CHAPTER 3

RESULTS AND DISCUSSION

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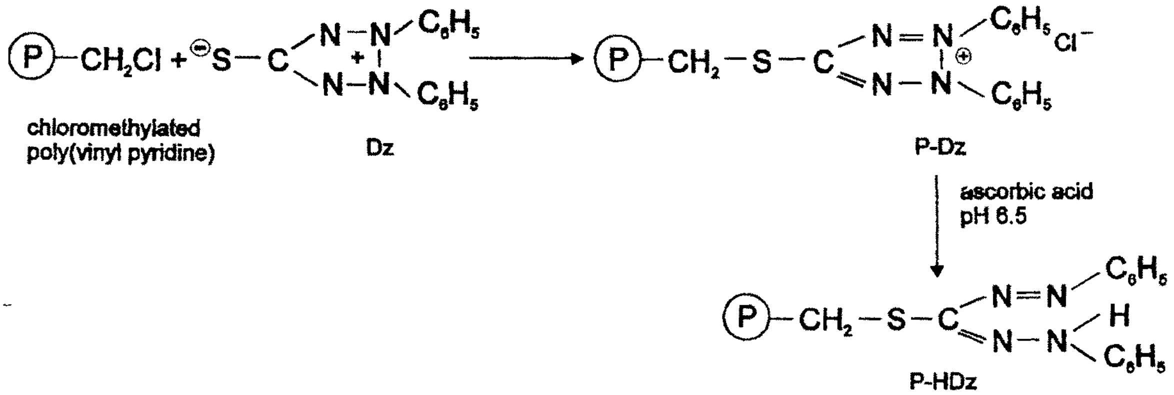
The synthesised resin was brown in colour. The resin beads of 20 - 60 mesh size were used through out the work. The resin was insoluble in most of the organic solvents and was stable to mineral acids upto 6 M strength. However, it was not stable even at 1 M alkalies. The colour of the resin became intense in alkaline medium. The change in colour was observed to be reversible but the resin lost its exchange capacity during the process. The resin showed good storage stability over the period of 3 years.

For the anchoring of dithizone to chloromethylated poly (vinyl pyridine), dehydrodithizone[1,2], an oxidized form of dithizone was used. Because of the enhanced nucleophilic properties of the mesoionic compound, displacement reactions at the chloromethylated group of the reactive polymer proceed successfully, resulting in a support carrying sulfur-bonded dehydrodithizone denoted as P-Dz. Opening of the heterocycle was achieved by reducing the orange resin, P-Dz with a neutralised solution of ascorbic acid which gave rise to a support carrying S-bonded dithizone denoted as P-HDz. The reactions involved in the preparation of the resin containing dithizone group are given in Fig. 3.1.

3.1 Structure of the chelating resin

The probable structure of the resin was deduced from the C,H,N, and Cl analysis and the results of the analysis are given in Table 3.1. From the C,H,N, and Cl analysis, it was found that chloromethylated poly (vinyl pyridine) contains 1.4 mmol g^{-1} chlorine where as dithizone anchored on chloromethylated poly (vinyl pyridine) contains ~1.1 mmol g^{-1} dithizone (based on nitrogen analysis) and 0.38 mmol g^{-1} of chlorine. Further the presence of dithizone was confirmed by FTIR spectrum of the resin. The FTIR spectra of (a) poly (vinyl pyridine), (b) chloromethylated poly (vinyl pyridine) and (c) dithizone anchored chloromethylated poly (vinyl pyridine) are given in Fig. 3.2. In the spectrum of poly (vinyl pyridine) a strong band at ~993 cm^{-1} for vinyl group was observed. Whereas in the spectrum of chloromethylated poly (vinyl pyridine), a stretching band at ~832 cm^{-1} for C-Cl group was observed. The FTIR spectrum of the dithizone anchored chloromethylated poly (vinyl pyridine) shows a sharp and intense band for C=S group linked to N between 1450-1400 cm^{-1}. This was taken as a proof for the presence of dithizone in the resin. The structure of the resin is given in Fig. 3.1

Fig. 3.1



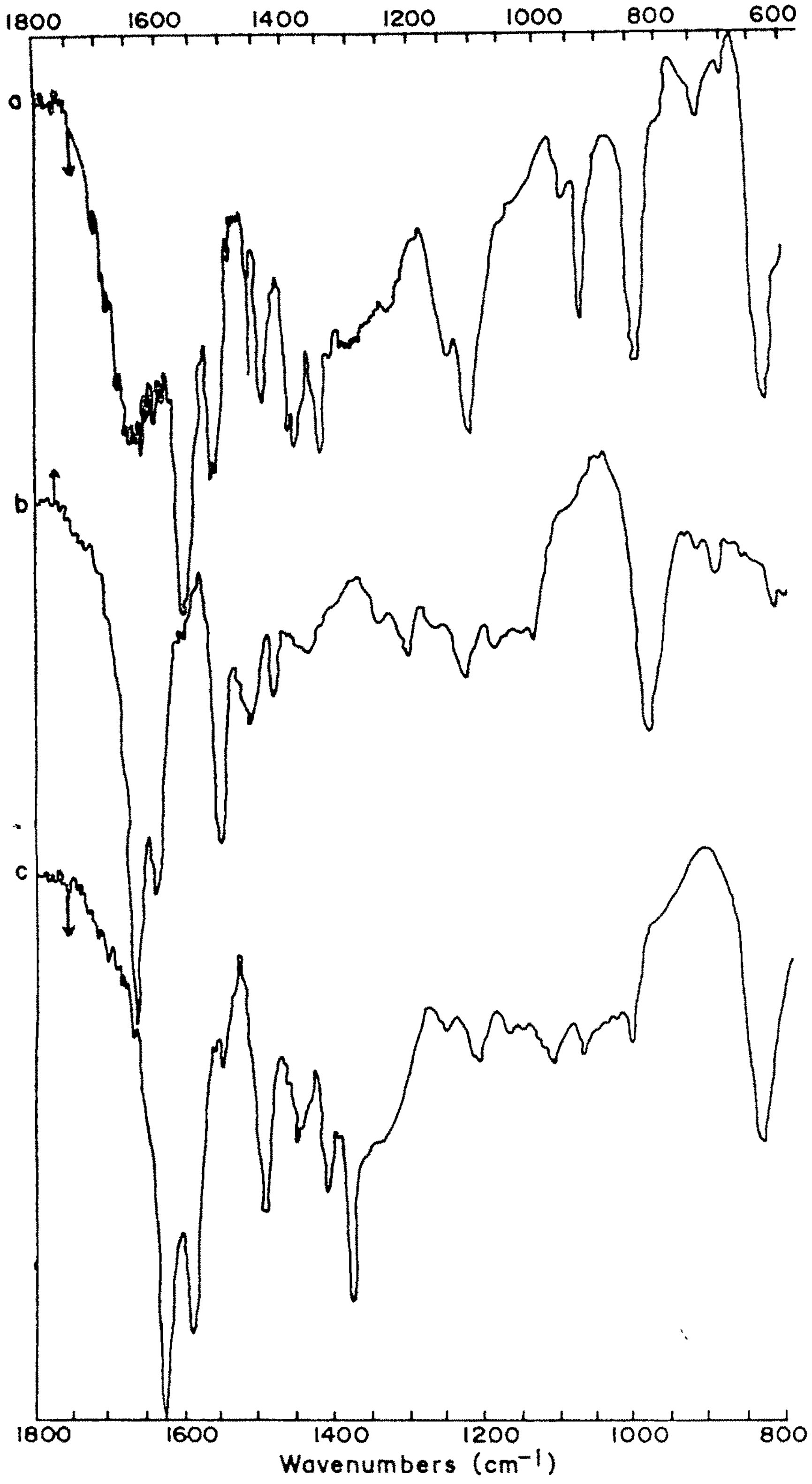
Dz = dehydrodithizone
HDz = dithizone

Table 3.1 : Elemental Analysis

Element	% content in		
	poly (vinyl pyridine)	Chloromethylated poly (vinyl pyridine)	Dithizone anchored resin
C	59.37	60.95	72.65
H	6.57	6.85	6.94
N	8.65	7.27	13.39
Cl	-	4.97	1.35

Fig. 3·2

i.r. Spectra



a = Poly (Vinyl Pyridine)

b = Chloromethylated Poly (Vinyl Pyridine)

c = Dithizone anchored chloromethylated Poly (Vinyl Pyridine)

3.2 Physicochemical properties

The physicochemical properties of the polymeric support are listed in Table 3.2. The lower moisture content value is due to crosslinked polymer. The resin did not show any loss in exchange capacity even after 25 cycles.

3.2.1 Stability of the resin

Storage stability of the resin depends on the regeneration efficiency, swelling and solubility of the resin. From preliminary studies it was observed that the resin shows good regeneration efficiency and considerable swelling in the aqueous medium (Table 3.2). No change in the copper exchange capacity was observed when the resin was heated to 30 -150 °C for 8 h indicating good thermal stability. From the TGA study it was observed that even at temperatures as high as 575°C only 50% decomposition of the resin takes place indicating good thermal stability. From TGA curve activation energy for the decomposition of the resin was calculated and was found to be 16.12 Kcal and 8.90 Kcal for first and second stage decomposition of the resin respectively.

3.2.2 True and apparent densities

Floating of resin particles is undesirable in column chromatographic studies as it hampers the formation of compact columns. Hence resins with higher true densities are desirable. The resin used in the present work showed 1.24 g cm^{-3} true density and 0.34 g cm^{-3} apparent density (Table 3.2).

3.2.3 Void Volume Fraction

The higher values of the void volume fraction facilitates the diffusion of ions in the resin and hence increases the rate of exchange of ions. The resin under study exhibited reasonably high void volume fraction (Table 3.2) which was measured as discussed earlier in sec. 2.4.2.

3.2.4 Concentration of fixed ionogenic groups

The extent of ion exchange process[3] can be explained through the knowledge of concentration of fixed ionogenic groups (Cr). This value for the synthesised resin was calculated[4] as discussed in section 2.4.3 from the data of copper exchange capacity and true and apparent densities. The results obtained are given in Table 3.2.

3.2.5 Volume capacity

Volume capacity is not a constant parameter, it can be understood as the capacity of the number of ionogenic groups per unit volume of packed column in terms of equivalents per unit volume[3] of fully swollen resin bed. Volume occupied by a given amount of the ion exchanger depends on the experimental conditions like ionic form of the resin and composition of the solution with which it is in contact. It also depends on the swelling capacity of the ion exchanger and hence on the degree of crosslinking. A weakly crosslinked resin swells more strongly and this has a lower capacity per unit volume. Usually it is observed that volume capacity of a highly crosslinked resin is higher when the resin bed is treated with

Table 3.2 : Physicochemical properties of the dithizone anchored poly (vinyl pyridine)

Sr.No.	Properties	
1	% Moisture	4.77
2	% Swelling	36.00
3	% Solid	95.23
4	True density, g cm^{-3}	1.24
5	Apparent density, g cm^{-3}	0.34
6	Void volume fraction	0.73
7	Chelating capacity, m mol g^{-1} for Cu^{2+}	0.51
8	Concentration of fixed ionogenic group (Cr), m mol g^{-1} for Cu^{2+}	0.61
9	Volume capacity (Q), eq cm^{-3} for Cu^{2+}	0.17
10	$t_{1/2}$ value for Cu^{2+}, min	35.5

electrolyte solution as it contracts in the presence of electrolyte. In the present work, the synthesised resin shows considerable swelling (~36%) indicating weakly crosslinked resin and therefore low volume capacity was observed. The results are given in Table 3.2.

3.2.6 Rate of exchange of metal ions

Rate of exchange of the metal ions with the resin is a useful property which determines the effectiveness and economical viability of the ion exchange process. Hence rate of exchange for the metal ions under study was determined as discussed earlier in sec. 2.3.8. The results obtained are discussed later in the relevant sections. It was observed that complete exchange of metal ions takes place within 3 to 15 h whereas time required for 50% of exchange ($t_{1/2}$) was considerably shorter for the metal ions under study. The faster rate of exchange observed in the begining is due to the law of mass action and the rate gradually decreases because of the slow diffusion in the interior of the resin.

3.2.7 Mechanism of the exchange processes

Exchange process is controlled by the nature of diffusion of ions from the solution towards resin. The nature of diffusion of metal ions was studied through the interruption test[3,4] as discussed earlier in sec. 2.4.4. From the results obtained (Fig. 3.6, 3.11 and 3.16) it was observed that metal exchange is a particle diffusion controlled process. The 10.0 min interruption pause during the test gives time for the concentration gradients developed in the beads to level out resulting in the increase in exchange rate after reimmersion. On the other hand in film diffusion no concentration gradient exists in the beads and hence the interruption does not affect the concentration gradient across the beads resulting into no effect on exchange rate.

Particle diffusion was also confirmed with the mathematical model proposed by Nativ et al[5] as discussed below. According to this model,

$$t = \frac{C_{So}R^2}{6D_eC_{Ao}}\left[1 - 3(r_c/R)^2 + 2(r_c/R)^3\right] \tag{3.1}$$

where Cso is the concentration of the solid resin.

