CHAPTER 4

KINETICS OF EXTRACTION

This chapter deals with kinetics of sorption of Pu from nitric acid. Studies show that introduction of sulphonic acid group into the specific phosphinic acid resin enhances the complexation as well as the kinetics of extraction. Hence a study was initiated to find the effect of sulphonation on rate of exchange. A detailed description on the studies done with Pu(IV) at different acidities i.e. 0.5M, 1 M, 3M and 6M nitric acid is presented in this chapter. Samples were drawn at regular intervals and the fractional attainment of equilibrium is calculated. An attempt is made in this chapter to explore the probable mechanism of enhanced extraction. This chapter also includes the kinetics studies of Pu(IV) on Dowex 50WX8, a conventional strong acid cation exchange resin, from HNO₃ media and the performance of these resins are compared.

4.1 Introduction:

Selective ion exchange resins represent an important class of materials and finds wide applicability in trace metal ion separations [1]. The success of organophosphorus solvents led to the preparation of phosphorus based ion exchangers. It is known that the phosphorus based resins outperform sulphonylic acid cation exchangers for actinide separation in high acid region due to strong
coordinating ability. But this advantage is masked by the slow rates of complexation exhibited by the phosphorus based resins. The most important reason for the slow rates of complexation is their low hydrophilicity [2]. The phosphorus based ligands comes under intermediate/ weak acids with little or no ionic dissociation.

The complexation rates can be increased by a number of ways. Some of the parameters such as particle size, matrix rigidity as determined by degree of cross linking and type of cross linking, macroporosity etc. have been proposed in a number of studies and some experimental verifications are also reported.

Apart from the above mentioned methods, incorporation of adequate quantities of water to the polymer matrix also has been reported to give enhanced rate of exchange [3]. In such methods getting reproducible results is difficult and utmost care has to be taken to obtain reproducible results.

In order to overcome all these difficulties, it is essential to have an easier technique. It is reported that introduction of sulfonic acid group to 8-hydroxyquinoline resins, show excellent results [4]. Results obtained from the study had explained that introduction of sulphonic acid ligand which is highly polar, imparts the required hydrophilicity to the matrix, thereby enhancing rapid water gain, good swelling and good kinetic properties.

S.D.Alexandratos introduced Diphonix resin, which is a polystyrene-DVB resin containing gem diphosphonic acid groups along with sulphonic acid
group [5]. The results from the uptake data of actinides from highly acidic solutions suggest that the presence of sulfonic acid ligand provide the polymer matrix with faster kinetics while the specificity is due to the complexation by the gem phosphonic acid groups.

In view of the results reported by K.N. Sabharwal by phosphinic acid resin for actinides from highly acidic solutions, it is proposed that application of phosphinic acid resin can be extended to the separation of actinides from acidic HLW produced during PUREX process [6]. But as mentioned earlier, they suffer from slow rates of complexation. Based on the results given by S.D. Alexandratos, it was proposed to incorporate the sulfonic acid ligand into phosphinic acid resin. Accordingly a novel ion exchange resin, sulphonated phosphinic acid resin has been synthesised in our laboratory [7]. Uptake studies were carried out for the separation of actinides from nitric acid medium. Results obtained showed that the resin has very high affinity for actinides even in highly acidic solutions. Performance of the sulphonated phosphinic acid resin was compared with a commercially available strong acid cation exchanger. It was found that the sulphonated phosphinic acid resin is much more effective than the commercial cation exchanger in removing actinide ions from very acidic solutions. Results obtained from the distribution studies carried out with actinides and lanthanides suggest that the presence of sulfonic acid ligand is responsible for the enhanced rates of complexation. The prime
idea of incorporation of sulfonic acid ligand is to have faster rates of complexation.

Experimental work discussed in this chapter is aimed to establish the role of sulphonate acid ligand in enhancing the kinetics of extraction. Since the main aim is to find how fast the system approaches equilibration, Ft Vs t plots are used. The tests commonly applied are Boyd’s “Bb Vs t plot” which is readily useful for distinguishing between particle diffusion and film diffusion control.

