CHAPTER 4

SEPARATION OF CALCIUM, MAGNESIUM, MANAGANESE, LEAD, CADMIUM, COPPER, ZINC, NICKEL, COBALT, THORIUM, ALUMINIUM, MERCURY, BARIUM AND STRONTIUM

IN

AQUEOUS, ACETONE-SUCCINIC ACID MEDIUM

ON

DOWEX 50 W-X8 (H^+) RESIN

THEORY OF ION-ECHANGE PROCESS IN WEAK ORGANIC ACID MEDIUM

(A) ADSORPTION OF WEAK ORGANIC ACIDS

Acetic acid is adsorbed by cation exchangers in H^+ form and by anion exchangers in acetate form. This adsorption is almost completely non-ionic since the high concentration of H^+ or acetate ions in the ion-exchangers suppresses the dissociation of the acid.[1] In a similar way, weak bases such as ammonia, pyridine and piperdine are adsorbed by anion exchangers in OH^- or free base form and by cation exchangers in ammonium, pyridinium or piperidinium form. Resins may take up weak electrolytes by non-ionic sorption well in excess of their ion exchange capacity. The dissociation of weak electrolytes and hence, this uptake by ion-exchangers depend on the pH of the solution[2]. The pH dependence can be used for elution for example, weak acids which are taken up in un-dissociated form by cation exchangers in H^+ form are efficiently eluted with alkali, the resin and the acid are neutralized by the alkali, and the dissociated salt of the acid is expelled by the Donnan effect[3]. Weak electrolytes can also be sorbed, without simultaneous ion-exchange, by resins containing multivalent counter-ions. The uptake of acid lowers the internal pH. As a consequence, the counter ions associate partly with the H^+ ions of the penetrating acid. This association decreases the charge of the original counter ions, and ionic groups of the resin become available for holding the anions of the penetrating acid. The net effect is an uptake of acid without exchange of original counter ions.

This mechanism is called as 'Site Sharing'[4]. A necessary condition for acid sorption by site sharing is that H^+ ion of the penetrating acid associate with the counter ion in the resin. Hence, the pK of the penetrating acid must be lower than the highest pK of the multivalent acid anion in the resin. A higher site sharing capacity is attained if the pK of the penetrating acid is lower than the second-highest pK of the anion in the resin. On the other hand, the pK of the penetrating acid should be higher than the pK of the anion in the resin since, otherwise, this anion will form un-dissociated acid which is no longer electrostatically held by the fixed charges. The condition for site sharing thus is (pK_1) counter ion $<$ (pK) sorbed acid $<$ (pK_n) counter ion.

(B) ION-EXCHANGE PROCESS IN MIXED SOLVENTS

Ion-exchange between a solid and a solution can only occur if there is a solvent in which the exchanging species are soluble. There should not be destruction or dissolution of the solid ion-exchanger in the solvent. Water, because of its high dielectric constant is an excellent solvent for most inorganic and quite a number of organic acids, bases and salts. Strong electrolytes dissociate largely or completely when dissolved in water, and aqueous solutions even of weak electrolytes and strong complexes contain ions in measurable concentrations. There are other solvents with high dielectric constants in which electrolytes can dissolve and dissociate and in which most of the common ion exchangers are stable. Many organic acids, are more readily dissolved in these solvents than in water. In quite a number of cases, organic solvents can be used for achieving effects which can not be obtained with water. The nature of the solvents affects the solubility, dissociation and solvation of the solutes and the behaviour of the ion-exchanger and certain peculiarities and side effects are more pronounced with organic solvents than with water.

HISTORICAL REVIEW

The separation of metal ions as halogen complexes by elution from a cation exchange column with hydrochloric acid organic solvent media is now an established analytical technique. Kember et al[6] probably were the first to employ addition of water-miscible non-aqueous solvents to promote metal halide complex formation for the selective elution of transition metal ions from cation exchange resins.

Fritz, Garralda and Karraller[7] separated many metal ions using 0.1 M 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 using Dowex 50 W-X8, cation exchange resin in H^{+} and ethylene diammonium forms. Yoshimo and Kojima[8] and Strelow[9] separated cadmium from zinc and other metal ions by elution with 0.5 M hydrochloric acid. Frits and Garralda[7] separated Al^{3+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Th^{4+} using nitric acid. The studies indicated that the nitric acid in non-aqueous solvent separations required larger volumes of eluent for quantitative elution and a slower flow rate had to be employed. Strelow[10], Mann and Swanson[11] measured the equilibrium distribution coefficients which are a useful guide to possible cation exchange separations in aqueous solution. Equilibrium distribution coefficients of cations in hydrocholoric acid[12], nitric acid and sulphuric acid media using BIO-RAD AG 50W-X8 sulfonated polysterene resin have been worked out. The possibilities of separation of various metals are indicated with the help of the distribution coefficients. It has been shown that metal ions are taken up more strongly and at lower hydrochloric acid concentrations by an anion exchange column if an appreaciable amount of a water-miscible organic solvent is added to the aqueous hydrochloric acid[12,13]. This behaviour indicated the possibility of using a non-aqueous solvent to promote metal-halide complex formation for the selective elution of metal ions from a cation exchange column. Preliminary work by Piettryzyk[14] indicated that acetone is the most effective of the solvents tested.

The attempts made to investigate systematically the broad fields of mixed aqueous organic solvent media containing hydrochloric acid is limited in comparision to the data available for the cation exchange behaviour of the eluents in aqueous hydrochloric acid. The exchange behaviour of lithium, sodium and potassium and of magnesium, calcium, strontium and barium [7,9,10,13] in methanol hydrochloric acid media has been investigated. Some of the sys-tems were applied to the effective separation of lithium from other alkali metals e.g. by using 90% methanol-10% 2 M hydrochloric acid as eluent for lithium[9] under these conditions the distribution coefficients of lithium and sodium are 2 and 41 respectively. In media containing phenol as well as methanol and hydrochloric acid, lithium was separated from sodium and potassium[15].

Cation exchange separations of alkali metals, alkaline earths and transition metals like copper, cobalt, nickel, manganese and vanadium in ethanol-hydrochloric acid media have been reported [16]. In this case the media offer many attractive possibilities for separations. Its advantages over the acetone-HCl system are (i) Ethanol has high boiling point, (ii) It has no possibility of polymerization in acid solutions and (iii) non-toxic nature of ethanol. Its disadvantages are the case of chloride complex formation and increase in viscosity at higher concentration of acid. Exchange rates for elements which require these kind of eluents often are slow in aqueous solution. In ethanolic solutions they are even slower and resin of a fine particle size leads to considerably improved separations. High viscosities in such cases limit the maximum flow rates attainable without the application of external pressures. Relatively great attention has been paid to cation-exchange studies and separations of various elements with acetone-hydrocholoric acid mixtures as eluents. Buzena, Constantinescu and Topar[17] and Ionescu Negoescu and Gainin[18] have effected the separation of copper and zinc on phenol formaldehyde type cation-exchange resin using acetone-water-hydrocholoric acid solutions as eluting agents. Kember, Macdonald and Wells[19] have studied the behaviour of several metals on Zeokarb 225, cation-exchange resin using acetone-water-hydrochloric acid eluents but were able to separate only copper and nickel. Van Erkelens[20] has studied the ion exchange separation of complex mixtures of metal cations and anions in trace quantities using acetone-water-hydrocholoric acid solutions as eluting agents. He observed that certain separations such as the mixture of cobalt, manganese and iron or the mixture of copper and zinc could not be effected and that the addition of potassium iodide to the eluent is necessary to effect the separation of the mixture of copper and cobalt.

Systematic investigations for the separation of bismuth, cadmium, zinc, iron, copper, uranium, cobalt, gallium and manganese were carried by Fritz and Rettig[21].

The use of organic solvents like iso-propanol, methyl ethyl ketone, glycol, tetra-hydrofuran was made by several workers. The behaviour of praseodymium[22,23] was investigated in hydrochloric acid systems containing methanol, ethanol, iso-propanol, methyl ethyl ketone and glycol. An effective separation of large amounts of iron from cobalt, nickel and aluminium is possible by using the mixture of tetraphydrofuran and hydrochloric acid as eluents[24].

It is seen that cation-exchange in hydrochloric acid organic solvent media has received attention only with respect to the solution of specific separation problems or has been used to study the adsorption behaviour of several metal ions in only one solvent or of only one or a small group of elements in several different organic solvents. The correlation of the various adsorption data obtained in these media by the various authors is extremely difficult because cation exchange resins of various type were used for this purpose. The effect of increasing concentration of organic solvent from o to 90% in solutions with a constant over all acidity of 0.6 M -hydrochloric acid, and the effect of acidity ranging from 0.15 to 1.2 M overall acidity at constant concentration of organic solvent of 90% were investigated by measuring the distribution-coefficient in the same media. From the distribution-coefficients thus obtained, the possibilities of separating the elements from one another was investigated.