R is the radius of the resin bead

D_e is the effective diffusivity of the counter ion

C_{Ao} is the concentration of counter ion A

r_c is the radius of diffusion shell

The fraction conversion 'X' of the resin which is a ratio between the measured and maximum capacity is given as,

$$1 - x = (r_c / R)^{1/3} \tag{3.2}$$

The rate expressed in terms of the fraction conversion is,

$$t = \frac{C_{So}R^2}{6D_eC_{Ao}}\left[1 - 3(1-x)^{2/3} + 2(1-x)\right] \tag{3.3}$$

As C_{So}, R, D_e and C_{Ao} are constant for a given system,

$$t \propto \left[1 - 3(1-x)^{2/3} + 2(1-x)\right]$$

According to this model straight lines not passing through origin obtained in the plots of t vs $[1-3\ (1-x)^{2/3} + 2\ (1-x)]$ confirm the shell progression mechanism controlled by the particle diffusion through the reacted layer. In the present work, we have obtained plots with intercept on X and Y axis supporting the particle diffusion process.

3.3 Role of chromatography

Many transition, heavy and rare earth metals are known as toxic for human and aquatic life. Even the presence of very low concentration of these metal ions in water and food is undesirable. Industrial effluents and minerals show a considerable amount of such metal ions. In the analytical chemistry, it is always challenging to estimate and separate the specific metal ion in the presence of others. Chromatography is one of the techniques used for this purpose. Preconcentration and separation of a given metal ion on the ion exchange resin takes place at the optimised pH, time of contact, rate of exchange and strength of eluting reagent. Optimisation of conditions for the chromatographic studies of copper, nickel, zinc, lead, cadmium, mercury, gold, platinum and palladium is discussed in the later sections. For the sake of the convenience of data representation the metal ions are grouped into 3 categories:

(i) Essential metals : copper, nickel and zinc
(ii) Heavy (toxic) metals : lead, cadmium and mercury
(iii) Noble metals : gold, platinum and palladium

The results obtained are discussed in the following sections.

3.4 Preconcentration of copper, nickel and zinc

Traces of copper, nickel and zinc are essential for life. But imbalance of these elements has adverse effects resulting into metabolic disorders due to both deficiencies and excess amounts of these metal ions.

Higher concentration of copper in body causes sickness and liver damage. Even a trace quantity of copper sulphate causes acute poisoning to the living system when injected. It also causes detrimental effect on biological environment. It accumulates in soil whenever copper fungicides are used.

Common nickel compounds have produced toxic effects in human and other animals. Traces of nickel in water, soil or food are not considered hazardous but larger amounts lead to toxicity. Nickel(II) ions can bind to nucleic acids and can have significant genetic effects. Certain enzymes are inhibited by nickel ions. Alteration of the normal level of nickel in the blood causes a number of diseased states. It is carcinogenic and it also causes dermatitis.

Zinc is in fact, an essential element for growth and development of the body. Zinc ion is an essential component of some of the enzymes and hormones. But inhalation of zinc fumes from galvanising baths sometimes produces 'Zinc fever' characterised by chills and fever, nausea and aching. Edema of the lungs from fumes of zinc chloride has sometimes proved fatal. Soluble and astringent acidic salts such as $ZnSO_4$ in large doses have caused internal organ damage and death.

Copper, nickel and zinc being transition elements, can form complexes with many organic compounds present in any materials. Therefore, estimation of microquantities of copper, nickel and zinc in various types of samples is all time a favourite problem. These metals have high affinity towards dithizone reagent. Hence, preconcentration and separation of copper, nickel and zinc from other metal ions by batch and column chromatographic methods using dithizone anchored poly (vinyl pyridine) is discussed here and conditions are established for the removal and separation of these metal ions.

3.4.1 Effect of pH on copper, nickel and zinc exchange

The results obtained in the study of effect of pH on copper, nickel and zinc exchange capacity of the resin are given in Fig. 3.3 and Table 3.3. It was observed that in acetate buffer exchange of copper and nickel was quantitative but zinc was not exchanged with the resin under study. Hence, zinc exchange was carried out in citrate-phosphate buffer. The optimum pH for the metal exchange was observed to be 5. However, copper and zinc showed slight decrease in exchange capacity above pH 5 but nickel shows no effect of pH on exchange capacity above pH 5. The selectivity order of the dithizone anchored poly (vinyl pyridine) resin towards copper, nickel and zinc based on distribution coefficient was observed to be Cu(II) > Zn(II) > Ni(II).

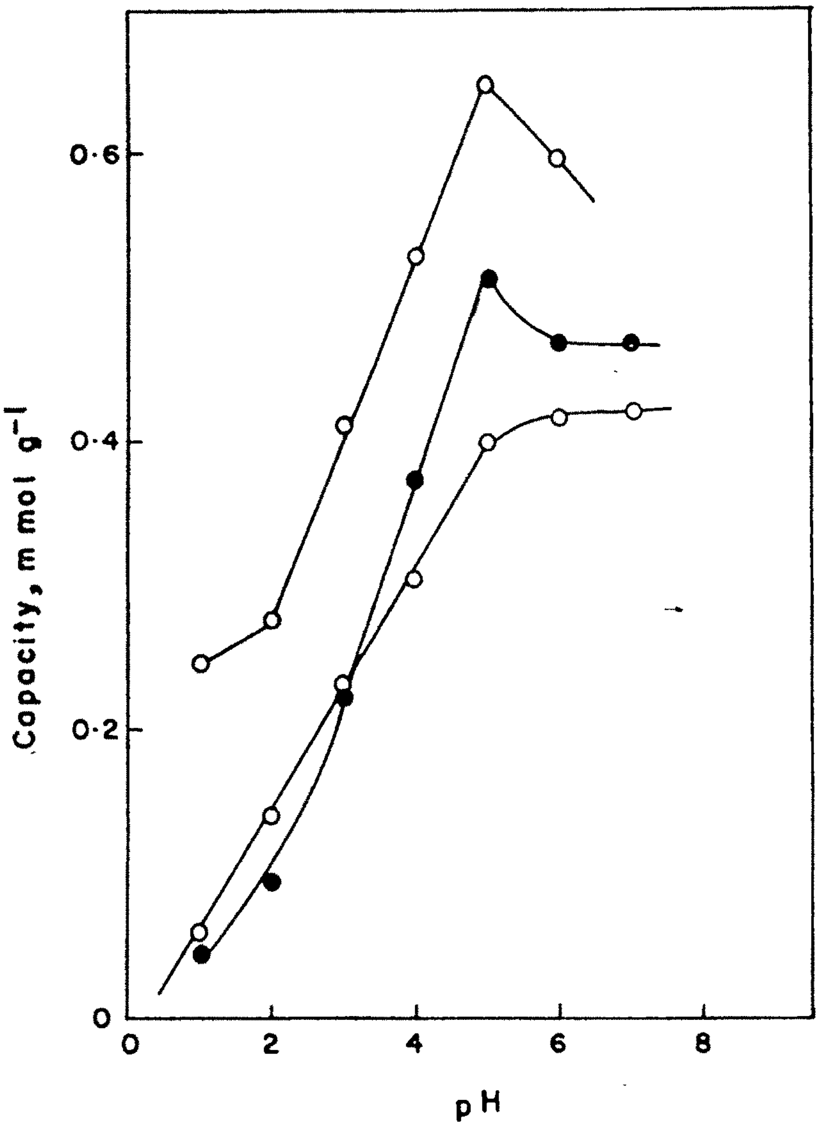
The variation in copper, nickel and zinc exchange capacities and hence distribution coefficients is due to variable chelate forming capacities of the resin towards these metal ions.

3.4.2 Effect of copper, nickel and zinc ion concentration on exchange capacity

From the results presented in Fig. 3.4 and Table 3.3 it was observed that uptake of all the three metal ions by chelating resin increases with increasing concentration of copper, nickel and zinc and attains a constant value. In the present study at the initial concentration of 200 $\mu g\ cm^{-3}$ of Cu(II), 800 $\mu g\ cm^{-3}$ of Ni (II) and 400 $\mu g\ cm^{-3}$ of Zn (II), resin attains saturation exhibiting 0.51, 0.59 and 0.65 mmol g^{-1} exchange capacity for copper, nickel and zinc respectively.

Fig. 3·3

Effect of pH on Copper, Nickel and Zinc exchange



Resin taken 0·1 g ; Copper, Nickel, Zinc concentration 200, 400, 400 µg cm^{-3} respectively ; equilibration time 24 h ; reaction volume 25 cm^{3}.

● Copper, ○ Nickel, ⊙ Zinc.

Table 3.3 : Optimum conditions for copper, nickel and zinc exchange

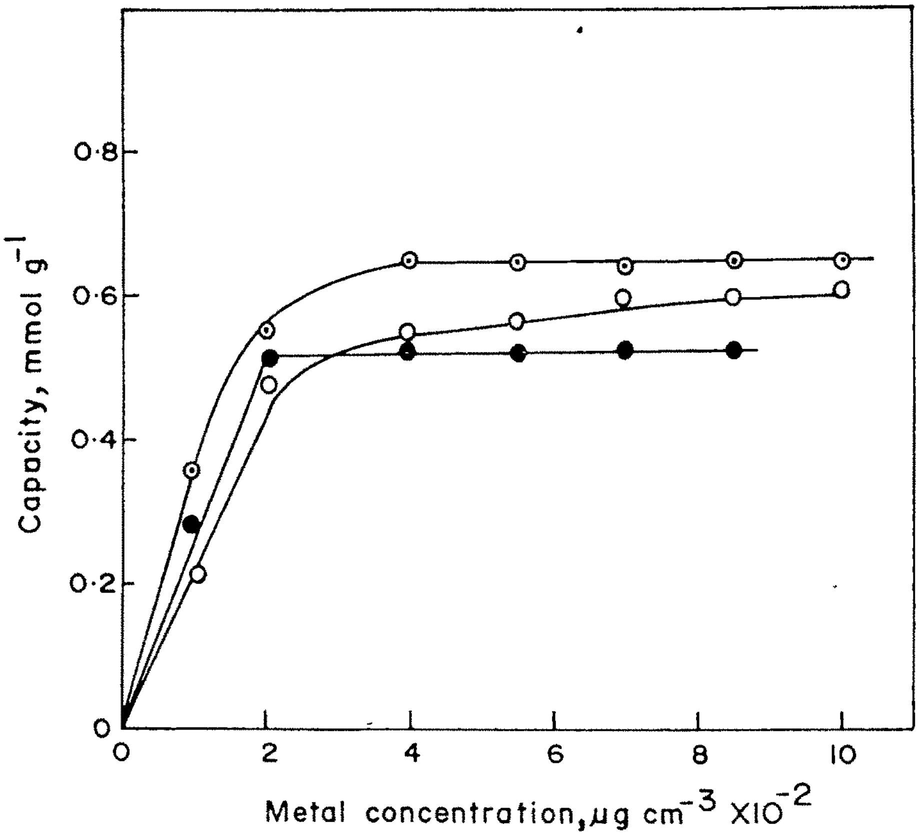
Equilibration time 24 h, reaction volume 25 cm^3, resin 0.1 g

Metal	**pH**	**Optimised Metal concentration $\mu g\ cm^{-3}$**	**Capacity m mol g^{-1}**	**Kd * values**	**$t_{1/2}$ min.**
Cu(II)	5.0	200	0.51	472.0	35.5
Ni(II)	5.0	800	0.59	305.0	30.0
Zn(II)	5.0	400	0.65	375.0	45.5

* Kd values for 200 $\mu g\ cm^{-3}$ copper, nickel and zinc concentration

Fig. 3·4

Effect of Copper, Nickel and Zinc ion concentration on exchange process



Resin taken 0·1 g ; pH – 5 ; equilibration time 24 h ; reaction volume 25 cm^3

● Copper, ○ Nickel, ⊙ Zinc,

3.4.3 Kinetics of copper, nickel and zinc exchange

Ion exchange is a purely diffusion controlled process. Ion exchange is inherently a stoichiometric process. Any counter ion which leaves the ion exchanger is replaced by an equivalent amount of other counter ion. Deviation from stoichiometric behaviour can occur because of electrolyte sorption on the ion exchange material which changes the co-ion content of the ion exchanger. Under normal conditions, according to Donnan theory at equilibrium a considerable potential difference is developed between an ion exchanger and the electrolyte solution in contact with it. This potential difference prevents the accumulation of electrolyte solution in the interior of the ion exchange resin so that deviation from stoichiometric exchange remains small.

