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## Adsorption Behavior of Cu, Al, Mn, Sr, Pb, Cd, Zn, and Ca Metal Ions on Cation Exchange Resin Dowex 50 WX8 (NH<sub>4</sub><sup>+</sup> form) from Aqueous Acetone – Ammonium Propionate 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. 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 and the reaction with resin and electrolytes which determine the equilibrium. The metal ion exchange on action exchangers and their uses has been done.*

*Keywords- Dowex 50 WX8 (NH<sub>4</sub><sup>+</sup> form), Ammonium Propionate, Distribution Coefficients, Binary mixtures, Eluting agent.*

### 1. INTRODUCTION

The use of mineral acids and their salts has been done in variety of non-aqueous and mixed aqueous solvent. Firtz et al [3] separated many metal ions using 0.1 or 1M hydrochloric acid as the eluting agent. Strelow [4] Maan and Sanson [5] measured the equilibrium distribution coefficients which are useful guide to possible. The distribution coefficients (K<sub>D</sub>) were found at various percentages of acetone and at various concentrations of ammonium propionate. The data on distribution coefficients are used to find out the optimum conditions of metal ion separations. The result of column chromatographic separations of binary mixtures containing Cu, Al, Mn, Sr, Pb, Cd, Zn and Ca are given. Carboxylic acid media have shown great potential for the separation of metal ions which are otherwise very difficult to separate. Fridman and Yudinazh [6] extracted and separated Nb<sub>5</sub><sup>+</sup> and Ti<sub>4</sub><sup>+</sup> from oxalic acid solution using cation exchange separation is determining trace elements by neutron activation analysis is described by Brooksbank and Leddicote [7]. Lanthanides are separated on the column of Dowex-50 using ammonium citrate as eluent at pH 3.26 Tartaric acid [8], citric acid and formic acid [9] have proved to be very effective for metal ion separations to separate the metal ions in aqueous acetone propionic acid media by using Dowex 50WX8 in H<sup>+</sup> form. The distribution coefficients of various metal ions were found to be very high and therefore the separations were not achieved. The effect of acetone percentage on the distribution coefficient is explained on the basis of variations in dielectric constants of mixed solvents. The data of distribution coefficients are used to find out the optimum conditions of metal ion separations.

### 2. MATERIAL AND METHODS

The distribution coefficient, K<sub>D</sub> was determined by batch equilibrium method. 1g of air dried Dowex 50WX8 (NH<sub>4</sub><sup>+</sup> form) resin was taken in 250 ml glass stoppered bottle Erlenmeyer flask. 4 ml of 0.05M metal ion solution and 50ml of proper aqueous acetone - ammonium propionate was taken. The flask was stoppered and kept for 24 hrs. After 24 hrs a 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 50ml capacity were used. The columns were provided with safety device to maintain the ion exchanger under liquid. The column was packed with a glass wool at the bottom and a 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 equilibration with the resin by passing 20ml of aqueous acetone - ammonium metal ions were prepared. It was allowed to pass down the column slowly without allowing the level of 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 1ml/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 fraction. The metal ion contents in the collected fractions were estimated by standard volumetric procedures.

**3. RESULTS AND DISCUSSION**

The distribution coefficients of Cu, Al, Mn, Sr, Pb, Cd, Zn and Ca were found out at 0, 20, 0.06, 0.1, 0.2, 0.4, 0.6 M ammonium propionate solutions. The values are given in tables 1 to 6. The distribution coefficients of all metal ions are high at all percentages of acetone at 0.02M solution of ammonium propionate. From the  $K_D$  data of the metal ions, the selectivity sequences 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 contents

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

The distribution coefficient of Cu, Mn, Pb, Ca, Sr, Zn, Cd and Al decrease with the rise in percentage of acetone and the concentration of ammonium propionate. The values of  $K_D$  are small at 0.2M ammonium propionate and becomes negligible means no adsorption at 0.4 and 0.6M  $C_2H_5COONH_4$  solution. The presence of water, the salt like  $C_2H_5COONH_4$  undergo hydrolysis.. This salt is a weak base  $NH_4OH$  and weak acid like  $C_2H_5COOH$ .  $C_2H_5COONH_4$  is a mono-valent non-ampholytic anion ( $C_2H_5COO^-$ ) and mono valent non-ampholytic cation ( $NH_4^+$ ) are simultaneously present in ammonium propionate. The results of ,the quantitative separation of synthetic multi-component mixtures in aqueous presented in table 7.

**3.1 Separation of Ca from Zn, Ca, Pb, Cu, Mn, Al**

It is observed that 70%  $CH_3COCH_3$  -0.2M  $C_2H_5COONH_4$  was the best eluent for Zn / Pb / Cu, Mn, Al, Cd and 40%  $CH_3COCH_3$  - 0.4M  $C_2H_5COONH_4$  eluent is used for the separation of Ca.

**4. CONCLUSION**

Ion exchange chromatography has been used to separate mixtures of calcium, magnesium or of iron, chromium that occur together in the Qualitative scheme of analysis and also in minerals and ores such as limestone, dolomite and chromeiron Ore.