J. Korkisch and S.S. Ahluwalla [25] investigated 20 elements on the strongly acidic cation-exchange resin Dowex 50x8 in media containing varying concentrations of aqueous hydrochloric acid and organic solvents like methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetraphydrofuran and acetic acid. Ion exchange equilibrium distribution of Ca, Mg, Co, Ni, Cu and Fe (III) on Imac-Ar Cation exchange resin was studied by Hassan et al[26] in hydrochloric acid containing methanol, ethanol, isopropanol and acetone. The possibilities of several useful separations were suggested from the distribution results.

Distribution coefficients have been measured for the partition of metal ions between cation exchange resin and acetone-water-hydrochloric acid solutions. The differences in distribution coefficients of a metal ion are greater in acetone water media than in aqueous media of the same hydrochloric acid concentration. By using distribution coefficient data, conditions for column separations of mixtures can be effected by eluting with acetone-water-hydrochloric acid solutions of different compositions.

Ion exchange is extensively used for the concentration of uranium or its complete separation from associated elements. For a separation from the rare earths, a non-complexing elution was inadequate owing to the insufficient difference in their ion exchange affinities. Among the complexing eluants proposed may be mentioned oxalate, acetate, fluoride, sulphate, carbonate and EDTA, but few of them have found favour. The anion exchange methods were based on[27] the retention of uranium as its chloro or sulphato complex appeared to be more useful. The popular aminocarboxylic acid eluants are less staisfactory in this case because of the comparatively weak co-ordinating tendency of uranium with nitrogen. The Lanthanides plus yttrium and scandium were separated[28] from Ba, Sr, Ca, Mg, Pb(II), Bi(III), Zn, Mn(II) and U(VI) by eluting these elements with 2.0 M nitric acid from a column of AG 50 W-X8 cation exchange resin (200-400 mesh). The lanthanides were retained and were eluted with 4 M nitric or hydrochloric acid. Elements such as Cu (II), Co(II), Ni(II), Cd, Hg (II), Tl (I), Ag, Be, Ti (IV) and the alkali metals should accompany barium quantitatively according to their known distribution coefficients.

Cation exchange chromatographic studies of scandium on Dowex 50W-X8 were reported by Khopkar[29]. Mineral acids and their salts were tested as eluants. Their efficiency was evaluated in terms of the elution constant and the bed distribution coefficient as $H_2SO_4 > CH_3COONH_4 > NH_4Cl > NaCl > HNO_3 > HCl > NH_4NO_3$.

Scandium was separated from alkali, alkaline earths, iron, zinc, cadmium, mercury, copper, indium, aluminium, vanadium, uranium, and bismuth by the process of selective elution. It was separated from titanium, zirconium, hafnium and antimony by the process of selective sorption. Separation of cobalt, nickel, manganese, lead and silver from scandium was accomplished with sodium chloride as an eluent. The separation from thorium was carried out by gradient elution with hydrochloric acid.

Complex formation of the metals with organic compounds has been advantageously used to achieve difficult seperations. A cation exchange separation methods for uranium in dimethyl sulphoxide [30] and in tetrahydrofuran-nitric acid media containing trioctylphosphineoxide[31] have been developed. Carboxylic acid media have shown great potential for the seperation of metal ions which are other wise very difficult to separate. Fridman and Yudina[32] 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[33]. Lanthanides were separated on Dowex-50 column using ammonium citrate as eluent at pH 3.26. Tartaric acid[34], citric acid and formic acid[35] 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 50x8 in media containing varying concentrations of formic acid and mixtures of formic acid with aqueous dioxan were investigated. The mixture of bismuth and copper solutions was separated. The bismuth was eluted by passing 23 M formic acid through the column at a flow rate of 3.0 ml/min. The copper was then eluted with 2.5 M hydrochloric acid at a flow rate of 1.5 ml/min.

The distribution coefficients in aqueous dioxan-3 M formic acid (1:1) mixtures for the various metal ions were calculated and the separations of the mixtures of lead and copper, barium and lanthanum, cadmium and copper were predicted[35]. A selective study of titanium, vanadium, iron, niobium and uranium in formic, axalic, tartaric and citric acid media was carried out by Quereshi, Varshney and Kaushik[36].

The distribution coefficients in these media at various concentrations were calculated and mixtures of titanium and uranium or titanium and vanadium were separated. Tartaric acid was used as eluent for titanium, formic acid for niobium and nitric acid for vanadium, uranium and iron. Electrophoretic movements of these metal ions were studied in 2% tartaric acid, 10% tartaric acid and 2 M nitric acid in order to ascertain the nature of the charged species of these metals.

Cation exchange distribution coefficients were presented for 46 elements in tartaric acid - nitric acid and in tartaric acid - ammonium tartrate mixtures[37] with AG 50 W-X8, a sulphonated polystyrene resin. The Ionexchange behaviour of the elements in tartrate-containing media was discussed. A selectivity series of elements in tartrate media according to their tendency to tartrate complex formation was presented together with three multielement elution curves demonstrating the separation of the element combinations Sn(IV)-In-Zn-Cd, Mo(VI)-U(V-I) Ni(II) - Mn(II), and Ti (IV)-Sc-Al-Ca.The same study was carried further with the help of Dowex 1x8 anion exchanger. The results obtained by both types of resins were compared and the possible separations of various metal ions were proposed[17]. Cation exchange studies[38] of Yttrium and its separation from various other elements were carried out by Khopkar using malonic acid, tartaric acid as eluting agents.

PRESENT WORK

It is observed that the carboxylic acid-organic solvent media have shown a great potential in the separation of metal ions. In the present work the distribution coefficients for calcium, magnesium, manganese, lead nickel, thorium, aluminium mercury, strontium, barium, zinc, cobalt, copper and cadmium ions in acetone-succinic acid, has been worked out. The data is used for working out the optimum conditions for analytical separations of binary system.

EXPERIMENTAL

(A) Measurement of distribution coefficients

1.00 gm of air dried cation exchange resin was taken in 250 ml glass stoppered conical flask. 4 ml of 0.05 M metal ion solution and 50 ml of the appropriate acetone-water-succinic -acid mixture was taken. The flask was stoppered and kept for 24 hrs. An aliquot from the supern--ent liquid was pipetted out and acetone was evaporated. The metal ion content was determined by suitable titration method.

(B) 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 exchanger under liquid. The column was packed with a small wad of glass wool at the bottom and a slurry of 10 g soaked resin was passed and was allowed to settle by occassional tapping. A care was taken to prevent the formation of air pockets or strata of the ion exchange resin.

PROCEDURE

The column was equilibrated with the resin by passing 20 ml of acetone-water-carboxylic acid mixture at maximum flow rate[39,40]. 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 requisite amount of eluting agent was added. After about ten minutes the effluent fractions were collected in test tubes by maintaining a flow rate of 4.6 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 by 2M HCl or 3 M HNO_3 or 6 M HNO_3, and gets completely eluted at a particular fraction. After complete removal of the two metals, elution is stopped, and the fractions containing first metal are mixed together and the fractios containing second metal ion are also mixed together. The metal ion contents of the two mixtures were carried out by standard titrimetric procedures. Under certain conditions the separation is not complete, some middle fractions were found to contain both the ions, such experimental conditions were avoided.

DISCUSSION :

(A) Distribution Coefficients

The distribution coefficients of Cu, Zn, Mg, Ni, Cd, Co, Mn, Ca, Pb, Th(IV), Al(III), Hg(II), Sr and Ba were found out at 0, 20, 40, 60, and 80 percentages of acetone and at 0.1, 0.3, 0.5 and 0.7 M concentrations of succinic acids. The values of distribution coefficients are presented in tables $4C_1$ to $4C_4$

TABLE-4C$_1$

CATION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-SUCCINIC ACID (0.7 M) MEDIA ON DOWEX 50W-X8 (H^+)

ION	ACETONE PERCENTAGE % (v/v)				
	0	20	40	60	80
Cu(II)	-	T.A.	T.A.	T.A.	t.A.
Zn(II)	-	144	157	176	190
Mg(II)	-	203	353	461	594
Ni(II)	-	T.A.	T.A.	T.A.	T.A.
Cd(II)	-	1728	1728	1728	2619
Co(II)	-	1147	1296	1746	2646
Mn(II)	-	72.2	81	85.4	95.3
Ca(II)	-	T.A.	T.A.	T.A.	T.A.
Pb(II)	-	4158	4806	4806	9666
Th(IV)	-	2806	2443	2443	2443
Al(III)	-	693	693	1066	1066
Hg(II)	-	1458	T.A.	T.A.	T.A.
Sr(II)	-	T.A.	T.A.	T.A.	T.A.
Ba(ii)	-	T.A.	T.A.	T.A.	T.A.

T.A. = Total Adsorption

TABLE- 4C$_2$

CATION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-SUCCINIC ACID (0.5 M) MEDIA ON DOWEX 50 W-X8 (H$^+$)

ION	ACETONE PERCENTAGE % V/V				
	0	20	40	60	80
Cu(II)	972	972	1198	1198	T.A.
Zn(II)	486	576	667	667	667
Mg(II)	385	491	474	482	592
Ni(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Cd(II)	266	705.5	814	1296	1730
Co(II)	918	918	918	918	918
Mn(II)	12.56	12.56	15.43	15.43	22.74
Ca(II)	1566	1566	1296	1296	1192
Pb(II)	1566	2376	2376	2376	4804
Th(IV)	4941	4941	3276	2443	1611
Al(III)	693	693	1066	5063	5063
Hg(II)	324	324	450	702	1458
Sr(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Ba(II)	T.A.	T.A.	T.A.	T.A.	T.A.

