CHAPTER - III

CATION EXCHANGE SEPARATION OF COBALT NICKEL, ZINC, MANGANESE, COPPER, CALCIUM CADMIUM; MERCURY, LEAD, STRONTIUM, BARIUM, ALUMINIUM, THORIUM, MAGNESIUM, IN AQUEOUS ACETONE AMMONIUM TARTRATE. MEDIUM.

HISTORICAL REVIEW :

Carboxylic acid media have shown a great potential for the separation of metal ions which are otherwise very difficult to separate. Firdman and Yudinazh[5] extracted and separated Nb^{5+} and Ti^{4+} from oxalic acid solution using cation exchanger KY-2 in protonated form. The use of ion exchange separations in determining trace elements by neutron activation analysis is described by Brooksbank and Leddicotte[6]. Lanthanides were separated on the column of Dowex 50 using ammonium citrate as eluent at pH 3.26. Tartaric acid,[7] citric acid and formic acid[8] have proved to be very effective for metal ion separations. Boron and magnesium were separated from iron by a simple procedure with a cation exchange resin, ' Diaron K'. H_3BO_3 in an acidic solution of the sample is passed through the resin, and iron or other cations are adsorbed. Boron was detected titrimetrically or colorimetrically. Magnesium was adsorbed quantitatively by the resin even in the presence of tartaric acid, but iron is passed into the eluate through the resin by 20% tartaric acid.

The cation exchange characteristics of a large number of elements towards the strongly acidic cation exchange resin Dowex 50W-X8 in media containing varying concentrations of formic acid and mixture of formaic acid with aqueous dioxan were investigated by Qureshi et al.[8] The mixture of bismuth and copper solutions was separated. Bismuth was eluted by passing 23 M formic acid through the column at a flow rate of 3 ml/min, copper was then eluted with 2.5 M hydrochloric acid at a flow rate of 1.5 ml/min. Also the separations of the mixtures of lead and copper, barium and lanthanum, cadmium and copper were predicted.

Attempts were made to employ addition of water-acetone to promote metal-carboxylate complex formation for the selective elution of Ni, Cu, Co and Zn ions from Dowex 50W-X8 resin.[9] The distribution coefficients of Ni, Cu, Co and Zn ions in aqueous acetone-acetic, chloroacetic, dichloroacetic and trichloroacetic acids were found out at various compositions of the latter. The data were used for working out the optimum conditions for metal ion separations. Results on the separation of binary and ternary mixtures of metal ions were presented.

Cation exchange chromatographic studies of manganese on Dowex 50W-X8 are recently reported in out laboratory.[10] The distribution coefficients for Cu, Zn, Mg, Ni, Cd, Co, Mn, Ca, Pb, Th, Al, Hg, Sr and Ba were found out in aqueous acetone-succinic acid media. The effect of varying concentrations of acetone and the acid on distribution coefficients were studied to find out the suitable conditions for the separations. The quantitative separations of manganese from other elements were carried out.

A systematic study of the cation exchange behaviour of metals on $R-NH_4$ type resin in aqueous-ammonium acetate and ammonium acetate containing other solvents (mixed media) has been reported by some workers. Minami and Ishimori[11] explored the possibility of separating barium from lead on a cation-exchanger by first eluting the adsorbed lead with ammonium acetate at pH 6 and then barium, with 10%, ammonium chloride solution. The difference in the stability of the anionic complexes of barium and lead with ethylenediaminetetraacetic acid at pH 4.5 and 10.5 respectively has been utilised for their separation.[12] Lead (pH = 4.5) passed out of bed and adsorbed barium was eluted with EDTA (disodium salt) at pH 10.5. Khopkar and De[13] studied the cation exchange behaviour of barium on Dowex 50W-X8 (H^+). Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA has been used as the eluting agents. Barium has been separated from U(VI), Cu(II),Hg(II), Cs, Zn, Cd, Ag, Ce(IV), Zr, Th, Fe (III) and Bi(III) by 4 M ammonium acetate. Kemula and co-workers[14] developed a procedure for the separation of silver from the copper based on the adsorption of both ions on the cation exchanger, wolfatit KPS-200. Copper was eluted as the complex $CuCl_4^{-2}$ by hydrochloric acid, while silver was precipitated on the column. A method[15] had been developed for separation of silver, lead and mercury (II) in their mixtures at the milligram level, based on their differences in ion exchange potential on a cation exchanger, Dowex 50W-X8 (H^+). Out of the two common eluting agents nitric acid and ammonium acetate[16,17] the latter is preferable in view of the more favourable separation factors. It was observed that 300 ml of 0.25 in ammonium acetate eluted lead alone, the effluent was free from silver and mercury. Further 0.5 M ammonium acetate offers a good separation of silver from mercury, 150 ml of this eluent removed silver alone and the effluent was free from mercury. Finally mercury was removed from the resin bed by 100 ml of 4 M ammonium acetate.

Janauer et al. separated barium from other metal ions by means of cation exchange in an aqueous 20%, v/v DMSO medium containing 0.25 mol/l of thiocyanate.[18,19] As the DMSO offers numerous advantages as an eluent in cation-exchange chromatography because of its complex forming tendency with almost all metal ions, it is used as solvent in many analytical procedures. Diehl et.al[20] studied the behaviour of Bi^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Sn^{4+} and Zn^{2+} on a cation exchange resin (Bio Red AG 50-X8) in DMSO-hydrochloric acid-water systems. On the basis of K_D values they predicted the possibilit of separating these cations from mixtures. The anion-exchange behaviour of several cations in methanol-hydrochloric acid-DMSO-water systems has been explored by Fritaz and Lehoczky,[21] who showed the usefulness of these systems by separating various mixtures of metal ions. Phipps[22] has studied the selectivity sequence of monovalent anions on an anion exchange resin in DMSO systems. Earlier studies[23,24] have shown that formic acid offers unusual possibilities in cation-exchange chromatography and zirconium can be separated from thoriumand hafnium by cation-exchange in formic acid media.

Present Work

The adsorption characteristics of Co, Mg, Ca, Cd, Zn, Th, Ni, Pb, Al, Hg, Mn, Sr, Ba, Cu and metal ions on Amberlite IR-120 (NH_4^+) form in aqueous acetone Ammonium Tartrate media were studied. The distribution coefficient of these ions were found out at various percentage of acetone and at various concentration of δAmmonium Tartrate. The probable seperations of metal ions were predicted from the distribution coefficient data. The results of seperation of M binary, and terna y mixtures are presented in this chapter. The elution characteristics are discussed from the elution curves. The separation limits are recorded which suggest the efficiency of the separations by ion exchange chromatography techniques.

