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Cation Exchange Distribution Studies Of Th(IV), Mg(II), Ni(II) & Cu(II) Ions in Aqueous-organic Solvent-HCl Media

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Summary: Distribution coefficients have been measured for the partition of metal ions, Th(IV), Mg(II), Ni(II) and Cu(II) between cation exchange resin of Dower HCR-S and water-, water - organic solvent - HCl solutions. The effect of variation in concentration of isopropanol, acetone and dioxane on the distribution coefficients of the metal ions have been studied. The effect of change in the acidity of the medium has also been studied by varying (HCl). The possibilities of several useful separations has been suggested and the distribution coefficient data was calculated.

Introduction

Previous investigations have shown that, a number of metal ions in aqueous solution were found to be affected by using varying concentration of HCl as eluting agent[1,2]. A study has been made of the ion exchange behaviour for Mg(II), Cu(II), Ni(II) and Th(IV) in HBr and HF solutions in presence of Dower 50-x8. As the results show useful cation exchange separation of elements can be achieved[3,4].

The behaviour of several metal ions on Zeo-Karb 225 cation exchanger has been studied using acetone-water-HCl system as eluent, for possible separation of Cu(II) and Ni(II) ions. On the other hand, such system was found to be less effective in certain separation; such as Co(II)-Mg(II) and Fe(III)-Cu(II)-Zn(II)[5].

In addition a large amount of Ca(II) can be separated from Mg(II) and also Co(II) from Ni(II) by means of cation exchanger using Imac-20Ar at 90% (vol/vol) ethanol or acetone and at isopropanol-0.6$\underline{N}$ HCl system for Mg(II) and Ni(II) ions[6].

The aim of the present work is to determine and evaluate the values of the distribution coefficients for some di-and tetravalent ions using Dower HCR-S cation exchange resin, in presence of 0.005$\underline{N}$-1.0$\underline{N}$ HCl. The effect of variation in concentration of metal ions on the distribution coefficients were also investigated. Some possible separation are discussed and tabulated results given from the distribution data.

EXPERIMENTAL

The exchange resin Dower HCR-S (cation exchanger), (250-420 mesh size, hydrogen form) was used for batch and column separation[6-7]. The capacity was 3.85 meq/g dry resin.

Standard solutions: stock solution of Ni(II), Mg(II), Cu(II) and Th(IV) ions were prepared by dissolution of the chloride of these metal ions in aqueous, aqueous - organic media. Each solution containing different concentration of HCl in presence of different variation of isopropanol, acetone and dioxane.

Most investigated elements were determined by titrations with EDTA-disodium salt as the titrant. The indicators used were; Muroxide for Ni(II), Erichrom Black T for Mg(II), methyl thymol blue for Cu(II)[8] and Solochromate Fast Red is used as the colour for Th(IV).

In case of separation procedure (Beckman Model B spectrophotometer type)-1cm cell was used.

Procedural studies were carried out by equilibrating in glass stoppered flask (100ml) at 25°C $\pm$ 0.1°C, each system containing 1g of resin and 50ml of the respective metal ion solution (0.005-0.025M) in aqueous or aqueous-organic-HCl media. After shacking in thermostate for 8hr. each solution was analysed for the studies of metal ions.

Determination of k_d-values were assumed from the following relation[7].

$$K_d = \frac{\text{meq metal / g of dry resin}}{\text{meq metal / ml of solution}}$$

The column separation procedure was the same as reported earlier by several authors[10-11].

Results and Discussion

Distribution coefficient values of Mg(II), Ni(II) Cu (II) and Th(IV) ions in different concentrations were measured in aqueous - 0.005N HCl are given in Table 1. The obtained results indicate that the k_d - value decreases with increasing metal ions concentration. The dependence of the k_d-values on the metal ion concentrations are accordance with Pauling's electronegativity values of these metal ions[12]. However k_d-values of Cu(II) and Ni(II) ions give the highest values as the corresponding values for other metal ions.

Investigation with respect to the effect of HCl acid concentration on the distribution coefficients of the studied metal ions, indicate that the sorption of the investigated metal ions decrease rather strongly with increasing concentration of HCl. At 0.005M of metal ions, the k_d-values of Ni(II), Cu(II) and Mg(II) decrease consequently with increasing the concentration of HCl, whereas for Th(IV) the k_d-values increase with increasing of HCl concentration up to 0.2N. The chloro-complex of thorium has been found to be less stable in HCl of 0.2N[13], as shown in Table-2.

Results given in Table-3, indicate that the elements studied in the present work can be divided into two groups; with varying isopropanol concentration 0-90% (vol/vol) and at constant acidity of 0.05N HCl, one group of metal ions is completely absorbed on the cation exchange resin Cu(II) and Ni(II) ions. The other group of k_d values increase with increase in isopropanol solution Mg(II) ion. However the distribution coefficients of Th(IV) is dropped sharply. The decrease in the k_d-values at higher isopropanol concentration may be attributed to the formation of chloro-complex of this element which is held less strongly with uptack by the resin. It is interesting to show that the addition of polar organic solvent such as isopropanol to water solution at HCl of (0.05-1.0N), modifies the selectivities in a number cases which are otherwise unattainable

Table 1: Distribution Coefficients for Various Metal Ions Concentrations at 0.005N HCl Solution.

