

Ligand Exchange Studies with an Iminodiacetic Acid Ion Exchange Resin

by

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Iminodiacetic Acid 이온 교환수지를 사용한 Ligand Exchange 에 대한 연구

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Abstract

Mixtures of amines can be separated by elution chromatography on a chelating resin, Dowex A-1 loaded with nickel ions based on ligand exchange. Aqueous ammonia is used as the eluent. The method has proved particularly effective for separating aromatic amines.

요 약

Ligand Exchange 를 원리로 하여 Nickel Ion 을 포함하고 있는 Chelating Resin 인 Dowex A-1 을 써서 Elution Chromatography 에 의하여 Amine 의 혼합물을 분리하는 방법을 기술하였다. 이 실험에서 암모니아 수용액을 Eluent 로 썼다. 이 방법은 특히 방향족아민의 분리에 효과 있음을 알게 되었다.

Introduction

The term "ligand exchange" was introduced by Helfferich (1) to describe the exchange of electron donating ligands coordinated to metal ions held by a cation exchange resin. He showed that ammonia molecules coordinated with ions of nickel and copper in resin could be exchanged reversibly for molecules of an amine, and that such exchanges could be used for column separations. He recovered 1,3-diaminopropane-2-ol from a dilute aqueous solution containing ammonia by passing the solution through a column of cation exchange resin loaded with nickel-ammonia complex ions. The diamine was selectively adsorbed

from the dilute solution, but could be displaced by passing concentrated aqueous ammonia. Two ammonia molecules displaced one diamine molecule, so that the displacement was favored by high concentration (1).
$$\text{Ni}(\text{NH}_2\text{RNH}_2)_3^{2+} + 6\text{NH}_3 = \text{Ni}(\text{NH}_3)_6^{2+} + 3\text{NH}_2\text{RNH}_2$$
 (1)
Application of the mass-action law in its simplest form gives

$$\frac{[\text{Ni}(\text{NH}_3)_6]^{2+} [\text{NH}_2\text{RNH}_2]^3}{[\text{Ni}(\text{NH}_2\text{RNH}_2)_3]^{2+} [\text{NH}_3]^6} = K \quad (2)$$

where K = molal equilibrium constant of reactions after rearrangement,

$$\frac{[\text{Ni}(\text{NH}_3)_6]^{2+}}{[\text{Ni}(\text{NH}_2\text{RNH}_2)_3]^{2+}} = K \left[\frac{\text{NH}_3}{\text{NH}_2\text{R NH}_2} \right]^3 [\text{NH}_3]^3 \quad (3)$$

Applications of ligand exchange to the elution chromatography of amine mixtures have been explored in a preliminary way by Lattrell and Walton^{(2),(3)} and found that 1,2-diamines were very difficult to displace from the nickel form of Dowex 50W×8 with an ammonia solution because the 1,2-diamines were held so strongly by the resin.

This report describes an elution of aromatic amines and aliphatic diamines by elution chromatography using a column of the nickel loaded Dowex A-1, which contains iminodiacetic acid as the active group. The properties of this chelating resin should differ essentially from those of the classical resins in that the possibilities of separation are to a high degree determined by the stability constants of the metal-resin complexes. In this study the cations are complexed with ammonia beforehand, and amine molecules exchange with ammonia molecules as ligand and aqueous ammonia solution was used as the eluant. And also elution behavior of amines was studied on the Dowex A-1 and zirconium phosphate, all loaded with nickel ions.

Experimental

(1) Materials. The Chelex 100(50-100mesh), a sized and purified form of Dowex A-1(Bio-Rad Laboratories, Richmond, California), was used without further treatment. The Chelex 100 was converted to the nickel-ammonia complex form by treating with 0.1M nickel nitrate solution and dilute aqueous ammonia solution in a column. The exchange process was followed by rinsing with deionized water. Tests were also made with sulfonated crosslinked polystyrenes, Dowex 50W, 50-100 mesh, with 8% crosslinking and a zirconium-base ion exchanger Bio-Rad ZP-1, 50-100 mesh. The amines used were obtained in high purity and were used without further purification. Deionized water was used throughout.

(2) Columns. The columns used had an internal diameter of 1cm; the bed volume was usually 10-15ml. Flow rates of 0.3-0.5 ml/min were used, and fractions of 10 ml collected.