T.A. = Total adsorption

TABLE-4C$_3$
b

CATION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-SUCCINIC ACID (0.3 M) MEDIA ON DOWEX 50 W-X 8 (H^+)

ION	ACETONE CONCENTRATION % V/V				
	0	20	40	60	80
Cu(II)	961	992	1215	2484	2484
Zn(II)	871.8	1242	1242	1242	1566
Mg(II)	441	625	677	688	738
Ni(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Cd(II)	1366	1435	1433	2025	2043
Co(II)	1486	2145	2145	2145	5076
Mn(II)	47	76	78	751	798
Ca(II)	507	161	161	105	103
Th(Iv)	2844	2119.5	2119.5	737	ppt.

T.A.= Total adsorption

TABLE-4C$_4$

CATION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-SUCCINIC ACID (0.1 M) MEDIA ON DOWEX 50 W- X8 (H^+)

ION	ACETONE CONCENTRATION % v/v				
	0	20	40	60	80
Cu(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Zn(II)	231.4	478.8	611.9	634.9	670
Mg(II)	307	472	525	532.5	602
Ni(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Cd(II)	854	854	870	944	944
Co(II)	522	876	876	954	1458
Mn(II)	203	206	382.3	400	400.5
Ca(II)	873.4	454	356.2	356.2	206.0
Th(IV)	2844	1395	912.0	737	ppt.

T.A. = Total adsorption

The distribution coefficients of Mn are low at 0.7, 0.5 M succinic acid(SA) at all percentages of acetone, 0.3 M SA upto 40% acetone. This indicates that Mn has very little tendency of forming complexes with succinic acid. The distribution coefficients of Mn at 0.3M SA(above 60% acetone) and 0.1 M SA are higher showing that low concentration of succinic acid is favourable for complex formation.

The distribution coefficients of Zn, Mg, Ca, Co, increase as the percentage of acetone increases and the KD values suggest that the amount taken up on the resin is 4 to 8 times greater than the amount of these metalions remain in the solution,

The distribution coefficients of Cu, Ni, Th(IV), Sr, Ba are very high indicating that these metal ions are preferred strongly by a cation exchange, Dowex 50 WX8. The KD data of the metal ions in tables $4C_1$ - KC_4 suggest the following selectivity sequence.

$\mathrm{Mn} < \mathrm{Zn} < \mathrm{Mg} < \mathrm{Al} < \mathrm{Co} < \mathrm{Cd} < \mathrm{Th} < \mathrm{Pb} < \mathrm{Hg} \lesssim \mathrm{Sr} \lesssim \mathrm{Ba} \lesssim \mathrm{Ca} \simeq \mathrm{Ni} \simeq \mathrm{Cu}$
(0.7 M SA)

$\mathrm{Mn} < \mathrm{Hg} < \mathrm{Mg} < \mathrm{Zn} < \mathrm{Cd} < \mathrm{Al} < \mathrm{Co} < \mathrm{Cu} < \mathrm{Ca} < \mathrm{Pb} < \mathrm{Th} < \mathrm{Ni} < \mathrm{Sr} < \mathrm{Ba}$ (0.5 M SA)

$\mathrm{Mn} < \mathrm{Ca} < \mathrm{Mg} < \mathrm{Cu} < \mathrm{Zn} < \mathrm{Th} < \mathrm{Ni}$ (0.3 M SA)

$\mathrm{Mn} < \mathrm{Mg} < \mathrm{Zn} < \mathrm{Co} < \mathrm{Cd} < \mathrm{Th} < \mathrm{Ni} < \mathrm{Cu}$ (0.1 M SA)

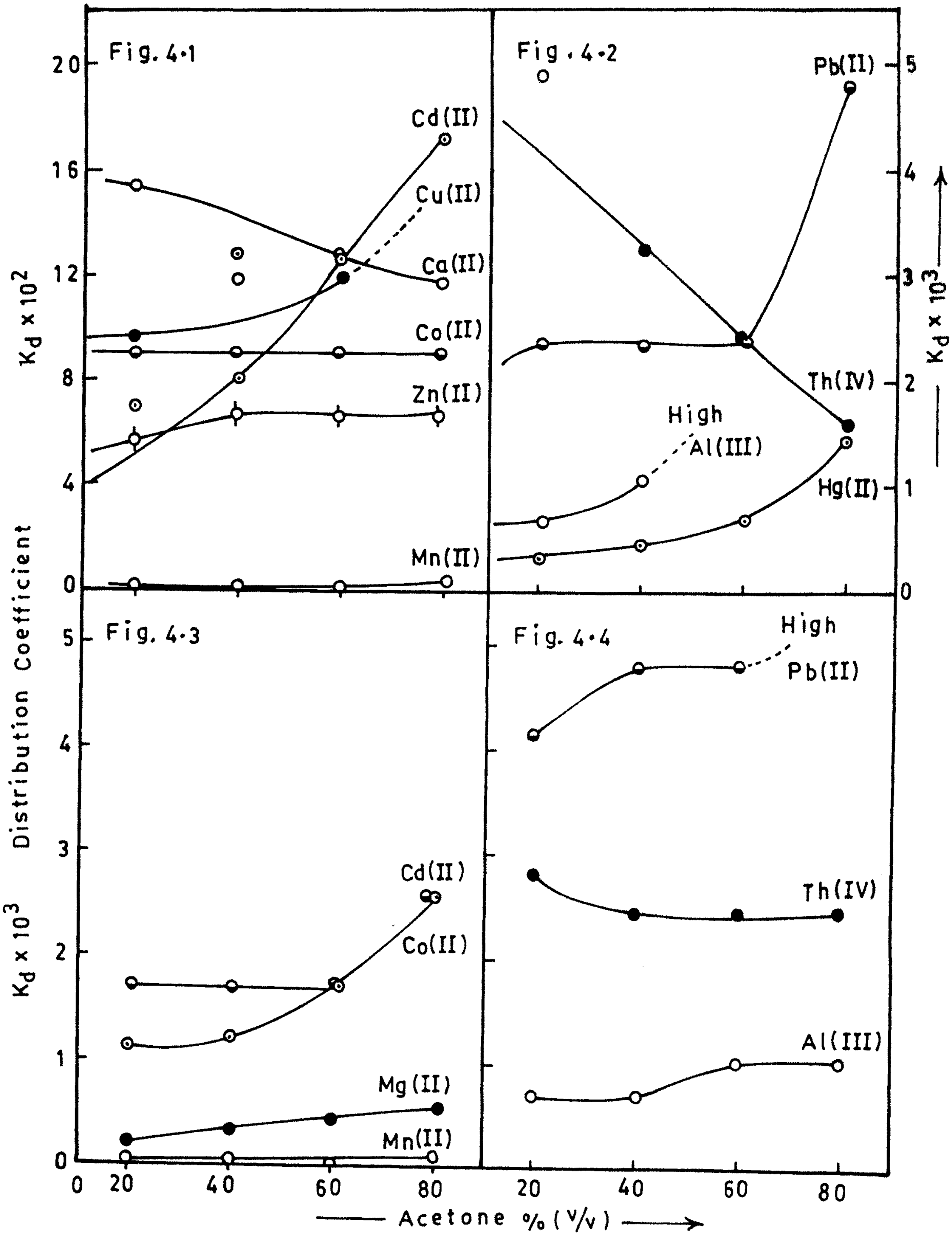
The distribution coefficients for 14 metals are reported at 0.1, 0.3, 0.5 and 0.7 M of succinic acid. The values could not be obtained at concentrations more than 0.7M and the reason is that the succinic acid is soluble at various percentages of acetone only upto 0.7 M. This limit of concentration of succinic acid is the serious obstacle in the studies and the achievements are restricted by this behaviour. The distribution coefficients at 0.7M SA could not be obtained at zero percentage of acetone, the reason being the insolubility of succinic acid.

It is seen that the distribution coefficients vary with the change in concertration of acetone (fig.4.1 to 4.4.) and acid (fig.4.5. to 4.8). The role of acetone and acid on the distribution coefficient is discussed below.