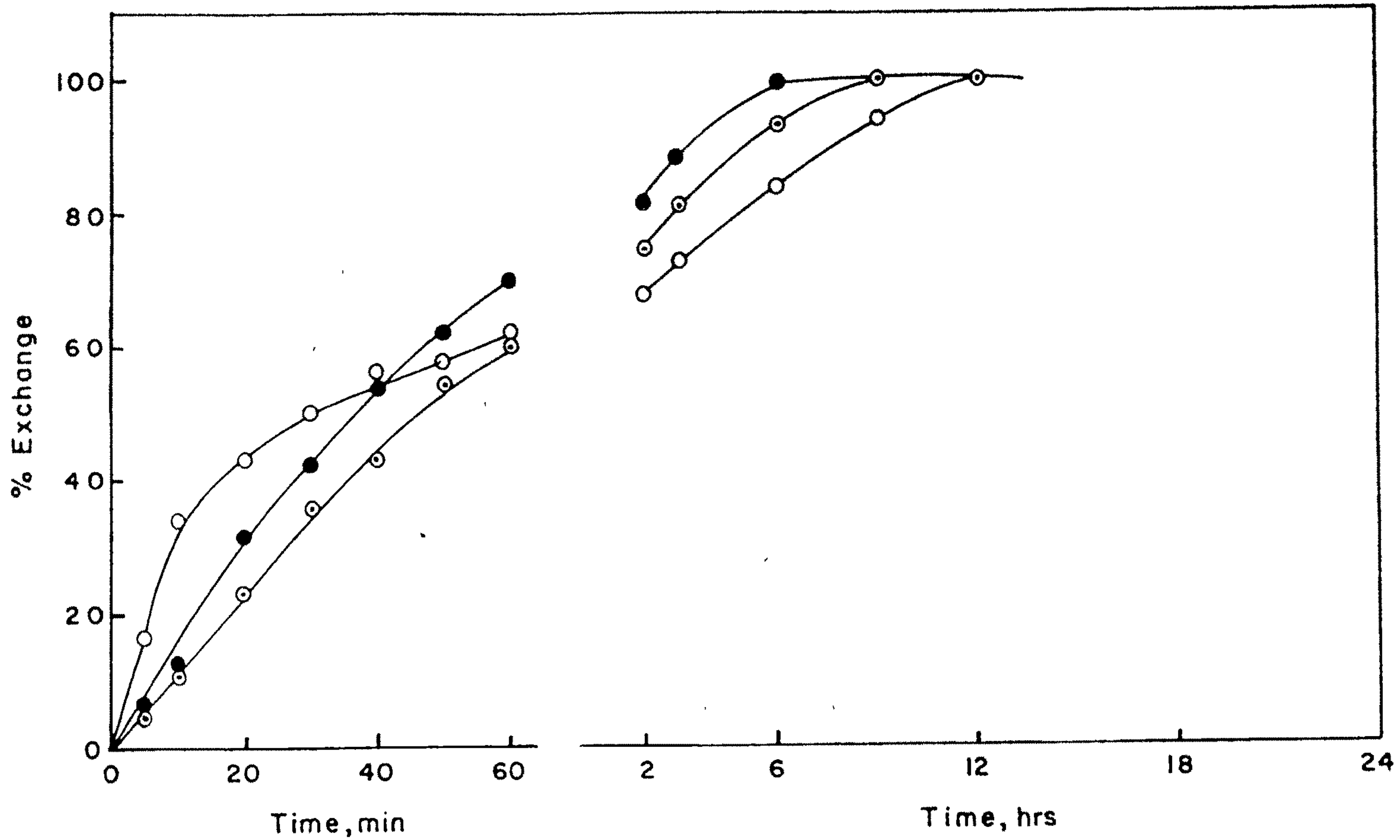
For the ion exchange process, rate determining step is the interdiffusion of counter ions. Boyd[6] studied the ion exchange kinetics by applying the Nernst concept of a liquid diffusion layer. In the process of ion exchange, a counter ion A must migrate from its place within the ion exchanger into the solution. Simultaneously, a counter ion B must go the other way and occupy the place left by ion A. There is transfer of ions in both the ion exchanger and the solution. Two rate determining steps are involved in the process:

1. Interdiffusion of counter ions within the ion exchanger itself i.e. particle diffusion.
2. Interdiffusion of counter ions in the adherent films i.e. film diffusion.

In practice, either step can be rate controlling. In intermediate cases the rate may be affected by both steps.

Fig. 3·5

Rate of Copper, Nickel and Zinc exchange



Resin taken 0·1 g ; Copper , Nickel , Zinc concentration 200,800, 400 $\mu g\ cm^{-3}$ respectively ; pH optimum ; reaction volume 25 cm^3

● Copper, ○ Nickel, ⊙ Zinc

The results of the rate of exchange of copper, nickel and zinc with the chelating resin under study are plotted in Fig. 3.5. It was observed that 6, 9 and 12 hours contacting time is required for the 100% exchange of copper, zinc and nickel respectively. The time required for the 50% exchange of zinc, copper and nickel ($t_{1/2}$) was observed to be 45.5, 35.5 and 30.0 min respectively. The lowest $t_{1/2}$ value for nickel can be explained on the basis of size of the counter ion. Smaller the size of the counter ion, faster will be the exchange rate.

Initial fast exchange can be explained on the basis of law of mass action. In the begining, the exchange of ions from the solution to the surface of the resin is faster and when all available sites on the resin surface are occupied by the metal ions from the solution, metal ions penetrate the interior resin sites, resulting into the lower exchange rate. The shorter time for 50 % exchange indicates the faster rate of exchange which facilitates the chromatographic separations.

To understand the exchange mechanism of copper, nickel and zinc interruption test[3] was carried out as described earlier. According to shell progression mechanism, exchange of metal ions is governed by either particle diffusion or film diffusion. From the results obtained in interruption test (Fig.3.6), it was observed that copper, nickel and zinc exchange is controlled by particle diffusion process.

As it is observed that 10 min interruption pause during the interruption test gives time for the concentration gradients developed in the beads to level out, resulting in the increase in exchange rate after reimmersion. In the film diffusion process, no concentration gradient exists in the beads and hence the interruption does not affect the concentration gradient across the beads resulting into no effect on exchange rate. The particle diffusion is also confirmed through the mathematical model proposed by Nativ et al[5] for the film diffusion process as described earlier in sec.3.2.8. A plot $[1 - 3\,(1-x)^{2/3} + 2(1-x)]$ vs time was constructed (Fig.3.6), where x is the fraction conversion of the resin which is a ratio between the measured and maximum exchange capacity. According to this model straight line passing through origin, confirms the shell progression mechanism controlled by film diffusion through the reacted layer. However, the plots are linear with intercept on x or y axis indicating that it is not a film diffusion but is a particle diffusion process.

For the exchange process, the reaction can be written as,

$$y\overline{R}A + B^{y+} \rightleftharpoons \overline{R}yB + yA^{x+} \qquad (3.4)$$

Where $\overline{R}A$ indicates solid phase having yA^{x+} exchangeable ions and B^{y+} is exchangeable counter ions in the solution phase. In the present study for copper, nickel and zinc, charges on A and B are 1 and 2 i.e. x = 1 and y = 2. Adsorption of ions from solution to solid is governed by Langmuir adsorption isotherm. This can be applied to ion exchange process with specific assumptions[12].

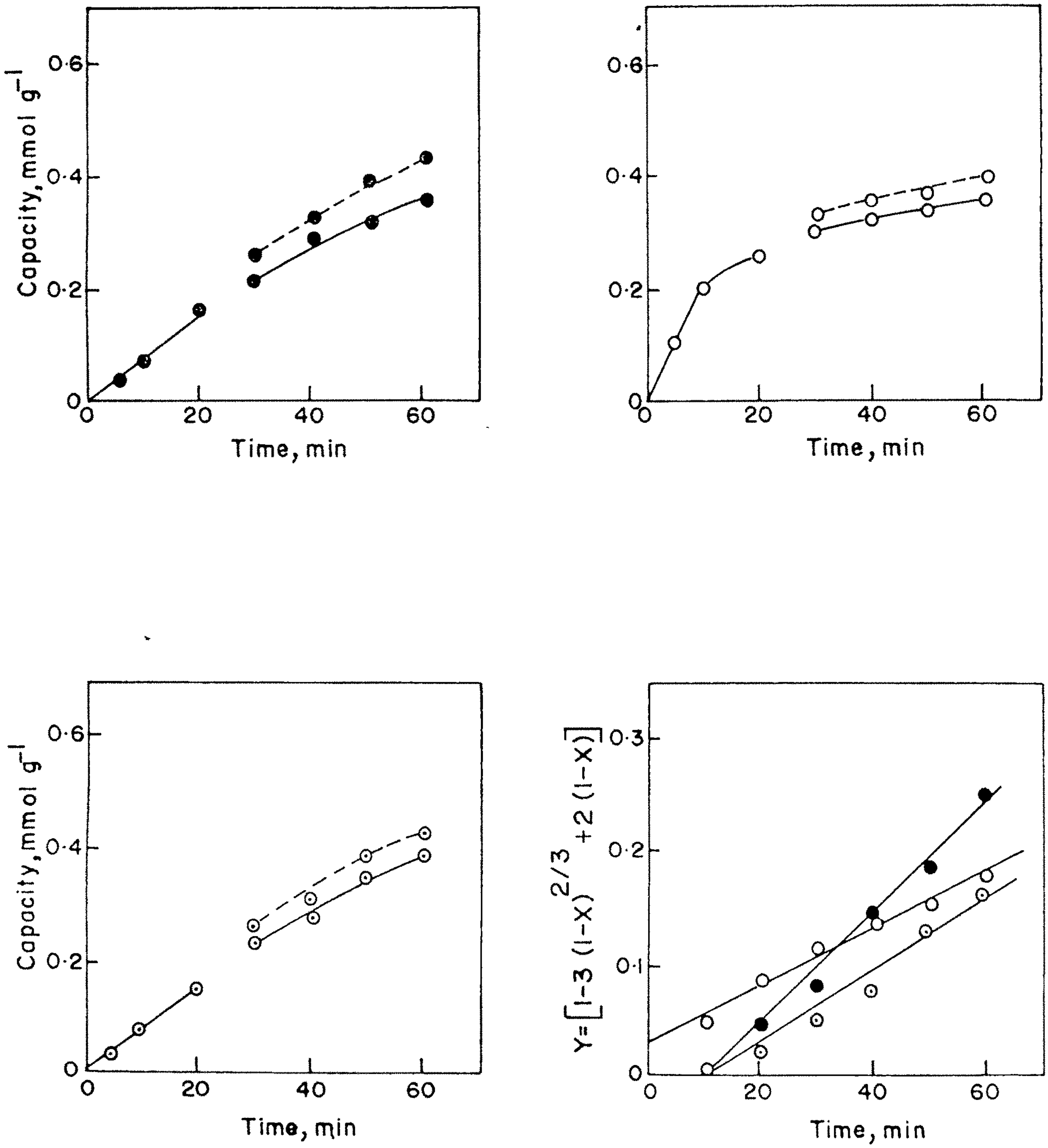
(i) The first assumption is that the selectivity coefficient factor remains unchanged or little changed over the exchange involved.

(ii) Secondly for homovalent and heterovalent exchange, the concentration of one of the ions or of the total solution is constant.

(iii) Unlike selectivity coefficient, the separation factor obtained for the Langmuir plot can not be regarded as a constant depending on site adsorption energy.

