agent. The migration of the zones and boundaries is clearly visible since the resin is sky blue in the (water-washed) diamine form, dark violet in the sweep wave and pale violet in the ammonia zone.

According to Fig. 1, about 1.36 bed volumes (445 ml.) of concentrated ammonia are needed for complete displacement. All the diamine (56 g.) appears within an effluent fraction of about 0.85 bed volumes (280 ml.) with a peak concentration of 40.5% weight. A product cut of only about 0.34 bed volumes (110 ml.) can be taken which contains 75% of the total diamine in an average concentration of 37% weight and is contaminated by only about 3.2% weight ammonia. No detectable loss of nickel from the bed occurred. It is conceivable that an even more concentrated product fraction could be obtained by displacement with ammonia of higher concentration under pressure.

Both the front and the rear boundary of the sweep wave are self-sharpening since the equilibria both of sorption of "free" diamine by the diamine-form resin at the front boundary and of the ammonia–diamine exchange at the rear boundary are "favorable," *i.e.*, have negatively curved isotherms.[4] A rather sharp sweep wave, as in Fig. 1, thus results unless the boundaries become distorted. In the experiment at room temperature, no significant distortion of either boundary occurred. However, a curious phenomenon was

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[4] For a detailed discussion of "favorable" and "unfavorable" sorption and exchange equilibria which lead to self-sharpening and non-sharpening boundaries see, for example, T. Vermeulen, *Adv. Chem. Eng.*, **2**, 147 (1958), and F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York, N. Y., 1962, Sec. 9-1.

observed when the experiment was repeated under identical conditions, but with flood lights (for the purpose of filming the operation) which raised the bed temperature to about 40 to 50°. Here, the rear boundary remained even sharper while the front boundary showed severe distortion, with long and surprisingly uniform-sized "fingers" protruding deeply into the diamine zone downstream. The following hydrodynamic explanation is offered. The liquids in the three zones differ significantly in their specific gravities and viscosities. Such differences are known to affect the hydrodynamic stability of boundaries. As a general rule, gravitation has a stabilizing effect on a boundary between two zones if the upper zone has the lower specific gravity and has a destabilizing effect in the opposite case. Also, the viscosity difference has a stabilizing effect on the boundary if the driving liquid is the more viscous one and has a destabilizing effect in the opposite case. The viscosity effect becomes more important when the flow rate is increased. Hill[5] and others[6,7] have derived a quantitative criterion for the hydrodynamic stability of such boundaries in liquid–liquid displacement. Hydrodynamic instability usually results in the characteristic "fingering" pattern. In the diamine displacement by concentrated ammonia, the sweep wave has a higher specific gravity and higher viscosity than both liquids in front and behind the wave. In downflow operation (as in the reported experiments), the front boundary of the wave thus is gravitationally unstable but may be stabilized by the viscosity effect, and the rear boundary is gravitationally stable but may become unstable because of the viscosity effect. It is likely that in the experiment at room temperature the viscosity effect was predominant, so that the front boundary was hydrodynamically stable while the rear boundary was not. The increase in temperature, by greatly reducing the viscosity differences, stabilized and sharpened the rear boundary but made the front boundary unstable so that, here, the fingering pattern developed. A decrease in flow rate, by reducing the importance of the viscosity effect, should have the same result. On the other hand, an increase in flow rate should enhance the viscosity effect and thus sharpen the front boundary and widen the rear boundary; this latter prediction was confirmed experimentally.

Conclusions.—The experiments confirm that ligand-exchange cycles with selectivity reversal are feasible and can be used for efficient removal and recovery of polydentate ligands from dilute streams or mixtures. Ligand-exchange equilibria, studied in Part I, indicated this possibility. However, it remained to be seen whether ligand-exchange rates are high enough for such chromatographic separations. The fixed-bed experiments show that this is the case, at least for the systems studied. Of course, the possibility cannot be excluded that low rates will interfere in other systems. The "fingering" observed in the displacement experiment at elevated temperature shows that attention must be devoted to the hydrodynamic stability of boundaries between concentrated chromatographic zones.

Experimental

The same resin, reagents and analysis methods as in Part I, and standard Pyrex glass laboratory columns were used.

Diamine Uptake from Dilute Solutions and Mixtures.—The column was filled with resin in the swollen $Ni(NH_3)_4^{2+}$ form. The bed was then washed with *ca.* 20 bed volumes of deionized water and was briefly backwashed and allowed to settle to insure adequate packing. The dilute diamine or ammonia–diamine solution was fed from a reservoir bottle and passed downflow through the column. The usual procedure of detecting breakthrough by analysis of effluent cuts is cumbersome and not very reliable in these experiments since very small amounts of the diamine in the presence of a large excess of ammonia would have to be determined by difference after a lengthy distillation. Therefore, feed was discontinued at the visual breakthrough point, *i.e.*, when the front boundary of the diamine zone came within about 1 mm. of the end of the bed. The nickel–diamine and –ammonia complexes were then displaced from the bed by 2 *M* HCl and the diamine was determined in the displacement effluent. The amount of diamine recovered from the bed is given as the breakthrough capacity. In both experiments this amount of diamine agreed within the experimental error (0.1%) with the diamine content of the original feed; this shows that sorption was not carried beyond the breakthrough point. The equilibrium capacities of the resin were determined by separate equilibrium measurements as described in Part I.

Diamine Displacement by Concentrated Ammonia.—The column was filled with resin in the swollen $Ni(NH_3)_4^{2+}$ form. The bed was then converted to the diamine form by passing a 0.05 *M* solution of the diamine through the column until the effluent was free of ammonia. Now, the bed was washed with deionized water (*ca.* 30 bed volumes) and was briefly backwashed and allowed to settle to insure adequate packing. Concentrated ammonia was fed from a reservoir bottle and passed downflow through the column. For determining the effluent concentration history, effluent cuts (*ca.* 0.5 to 1 ml. each) were taken and weighed in stoppered 100 ml. volumetric flasks which were then filled to the mark with deionized water. The amounts of ammonia and diamine in the cuts were determined by analysis of aliquots as described in Part I.

Acknowledgment.—The help of Mr. D. Dere in carrying out the experiments is gratefully acknowledged.

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(7) P. G. Saffman and G. Taylor, *Proc. Roy. Soc.* (London), **A245**, 312 (1958).