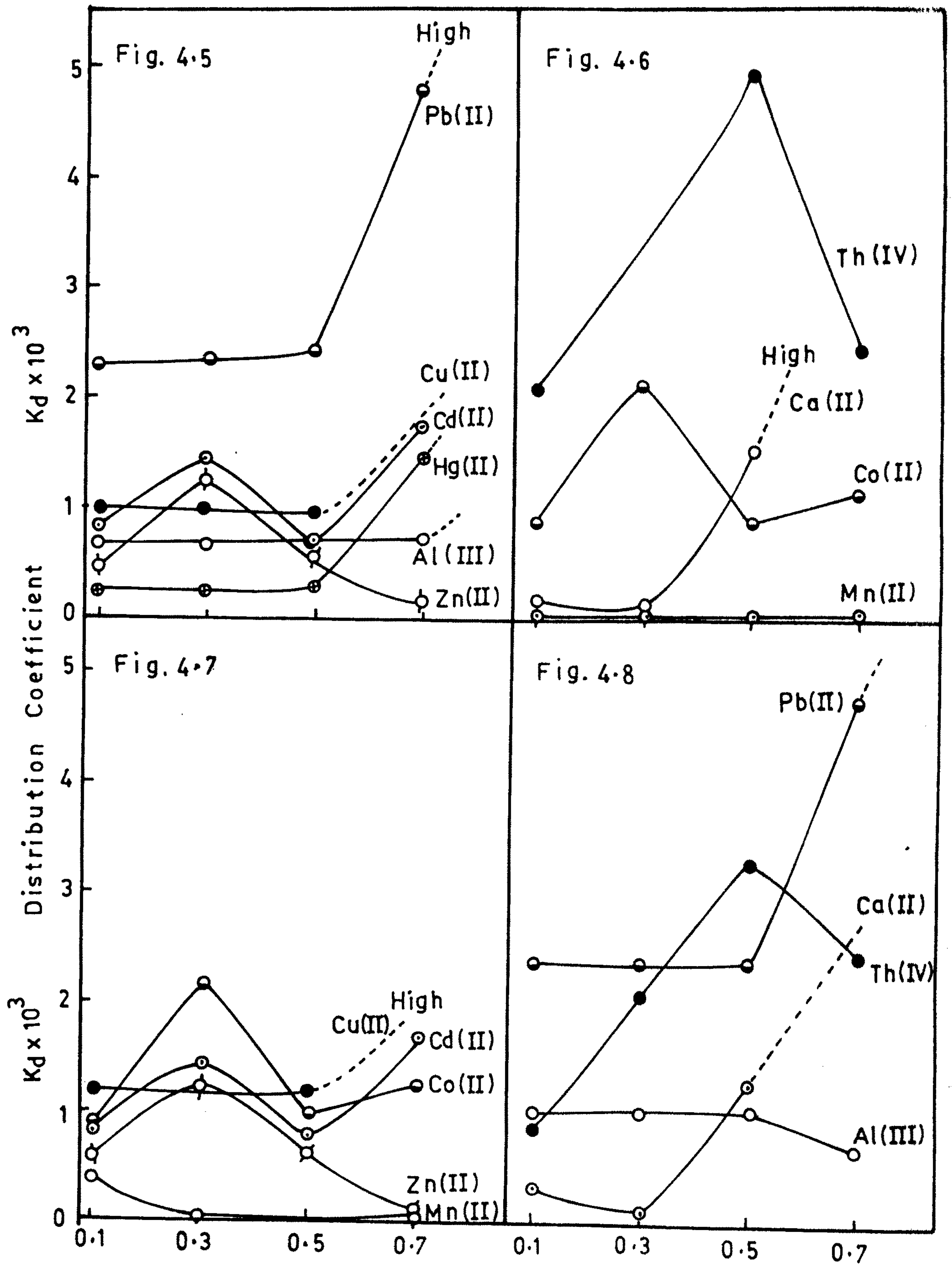
The dielectric constant of a solvent, and the polarity and polarizability of solvent molecules are the properties which effect strongly their interactions with solutes and hence their solvent power. Onsagar and Kirkwood[41] gave the relationship between dielectric constant and dipole moment as

$$(\epsilon - 1)(2\epsilon + 1)/9 = \frac{4x}{3} N(\alpha + g\mu^2/3KT)$$

where α is the polarizability, μ dipolemoment, g coefficient, K Boltzman constant and T absolute temperature. The solvents are classified as non polar ($\mu = 0$), polar ($\mu > 0$), slightly polarizable ($\alpha < 2$ A°) and highly polarizable ($\alpha <$ 10 A°). The symmetrical molecules such as cyclohexane, p-xylene and carbontetrachloride are non polar, the molecules of lower symmetry (toluene, p-dioxane), show a small dipolemoment and the very unsymmetrical molecules, with functional groups such as C = O, $-NO_2$, - CN show high dipolemoments, e.g. acetone (2.72 Debye), nitrobenzene (3.99 Debye). Multiple bonds and bonds between carbon and the heavier halogen and sulphur atoms highly contribute to the polarizability of organic



Distribution Coefficients of metals on Dowex 50W-X8 in 0·5 M $(CH_2COOH)_2$ (4·1, 4·2), 0·7 M $(CH_2COOH)_2$ (4·3, 4·4) media.



Distribution Coefficients of metals on Dowex 50W–X8 at Acetone 20 % (v/v) (4·5, 4·6) and 40 % (v/v) (4·7, 4·8) in $(CH_2COOH)_2$.

molecules, whereas singly C-C or C-O bonds, C-H and C-F bonds contribute less.

The solvents like acetic acid or dibutyl phosphoric acid are hydrogen-bonded dimers and alcohols and water are hydrogen-bonded chains or larger aggregates. Cyclic aggregates and a low dipolemoment, while chain polymers have a low and high dipolemoments respectively[40].

It is observed that the distribution - coefficients of calcium, magnesium, maganese, mercury in zinc, cadmium, aluminium, lead cobalt, copper, thorium in succinic acid increase with the rise in concentration of acetone. It is reported that the distribution coefficients increase with the decrease in dielectric constant. Akerolof[42] has determined the dielectirc constants of a number of aqueous organic solvent mixtures.

TABLE 4 A_1

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

Mixture of such polar solvents as alchols, water and acetone follow Kirkwood's equation[37].

$$\epsilon = \epsilon 1 - \delta 2 \quad C_2$$

where δ_2 is the molar dielectric decrement for dilute solutions of the less polar component 2 = (acetone) ϵ = 21.1 in the highly polar component 1 (water ϵ = 78.4).

A similar change in distribution coefficients of uranium in methanol-water mixtures containing 10% of 6 M nitric acid has been reported earlier[25].

Ionic dissociation leading to electrical conductivity is the most important distiguishing feature of electrolyte solutions and this makes the dielectric constant of the solvent a property of prime importance. Active solvents, being usually highly polar, have appreciable dielectric constants, so that some ionic dissociation occurs (e.g. acetone ϵ = 20.7). Active solvents permit strong ion-dipole interactions, having in many cases atoms with donor properties, so that they can co-ordinate and solvate metal ions. Oxygen and nitrogen atoms with unshared electron pairs are the most important donar atoms. The solvation reaction can be envisaged as a generalized acid base reaction. Solvation is thus one of the main features of electrolyte solutions in active solvents.

The dissolution of a salt in an organic solvent is furthered by a favourable entropy and heat of the solution, the former is always positive and the latter is within the range of ± 10 K.cal/mole. The heat of solution depends strongly on whether the salt is anhydrous, a hydrate or a solvate with the solvent employed, as does the solubility itself. Anhydrous salts are more soluble than the hydrated salts in organic solvents. The heat of solvation of the ions by the solvent, which must overcome the lattice energy of the salt, is an important term in the heat of solution. Only very strong Lewis base solvents can supply the heats of solution so these salts are insoluble in most organic solvents. The same is true for the alkali and alkaline earth metal halides.

The phase diagram in the ternary system CoCl2 - 2H_2O--CH_3 $COCH_3$ is presented in figure. At 25°C above about 30% acetone, there is a two liquid phase region, where the solution splits into a light blue acetone-rich phase containing tetrahedral($CoCl_2 \cdot CH_3COCH_3, H_2O)_4$ and a magenta-coloured water-rich phase, containing more cobalt, as the octahedral $Co(H_2O)_6^{2+}$ mixed with $CoCl_2$ $(CH_3\ COCH_3, H_2O)_4$. Above about 86% acetone in the mixture, the two phases coalesce again, and a minimum solubility is observed at Ca 90% acetone. At still higher acetone concentration, however, there is a sharp upturn in the solubility and cobalt chloride tetra- and trihydrates are at equilibrium with above 20% cobalt chloride in solution. When more acetone is added the solubility again drops, but rises at still higher acetone concentrations again, to yield a 25% Cobalt chloride solution, containing only 3% water, at equilibrium with cobalt chloride dihydratex and various acetonate crystals. The solubility drops to rather low values for the anhydrous salt in pure acetone.

