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Effect of gamma irradiation on the kinetics of ion exchange of Mg (ii), Zn (ii), Co (ii), Pb (ii) on DOWEX 50 wx8 (NH^{4+}) in aqueous acetone – ammonium propionate media.

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ABSTRACT

Dedgaonkar [1] studied radiation effects on self diffusion in polystyrene ion exchangers with functional groups So^{-3} in Mn^{+2} form and N (CH3) I^{-1} form. Samples exposed to gamma radiations up to a dose of 0.35 MGY showed lower values of diffusion coefficient at any given temperature than those of normal resins. Irradiation increased the energy of activation from 25.6 – 46. 5 kJ / mol^{-1} for the cation exchangers. Exchanger capacity of cation exchanger was un- influenced up to a dose of 2.5 MGY. The effect of gamma irradiation on the physico-chemical properties of weakly basic polystyrene anion exchanger. Effect of gamma irradiation on ion exchange characteristics of titanium vanadu phosphate was studied by Singh [2] After irradiation by gamma rays (10^{-9} rads) the colour of the resin changed from yellow to greenish yellow. The capacity values and distribution coefficient values showed a slight increase up on irradiation the rates of exchange of Rb^{+}/ h^{+} system was investigated on un irradiated and irradiated resin.

Keywords- *Aqueous Ammonium Propionate, Un-Irradiated and Gamma Irradiated, Dowex 50 Wx_8, Half Exchange Time ($T\ ^1/_2$), Inter Diffusion Coefficient (D), Exchange Rate Constant (K)*

1. INTRODUCTION

The ion exchangers are generally used in hydrogen and hydroxyl forms. 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 condition of the ionic species in solution which in turn are influenced by radiation. Hence the kinetics also should be affected by gamma radiation treatment. With this views kinetic studies ion exchange reactions with various metal ions like Zn, Pb, Mg, and Co have been made on un irradiated and gamma irradiated resin.

The resin on irradiation the rate of exchange of Zn, Pb, Mg, and Co on Dowex 50 WX_8 in aqueous acetone ammonium propionate (0. O2M) was studied. The effect of percentage of the acetone on the kinetics of exchange of metal ions on irradiated and un-irradiated samples of resins was compared. The kinetic parameters such as half exchange time ($t\ ^1/_2$), inter diffusion coefficient (D) and the exchange rate constant (K) were computed. The probable mechanism of difference in the properties of irradiated and normal resin is discussed.

2. MATERIAL AND METHOD

2.1 Conditioning of Resin

The soluble impurities from resin were removed by repeated Soxhlet extractions using water. 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. Between 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.

Irradiation of resin

The samples were irradiated using cobalt ⁻60 sources. ^{60}Co decays by emission of β particles to an excited ^{60}Ni nucleus which gets stability by emitting two gamma photons, each of 1.7323 MeV and 1.33248 MeV energy. This decay scheme is shown in fig no 1.

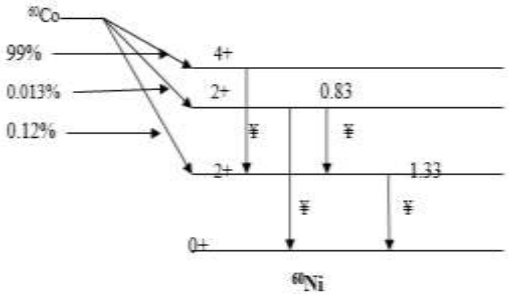


Fig 1: ^{60} Co Decay Scheme

2.2. Dose Rate Measurement

The dose rate was evaluated using the relation

$$\text{Dose rate} = \frac{0.647 \text{ X } 106 \text{ X } \Delta A}{\text{Ed eG (Fe3+)}2a} \qquad \text{Gy min}^{-1} \text{ (Cm}^3\text{)}$$

Here Δ A is the difference in absorption between the irradiated and non irradiated solution of density, d is the optical path length in centimeters and the value of G is taken as 15.6.

2. 3 Sample Irradiation

15 g air dried sample was irradiated up to the desired dose by placing it in the pyrex tube but without water.

2. 4 Capacity Measurements

The change in the exchange capacity after irradiation was determines by,

$$\text{Capacity} = \frac{(50 \text{ M NaOH}) - (\text{X M Acid})}{\text{Sample weight}}$$

2.5 Weight Loss Measurement

Already weighed air dry sample after radiation treatment were washed thoroughly with distilled water to remove degradation. Products were dried over P_2O_5 in a desiccator for long time and reweighed. The difference in weight is considered as a measure of degradation. **[3]**

2.6 Solutions

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

3. PROCEDURE

For kinetic study exactly 1 g of air dried resin Dowex 50 W X_8 (NH_4^+ form) was taken in an Erlenmeyer flask. The mixture containing acetone-ammonium propionate (0.02M) was then added. Appropriate quantity of metal ion solution was poured into it at noted time, so that the total volume of the mixture becomes 50 ml. The 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 Zn, Pb, Mg and Co (0.004 M) were carried out at 296° K. The experiments were performed using un- irradiated and gamma irradiated (0.45 X 10^6 rads) resins.

