Separation and Speciation of Ruthenium from Nitrate Medium by Ira-410 Anion Exchangers Kinetic, Thermodynamics and Reaction Mechanism

H.F. Aly, N. EL-said and A.T. Kassem

Hot Labs. And Waste Management Center,
Atomic Energy Authority, P.O. Box: 13759, Cairo, Egypt

Abstract: The kinetics of exchange of Ru(III) at extremely low concentration on the strongly basic anion exchanger IRA-410 has been studied by means of finite volume method. The rate of exchange of Ru(III) studied as function of different parameters, the concentration, the particle size of the exchanger and temperature. The apparent activation energy obtained is 48.75±0.07 and 16.8 kJmol^{-1} for IRA-410. The adsorption of ruthenium goes through a chemical reaction mechanism IRA-410 and a particle diffusion mechanism in the case of macroreticular resin. The free energy of activation and the entropy of activation were found to be, -17.71Kjmol^{-1} and 143.40 Jkmol^{-1} respectively. In order to understand the exchange behavior of IRA-410, The distribution coefficient was studied as a function of pH and temperature. The equilibrium study of Ru(III) ions with the two exchangers has been studied at 25, 35, 45, 55 and 65°C. The extraction of Ru(III)depends strongly on the change of pH rather than on the temperature.

Key words: Kinetic Separation ⋅ Adsorption of ruthenium ⋅ IRA-410 and ⋅ Anion Exchangers

INTRODUCTION

The occurrence of the relatively long-lived isotopes of ruthenium, [103]Ru and [106]Ru, amongst the fission products, Ruthenium has seven naturally occurring isotopes: [96]Ru, [98]Ru, [99]Ru, [100]Ru, [101]Ru, [102]Ru and [104]Ru with the relative abundance of 5.5, 1.9, 12.7, 12.6, 17.0, 31.6 and 18.7 % respectively. Additionally, 34 radioactive isotopes have been discovered. Of these radioisotopes, the most stable ones are [106]Ru, [103]Ru and [97]Ru with half-lives of 373.6, 39.3 and 2.9 days respectively. [106]Ru, which is a soft beta emitter (Ebmax = 39 keV) is used for treatment of eye cancerand hence their presence in solutions of irradiated fissile material dissolved in nitric acid, has drawn attention to extensive gaps in the knowledge of ruthenium chemistry.Such solutions contain tetra valent nitrosyl ruthenium complexes in which the ligands are nitrato, nitro, hydroxo and aquo groups [1-8]. Although a large number of RuNO complexes (containing the ligands NH$_3$, halide ions, OH$^-$, SO$_4^{2-}$, C$_2$O$_4^{2-}$ and in a few cases NO$_2$) have been identified, the aquo-nitrato complexes have been neglected since Joly (1) prepared them in solution; furthermore, in spite of the general similarity of RuNO complexes to those of Ru(III) and Pt(IV), amongst which nitro complexes are well known, no nitro complex of RuNO has hitherto been formulated; has partly arisen from the tetra nitro complex having hitherto been regarded as a penta nitro complex of Ru(III) [9-13]. The particular nitrosylruthenium compounds prepared are formulated on the assumption that, as in the amino-nitrosylruthenium complexes, the ruthenium atom has a co-ordination number of 6, one position being occupied by the nitrosyl group: thus the mononuclear nitrato complexes are represented by the general formula [RuNO(NO$_3$)$_4$(OH)$_{2-4}$(H$_2$O)$_2$]. Their identity as nitrosylruthenium complexes has been established by their conversion to nitrosyl-ruthenium hydroxide or hydrosulphide, in both of which the ratio [N]: [Ru] is unity. Among many other fission products, [103]Ru and [106]Ru also are found after nuclear fission. On dissolving the fuel elements in HNO$_3$, numerous neutral, anionic and particularly, cationic ruthenium nitrosyl nitrato complexes are formed which are converted into one another more or less quickly, depending on the external conditions. During the PUREX process, Ru is distributed uncontrollably between the organic and the aqueous phases and interferes with the decontamination during the process [14]. A important way of treatment of radioactive

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Corresponding Author: H.F. Aly, Hot Labs. And Waste Management Center, Atomic Energy Authority,
P.O. Box: 13759, Cairo, Egypt. E-mail-nessem.abdel@yahoo.com.

waste solutions is to know the knowledge and give highlights on the kinetics and thermodynamics of one of the interested fission products which is the ruthenium isotopes. In context the starting complexes and the behavior of the ruthenium during the single steps of the process are of interest. Till now there have been only few reliable results on the kinetics and thermodynamics and separation of ruthenium nitrosyl complexes and the determination of their composition [15]. In dilute nitric solutions different mononuclear complexes are present [16, 17]. For the isolation of the ruthenium nitrosyl complexes on a preparative scale, column chromatography is suitable. It allows on the one hand the clear separation of the complexes, on the other hand their elution as in chromatography. This advantage plays an important role in the elucidation of the extraction behavior of the complexes [1-10].

MATERIALS AND METHODS

Materials: Two strongly basic anion exchangers namely; IRA-410 (16-50 mesh) was used. The two resins are of Amberlyte type in Cl-form and obtained from Aldrich. Sodium nitrate, nitric acid and all other elements used were from Merck. Formic acid was obtained from GEB Laborchemi Apolda. Other chemicals and reagents were of analytical reagent grade. Were obtained from Merck.

Preparation of Mother Solution (Simulated Waste Solution): The pure nitric ruthenium solutions was prepared by dissolving $Ru_2N_6O_{15}$ in 100ml of 0.15 M HNO_3 The solution was adjusted to prepare aqueous solutions of ruthenium ($\sim10^{-3}$M Ru) of the nitrato complexes. An inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) of ARL type model 3520, was used for element analysis where argon is used and the power was 1.5 kilo watt and the temperature of the plasma was about 6000°C.

Batch Investigation: For batch investigations, ten samples from the mother solution, each of 40 ml were adjusted to different pH's (1-11). These samples were shaken for half hour with one grame of the exchange. The distribution coefficient was calculated as:

$$K_d = \frac{C_o - C}{C} x \frac{V}{m} ml/g \qquad (1)$$

Column Application: A chromatographic double jaket column was used in connection with a Julabo circulator which control the temperature with an a quracy of ± 0.01°C. The column was of 1 cm diameter and 25 cm long

and filled with 7.5 gm of either IRA-410 or IRA-900 anionic exchangers to give ~22 cm bed length. Before use, the column was preconditioned by 300ml of the loading solution and in all cases the follow rate of the mobile phase was 2 ml/min.