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 mixtures of solvents too. Walden[43] has shown that there is a direct proportionality between the mole fraction of the solute 'i' in the saturated solution and the cube of the

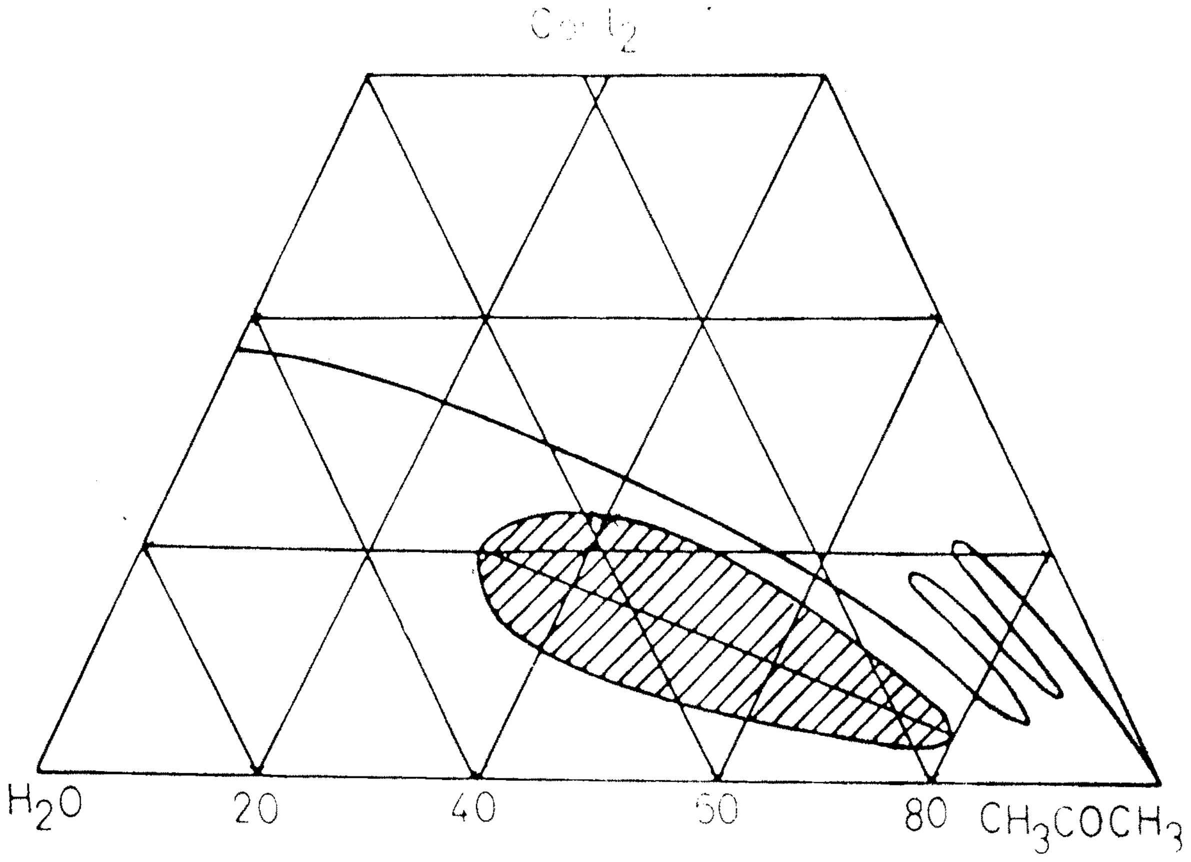


Fig. A Ternary phase diagram of the system $CoCl_2-H_2O-CH_3COCH_3$.

Compositions in the shaded area split into two liquid phases.

dielectric constant of the solvent 'j'

$$X, i, j \ (\mathrm{S\text{-}atd.}) = k \quad i \ \epsilon \ j^3$$

The relative binding energies of water and to organic solvent in mixed solvates were obtained from measurements of the heat of solution of metal salt, hydrates in the organic solvents and in their mixtures with water[44]. Octahedral cobalt(II) is capable of binding two solvent molecules, in addition to two water molecules and two nitrate ions in organic solution, so that the heats of solution of $Co(NO_3)_2 \cdot 2H_2O$ depend directly on the binding of the organic solvent, ranging from ΔH soln = 17.76 K cal/mole for dimethyl formamide to - 1.65 K cal/mole for acetone. The difference between the heats of solution of the tetrahydrate and the dihydrate - -8.78 K cal/mole is the corresponding heat of addition of two water molecules. The value is reasonable with respect to the relative base strengths of the choosen solvent pair. Addition of a small amount of water to an acetone solution of the nitrate dihydrate gives essentially the same value. The cryoscopic measurements in dioxane indicate that acids which associate strongly with water i.e. perchloric acid forms $HClO_4$, $2H_2O$, hydrochloric acid forms $(HCl \cdot H_2O)_2$ and sulphuric acid forms $H_2SO_4 \cdot H_2O$ get solvated to an unknown extent with dioxene[45].

The number of moles of solvent transported with a mole of calcium chloride electro-osmotically has been measured in aqueous methanol[46]. At a mole fraction of 0.7 of methanol there are 7 moles of each solvent transported with the calcium ions, 2 moles of each with the chloride ions. They hydration of closed-shell ions such as the alkaline earths (e.g. Ca^{2+}, Mg^{2+}), cadmium in 50% by volume of aqueous dioxane has been estimated from the chemical shifs of n.m.r. singals[47].

The relative solvating power of water, formamide, methanol and ethanol for cadmium and lead has been measured polarographically[48]. Thallium(I) prefers methanol to water even up to 5 M of the latter solvent, while lead forms hydrates upto $Pb(OH_2)_2^{2+}$ and cadmium and zinc upto the trihydrate. Water can displace all, and methanol most, of the solvent around cadmium ions in acetone, but ethanol cannot, while it can displace some of the solvent from lead ions. Zinc is most hydrated, and least solvated by formamide, while lead shows the opposite behaviour.

A cation is surrounded by the hydration field. As the acetone concentration is increased the distribution coefficient increases without disturbing this hydration field. In some cases the hydration field is weakened enough to allow replacement of the water ligands in the coordination shell by the anions. This causes a sudden decrease in the values of the coefficients, often very much bel-ow their value in pure aqueous acid. When the distribution coefficients reach to their high or saturation values, the state of equilibrium is established between the anions and the water ligands in the coordination shell. At the steady state free cations under study are in equilibrium with those already deposited on the resin, and the process stands out as a limiting case of polar adsorption[49]. Arnikar, Daniels and Kulkarni have observ-ed the steady state in the adsorption of Sr^{2+} and Ca^{2+} ions on aluminium surfaces[50].

In order to know the behaviour of succinic acid towards

TABLE 4C$_5$

CATION EXCHANGE DISTRIBUTION COEFFICIENTS ON DOWEX 50 W-X8 H$^+$

METAL ION	ACETONE CONCENTRATION % V/V							
	0		20		40		60	
	a	b	a	b	a	b	a	b
Cu(II)	972	high	972	high	1198	high	1198	high
Zn(II)	486	216	576	216	667	413	667	413
Mg(II)	385	400	491	450	474	641	482	high
Ni(II)	T.A.	19	T.A.	40	T.A.	495	T.A.	high
Cd(II)	266	480	705.5	high	814	high	1296	high
Co(II)	918	3	918	19	918	10	918	6
Mn(II)	12.56	18	12.56	22	15.43	30	15.43	44
Ca(II)	1566	400	1566	444	1296	660	1296	high
Pb(II)	1566	486	2376	high	2376	high	2376	high

T.A. = Total adsorption.

a = Aqueous acetone-succinic acid (0.5 M)

b = Aqueous acetone-acetic acid (0.5 M)

the metal ions in aqueous acetone media, the values of distribution coefficients of some of the metalions like Cu, Ni, Co, Zn, Ca, Mg, Pb, Cd and Mn in 0, 20, 40, and 60 percentages of acetone at 0.5M succinic acid are compared with those in 0.5M acetic acid. The values are presented in table $4C_5$. It is observed that the distribution coefficients in succinic acid is higher than the corresponding values in acetic acid.

Acetic acid (HA) is a monocarboxylic acid while succinic acid is a dicarboxylic acid. The strength of the acid depends on its capacity to donate protons in aqueous solution. Mono-Carboxylic acid undergoes ionization to an appreciable extent according to

$$HA \rightleftharpoons A^- + H^+$$

If there is a base present to accept the proton which is being lost water is capable of acting as a base and the ionisation of an acid HA in water is represented by

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

In monocarboxylic acids the equilibrium in solution exists as

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad \text{----(1)}$$

The ionization of acid in water increases the concentration of H_3O^+ ions in the solution. The extent of dissociation in aqueous solution expressed as

$$Ka = \frac{(RCOO^-)\,(H_3O^+)}{RCOOH}$$

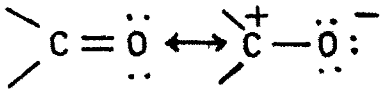
where Ka is acidity constant or ionization constant.