**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 |
| Mn (II)  | 3943            | 1376  | 516.9 | 309.4 | 293.5 |
| Pb (II)  | 837             | 415   | 153.2 | 20.25 | N. A. |
| Sr (II)  | 719.9           | 719.9 | 719.9 | 266.3 | 266.3 |
| Zn (II)  | 224.1           | 224.1 | 217.3 | 80.84 | 56.14 |
| Cd (II)  | 578.6           | 215.6 | 104.0 | 6.37  | 31.97 |
| Al (III) | 195.0           | 105.7 | 86.08 | 67.14 | 55.31 |
| Ca (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 Propionate (0.06M)**

| Ion      | Acetone % $V/V$ |       |       |       |       |
|----------|-----------------|-------|-------|-------|-------|
|          | 0               | 20    | 40    | 60    | 80    |
| Cu (II)  | 71.36           | 49.06 | 36.45 | 36.45 | 28.01 |
| Mn (II)  | 345.6           | 203.7 | 99.70 | 770.  | 31.94 |
| Pb (II)  | 69.76           | 12.49 | N. A. | N. A. | N. A. |
| Sr (II)  | 236.2           | 211.3 | 111.9 | 103.4 | 103.4 |
| 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. |
| Ca (II)  | 359.5           | 216.0 | 149.6 | 79.66 | 51.85 |

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

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**Table-3: Distribution Coefficient (K<sub>D</sub>) in Aqueous Acetone Ammonium Propionate (0.1M)**

| Ion      | Acetone % <sup>V</sup> / <sub>V</sub> |       |       |       |       |
|----------|---------------------------------------|-------|-------|-------|-------|
|          | 0                                     | 20    | 40    | 60    | 80    |
| Cu (II)  | 32057                                 | 23.36 | 23.36 | 23.36 | 21.75 |
| Mn (II)  | 156.3                                 | 88.72 | 86.20 | 52.55 | 52.55 |
| Pb (II)  | 26.27                                 | N. A. | N. A. | N. A. | N. A. |
| Sr (II)  | 106.1                                 | 103   | 88.90 | 59.27 | 5.27  |
| 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 |
| Ca (II)  | 89.80                                 | 82.39 | 18.50 | 37.24 | 14.90 |

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

**Table-4: Distribution Coefficient (K<sub>D</sub>) in Aqueous Acetone Ammonium Propionate (0.2M)**

| Ion      | Acetone % <sup>V</sup> / <sub>V</sub> |       |       |        |       |
|----------|---------------------------------------|-------|-------|--------|-------|
|          | 0                                     | 20    | 40    | 60     | 80    |
| Cu (II)  | 17.76                                 | 12.11 | 5.241 | 5.242  | 5.241 |
| Mn (II)  | 21.39                                 | 17.36 | 2.282 | 0.7396 | N. A. |
| Pb (II)  | 15.61                                 | N. A. | N. A. | N. A.  | N. A. |
| Sr (II)  | 34.45                                 | 27.48 | 22.13 | 22.13  | 7.509 |
| 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. |
| Ca (II)  | T. A.                                 | T. A. | T. A. | T. A.  | T. A. |

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

**Table-5: Distribution Coefficient (K<sub>D</sub>) in Aqueous Acetone Ammonium Propionate (0.4M)**

| Ion      | Acetone % <sup>V</sup> / <sub>V</sub> |        |       |       |       |
|----------|---------------------------------------|--------|-------|-------|-------|
|          | 0                                     | 20     | 40    | 60    | 80    |
| Cu (II)  | 2.518                                 | 2.227  | 1.403 | 1.403 | 1.403 |
| Mn (II)  | N. A.                                 | N. A.  | N. A. | N. A. | N. A. |
| Pb (II)  | N. A.                                 | N. A.  | N. A. | N. A. | N. A. |
| Sr (II)  | 0.6353                                | 0.6353 | 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. |
| Ca (II)  | N. A.                                 | N. A.  | N. A. | N. A. | N. A. |

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

**Table-6: Distribution Coefficient (K<sub>D</sub>) in Aqueous Acetone Ammonium Propionate (0.6M)**

| Ion      | Acetone % <sup>V</sup> / <sub>V</sub> |       |       |       |       |
|----------|---------------------------------------|-------|-------|-------|-------|
|          | 0                                     | 20    | 40    | 60    | 80    |
| Cu (II)  | 0.500                                 | 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. |
| Sr (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. |
| Ca (II)  | N. A.                                 | 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     | Cu (II) + Ca(II)  | Cu (II)          | b             | 0.280         | 0.277         |
|       |                   | Ca (II)          | d             | 0.150         | 0.144         |
| 2     | Al(III) + Ca (II) | Al (III)         | b             | 0.240         | 0.234         |
|       |                   | Ca (II)          | d             | 0.150         | 0.144         |
| 3     | Mn(II) + Ca (II)  | Mn (II)          | b             | 0.240         | 0.226         |
|       |                   | Ca (II)          | d             | 0.150         | 0.144         |
| 4     | Sr (II) + Ca (II) | Sr (II)          | b             | 0.290         | 0.282         |
|       |                   | Ca (II)          | d             | 0.150         | 0.144         |
| 5     | Pb (II) + Ca (II) | Pb (II)          | b             | 0.118         | 0.161         |
|       |                   | Ca (II)          | d             | 0.150         | 0.141         |
| 6     | Cd (II) + Ca(II)  | Cd (II)          | b             | 0.130         | 0.126         |
|       |                   | Cs (II)          | d             | 0.150         | 0.144         |
| 7     | Zn(II) + Ca(II)   | Zn (II)          | b             | 0.220         | 0.204         |
|       |                   | Ca (II)          | d             | 0.150         | 0.144         |

e = 60% CH<sub>3</sub>COCH<sub>3</sub> – 0.02 M C<sub>2</sub>H<sub>5</sub>COONH<sub>4</sub>

d = 40% CH<sub>3</sub>COCH<sub>3</sub> – 0.4 M C<sub>2</sub>H<sub>5</sub>COONH<sub>4</sub>

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