4.2 Kinetics study:

In general kinetics studies deals with the following aspects of ion exchange process. 1) mechanism of ion exchange 2) rate determining step and 3) rate laws obeyed by the ion exchange system.

4.2.1 Ion exchange mechanism:

The theory of ion exchange kinetics is not clearly as advanced as ion exchange equilibria [8]. Ion exchange resin consists of a three dimensional polymer network of relatively large porous structure, carrying fixed ionic groups known as co-ions and exchangeable or mobile ions called counter ions. When a system of ion exchanger is in contact with an electrolyte, the counter ions diffuses out of the beads into the electrolyte solution. At the same time exchangeable ions from the electrolyte diffuses from the solution into the beads and occupies the space left by the counter ions, maintaining stoichiometry as
well as electroneutrality. Electroneutrality is preserved by the exchange of counter ion A in an equivalent charge transfer by counter ions B. No co-ions transfer is required.

4.2.2 Rate determining step:

Though there had been a lot of studies about the rate determining process in an ion exchange mechanism, Nachod and Wood had given a serious attempt to explain the same.

Earlier it was assumed that solely diffusion in the resin (particle diffusion) is the rate controlling process and in the solution, equalisation of the concentration on film at the surface of the spherical particles takes place instantaneously [9].

During an ion exchange mechanism there is a transfer of ions in both the ion exchanger and the solution. The rate of ion exchange depends upon the rates of the various transport mechanisms involved and the rate of the exchange reaction itself. Within the beads and through the film (a liquid layer adhered to the bead surface) transport can occur by diffusion only. So the rate determining steps are divided into

1) Inter diffusion of counter ions within the ion exchanger itself (Particle diffusion)
2) Inter diffusion of counter ions in the film adherent to the bead surface (film diffusion)

3) Counter ion exchange across the interface between the ion exchanger and solution phase

4) Chemical exchange reaction at the fixed ionic group.

The rate determining step was first shown by Boyd to be diffusion of ion either in the solid phase (particle diffusion) or across the surrounding liquid film (film diffusion) after conducting a series of studies [10], they concluded that for solutions of very low concentrations (<0.003N) film diffusion is the rate controlling, while at higher concentrations (>0.1 N) particle diffusion is the rate controlling. The film model was first introduced by Nernst in which the Nernst film is assumed as a completely stagnant one with sharp boundary separating it from the solution. The Nernst film thickness cannot be measured directly, but can be estimated from hydrostatics or kinetics measurements and of the order of $10^{-3} - 10^{-2}$ cm. The rate of ion exchange is determined by the slower of the above two processes. In the above cases migration of ions is defined by the properties of the system. Rate of these step can be changed by altering the system itself rather than by external forces.

Of various processes, ion exchange controlled by particle diffusion is the most widely studied.
In the case of film diffusion controlled mechanism, the overall rate of ion exchange is controlled solely by the rate of diffusion in the Nernst film. In this case rate of diffusion taking place inside the resin particles is much higher than that in the solution layer.

Considering that the overall rate of the ion exchange is controlled by the rate of the slowest step, factors which increase the rate of diffusion in the resin predominate in the film diffusion nature of the ion exchange process. Accordingly film diffusion is rate controlling if 1) ionic concentration in the resin is very high 2) degree of cross linking of resin is low 3) grain size is small 4) the concentration of the solution is low 5) the solution is not well mixed.

4.2.3 Rate laws:

The rate of ion exchange is determined by diffusion processes. Particle diffusion and film diffusion controlled ion exchange differ in their rate laws and the rate dependents on the particle size, solution concentration and degree of agitation. Rate laws can be derived by applying the well-known equations arising from diffusion induced electric forces, from selectivity, specific interaction and changes in swelling. To express the rate data in terms of fractional attainment of equilibrium, a simplified rate equation has been derived, following one of the approaches as suggested by Helfferich [11].
In this approach the ion exchange process is considered formally analogous to a reversible, pseudo first order chemical reaction.

\[
\frac{k_f}{k_r} \begin{array}{c} \text{M} \\ \hline \text{M} \end{array}
\]  

(1)

where the bar represents the resin phase species, M is the metal cation and kf and kr are forward and reverse rate constants, which include constant geometric factors such as interfacial area and solution volume.

