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Adsorption Behavior of Thorium and some Metal Ions on Cation Exchange Resin Dowex 50 WX₈ (NH₄⁺Form) from Aqueous Acetone-Ammonium Propionate Media.

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ABSTRACT

In the field of inorganic separations, the incentive to explore the use of non-aqueous or mixed solvents has been the enhanced selectivity, 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 solvation 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 an electrolyte. All these changes are mutually dependent and affect the distribution of the metal ion. From the investigations of ion exchange in mixed solvents, it is apparent that the adsorption equilibrium depends markedly on the properties of the organic solvent and reactions with the resin and electrolytes which determine the equilibrium.

Keywords: Aqueous Ammonium Propionate, Un-Irradiated and Gamma Irradiated, Dowex 50 WX₈, Half Exchange Time ($t^{1/2}$), Inter Diffusion Coefficient (D), Exchange Rate Constant (K).

1. INTRODUCTION

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. Cation exchange separation of alkali metals, alkaline earths and transition metal like copper, cobalt nickel, manganese and vanadium in ethanol-hydrochloric acid media have been reported. ^[3] In this case the media offer many attractive possibilities for separation. Korkisch et al ^[5] used propanal HCl medium for the separation of alkali metal ions. Propanol- α -OH- isobutyric acid is used for the separation of lanthanide mixtures by Mazzei et al^[6], the same authors tried the propanol-NaClO₄ medium for lanthanide separation. The distribution coefficients (K_D) were found out at various percentages of acetone and at various concentrations of ammonium propionate and ammonium butyrate solution. The effect of acetone percentage on 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.

2. MATERIAL AND METHODS

2.1 Measurement of Distribution Coefficient

The distribution coefficient K_D was determined by batch equilibrium method. 1 g of air dried Dowex 50 WX₈ (NH₄⁺ form) resin was taken in 250 ml glass stoppered Erlenmeyer 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.

2.2 Ion Exchange Separation of Metal Ions

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 or strata of the ion exchange resin.

2.3 Procedure

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 requisite 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 procedure. In case of tertiary mixtures the first and second metal ions were eluted by suitable eluting agents and finally third metal is eluted by proper eluting agent.

2.4 Solutions

1. 0.05M metal ion solution.
2. 50 ml aqueous acetone- ammonium propionate.
3. Acetone- 0, 20, 40, 60, and 80 %.
4. 0.02 M Ammonium propionate.

3. RESULTS AND DISCUSSION

3.1 Distribution Coefficients in Aqueous Acetone- Ammonium Propionate Medium

The distribution coefficients of Cu, Co, Ni, Mn, Pb, Mg, Ca, Sr, Ba, Zn, Cd, Hg, 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, 0.6M 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 values are maximum at 0 and 20 percent of acetone and goes on decreasing with the rise in percentage of acetone. The uptake of thorium on the resin is maximum i. e. total adsorption at all percentages of acetone and at 0.02-0.6 M ammonium propionate concentrations. Mercury shows total adsorption at all percentages of acetone. K_D values for Mg are higher up to 40 percent acetone at all concentrations of ammonium propionate but decrease at later percentages of acetone. Very high values of K_D for all metal ions at 0.02 ammonium propionate and those of thorium indicate the formation of stable $M^n (C_2H_5COO)^{n-1}$ complex. From the K_D data of the metal ions, the selectivity sequence can be given for the cation exchanger (NH_4^+ form) studied. As most of the separations are carried out at 40% acetone, the selectivity sequence is given for this acetone content.

0.02 M – Th > Mn > Ni > Ca > Sr > Zn > Cd > Pb > Cu > Al.
0.1 M - Th > Mn > Ni > Sr > Ca > Zn > Cd > Cu > Pb > Al.
0.2 M - Th > Sr > Ca > Mn > Cu > Ni > Al > Pb > Cd > Zn.
0.4 M - Th > Zn > Cu > Al > Sr > Ni > Mn > Pb > Ca > Cd.
0.6 M - Th > Al > Zn > Cu > Ni > Mn > Pb > Ca > Sr > Cd.

The distribution coefficient of Cu, Ni, Mn, Pb, Ca, Sr, Zn, Cd and Al decrease with the rise in percentage of acetone and the concentrations of ammonium propionate as well.

The values of K_D are small at 0.02 M ammonium propionate and become negligible i. e. no adsorption at 0.4 and 0.6 M $C_2H_5COO NH_4$ content. These metals show no tendency to form the adsorbable cationic propionate complexes at these concentrations of $C_2H_5COO NH_4$ solution.