Metal ion Conc., M	kd-values			Th(IV)
	Ni(II)	Cu(II)	Mg(II)	
0.005	737.032	1230.269	758.578	645.654
0.010	239.883	371.535	208.930	288.403
0.015	151.356	177.828	60.256	125.893
0.020	104.713	104.713	14.125	35.48
0.025	83.176	74.131	4.786	14.791

Table 2 - Distribution Coefficients of Some Elements in Various HCl Concentrations Containing a Fixed Concentration of 0.005M Metal Ions.

HCl Conc., (M)	kd-values			Th(IV)
	Ni(II)	Cu(II)	Mg(II)	
1.00	0.000	22.909	0.000	398.107
0.50	43.652	114.815	0.000	450.550
0.20	117.828	301.995	14.791	1778.279
0.10	316.228	354.813	39.811	1819.701
0.05	457.088	436.516	353.813	1584.890
0.01	691.831	645.000	794.328	1071.519

Table 3: Distribution Coefficients in 0.05.0.1, 0.5 and 1.0M HCl with Various Isopropanol Concentrations.

Isopropanol; %	HCl, Conc. (N)	Kd-values			
		Mg(II)	Ni(II)	Mg(II)	Th(IV)
00	0.05	354.813	457.088	436.516	1584.890
30	0.05	528.571	C.S.	C.S.	866.670
60	0.05	617.660	C.S.	C.S.	975.090
90	0.05	739.850	C.S.	C.S.	300.000
00	0.10	39.811	316.288	354.813	1819.701
30	0.10	514.290	C.S.	C.S.	C.S.
60	0.10	542.940	C.S.	C.S.	C.S.
90	0.10	690.870	C.S.	C.S.	200.000
00	0.50	0.000	4.30	114.815	700.000
30	0.50	27.273	32.42	186.175	1466.670
60	0.50	68.420	C.S.	230.760	600.000
90	0.50	266.636	C.S.	241.700	146.141
00	1.00	0.000	0.000	22.909	398.107
30	1.00	0.000	0.000	40.820	1300.375
60	1.00	11.045	0.000	77.280	362.430
90	1.00	175.756	0.000	18.510	74.273

in aqueous medium as shown in case of Th(IV) ions. Ni(II) and Cu(II) ions are completely adsorbed at 0.1N HCI-30-90% (vol/vol) isopropanol, Ni(II) is completely adsorbed at 60-90% (vol/vol) isopropanol -0.5N HCl solution.

Moreover, an increase in hydrochloric acid concentration up to 1.0N HCl, considerably lower the distribution coefficient values, this change become more pronounced as the ability of the elements Mg(II) and Ni(II) ions to form negatively charged ions.This behaviour gave a zero kd-values at all percentage of isopropanol. Our results agree well with those of Korkisch[14], who used THF-water-20% HCl mixtures.

Moreover, the distribution coefficient values decrease considerably in a number of cases rather than in case of Th(IV) according to the following order; 0.05 > 0.1 > 0.5 > 1.0M in case of divalent ions, whereas in case of Th(IV) the sequence is found; 0.1 > 0.05 > 0.5 > 1.0N.

Studies carried out in aqueous-acetone and dioxane solutions with varying HCl concentration gave useful indication regarding exchange trends as compared with isopropanol, except for Mg(II) with increasing percentage of acetone the adsorption of Mg(II) ion decreases[13] up to 50% (vol/vol). In Ni(II) and Cu(II) ions the kd values increase up to 30% (vol/vol) of dioxane. Mg(II) show a decrease in kd-values at low dioxane composition up to 30% (vol/vol). The observed rise or fall in the kd values with varying concentration of organic solvents may be due to solvent partition phenomena[16].

Separation of elements:

The Dowex HCR-S resin column had a length of 30cm and diameter 1.2cm. It was first washed with 0.5N HCl; 2ml of CuCl2 solution was mixed with MgCl2, the mixture was passed through the column at a flow rate of 0.3ml. 30ml of the 0.5N HCl solution was passed through the column at the flow rate as·mentioned above. This is quantitatively

Table 4: Distribution Coefficients of Mg(II), Ni(II) and Cu(II) in 0.05N HCl-Water-Acetone Mixtures

	Kd-Values					
Acetone, %						
		Metal ion concentrations				
	0.005M			0.01M		
	Mg(II)	Ni(II)	Cu(II)	Mg(II)	Ni(II)	Cu(II)
30	1059.25	645.64	1348.96	457.08	316.22	380.18
50	831.76	792.33	1972.42	323.594	446.68	416.87
70	1174.89	1273.50	2041.74	495.45	402.71	466.68
90	1659.59	2187.76	1698.76	478.63	436.51	426.58
00	1109.17	1230.26	1412.53	530.88	316.22	473.15