Fig.3·6

Interruption test



Resin taken 0·1g; Copper, Nickel, Zinc concentration 200, 800, 400 µg cm^{-3} respectively; pH Optimum; reaction volume 25 cm^{3}

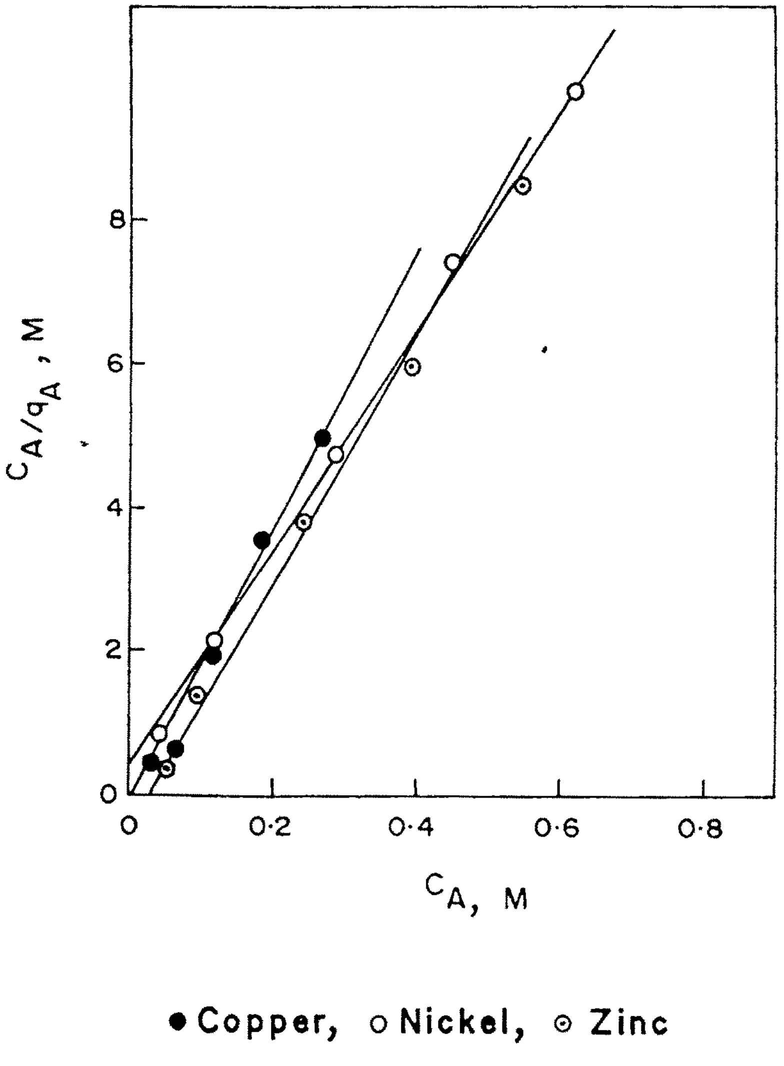
● Copper, ○ Nickel, ⊙ Zinc

Table 3.4 : Data for extended Langmuir adsorption hypothesis for ion exchange

	M Concentration of metals						
	C_o	C_A	q_A	C_A/q_A	α	Q (calculated) mmol g^{-1}	Q (experimental) mmol g^{-1}
Copper (II)							
	0.039	0.011	0.028	0.404	9.62	0.42	0.28
	0.079	0.027	0.051	0.530	17.39	0.47	0.51
	0.157	0.105	0.052	2.002	32.73	0.47	0.51
	0.236	0.185	0.051	3.590	48.19	0.47	0.51
	0.314	0.262	0.052	5.004	63.46	0.47	0.51
Nickel (II)							
	0.085	0.038	0.047	0.83	5.81	0.42	0.47
	0.170	0.117	0.054	2.18	9.64	0.51	0.54
	0.340	0.282	0.058	4.83	17.24	0.57	0.59
	0.511	0.450	0.061	7.43	24.90	0.59	0.60
	0.681	0.618	0.063	9.81	32.52	0.60	0.60
Zinc (II)							
	0.076	0.021	0.054	0.390	28.36	0.60	0.55
	0.153	0.089	0.064	1.38	55.03	0.62	0.65
	0.306	0.242	0.063	3.83	108.00	0.64	0.65
	0.459	0.393	0.065	6.02	161.14	0.64	0.65
	0.611	0.547	0.064	8.50	213.93	0.64	0.65

Fig. 3·7

Extended Langmuir adsorption isotherm for Copper, Nickel and Zinc exchange



Based on these assumption Misak[12] has modified Langmuir adsorption isotherm for the ion exchange process. Accordingly exchange process can be governed by the equation.

$$\frac{C_A}{q_A} = \frac{C_A}{Q}\left[1 - \frac{X}{\alpha y}\right] + \frac{C_0}{\alpha y Q} \qquad (3.5)$$

Where q_A is the amount of metal 'A' sorbed , C_A is equilibrium concentration of metal 'A' in the solution, C_0 is initial concentration of metal ion in the solution, Q is the maximum exchange capacity and α is a selectivity coefficient. From the above equation, a plot of C_A/q_A vs C_A (Fig. 3.7) was constructed. α and Q were calculated from the slope and intercept respectively. The theoretically calculated Q values (Table 3.4) for copper, nickel and zinc respectively are in good agreement with the observed values.

3.4.4 Thermodynamics of exchange process

The reaction rates for the exchange of copper, nickel and zinc on the resin were determined at three different temperatures. The rate constant k (for the initial exchange) was calculated using equation for the first order reaction[7].

$$-dc/dt = kC \qquad (3.6)$$

and

$$-\log(a-f) = kt/2.303 \qquad (3.7)$$

Where 'a' is the initial concentration of metal ion and 'f' is the concentration of metal ion exchanged on the resin. It was observed that the plot of -log (a-f) vs time is a straight line not passing through the origin. From the slope of the straight line rate constant k was calculated. If straight line is not obtained, a mirror method[8] was used to calculate the rate constant from the initial rate of the exchange reaction.

The activation energy required for complexation of metal on resin was determined using Arrhenius equation[7].

$$k = Ae^{-\Delta E/RT} \tag{3.8}$$

From the slope of the plot of log k vs 1/T energy of activation ΔE was calculated. The results are given in Table 3.5. In general higher rate of exchange was observed with increasing temperatures.

3.4.5 Elution of copper, nickel and zinc from the resin

Various eluting reagents of different strengths were tried for the quantitative elution of metal ions from the resin. The results are given in Table 3.6. It was observed that 0.1 M HCl could elute copper, nickel and zinc quantitatively where as 0.1 M HNO_3 and 0.1 M H_2SO_4 could elute copper and zinc quantitatively but even with higher concentration of HNO_3 and H_2SO_4 only 44 % and 55 % of nickel was eluted. Nickel was quantitatively eluted with 2.0 M CH_3COOH. Whereas copper and zinc were not at all eluted with CH_3COOH. With 1 % thiourea incomplete elution of copper and nickel was achieved where as zinc was eluted quantitatively.

Table 3.5 : Thermodynamics of exchange process

Copper, nickel and zinc concentration 400 μg cm^{-3}, resin 0.1 g, reaction volume 50 cm^3 at optimised pH, equilibration time 3 h.

Metal	Rate constant $k \times 10^4$ sec at °C 30	40	50	Activation energy ΔE J $mol^{-1} \times 10^{-4}$
Cu (II)	8.25	9.91	10.48	1.04
Ni (II)	1.70	2.02	3.32	2.72
Zn (II)	9.32	9.50	10.12	0.33

Table 3.6 : Elution of Copper, nickel and zinc

Copper, nickel and zinc concentration 200, 800 and 400 μg cm^{-3} respectively, reaction volume 25 cm^3, resin 0.1 g, equilibration time 24 h, volume of eluent 15 cm^3.

Sr. No.	Eluting reagent	% Elution copper	 nickel	 zinc
1	M HCl			
	0.1	100	100	100
	0.2	100	100	100
	0.5	100	100	100
	1.0	100	100	100
	2.0	100	100	100
	3.0	100	100	100
2	M H_2SO_4			
	0.1	100	42	100
	0.2	100	44	100
	0.5	100	48	100
	1.0	100	55	100
	2.0	100	55	100
	3.0	100	55	100
3	M HNO_3			
	0.1	100	28	100
	0.2	100	35	100
	0.5	100	40	100
	1.0	100	44	100
	2.0	100	46	100
	3.0	100	45	100
4	M CH_3COOH			
	0.1	00	82	00
	0.2	00	100	00
	0.5	00	100	00
	1.0	00	100	00
	2.0	00	100	00
	3.0	00	100	00

5	M H_3PO_4			
	0.1	100	100	100
	0.5	100	100	100
	1.0	100	100	100
	2.0	100	100	100
	3.0	100	100	100
6	M $HClO_4$			
	0.1	100	30	100
	0.5	100	38	100
	1.0	100	50	100
	2.0	100	50	100
	3.0	100	50	100
7	% Thiourea			
	1.0	100	45	100
	2.0	100	48	100
	3.0	100	48	100
8	M NaCl			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
9	M Na-Citrate			
	3.0	00	00	00
10	M Na-tartarate			
	3.0	00	00	00

3.5 Preconcentration of lead, cadmium and mercury

Environmental pollution has gained a prime concern in recent years. Among the metallic pollutants lead, cadmium and mercury can be grouped together as major pollutants[9].

Some 20,000 tons of lead is deposited on the earth annually due to the use of tetraethyl lead and tetramethyl lead in fuels. Alkyl mercury compounds are present in many lakes at toxic level concentration. Cadmium poisoning increases due to its use in electroplating units for the corrosion protection of iron and steel. Because of the poisoning effect of lead, cadmium and mercury it is necessary to remove these toxic metals from the water and air.

Inappropriate use and over-exposure of lead compounds lead to the toxicity. Inhalation of lead vapor or dust has worst effect. In the case of organo-lead compounds, absorption through the skin causes head-aches, dizziness and insomnia. In acute cases, there is usually stupor which progresses to coma and terminates in death. Lead occurs naturally in plants and soil through out the world to the extent upto 8.20 mg kg^{-1} in virgin soil and upto 300 mg kg^{-1} in cultivated areas[10]. Settle and patterson[11] estimated 6.4 μg lead in the average person's blood from inhalation of lead aerosols and lead dusts. High content of lead are found in industrial areas and also found in vegetables like lettuce, potato, tomato and cucumber. It accumulates in hair and is highly toxic and cumulative poison. Hence estimation and removal of lead from the waste water is essential.

Cadmium accompanies zinc to the extent of about 0.5 % in many of its ores, and is obtained as a byproduct of its manufacture. Microgram quantities of cadmium can cause serious symptoms. Acute cadmium poisoning leads to nausea, salivation, vomiting, diarrhoea and abdominal pain. A severe out break of chronic cadmium poisoning occurred along the Jintsu river of North-West Japan and was known as Itai Itai disease. It also gives hypertension and cardiovascular problems. On inhalation gives emphysema and bronchitis. It enters into the biosystem through drinking water and food products. It also affects the functioning of kidney, liver and heart. Substantial amount of cadmium is continuously added to soil, water and air as a consequence of human pollution. Hence it is necessary to measure cadmium content in water and food products and develop necessary methods for removal and separation of cadmium.

Almost all compounds of mercury are quite poisonous to human being and animals. Three types of mercury poisoning can be catagorised as mercury vapor, inorganic mercury and alkyl mercury. Soluble inorganic mercury salts are highly toxic. Excess $HgCl_2$ causes corrosion of the intestinal track, kidney failure and ultimately death. The use of $Hg(NO_3)_2$ in the felting process resulted in mercury poisoning becoming an occupational hazard of hatters. Mercury poisoning causes difficulty in walking, tremors and mental disability. In chronic mercury poisoning, reddening and bleeding of the gums, digestive disturbances, deafness and tremors of the hands occurs. Mercury (II) binds to thiol groups, thus almost all proteins can bind mercury to some extent and are potential targets for mercury poisoning which causes biological disorder. Hence estimation and separation of mercury has a special importance.

Hence in the present work lead, cadmium and mercury are studied together and conditions are established for the removal and separation of these elements by using dithizone anchored poly (vinyl pyridine) resin.

3.5.1 Effect of pH on lead, cadmium and mercury exchange

Exchange of metal ions with resins is governed by various parameters. pH of the medium is one of them. The results obtained in the study of effect of pH on lead, cadmium and mercury exchange are given in Fig.3.8 and Table 3.7. It was observed that the resin shows maximum exchange capacity for cadmium and mercury at pH 5 and 3 respectively. Where as lead exchange was observed to be pH independent although the exchange capacity for lead was observed to be poor. Cadmium exchange did not take place in acetate buffer but was achieved in citrate-phosphate buffer.

The results obtained for the resin selectivity towards lead, cadmium and mercury based on distribution coefficient showed an order of Hg > Cd > Pb.

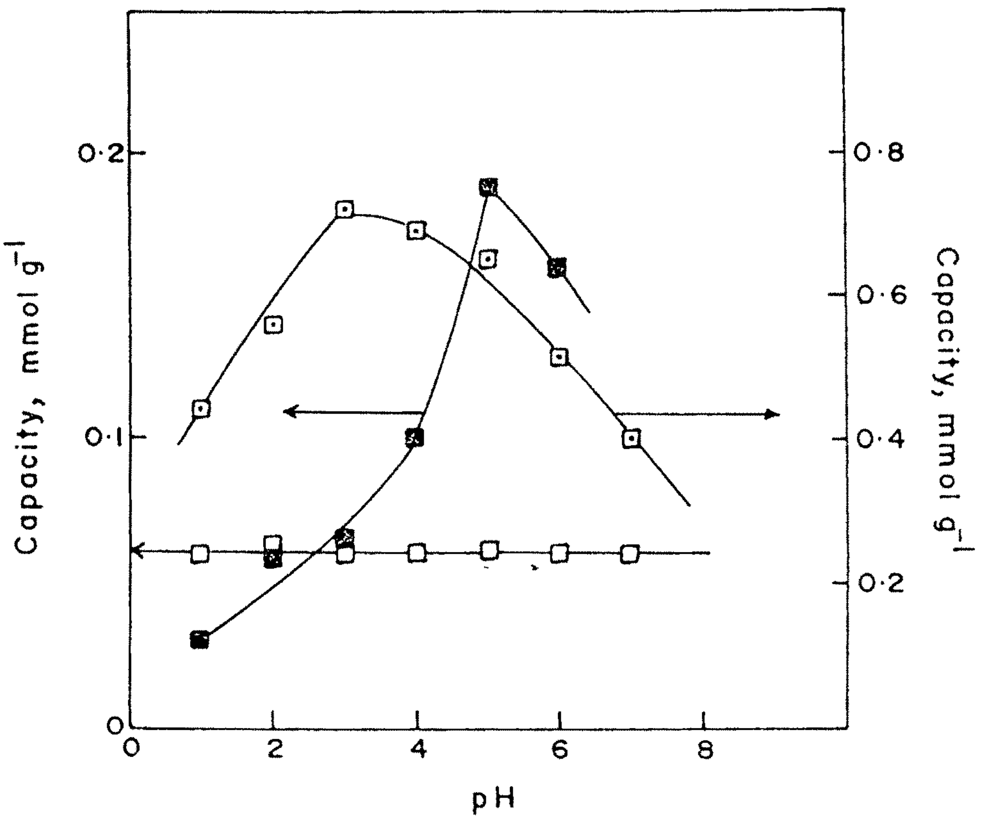
High distribution coefficient and exchange capacity for mercury is observed because of the high affinity of the resin for noble metal ions than for the base metal ions.