By using the mass balance relation, valid throughout the uptake process

\[ C = [M] + [\text{M}] \]  

(2)

(C is the total concentration of the metal ion in the system), it follows

\[ \frac{d[\text{M}]}{dt} = k_fC - (k_f+k_r) [\text{M}] \]  

(3)

which upon integration with the initial condition \([\text{M}]=0\) at \(t = 0\) and rearrangement, gives

\[ \ln \left(1 - \frac{(k_f+k_r)[\text{M}]}{k_fC}\right) = -(k_f+k_r)t \]  

(4)

by introducing the equilibrium condition

\[ D = k_f/k_r = [\text{M}]_{\text{eq}}/ [M]_{\text{eq}} \]  

(5)

and the fractional attainment of equilibrium defined as

\[ F = [\text{M}]_t/ [\text{M}]_{\text{eq}} \]  

(6)
Where \([\bar{M}]_t\) is the concentration of metal ion in the resin at time \(t\) and \([\bar{M}]_{eq}\) is that at equilibrium.

we obtain the rate equation

\[
\ln (1-F) = -(k_f+k_r)t = -kt
\]  \(\text{(7)}\)

where \(k(s^{-1})\) is the experimentally observed overall rate constant. The above equation is analogous to the rate law obtained by Boyd et al for film diffusion control when the ingoing ion is a micro component of the system.

To investigate the mechanism of extraction of Pu(IV) on resin, the kinetic data obtained for the adsorption were evaluated using Boyd’s kinetic model.

Boyd’s model is expressed as

\[
F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2Bt}}{n^2} \quad \text{(for particle diffusion)} \tag{8}
\]

where \(F\) is the fractional attainment of equilibrium at various time \(t\), and \(Bt\) (min\(^{-1}\)) is Boyd’s constant. \(Bt\) can be used to calculate the effective Diffusion coefficient (cm\(^2\).s\(^{-1}\)) using the equation

Where

\[
Bt = \pi^2 \frac{\bar{D}}{r^2}
\]  \(\text{(9)}\)

where \(r\) is the radius of particle (calculated from sieve analysis).
Reichenberg [12] modified Boyd’s kinetic expression by applying the Fourier transformation, and its approximations are obtained by

For F values >0.85, \[ B_t = -0.4977 - \ln(1 - F) \] \hspace{1cm} (10)

and for F values 0<0.85 \[ B_t = (\sqrt{\pi} - \sqrt{\pi^2 F/3})^2 \] \hspace{1cm} (11)

For values of F calculated from equation (6), corresponding values of Bt can be obtained from equation (9) or equation (10). The linearity test of plots of Bt vs. time was employed to predict the type of mechanism.

Rate laws have been derived based on Nernst-Planck equation for both film – diffusion and particle diffusion control but they apply only to specific cases, for e.g. when the resin shows no selectivity or when equal valence of the exchanged ions are involved.

When the exchanged species is present in trace level concentrations, all changes in solution and in the ion exchanger remain on a trace level and the diffusion coefficients, activity coefficients, swelling, composition of solution, resin etc. remain practically constant. It has been demonstrated that the diffusion of trace ion is always rate-controlling. Thus, the rate laws derived for isotopic exchange apply with the diffusion coefficients of the trace component appearing in the rate constant.
4.3 Experimental:

Pu(IV) stock solution of concentration 8 µg/mL was prepared at different acidities i.e. 0.5M, 1 M, 3M and 6M nitric acid. Care was taken to maintain the valence control by the addition of NaNO₂. About 100 mg of resin was contacted with 100 mL of Pu(IV) solution prepared. All the experiments were carried out at room temperature [24°C ± 2°C] and in duplicate. Precision of Kᵋ values are within ± 5%. At various time intervals the test tube was centrifuged, a sample of solution was withdrawn and the stirring was started again. At times volumes of sample with drawn was maintained as very small (50 µL), so that the total volume of solution can be considered constant throughout the experiment. In all the cases Pu(IV) concentration in the aqueous phase was measured by radiometry. From the concentration obtained percentage of extraction was calculated at different intervals of time using

\[
%E = \frac{(C_i - C_f)}{C_i} \times 100
\]  

(12)

Continuous kinetic experiments, were carried out where the rates were measured on the same solution using one single test tube for the whole experiment. The advantage of continuous kinetic experiments, compared to discontinuous kinetic experiments are that the whole experiment was followed in a system while keeping the resin weight constant. The advantage of continuous procedure is less production of waste, while it suffers from the
uncertainty due to subtracting the centrifugation time from the total reaction time.