Analytical Procedure: For Ruthenium loading, 300 ml of the simulated waste solution containing the studied elements in 0.1N $NaNO_3$ at pH~ 1 was run down the column where ruthenium was loaded as a brown zone at the top of the column.

Separation of Ruthenium by the Batch Technique: In this concern, 1 gm of the anionic exchanger; IRA-410 was preconditioned with 100 ml 0.1N $NaNO_3$, 40 ml of the simulated waste solution containing the ions under investigation in 0.1N $NaNO_3$ were adjusted to pH~ 1 and shaked in contact with the applied resin. After equilibration (1-2h), filtraction was carried out. Filtrate analysis (by ICP) showed the fraction of uptake of Ru (III). These separations of ruthenium from were experimented as follows: A solution of 0.1N $NaNO_3$ (40 ml) of pH~ 1, shaken equilibrated together with the used resin. However, filtrate analysis showes ruthenium presence.

RESULTS AND DISCUSSION

Adsorption Behavior of Ruthenium Ions on the IRA-410: In order to discuss the distribution data experimentally obtained for the ruthenium ions studied in the present work, the exchange process is considered. It has been found experimentally for organic ion exchangers and organic resins that:

- The adsorption of a given cation with decrease as the concentration of foreign cations is increased at any given pH.
- No significant adsorption of anions or neutral species in true solution takes place.
- The affinity of a cation for the adsorption increases with its increasing valence.
- The affinity of ions having the same charge for the adsorption tends to decrease as the size of the hydrated ion increases. In case of organic exchangers the exchange process involves mainly, replacement of the hydrogen ions in the exchanger by the cationic species in solution. If a metal ion M^{n+} and the proton H^+ are competing for the exchanger, the equilibrium encountered can be represented by the following:

where a denote the activity, R^-, the matrix anion of the exchanger, f, the activity coefficient of the N^{n+} *ion in* the exchanger and the y_N, the activity coefficient of the N^{n+} in the solution. The distribution coefficient, K_d of the N^{n+} ions is expressed by this.

$$K = \frac{a_{NR_n}(a_M)^n}{(a_{MR_n})^n a_N} = \frac{f_N[NR_n](a_M)^n}{\gamma_N[N]^{n+}(a_{NR_n})^{n+}} \qquad (2)$$

Equation:

$$K_d = \frac{[NR_n]}{[N]^{n+}}\ldots\ldots\ldots ml/g \qquad (3)$$

by combining Eqs. 3 and 4, we obtain:

$$K = \frac{f_N(a_M)^n}{\gamma_N(a_{MH})^{n+}} \qquad (4)$$

$$\log K_d = cons\tan t - n \log a_H \qquad (5)$$

when the amount of N^{n+} is negligible as compared with the that of M^+, a_{MR}, f_N are regard as constant. Moreover, y_N is also constant if the ionic strength is kept constant. Under such conditions, the following equation holds by taking logarithm of Eq. 5: That is, if the logarithm of the distribution coefficint of N^{n+} is plotted against pH or the D against hydrogen ion concentration on log-log scale, a straight line possessing the slope of -n should be obtained.

Adsorption Behavior of Ru (III)

The Effect of pH: The results of the uptake behavior of Ru (III) by zirconium phosphate in HNO_3 acids are shown graphically in Fig. 1 as D vs acid concentration on log-log scale. From the plot in this figure it could be seen that the adsorption behavior of Ru (III) in HNO_3 has D-values are low at low acid concentration, then it slightly increases with increasing acid concentration and finally decreases at higher acid concentration, It is, however, noticed here that Ru (III) in aqueous solution of dilute acid is present mainly as the hexa-aquo ion. So the low distribution ratio at low acid concentration may be related to hydrolysis in acidic medium. From nitric acid medium the log D vs acid concentration r elation gives a negative slope of -2.65 (0.1-2.0M acid range). This indicates that Ru(III) is the main cation from nitric acid, Fig. (1) [11-20].

From Figs. (2-6) it is obvious that, in the acidic range lower than 0.1M the results cannot be explained by this argument because the slopes are about half of the valency of the exchanging cation, N^{n+}. Since the experimental

conditions satisfies the assumption for deducing Eq, 6. This contradiction compels us to consider that K_{equ} on the pH. The uptake of Ru(III) was found to be from 30-80% in the pH(1-11) at 25°C while at 65°C was found to be from 60-80% in range of pH (1-11). If the solution is acidic enough to permit the participation of only ion exchange sites with lowest apparent pK_a value in the ion exchange reaction. And if the cation to be exchanged is present as hydrated ions, it can regarded that the reaction of the H^+ Eq. 2 is a combination of the following two reactions. Accordingly, equation. 7 represents the acid dissociation of the exchanger and Eq. 8, the variation of the anionic form of the exchanger with the exchanging cations, N^{n+}, a similar conflict between the Eq. 6 and the experimental results of the ion examined., it was considered that the contradiction was attributable to the gradual decrease in the acid dissociation constant. K_H of the ion exchanger with pH. Accordingly, it is considered that the pKa is not constant, but a certain average value. If this discussion holds true, the ralation of Eq. 6 should in the ion exchange between Ru (III) metal ions in an alkaline medium. Where the acid dissociation can be ignored. In a dilute aqueous solution, i.e. solution of activity coefficient ≈ 1,

$$K = K_n^n . K_N \qquad (6)$$

$$HR = H^+ + R^-,\ldots\ldots\ldots\ldots K_d = \frac{a_H \, a_R}{a_{HR}} \qquad (7)$$

$$nR^- + N^+ = NR_n.,\ldots\ldots\ldots K_N = \frac{a_{NR_n}}{(a_R)^n a_n} \qquad (8)$$

$$m^{n+} + \overline{HR} \leftrightarrow nH + \overline{M(R)_n} \qquad (9)$$

where m^{n+} is the cation to be exchanged in the solution and the superscript bar denotes the exchanger phase. In the reaction the ion hydration is omitted for simplicity. For metal ion-proton the equilibrium constant K_H^M is given by:

$$K_H^m = \frac{[H]^n[\overline{MR_n}]}{[RH]^n[M^{n+}]} \qquad (10)$$

Experimentally, the metal ion concentration used is generally less than the hydrogen ion and the $[RH]_n$ can be considered constant in equation (10). On the other hand, the distribution ratio at equilibrium is given by:
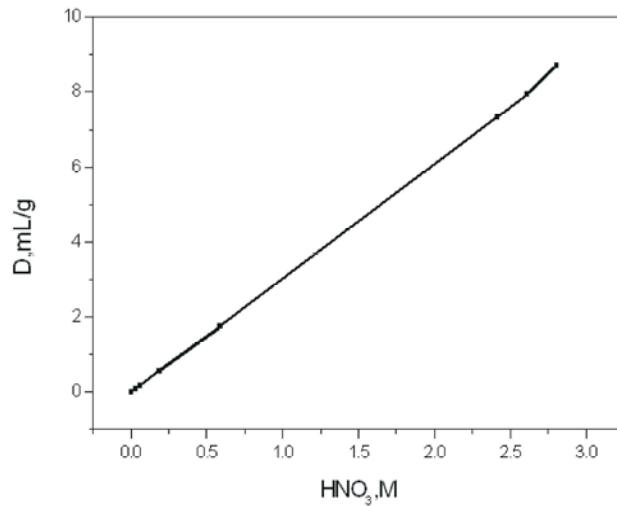
$$D = \frac{[\overline{MR_n}]}{[M^{n+}]} \qquad (11)$$

Fig. 1: Adsorption behaviour of Ru(III)on IRA-410 from different acid solutions
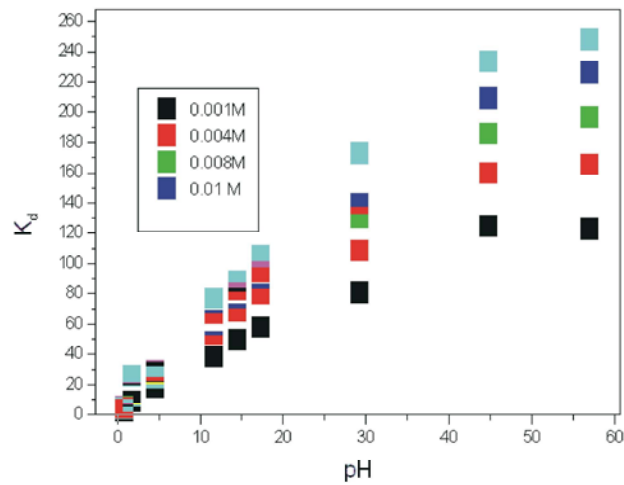

Fig. 2: Effect of pH on the uptake of Ru(III) using IRA-410 anion exchanger (0.02g) from 0.1M NaNO3 solution at different concentrations
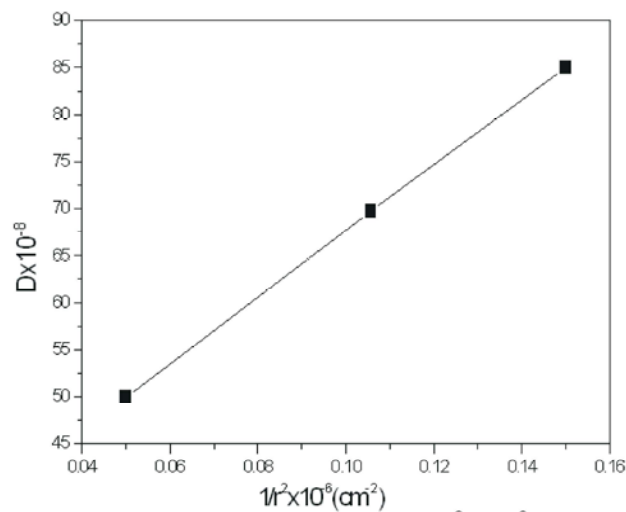

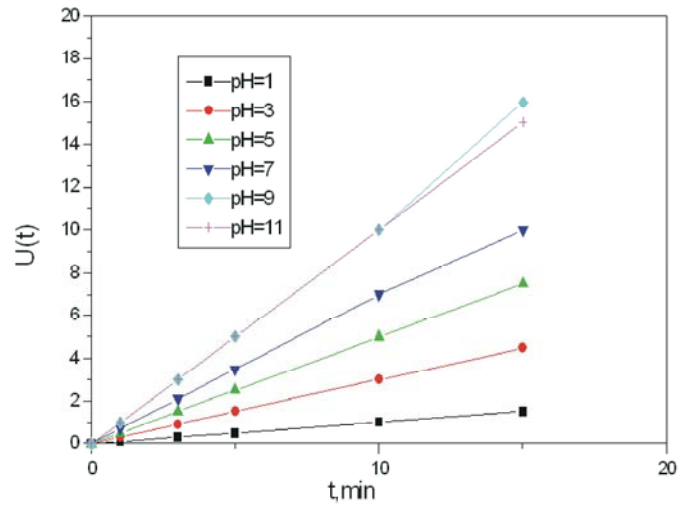Fig. 3: Plot of the diffusition coefficient D x10^{-8} VS 1/r^2 for Co(III) at 25°C onIRA-410

Fig. 4: Kinetics of the uptake of Ru(III) using IRA-410 anion exchanger (0.02g) from 0.1M NaNO$_3$ solution at different pH media at 25°C
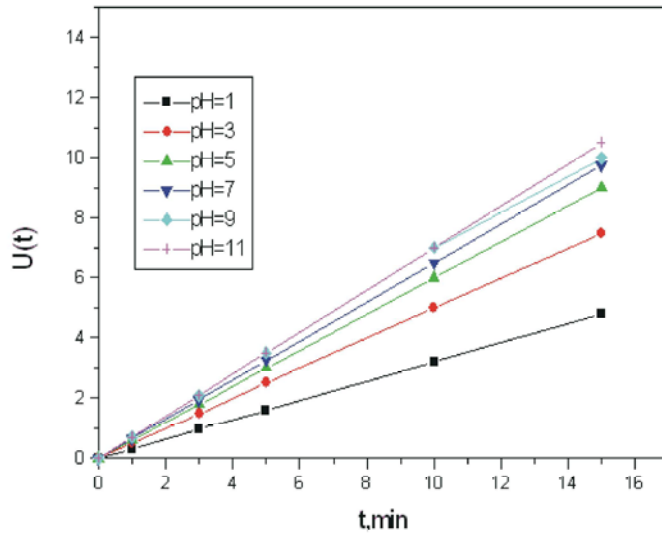