3.5.2 Effect of lead, cadmium and mercury ion concentration on exchange capacity

It was observed that the uptake of mercury by the resin increases with the increasing concentration. However, the uptake of lead and cadmium by the resin remained constant with the increasing concentration. Saturation of the resin takes place with the initial concentration of 100 $\mu g\ cm^{-3}$ of lead. 200 $\mu g\ cm^{-3}$ of cadmium and 1000 $\mu g\ cm^{-3}$ of mercury exhibiting 0.06, 0.19 and 0.72 mmol g^{-1} exchange capacity for lead, cadmium and mercury respectively. The results obtained are presented in Fig.3.9 and Table 3.7.

Fig. 3·8

Effect of pH on Lead, Cadmium and Mercury exchange



Resin taken 0·1g; Lead, Cadmium, Mercury concentration 400, 400, 1000 µg cm^{-3} respectively; equilibration time 24 h; reaction volume 25 cm^3

□ Lead, ■ Cadmium, ⊡ Mercury

Table 3.7 : Optimum conditions for lead, cadmium and mercury exchange

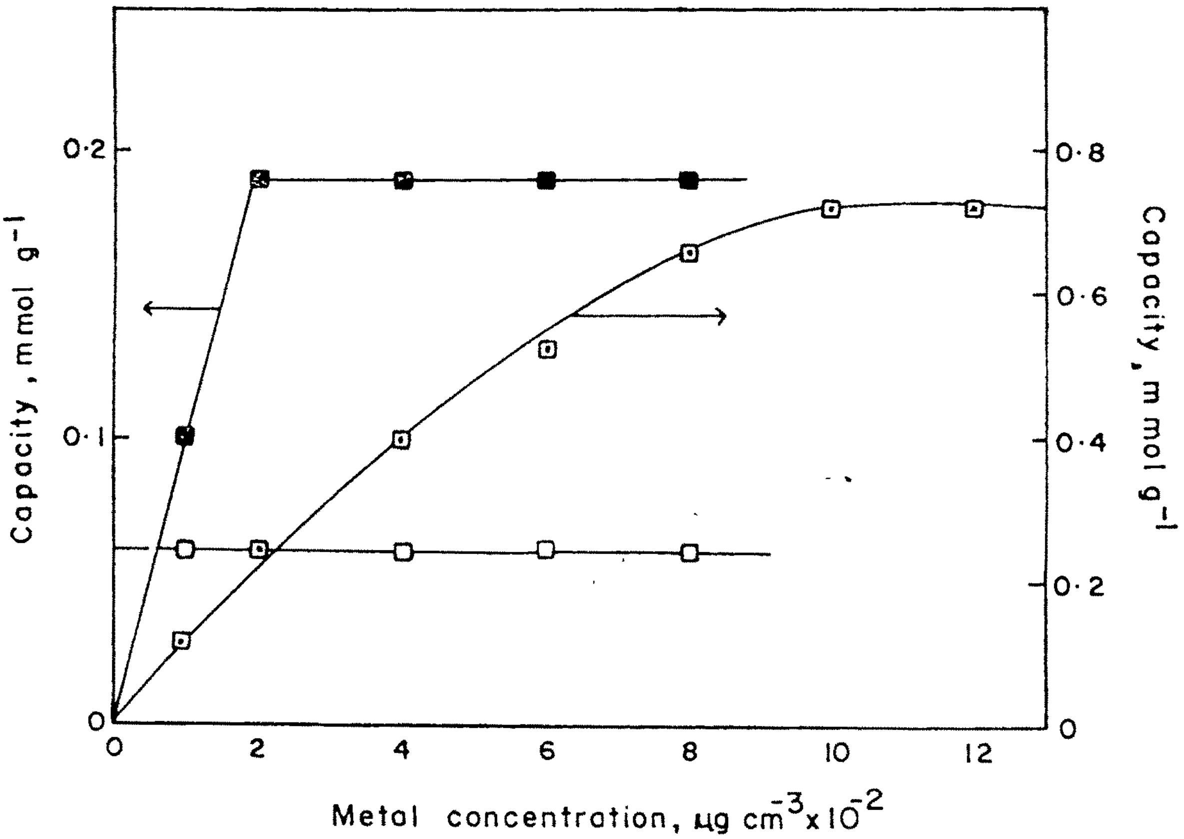
Eqilibration time 24 h, reaction volume 25 cm^3, resin 0.1 g

Metal	**pH**	**Optimum Metal Concentration $\mu g\ cm^{-3}$**	**Capacity mmol g^{-1}**	**Kd * values**	**$t_{1/2}$ min**
Pb(II)	1.0-7.0	100	0.06	83.0	160.0
Cd(II)	5.0	200	0.19	185.0	30.0
Hg(II)	3.0	1000	0.72	6000.0	20.0

* kd values for 200 $\mu g\ cm^{-3}$ of lead, cadmium and mercury concentration

Fig.3·9

Effect of Lead, Cadmium and Zinc ion concentration on exchange process



Resin taken 0·1 g, pH optimum, equilibration time 24h ; reaction volume 25 cm^3

□ Lead, ■ Cadmium, ⊡ Mercury.

3.5.3 Kinetics of lead, cadmium and mercury exchange

The results obtained in the study of kinetics of lead, cadmium and mercury exchange are illustrated in Fig.3.10. From the results it was observed that 3, 12 and 15 h time is required for the 100 % exchange of cadmium, mercury and lead respectively. Higher $t_{1/2}$ value (160 min) was observed for lead exchange. Mercury being a noble metal, resin shows high affinity towards mercury. Hence $t_{1/2}$ value for mercury is lower than that for cadmium. Though initial exchange rate for mercury is very fast, complete exchange requires 12 h where as for cadmium, complete exchange takes place within 3 h.

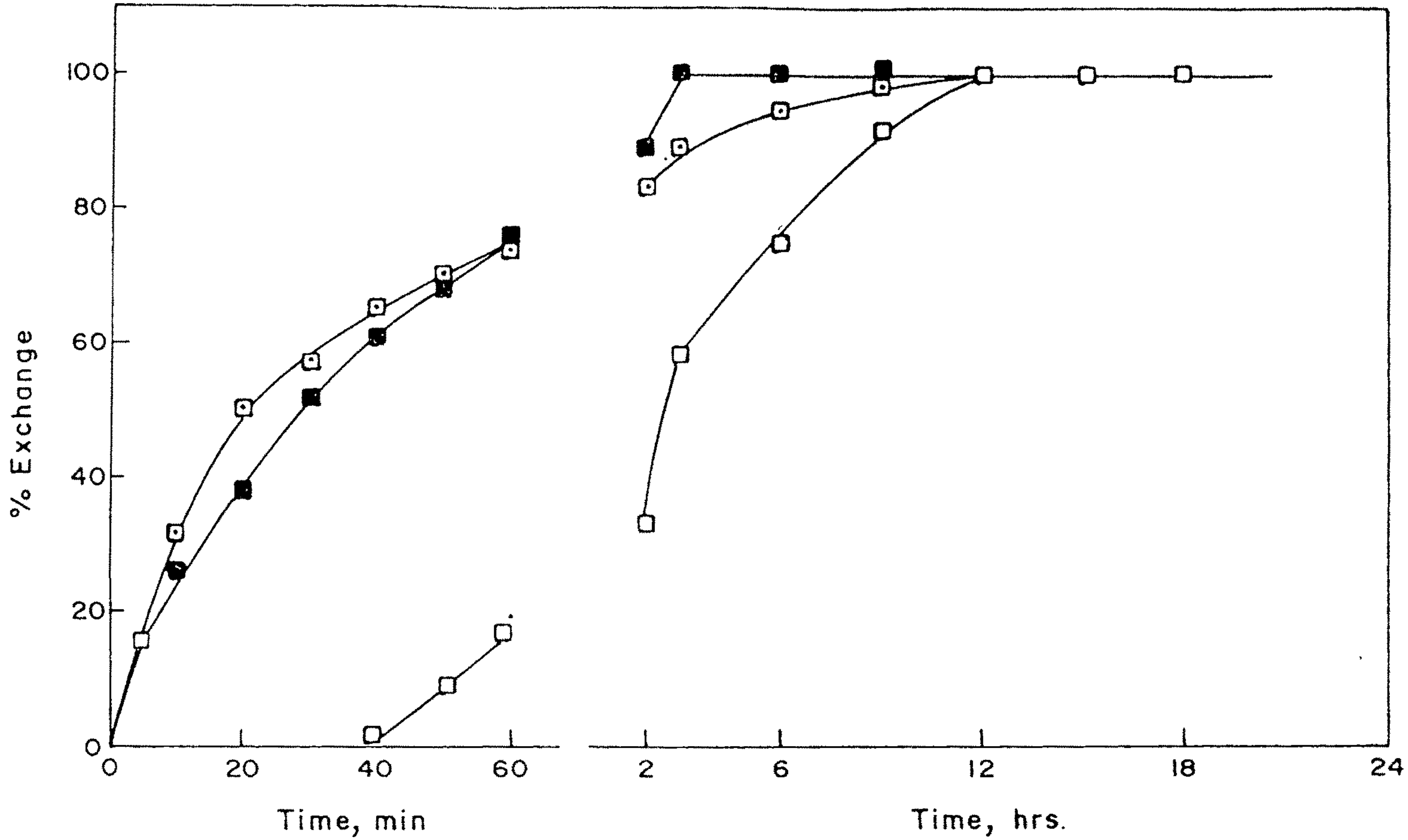
From the nature of the plots obtained in the interruption test[3] (Fig.3.11) it can be inferred that the exchange process is a particle diffusion controlled one and not the film diffusion controlled as discussed earlier in section 2.4.4. This was further confirmed by following the method suggested by Nativ et al[5] for the determination of the nature of diffusion process. The results given in Fig.3.11 are in good agreement with the particle diffusion model, as a straight line obtained in the $[1 - 3(1 - x)^{2/3} + 2 (1 - x)]$ vs time plot does not pass through the origin.

For the exchange process, the reaction can be written as given in equation 3.4. In the present study for cadmium and mercury charges on A and B are 1 and 2. i.e. $x = 1$ and $y = 2$. Adsorption of ions from solution to solid is governed by Langmuir adsorption isotherm. This can be applied to ion exchange process with specific assumptions which are discussed in sec.3.4.3.