EXPERIMENTAL

Ion exchange resin

Amberlite IR -120 (14-52) mesh in Na^+ form was treated in a column with 2 NHCl to convert it into H^+form. The resin was then converted into NH_4^+ form by adding 10% NH_4Cl solution in 10% liquor ammonia and then washing with deionised water till effluent was free from chloride. The resin was air dried.

Metal ion solutions :

The metal salt solutions (0.05 M) were prepared by dissolving nitrates of Zn, Co, Ca, Mg, Pb, Cu, Hg and chlorides of Sr, Ba , Mn and Ni in distilled water.

Acetone - water - Ammonium tartrate mixture.

A stock solution of 2 M Ammonium tartrate was prepared by mixing equimolar (4M) solution of Ammonia and Tartaric acid.

Excess ammonia was removed by boiling the mixture. The mixtures were prepared so that the amount of acetone and water was expressed as percentage by volume and the ammonium tartrate concentration as molarity.

Determination of Distribution coefficient.

The distribution coefficient, K_D was determined by batch equilibrium method[1]. 1 gm. of the resine was equilibriated with 50 ml. of the solution containing the same quantity (4 ml.) of the metal ion (0.05 M) in aqueous acetone - ammonium tartrate media for 24 hours. Batch solution was then analysed for the metal ion titrimetically with disodium EDTA using appropriate indicator. The values of the distribution coefficient (K_D) were calculated by

$$KD = \frac{\text{meq. metal ion per g. resin.}}{\text{meq. metal ion per ml. solution.}}$$

SEPARATION OF MIXTURES :-

The Pyrex glass chromatographic columns of 50 ml. capacity were used. The column was packed by a slurry of 10 g. soaked resin. The feed metak was prepared by mixing standard solutions of metal ions. It was then passed through resin bed. The metal ions eluted by eluting agents as shown in table 3.5 to 3.7. The metal ions were estimated in 5 ml. effluent fractions.

PROCEDURE :-

The column was equilibrated with the resin by passing 20 ml of acetone-water ammonium tartrate mixture at mximum period flow rate. The binary, and ternary 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. After about an hour the effluent fractions were collected in test tubes by maintaining a flow rate of 2 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 fraction. After complete removal of the two metals elution is stopped. The metal ion contents in the collected fractions were estimated by standard volumetric procedures and total metal ion concentration was calculated.

In case of ternary mixtures the first two metal ions were elluted by suitable eluting agents and finally the last metal ion is eluted by proper eluting agent. The experimental details were the same as described above. The concentration of metal ion versus effluent volumes are plotted.

–: RESULTS AND DISCUSSION :–

A) DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE AMMONIUM TARTRATE MEDIUM.

The distribution coefficients of the metal ions under study were found out at 0,20,40,60 and 80 percentages of acetone at 0.06, 0.1, 0.2 and 0.4 M concentrations of ammonium tartrate.

The distribution coefficients of most of the metal ions like Mg, Sr, Ba, Pb, Zn, Cd, Cu, Mn, Co, Ni, Al are low at 0, 20, 40, 60, and 80% of acetone and at 0.06 , 0.1, 0.2 and 0.4 M ammonium tartrate. Ca, Sr, and Th, shows high values of distribution coefficients at 80% of acetone in 0.4 M ammonium tartrate. While they have low distribution coefficients at 0, 20, 40, 60 percentages of acetone in 0.06, 0.1, 0.2 M ammonium tartrate. Ba(II) shows no affinity for complexion at all percentages of acetone and in all concentrations of ammonium tartrate. Metal ion Sr (II) shows total adsorption at all percentages of acetone in all concentrations of ammonium tartrate. This suggests that strantium tartrate complex formed is preferred by the resin.

The tendency of adsorption of Th (IV) on resin is low at 0,20,40 percentages of acetone and in 0.06, 0.1, 0.2 M concentrations of ammonium tartrate. But it has very high adsorption tendency at 60 and 80% of acetone and in 0.4M ammonium tartrate. Thus Th (IV) forms a cationic tartrate complex which exchanges NH_4^+ ions on the resin.

The distribution coefficients of Ca has high values at 60 and 80 percentages of acetone and in 0.06, 0.1, 0.2, 0.4 M. ammonium tartrate. Which suggests it's higher adsorption tendency resulting in formation of calcium tartrate complex on the resin. Calcium shows low distribution coefficients at 0, 20, 40 percentages of acetone in 0.06, 0.1, 0.2 and 0.4 M ammonium tartrate.

Ba (II) shows no adsorption tendency at 0, 20 and 40 percentages of acetone in 0.06, 0.1, 0.2 and 0.4 M ammonium tartrate. At higher percentage of acetone Ba(II) forms preciptate in all concentrations of ammonium tartrate. Mn(II) also shows descreasing values of distribution coefficients at 0,20,40 percentages of acetone in 0.06, 0.1, 0.2 and 0.4 M ammonium tartrate. But it shows no adsorption tendency at 60 and 80 percentages of acetone in 0.06, 0.1, 0.2 and 0.4 M ammonium tartrate. From the K_D data of the metal ions in Tables

3.1 to 3.4 following selectivity sequence for the cation exchange can be given.

1) Ammonium tartrate = 0.06 M
   a) Acetone percentage = 0.
      Pb > Mg > Cd > Mn > Ni > Co > Hg > Cu > Zn > Ca > Al > Th

   b) Acetone percentage = 80
      Th > Ca > Zn > Hg > Cu > Pb > Mg > Co > Mn > Cd

2) Ammonium tartrate = 0.1 M
   a) Acetone percentage = 0
      Sr > Mg > Ca > Cd > Ni > Mn > Co > Cu > Zn > Al > Th > Ba

   b) Acetone percentage = 80
      Th > Sr > Ca > Zn > Hg > Mg > Ni > Al > Pb > Cd > Mn >
      Co > Ba .