(3) Static adsorption studies. To evaluate resin sorption of aromatic amines from their aqueous solutions, weighed 2-3 grams quantities of nickel loaded

resins were placed in flasks with 100ml of solutions of aromatic amines. For the experiments, air-dried resins were used. The flasks were closed and left to stand at 20-25°C for 48 hours, shaking intermittently, after which a small aliquot was withdrawn for analysis. The amount of adsorbed amines was calculated from the analysis of the solution. Adsorption is from 0.05M aqueous amine solutions.

(4) Diamines and nickel loaded chelating resin. In order to predict the possibilities for the separation of diamines by aqueous ammonia solution, the competition of ammonia and diamine for the resin was measured in different concentration of ammonia and the distribution of diamines between the resin and aqueous ammonia solutions was determined using the following relationship:

$$\lambda = \frac{(\text{Amine in resin})}{(\text{Ammonia in resin})} \times \frac{(\text{Ammonia in solution})}{(\text{Amine in solution})}$$

This is an apparent and not a thermodynamic constant, because the activity coefficients of the ligands in solution and in the resin phase been neglected; but it provides practical information as to the separation possibilities of two ligands with the aid of Dowex A-1.

A number of equilibrium distributions were measured by weighed 0.5 gram quantities of nickel loaded chelating resin (50-100 mesh) were placed in flasks with measured volumes of aqueous solutions containing amines and ammonia. The flasks were closed and left to stand at 20-25°C for twenty four hours, shaking intermittently, after which a small aliquot was withdrawn for analysis. Because of analytical difficulties the resin compositions were found by difference from the solution compositions, these results were not very accurate. The diamines were determined by titration with standard hydrochloric acid, the accompanying ammonia could be removed by boiling.

(5) Analytical methods. (a) Ultraviolet absorption. Pyridine, aniline, and benzylamine in the effluents were determined in the presence of ammonia by spectrophotometry in the ultraviolet. Measurement of ultraviolet absorbances at different wave lengths was used for the simultaneous determination of amines in pyridine-benzylamine and aniline-benzylamine mixtures.

(b) Absorption, in the visible region, by copper:

(II) complexes. This was applicable to 1,2- and 1,3-diamines. A small, measured amount of copper sulfate solution was added and the absorbance measured in a cm cell at 550 and 620 $m\mu$, where the copper-diamine complexes absorb considerably more strongly than the copper-ammonia complex, but ammonia interferes significantly.

Results and Discussion

(a) Static adsorption studies. The adsorption from aqueous solutions is summarized in Table 1. Benzylamine is the most strongly adsorbed on both of the resins, then pyridine, then aniline on the chelating resin. It was that the greatest adsorption of benzylamine is due to the molecular structure of benzylamine is the closest to that of the monomer of the resin.

(b) Aromatic amines and nickel loaded chelating resin. An extensive series of tests was made in which columns of the cation exchange resin were saturated with nickel-ammonia complex. Experiments were made to separate two pairs of amines, pyridine from benzylamine and aniline from benzylamine, by elution chromatography. Small quantities of the mixed amines were placed on the top of the column and aqueous ammonia solutions were passed to elute the amines from the column. For determining effluent concentration history, effluent cuts were taken and amines were determined in the effluent by ultraviolet absorption at different wave lengths.

The flow rate of eluting solution through the column had a marked effect on resolution. Flow rates of 0.3, 0.5, and 1.0 ml/min were compared. The slowest flow rate gave the best resolution. The more rapid flow rates, however, reduced the length of time required to complete a chromatogram and still gave adequate resolution of the amines present in the resin. The flow rate of 0.3-0.5 ml/min adopted as standard was a compromise between resolution and speed.

Concentrations of ammonia solution as an eluant is less critical, lower than 2.0M resulted in longer retention times for benzylamine or its failure to be eluted quantitatively. Concentrations in the reservoir higher than 2.0 M slightly reduced the time required to complete the chromatography, but very high concentrations appeared to cause excessive compaction of

the column which resulted in higher operating pressures.

Elution curves for mixtures of amines on nickel loaded chelating resin are shown Figures 1 and 2. The elution of nickel ions during this run was not detected. Even here the benzylamine recovery is a little less, the aniline and pyridine recoveries a little more than 90%. The incomplete recovery can be attributed to insufficient slow flow rates. One can visualize a certain fraction of the amines being held in the centers of the beads and not having time to elute out. For quantitative analytical use, however, it would be wise to use fine mesh resins on account of the slowness of diffusion of amine molecules within the resins.

(c) Diamines and nickel loaded chelating resin. The data presented in this experiment are still quite rough. Attempts were made to measure ligand exchange distributions over a range of amine : ammonia ratios by equilibrium tests, but as was mentioned previously, these measurements are not very reliable. Such data, however, shown several points of interest. The data are shown in Table 2.

