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Effect of Gamma Irradiation on Kinetics of Ion Exchange of Mg (Ii), On Dowex 50 Wx_8 (Nh_4^+) In Aqueous Acetone – Ammonium Propionate Media.

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ABSTRACT
The vast majority of exchangers used today are synthetic organic resins. The ion exchangers are generally used in hydrogen and hydroxyl forms in the process applications. During their use in nuclear process industry the exchanger changes to the salt form and constitutes significant part of a column by the time resin bed accumulates increased radiation dose. Investigations have been made on the stability of cation exchange resin Dowex 50 WX_8 in H+ and NH_4^+ forms. These studies are done by irradiating the resin under different irradiation conditions.
Many factors change the ion exchange kinetics including exchange capacity, moisture content, cross linkage, rate of diffusion and concentration of the ionic species in solution which in turen are influenced by radiation. Hence the kinetic also should be affected by gamma radiation treatment. The ion exchange reactions with various metal ions like Zn, Pb, Mg and Co have been made on un-irradiated and gamma irradiated resin.
Different types of sources have been employed for exposing ion exchange materials to ionizing radiation. Among these are the **X-ray machines[1], electron accelerates[2], ^{60}Co gamma facilities[3] and research reactors.[4]** Variety of irradiation conditions have been used in the experimental studies which include ion exchanger exposed to radiation while immersed in water at different pH-5 or in HNo3 of different **concentration [6] or in acetic acid[7]** under vaccum[8] and under air dried state. [9] This results into different radiation chemical effects on ion exchange materials.
H_2, Co_2 Co, So_2, O_2 and CH_4 have been identified during irradiation of cation exchangers while, H_2, Co_2, Co, N_2, N_2O and NO have been reported as the gaseous products of radiolysis of anion **exchangers.[9]** In case of Dowex 50 WX_8 a cation exchanger, it is reported[10] that evolution of hydrogen is linear function of absorbed dose.

KEY WORDS :Dowex 50 WX_8, Aqueous acetone-ammonium propionate, half exchange time (($t^1/_2$), exchange rate constant (K), inter diffusion coefficient (D)

I. INTRODUCTION

Many factors change the ion exchange kinetics including exchange capacity, moisture content, cross linkage, rate of diffusion and concentration of the ionic species in solution which in turn are influenced by radiation. The effect of gamma irradiation on the physical properties of Dowex 50 WX_8 is studied. The effect of percentage of acetone on the kinetics of exchange of acetone on the kinetics of exchange of metal ion on irradiated and un irradiated samples of resins was **compared [1-3}.** The kinetic parameters such as half exchange time ($t^1/_2$), inter diffusion coefficient (D) and the exchange rate constant (K) were computed.

II. MATERIAL AND METHODS

Conditioning of resin:-

The resin was conditioned prior to use. The resin sample soaked in water placed in a 3 cm x 50 cm column and repeatedly 1M NaOH and 1M HCl solutions were passed through it. During each cycle, the resin was washed with de-ionized water and occasionally with ethanol which removes the non-polymerized organic impurities. After five – six cycles, the resin was converted into the desired form.
The sample was irradiated using cobalt ⁻ 60 sources. 15 g of air dried sample was irradiated up to the desired dose by placing it in the pyrex tube but without water
1 g of air dried resin Dowex 50 WX_8 (NH_4^+ form) was taken in Erlenmeyer flask. The mixture containing acetone – ammonium propionate 0.02 M was then added. Appropriated quantity of metal ion solution was poured into it at noted time so that the total volume of the mixture becomes 50 ml. The

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amount of metal ions exchanged on the resin was estimated at different time intervals from the concentration difference before and after the ion exchange. The kinetic studies for Mg was carried at 296 ° K 0.002, 0.004, 0.008 M at 296°K in a mixture acetone – ammonium propionate solution was used. The experiments were performed using un-irradiated and gamma irradiated (0.45 x 10^6 rads) resins.

Estimation of Magnesium –

The magnesium ions were estimated titrimetrically using standard EDTA solution. 10 ml of magnesium salt solution was pipette out in a conical flask and it was diluted to 50 ml with distilled water. 40 ml of buffer solution ($_P$H-10) and a few drops of Eriochrome black-T indicator was then added and the mixture was titrated with 0.1M EDTA solution until the colour changes from wine red to blue. The amount of magnesium was calculated by using the relation. 1 ml 0.1 M EDTA = 2.432 g of Mg

Solutions

1. 0.1 N stock solutions of cobalt was prepared from A. R. grade salts of B. D. H by using double distilled water.
2. Acetone- 0, 30, and 50 %
3. Ammonium butyrate solution – 2M
4. E. D. T. A. – 0.001M

