Adsorption Behavior of Pb, Cd, Ca, Al, Zn And Co 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 chemistry 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 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 an electrolytes. All these changes are mutually dependent and affect the distribution of the metal ion. It is already known that, at equilibrium with a mixed solvent, because of the preferential up take of water by the resin, 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.

Keywords: Ion exchange resin Dowex 50 WX8 (NH4+ form), Ammonium propionate, Synthetic binary mixtures, Distribution coefficient (K_D), Dielectric constant, Total adsorption (T. A.), No adsorption (N.A.).

Introduction
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.

The presence of water miscible polar solvents proved to be advantageous in the metal ion exchange in complexing media. Firtz et al [3] 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 [4] and Strelow [5] separated cadmium from zinc and other metal ions by eluting them with 0.5 M hydrochloric acid. The studies indicated that when nitric acid is used with non aqueous solvent, the larger volume of eluent is required for quantitative 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. Cation exchangers permit the phenomenon of combined ion exchanger-solvent extraction (CIESE) to be exhibited 8, 9, 10 complex formation of the metal ions with organic compounds has been advantageously used to achieve difficult separations. Attempts were made to separate the metal ions in aqueous acetone propionic acid media by using Dowex 50 WX8 in H\(^+\) form. The distribution coefficients of various metal ions were found to be very high and therefore the separations.

The distribution coefficients of various metal ions were found to be very high and therefore the separations were not achieved. The distribution coefficients (K_D) were found out at various concentrations of ammonium propionate solutions. The effect of acetone percentage on the distribution coefficient is explained on the basis of variations in di-electric constants of mixed solvents.
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 propionate mixtures was taken. The flask was stoppered and kept for 24 hr. After 24 hrs, supernatant 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 column was packed with a small glass wool at the bottom and a 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 binary 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 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.

Results And Discussion

The distribution coefficients of Pb, Cd, Al, Zn and Co, 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 propionate solutions. The values are given in table 1-6. The distribution coefficients of Pb, Ca, Zn, Cd, Al, decrease with the rise in percentage of acetone and the concentrations of ammonium propionate as well. The values of KD are small at 0.2M- ammonium propionate and becomes negligible i.e. no adsorption at 0.4 and 0.6 M C$_2$H$_5$COONH$_4$ content. These metals show no tendency to form the absorbable cationic propionate complexes at these concentrations of C$_2$H$_5$COONH$_4$ solutions.

The dissociation of CH$_3$CH$_2$COONH$_4$ in aqueous solution takes place as:

$$\text{CH}_3\text{CH}_2\text{COONH}_4 \rightleftharpoons \text{CH}_3\text{CH}_2\text{COO}^- + \text{NH}_4^+$$

The dissociation in liquid phase is due to the dielectric constant. The distribution coefficients for Zn, Ca decrease with the increasing acetone constant. Cobalt forms a stable complex at 0.02 and 0.06 M solutions of C$_2$H$_5$COO NH$_4$. The tendency to form propionate was found to decrease with increase in the concentration of C$_2$H$_5$COO NH$_4$. In presence of water, the salts like C$_2$H$_5$COO NH$_4$ undergo hydrolysis. These salts are of weak base NH$_4$OH and weak acid like C$_2$H$_5$COOH. 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$_2$H$_5$COO$^-$) ion.
3. Changes in t 0.02 M he salvation shell of each metal ion other than those due to complex ion formation i.e. dehydration.
4. Shrinkage of the resin.

$$\text{M} (\text{H}_2\text{O})_n^{x+} \rightleftharpoons \text{M} (\text{H}_2\text{O})_{n-1}^{x+} + \text{H}_2\text{O}$$

The results of the quantitative separation of synthetic multi-component mixtures in aqueous acetone–ammonium propionate media are presented in table no-7. Separation of Pb/Cd/Ca/Al/Zn-Co shows that lower distribution coefficients in 60% CH$_3$COCH$_3$- 0.02 M C$_2$H$_5$COO NH$_4$ and hence the metal ion in the binary mixtures was eluted first in this medium. Cobalt was eluted by 40% CH$_3$COCH$_3$- 0.04 M C$_2$H$_5$COO NH$_4$ successively one after the other.