TABLE - $4A_2$

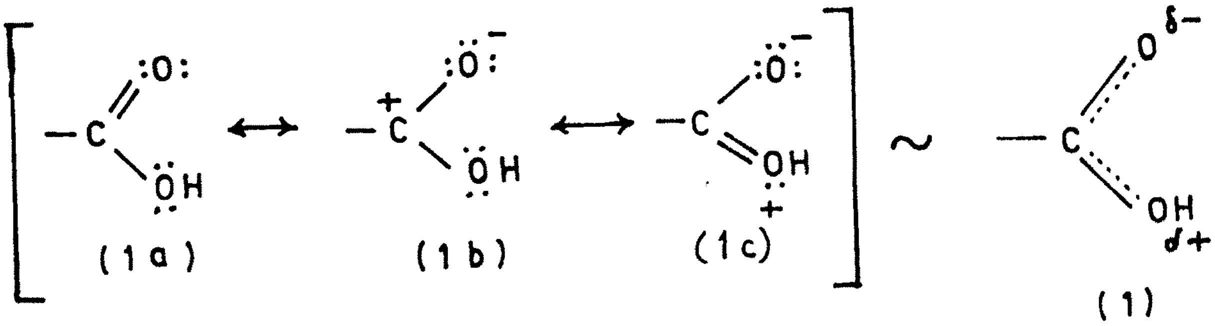
IONIZATION CONSTANTS [53,54] OF ACIDS

Acid	Temp. °C	M.P.	B.P.	- log K_1	-log K_2
Acetic	25	16.6	118.1	4.76	-
Succinic acid	25	18.5	-	4.2066	5.57
	30	-	-	4.1980	-,,-
	35	-	-	4.1914	-,,-
	40	-	-	4.1878	-,,-
	45	-	-	4.1869	-,,-
	50	-	-	4.1863	-,,-

The acidity to the carboxyl group stems, at least in part, from the polar nature of the carboxyl group, the polarity of which can be ascribed to contribution of the structures.

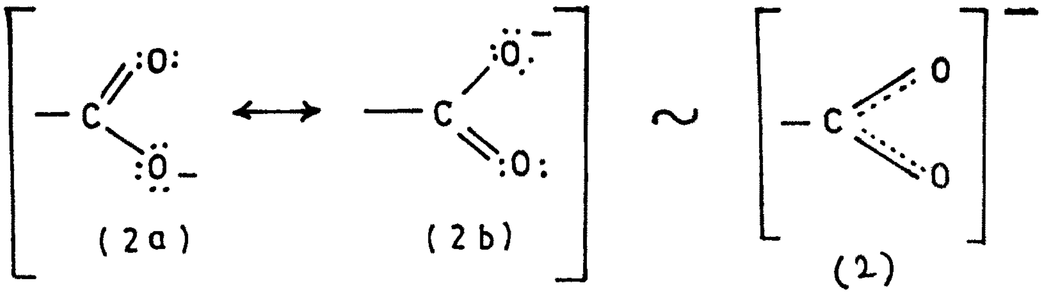


For a carboxyl group the following structures may also contribute.



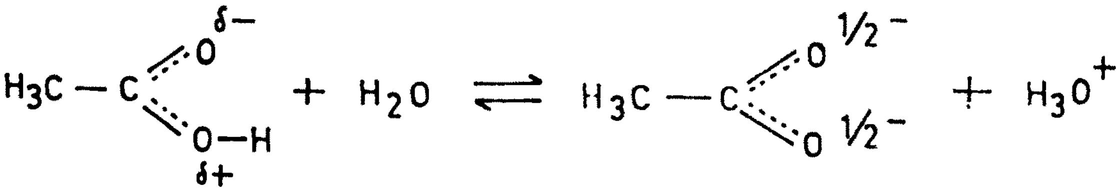
(1)

The stabilization energy of the carboxylate anion is expected to be greater than that of the acid, because the anion can be regarded as a resonance hybrid of two energetically equivalent structures (2a) and (2b) while the acid is represented by a hybrid of non-equivalent structures.



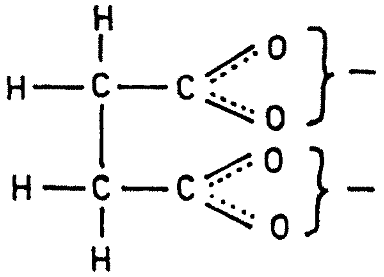
(2)

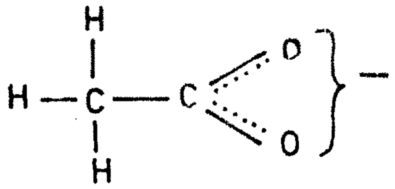
The higher degree of stabilization is achieved when the contributing structures are energetically equivalent. The resonance energy of the carboxylate anion should be greater than that of the acid. A driving force is hence expected to promote the dissociation of carboxylic acids.



Inductive Effects as Measured by Acid strengths

From acid-strength data we can set up a series of relative electron-attracting or electron-donating properties for atoms or groups. Because the induced polarizations set up by bond dipoles are roughly additive. Succinic acid is stronger than acetic acid.





We see that the acid strength of the dicarboxylic acids, as measured by the first acid-dissociation constant, K_1, is higher than that of acetic acid (K_A, $1.75 X 10^{-5}$) and falls off with increasing distance between the two carboxyl groups. The second-dissociation constant, K_2, is smaller than K_A for acetic acid (with exception of oxalic acid) for the reason that it is more difficult to pull off a proton under the electrostatic attraction of the nearby carboxylate anion. This inductive effect of one carbonyl group is expected to enhance the acidity of the other.

The exact mechanism of the uptake of metal ions on the resin is not known. In absence of succinic acid the metalions get exchanged with H^+ ions of the resin. In presence of weak acids like acetic acid or succinic acid the behaviour of the acid in solution may suggest some mechanism. The acid like acetic acid gets dissolved in water, produces a solution containing rather small amounts of hydrogen ion, H^+, and acetate ion $CH3COO^-$, and a large amount of undissociated molecules of acetic acid $H_2C_2H_3O_2$. Similarly succinic acid, when dissolved in water, produces a solution containing small amounts H^+, $\left[\begin{array}{l} CH_2COO \\ | \\ CH_2C{-}O \\ \quad OH \end{array}\right]^-$, $\left[\begin{array}{l} CH_2COO \\ | \\ CH_2COO \end{array}\right]^{--}$ and undissociated succinic acid molecule. Succinic acid forms +vely charged complexes in order to exchange with H^+ ions of the resin. The ultimate structures of complexes may be represented by $M^n({}_nSA)^{n+}$. The details are expresed on page 57 . In case of compounds like H_gCl_2, it is partially ionised in aqueous solution and contains molecular species H_gCl_2, H_gCl^+, H_g^{2+} and Cl^-, all in appreciable concentrations. The exchange between H_gCl^+, H_g^{2+} or $Hg\ (2SA)^{2+}$ and H^+ of resin may take place. The distribution coefficients of metal ions is higher in aqueous acetone succinic acid than aqueous acetone solution.

(B) Separations :

The results of the quantitative separation of synthetic binary mixtures in aqueous acetone-succinic acid are presented in table $4C_{6-7}$ and by figs. 4.9, 4.10, 4.11.

Separation of Mn from Zn/Co/Cu/Ca/Cd/Mg/Ni/Al/Sr/Ba.

Manganese was weakly bound to the resin in comparison with the co-ion in the binary mixtures. Therefore, Manganese was first eluted by 20% acetone - 0.5M Succinic acid solution. The distribution coefficients of Zn, Co, Cu, Ca, Cd, Mg, Ni, Al, Sr, Ba are higher at all concentrations of succinic acid and

TABLE-$4C_6$

QUANTATIVE SEPARATION OF SYNTHETIC BINARY MIXTURES (FIRST ION IN THE MIXTURE IS ELUTED, WHILE THE SECOND ION IS RETAINED)

Mixture	Metalion eluted	Eluting agent	m moles taken	m moles found
1	2	3	4	5
1 Mn(II)+	Mn(II)	a	0.241	0.231
Zn(II)	Zn(II)	b	0.249	0.248
2 Mn(II)+	Mn(II)	a	0.241	0.231
Co(II)	Co(II)	b	0.244	0.243
3Mn(II)+	Mn(II)	a	0.241	0.231
Cu(II)	Cu(II)	b	0.252	0.232
4Mn(II)+	Mn(II)	a	0.241	0.231
Ca(II)	Ca(II)	b	0.244	0.231
5 Mn(II)+	Mn(II)	a	0.241	0.231
Cd(II)	Cd(II)	b	0.249	0.246
6 Mn(II)+	Mn(II)	a	0.241	0.231
Mg(II)	Mg(II)	b	0.256	0.248
7 Mn(II)+	Mn(II)	a	0.241	0.231
Ni(II)	Ni(II)	b	0.251	0.248

Contd. on next page

1	2	3	4	5
8 Mn(II)+	Mn(II)	a	0.241	0.231
Th(IV)	TH(IV)	c	0.255	0.253
9 Mn(II)+	Mn(II)	a	0.241	0.231
Pb(II)	Pb(II)	d	0.256	0.238
10 Mn(II)+	Mn(II)	a	0.241	0.231
Al(III)	Al(III)	b	0.248	0.235
11 Mn(II)+	Mn(II)	a	0.241	0.231
Hg(II)	Hg(II)	c	0.263	0.231
12 Mn(II)+	Mn(II)	a	0.241	0.231
Sr(II)	Sr(II)	b	0.23	0.228
13 Mn(II)+	Mn(II)	a	0.241	0.231
Ba(II)	Ba(II)	b	0.248	0.246

a = 20 % Acetone + 0.5 M Succinic acid

b = 2 M HCl

c = 4 M HNO_3

d = 6 M HNO_3

at 0, 20, 40, 60, 80 perc-entages of acetone and hence these metal ions could not be eluted by medium containing succinic acid. These metal ions form chlorocomplexes[51] with hydrochloric acid, these were eluted by 2M HCl.