Based on these assumptions Misak[12] has modified Langmuir adsorption isotherm which was applied to cadmium and mercury exchange using the equation 3.5. A

Fig. 3·10

Rate of Lead, Cadmium and Zinc exchange

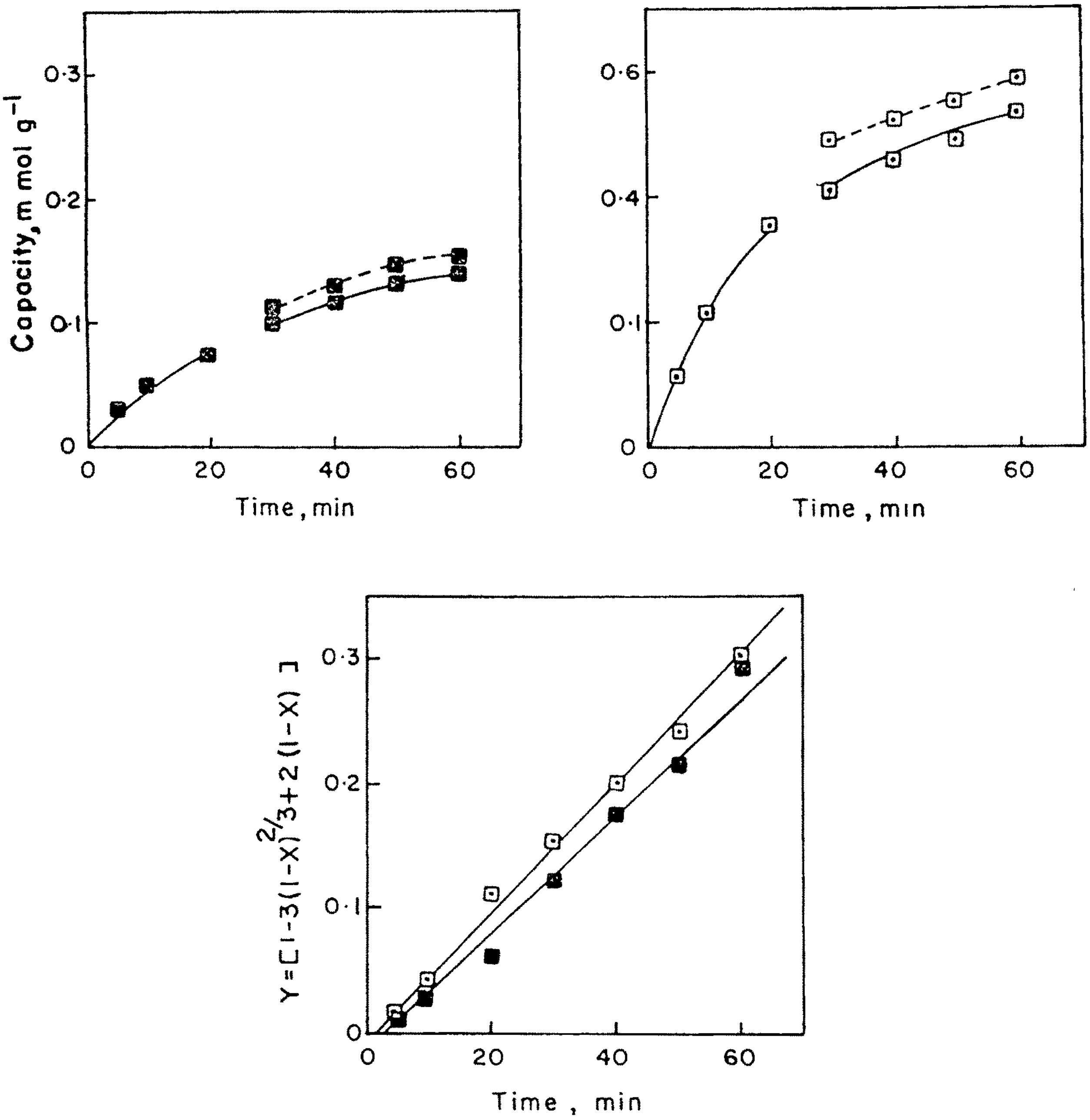


Resin taken 0·1g; Lead, Cadmium, Mercury concentration 100, 200, 1000 μg cm^{-3} respectively; pH Optimum; reaction volume 25 cm^3

□ Lead, ■ Cadmium, ⊡ Mercury

Fig. 3·11

Interruption Test



Resin taken 0·1 g ; Cadmium , Mercury concentration 200, 1000 µg cm^{-3} respectively ; pH optimum ; reaction volume 25 cm^3

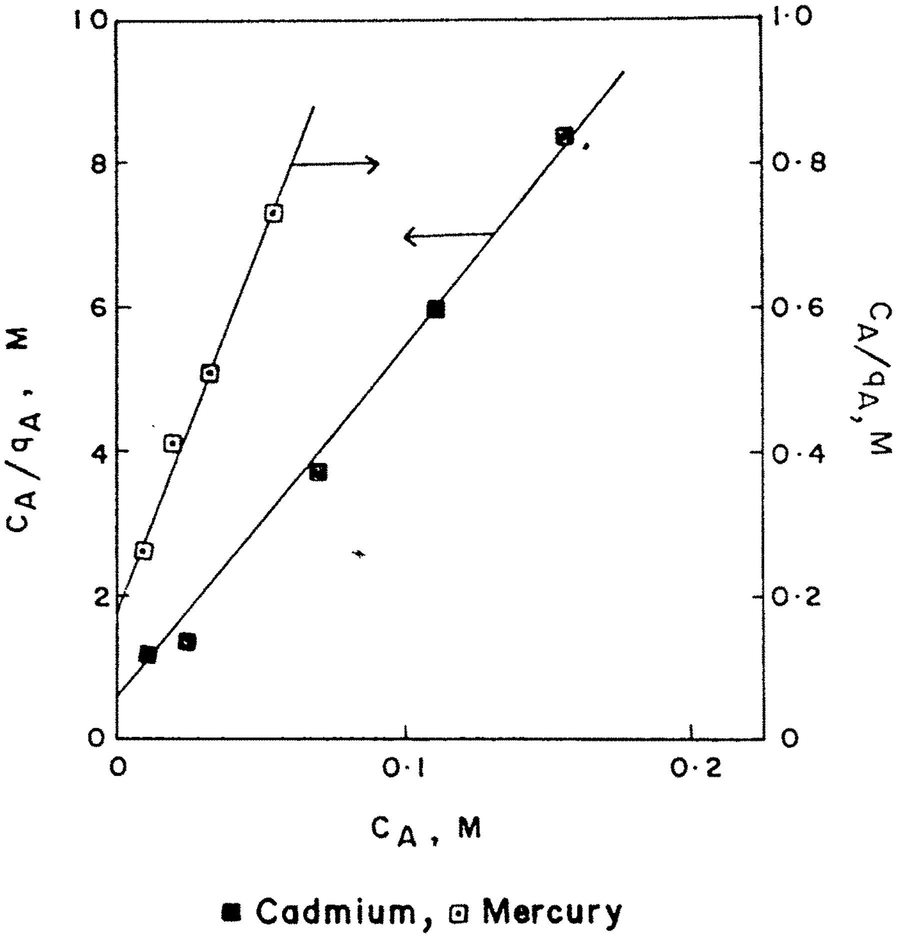
■ Cadmium , ⊡ Mercury

Table 3.8 : Data for the extended Langmuir adsorption hypothesis for ion exchange

	M Concentration of metals						
	C_o	C_A	q_A	C_A/q_A	α	Q (calculated) mmol g^{-1}	Q (experimental) mmol g^{-1}
Cadmium (II)							
	0.022	0.012	0.001	1.23	5.65	0.12	0.10
	0.044	0.025	0.019	1.34	9.30	0.15	0.19
	0.088	0.069	0.187	3.69	16.59	0.17	0.19
	0.132	0.113	0.188	6.01	23.88	0.18	0.19
	0.176	0.157	0.187	8.39	31.18	0.18	0.19
Mercury (II)							
	0.048	0.010	0.038	0.26	13.39	0.61	0.39
	0.072	0.021	0.050	0.42	19.08	0.64	0.52
	0.096	0.032	0.064	0.51	24.78	0.65	0.66
	0.120	0.051	0.069	0.73	30.47	0.66	0.72

Fig. 3·12

Extended Langmuir adsorption isotherm for Cadmium and Mercury exchange



plot of C_A/q_A vs C_A was constructed and is illustrated in Fig.3.12. α and Q were calculated from the slope and intercept respectively. The theoretically calculated Q values were observed to be in good agreement with the observed values for cadmium and mercury (Table 3.8).

3.5.4 Thermodynamics of lead, cadmium and mercury exchange

Rate of lead, cadmium and mercury exchange with the resin was determined at different temperatures. The rate constant k was calculated for the initial exchange process. As the temperature increases, rate constant (k) increases. But in the case of lead exchange, it was observed that exchange rate does not increase with temperature. For cadmium and mercury exchange, rate constant k was calculated for the initial exchange process at different temperature as discussed in section 3.4.4.

The activation energy ΔE required for the complex formation in the case of cadmium and mercury was determined using Arrhenius equation.

$$k = A\ e^{-\Delta E/RT} \tag{3.8}$$

From the slope of the plot of log k vs 1/T energy of activation ΔE was calculated as discussed in section 3.4.4. The results are given in Table 3.9. It was noticed that lower the activation energy faster the exchange rate.

Table 3.9 : Thermodynamics of exchange process

Cadmium and mercury concentration 200 and 400 μg cm^{-3} respectively, resin 0.1 g, reaction volume 50 cm^3 at optimised pH, equilibration time 3 h.

Metal	**Rate constant k x 10^3 sec at °C**					**Activation energy ΔE J mol^{-1} x 10^{-4}**
	30	**35**	**40**	**45**	**50**	
Cd (II)	1.13	1.47	1.66	2.18	2.15	2.51
Hg (II)	8.23	8.53	n.d	9.91	10.48	1.04

n.d = not determined

3.5.5 Elution of lead, cadmium and mercury

Various eluting reagents of different strengths were used to elute lead, cadmium and mercury from the resin. The results are given in Table 3.10. It was observed that lead can be quantitatively eluted with 0.5-1.0 M HCl where as other reagents were unable to elute lead from the resin. Cadmium can be quantitatively eluted with 1.0-2.0 M CH_3COOH, 3.0 M HCl and 1.0-3.0 M H_2SO_4. Higher concentration of HNO_3, thiourea, H_3PO_4, $HClO_4$, citrate and tartarate were unable to elute cadmium from the resin. Where as mercury can be eluted quantitatively with 1:1 mixture of 0.2 M HNO_3 and 2.0 % NH_4NO_3. Higher strength of H_2SO_4, HNO_3 and thiourea could elute only 80-90 % mercury from the resin. HCl, H_3PO_4, $HClO_4$ could not elute mercury from the resin. From the study of eluting reagents it can be predicted that separation of lead, cadmium and mercury from each other is possible.

3.6 Preconcentration of gold, platinum and palladium

Gold, platinum and palladium are noble metals. They are generally associated with each other as well as with copper, nickel and zinc. They are generally found in rocks, soil and natural ores. All three metals are toxic as well as precious.

Gold salts are not considered to be among the more poisonous compounds of metals, but some toxicity has been observed. Most of the toxic reactions of gold are with the skin, which may develop a rash or other dermatitis. Excessive injection of gold may causes gastrointestinal upset and serious internal disorders. Gold is known to be carcinogenic when accumulated in the biological system during ageing.

Table 3.10 : Elution of lead, cadmium and mercury

Lead. cadmium and mercurv concentration 100. 200 and 1000 µg cm^{-3} respectively, reaction volume 25 cm^3, resin 0.1 g, equilibration time 24 h, volume of eluent 15 cm^3.

Sr. No.	Eluting reagent	Pb	% Elution Cd	Hg
1.0	M HCl			
	0.1	58.0	38.0	10.0
	0.5	71.0	43.0	8.0
	1.0	94.0	91.0	5.0
	2.0	94.0	91.0	3.0
	3.0	94.0	92.0	3.0
2	M H_2SO_4			
	0.1	00	34.0	-
	0.5	00	54.0	-
	1.0	00	69.0	70.0
	2.0	00	93.0	74.0
	3.0	00	96.0	92.0
3	M HNO_3			
	0.1	00	6.0	-
	0.5	00	15.0	63.0
	1.0	00	21.0	74.0
	2.0	00	23.0	92.0
	3.0	00	31.0	92.0
4	M CH_3COOH			
	0.1	00	87.0	00
	0.5	00	99.0	00
	1.0	00	99.0	00
	2.0	00	89.0	00
	3.0	00	63.0	00
5	M H_3PO_4			
	0.1	00	00	00
	0.5	00	6.0	00
	1.0	00	14.0	00
	2.0	00	14.0	00
	3.0	00	15.0	00

6	M $HClO_4$			
	0.1	00	00	00
	0.5	00	00	00
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
7	M HNO_3 + % NH_4NO_3 (1:1)			
	0.1 + 2	00	00	100
	0.5 + 2	00	00	100
	1.0 + 2	00	00	100
	2.0 + 2	00	00	100
	0.1 + 1	00	00	62.0
	0.1 + 0.5	00	00	77.0
	0.1 + 2.0	00	00	100
8	% Thiourea			
	1.0	00	00	54.0
	2.0	00	00	61.0
	3.0	00	00	85.0
9	M NaCl			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00

The concentration of platinum in the earth's crust is 5 µg/kg. Platinum can be obtained from alloys of metals or from sulfide ores. There is no detectable platinum in blood or urine of normal humans. Inhalation of platinum compounds leads to platinosis. Platinum compounds bind to DNA and RNA molecules inhibiting DNA, RNA and protein synthesis. Nephrotoxicity and kidney failure are the major side effects of platinum poisoning but ototoxicity, nausea, vomiting and bone marrow depression are also observed.

Palladium is one of the heavy metals which is always associated with silver, copper, nickel, gold and platinum. It is always found in the waste of electroplating units and in the jewelery producing units. Palladium supported on carbon or alumina is used as a catalyst for hydrogenation and dehydrogenation in liquid and gas phase reactions. When the excess of palladium accumulates in the living system, due to its catalytical effect it causes some reactions in the biological systems resulting into biological disorders.

All the three heavy metals gold, platinum and palladium are toxic but are precious metals. They have very high affinity for -SH group. In biological systems, proteins contain -SH group. Hence the metals under study readily forms complexes with -SH group of the enzymes and inhibit the activity of the enzymes. Hence, estimation, preconcentration and separation of gold, platinum and palladium from other metal ions by batch and column chromatographic method is discussed here.

3.6.1 Effect of pH on gold, platinum and palladium exchange

The results from the study of effect of pH on gold, platinum and palladium exchange with the resin are given in Fig.3.13 and Table 3.11. It was observed that gold, platinum and palladium exchange capacities are pH independent. The resin shows same exchange capacity over the pH range 1.0 - 7.0 and hence further study was carried out at pH 5.0 using 0.2 M acetate buffer.