In all kinetic experiments, the ratio of volume of solution to amount of resin is typical of the so called “limited bath” technique [13]. However because the metal concentration was always at trace level, the experimental conditions employed in this work was indistinguishable from those of the “infinite bath” technique where a practically constant thermal composition of the system is maintained throughout the kinetic experiment [12].

4.4 Results and Discussion:

The $K_D$ values of Pu(IV) ions on phosphinic acid resin from nitric acid of different strengths for a constant contact time of 24 hours has been given in earlier chapter. The result shows that at lower acidity ion exchange is the predominant mechanism. At higher acidity ion exchange mechanism becomes ineffective and changes to coordination of Pu through phosphoryl oxygen. However from practical application of ion exchange resins, a major concern is the kinetics of the metal uptake. This drawback limits its advantage of high selectivity.

In order to find out the time required to reach equilibrium, experiments were carried out as a function of time from different acidities. Fig 4.1 shows the extraction of Pu from varying concentrations of $\text{HNO}_3$ by phosphinic acid resin
as a function of time. It can be seen that the exchange is very slow in all the cases.

![Figure 4.1 Extraction of Pu(IV) by phosphinic acid resin](image)

**Fig. 4.1 Extraction of Pu(IV) by phosphinic acid resin**

From Fig 4.1 it is clear that it takes long time to reach equilibrium. There is no appreciable change in percentage of sorption by varying the nitric acid concentration. Under the experimental conditions, the equilibrium Pu(IV) values correspond to the total uptake of Pu(IV).

The primary kinetic data obtained in this work is expressed as % of sorption vs. time. By normalising the data in terms of fractional attainment of equilibrium, it is possible to compare how rapidly a stable equilibrium is
reached under different experimental conditions, independent of equilibrium parameters. Normalisation of fractional attainment of equilibrium values were carried out by maintaining ratio of solution volume to resin weight (100 mg resin with 100 mL solution). The Ft values were calculated using equation (6). Since in all the cases the C (quantity of metal ion per mL of the raffinate at infinite time) value is taken as zero, the [M]eq used in the calculation of Ft is constant for all exchange systems. The corresponding Ft vs. time plot is given in Fig. 4.2. The results clearly indicate the slow kinetics of Pu(IV) by phosphinic acid resin. It can be seen that even after 10 hours of equilibrium the system could achieve only 50 % of equilibrium.

![Fig 4.2 Ft vs. time of Pu(IV) on phosphinic acid resin](image)
Fig 4.3 Bt vs. time of Pu(IV) on phosphinic acid resin

Fig 4.3 shows the Bt vs. time plots for the extraction of Pu(IV) by phosphinic acid resin. It can be seen that plots are linear passing through origin. It can be assumed that the predominant mechanism in these cases can be particle diffusion.

The prime idea of incorporation of sulphonic acid group is the enhancement of kinetics. It is postulated that the sulphonic acid ligand due to its high polarity nature imparts the required hydrophilicity to the ion exchange resin, where by increasing its rate of uptake of metal ions. Hence uptake studies were carried out similar way to that performed using phosphinic acid ligand. The results obtained show the effect of sulphonation as the sulphonic acid ligand is incorporated into the phosphinic acid resin.
Fig. 4.4 Extraction of Pu(IV) by sulphonated phosphinic acid resin