Fig. 5: Kinitics of the uptake of Ru(III) onto IRA-410 exchanger (0.02g) from 0.1M NaNO$_3$ solution at different pH media at 35°C
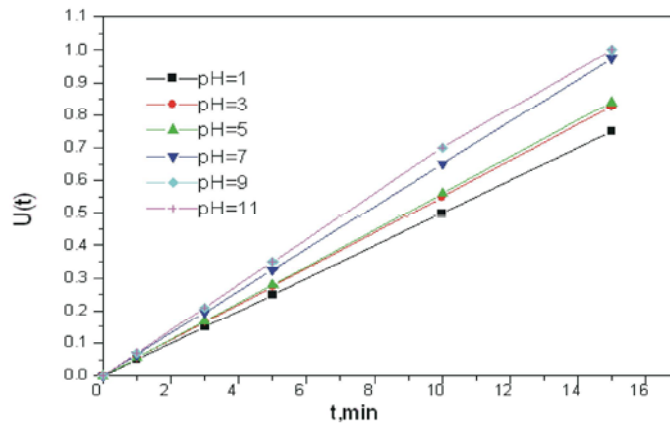

Fig. 6: Kinitics of the uptake of Ru(III) onto IRA_410 anion exchanger (0.05g) from 0.1M NaNO$_3$ solution at different pH media at 45°C

Substituting equation (10) into equation (11) it becomes:

$$D = K_H^m = \frac{\overline{[MR]^n}}{[H^+]^n} = \frac{K^/}{[H^+]^n} \qquad (12)$$

In logarithmic form, equation (12) becomes,

$$\log D = \log K^/ - n\log[H^+] \qquad (13)$$

Thus, if the law of mass action is obeyed, a plot of D vs H$^+$ on log-log scale for a certain metal cation of charge n$^+$ should give a straight line of a slope (-n). In this work the adsorption behaviour of Ru(III) in nitric acid solutions is studied. The study was carried out by the batch technique in duplicate and the main value of the final results is taken. Deviation of singlets from the main value is found not to exceed 3%.

Adsorption and Speciation: Prior to evaluate the possibility of studying the effect of pH concentration on the adsorption of different Ru (III) on IRA-410, the kinetics of ion exchange process is studied. Our aim is to study the mechanism of ion exchange process (film and/or particle diffusion or chemical reaction), not only to determine the equilibrium time. The rate of adsorption of the activity is followed by contacting 0.01g of the exchanger with 10 ml of the spiked investigated ruthenium ions solution. The solution is then shaken at a fixed rate and samples are removed periodically for analysis. The percentage uptake of ruthenium ions at different intervals of time is calculated from the following equation:

$$\%uptake = (\frac{A_o - A_t}{A_o})100 \qquad (14)$$

where,

A$_o$ = Initial activity in ml solution.
A$_t$ = Activity at time t in ml solution.

A quantity of 10 mg of the IRA-410 ion-exchanger to be studied was shaken with 10 ml of the aqueous solution containing the radioactive isotope of suitable activity for a sufficient time to attain equilibrium. This time was determined for Ru(III) from a separate experiment carried out specifically for this purpose. The distribution ratio in all the series of the measurement was calculated according to the following equation:

$$K_d = \frac{1-F}{F} X V \bigg/ m ....ml/g \qquad (15)$$

where,

I : The initial activity (counts/sec.).
F : The residual activity after equilibrium (counts/sec.).
V : The volume of the aqueous phase (ml.).
m : The weight of the ion exchanger (g).

The value of the distribution ratio in each study is the mean value obtained from the experiments carried out for each. The effect of pH is clear in Fig. 7. Which that K$_d$ increase as the pH increase in the pH range (3-7) while at 7<pH<3 it remains constant. Fig. 2. depict the effect of pH at different temperature on the exchange in range (25-65°C) on the K$_d$ was value and outlined in Fig. 7. It is obvious that as the temperature increases, the K$_d$ increases from 25 to 35°C. While the K$_d$ remains constant at temperatures higher than 55°C. The expected chemical strictly of Ru(III) in the solution was as follows:
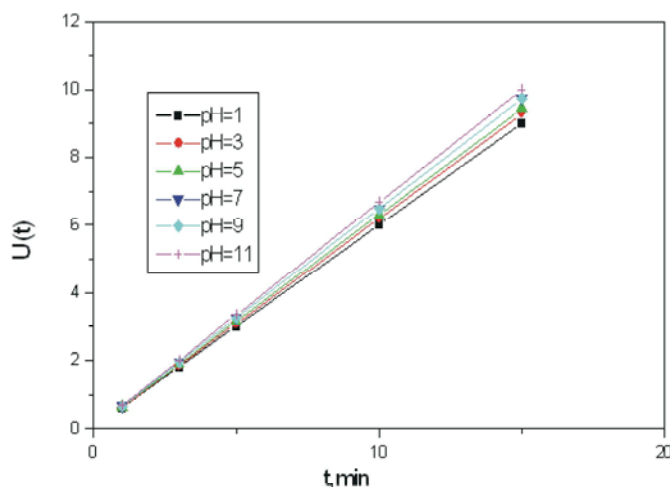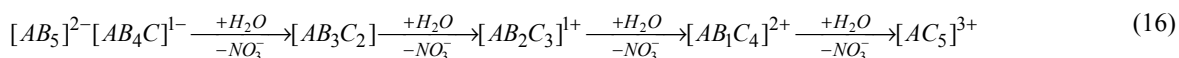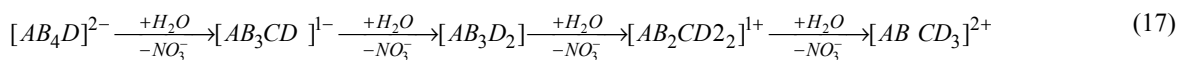

Fig. 7: Kinitics of the uptakeof Ru(III) using IRA-410 exchanger (0.02g) from 0.1M NaNO₃ solution at different pH media at 55°C

Speciation:

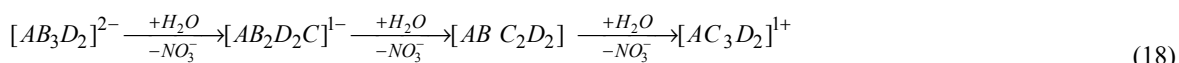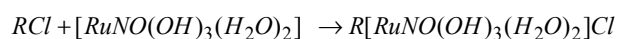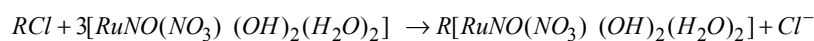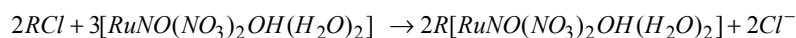$$[AB_5]^{2-}[AB_4C]^{1-}\xrightarrow[-NO_3^-]{+H_2O}[AB_3C_2]\xrightarrow[-NO_3^-]{+H_2O}[AB_2C_3]^{1+}\xrightarrow[-NO_3^-]{+H_2O}[AB_1C_4]^{2+}\xrightarrow[-NO_3^-]{+H_2O}[AC_5]^{3+} \qquad (16)$$

$\downarrow$

$$[AB_4D]^{2-}\xrightarrow[-NO_3^-]{+H_2O}[AB_3CD]^{1-}\xrightarrow[-NO_3^-]{+H_2O}[AB_3D_2]\xrightarrow[-NO_3^-]{+H_2O}[AB_2CD2_2]^{1+}\xrightarrow[-NO_3^-]{+H_2O}[AB\,CD_3]^{2+} \qquad (17)$$

$\downarrow$

$$[AB_3D_2]^{2-}\xrightarrow[-NO_3^-]{+H_2O}[AB_2D_2C]^{1-}\xrightarrow[-NO_3^-]{+H_2O}[AB\,C_2D_2]\xrightarrow[-NO_3^-]{+H_2O}[AC_3D_2]^{1+} \qquad (18)$$

-NO$_3$ $\downarrow$

$$[AB_2D_3]^{2-}\xrightarrow[-NO_3^-]{+H_2O}[AB\,D_3C]^{1-}\xrightarrow[-NO_3^-]{+H_2O}[AC_3D_2] \qquad (19)$$

OH,- $\downarrow$

$$[ABD_4]^{2-}\xrightarrow[-NO_3^-]{+H_2O}[AD_4C]^{1-} \qquad (20)$$

where A = RuNO, B = NO$_3^-$, C = H$_2$O, D = OH$^-$, Reactions in equations [16-20].

While the reaction mechanism can be described as below and thaexchange speces positive and neutral species and the reaction species in the solution was shown below.

Mechanism and Chemical Reaction: The expected species in aqueous nitrate medium evaluated by soft ware programme Mintque. A series of nitratoaquo nitrosylruthenium complexes of general formula [RuNO (NO$_2$)$_3$(OH)$_{2-3}$(H$_2$O)$_2$]$_5$ has been identified. In aqueous solution they give rice to anionic and cationic ruthenium apecies; the higher nitrato complexes are hydrolysed at room temperature at a rapid but measurable rate to lower nitrato complexes; condensation to polynuclear species accompanies these reactions. The trinitrato complex has been.

$$HNO_3 \rightarrow H^+ + NO_3^-$$
$$RCl + [RuNO(NO_3)_5]^{-2} \rightarrow R[RuNO(NO_3)_5]^{-2} + 2Cl^-$$
$$RCl + [RuNO(NO_3)_4O\,H]^{-2} \rightarrow R[RuNO(NO_3)_4OH]^{-2} + 2Cl^-$$
$$RCl + [RuNO(NO_3)_3(OH)_2]^{-2} \rightarrow R[RuNO(NO_3)_3(OH)_2]^{-2} + 2Cl^-$$
$$RCl + [RuNO(NO_3)_2(OH)_3]^{-2} \rightarrow R[RuNO(NO_3)_2(OH)_3]^{-2} + 2Cl^-$$
$$RCl + [RuNO(NO_3)\,(OH)_4]^{-2} \rightarrow R[RuNO(NO_3)_2]^{-2} + 2Cl^-$$
$$RCl + [RuNO(NO_3)_4(H_2O)]^{-1} \rightarrow R[RuNO(NO_3)_4(H_2O)]^{-1} + Cl^-$$
$$RCl + [RuNO(NO_3)_3OH(H_2O)]^{-1} \rightarrow R[Ru(NO)_3OH(H_2O)]^{-1} + Cl^-$$
$$RCl + [RuNO(NO_3)_2(OH)_2(H_2O)]^{-1} \rightarrow R[RuNO(NO_3)_2(OH)_2(H_2O)]^{-1} + Cl^-$$
$$RCl + [RuNO(NO_3)\,(OH)_3(H_2O)]^{-1} \rightarrow R[RuNO(NO_3)(OH)_3(H_2O)_2]^{-1} + Cl^-$$
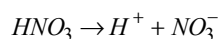$$RCl + [RuNO(OH)_4(H_2O)]^{-1} \rightarrow R[RuNO(OH)_4(H_2O)_2]^{-1} + Cl^-$$

$$3RCl + 3[RuNO(NO_3)_3(H_2O)_2] \rightarrow 3R[RuNO(NO_3)_3(H_2O)_2] + 3Cl^-$$
$$2RCl + 3[RuNO(NO_3)_2OH(H_2O)_2] \rightarrow 2R[RuNO(NO_3)_2OH(H_2O)_2] + 2Cl^-$$
$$RCl + 3[RuNO(NO_3)\,(OH)_2(H_2O)_2] \rightarrow R[RuNO(NO_3)\,(OH)_2(H_2O)_2] + Cl^-$$
$$RCl + [RuNO(OH)_3(H_2O)_2] \rightarrow R[RuNO(OH)_3(H_2O)_2]Cl$$

$$2RCl + 2[RuNO(NO_3)_2(H_2O)_3]^{+1} \rightarrow R[RuNO(NO_3)_2(H_2O)_3]^{+1} + 2Cl^-$$

$$RCl + [RuNO(NO_3)\ OH(H_2O)_3]^{+1} \rightarrow R[Ru(NO_3)\ OH(H_2O)_3]^{+1} + Cl^-$$

$$RCl + [RuNO(OH)_2(H_2O)_3]^{+1} \rightarrow R[RuNO(OH)_2(H_2O)_3]^{+1}Cl$$

$$2RCl + 2[RuNO(NO_3)(H_2O)_4]^{+2} \rightarrow 2[RuNO(NO_3)(H_2O)_4]^{+2} + 2Cl^-$$