Conclusion

The distribution coefficient of Co, Cd, Pb, Ca, Al, Zn were found out at 40% acetone. The selectivity sequence is given for this acetone content in C$_2$H$_5$COO NH$_4$ is below:

0.02 M – Co > Ca > Zn > Cd > Pb > Al.

0.1 M - Co > Ca > Zn > Cd > Pb > Al.
0.2 M – Co > Ca > Al > Pb > Cd > Zn.  
0.4 M – Co > Zn > Al > Pb > Ca > Cd.  
0.6 M – Co > Al > Zn > Pb > Ca > Cd.

**Table-1** Distribution Coefficient ($K_D$) in Aqueous Acetone Ammonium Propionate (0.02M)

| Ion     | Acetone % V/V | 0    | 20   | 40   | 60   | 80   |
|---------|---------------|------|------|------|------|------|
| Pb (II) |               | 837  | 415  | 153.2| 20.25| N. A.|
| Ca (II) |               | 963.8| 772.9| 607.5| 547.4| 436.0|
| 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|
| Co (II) |               | 772.8| 757.8| 681.7| 681.7| 681.7|

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   |
|---------|---------------|------|-----|------|------|------|
| Pb (II) |               | 69.76| 12.49| N.A  | N.A  | N.A  |
| Ca (II) |               | 359.5| 216.0| 149.6| 79.66| 51.85|
| 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| 18.29| 12.89| N.A  |
| Co (II) |               | 569.5| 99.3 | 96.35| 86.99| 86.99|

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   |
|---------|---------------|------|-----|------|------|------|
| Pb (II) |               | 26.27| N. A| N.A  | N.A  | N.A  |
| Ca (II) |               | 89.80| 82.39| 18.50| 37.24| 14.90|
| 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|
| Co (II) |               | 9.3  | 90.99| 78.44| 62.47| 84.34|
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  |
| Pb (II) | 15.61 | N. A | N.A | N.A | N.A |
| Ca (II) | 31.35 | 17.52 | 8.112 | 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 |
| Co (II) | 71.41 | N.A62.42 | 43.57 | 42.57 | 139.9 |

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  |
| Pb (II) | N.A | N.A | N.A | N.A | N.A |
| Ca (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 |
| Co (II) | 27.51 | 0.774 | 61.43 | 61.43 | 60.35 |

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  |
| Pb (II) | N. A | N.A | N.A | N.A | N.A |
| Ca (II) | N.A | N.A | N.A | N.A | N.A |
| Zn (II) | 1.929 | 1.929 | 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 |
| Co (II) | 3.38 | 3.38 | 88.51 | 309.0 | 833.6 |
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) + Co (II)        | Pb (II)          | a             | 0.245         | 0.240         |
|        |                          | Co (II)          | d             | 0.240         | 0.223         |
| 2      | Cd (II) + Co (II)        | Cd (II)          | a             | 0.190         | 0.188         |
|        |                          | Co (II)          | d             | 0.240         | 0.223         |
| 3      | Ca (II) + Co (II)        | Ca (II)          | a             | 0.240         | 0.220         |
|        |                          | Co (II)          | d             | 0.240         | 0.223         |
| 4      | Al (III) + Co (II)       | Al (III)         | a             | 0.218         | 0.211         |
|        |                          | Co (II)          | d             | 0.240         | 0.223         |
| 5      | Zn (II) + Co (II)        | Zn (II)          | a             | 0.222         | 0.212         |
|        |                          | Co (II)          | d             | 0.240         | 0.223         |

e = 60% CH₃COCH₃ – 0.02 M C₂H₅COONH₄  
d = 40% CH₃COCH₃ – 0.4 M C₂H₅COONH₄

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