The dielectric constant of a solvent, and the polarity and polarizability of solvent molecules are the properties which affect strongly their interactions with the properties which affect strongly their interactions with the properties which affect strongly their interactions with solutes and hence their solvent power. Osager^[7] and Kirkwood^[8, 9] gave the relationship between dielectric constant and dipole moment. The chain polymers have a low and high dipole moments respectively^[10]

In presence of water, the salts like $C_2H_5COO NH_4$ undergo hydrolysis. It is observed that the distribution coefficients of Cu, Ni, Zn, Cd, Pb, Co, Sr, Ca, Mn, Al are continuously decrease with increase in the $C_2H_5COO NH_4$ concentration at the respective percentages of acetone.

There are at least four main factors involved in such exchange equilibrium 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. The changes in the solvation shell of each metal ion other than those due to complex ion formation i.e. hydration.
4. Shrinkage of the resin.

3.2 Column Chromatographic Separations

The results of the quantitative separation of synthetic multi - component mixtures in aqueous acetone ammonium propionate media are presented in tables 7 and 8. The separation of metal ions in aqueous acetone ammonium propionate media were carried out at equal quantities (0.25 M of each). The separations were further carried out at 0.15, 0.10 and 0.05 M moles of the metals. It is

generally observed that the separation of copper in binary and tertiary mixture is affected by its concentration and also 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.

Table1. 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
Co (II)	772.6	757.8	681.7	681.7	681.7
Ni (II)	1262	1262	1091.0	1091.0	531.0
Mn (II)	3943	13.76	516.9	309.4	293.15
Pb (II)	837	415	153.2	20.25	N.A
Mg (II)	675	362.5	362.5	362.5	154.3
Ca (II)	963.8	772.9	607.5	547.4	436.0
Sr (II)	719.9	719.9	719.9	266.3	266.3
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
Hg (II)	7.764	T.A	T.A	T.A	T.A
Al (II)	195.0	105.7	86.08	67.14	556.31
Th (II)	T.A	T.A	T.A	T.A	T.A

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

Table2. 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
Co (II)	569.4	99.3	96.35	86.99	86.99
Ni (II)	248.8	170.0	115.8	64.31	51.30
Mn (II)	345.6	203.7	99.70	77.0	31.94
Pb (II)	69.76	12.49	N.A	N.A	N.A
Mg (II)	46.7	295.9	295.9	219.4	154.3
Ca (II)	359.5	216.0	149.6	79.66	51.85
Sr (II)	236.2	211.3	111.9	103.4	103.4
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
Hg (II)	75.46	T.A	T.A	T.A	T.A
Al (II)	86.08	32.20	18.31	12.89	N. A
Th (II)	T.A	T.A	T.A	T.A	T.A

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

Table3. 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
Co (II)	9.3	90.99	78.44	62.47	84.34
Ni (II)	108.9	108.9	48.23	0.92	30.92
Mn (II)	156.3	88.72	86.20	52.55	52.55
Pb (II)	26.27	N. A	N.A	N.A	N.A
Mg (II)	675	675	295.5	258.4	159.3
Ca (II)	89.80	82.39	18.50	37.24	14.90
Sr (II)	106.1	103.0	88.90	59.27	5.27

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
Hg (II)	98.42	T.A	T.A	T.A	T.A
Al (II)	24.63	20.69	6.262	1.333	1.333
Th (II)	T.A	T.A	T.A	T.A	T.A

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

Table4. 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
Co (II)	71.41	62.42	43.57	42.57	139.9
Ni (II)	17.63	9.126	N.A	N.A	N.A
Mn (II)	21.39	17.36	2.282	0.740	N.A
Pb (II)	15.61	N. A	N.A	N.A	N.A
Mg (II)	270	270	237.6	203.2	N.A
Ca (II)	31.35	17.52	8.112	N.A	N.A
Sr (II)	34.45	27.48	22.13	22.13	7.509
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
Hg (II)	164.0	T.A	T.A	T.A	T.A
Al (II)	17.4	9.126	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

Table5. 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
Co (II)	27.51	0.774	61.43	61.43	60.35
Ni (II)	N.A	N.A	N.A	N.A	N.A
Mn (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
Ca (II)	N.A	N.A	N.A	N.A	N.A
Sr (II)	0.635	0.635	N.A	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
Hg (II)	47.61	T.A	T.A	T.A	T.A
Al (II)	2.735	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

