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CARBOXYLIC ACID EXCHANGERS IN ANALYTICAL CHEMISTRY

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भाभा परमाणु अनुसंधान केन्द्र

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ABSTRACT

The literature on the use of carboxylic acid exchangers in inorganic analytical chemistry is reviewed. It is classified under two heads, based on the ionic form in which the exchanger is employed, viz., the salt form and the acid form.

In the salt form, the separations reported in the beginning are mostly carried out in alkaline medium, employing ammonia and its derivatives as complexing agents to hold cations in solution. This was followed by the use of ammonium ion as an eluent from very weakly acidic or neutral solutions. There are a few separations reported making use of EDTA as eluent. It appears that separation of some anions from cations can be achieved with greater ease with these exchangers than with sulphonic acid type.

Contrary to the general belief, carboxylic acid exchangers are used in H^+ form to achieve some analytical separations of cations of interest. These exchangers exhibit better sorption of some cations in presence of complexing agents containing basic nitrogen as a donor. In fact, a careful study of these exchangers with different matrices might yield really selective exchangers, than the chelating ones known commercially.

From the separations cited, carboxylic acid exchangers appear to have greater potentialities in their applications, than what is normally expected.

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1. INTRODUCTION

In most of the inorganic applications in the laboratory as well as in industry, strong cation or anion exchangers are employed as they function well over a wide range of acidity. The weaker ones, on the contrary, exchange well with many counter ions only in their salt forms. In spite of this limitation, interesting studies are reported now and then, revealing their advantages over the strong ones. This article deals with the carboxylic acid type of exchangers in general, and their use in analytical chemistry, in particular.

Carboxylic acid exchangers can be synthesized by copolymerising acrylic or methacrylic acid derivatives with divinyl-benzene⁽¹⁾, condensation of hydroxybenzoic acids with formaldehyde⁽²⁾, cyanation and hydrolysis of polymeric vinylbenzyl chloride⁽³⁾ etc. Zeckarb 226, Amberlite IRC-50, Biorex-70, Permutit H-70, Kationite SG-1, KB-4P and Merck IV are some of the commercially available exchangers, mostly prepared by copolymerisation reaction. The same functional group is present in furan-carboxylic acids⁽⁴⁾, graft copolymers of cellulose with poly acrylic or methacrylic acids⁽⁵⁾ etc.

These exchangers are used in the recovery of valuable metals⁽⁶⁻¹²⁾, water softening⁽¹³⁾, preparation of acids from the corresponding metal salts⁽¹⁴⁾, purification of antibiotics^(15,16), exchange of ligands^(17,19), separation of aminoacids⁽²⁰⁾, etc.^(21,22).

2. SAIT FORM

Alkaline medium: Carboxylic acid exchangers possess an unusually high affinity for H^+ . Accordingly sorption of some metal ions is found to be poor against H^+ ⁽²³⁻²⁶⁾. In neutral and alkaline media, it is difficult to

keep many cations in solution without using complexing agents. These factors may be partly responsible for the lack of interest shown by Analytical Chemists for a long time in the use of these exchangers in inorganic analysis. While working with organic cation exchangers with ionogenic groups of different acid strengths, Nelson and Walton⁽²⁷⁾ have realized that the increased exchange capacity in alkaline solutions could be of value in the sorption and separation of heavy metals, which form complexes with ammonia. Subsequently, Honda⁽²⁸⁾ reported a separation of copper and nickel on Amberlite IRC-50 (XE-88) in NH_4^+ form using ammonium chloride (0.8N) and ammonium hydroxide (3N) mixture as the eluent. Edge⁽²⁹⁾ reported the separation of copper from chromated wood preservatives by making an aliquot ($\text{CuSO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7/\text{CuSO}_4 + \text{ZnSO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7/\text{CuSO}_4 + \text{Na}_3\text{AsO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7/\text{CuSO}_4 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{Cr}_2\text{O}_7$) alkaline with ammonium hydroxide to dissolve the basic copper salt and passing through a column of Amberlite IRC-50. Copper alone is retained on the column. More recently Grays and Walton⁽³⁰⁾ separated lead from silver on Biorex-70 using a mixture of diethanolamine (1.0M) and its nitrate (0.5M) as the eluent. Silver was eluted rapidly and was free from lead. In the above mentioned separations, metal ions are kept in solution in alkaline medium by complexation with ammonia and its derivatives.