Separation of Mn from Th/Hg :

It was seen that 20% acetone - 0.5 M - succinic acid was the best eluent for manganese but not for thorium and mercury. Hence in a mixture of thrium, mercury with manganese, manganese was separated by 20% acetone - 0.5 M succinic acid solution. The distribution coefficients of Th and Hg was found to be higher at all concentrations of succinic acid and at 0, 20, 40, 60, 80 percentages of acetone and hence these metal ions could not be eluted by mixed medium containing succinic acid. The distribution coefficients of Th and Hg are low in 4M HNO_3 and hence these were eluted by 4M HNO_3.

Separation of Mn from Pb:

Lead was taken up very strongly in comparison to manganese. Manganese was eluted first by 20% acetone-0.5 M succinic acid. The distribution coefficient of lead was found[52] to be low in 6 M HNO_3, it is eluted by + 6 M HNO_3.

Elution curves :

The elution curves for the separation o f binary mixtures are presented by figs. 4.9, 4.10, 4.11. The curves indicate how the systematic information contained in tables of distribution coefficients can be applied to develope analytical separation procedures. The clear out separations of metal ions are indicated by no overlap of the elution curves. The various shapes of the elution curves are discussed below.

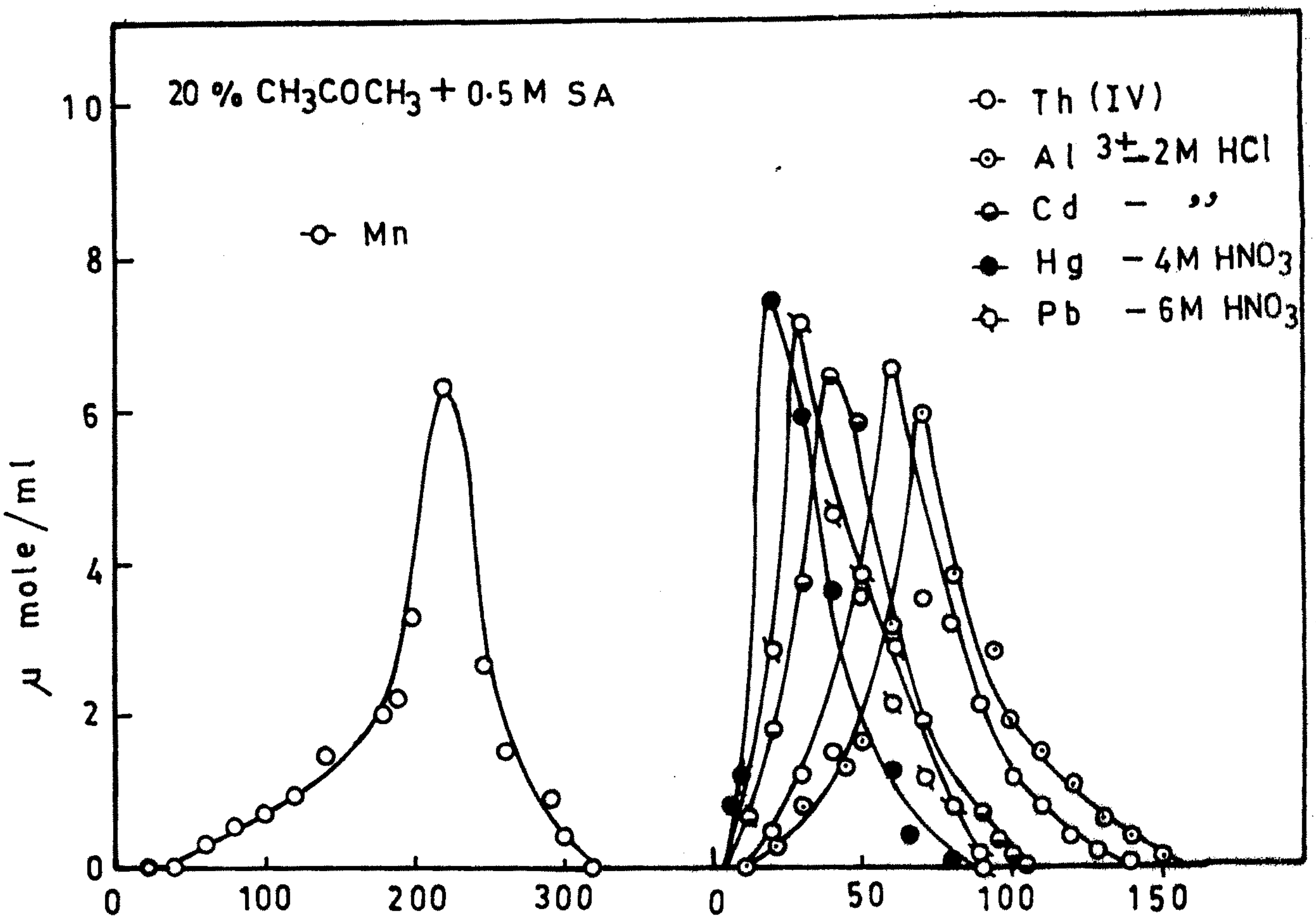


Fig. 4.9 – Elution Curves of Mn – Hg/Th(IV)/Pb/Al/Cd.

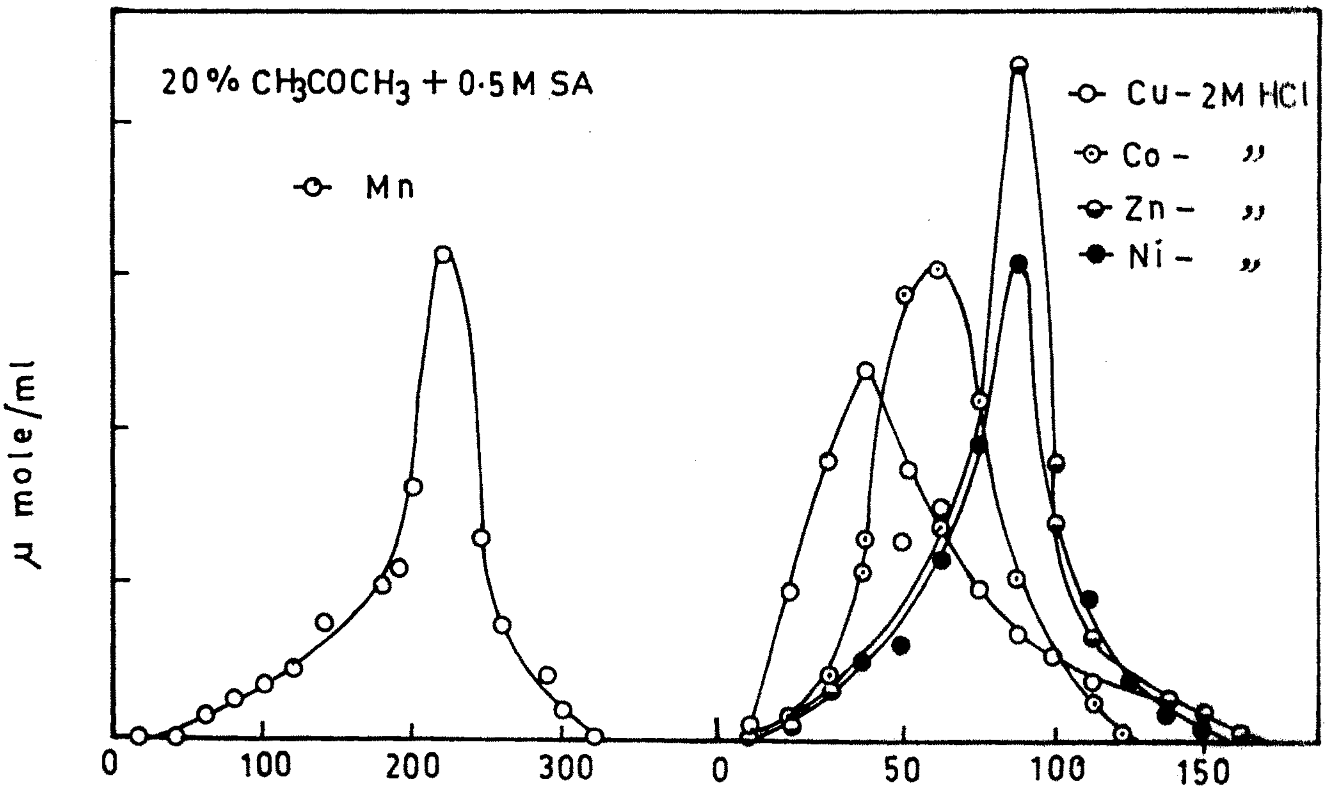


Fig. 4.10 – Elution Curves of Mn – Cu/Co/Zn/Ni.