The resin showed selectivity order towards the metals as Pt > Au > Pd which is based on distribution coefficient as well as exchange capacity.

3.6.2 Effect of gold, platinum and palladium ion concentration on exchange capacity

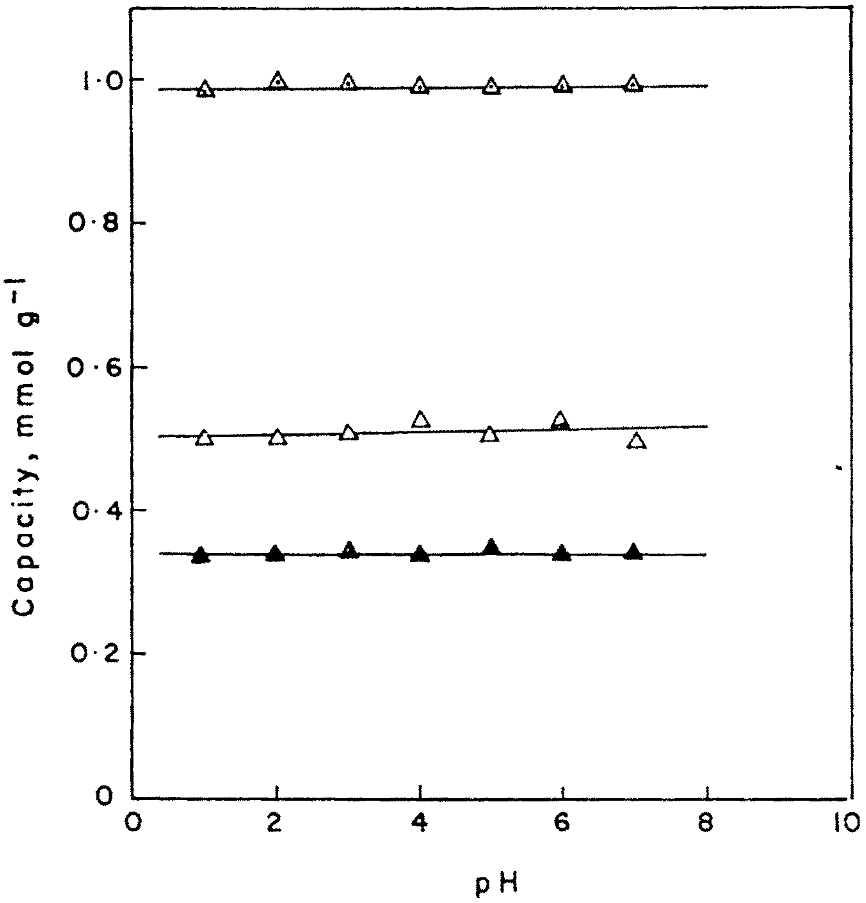
From the results presented in Fig.3.14 and Table-3.11 it is observed that uptake of all the three metal ions by ion exchange resin increases with increasing concentration of gold, platinum and palladium and attains a constant value. In the present study at the initial concentration of 1080 $\mu g\ cm^{-3}$ of gold, 1120 $\mu g\ cm^{-3}$ of platinum and 465 $\mu g\ cm^{-3}$ of palladium, resin attained saturation exhibiting 1.24, 1.29 and 0.99 mmol g^{-1} exchange capacities respectively.

3.6.3 Kinetics of gold, platinum and palladium exchange

The results obtained in the study of kinetics of gold, platinum and palladium exchange are given in Fig.3.15. From the results it was observed that 3, 12 and 15 h are required for the complete exchange of platinum, palladium and gold respectively. But the time required for 50 % exchange was observed to be 10, 50 and 60 min for platinum, palladium and gold respectively.

Fig. 3·13

Effect of pH on Gold, Platinum and Palladium exchange



Resin taken 0·1g; Gold, Platinum, Palladium concentration 440, 280, 460 µg cm^{-3} respectively, equilibration time 24 h; reaction volume 25 cm^3

△ Gold, ▲ Platinum, ◬ Palladium

Table 3.11 : Optimum conditions for gold, platinum and palladium exchange

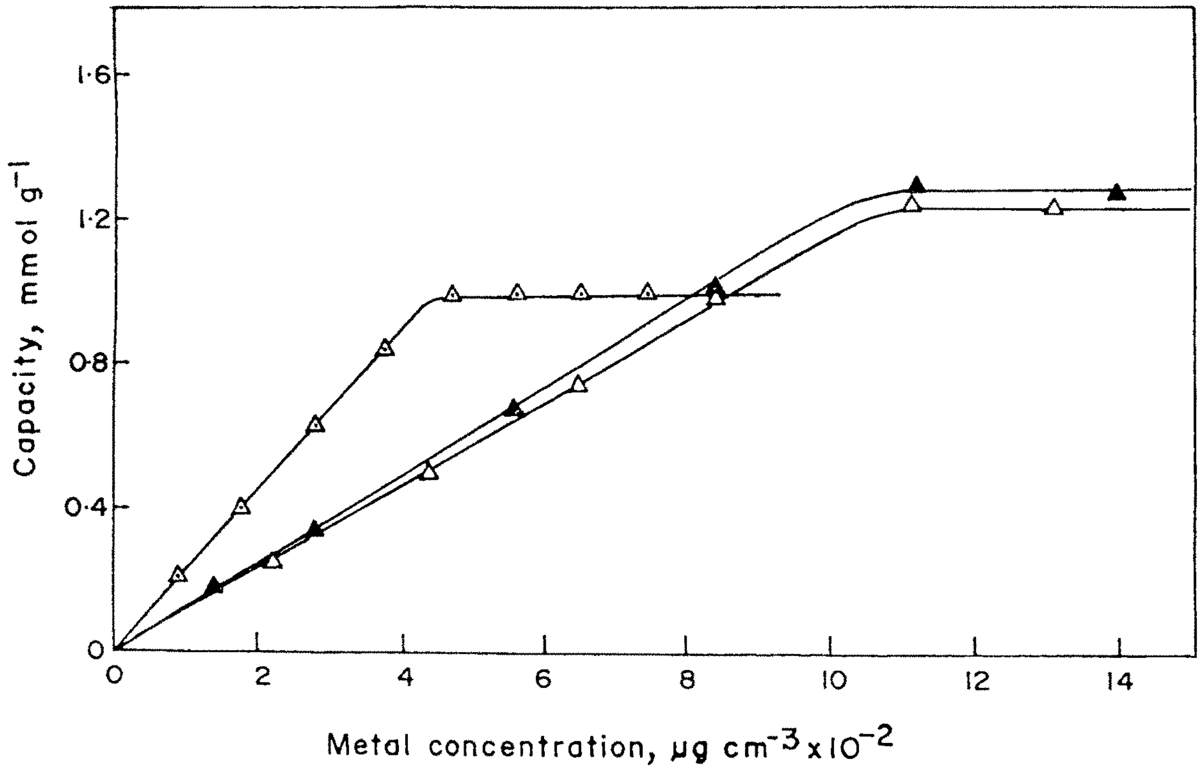
Equilibration time - 24 h, reaction volume 25 cm^3, resin 0.1 g.

Metal	Optimum pH	Optimum Metal Concentration $\mu g\ cm^{-3}$	Capacity mmol g^{-1}	Kd * values	$t_{1/2}$ min.
Au (III)	1.0-7.0	1080	1.24	2345	60.0
Pt (IV)	1.0-7.0	1120	1.29	2250	10.0
Pd (II)	1.0-7.0	465	0.99	5578	50.0

* Kd values for 440 $\mu g\ cm^{-3}$ of gold, platinum and palladium concentration.

Fig. 3·14

Effect of Gold, Platinum and Palladium ion concentration on exchange Process



Resin taken 0·1 g ; pH-5 ; equilibration time 24h ; reaction volume 25 cm^3

△ Gold, ▲ Platinum, ◬ Palladium

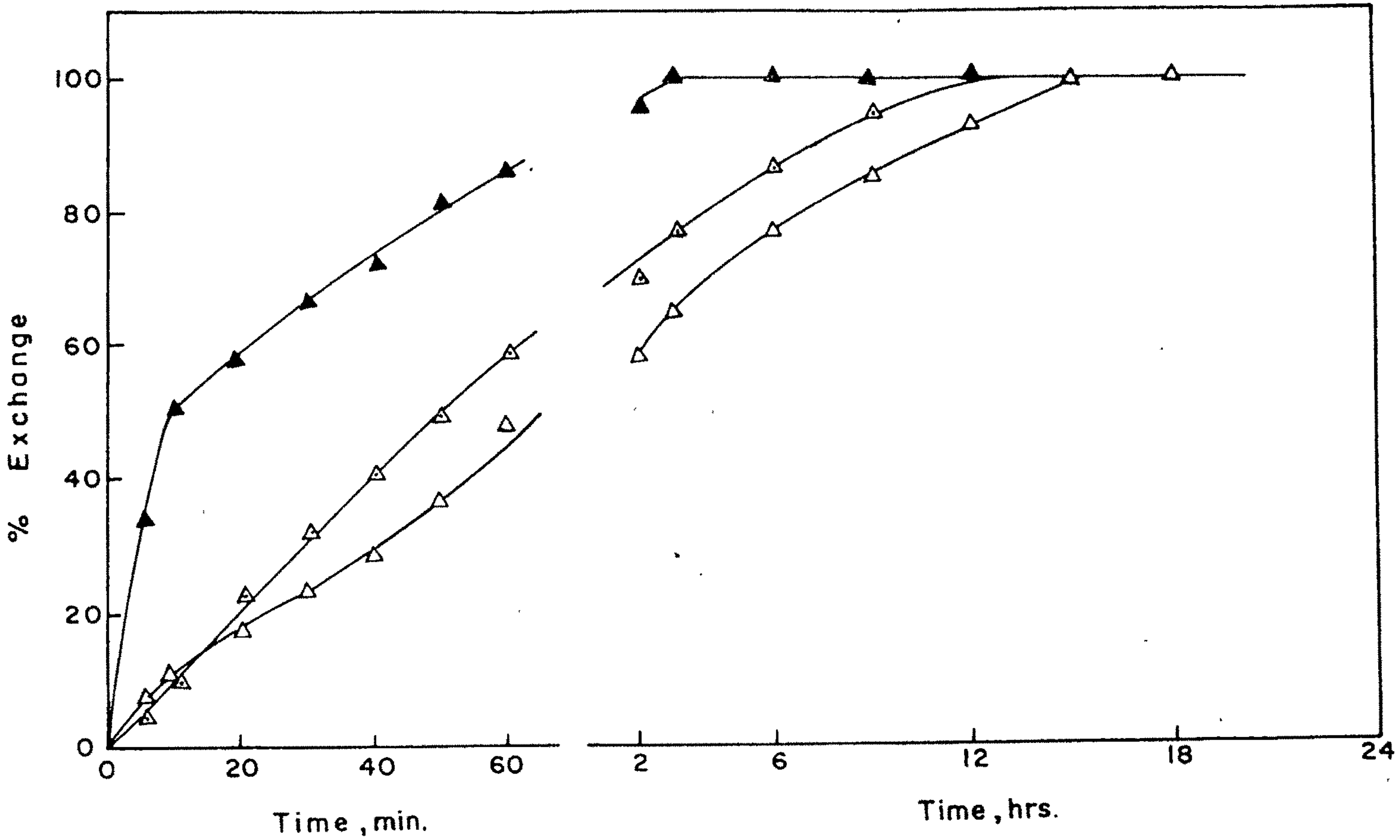
The exchange of metal ions with the resin is a diffusion controlled process. Hence, nature of diffusion of gold, platinum and palladium ions was determined through interruption test[3] and results are given in the Fig.3.16. From the nature of the plot of capacity vs time it is observed that metal exchange is governed by a particle diffusion process. The higher exchange rate after interruption was observed because interruption pause gave time for the concentration gradients developed in the beads to level out. The results of the initial exchange rate were also treated by the method proposed by Nativ et al[5]. It was observed that a straight line plots of $[1-3\ (1-x)^{2/3} + 2\ (1-x)]$ vs t as discussed earlier, do not pass through origin and hence support the particle diffusion process (Fig.3.16).

For the ion exchange process, the exchange reaction can be written as in equation 3.4. In the present study of gold, platinum and palladium charge on A is 1 and charges on B are 3, 4 and 2 for gold, platinum and palladium respectively. Hence $x=1$ and $y=3$, 4 and 2 for gold, platinum and palladium respectively. Adsorption of ions from solution to solid is governed by Langmuir adsorption isotherm. This can be applied to ion exchange process with specific assumptions which are discussed in sec.3.4.3.

Based on the assumptions Misak[12] has modified Langmuir adsorption isotherm which was applied for gold, platinum and palladium exchange using the equation 3.5. A plot of C_A/q_A vs C_A was constructed and is illustrated in Fig.3.17. α and Q were calculated from the slope and intercept respectively. The theoretically calculated Q values were observed to be in good agreement with the experimental values. The results are given in Table 3.12.