Neutral or weakly acid medium: Based on the observation that NH_4^+ is preferred over Li^+ by a carboxylate exchanger (Merck IV)⁽³¹⁾, conditions are worked out in our laboratory for the separation of alkalis from reactor grade uranium employing 1.0N ammonium chloride as the eluent⁽³²⁾. Under these conditions, alkaline earths are also retained by the exchanger. Studying the conditions of quantitative elution of lithium with ammonium chloride from a column of ZeoKarb 226 (NH_4^+), a method of separation of alkalis from Mg, Ca, Sr, Ba, Mn, Cu, Co, Ni, Zn, Fe, Al, Th, U and rare earths is worked out and applied for the determination of alkalis in silicate ores⁽³³⁾. The alkalis are quantitatively eluted with

0.1N ammonium chloride. Soldatov et al⁽³⁴⁾ have studied the distribution of Na^+ , K^+ , Mg^{2+} and Ca^{2+} between KB-4 exchanger and ammonium chloride solution. Though a complete separation of all the four cations is not achieved, separation of Na^+ and K^+ together from Ca^{2+} and Mg^{2+} was reported to be easier than on a sulphonic acid type of exchanger.

Ag^+ and Tl^+ are not only preferred to NH_4^+ but also sorbed strongly on carboxylate exchangers. However, studies of K_d values of these and some polyvalent cations (Table 1) as a function of ammonium ion concentration in the solution phase⁽³⁵⁾ reveal that those of Ag^+ and Tl^+ are lower than those of polyvalent ions like Zn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , UO_2^{2+} , Al^{3+} and Th^{4+} in presence of, say, 1.0N ammonium ion. On this basis, conditions for the separation of Tl^+/Ag^+ from many polyvalent cations are worked out in our laboratory employing 1.0N ammonium salt as the eluent^(35,36). This principle is successfully applied for the separation of thallium at 5 ppm level from high purity zinc and zinc-base alloys used in die casting industry⁽³⁶⁾ and for the separation of thallium from lead in their alloys⁽³⁶⁾. It is shown that small amounts of silver can also be separated from zinc-cadmium phosphors with ammonium nitrate as the eluent⁽³⁷⁾. In these methods, the sample solution is mixed with the exchanger in a beaker and then the contents of the beaker are transferred to a column of the exchanger. This obviates channelling of the column due to significant shrinkage of the exchanger on sorption of polyvalent cations.

For the determination of copper at ppb levels in distilled water, used in biochemical work, it is shown that copper⁽³⁸⁾ is collected quantitatively from a litre of sample on a very small column of 0.1 g exchanger (0.4 x 2.0 cm) and determined by neutron activation analysis. The sodium activity is eluted with 10 ml of 1.0M ammonium chloride.

Just as in the case of alkali ions a reversal of the selectivity order for alkaline earths is suggested⁽³⁹⁾ on carboxylic acid exchanger compared to

that reported on a sulfonic acid one. However, the experimentally observed one is $Ra < Ba < Sr < Mg < Ca$ ⁽⁴⁰⁾. Employing 1M ammonium chloride as the eluent on ZeoKarb 226 in NH_4^+ form, separation of calcium from strontium, and radium from other alkaline earths appears feasible⁽⁴¹⁾. Experiments are in progress to determine the optimum conditions for quantitative separations.

For the separation of copper from nickel⁽²⁸⁾ or silver from lead⁽³⁰⁾, earlier workers have employed mixtures of a base and its salt as eluents. These two separations can easily be achieved using ammonium salt alone as the eluent as per the data in Table 1. Further, K_d values of copper, nickel and silver in ammonium hydroxide, ammonium nitrate and a mixture of base and salt (Table 2)⁽⁴²⁾ indicate that the separation is easier with salt alone as the eluent than a mixture of base and its salt. It is interesting to note that the order of K_d values of copper and nickel in a mixture of base and salt is the reverse to that in presence of either component in the solution phase.

There are two other advantages of using ammonium salt alone as the eluent in the above mentioned separations. No complexing agent is used. There is no necessity of working in ammonical solutions, as suggested earlier by Nelson and Walton⁽²⁷⁾. As such cations which do not form complexes with bases can also be handled.

Differences in the stability constants of complexes of metal ions with a ligand are also made use of for analytical separations. Uranium^(43,44) and beryllium⁽⁴⁵⁾ are separated from many others in presence of EDTA. It is shown that this principle is applicable for the separation of silver from zinc-cadmium phosphors also⁽⁴⁶⁾. All the zinc and cadmium in a sample, but for a millimole, is complexed with EDTA at pH 7.0. The solution is passed through a column of ZeoKarb 226, followed by 100 ml of 0.0025M EDTA. The effluent contains all the zinc and cadmium. It may be pointed out that chromatographic separation of cations with complexing agents will generally be easier on sulphonic acid

exchangers than on the carboxylate ones.

