Adsorption behavior of *Cu, Co, Mn, Pb, Mg, Ca, Ba, Zn, Cd, Al,* and *Th* metal Ions on cation exchange resign Dowex 50WX8 (NH$_4^+$ Form) From Aqueous Acetone – Ammonium Butyrate media

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ABSTRACT

In the field of inorganic separation, the incentive to explore the use of non-aqueous or mixed solvent has been enhanced selectivity's, discovered quite early in such media for Zeolites [1] and ion exchange resins [2]. The partial substitution of aqueous solution by organic solvent produces a number of changes in an exchange system. Such as change in the solution structure due to the interaction between water and the organic solvent, change in the hydration and salvation of the electrolyte, change in the solvent composition in the resin phase, change in the activity coefficients of the electrolyte in the solution phase as well as in the resin phase, change in the complexation of the metal ion and change in the extent of invasion by and electrolyte. All these changes are mutually dependent and affect the distribution of the metal ion. The solution composition in the resin phase often differs very much from that in the outer solution and the difference becomes greater with less polar organic solvents. Such behavior the selective swelling is mainly attributed to the hydration and salvation proportion of the functional resin group, namely the fixed ion and counter ion. The difference in the composition of the resultant solution in the two phases enhances the invasion of electrolyte so that it is larger than in the pure aqueous solution. The electrolyte plays a significant role in the ion exchange equilibrium with aqueous solutions. This effect is expected to be even more important in the adsorption equilibriums of metal ions from mixed aqueous organic solvents. Adsorption equilibrium depends on the properties of the organic solvent reactions with resin and electrolytes which determine the equilibrium.

Keywords— Dowex 50 WX8 (NH$_4^+$ form), Aqueous acetone ammonium Butyrate, Distribution Coefficients, (K$_D$), Total adsorption (T. A.), No Adsorption (N. A.), Chromatographic separation.

1. INTRODUCTION

Firtz et al [3] separated many metal ions using 0.1 or 1 M hydrochloric acid as the eluting agent. Yoshimo and Koiima[4] and Strelow [5] separated cadmium from zinc and other metal ions by eluting them with 0.5 M hydrochloric acid. When the nitric acid is used with non-aqueous solvent, larger volume of effluent is required for qualitative elution and a slower flow rate had to be employed. Strelow[6] Mann and Swanson [7] measured the equilibrium distribution coefficients which are a useful guide to possible cation exchange separations in aqueous solution. It has been shown that metal ions are taken up more strongly at lower hydrochloric acid concentrations by an anion exchange column, if an appreciable amount of a water miscible organic solvent is added to the aqueous hydrochloric acid. [8, 9] The data on distribution coefficients are used to find out the optimum conditions of metal ion separations.

2. MATERIAL AND METHODS

The distribution coefficient, K$_D$ was determined by batch equilibrium method. 1 g of air dried Dowex 50 W X8 (NH$_4^+$ form) resin was taken in 250 ml glass stoppered Erlynmeyer flask. 4 ml of 0.05M metal ion solution and 50 ml of the appropriate aqueous acetone-ammonium butyrate mixtures was taken. The flask was Stoppard and kept for 24 hrs. After 24hrs **supernatan**t liquid was pipetted out and acetone was evaporated. The metal ion content was determined by suitable titration method. The pyrex glass chromatographic columns of 50 ml of capacity were used. The columns were provided with safety device to maintain the ion exchanger under liquid. The column was packed with a small glass wool at the bottom and slurry of 10g 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 butyrate mixture at maximum flow rate. The binary and 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 required amount of eluting agent was added. The effluent fractions were collected in test tubes by maintaining a flow rate of 1 ml/min. The presence of metal ion was tested by suitable analytical reagents in the effluent fractions. Under specified experimental conditions the first metal ion starts eluting and it is completely removed in a series of fractions collected. The second metal ion starts eluting and gets completely eluted at a 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 (Table no. 7). In case of tertiary mixtures, the first and second metal ions were eluted by suitable eluting agents and finally the third metal ion eluted by proper eluting agent (Table no. 8). The distribution coefficient (K_D) in aqueous acetone ammonium butyrate was given in table 1 to 6.