$$2RCl + 2[RuNO(OH)(H_2O)_4]^{+2} \rightarrow 2[RuNO(OH)(H_2O)_4]^{+2} + 2Cl$$

$$3RCl + 3[RuNO(H_2O)_5]^{+3} \rightarrow 3R[RuNO(OH)_2(H_2O)_3]^{+3} + 3Cl$$

It has long been established the ion exchange reaction in anion exchange resin is controlled either by film or by particle diffusion [18-22]. In this work, an attempt was made to establish the kinetic behavior of strongly basic anion exchangers IRA-410 resin as exchanger to elucidate which type of the reaction mechanism for separation of Ru (III) is going on. Since the concentration of the adsorbing ion is extremely low; the changes of the composition of the resin and external solution remains insignificant. In such a system the conventional rate low for an Ru (III) isotope exchange

$$U(t) = 1 - \frac{2}{3w} \sum_{n=1}^{\infty} \left(\frac{\exp(-nS^2\tau)}{(1 + S_n^2/(9w(1+w))} \right) \qquad (21)$$

reaction is valid, The kinetic equation [21-29] for an exchange reaction controlled by film diffusion under the condition of finite volume is given by the Paterson equation; [10] where C_o is the initial metal concentration, $C(t)$ the metal concentration at time (t) and C_∞ is the equilibrium metal concentration. Paterson equation for solid diffusion process was applied to the experimental data. Paterson 's approximation is widely applied to the ion exchange between spherical beds of exchanger containing the counter ion A^+ and a well stirred solution of B^+ when the diffusion coefficient may be supposed constant (isotopic exchange) and the concentration of A^+ entering the solution is not necessary negligible thought the process. Equation. (21), predicts that, if the rate determining step is film diffusion, Log [1-U(t)] is directly proportional to the reaction time and inversely to the particle radius and film thickness.

$$U(t) = \left(\frac{6Q_o\sqrt{Dt}}{r(Q_0 - Q\infty)\sqrt{\pi}} \right) \qquad (22)$$

The film thickness decreases with an increase of the ionic radius. Thus the rate of exchange reaction increases with increase the ionic strength, [22, 23]. From Eq. (24), we see that U(t) in the reaction controlled by particle diffusion is

proportional to the square root of the time, and inversely proportionally to the particle radius Similarly for particle diffusion controlled exchange with a finite volume condition, the kinetic equation. Where $w=CV./CV$, $Q_\infty =Dl/r^2$, S_n is the roots of equation $S_n \cot S_n =1+(S_n^2/3w)$. Under the experimental conditions, the volume of the solution is significntly higher than that of the resist since this system may be taken as semi-finite. Equation (2) can be approximated by [21, 22]: Where Q is the amount of the reaction group in the reaction, Q_∞ is the amount of the exchange at equilibrium. The deviation from linearity between U(t) and $t^{1/2}$ is less than 2.5%if U(t) doesn't exceed 0.5. For the exchange reaction controlled by a chemical reaction, the rate is expressed by a conventional rate equation for chemical instead of such equation as Eqs. (21, 22) and (18) drived from Fick diffusion law. Taking in to consideration the fact that the amount of functional group in the reaction system is significantly larger than that of exchanging ion, this reaction can be regarded as first-order with respect to the exchanging ion [23, 24]. The rate equation is where Q_1 is the initial amount of exchanging ion. Q_t is amount of exchange at time t and k is the rate constant was assumed that the reaction in the chelating resin was controlled either by diffusion (film or particle) or by a pseudo-first-order chemical reaction. The kinetics of exchange of Ru(III) in the solution for H^+ in the resin was studied and the results were given in Fig. (10). It can be seen that the relationship between $\log[Q_1/(Q_1-Q_t)]$ or $-\log[1-U(t)]$ and t is linear corresponding to Eq. (16-18), no linearity being obtained in U(t)-t relation. Each value of log $[Q_1/(Q_1-Q_t)]$ at corresponding time does not so much differ from that of $-\log[1-U(t)$, Fig. (8-11). This makes it difficult to determine which mechanism is operating as the rate determining step. For sake of clarification, the effects of ionic strength (0.05-0.001) and the particle radius [0.15-0.2mm] on the rate of exchange reaction were examined. The effect of particle size seems to have a marked effect on the ion exchange rate. Aplot of D vs.$1/r^2$. Fig. 3. Shows a reciprocial proportionality between the rate of exchange and square
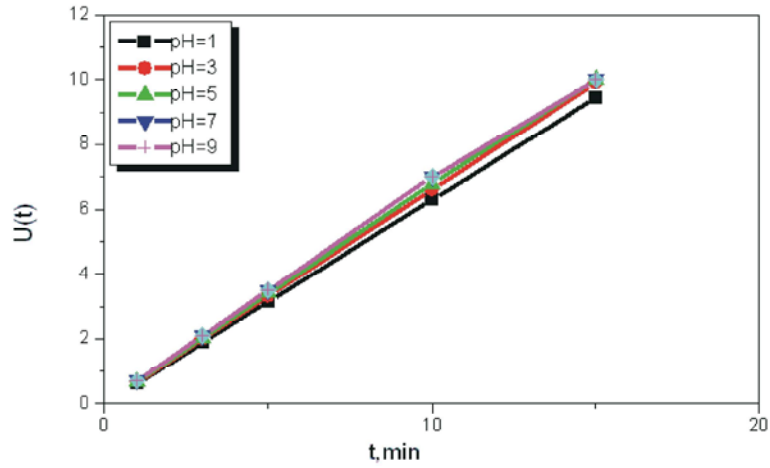
Fig. 8: Kinitics of the uptakeof Ru(III) using IRA-410 exchanger(0.02g) from 0.1M NaNO$_3$ solution at different pH media at 65°C
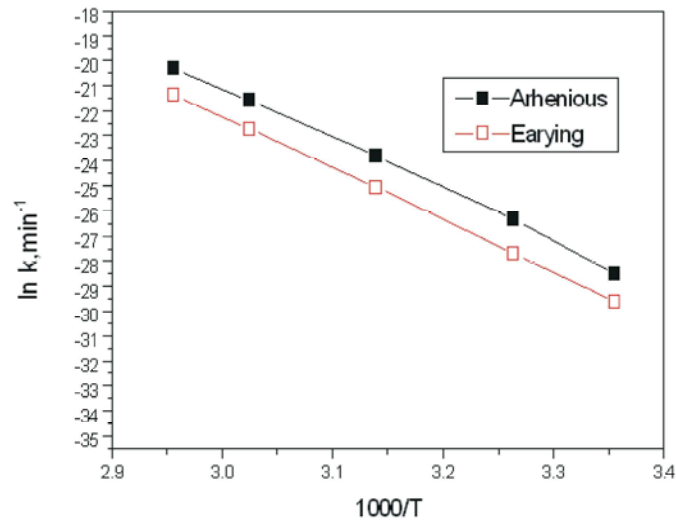