Separation of cations from anions: Copper is separated from chromate, borate and arsenate employing Amberlite IRC-50⁽²⁹⁾. On ZeoKarb 226 uranyl ion is separated from borate⁽⁴⁷⁾. Separations of cations from anions will be easier on carboxylate exchangers than the sulphonic acid type.

3. ACID FORM

Without using complexing agents: It has been mentioned earlier⁽²³⁻²⁶⁾ that sorption of cations is poor against H^+ of a carboxylic acid exchanger. In 1960s Kazantsev et al⁽⁴⁸⁻⁵⁰⁾ reported sorption of some cations, on saturation of a column with concentrated metal solutions (0.1M). Recently a systematic study of K_d values of several cations on ZeoKarb 226 as a function of pH (1-6) is reported (Fig.1)⁽⁵¹⁾. From solutions at pH 1.0, Bi^{3+} is the only cation that is strongly sorbed. As the pH increases, sorption of other cations also increases.

Separation of nickel from uranium⁽⁴⁹⁾ is easily achieved in view of the large difference in sorption from solutions at pH 3.0. When the separation of calcium from thorium⁽⁵²⁾ as well as gadolinium from uranium⁽⁵³⁾ are tried based on similar differences, a small fraction of calcium and gadolinium is retained on the column rather tenaciously. However, quantitative separations are obtained when lanthanum⁽⁵²⁾, aluminium⁽⁵²⁾ or o-phenanthroline⁽⁵³⁾ are added to the solutions of calcium and gadolinium before passing through the exchanger. While working out a procedure for the sequential separation of uranium, thorium and rare earths also⁽⁵⁴⁾, a similar retention of rare earths and their elution in presence of phenanthroline is observed. When a mixture of thorium, uranium and rare earths in nitrate medium in presence of phen at pH 2.0 is passed through ZeoKarb 226, rare earths pass through. These procedures bring out two points of interest for further investigation. How a small fraction of cations with little sorption are retained on a column rather

tenaciously? How does the presence of aluminium, lanthanum or phen facilitate their quantitative elution? In a very qualitative way, this may be compared to surface modified (gas) chromatography⁽⁵⁵⁾ in which tailings of components are minimised.

Another useful application is the separation of traces of thallium and indium from zinc and zinc-base alloys employing ZeoKarb 226(H⁺)⁽³⁶⁾. From sample solutions at pH 3.0, these elements are retained by the exchanger (along with iron), while other associated elements readily pass through the column.

High selectivity: A very selective sorption of gold(III) is reported by Fritz and Millen⁽⁵⁶⁾ on a porous polyacrylate resin XAD-7 from 0.1N acid solutions. Similarly bismuth in 0.1N nitric acid medium is very selectively sorbed by ZeoKarb 226 and is being made use of for practical applications⁽⁵⁷⁾.

Use of complexing agents: It has been observed earlier that ZeoKarb 226 sorbs phen and, in its presence, cations which form complexes with it⁽⁵⁸⁾. K_d values of several cations in presence of phen as a function of pH are reported subsequently⁽⁵¹⁾. Though many cations are reported to form complexes with phen⁽⁵⁹⁾, K_d values of some cations like alkaline earths, and thorium are lower than those in absence of phen. The utility of phen for a quantitative elution of calcium⁽⁵³⁾, gadolinium⁽⁵³⁾ and rare earths⁽⁵⁴⁾ is already mentioned earlier.

K_d of thorium decreases from 1720 to 340 in presence of phen on ZeoKarb 226 at pH 2.0, while that of uranium(VI) increases from 230 to 2770. In such a situation 0.05M EDTA at pH 4.5 is successfully used as an eluent to separate thorium from uranium⁽⁵¹⁾. The same eluent might work in the absence of phen also in view of the large difference in the stability constants but with a lower separation factor. Podcr⁽⁶⁰⁾ reported that uranium is selectively sorbed from solutions containing EDTA (pH 7.0) by Amberlite IRC-50, while many

other cations pass through the column as anionic complexes. Blasius et al⁽⁶¹⁾ separated palladium from rhodium, iridium and platinum by sorbing the former on Amberlite IRC-50, charged with salicylaldehyde.