3. RESULTS AND DISCUSSION

The distribution coefficients of Cu, Co, Mn, Pb, Mg, Ca, Ba, Zn, Cd, Al, and Th were found out at 0, 20, 40, 60 and 70 percentages of acetone at 0.02, 0.06, 0.1, 0.2, 0.4, 0.6 M ammonium butyrate solutions. The values are given in table 1-6. The K_D values of thorium show total adsorption at 0.02, 0.06, 0.1 M ammonium butyrate at all percentages of acetone. Thorium shows negligible adsorption at 60, 70 % of acetone and at 0.4 and 0.6 M ammonium - butyrate. Most of the column chromatographic separations were carried out by using media containing 40% of acetone. It is observed that the distribution coefficients of all metal ions decrease with the rise in percentages of acetone. The dissociation of CH_3-CH_2- CH_2-$COONH_4$ in aqueous solution takes place as

$$CH_3\text{-}CH_2\text{-} CH_2\text{-}COONH_4 \leftrightarrow CH_3CH_2CH_2COO^- + NH_4^+$$
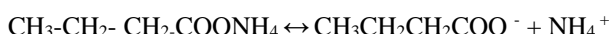
The dissociation is due to the dielectric constant. The present findings are similar to those reported earlier by Piters and Flore. [9] Akerlof [10] has determined the dielectric constants of a number of aqueous organic solvent mixtures. It is observed that the distribution coefficients of Cu, Th, Zn, Cd, Pb, Co, Ba, Mg, Ca, Mn and Al continuously decrease with increase in the ammonium propionate concentrations 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 butyrate ($C_3H_7COO^-$) ion.
3. The change in salvation shell of each metal ion other than those due to complex ion formation i.e. dehydration.
4. Shrinkage of the resin.

$$M (H_2O)_n^{x+} \leftrightarrow M (H_2O)_{n-1}^{x+} + H_2O$$
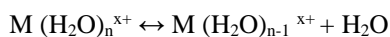
The first factor should cause the equilibrium distribution constants of the metal ions to decrease continuously with increasing ammonium ion concentration. It is observed that K_D values of all the metal ions decrease with the rise in the concentration of ammonium butyrate solutions. As per the second factor, association and complex ion formation with acetate and formate ions, the charge on complex decreases with rise in the concentration of the anions and ultimately neutral species are formed which support to the findings of decrease in K_D with increase in the concentration of anions. The results of the quantitative separation of synthetic multi-component mixtures in aqueous acetone-ammonium butyrate are presented in tables 7 and 8.

Separation of Ca/Cu/Ba/Cd/Pb/Co/Zn/Mg/Mn/Al from Th

The distribution coefficients of Ba and Th metal ions are higher than the Co ion. Al/ Mg/ Pb/ Cd/ Cu/ Zn/ Co was eluted first by 40% CH_3COCH_3- 0.1 M 40% CH_3COCH_3- 0.04 M C_3H_7COO NH_4 and Th was finally obtained by using 60% CH_3COCH_3- 0.04 M C_3H_7COO NH_4 solution as an eluent. The recovery of copper depends on the concentration of the Co ions. In case of other metal ions, there is no effect of the concentration of Co ions on the recovery.

4. CONCLUSION

The quantitative separation of various metal ions can be effectively carried out at trace level also.

Table-1: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Butyrate (0.02M)

Ion	Acetone % $^V/_V$				
	0	**20**	**40**	**60**	**70**
Cu (II)	5616	5616	2729	2781	891
Co (II)	1331	1331	444	324	324
Mn (II)	283.1	252.0	152.0	53.16	125.5
Pb (II)	1386	1023	1023	810.0	666.1
Mg (II)	966.6	966.6	966.6	955.6	955.8
Ca (II)	502.3	429.5	429.5	322.0	206.3
Ba (III)	1040.7	1952.9	3954	3954	596.7
Zn (II)	1971	1296	372.3	351.0	351.0
Cd (II)	1755	1755	1755	17.55	1755
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	T. A.	T. A.	T. A.	T. A.	T. A.

T.A = Total Adsorption,
N. A = No Adsorption

Table 2: Distribution Coefficient (K$_D$) in Aqueous Acetone Ammonium Butyrate (0.06M)

Ion	Acetone % ^{V}/$_V$				
	0	20	40	60	70
Cu (II)	252	172	135	101	101
Co (II)	777	488	292	176	513
Mn (II)	149.3	143.5	108.6	71.68	55.71
Pb (II)	10.31	9.065	N. A.	N. A.	N. A.
Mg (II)	338.6	264.9	150.1	87.7	63.3
Ca (II)	284.4	236.0	149.0	13.38	7.526
Ba (III)	1666	806	1040	1451	N. A.
Zn (II)	216	134.4	29.5	10.8	10.6
Cd (II)	172.1	88.8	25.8	2.2	N. A.
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	T. A.	T. A.	T. A.	T. A.	T. A.