Fig . 3·15

Rate of Gold , Platinum and Palladium exchange

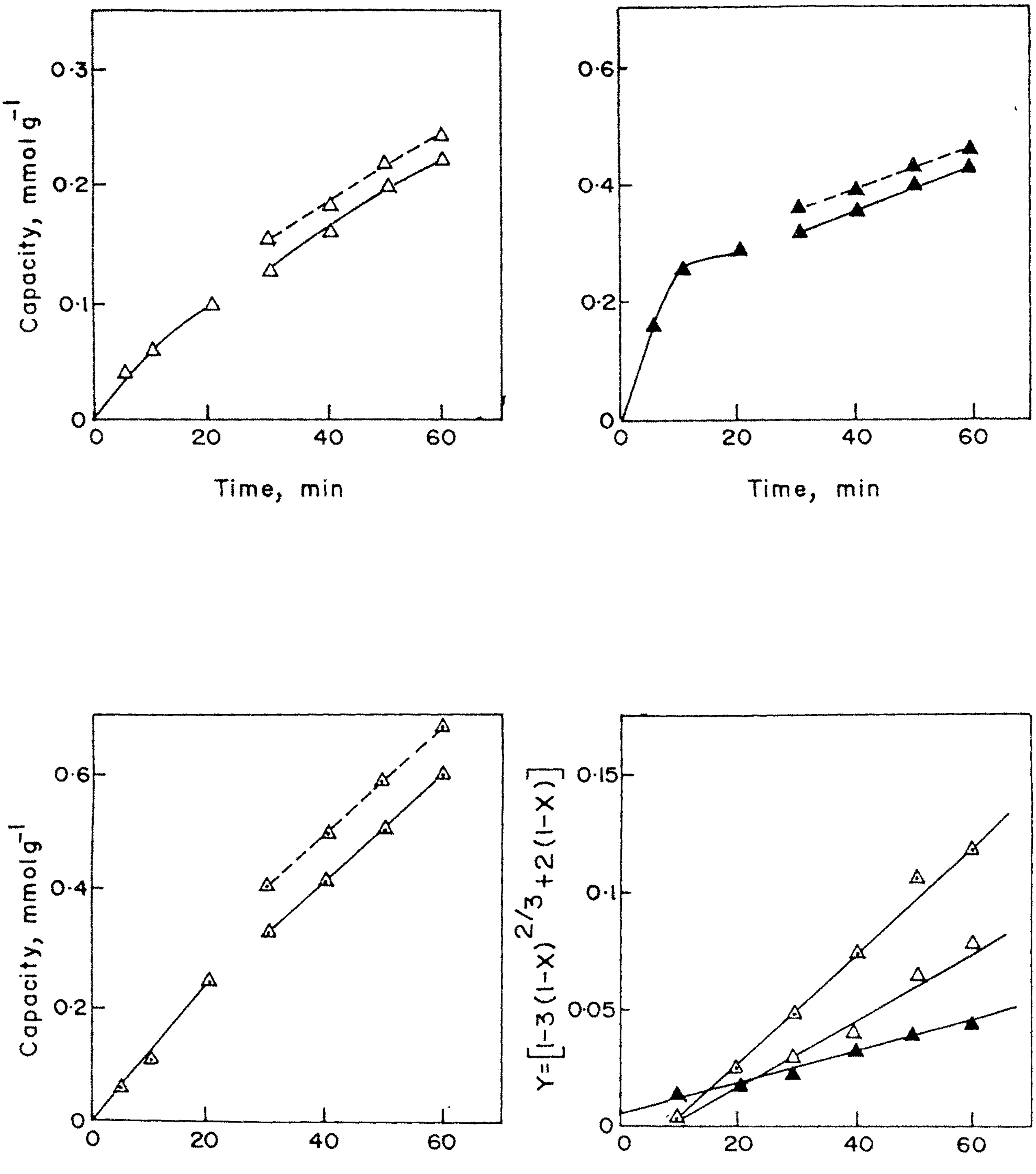


Resin taken 0·1 g ; Gold , Platinum and Palladium concentration 440, 420, 460 µg cm^{-3} respectively ; pH 5 ; reaction volume 25 cm^3

△ Gold , ▲ Platinum , ◭ Palladium

Fig. 3·16

Interruption test



Resin taken 0·1 g ; Gold, Platinum, Palladium concentration 440, 420, 460 µg cm^{-3} respectively ; pH 5 ; reaction volume 25 cm^{3}

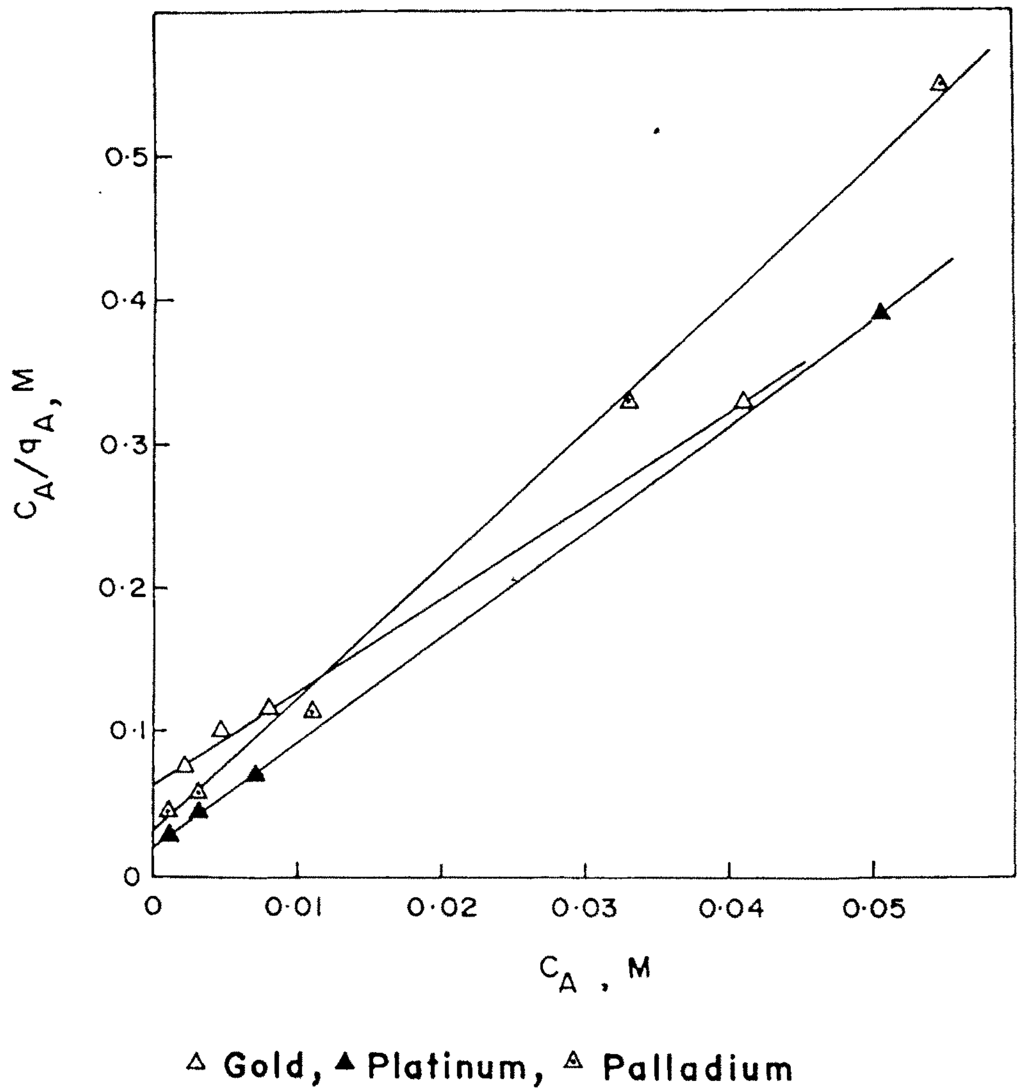
△ Gold, ▲ Platinum, ◬ Palladium

Table 3.12 : Data for extended Langmuir adsorption hypothesis for ion exchange.

	M Concentration of metals						
	C_o	C_A	q_A	C_A/q_A	α	Q (calculated) mmol g^{-1}	Q (experimental) mmol g^{-1}
Gold (III)							
	0.028	0.0002	0.025	0.008	32.2	1.14	0.26
	0.055	0.0005	0.050	0.010	61.2	1.20	0.50
	0.083	0.0008	0.075	0.011	90.9	1.22	0.75
	0.110	0.0103	0.010	0.103	119.5	1.23	1.00
	0.138	0.0134	0.125	0.107	149.2	1.23	1.24
	0.165	0.0413	0.134	0.334	177.7	1.24	1.24
Platinum (IV)							
	0.036	0.001	0.037	0.029	3.9	0.7	0.35
	0.072	0.003	0.069	0.050	5.8	0.94	0.69
	0.108	0.007	0.101	0.069	7.7	1.06	1.00
	0.144	0.014	0.130	0.108	9.6	1.14	1.29
	0.216	0.051	0.129	0.396	13.5	1.22	1.29
Palladium (II)							
	0.022	0.001	0.021	0.048	6.5	0.72	0.21
	0.044	0.003	0.041	0.073	11.1	0.86	0.41
	0.066	0.002	0.064	0.031	15.6	0.91	0.64
	0.088	0.003	0.085	0.035	20.2	0.94	0.85
	0.101	0.002	0.099	0.020	22.9	0.95	0.99
	0.132	0.033	0.099	0.333	29.3	0.97	0.99

Fig. 3·17

Extended Langmuir adsorption isotherm for Gold, Platinum and Palladium exchange



3.6.4 Thermodynamics of gold, platinum and palladium exchange

Exchange rate constant[8] (k) and activation energy[7] (ΔE) were calculated for gold, platinum and palladium exchange by determining the gold, platinum and palladium exchange at three different temperatures. The results obtained for the rate constant k show that it is a first order reaction. The details are discussed in sec.3.4.4. The rate constant k was observed to be higher at higher temperature. Activation energy was calculated using Arrhenius equation as discussed earlier. The results obtained are given in Table 3.13. Due to lower activation energy $t_{1/2}$ for Pt(IV) exchange was observed to be very small (10 min).

3.6.5 Elution of gold, platinum and palladium

Various eluting reagents of different strengths were tried to elute gold, platinum and palladium quantitatively from the resin. The results are given in Table-3.14. It was observed that 1:1 mixture of 0.1 M HCl and 1.0 - 5.0 % thiourea could elute all the three metals quantitatively. A 1:1 mixture of 5.0 M HCl and 1.0 M HNO_3 could elute only gold quantitatively. The variation in eluting agents can be used for the separation of these metal ions. Different complexing agents like sodium diethyl dithiocarbamate, 8-hydroxy quinoline, semithiocarbazide could also elute these metals but regeneration of the resin was not possible. 5.0 % ammonia solution also eluted gold, platinum and palladium but the resin was destroyed because of highly alkaline medium and lost its chelating capacity.

Table 3.13 : Thermodynamics of exchange process

Gold, Platinum and Palladium concentration 220, 280 and 235 μg cm^{-3} respectively, resin 0.1 g, reaction volume 50 cm^3 at pH 5.0, equilibration time 3 h.

Metal	Rate constant k x 10^3 sec at °C 30	 40	 50	Activation energy ΔE J mol^{-1} x 10^{-4}
Au (III)	2.51	3.80	4.26	2.19
Pt (IV)	19.90	23.70	32.20	1.95
Pd (II)	6.66	9.05	11.45	2.23

Table 3.14 : Elution of gold, platinum and palladium

Gold, Platinum and Palladium concentration 435, 280 and 465 μg cm^{-3} respectively, resin 0.1 g, reaction volume 25 cm^3, equilibration time 24 h, volume of eluent 15 cm^3.

Sr. No.	Eluting reagent	% Elution		
		Au	Pt	Pd
1	M HCl			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
2	M H_2SO_4			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
3	M HNO_3			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
4	M HCl + HNO_3 (1:1)			
	1 + 1	20.0	00	00
	2 + 1	29.0	00	00
	3 + 1	65.0	00	00
	5 + 1	100	00	00
5	M CH_3COOH			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
6	M $HClO_4$			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00

7	M H_3PO_4			
	1.0	00	00	00
	2.0	00	00	00
	3.0	00	00	00
8	% NH_3			
	5.0	95.0	92.0	90.0
9	% Thiourea			
	1.0	88.0	90.0	85.0
	2.0	88.0	90.0	86.0
	3.0	88.0	90.0	88.0
10	M Hcl + % thiourea			
	0.1 + 1.0	100	92.0	100
	0.2 + 1.0	100	90.0	100
	0.2 + 2.0	100	96.0	100
	0.2 + 5.0	100	100	100
	0.1 + 5.0	100	100	100

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