3) Ammonium Tartrate 0.2 M
   a) Acetone % = 0.
      Sr > Zn > Mg > Cd > Ni > Ca > Hg >Cu
      Co > Th > Pb > Mn > Ba

   b) Acetone percentage = 80
      Th > Sr > Ca > Zn > Cu > Hg > Al > Mg > Co
      Pb > Mn > Cd > Ni > Ba

It is seen that the distribution coefficients vary with change in percentage of acetone and concentration of ammonium tartrate. The role of acetone and ammonium tartrate on the distribution coefficients is discussed below.

Affect of concentration of Acetone :

It is observed that the values of distribution coefficients of metal ions under study increase with the rise in concentration of acetone at 0.06, 0.1, 0.2, and 0.4 M ammonium tartrate.

Ion exchange between a solid and a solution can only occur if certain requirements are met. A solvent must be used in which the exchanging species are soluble. There must be ions in both the solutionand the solid. The solute and the functional groups of the solid (resin) must ~~be~~ dissociate at least partially. The ions must be free to move to exchange with one another. This requires porous structure of the resin which is expanded by swelling in the solvent. Water, because of its high dielectric constant, is an excellent solvent for most inorganic and quite number of organic acids, bases and salts. There are other solutions with high dielectric constants in which electrolytes can dissolve and disociate and in which most of the common ion exchangers are stable. Such solvents are formamide ($\epsilon = 126$), anhydrous ammonia ($\epsilon = 22$), ethylene glycol ($\epsilon = 41$), methanol ($\epsilon = 32$), ethanol ($\epsilon = 26$) and acetone ($\epsilon = 27$). These solvents can be used with or without addition of water. Many organic acids, are more radially dissolved in these solvents than in water. The nature of the solvent like acetone affects the solubility, dissociation and the solvation of the solutes and the behaviour of the ion exchanger and certain peqularities and side effects are more pronounced with acetone than with water.

The metal ions under study are preferred at higher percentage of acetone because of the variation in dielectric constant. It is reported that the distribution coefficients increase with decreasing dielectric constant. Akerlof[42] has determined the dielectric contants of a number of aqueous organic solvent mixtures.

Table 3.5 The dielectric constants of acetone-water mixtures v/v

Acetone %	100	70	30	20	10	0
Dielectric constant.	21.1	35.7	61	67	73	78.4

A similar change in distribution coefficients of some metal ions in aqueous acetone carboxylic acid media using cation[43] and anion[40] exchangers are reported earlier.

A fairly reliable measure for the affinity is the extent of swelling of the resin in the solvent. The swelling by the total solution, water and organic solvent as a function of the mole fraction of organic solvent can be described as moles of solution per equivalent resin. The moles of organic solvent taken up by the resin as a function of their mole fractions vary somehow in proportion to their polarities, giving a relatively large increase with the more polar solvents like methanol, glycol, acetic acid and little or no increase with the less polar solvents like dioxane, acetone, n-propenol, isopropenol, t-butanol, propinic acid. The decrease in the total absorbed solution as a function of the mole fraction of organic solvent shows that the mixed solvent in general becomes a poorer solvating agent for ions in the resin. The quaternary amine bound to a polystymene skeleton probably behaves much like a large organic ion with a low density of surface charge and only reacts with the less polar, more organic component of a mixed solvent. This conclusion is based on the experimental evidence of the uptake of solvent, dioxane, acetone, isopropanol and n-propanol by the resin, when a very small change in the uptake of organic solvent is observed for substantial change in ~~uptak~~ its mole fraction in the outer solution (from Ss = 0.1 to ~~Sx~~ Xs = 0.9). It is quite probable that this large ion retains merely a constant solvation shell irrespective of the solution composition. In support of this view, there are a number of examples where a carbonium ion attracts the more organic component of a mixed solvent.[44,45] on this evidence we may suppose that the resin particle is solvated by one or two less polar organic solvents like acetone, dioxane, n-propanol, etc. the more polar organic solvents like methanol, acetic acid, glycol probably solvate the cation as well as the anion in the functional resin group.

When the counter ion is a simple inorganic cation as in the present case NH_4^+, there is strong evidence that this cation is primarily surrounded by water molecule regardless of which reasonable model is used to interprete the results[45]. On this basis one must suppose that the water and organic solvent molecules is the resin phase are somehow partly separated from each other at the resin functional group. Such an occurence is in fact not improbable in view of the behaviour of salts in a mixed solvent. In the mixed aqueous organic solvent with less polar solvants like acetone, dioxane, dioxane, propanol, etc. the salting out effect of NaCl or KCl separates the water from organic solvent, resulting in phase separations whereas with a perchlorate, such separation does not take place because of the small affinity of the perchlorate ion for water molecules. In another mixed solvent with a more polar organic solvant like methanol or even methanol, phase separation does not become possible by addition of a chloride. However, a sulphate separates water and ethanol, which shows the necessity of supposing a large excess of the more polar componanets in the viscinity of the cation. The hydration number of the sulphate ion is aqueous solution is known to be 8 to 11[46]. These data demonstrate that in a mixed solvent the affinity for water molecule is greater for an anion for cation.

In the water rich region, the uptake of organic ion is in general much preferred compared with other solution compositions. This preferential uptake of organic solvent is more pronounced with the more polar organic solvents than with the less polar. It is seen that, whereas the cations are in a state of lower free energy of transfer in mixed aqueous methanol than in water, the reverse is the case for the anions[48].

The quarternary methyl amion fixed to polystyrene attracts methanol molecules to form a complex structure $-C(CH_3)_3N\ (ROH)_n$ in which the number of methanol molecules remains nearly constant irrespective of change in the solution composition. The same is true for the case of other organic solvents, the value n being different, depending on the nature of the solvent.

Table 3.1 Cation Exchange distribution coefficient (K_D) in aqueous acetone Ammonium Tartrate (0.06 M) Media on Amberlite I R-120 (NH_4^+) form.