Table 5: Distribution Coefficients of Mg(II), Ni(II) and Cu(II) in 0.05N HCl-Water-Dioxane Mixtures

	Kd-Values					
Dioxane, %						
		Metal ion concentrations				
	0.005M			0.01M		
	Mg(II)	Ni(II)	Cu(II)	Mg(II)	Ni(II)	Cu(II
30	1380.40	3467.40	1513.60	478.63	426.58	501.18
50	1230.27	851.14	1949.85	537.03	407.38	436.51
70	489.78	1288.25	1148.15	575.44	354.81	338.84
90	707.94	1737.80	338.84	489.77	281.83	147.91
00	1122.00	1258.92	1412.53	595.66	316.22	473.15

enough to elute out Mg(II). Copper was next eluted with 80ml of 1.0N HCl. The concentration of Mg(II) and Cu(II) ions were determined, Fig-1A. Amount taken (amount recovered) for the two ions was: Mg(II) 10.0mg (9.90mg) Cu(II) 10.0mg (9.96mg). Fig1C. Amount taken (amount recovered) 5.0mg (5.0mg); Cu(II) 5.0mg (4.99mg).

The values of distribution coefficients measured in different orgnic media, could be used to arrive at optimum conditions for the separation of different metal ions. Thus in a medium such as 0.05N HCl- 30% (vol/vol) acetone, it is possible to separate Ni(II) from Cu(II) because of large difference in their kd values. A 0.05N HCl -90% (vol/vol) dioxane seems to best medium to separate Cu(II) from Mg(II) ions.

Based on the results in the present study, Cu(II) was separated from Th(IV) using the procedure mentioned above. The first elution solvent required to elute Th(IV) was 0.1N HCl-90% (vol/vol)
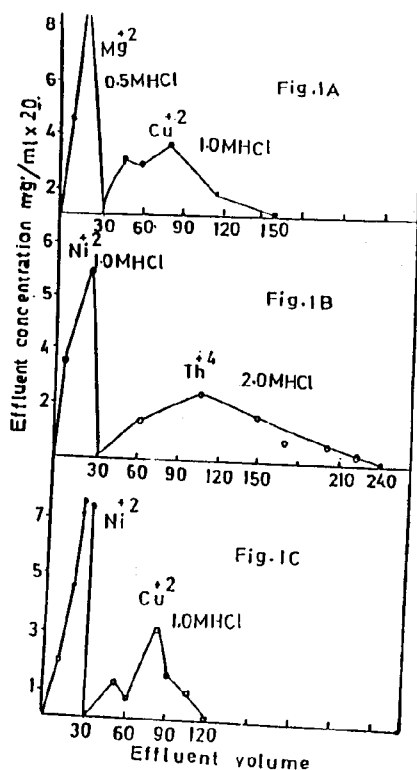
Fig. 1: Elution curves for the separation of Mg(II) and Cu(II) (A), Ni(II) and Th(IV), and Ni(II) and Cu(II) using Doewx HCR-S cation exchanger.
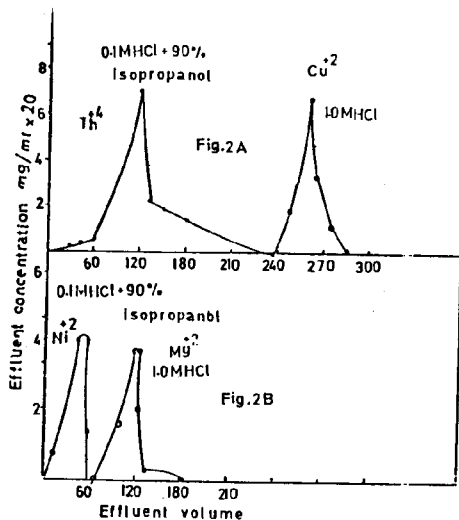

Fig. 2: Elution curvesffor the separation ofTh(IV) and Ni(II) (A) and Ni(II) and Mg(II) (B) using Dowex HCR-S cation exchanger.

isopropanol 280ml. Cu(II) was next eluted with 1.0N HCl Fig.2A. Amount taken (amount recovered); Th (IV) 5.0mg (4.775mg); Cu(II) 5.0mg (5.0mg).

Next Mg(II) was separated from Ni(II) following the same procedure except that the first elution solvent was 1.0N HCl-90% (vol/vol) isopropanol which eluted Ni(II) in 3 fractions. Mg(II) was next eluted with 1.0N HCl in 6 fractions of 20ml. Fig.2B. Amount taken (amount recovered) Mg(II) 10.0 mg (10.0mg); Ni(II) 10.0mg (10.0mg).

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