Table6. Distribution Coefficient (K_D) in Aqueous Acetone Ammonium Propionate (0.6M)

on	Acetone % ^v / _v				
	0	20	40	60	80
Cu (II)	0.500	N.A	N.A	N.A	833.6
Co (II)	3.38	3.38	88.51	309.0	60.35
Ni (II)	N.A	N.A	N.A	N.A	N.A
Mn (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
Ca (II)	N.A	N.A	N.A	N.A	N.A
Sr (II)	N.A	N.A	N.A	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
Hg (II)	43.42	T.A	T.A	T.A	T.A
Al (II)	7.398	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

Table7. 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	Zn (II) + Th (IV)	Zn (II)	d	0.27	0.261
		Th (IV)	e	0.234	0.210
2	Mg (II) + Th (IV)	Mg (II)	d	0.224	0.208
		Th (IV)	e	0.234	0.210
3	Ca (II) + Th (IV)	Ca (II)	d	0.200	0.180
		Th (IV)	e	0.234	0.210
4	Pb (II) + Th (IV)	Pb (II)	d	0.244	0.234
		Th (IV)	e	0.234	0.210
5	Ni (II) + Th (IV)	Ni (II)	d	0.260	0.254
		Th (IV)	e	0.234	0.210
6	Co (II) + Th (IV)	Co (II)	d	0.267	0.261
		Th (IV)	e	0.234	0.210
7	Cu (II) + Th (IV)	Cu (II)	d	0.180	0.168
		Th (IV)	e	0.234	0.210
8	Mn (II) + Th (IV)	Mn (II)	d	0.200	0.186
		Th (IV)	e	0.234	0.210
9	Al (II) + Th (IV)	Al (II)	d	0.205	0.200
		Th (IV)	e	0.234	0.210
10	Ba (II) + Th (IV)	Ba (II)	d	0.180	0.153
		Th (IV)	e	0.234	0.210

d = 40% CH₃CooCH₃ – 0.4 M C₂H₅CooNH₄

e = 60% CH₃CooCH₃ – 0.4 M C₂H₅CooNH₄

Table8. Quantitative Separation of Synthetic Ternary Mixtures

Sr. No	Mixture	Metal ion eluted	Eluting agent	m moles taken	m moles found
1	Pb (II) + Co (II)+ Th (IV)	Pb (II)	a	0.200	0.156
		Co (II)	d	0.250	0.240
		Th (IV)	e	0.200	0.151
2	Ca (II) + Co (II)+ Th (IV)	Ca (II)	a	0.192	0.162
		Co (II)	d	0.250	0.240
		Th (IV)	e	0.200	0.181
3	Al (II) + Co (II) + Th (IV)	Al (II)	a	0.210	0.198
		Co (II)	d	0.250	0.240
		Th (IV)	e	0.260	0.181
4	Zn (II) + Co (II)+ Th (IV)	Zn (II)	a	0.210	0.198
		Co (II)	d	0.250	0.240
		Th (IV)	e	0.200	0.181

5	Cd (II) + Co (II)+ Th (IV)	Cd (II)	a	0.201	0.179
		Co (II)	d	0.250	0.240
		Th (IV)	e	0.200	0.181
6	Cu (II) + Ca (II)+ Th (IV)	Cu (II)	b	0.201	0.157
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.22	0.226
7	Al (II) + Ca (II)+ Th (IV)	Al (II)	b	0.156	0.138
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.250	0.226
8	Pb (II) + Ni (II)+ Th (IV)	Pb (II)	b	0.20	0.160
		Ni (II)	d	0.201	0.190
		Th (IV)	e	0.250	0.215
9	Zn (II) + Ca (II)+ Th (IV)	Zn (II)	b	0.185	0.149
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.250	0.226
10	Cd (II) + Ca (II)+ Th (IV)	Cd (II)	b	0.212	0.206
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.250	0.226
11	Pb (II) + Ca (II)+ Th (IV)	Pb (II)	b	0.224	0.207
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.250	0.226
12	Sr (II) + Ca (II)+ Th (IV)	Sr (II)	a	0.250	0.232
		Ca (II)	d	0.194	0.161
		Th (IV)	e	0.250	0.226

b = 70% CH₃CooCH₃ – 0.2 M C₂H₅CooNH₄

d = 40% CH₃CooCH₃ – 0.4 M C₂H₅CooNH₄

e = 60% CH₃CooCH₃ – 0.4 M C₂H₅CooNH₄

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