Metal Ion	Acetone % , v/v				
	0	20	40	60	80
Mg (II)	339.1	275.6	162.0	82.0	46.2
Ca (II)	6.0	15.3	191.5	306.0	666.0
Sr (II)	TA	TA	TA	PPt	PPt
Ba (II)	NA	NA	NA	PPt	PPt
Pb (II)	486.0	306.0	306.0	186.0	66.0
Zn (II)	18	23.14	31.5	39.2	202.0
Cd (II)	216	100.00	26.0	10.0	NA
Hg (II)	30	49	77.0	101.0	128.0
Cu (II)	19.8	29.8	42.2	69.0	71.0
Mn (II)	99.0	44.8	25.0	14.0	2.2
Co (II)	62.1	26.0	17.2	14.6	70
Ni (II)	85.5	65.5	50.6	48.0	40.0
Al (III)	2.5	2.5	8.5	8.5	PPt
Th (IV)	0.8	1.35	9.5	38.25	2160.0

Where,

NA = No Adsorption
PPt = Precipitation
TA = Total Adsorption

Table 3.2 Cation Exchange distribution coefficient (K_D)
in aqueous acetone Ammonium Tartrate 0.1 M
Media on Amberlite I R-120 (NH_4^+) form.

Metal Ion	Acetone %, V/V				
	0	20	40	60	80
Mg (II)	224.4	138.7	71.2	35.8	15.0
Ca (II)	84.5	162.0	270.0	486.0	666.0
Sr (II)	TA	TA	TA	PPt	PPt
Ba (II)	NA	NA	NA	PPt	PPt
Pb (II)	11.4	11.4	11.4	9. 5	6.8
Zn (II)	22.0	35.0	42.0	74.0	174.0
Cd (II)	77.7	23.1	18.0	9.0	1.4
Hg (II)	27.0	47.0	70.0	95.0	121.0
Cu (II)	25.0	35.25	42.26	56.0	73.0
Mn (II)	31.15	17.4	13.0	NA	NA
Co (II)	26.0	20.0	15.5	14.0	NA
Ni (II)	57.6	41.1	23.5	10.3	7.6
Al (III)	2.5	2.5	10.2	18.0	PPt
Th (IV)	0.8	1.35	4.2	19.8	TA

Where NA = No Adsorption
PPt = Precipitation
TA = Total Adsorption

Table 3.3 Cation Exchange Distribution coefficient (K_D) in aqueous acetone Ammonium Tartrate (0.2 M) Media on Amberlite I R-210 (NH_4^+) form.

Metal Ion	Acetone % , v/v				
	0	20	40	60	80
Mg (II)	50.0	46.2	24.0	16.8	8.1
Ca (II)	29.0	162.0	216.0	306.0	1026.0
Sr (II)	TA	TA	TA	PPt	PPt
Ba (II)	NA	NA	NA	PPt	PPt
Pb (II)	9.5	9.5	2.8	2.8	1.6
Zn (II)	112.0	131.0	139.0	222.0	412.0
Cd (II)	54.0	40.0	13.5	12.6	NA
Hg (II)	23.8	26.6	32.7	39.8	114.3
Cu (II)	22.34	25.0	29.45	30.0	167.0
Mn (II)	2.76	NA	NA	NA	NA
Co (II)	20.0	15.0	13.0	9.0	7.0
Ni (II)	37.0	24.9	11.3	2.5	PPt
Al (III)	20.0	25.0	28.9	35.0	48.1
Th (IV)	15.1	28.0	TA (	TA	TA

Where,

NA = No Adseprtion
PPt = Precipitation
TA = Total Adsorption

Table 3.4 Cation Exchange Distribution coefficient (K_D) in aqueous acetone Ammonium Tartrate (0.4 M) Media on Amberlite IR-120 (NH_4^+) form.

Metal Ion	Acetone %, v/v				
	0	20	40	60	80
Mg (II)	11.0	6.4	5.2	2.1	NA
Ca (II)	16.6	81.0	90.0	378.0	TA
Sr (II)	TA	TA	TA	PPt	PPt
Ba (II)	NA	NA	NA	PPt	PPt
Pb (II)	NA	NA	NA	NA	NA
Zn (II)	31.5	36.7	25.8	66.7	972.0
Cd (II)	NA	23.1	18.0	13.5	8.0
Hg (II)	9.8	16.6	19.8	26.6	53.3
Cu (II)	23.4	23.4	30.6	46.0	167.0
Mn (II)	3.3	2.1	NA	NA	NA
Co (II)	16.0	14.0	10.5	8.0	NA
Ni (II)	13.0	3.7	1.4	PPt	PPt
Al (III)	22.6	28.0	35.0	38.0	PPt
Th (IV)	TA	TA	TA	PPt	PPt

Where,

NA = No Adsorption
PPt = Precipitation
TA = Total Adsorption

Table 3.5 Quantitative seperation of binary mixtures

(First ion is the mixture is eluted, while the Second ion is retained).

Mixtures 1	Metal ion eluted 2	Eluting agent 3	m moles taken 4	m moles found 5
Co(II)+Th(IV)	Co(II)	a	0.250	0.249
	Th(IV)	b	0.240	0.235
Ni Ni(II)+Th(IV)	Ni(II)	a	0 .240	0.238
	Th(IV)	b	0.240	0.235
Zn(II)+Th(IV)	Zn(II)	a	0.250	0.247
	Th(IV)	b	0.240	0.235
Cu(II)+Th(IV)	Cu(II)	a	0.245	0.245
	Th(IV)	b	0.240	0.235
Mg(II)+Th(IV)	Mg(II)	a	0.240	0.238
	Th(IV)	b	0.240	0.235
Ca(II)+Th(IV)	Ca(II)	a	0.240	0.237
	Th(IV)	b	0.240	0.235
Pb(II)+Th(IV)	Pb(II)	a	0.280	0.278
	Th(IV)	b	0.240	0.235
Cd(II)+Th(IV)	Cd(II)	a	0.260	0.259
	Th(IV)	b	0.240	0.235
Co(II)+Sr(II)	Co(II)	a	0.250	0.248
	Sr(II)	c	0.245	0.240
Sr(II)+Ni(II)	Ni(II)	a	0.240	0.240
	Sr(II)	b	0.245	0.240
Zn(II)+Sr(II)	Zn(II)	a	0.250	0.248
	Sr(II)	b	0.245	0.240
Cu(II)+Sr(II)	Cu(II)	a	0.245	0.244
	Sr(II)	c	0.245	0.240
Mg(II)+Sr(II)	Mg(II)	a	0.240	0.239
	Sr(II)	c	0.245	0.240
Ca(II)+Sr(II)	Ca(II)	a	0.240	0.238
	Sr(II)	c	0.245	0.240
Pb(II)+Sr(II)	Pb(II)	a	0.280	0.278
	Sr(II)	c	0.245	0.240
Cd(II)+Sr(II)	Cd(II)	a	0.260	0.258
	Sr(II)	c	0.245	0.240
Al(III)+Sr(II)	Al(III)	a	0.245	0.240
	Sr(II)	c	0.245	0.240

contd..

