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ADSORPTION BEHAVIOR OF Mg (II), Cu (II), Ni (II), Pb (II), Ba (II), Zn (II), Cd (II) AND Al (III) IN AQUEOUS ACETONE- AMMONIUM PROPIONATE MEDIA

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ABSTRACT

From the investigations of ion exchange in mixed solvents, it is apparent that adsorption equilibrium depends markedly on the properties of the organic solvent and reactions with the resin and electrolytes which determine the equilibrium. A variety of complexing media have been used to study the metal ion exchange on cation exchangers and their uses has been done in many analytical separations. Almost the mineral acids and their salts from a class of complexing agents which has been used by many workers. As the presence of water miscible polar solvents proved to be advantageous in the metal ion exchange in complexing media. The use of mineral acids and their salts has been done in a variety of non aqueous and mixed aqueous solvent**.** Fritz et al[1] separated many metal ions using 0.1 or 1 M hydrofluoric acid as the eluting agent, the method of separation of Al^{3+}, Ti^{4+} , V^{4+} and Nb^{5+} ions was studied by Dowex 50 WX8 resin in H^{+} and ethylene di -ammonium forms. Yoshimo and Koiima[2] and Strelow[3] separated cadmium from zinc and other metal ions by eluting them with 0.5 M hydrochloric acid. Strelow[4] Mann and Swanson[5] measured the equilibrium distribution coefficients which are a useful guide to possible cation exchange separations in aqueous solution. Equilibrium distribution coefficients of cations in hydrochloric acid[6], nitric acid, sulphuric acid media using BIO-RAD AG, 50 WX8, Sulforated polysterene resin have been worked out and the possibilities of separation of various metal ions indicated with the help of the distribution coefficients.

KEYWORDS: Dowex 50 WX_8 (NH_4^+ form), Aqueous ammonium propionate, Diffusion coefficient (K_D), Binary mixtures, Eluting agent.

INTRODUCTION

Selective sorption and elution of metal complexes on cation exchangers has been shown in recent years to be an extremely powerful tool for metal ion separations. The distribution coefficients (K_D) were found out at various percentages of acetone and at various concentrations of ammonium propionate solutions. The distribution coefficient is explained on the basis of variations in dielectric constants of mixed solvents. The data on distribution coefficients are used to find out the optimum conditions of metal ion separations. The results of column chromatographic separations of binary mixtures containing Cu (II), Ni(II), Pb (II), Mg (II), Ba (II), Zn (II), Cd (II), Al (II), are given (table no. 7).

MATERIAL AND METHODS

The distribution coefficients (K_D) The distribution coefficient K_D was determined by batch equilibrium method. 1 g of air dried Dowex 50 WX8 (NH_4^+ form) resin was taken in 250 ml glass stoppered Erlynmeyer flask. 4 ml of 0.0N metal ion solution and 50 ml of the appropriate aqueous acetone-ammonium propionate mixtures was taken. The flask was stoppered and kept for 24 hr. after 24 hrs an aliquot from the supernatant liquid was pipette out and acetone was evaporated. The metal ion content was determined by suitable titration method.

The pyrex glass chromatographic columns of 50 ml capacity were used. The columns were provided with safety device to maintain the ion exchangers under liquid. The column was packed with a glass wool at the bottom and slurry of 10 g soaked resin was passed and was allowed to settle by occasional tapping. A care was taken to prevent the formation of air pockets.

The column was equilibrated with the resin by passing 20 ml of aqueous acetone - ammonium propionate mixture at maximum flow rate. The binary or tertiary mixtures of various metal ions were prepared. It was allowed to pass down the column slowly without allowing the level of the liquid to drop below the surface of the exchanger. The proper quantity of eluting agent was added. The effluent fractions were collected in test tunes by maintaining a flow rate of 1ml/min. Under specified experimental conditions the first metal ion starts eluting and gets completely eluted at particular fractions. After complete removal of the two metals elution is stopped. The metal ion contents in the collected fractions were estimated by standard volumetric procedures.

RESULTS AND DISCUSSION

The distribution coefficients of Pb, Cd, Zn, Cu, Al, Ba, Ni and Mg, were found out at 0, 20, 40, 60 and 70 percentages of acetone at 0.02, 0.06, 0.1, 0.2, 0.4, 0.6M ammonium propionate solutions. The values are given in Tables 1-6. The distribution coefficients of all metal ion are high all percentages of acetone at 0.02 M solution of ammonium propionate. The dissociation of ammonium propionate in liquid phase is due to the low dielectric constant. The dissociation takes place as

$$CH_3\text{-}CH_2\text{-}COOH_4 \longleftrightarrow CH_3CH_2\text{-}COO^- + NH_4$$

In presence of water, the salts like $C_2H_5COOH\ NH_4$ undergoes hydrolysis. These salts are of weak base NH_4OH and weak acid like C_2H_5COOH. The distribution coefficients of Cu, Ni, Zn, Cd, Pb, Ba, Al and Mg are continuously decrease with increase in the $C_2H_5COOH\ NH_4$ concentration at the respective percentages of acetone. There are at least four main factors involved in such exchange equilibriums are –

1. The mass action effect of ammonium ion in the exchange reaction.
2. Complex ion formation of the metal ion with propionate ($C_2H_5COO^-$) ion.
3. Changes in the salvation shell of each metal ion other than those due to complex ion formation i.e. dehydration.
4. Shrinkage of the resin.