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

Table – 2: Kinetic parameters for the exchange of Mg, Zn, Co, Pb on un irradiated and Irradiated Dowex 50W X8 (NH_4^+) in Aqueous Acetone Ammonium Propionate (o.02M) at 296°K.

Acetone % V/V	$t^1/_2$ (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})
	Magnesium (II)							
	a	b	a	b	a	a	b	b

0	175	140	0.154	0. 192	2.76	-	6. 5	8.7
30	195	160	0.138	0.168	5.48	5.75	5.75	13.4
50	230	170	0.117	0.158	3.98	-	4.97	7.83
Zinc (II)								
0	130	65	0.207	0.415	4.60	-	6.1	6.9
30	180	75	0.15	0.30	5. 98	6.721	5.75	-
50	200	70	0.135	0.385	4.06	6.44	5.70	-
Cobalt (II)								
0	120	80	0.225	0. 337	15	-	4.72	20.26
30	155	135	0. 174	0.2	7.59	-	3.91	18.42
50	235	190	0.114	0.142	14	-	3.45	3.68
Lead (II)								
0	120	85	0.225	0.317	20.2	-	6.05	14.0
30	110	115	0.245	0.234	20.2	-	5.27	7.06
50	125	135	0. 216	0. 2	23.2	-	5.0	5.52

Where
a = gamma irradiated resin
b = un-irradiated resin.

4. RESULTS AND DISCUSSION

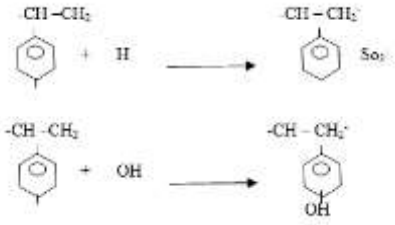
The kinetics of exchange of Zn, Pb, Mg and Co on irradiated (0.45 x 10^{-6} rads) and un irradiated Dowex 50 W X_8 (NH_4^+) resin in aqueous acetone ammonium propionate (0.02M) was studied [4,5,6].

The kinetic parameters such as half exchange time ($t^1/_2$), diffusion coefficient (D), exchange rate constants (K) are presented in table. The kinetic parameters were computed at, 0, 30, 50 percentages of acetone.

The colour of the resin changes from golden yellow to brownish on **irradiation [7].** The colour changes of an ion exchange resin and the decrease in capacity occur as a result of some structural change in the skeleton of the resin such as cross linkage.

The weight loss in H+ form was more than that in NH_4^+ form on irradiation. The resin in NH4- form is less affected than that in H^+ form on irradiation. Under the influence of ionizing radiation, the sulphonic acid groups are split off and new weakly acidic groups enter the aromatic nuclei. The degradation and formation of new groups in Dowex 50 W X_8 **(NH_4^+ form)** may be explained as follows

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



Induce further degradation of the resin. 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 (NH_4^+) resin at a gamma ray dose of 0.4 x 10-6 rads / hr was found to be 15% for air dry resin in NH_4^+

It is observed that the value of half exchange time ($t^1/_2$) increase on irradiation of the resin. It indicates that the exchange reaction becomes slower on irradiation. This effect is observed at all percentages of acetone. The half exchange time for all the metal ions, show the following order at 50% acetone.

Mg > Co > Zn > Pb

The exchange reaction becomes slow due to irradiation and acetone **content [8].** The values of diffusion coefficients decrease on irradiation of the resin. The overall change in the rate constant is not very much affected on irradiation. The values of rate constant (K) indicate that, rate constant decreases on irradiation.

Diffusion coefficient value decreased when the resin is exposed to gamma radiation. For un irradiated and irradiated resins D decreases with increase in acetone percentage for all the metal ions. The change in chemical structure of the irradiated resin should

account for the change in diffusion properties of the resin. The structural and cross linking properties of the resin matrix are important. On exposure to ionizing radiation, macromolecular structures have been formation, 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 irradiation.

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 (Table 1, 2).

5. CONCLUSION

For all percentages of acetone, the exchange reaction becomes slower on irradiation. The diffusion coefficients decrease on irradiation. The exchange rate constant (K) decreased when the resin is exposed to gamma radiation.

6. APPLICATIONS

Ion exchange is often used for removing another ion. The quantitative separation of various metal ions can be effectively carried out at trace level also. The utility of ion exchange phenomena is not restricted to anyone field. From the point of view of national defense and public welfare ion exchange is found out to be of vital importance to the collection of blood, isolation and to the problem of radioactive waste disposal. Ion exchange is most selective and the most widely applicable separatary techniques. Synthetic ion exchangers are used in analytical chemistry, hydrometallurgy and water treatment.

Ion exchange resins are used for the application of esters, amides, imides, anilides, aliphatic and aromatic aldehydes.

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