Table 3.5 contd...

1	2	3	4	5
Co(II) + Ca(II)	Co(II)	d	0.250	0.248
	Ca(II)	e	0.245	0.240
Ni(II) + Ca(II)	Ni(II)	d	0.240	0.240
	Ca(II)	e	0.245	0.240
Zn(II) + Ca(II)	Zn(II)	d	0.250	0.248
	Ca(II)	e	0.245	0.240
Cu(II) + Ca(II)	Cu(II)	d	0.245	0.240
	Ca(II)	e	0.245	0.244
Mg(II) + Ca(II)	Mg(II)	d	0.250	0.248
	Ca(II)	e	0.245	0.240
Pb(II) + Ca(II)	Pb(II)	d	0.240	0.239
	Ca(II)	e	0.240	0.240
Cd(II) + Ca(II)	Cd(II)	d	0.245	0.245
	Ca(II)	e	0.240	0.239
Al(III)+ Ca(II)	Al(III)	d	0.250	0.245
	Ca(II)	e	0.245	0.240

Where,

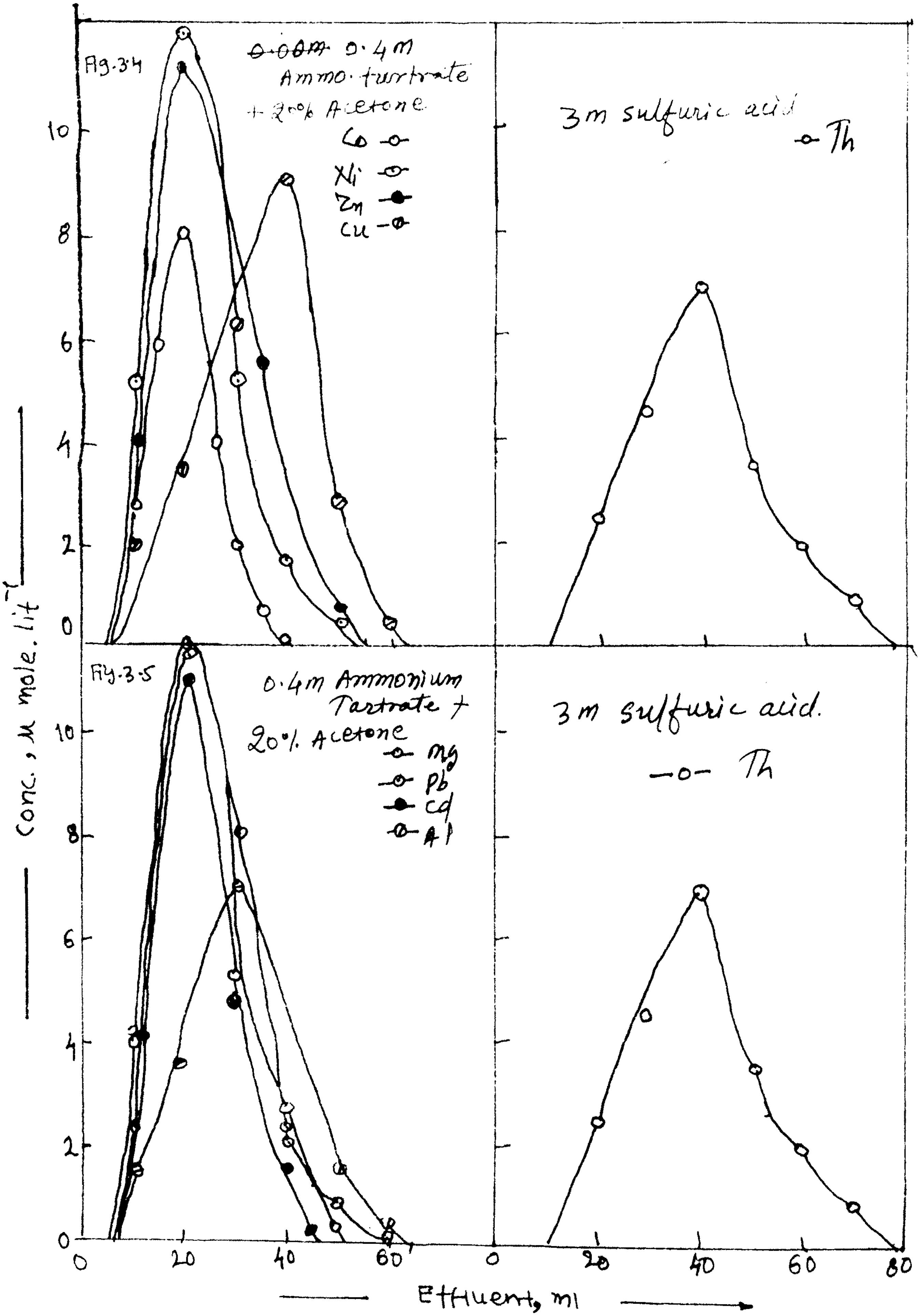
a - 20% Acetone + 0.4 M Ammonium Tartrate

