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Application of Tracer Isotopes in Kinetic Study of First Order Ion Exchange Reaction

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Analysis of first order ion exchange reaction rates at different temperatures [27°C to 50°C] and particularly at low concentration of KBr solution [electrolyte] ranging from 0.005 M to 0.1 M has been carried out by application of radioactive tracer isotope ^{82}Br with increase in concentration of electrolyte. Amounts of bromide ion exchanged in millimoles increases specific reaction rates of ion exchange reaction and are calculated for different temperatures and for different amounts of ion exchange resins. It is observed that with increase in temperature reaction rate increases but the increase is more pronounced for increase in amount of ion exchange resins. For 0.005 M solution of electrolyte, the reaction rate increases from 0.120 min^{-1} at 27°C to 0.209 at 50°C. For 0.005 M solution of electrolyte at 27°C reaction rate increases from 0.120 min^{-1} for 1.0 g of resin to 0.190 min^{-1} for 5.0 g of resin. From the reaction rate calculated at different temperatures energy of activation in KJ/mole is calculated. It is observed that for 0.005M solution of electrolyte, energy of activation is 6.801 kJ/mole which decreases to 6.120 kJ/mole for increase in concentration of electrolyte to 0.100 M.

INTRODUCTION

Radioactive tracers have gradually become integrated into process analysis as a measuring tool for diagnosing industrial systems.[1] As a result of development of methods for process analysis, the majority of radioactive tracer applications are now-a-days directed towards investigation of material transport in full-scale industrial process plants. Fission products[2, 3] of long half life Cs-137 and Sr-90 in millicurie quantities find a variety of applications in food irradiators and in systems for nuclear power. In the study of numerous migration problems other than self diffusion, particularly when movements of very small amounts of materials are involved, radioactive tracer isotopes are widely used for analysis as a sensitive and relatively convenient analytical tool.[4]

The present investigation is an important application of radioactive tracers for analysis of first order ion exchange reactions by using ^{82}Br as tracer isotope and duolite-161 as an ion exchanger.

EXPERIMENTAL

Duolite-161 which is a strongly basic anion exchanger in chloride form was converted into bromide form by using 10% KBr solution in a conditioning column. The conditioned resins were then air-dried and used for further study. In the present investigation KBr solution of different concentrations from 0.005 M to 0.100 M were prepared and by using diluted ^{82}Br solution the solutions of different concentrations were labelled, such that 1.0 mL of this labelled solution will have known initial activity between 10,000 to 11,000 counts per min. as measured on γ-ray spectrometer. To these solutions of different concentrations of known initial activity [c.p.m.], fixed amount of ion exchange resin [1.0 g] in bromide form are added and under continuous stirring of solutions the activity of 1.0 mL solution is measured at an interval of every minute. Due to rapid exchange of radioactive bromide ions in solution with bromide ions on ion exchange resins, activity of 1.0 mL solution decreases rapidly for the initial interval of time, but after some time interval it decreases slowly. The decrease in activity [c.p.m.] of solution will correspond to the activity on the resin surface. When the graph of log activity against time is plotted a composite curve is obtained which includes activity exchanged due to rapid as well as slow process. The composite curve so obtained is then resolved for calculating specific reaction rates [min^{-1}] of rapid process. Similarly the experiment is repeated for different temperatures ranging from 27°C to 50°C. The temperature of the solution is maintained accurately with deviation of ±0.1°C by using in surf water bath with automatic on and off control system. Similar set of experiments is performed by varying amounts of ion exchange resins from 1.0 g to 5.0 g for fixed temperature of 27°C and for fixed concentration 0.005 M of bromide ion solution.

RESULTS AND DISCUSSION

Kinetic study carried out in the present investigation reveals many interesting observations. The reaction rates [min^{-1}] were observed to increase with increase in temperature [Table-1] which is due to increase in number of effective collisions with rise in temperature. But increase is more sharp with increase in amount of ion exchange resin [Table-2]. With increase in amount of ion exchange resin the

TABLE-1
EFFECT OF TEMPERATURE ON REACTION RATES OF ION EXCHANGE REACTION

Concentration of labelled bromide ion solution: 0.005 M
Amount of ion exchange resin: 1.0 g

Temperature (°C)	27	35	40	45	50
Specific reaction rate [min^{-1}]	0.120	0.152	0.169	0.187	0.203

TABLE-2
EFFECT OF AMOUNT OF ION EXCHANGE RESIN ON ION EXCHANGE REACTION RATES

Concentration of labelled bromide ion solution: 0.005 M; Temperature: 27°C

Amount of ion exchange resin [g]	1	2	3	4	5
Specific reaction rate [min^{-1}]	0.120	0.143	0.161	0.184	0.190

number of exchangeable counter ions increases resulting in increase in specific reaction rates [Table-2]. From the specific reaction rates calculated at different temperatures the graph of reaction rates [min^{-1}] against temperature is plotted which gives a straight line with negative slope. From this negative slope, energy of activation (kJ/mole) is calculated by equation E = slope X 2.303R, where R is a gas constant with value of 1.987 Cals/mole. When energy of activation is calculated for different concentrations it is observed that energy of activation value decreases with increase in concentration of electrolyte [Table-3] which is due to increase in number of effective collisions with rise in temperature.

TABLE-3
EFFECT OF CONCENTRATION OF BROMIDE ION SOLUTION ON ENERGY OF ACTIVATION OF ION EXCHANGE REACTION

Amount of ion exchange resin: 1 g
Volume of labelled bromide ion solution: 200 cm^3

Concentration of labelled bromide ion solution [M]	0.005	0.01	0.02	0.04	0.1
Energy of activation [kJ/mole]	6.790	6.690	6.446	6.369	6.350

The amount of bromide ion exchanged in millimoles when calculated for different concentrations of bromide ion solution were observed to increase with increase in concentration of bromide ion solution [Table-4). This increase takes place for fixed temperature, fixed amount of ion exchange resin and for specific reaction rate which also remains constant.

TABLE-4
EFFECT OF CONCENTRATION OF BROMIDE ION SOLUTION ON AMOUNT OF BROMIDE ION EXCHANGED IN ION EXCHANGE REACTION

Amount of exchange resin: 1 g
Temperature: 27°C
Volume of labeled bromide ion solution: 200 cm^3

Concentration of bromide ion solution [M]	0.005	0.01	0.02	0.04	0.1
Millimoles of bromide ion in 200 cm^3 of solution	1	2	4	8	20
Amount of bromide ion exchanged [millimoles]	0.659	1.125	2.558	5.549	7.307

The amount of bromide ion exchanged in millimoles increases efficiently with increase in amount of ion exchange resins [Table-5]. For solution containing 1.0 millimoles of bromide ion, the amount of bromide ion exchanged is 0.659 millimoles for 1.0 g of resin and is maximum 7.020 millimoles for 5.0 g of resin at 27°C [Table-5].

TABLE-5
EFFECT OF AMOUNT OF ION EXCHANGE RESIN ON AMOUNT OF BROMIDE ION EXCHANGED IN ION EXCHANGE REACTION

Concentration of labeled bromide ion solution: 0.005 M
Amount of bromide ion in 200 cm^3 of solution: 1.0 millimoles
Temperature: 27°C

Amount of ion exchange resin [g]	10	2	3	4	5
Amount of bromide ion exchanged [millimoles]	0.659	1.141	2.497	5.170	11.0

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