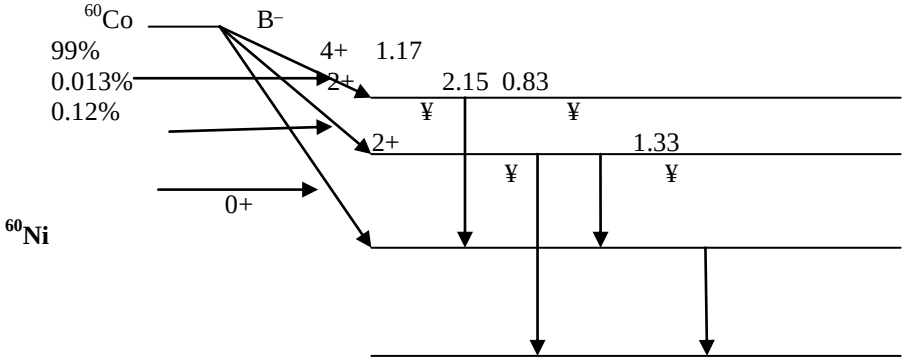

Fig. 1 ^{60} Co Decay Scheme

Table 1. Effect of the capacity of the state of resin during irradiation (Dose – 0.45 MGY)

Ion Exchanger	Form	Decrease in capacity %	
		Air dry	Under water
Dowex 50 WX_8	NH4 +	5.0	8.7

III. RESULTS AND DISCUSSION

The colour of resin was changed from golden yellow to brown on irradiation. By gamma irradiation the capacity of resin was found to be decreased and also causes decrease in the weight of the resin sample. The change in colour, capacity and weight loss are due to changes in the skeleton of the resin. [4-11]

The decrease in capacity and change in colour of resin by irradiation was due to the change in cross linking of resin. The resin in NH_4^+ form is less affected than that in H^+ form on irradiation.

The kinetics of exchange of Mg on irradiated (0.45 x 10-6 rads) and un-irradiated Dowex 50 W X_8 (NH_4^+) resin in aqueous acetone ammonium propionate (0.02M) was studied**.**

The kinetic parameters such as half exchange time ($t^1/_2$), diffusion coefficient (D), and exchange rate constants (K) are presented in **table no 1**. The kinetic parameters were computed at, 0, 30, 50 percentages of acetone.

The change in colour, exchange capacity and loss in weight on exposure to gamma irradiation was observed.

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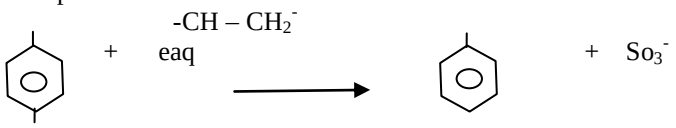
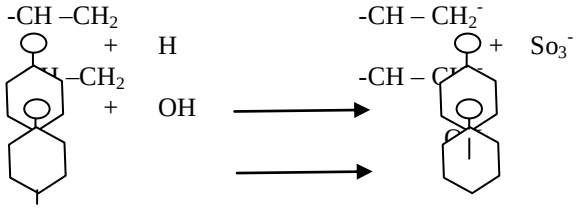
Under the influence of ionizing radiation the sulphonic acid groups are split off and new weakly acidic groups enter the aromatic nuclei. The anionic resins are less resistant in comparison with strongly acidic exchangers. Higher amines and ammonia are lost and strongly basic groups are changed into weaker bases. The resins with higher degree of cross linkage are more stable than those with looser network. The same observation is observed between the salt form and free acid form of the resin[12, 13]. Presence of air and water accelerates the decomposition which is confirmed in the present case by irradiating the resin in air dry and aquated state. Aromatic nuclei in the resin are more stable than aliphatic binding chains. Hydrogen, carbon dioxide, carbon monoxide and sulphur dioxide were formed during irradiation of Dowex 50 W X_8 under excess of water. It is probably because of a secondary oxidation to sulphuric acid or a different decomposition mechanism.

Degradation and formation of new groups in Dowex 50 W X_8 may be explained as follows.



The H- atom may also bring about scission of So_3 group and the formation of weak acid exchange group takes place.



So_3 radicals may react with water molecules near the exchange group to form H- atoms and the resulting H-atoms can be turn induce further degradation of the resin

$$So_3 + H_2O \longrightarrow HSo_4 + H$$

The loss of sulphonic acid group leads to capacity loss. The amount of degradation in terms of exchange capacity loss for Dowex 50 W X_8 resin at gamma ray dose of 0.4 x 10^6 rads /hr was found to be 15% for air dry resin in NH_4^+ form. Cation exchange resins show slight increase in volumes on irradiation indicating thereby degradation or de-cross linkage was predominant. The effect of radiations to produce swelling or shrinkage seems to be influenced by the nature of ionic sites present in the polymer.