T. A = Total Adsorption,

N. A = No Adsorption

Table-3: Distribution Coefficient (K$_D$) in Aqueous Acetone Ammonium Butyrate (0.1M)

Ion	Acetone % ^{V}/$_V$				
	0	20	40	60	70
Cu (II)	236.7	203	110	73	59
Co (II)	135	116	54	64	30.2
Mn (II)	90.55	75.19	33.55	40.04	39.23
Pb (II)	N. A.	24.55	N. A.	N. A.	N. A.
Mg (II)	194.9	113.3	76.85	58.15	28.3
Ca (II)	124.2	72.90	38.29	16.05	16.05
Ba (III)	654	654	427	N. A.	N. A.
Zn (II)	52.5	41.3	16.4	3.8	3.8
Cd (II)	57.8	22.9	.0.27	N. A.	N. A.
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	T. A.	T. A.	T. A.	T. A.	T. A.

T.A = Total Adsorption,

N. A = No Adsorption

Table-4: Distribution Coefficient (K$_D$) in Aqueous Acetone Ammonium Butyrate (0.2M)

Ion	Acetone % ^{V}/$_V$				
	0	20	40	60	70
Cu (II)	164	131	97	71	54
Co (II)	89	105	116	229	N. A
Mn (II)	34.05	25.91	25.0	10.59	10.59
Pb (II)	47.65	12.98	N. A.	N. A.	N. A.
Mg (II)	116.1	73.5	24.5	16.9	18.9
Ca (II)	16.05	16.05	7.157.	N. A.	N. A.
Ba (III)	253	146	N. A.	N. A.	N. A.
Zn (II)	35.9	35.9	5.1	5.1	N. A.
Cd (II)	47.43	13.41	N. A.	N. A.	N. A.
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	953	953	657	494	494

T.A = Total Adsorption,

N. A = No Adsorption

Table-5: Distribution Coefficient (K$_D$) in Aqueous Acetone Ammonium Butyrate (0.4M)

Ion	Acetone % ^{V}/$_V$				
	0	20	40	60	70
Cu (II)	87	70	52	33	33
Co (II)	92.7	265	T. A.	T. A.	T. A.
Mn (II)	10.30	4.084	3.599	3.124	N. A.
Pb (II)	14.57	N. A.	N. A.	N. A.	N. A.

Mg (II)	24.5	16.38	7.85	7.85	1.46.
Ca (II)	N. A.	N. A.	N. A.	N. A.	N. A.
Ba (III)	66.4	66.4	N. A.	N. A.	N. A.
Zn (II)	N. A.	N. A.	N. A.	N. A.	N. A.
Cd (II)	29.4	14.2	9.8	9.8	N. A.
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	618	494	145	N. A.	N. A.

T.A = Total Adsorption,
N. A = No Adsorption

Table-6: Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Butyrate (0.6M)

Ion	Acetone % $^V/_V$				
	0	20	40	60	70
Cu (II)	42	42	37.4	27	23.14
Co (II)	153	177	N. A.	N. A.	N. A.
Mn (II)	2.889	N. A.	2.656.	N. A.	N. A.
Pb (II)	21.13	N. A.	N. A.	N. A.	N. A.
Mg (II)	4.65	2.7	2.7	2.07	1.66
Ca (II)	N. A.	N. A.	N. A.	N. A.	N. A.
Ba (III)	38.6	38.6	N. A.	N. A.	N. A.
Zn (II)	N. A	N. A.	N. A.	N. A.	N. A.
Cd (II)	36.4	9.8	N. A.	N. A.	N. A.
Al (III)	N. A.	N. A.	N. A.	N. A.	N. A.
Th (II)	1150	523	214	N. A.	N. A.