Fig 4.4 shows the uptake of Pu(IV) from varying concentrations of nitric acid using sulphonated phosphinic acid resin. It is evident from the Fig 4.4 that the equilibrium is reached at a faster rate compared to that of phosphinic acid resin. At 0.5 M acidity the resin could extract more than 90% of Pu within a contact time of 4 hours, whereas at 6M acidity it takes longer time to reach equilibration. The reason for the difference in kinetic behaviour can probably due to the fact that at 0.5 M ion exchange is the predominant mechanism. At higher acidity ion exchange mechanism becomes ineffective and changes to coordination mechanism. Helfferich reports that at low and high acidity the difference in kinetic behaviour can be due to the effect of selectivity on ion exchange rate.
Fig 4.5 Ft vs. time of Pu(IV) on sulphonated phosphinic acid resin

As stated earlier Ft vs. t plots give idea about the attainment of equilibrium. Fig 4.5 presents the Ft vs. time plots of Pu by sulphonated phosphinic acid resin from varying concentrations of HNO$_3$. It can be seen from the Fig 4.5 in this case compared to phosphinic acid resin, the rate of approach of equilibrium is faster. The results confirm the role of sulphonic acid ligand in enhancement of rates of uptake.
Fig 4.6 Ft vs. time of Pu(IV) on different resins at 0.5 M HNO₃

Fig. 4.6 represents the kinetics of Pu(IV) on sulphonated phosphinic acid resin from 0.5 M HNO₃ along with phosphinic acid resin. The characteristics of the two resins are the same as sulphonic acid ligand is incorporated into synthesised phosphinic acid resin. A commercially available strong acid cation exchanger is also included in study for comparison purpose. The data shows that both the sulphonated phosphinic acid resin and Dowex resin have similar kinetic behaviour. However as the system selected is Pu(IV) from 0.5 M HNO₃, even the commercial cation exchanger also behaves same way, since ion exchange is the predominant mechanism for absorption of Pu(IV) by the resin.
When the same work was extended to higher acidity, the results indicate that conventional cation is ineffective for the extraction of Pu(IV), while sulphonated phosphinic acid can be used for effective removal with faster kinetics. Here again sulphonated phosphinic acid resin attained equilibrium at a faster rate compared to phosphinic acid resin. The results presented in Fig. 4.7 confirm the same.

Fig. 4.8 represents the plot of Bt vs. time on sulphonated phosphinic acid resin for Pu(IV) from varying concentrations of nitric acid. It is clear from the Fig 4.8 that at lower acidity the plot is almost linear and the predominant mechanism in this case is by particle diffusion. At higher acidity the plot show a marked deviation from linearity. It can be concluded that at high acidity film
diffusion is the predominant mechanism and switch to mixed mechanism as exchange progress.

Fig 4.8 Bt vs. time of Pu(IV) by sulphonated phosphinic acid resin

The results obtained from the kinetics study can be concluded as follows:

Introduction of sulphonic acid group enhances the rate of extraction and reduces the time taken to attain equilibrium. The rate of kinetics is found to be faster in sulphonated phosphinic acid which attained equilibrium in at a faster rate compared to unsulphonated phosphinic acid resin in which case it takes longer time to reach equilibrium. As the objective of our study is the removal of actinides from High active waste, the prime characteristic the resin should have

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is faster kinetics which helps in reduction of contact time. The results confirm the role of sulphonic acid ligand in enhancing the kinetics of metal uptake.

The increase in the capacity and kinetics of sulphonated resin is because of coupling of an access mechanism with a recognition mechanism. The access mechanism can be nonselective and it allows all ions into the proximity of the polymer matrix, while it is the recognition mechanism which selectively complexes the targeted metal ion. Here sulphonic acid ligand acts as the access mechanism for metal ions to gain entry into the polymer matrix even at high acid medium whereas the phosphinic acid ligand is responsible for the selective complexation of metal ions by coordination through P=O bond.

At lower acidity the rate of uptake of sulphonated phosphinic acid resin is comparable to conventional cation exchange resin, while at higher acidity it outperform cation exchanger which is ineffective at higher acidity. As far as mechanism is concerned it is concluded that sulphonated phosphinic acid resin follow a mixed mechanism.

4.5 References:

3. A.Warshawsky, Chelating Ion exchangers, in Ion exchanger and separation process in Hydrometallurgy, edited by M.Streat and D.Naden,