Experiments were conducted with 6 diamines, ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, 1,3-diamino-propane-2-ol, 1,4-butanediamine, and 1,6-hexanediamine. In most cases, similar results were obtained, viz., increasing the concentration of ammonia in the solution reduces the concentration of diamines in the resin because of competing complexation.

Column elution tests were made with 1,2-propanediamine and 1,3-propanediamine. Both of the diamines were detected by the visible absorption of their Cu (II) complexes, however, they were held so strongly by the resin that elution from a column by aqueous ammonia solution was virtually impossible. There must be a special reason for the very strong binding of these diamines. It was felt that the values of the stability constants of the diamine complexes are very high in comparison with that of ammonia, and therefore elution is difficult.

It has been also shown that ammonia concentration in the solution exerts little influence on the distribution coefficients.

Clearly, much development work remains to be

done before this type of resin will extend the separation of diamines.

(e) Effect of resin type. It is interesting to note that the affinity of the amines for the resin matrix is different for different resins. Between the chelating resin and zirconium phosphate the affinity of the amines for the resin matrix is different each other. The stabilities of the nickel-amine complexes in aqueous solution appear to have little to do with the affinity of the amines for the resin matrix.

It seems that the affinity of the amines for the resin matrix is more important than their affinity for the nickel ions. This is very obvious with benzylamine, which is held strongly by a polystyrene-base resin but very weakly by zirconium-base ion exchanger. Whatever the reasons, the changes in affinity of the amines between different exchangers are of obvious analytical interest.

Table 1. Adsorption of aromatic amines on nickel loaded resins

Amine	Adsorption (m mol/g of resin)	
	Dowex 50W	Dowex A-1
Benzylamine	0.131	0.862
Pyridine	0.103	0.471
Aniline	0.042	0.355

Table 2. Ammonia-amine distribution on nickel loaded chelating resins

Ammonia concn. (M)	Distribution Coefficient					
	en	1,2-pn	1,3-pn	1,3-AOH	1,4-bn	1,6-hn
1.02	1.84	4.08	3.97	1.04	0.91	0.60
1.76	2.68	4.21	2.97	0.63	1.22	0.81
3.55	1.39	1.84	0.98	0.43	1.57	0.46

en: Ethylene diamine

1,2-pn: 1,2-propane diamine

1,3-pn: 1,3-propane diamine

1,3-AOH: 1,3-diaminopropane-2-ol

1,4-bn: 1,4-butane diamine

1,6-hn: 1,6-hexane diamine

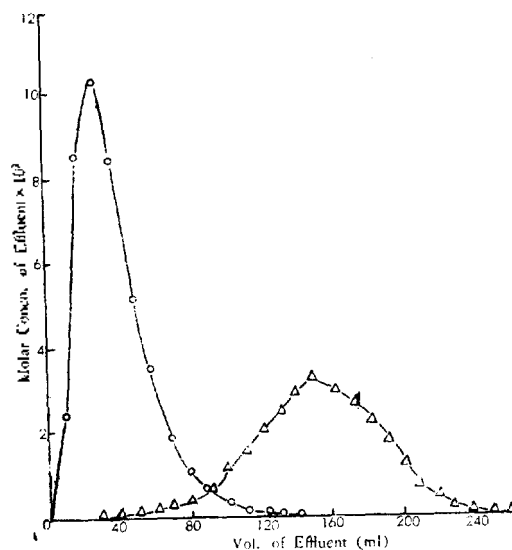


Figure 1. Ion exchange chromatogram of amine mixture

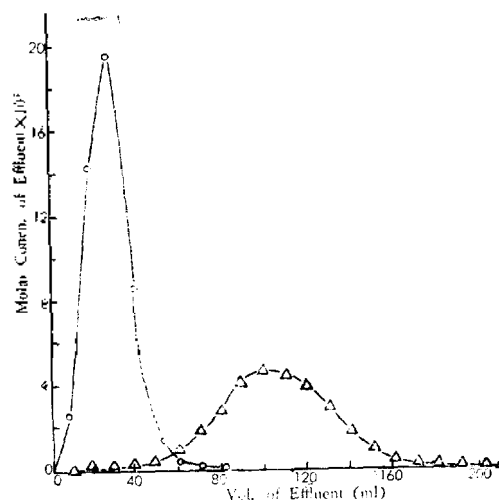


Figure 2. Ion exchange chromatogram of amine mixture

References

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