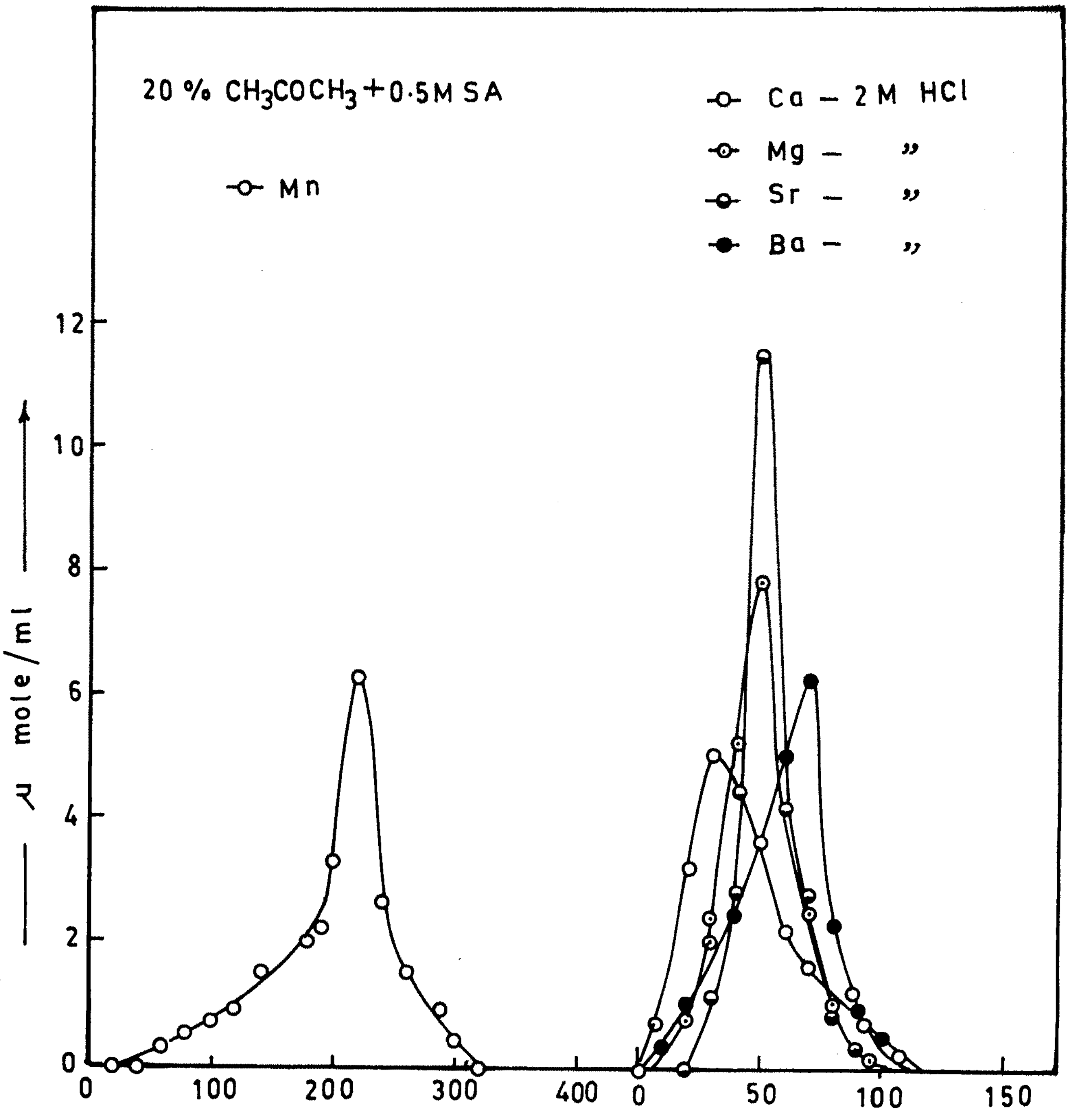


Fig. 4·11 — Elution Curves of Mn — Ca/Mg/Sr/Ba.

Ideally the concentration profile of a solute in the direction of movement of the mobile phase should remain Gaussian at all concentrations as it moves through the system. However, sorption characteristics of change at high concentrations resulting in changes in the distribution ratio. If no such changes occured, a plot of the concentration of solute in the mobile phase as a function of that in the stationary phase at constant temperature would be linear and the concentration profile symmetrical. Plots of this type, known as sorption isotherms, can show curvature towards eigher axis under which circumstances the concentration profiles will show tailing or fronting. Both these effects are undersirable as they lead poor separations and unreliable quantitive data. Fronting which produces peaks with sloping front and sharp near boundaries is more likely to occur in systems where partition forms the basis of the separation process, and where the solute has a small distribution ratio. Tailling produces peaks with sharp leading edges and long sloping near boundaries. It is particularly likely to occur where adsorption is involved in the separation process. Both effects become pronounced at high concentrations and are therefore symptomatic of overloading the column or surface with sample. Restricting the sample size so as to operate over the linear region of the sorption isotherm is a recognized means of preventing fronting and tailing.

In two component mixtures the second metal ion is separated by 2 M HCl 4M HNO_3/6 M HNO_3 and the curves represent

Linear isotherm or gaussion profile. Similar Gaussion profile is shown by most of the other metal ions indicating good separation. (Fig. 4.9, 4.10, 4,11) The elution curves for Ca^{2+} ions (fig.4.11) and the elution curves for Mn^{2+} ions (fig. 4.9, 4.10, 4.11) are non-linear isotherms and indicate fronting effect. These separation processes may be due to partition phenomenon. The most of the elution curves are linear isotherms i.g. gaussian profiles and few show slight curved isotherms. It can be concluded that the diagrams represent a considerable good separation.

Separation Limits

The separation of manganese from zinc, cobalt, copper, nickel, calcium, magnesium, mercury, thorium, lead, cadmium, strontium, barium, aluminium in water-acetone and succinic acid (0.5M) medium was carried at 0.05 M each. The separations were further carried out at 0.025 and 0.012 M of the metals.

It is generally observed that the metal ions calcium, manganese could be separated in the mixed media only upto 0.05 M. The recovery of 0.025 and 0.012 M of these metal ions in these media is only 35%. Thorium, mercury were eluted by 4 M HNO_3 and lead by 6 M HNO_3 up to 0.012 M concentration. Zinc, cobalt, copper, caldum, magnesium, nikel, aluminium, strontium and barium were eluted by 2 M HCl up to

TABLE-$4C_7$

ELUTION CHARACTERISTICS OF METAL IONS IN ACETONE WATER-SUCCINIC ACID MEDIA

Sr. No.	Metal Ion	BTV ml	VEP ml	TEV ml	Eluent
1	Cu(II)	8	40	144	b
2	Cd(II)	5	40	90	b
3	Hg(II)	3	20	90	c
4	Zn(II)	6	80	144	b
5	Mn(II)	25	220	320	a
6	Co(II)	6	60	112	b
7	Ni(II)	8	80	138	b
8	Al(III)	10	70	158	b
9	Th(IV)	12.5	60	145	c
10	Pb(II)	5	30	90	d
11	Mg(II)	5	50	100	b
12	Ca(II)	2.5	30	117	b
13	Sr(II)	20	50	100	b
14	Ba(II)	5	70	110	b

a = 20 % Acetone+ 0.5 M Succinic Acid

b = 2 M HCl c = 4 M HNO_3 d = 6 M HNO_3

0.012 M concentrations.

Elution Characteristics:-

The nature of elution of metal ions by various eluents from ion exchange columns is known by the elution characteristic values. BTV is break through volume and describes the initial volume required to start the elution. Once the elution is started, the effluents are collected in various fractions and the maximum amount of it is recorded which is termed as peak elution volume, VEP. The elution is continued till almost all concentration of metal ion is removed from the column. The total volume required for complete elution is called as terminal elution volume, TEV.

The elution characteristics of Cu, Cd, Hg, Zn, Mn, Co, Ni, Al, Th, Pb, Mg, Ca, Sr, Ba are presented in table $4C_7$. It is observed that the elution of Cu, Cd, Hg, Zn, Co, Ni, Pb, Mg, Ca, Ba, is very quick. The rate of flow for the elution of these metal ions was 2 ml/min and hence the average time required to start the elution is 2-3 minutes. The elution of thrium starts after 6-8 minutes and Sr required 10 minutes. The manganere ions require more time with the flow rate 2 ml/min and hence the rate of flow for the elution of Mn^2 was kept 4.6 ml/min. It requires 6-8 minutes with this higher rate. The values of VEP are in the range 30-80 for all metal ions except manganese. VEP = 220 for manganese. As regards the time required for complete elution of these metal ions, it is seen that these require nealy two hours. Manganese require about 1½ hrs but the flow rate is maintained high. If the same flow rates are adjusted manganese require more time. In the quantitative separation of binary mixture manganese is eluted first, i.e. the elution o-f manganese takes place in presence of its co-ion and hence it requires more time. In the elution of second metal ion from the binary mixture there is no interference of other ion and hence it is eluted fast.

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