Separation of Pb/ Cd/Zn/Al/Ba/Cu/Ni-Mg

Mg bound strongly as compared to the other cation. Hence it remain adsorbed on the column Pb/ Cd/Zn/Al/Ba/Cu/Ni are removed from the column by 20% $CH_3\ COCH_3$ – 0.1 $C_2H_5COO\ NH_4$ and Mg was stripped off by 40% CH_3COCH_3 - 0.4 M $C_2H_5COONH_4$.

CONCLUSION

Magnesium was separated from co-ion in binary mixtures. From the investigations of ion exchange in mixed media solvents, it is apparent that the adsorption equilibrium depends markedly on the properties of the organic solvent and the reactions with the resin and electrolytes which determine the equilibrium. Selective sorption and elution of metal complexes on cation exchange is powerful tool for metal ion separation.

Table 1: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.02M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	673.2	382.3	283	72.85	50.89
Ni (II)	1262	1262.0	1091.0	1091.0	531.0
Pb (II)	837	415	153.2	20.25	N.A
Mg (II)	675	362.5	362.5	362.5	154.3
Ba (II)	745.3	745.3	745.3	745.3	256.5
Zn (II)	224.1	224.1	217.3	80.84	56.14
Cd (II)	578.6	215.6	104.0	60.37	31.97
Al (III)	195.0	105.7	86.08	67.14	55.31

T.A = Total Adsorption,

N. A = No Adsorption

Table 2: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.06M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	71. 36	49.6	36.45	36.45	28.01
Ni (II)	248.8	170.0	115.8	64.31	51.30
Pb (II)	69.76	12.49	N.A	N.A	N.A
Mg (II)	460.7	295.9	295.9	219.4	154.3
Ba (II)	130.0	92.12	38.01	10.52	T.A
Zn (II)	152.1	112.6	47.68	14.09	71.71
Cd (II)	82.04	70.96	33.36	7.307	5.478
Al (III)	86.08	32.20	18.31	12.89	N. A

T. A = Total Adsorption,

N. A = No Adsorption

Table 3: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.1M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	32.52	23.36	23.36	23.36	21.75
Ni (II)	108.9	108.9	48.23	0.92	30.92
Pb (II)	26.27	N. A	N.A	N.A	N.A
Mg (II)	675	675	295.5	258.4	159.3
Ba (II)	51.70	20.15	6.750	N. A	N. A
Zn (II)	57.86	34.97	16.52	5.311	5.311
Cd (II)	3.638	33.36	14.02	N. A	N. A
Al (III)	24.63	20.69	6.262	1.333	1.333

T.A = Total Adsorption,

N. A = No Adsorption

Table 4: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.2M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	17.76	12.11	5.241	5.241	5.241
Ni (II)	17.63	9.126	N.A	N.A	N.A
Pb (II)	15.61	N. A	N.A	N.A	N.A
Mg (II)	270	270	237.6	203.2	N.A
Ba (II)	1.779	N.A	N.A	N. A	N. A
Zn (II)	N.A	N.A	N.A	N.A	N.A
Cd (II)	7.406	N.A	N.A	N. A	N. A
Al (III)	17.14	9.126	N.A	N.A	N.A

T.A = Total Adsorption,

N. A = No Adsorption

Table 5: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.4M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	2.518	2.227	1.403	1.403	1.403
Ni (II)	N.A	N.A	N.A	N.A	N.A
Pb (II)	N.A	N. A	N.A	N.A	N.A
Mg (II)	295.9	195.9	87.10	N.A	N.A
Ba (II)	N.A	N.A	N.A	N. A	N. A
Zn (II)	8.143	7.171	N.A	N.A	N.A
Cd (II)	N.A	N.A	N.A	N. A	N. A
Al (III)	2.735	N.A	N.A	N.A	N.A

T.A = Total Adsorption,

N. A = No Adsorption

Table 6: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.6M).

Ion	Acetone % $^V/_V$				
	0	20	40	60	80
Cu (II)	0.500	N.A	N.A	N.A	N.A
Ni (II)	N.A	N.A	N.A	N.A	N.A
Pb (II)	N.A	N. A	N.A	N.A	N.A
Mg (II)	295.9	189	189	N.A	N.A
Ba (II)	N.A	N.A	N.A	N. A	N. A
Zn (II)	1.929	1.129	N.A	N.A	N.A
Cd (II)	N.A	N.A	N.A	N. A	N. A
Al (III)	7.398	N.A	N.A	N.A	N.A

T.A = Total Adsorption

N. A = No Adsorption

Table 7: Quantitative Separation of Synthetic Binary Mixtures (First Ion in the mixture is eluted, while the second ion is that which is retained.).

Sr. No	Mixture	Metal ion eluted	Eluting agent	m moles taken	m moles found
1	Pb (II) + Mg (II)	Pb (II)	c	0.200	0.288
		Mg (II)	d	0.201	0.195
2	Cd (II) + Mg (II)	Cd (II)	c	0.200	0.196
		Mg (II)	d	0.201	0.195
3	Zn (II) + Mg (II)	Zn(II)	c	0.212	0.199
		Mg (II)	d	0.201	0.195
4	Cu (II) + Mg (II)	Cu (II)	c	0.220	0.215
		Mg (II)	d	0.201	0.195
5	Al (III) + Mg (II)	Al(III)	c	0.235	0.227
		Mg (II)	d	0.201	0.195
6	Ba (II) + Mg (II)	Ba (II)	c	0.200	0.189
		Mg (II)	d	0.201	0.195
7	Ni (II) + Mg (II)	Ni (II)	c	0.160	0.149
		Mg (II)	d	0.201	0.195

d = 20% CH_3COOCH_3 – 0.1 M $C_2H_5COONH_4$

e = 40% CH_3COOCH_3 – 0.4 M $C_2H_5COONH_4$

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