Kinetic studies:

It is observed that the values of half exchange time ($t^1/_2$) increases on irradiation of the resin. It indicates that the exchange reaction becomes slower on irradiation. This effect is common for all percentages of acetone. The exchange reaction becomes slow due to irradiation and acetone content. The values of diffusion coefficient decrease on irradiation of the resin. The overall change in the rate constant is not very much affected on irradiation. The values of rate the rate constant (K) indicate that the rate constant decreases on irradiation.

Diffusion coefficient (D) values calculated on irradiated and gamma irradiated resin at various concentrations of acetone **(Table no 2, 3a – 3e).** It is observed that diffusion coefficients (D) value decreased when the resin is exposed to gamma irradiation. For un-irradiated and irradiated resins D decreases with increase in the acetone percentage. The change in chemical structure of the irradiated resin should account for the changes in diffusion properties on the resin. The structural and cross linking properties of the resin matrix are important. On exposure to ionizing radiation macromolecular structures have been found undergoing changes such as bond breakage, bond formation and oxidation etc. Breakage of C – S bonds might be resulting into splitting of ion exchange groups as indicated by decreased capacity which is an important factor responsible for the decrease in diffusion coefficients upon radiation.

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The exchange rate constant (K) decreased when the resin is exposed to gamma irradiation. For all the metal ions K decreases with rise in the acetone percentage at 296^{o} K

IV. CONCLUSION

The distribution coefficient varies with the change in the concentration of acetone and ammonium propionate solutions and it decreases with rise in the propionate concentration.

The following factors involved in exchange equilibria.

1. The mass action effect of ammonium ion in exchange reaction.
2. Complex ion formation of the metal ion with propionate ion.
3. Change in the salvation shell of the metal ion.
4. Shrinking of the resin.

V. APPLICATION

Quantitative separation of various metal ions can be effectively carried out at trace level also.

Table 2: Kinetic Parameters For the Exchange of Mg on Un-irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})	$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})
	a	b	a	b	a		b	
0	175	140	0.154	0. 192	2.76	-	6.5	8.7
30	195	160	0.138	0.168	5.45	5.75	5.75	13.4
50	230	170	0.117	0.158	3.98	-	4.97	7.83

Table:3a Kinetic parameters for the exchange of Mg on un irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.
Magnesium (0.004M) Dose = 2.7 Mega Rad/hr.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})	$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})
	a	b	a	b	a		b	
0	50	140	0.154	0. 192	5.66	8.75	6.5	13.4
30	120	170	0.225	0.158	5.29	11.51	5.75	6.7
50	120	160	0.225	0.160	3.65	7.07-	4.97	7. 83

Table 3b. Kinetic parameters for the exchange of Mg on un-irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.
Magnesium (0.004M) Dose = 5.4 Mega Rad/hr.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})	$Kx\ 10^{-3}$ (min^{-1})	$Kx\ 10^{-4}$ (min^{-1})
	a	b	a	b	a		b	
0	130	140	0.207	0. 192	5.48	-	6.5	13.4
30	120	170	0.225	0.158	4.60	10.59	5.75	6.7

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50	190	160	0.142	0.168	3.52	7.07	4.97	7. 63

Table 3c. Kinetic parameters for the exchange of Mg on un-irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.
Magnesium (0.004M) Dose = 16.2 Mega Rad/hr.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})	Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})
	a	b	a	b	a		b	
0	140	140	0.27	0. 192	4.44	-	6.5	13.4
30	100	160	0.192	0.168	3.68	-	5.75	8.7
50	230	170	0.117	0.158	3.06	-	4.97	7. 83

Table 3d. Kinetic parameters for the exchange of Mg on un-irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.
Magnesium (0.004M) Dose = 21.6 Mega Rad/hr.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})	Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})
	a	b	a	b	a		b	
0	130	140	0.207	0. 192	7.59	7.59	6.5	13.4
30	120	160	0.225	0.168	5.06	5.0	5.75	8.7
50	170	170	0.158	0.158	3.13	-	4.97	7. 83

Table 3e. Kinetic parameters for the exchange of Mg on un-irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296^{o}K.
Magnesium (0.004M) Dose = 31.05 Mega Rad/hr.

Acetone % V/V	Mg (II)							
	$t^1/_2$ (min)		$Dx10^{-10}$ m^2 sec^{-1}		Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})	Kx 10^{-3} (min^{-1})	Kx 10^{-4} (min^{-1})
	a	b	a	b	a		b	
0	225	140	0.12	0.192	4.74	5.75	6.5	13.4
30	190	160	0.108	0.158	4.74	5.41	5.75	8.7
50	250	160	0.142	0.168	4.14	5-29	4.97	7. 83

a- gamma irradiated resin b- un irradiated resin

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