Separation of cations from anions: ZeoKarb 226 is found to be useful in the separation uranium from boric acid⁽⁶²⁾.

In the opinion of the author, the above mentioned separations serve as examples to indicate the potentialities of weak cation exchangers. One serious drawback is the large differences in swollen volumes of the exchanger in different ionic forms. With the availability of macroreticular and isoporous exchangers of this type commercially, they may find many more applications.

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Table 1

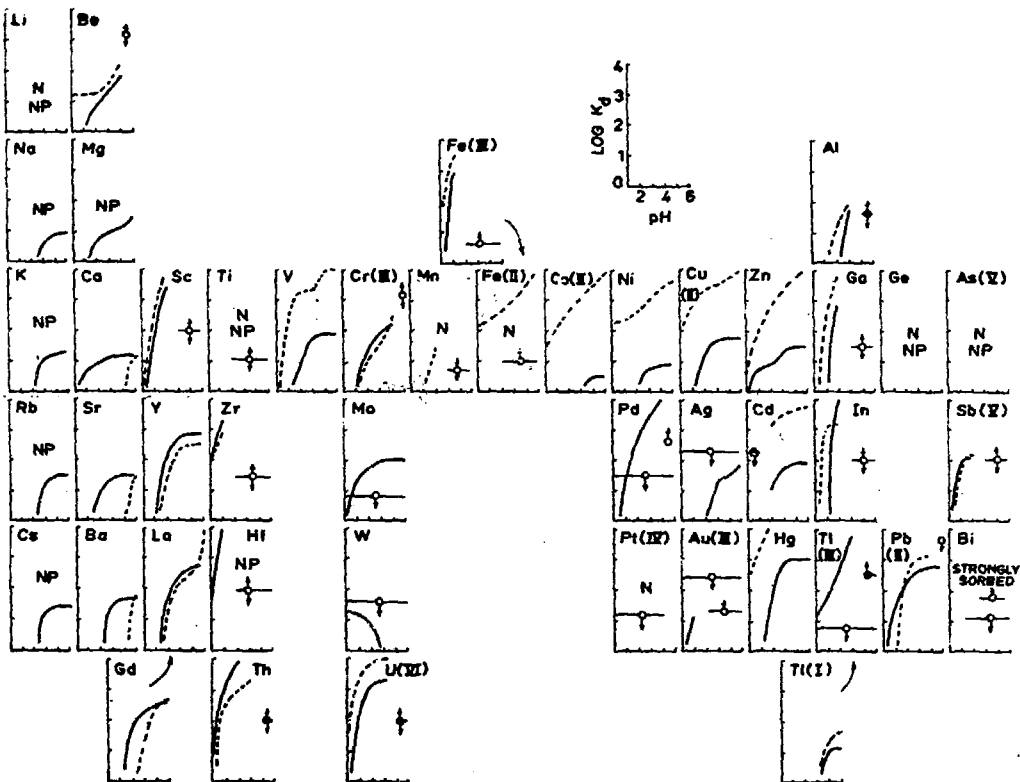
K_d OF METAL IONS IN PRESENCE OF AMMONIUM SALT

Metal ion	K_d in presence of ammonium salt				
	-	0.5M	1.0M	1.5M	2.0M
Tl ⁺	6560	25	9	7	< 5
Ag ⁺	>10 ⁴	100	60	43	30
Mg ²⁺	"	194	95	53	36
Ni ²⁺	"	910	290	181	105
Zn ²⁺	"	6560	4900	4030	3530
Cd ²⁺	"	7040	5960	5450	4900
Cu ²⁺	"	>10 ⁴	9900	6150	3350
Pb ²⁺ , UO ₂ ²⁺ , Al ³⁺ , Th ⁴⁺	"	"	>10 ⁴	>10 ⁴	>10 ⁴

Table 2

K_d OF METAL IONS IN PRESENCE OF A BASE, ITS SALT AND MIXTURE

Metal ion	K_d values in presence of		
	NH ₄ OH 1.0M	NH ₄ NO ₃ 1.0M	NH ₄ OH + NH ₄ NO ₃ (0.5M each)
Cu ²⁺	>10 ⁴	9900	80
Ni ²⁺	7785	290	96
Ag ⁺	260	60	5
K_d values in absence of base and salt are			>10 ⁴



K_d VALUES OF METAL IONS ON ZEO-KARB 226 (H^+)

N - NO ADSORPTION NP - NO ADSORPTION IN PRESENCE OF PHEN
 ○ - PRECIPITATION ○ - PRECIPITATION