Fig. 9: Linear plot of Arhenious and Eyring plots for ln k,min^{-1} vs 1000/T for extraction of Ru(III) from 0.1M HNO$_3$
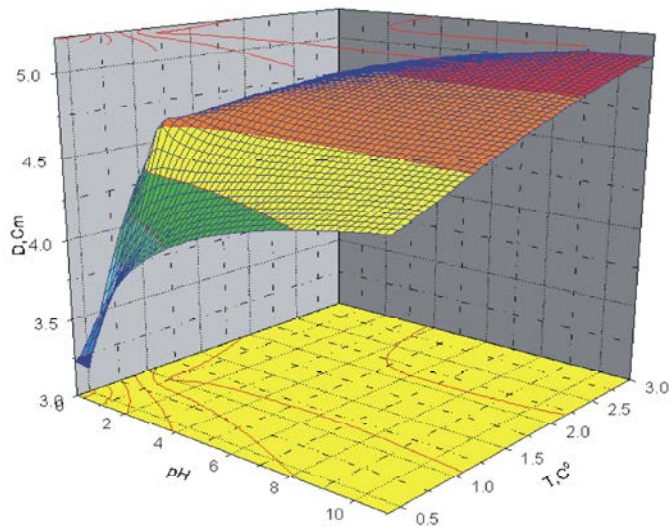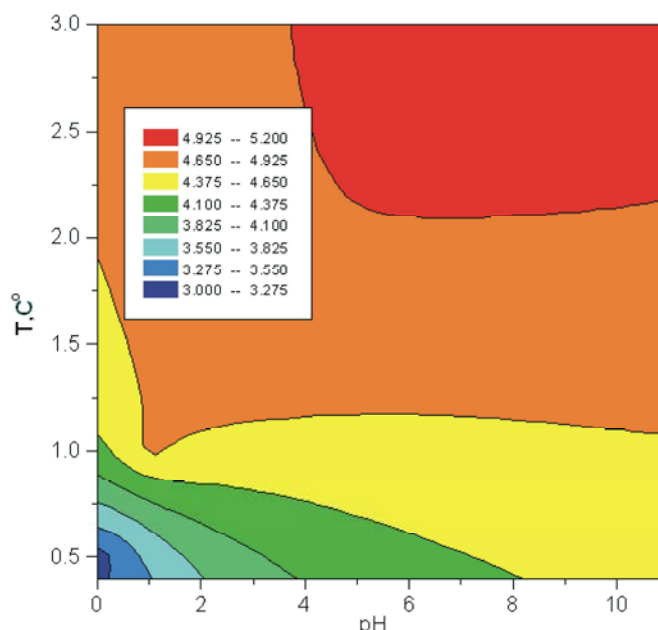

Fig. 10: 3D-Optimization

Fig. 11: Contour plot of exchange Ru(III) on IRA-410 where X=pH, Y=T,C° Z=K_d

of the particle size which again verifies that the diffusion exchanger particles is the rate govering step. The rate of exchange is independent of the above parameters. Thus, it might be concluded that the rate of exchange of Ru(III) in the resin should be controlled by insignificant particle diffusion mechanism and controlled by film diffusion mechanism.

Thermodynamics: The effect of temperature on the rate of exchange should be expected to afford a criterion of the mechanism, the Arhenious plot between ln D⁻ vs 100/T, Fig. 8., Equ. (25), Table (1). where D_o is the pre-exponential constant and R is the gas constant, a straight line is obtained and the activation energy is calculated from the slope of this line. The activation energy is calculated from Arhenious and Erying equations shows more closeness in Erying to the higher values than Aerhenious. The pre-exponential constants D_o are obtained from the intercepts of the lines were usesd for calculated of the entropy of activation (ΔS*) is obtained the D_o in calculated from the following equation.

$$D = D_o e^{-E_a/RT} \tag{25}$$

$$D_o = 2.72 d^2 \frac{KT}{h} \exp((\Delta S/R)) \tag{26}$$

where k and h the Boltzman and Plank constants, d is the ionic jump distance taken [25-28] as 0.5mm, R is the gas constants and T is taken as 273°K Equation (25). Since the

activation energy of exchange controlled by diffusion is supposed to be distinctly lower than that for the chelate formation reaction. This is certainly the case with such metal ion where the apparent activation energy is about 27.51 kJ mol⁻¹ The results support the view that the rate determining step of this reaction is particle diffusion mechsanism. Fig. 9 shows that the plot of ln D vs 1000/T is linear over a wide range of temperature the exchange reactions is thus endothermic. However it should be noted that values of ΔS/R were obtained from equation (25) the temperature dependence of the equilibrium constant nevetheless, it is interesing to note that ΔS is positive values and ΔG is negative values confirm that the reaction goes spontaneously in the forward directions negative Table (2). An appreciable decrease in ΔG and an increase in ΔS values. From these facts as well as the magnitude of ΔS we conclude that ΔG for the exchange reaction is not governed by enthalpy term which increase in a positive direction which reflect the energy required to distort the IRA-400 and IRA-900 for entry Ru(III) ions. For studing cations in the mixture of the, Pd^{3+}, Rh^{3+}, Ru^{3+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Al^{3+}, Ca^{2+} Ru^{3+}. With the two resins studied IRA-410, the behaviors of the studied ions were different the nitrate media employed in different concentrations, 0.1, 0.3 and 0.5N. In this concern, the distribution values of the studied cations are low at all the pH's experimented and are, also, different of the same order of magnetude. The only element which has high distributions in this case is palladium where its K_d's are maximum at lower pH's and

Table 1: Kinetics of the uptake of Ru(III) using IRA-410 exchanger(0.05g) from 0.1N NaNO$_3$ solution of different pH media and temperature. $_a$ is the activation energy, D is the effective diffusion coefficient