b - 3 M Sulfuric acid

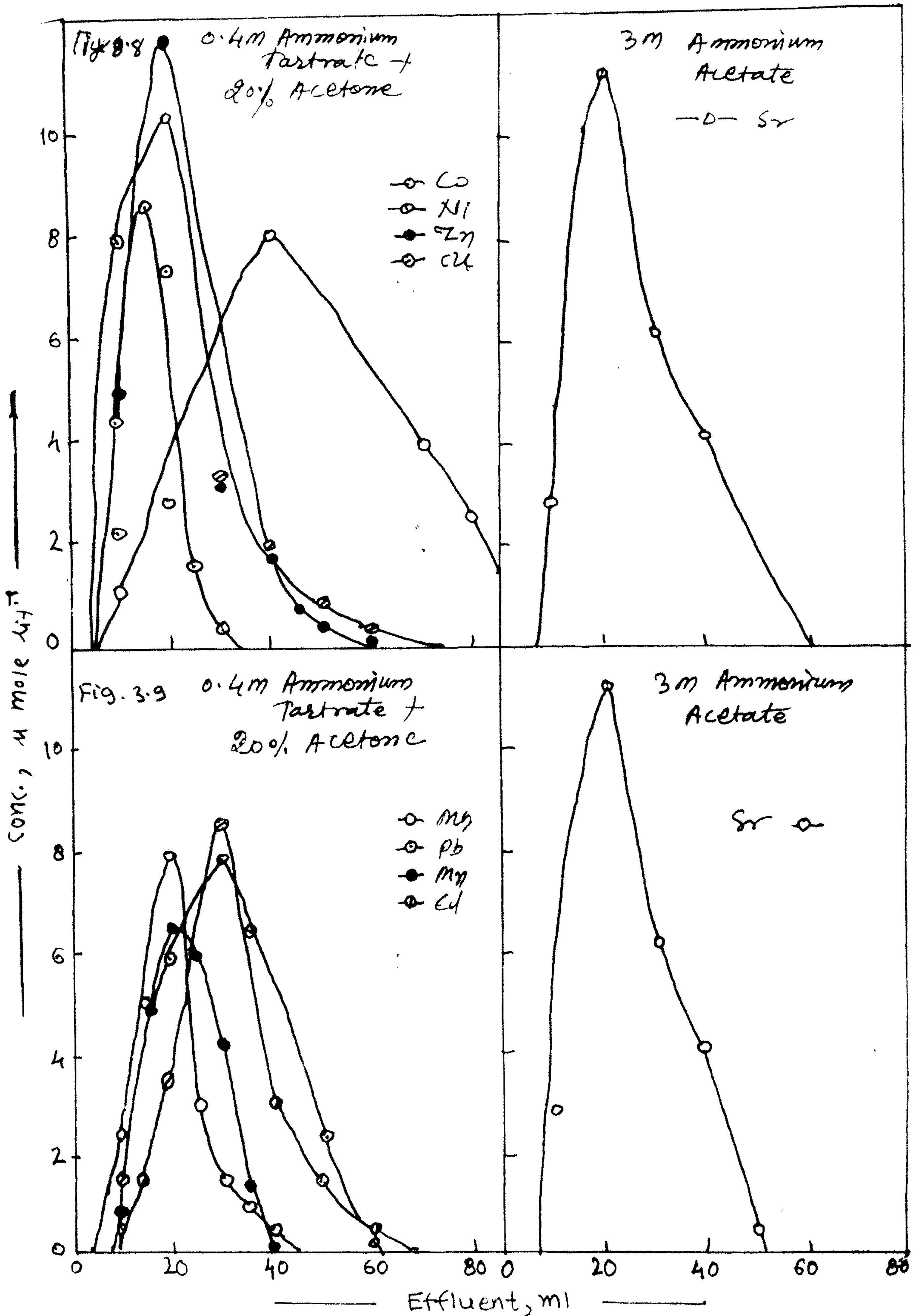
c - 3 M Ammonium Acetate

d - 80% Acetone + 0.4 M Ammonium Tartrate

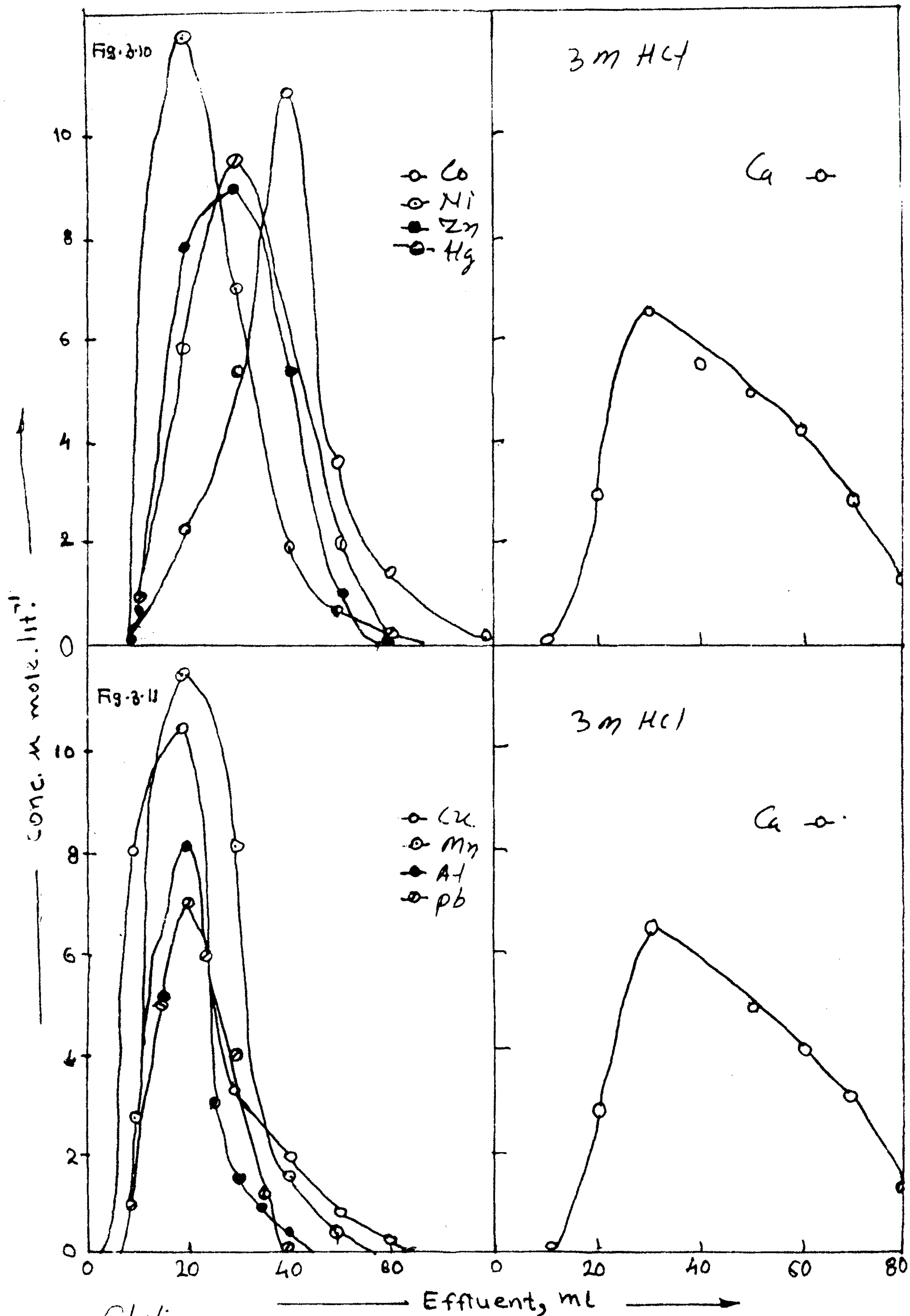
e - 3 M HCl



Elution curves of Th — Co/Ni/Zn/Cu/Mg/Pb/Cd/Al



Elution curves for Sr -- Co/Ni/Zn/Cu/Mg/Pb/Mn/Cd/Al



Elution curves for Ca – Co/Ni/Zn/Mg/Cu/Mn/Al/Pb/Hg

Table 3.6 Quantitative separation of Ternary Mixtures

Mixture 1	Metal ion eluted 2	Eluting agent 3	m moles taken 4	m moles found 5
Mg(II) + Ca(II) + Th(IV)	Mg(II)	a	0.245	0.240
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230
Ba(II) + Ca(II) + Th(IV)	Ba(II)	a	0.250	0.248
	Ca(II)	e	0.245	0.240
	Th(IV)	b	0.235	0.230
Pb(II) + Ca(II) + Th(IV)	Pb(II)	a	0.250	0.248
	Ca(II)	e	0.250	0.245
	Th(IV)	b	0.235	0.230
Zn(II) + Ca(II) + Th(IV)	Zn(II)	a	0.245	0.240
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230
Cd(II) + Ca(II) + Th(IV)	Cd(II)	a	0.240	0.238
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230
Hg(II) + Ca(II) + Th(IV)	Hg(II)	a	0.260	0.260
	Ca(II)	e	0.250	0.245
	Th(IV)	b	0.235	0.230
Cu(II) + Ca(II) + Th(IV)	Cu(II)	a	0.250	0.248
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230
Mn(II) + Ca(II) + Th(IV)	Mn(II)	a	0.260	0.258
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230
Co(II) + Ca(II) + Th(IV)	Co(II)	a	0.240	0.235
	Ca(II)	e	0.250	0.245
	Th(IV)	b	0.235	0.230
Ni(II) + Ca(II) + Th(IV)	Ni(II)	a	0.250	0.248
	Ca(II)	e	0.240	0.238
	Th(IV)	b	0.235	0.230
Al(III) + Ca(II) + Th (IV)	Al(III)	a	0.260	0.258
	Ca(II)	e	0.250	0.248
	Th(IV)	b	0.235	0.230

Contd...

Table 3.6 contd.

1.	2	3	4	5
Mg(II) + Ca(II) + Sr(II)	Mg(II)	a	0.245	0.240
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Ba(II) + Ca(II) + Sr(II)	Ba(II)	a	0.250	0.248
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Pb(II) + Ca(II) + Sr(II)	Pb(II)	a	0.250	0.245
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Zn(II) + Ca(II) + Sr(II)	Zn(II)	a	0.245	0.240
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Cd(II) + Ca(II) + Sr(II)	Cd(II)	a	0.240	0.238
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Hg(II) + Ca(II) + Sr(II)	Hg(II)	a	0.260	0.260