T.A = Total Adsorption
N. A = No Adsorption

Table-7: Quantitative Separation of Synthetic Mixtures

Sr. No	Mixture	Metal ion eluted	Eluting agent	m moles taken	m moles found
1	Ni (II) +Th (II)	Ni (II)	d	0.252	0.250
		Th (II)	e	0.120	0.115
2	Co (II) + Th (II)	Co (III)	d	0.240	0.239
		Th (II)	e	0.120	0.115
3	Cu (II) + Th (II)	Cu (II)	d	0.240	0.239
		Th (II)	e	0.120	0.115
4	Cd (II) + Th (II)	Cd (II)	d	0.249	0.247
		Th (II)	e	0.120	0.115
5	Pb (II) + Th (II)	Pb (II)	d	0.208	0.206
		Th (II)	e	0.120	0.115
6	Ca (II) + Th (II)	Ca (II)	d	0.215	0.198
		Th (II)	e	0.120	0.115
7	Ba (II) + Th (II)	Ba (II)	d	0.200	0.181
		Th (II)	e	0.120	0.115
8	Al (III) + Th (II)	Al (III)	d	0.220	0.205
		Th (II)	e	0.120	0.115
9	Mg (II) + Th (II)	Mg (II)	d	0.250	0.250
		Th (II)	e	0.120	0.115
10	Zn (II) + Th (II)	Zn (II)	d	0.192	0.178
		Th (II)	e	0.120	0.115
11	Mn (II) + Th (II)	Mn (II)	d	0.225	0.212
		Th (II)	e	0.120	0.115

d = 40% CH_3COOCH_3 – 0.4 M $C_3H_7COONH_4$
e = 60% CH_3COCH_3 – 0.4 M $C_3H_7COONH_4$

Table-8: Quantitative Separation of Synthetic Ternary Mixtures

Sr. No	Mixture	Metal ion eluted	Eluting agent	m moles taken	m moles found
1	Cd (II) + Co (II) + Th (IV)	Cd (II)	b	0.250	0.225
		Co (II)	d	0.250	0. 239
		Th (IV)	e	0.250	0.214

2	Zn (II) + Co (II) + Th (IV)	Zn (II)	b	0.250	0.185
		Co (II)	d	0.250	0.241
		Th (IV)	e	0. 250	0.214
3	Mn (II) + Co (II) + Th (IV)	Mn(II)	b	0. 250	0.242
		Co (II)	d	0.250	0.241
		Th (IV)	e	0. 250	0.214
4	Mg (II) + Co (II) + Th (IV)	Mg (II)	b	0. 240	0.178
		Co (IV)	d	0.250	0.241
		Th (II)	e	0. 250	0.214
5	Ca (II) + Co (II) + Th (IV)	Ca (II)	b	0. 250	0.240
		Co (II)	d	0.250	0.241
		Th (IV)	e	0. 250	0.214
6	Pb (II) + Co (II) + Th (IV)	Pb (II)	b	0. 242	0.199
		Co (II)	d	0.250	0.241
		Th (IV)	e	0. 250	0.214
7	Al (III) + Ba (II) + Th (IV)	Al (II)	c	0. 250	0.200
		Ba (II)	d	0. 250	0.245
		Th (IV)	e	0. 204	0.183
8	Mg (II) + Ba (II) + Th (IV)	Mg (II)	c	0.204	0.178
		Ba (II)	d	0.250	0.245
		Th (II)	e	0.212	0.183
9	Pb (II) + Ba (II) + Th (IV)	Pb (II)	c	0.212	0.187
		Ba (II)	d	0.250	0.245
		Th (II)	e	0.212	0.183
10	Cd (II) + Ba (II) + Th (IV)	Cd(II	c	0.250	0.233
		Ba(II)	d	0.250	0.245
		Th (IV)	e	0.212	0.183
11	Cu (II) + Ba (II) + Th (IV)	Cu (II)	c	0. 250	0.219
		Ba (II)	d	0. 250	0.245
		Th (IV)	e	0.212	0.183
12	Zn (II) + Ba (II) + Th (IV)	Zn (II)	c	0. 250	0.242
		Co (IV)	d	0. 250	0.245
		Th (II)	e	0.212	0.183
13	Co (II) + Ba (II) + Th (IV)	Co (II)	c	0.248	0.110
		Ba (II)	d	0. 250	0.245
		Th (II)	e	0.212	0.183

b = 20 % CH_3COCH_3 - 0.06 M $C_3H_7COONH_4$

c = 40% CH_3COCH_3 – 0.1 M $C_3H_7COONH_4$

d = 40% CH_3COCH_3 – 0.4 M $C_3H_7COONH_4$

e = 60% CH_3COCH_3 – 0. 4 M $C_2H_5COONH_4$

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