	Dx10^{-8}, m^2 Sec^{-1}				
Temperature,°C	25	35	45	55	65
pH	0.5	3.12	4.75	6.87	6.87
1	1	4.72	5.22	7.5	7.5
3	1.5	4.83	5.51	8.12	8.12
5	2	4.91	5.70	8.50	8.50
7	2.5	4.99	5.98	8.70	8.70
9	3	5.07	6.46	9.37	9.37
11	3	5.07	6.46	9.37	9.37

Table 2: Thermodynamic functions for extraction of Ru (III) by strongly basic anion exchangers IRA-410 from nitrate medium

T, °C	ΔH	ΔG	ΔS
KJmol^{-1}	IRA-410	IRA-410	IRA-410
25	14.19±0.01	-78.55±0.01	192.89±0.01
35	14.11±0.02	-81.83±0.05	187.91±0.15
45	14.21±0.05	-84.93±0.04	183.26±0.09
55	14.49±0.03	-87.85±0.06	178.89±0.1
65	14.86±0.06	-90.68±0.07	174.8±0.21

decreased by increasing the pH values. The distribution behaviors of the studied ions in presence of nitric acid can be explained on the bases of the nitrate salt formation which is bulky and can hinder the exchange process of the formed negatively charged nitric acid complexes with the anionic resins employed. The distribution behavior of ruthenium can be explained by considering the formation of ruthenium nitrate complexes which are positively and nutral charged and can be exchanged with the anionic resins investigated. Ruthenium can form also hydrolytic species where the stability constant log K$_{d1}$ for ruthenium to hydrolysis. Therefore, Ru^{3+} can form both nitrate complex [29] and hydrolytic species under the experimental conditions applied which can be exchanged with the anionic resins used.

Separation of Ruthenium: Separation of ruthenium was a chivied by advanced reduction process. From the aforementioned batch experiments carried out, ruthenium -III showed a unique behavior rather than the other twelve elements studied. In this concern, ruthenium had the higher distribution values at relatively high hydrogen ion concentrations from all the media experimented with the resin used; IRA-410. Therefore, it was of interest to carry out certain experiments for its separation from the other elements representing [ILLW] studied using the two investigated resins.

Characterization of Ruthenium (III) Aqua nitrato Species: From the literature it is evident that the bulk of research on ruthenium and especially ruthenium (III) was done in the 1950's and 60's. This was due to the fact that ruthenium was a by-product of nuclear processes and needed to be removed. Its chemistry needed to be understood before efficient removal could be achieved. Renewed interest in ruthenium was generated by its use in catalysis in the 1980's. The series of ruthenium(III) species in aqueous hydrochloric acid medium can be summarized as $[RuCl_{6-n}(H_2O)_n]^{n-3}$ and was first separated and characterized by various people before research could be done on the kinetics of the series. The focus was on the separation and characterization in the early stages.

Separation of Ruthenium by Column Technique: In this concern, 1 gm of the anionic exchanger; IRA-410 was firstly preconditioned with 100 ml 0.1N NaNO$_3$. 40 ml of the simulated waste solution containing the ions under investigation together in 0.1N NaNO$_3$ was adjusted to pH~ 1 and shaked in contact with the applied resin. After equilibration (0.5 or1.5 h), filtration was carried out. Filtrate analysis (by ICP) showed that all the experimented elements are found exept ruthenium [23-29].

The Separation of Ruthenium from the Resin Was Experimented as Follows: A solution of 0.1N NaNO$_3$ (40ml) of pH~ 1, was equilibrated together with the used resin. However, filtrate analysis did not show ruthenium presence. This process was experimented using the different media studied with the concentrations and pH's at which ruthenium had low K$_d$'s. However, in all cases, negative results were obtained i.e the filtrate had no ruthenium. Other media of strongly complexing agents were used such as sodium thiocyanate and sodium iodide with different concentrations and pH's. Negative results were, also, obtained. The difficulty of getting ruthenium from the solid phase was suggested to be due to the complexation of ruthenium with NO$_3^{-2}$ ions of the resin. Therefore, reduction and dissolution processes were suggested to get the complexed ruthenium from the resin. In this respect, concentrated formic (40 ml) was added to the solid phase and shaked for 20 min. After filtration, the used resin (IRA-410) was washed and a concentrated nitric acid solution (14N) was added (40ml) and shaked with the resin to dissolve ruthenium. After filtration, the analysis (by ICP) showed that the nitric acid solution contains ruthenium.

Separation of Ruthenium by the Column Technique:
Separation of ruthenium from the simulated waste solution [11] was successfully carried out using a chromatographic column by applying the previous concept. Systematic studies were carried out to reach the proper column conditions of the reduction with formic acid and the dissolution with nitric acid. The elution process of ruthenium was, also, investigated using the media. With the concentrations and pH's at which ruthenium had the low distribution values. However, in all cases, negative results were, also, obtained as with the batch experiments and ruthenium was not eluted. Other media was, also experimented for the elution with different concentrations and pH's, to complex ruthenium. But negative result obtained, using dithiocarbamate and N aBH_4 was used as reduced agent. The colour of change signified that Ru(III) (dark red) and was finally reduced to Ru(0) (dark brown), of the loaded ruthenium was changed to red and ruthenium was not eluted. It was obvious that the elution of ruthenium can be performed via two steps as with the batch technique. In this concern, the first step includes reduction of the uptake ruthenium on the solid phase using The reduced Ru(o) sorbed on IRA-410 was stabilized by 0.1M phenyl hydrazine while astreme of H_2 was used to continuous the reduction process. The second step involves the addition of nitric acid where the separated ruthenium on the solid phase is dissolved and directly eluted (dissolution process) which can be detected by (ICP). Different concentrations of formic and nitric acids were experimented. Moreover, temperature effect was, also laborated.
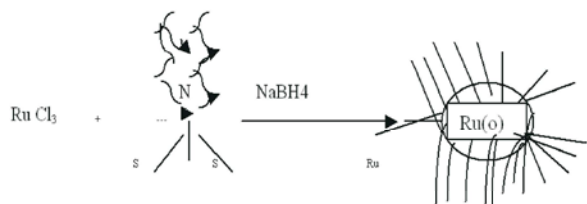
CONCLUSION

Separation of Ru(III) from nitrate medium by strongly basic anion exchangers IRA-410 was achieved. The separation of Ru(III) goes through a chemical reaction and particle mechanism for IRA-410 and respectively. Exchange has an activation energies were four 27.51 JK^{-1} M^{-1} which shows tat the reaction goes through particle mechanism.The reaction depends strongly on pH rater than the temperature.

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