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Cu(II) + Ca(II) + Sr(II)	Cu(II)	a	0.250	0.248
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Mn(II) + Ca(II) + Sr(II)	Mn(II)	a	0.260	0.258
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Co(II) + Ca(II) + Sr(II)	Co(II)	a	0.240	0.235
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Ni(II) + Ca(II) + Sr(II)	Ni(II)	a	0.250	0.248
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245
Al(III) + Ca(II) + Sr(II)	Al(III)	a	0.260	0.258
	Ca(II)	e	0.240	0.235
	Sr(II)	c	0.250	0.245

where,

a = 20% Acetone + 0.4 M Ammonium Tartrate
b = 3 M Sulfuric acid. c = 3 M Amm.Acetate
d = 80% Acetone + 0.4 M Ammo.Tartrate
e = 3 M HCl

Table 3.7 Elution characteristics of metal ions in aqueous acetone Ammonium tartrate media.

Sr. No. 1	Metal ion 2	BTV ml 3	VEP ml 4	TEV ml 5	Eluent 6
1	Pb(II)	20	50	90	a
2	Cd(II)	20	50	90	a
3	Mg(II)	30	50	100	a
4	Mn(II)	10	40	110	a
5	Zn(II)	20	40	140	a
6	Hg(II)	60	100	150	a
7	Cu(II)	10	40	80	a
8	Ni(II)	20	70	150	a
9	Co(II)	15	40	80	a
10	Th(IV)	15	40	80	b
11	Pb(II)	5	20	90	a
12	Cd(II)	5	20	80	a
13	Mg(II)	20	50	100	a
14	Mn (II)	20	60	120	a
15	Zn(II)	5	45	85	a
16	Hg(II)	10	60	110	a
17	Cu(II)	40	160	280	a
18	Ni(II)	20	50	115	a
19	Co(II)	5	25	80	a
20	Sr(II)	7	20	52	c

contd.......

Table 3.7 contd...

1	2	3	4	5	6
21	Al(III)	20	50	120	a
22	Ca(II)	5	45	75	a
23	Pb(II)	5	20	90	d
24	Cd(II)	20	50	100	d
25	Mg(II)	30	50	100	d
26	Mn(II)	10	40	10	d
27	Zn(II)	20	40	140	d
28	Hg(II)	60	100	150	d
29	Cu(II)	10	40	80	d
30	Ni(II)	20	70	150	d
31	Co(II)	15	40	80	d
32	Ca	10	25	125	e

Where,

a = 20% Acetone + 0.4 M Amm. Tartrate
b = 3M Sulfuric acid
c = 3 M Ammonium Acetate
d = 80% Acetone + 0.4 M Amm. Tartrate
e = 3 M HCl

EFFECT OF CONCENTRATION OF AMMONIUM TARTRATE :-

It is observed that from the data of distribution coefficient (Table 3.1 to 3.4) that the K_D values of metal ions under study decreases at higher concentrations of ammonium tartrate The values of K_D of metal ions at 0.06, 0.1, 0.2, and 0.4 M ammonium tartrate solutions and at all percentages of acetone. This indicates the tendency of forming tartrate complexes was found to decrease with increase in the concentration of ammonium tartrate.

It has been stated that the solubility of an electrolyte in a series of solvents is correlated with the dielectric constant of the solvents and the mixtures of the solvents too. The solubilities increase with increasing in dielectric constant.

SEPARATIONS :- The results of the quantitative separation of synthetic binary and ternary mixtures in aqueous acetone ammonium tartrato media are presented in Table 3.1 to 3.7 and Fig.3.1 to 3.6 (Ternary separations are not presented seperately).

A) BINARY MIXTURES :-

1) Seperation of Th from Co/Ni/Zn/Cu/Mg/Ca/Pb/Cd/Al/Hg

Th shows total adsorption at 0.2, 0.4 M ammonium tartrate and at 0.20 and 40 percentages of acetone. However at the same concentration of ammonium tartrate Th forms precipitate at 60 and 80 percentages of acetone. Hence 0.4 M ammonium tartrate medium is selected for separation. Co, Ni, Zn, Cu,Mg,Ca, Pb,Cd,Al,Hg show practically no a dsorption on Amberlite IR-120 in 0.4 M ammonium tartrate medium (K_D Very Very low). They were eluted first.

As Th shows T.A. in ammonium Tartrate media it was eluted by 3 M sulfuric acid solution.

2] SEPARATION OF Sr. from Co/Ni/Zn/Cu/Mg/Ca/Pb/Cd/Al/Hg

The metal ions Co, Ni, Zn, Cu, Mg, Ca, Pb, Al, Cd, Hg, show very small K_D values in 0.4 M ammonium tartrate at all percentage of acetone. However Sr shows T.A. in 0.4 M ammonium tartrate and at 0, 20, 40 percentages of acetone. Thus Sr remains onthe resin. The metal ions were eluted first.

As Sr shows T.A. in 0.4 M ammonium tartrate media, it was eluted by 3 M ammonium acetate.

3] SEPARATION OF Ca from Co/Ni/Zn/Cu/Mg/Hg/Pb/Cd/Al/Mn

Ca shows high K_D value in 0.4 M ammonium tartrate and at 20% of acetone. However the metal ions Co,Ni,Zn,Cu,Mg,Hg,Pb,Cd,Al,Mn shows very low K_D values. Hence these metal ions in 0.4 M ~~in~~ ammonium tartrate and at 20% of acetone do not shows any adsorption tendency. These metal ions were eluted first. As Ca shows high K_D value in 0.4 M ammonium tartrate at 20% of acetone on Amberlite IR -120, it remained on the resin. It was eluted lastly b 3 M HCl.

b) <u>TERNARY MIXTURES</u> :

1] Separation Co/Ni/Zn/Cu/Mg/Mn/Hg/Pb/Cd/Al–Ca–Th.

The distribution coefficients of Ca and Th are high in 20% acetone at 0.4 M ammonium tartrate media. Th shows T.A. hence it remains on the resin. The metal ions Co, Ni, Zn, Cu, Mg, Mn, Hg, Pb, Cd, Al shows very low K_D values hence they were eluted first Ca was th then eluted by 3 M HCl. Finally Th was separated by 3 M sulfuric acid solution.

2] Separation of Co/Ni/Zn/Cu/Mg/Mn/Hg/Pb/C/Al–Ca–Sr.

As Sr shows T.A. in 0.4 M ammonium tartrate and at 20% acetone it remains on the resin. Ca has a high K_D value. At the same time the

Co-metal ions Co, Ni, Zn, Al, Mg, Mn, Hg, Pb, Ba have very small K_D values in the same media. Hence they were eluted first. Ca was eluted separately by 3 M HCl. Lastly Sr was seperately by 3 M ammonium acetate.

ELUTION CURVES :- Two component elution curves are presented in fig. 3.1 to 3.6 The curves indicate hew the systematic information contained in the tables of distribution coefficients can be applied to develop analytical separation procedures. The clear-cut-separation of metal ions indicated by no overlap of the elution curves.

The curves for the separation of all metal ions from binary and ternary mixtures show Gaussian distribution curves indicating good chromatographic separations. The elution curves from binary and ternary mixtures eluted first show some amount of tailing as the the other cations interfere in separation, but fronting is not observed. Tailing descreases with second metal ion in both types of mixtures. The last metal shows practically no tailing. This indicates that the separation of ions become easier with less number of co-ions.

ELUTION CHARACTERISTICS :- The sequence of the seperation of metal ions from binary and ternary mixtures is presented in Tables 3.5 and 3.6 and fig. 3.1 to 3.6.

Break Through volume (BTV)

Some initial volume of the respective eluting agent is re required to start the elution of a particular metal ion. This initial volume is the break through volume.

Peak Elution volume(PEV): The volume of eluting agents required to obtain the peak in the elution curve of the metal ions is said to be peak elution volume (PEV).

Sharp peaks are obtained when the ion exchange rates are high and the migration rates are low. An increase in column length increases the distance between the peaks and thus the separation efficiency.

TERMINAL ELUTION VOLUME (TEV):-

The voolume of eluting agents required for completion of the elution of metal ions is reppesented by terminal elution volume (TEV).

The values of break through volume (BTV) , peak elution volume (PEV) and terminal elution volume (TEV) for the metal ion separa ions of Co, Mg, Ca, Cu, Zn, Th, Ni, Al, Mn, Ba, Sr, Pb, Cd, Hg, in aqueous acetone ammonium tartrate media are presented in Table 3.7. Generally it is bbserved that , BTV values ofe 5-10 ml for elution of metal ions. This indicates that the initial period required to start the separation is low. It is observed from BTV values that time required for separation of second metal ion ranges upto 5 minutes.

The values of VEP are 20-30 ml indicating the speady separation, Generally, it is observed that TEV are 40-80 ml. indicating that the process is completed in one hour.

SEPARATION LIMITS :- The separation of metal ions from binary
and ternary mixtures in aqueous acetone ammonium tartrate media
were carried out at equal quantities ($\simeq$ 0.250 n moles each).
The separations were further carried out at 0.100 and 0.050 m
moles of the metals. It is generally observed that the recovery
9 of all metal ions is more than 85%, indicating that the
separations were possible at low concentrations.

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