

Study of Reversible Ion-Isotopic Self Diffusion Reaction Kinetics Using ^{82}Br as a Radioactive Tracer Isotope

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Radioactive tracers as a sensitive analytical technique have been used to study the reversible ion-isotopic self-diffusion reactions. In forward self-diffusion reactions, the ion exchangers in bromide form were equilibrated with bromide ion solution (labelled with ^{82}Br as a radioactive tracer isotope) in the concentration range of 0.005–0.100 M. In reverse ion-isotopic self-diffusion reactions, the labelled ion exchangers in the range of 0.7500–1.2500 g were equilibrated with 0.0100 M bromide ion solution concentration. The results of reversible ion-isotopic self-diffusion reaction indicate that under identical experimental parameters, the reaction rates (in min^{-1}) are calculated to be nearly same, indicating that forward and reverse ion-isotopic self-diffusion reactions are complementary to each other.

Key Words: Reversible ion-Isotopic, Diffusion reaction, Kinetics, ^{82}Br , Radioactive isotope

INTRODUCTION

The study¹⁻²⁶ on ionic diffusion reaction reveals that film diffusion mechanism operates under different conditions of reaction, thereby affecting the rate. Boyd *et al.*² have derived separate equations governing the two types of mechanisms and by using radioactive tracer technique have verified the mechanism of film diffusion. Helfferich⁴ in the study of Na^+/H^+ exchanges on stacks of ion exchange discs of sulphonated phenol-formaldehyde type showed the predicted differences in rates and concentration profiles between the forward and reverse exchange. A comparison with the more rigorous solution shows that the earlier theory over-emphasises the difference in the rate between forward and reverse exchange²⁷.

In the present investigation to study the reaction rates (min^{-1}) of reversible ion-isotopic self-diffusion reaction using a radioactive tracer technique, a short lived radio isotope ^{82}Br was used to trace the system under study. The tracer concentrations recorded at various time intervals was analysed to draw information about the kinetics of reversible ion-isotopic self diffusion reaction. The results of the present investigation is expected to provide valuable information regarding the mechanism of ion-isotopic self-diffusion reaction and the factors influencing the same, thereby helping in standardisation of various industrial process parameters for which these ion exchangers are being widely used.

EXPERIMENTAL

The ion exchange resin Amberlite IRA-400, a strongly basic anion exchanger as supplied by the manufacturer in chloride form, was converted into bromide form by using 10% potassium bromide solution. The ion exchangers in bromide form were then air dried and used for further study.

The study on reversible ion-isotopic self diffusion reaction was performed in two sets of experiments. In the first set, the potassium bromide solutions in different concentration ranges from 0.005 to 0.100 M were labelled using diluted ^{82}Br radiotracer isotope solutions, such that 1.0 mL of every solution will be having known initial activity in counts per min (cpm) as measured on γ -ray spectrometer having NaI (TI) scintillation detector. Fixed amounts of ion exchange resins (1.0 g) in bromide form were added to each of these solutions and under conditions of uniform mechanical stirring at a constant temperature of 27°C ; the activity of the solutions was measured every minute. The temperature of the solutions was maintained constant $\pm 0.01^\circ\text{C}$ using insurf water bath. Due to the rapid self-diffusion reaction, the activity (in cpm) of the solution decreases sharply in the initial stages and then remains nearly constant (Fig. 1). The kinetics of ion-isotopic self-diffusion reaction studied here can be represented as

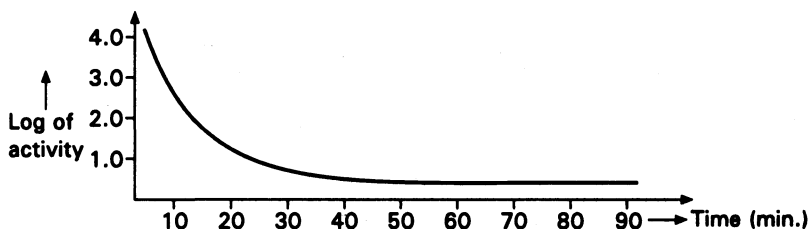
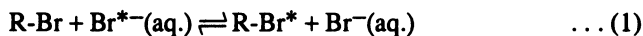
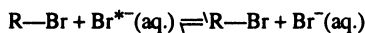


Fig. 1. Kinetics of ion-isotopic self-diffusion reaction.:

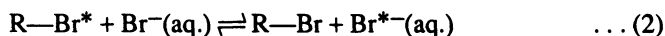


Amount of ion exchange resin in bromide form = 1 g; volume of labelled Br^{-} ion solution = 200 mL; temperature = 27°C ; concentration of labelled Br^{-} ion solution = 0.010 M

In the second set of experiments, the ion exchange resins in bromide form were labelled by placing them in diluted radioactive solution of known initial activity for 2 h under uniform mechanical stirring. From the results of our previous investigation²⁸, it was observed that this duration was sufficient for the radioactive bromide ions in solution to get completely transferred on the resin surface. After 2 h the activity (in cpm) of solution was again measured; the decrease in activity of solution corresponds to the activity transferred on to the resin surface. Different amounts of dried, labelled ion exchange resins in bromide form, in the range of 0.7500 to 1.2500 g, of known initial activity were transferred in potassium bromide solution of fixed concentration (0.0100 M) at a constant temperature of 27°C under continuous and uniform mechanical stirring. The activity of the solution was measured after every fixed interval of time, which increases rapidly

during the initial stages due to the rapid ion-isotopic self-diffusion reaction and then remains nearly constant due to the slow ion-isotopic self-diffusion reaction.

The self-diffusion reaction studied here can be expressed as



The kinetics of the reaction is graphically represented in Fig. 2.

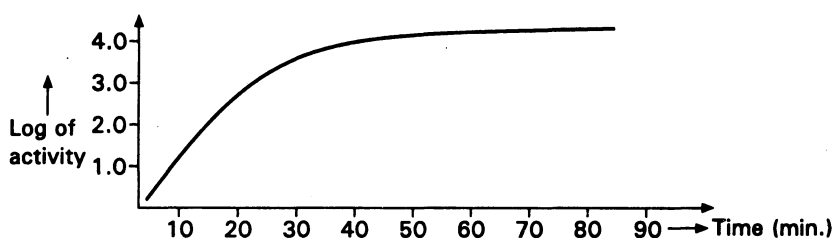
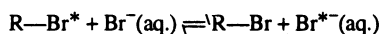


Fig. 2. Kinetics of ion-isotopic self-diffusion reaction.:



Amount of ion exchange resin in bromide form = 1 g; volume of Br^- ion solution = 200 mL; temperature = 27°C; concentration of Br^- ion solution = 0.010 M

RESULTS AND DISCUSSION

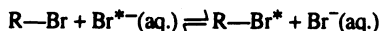
In the present investigation, it was observed that the activity of the solution changes rapidly during the initial interval of time due to the rapid ion isotopic self-diffusion reaction and after a certain time interval the rate of self-diffusion decreases and the activity of the solution remains nearly constant indicating the slow ion isotopic self-diffusion reactions. From the nature of composite curves (Figs. 1 and 2) of logarithm of activity (cpm) against time, it is evident that slow and rapid self-diffusion reaction occurs simultaneously, comparing the specific reaction rates of rapid and slow self-diffusion reactions. It was observed that rapid self-diffusion reactions contribute mainly to the overall reaction rate. Presumably the rapid process is film diffusion controlled while the slow process is particle diffusion controlled.

From the results, it was observed that the specific reaction rate increases very slowly (remains nearly constant) even though the bromide ion concentration in solution is varied 20 times using fixed amount of ion exchange resin (1.0) and at a constant temperature of 27°C (Table-1). However, as the amount of ion exchange resins increases, the number of exchangeable bromide ions on the exchanger phase increases and hence there is a pronounced rise in specific reaction rate for fixed concentration (0.010 M) of bromide ions in solution and at a constant temperature of 27°C (Table-2).

For both the forward and reverse ion-isotopic self-diffusion reactions, under identical conditions of 27°C using fixed amount of ion exchange resins (1 g and 0.01 M bromide ions in solution), the specific reaction rates of rapid self-diffusion reactions are calculated to be 0.152 min^{-1} and 0.153 min^{-1} respectively, indicating

that the forward and reverse ion isotopic self-diffusion reactions are complementary to each other.

TABLE-1
EFFECT OF BROMIDE ION CONCENTRATION ON KINETICS OF ION-ISOTOPIC SELF-DIFFUSION REACTION

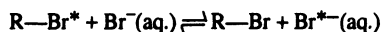


Amount of ion exchange resins in Br^{-} form = 1 g,

Volume of Br^{-} ion solution = 200 mL, Temperature = 27°C

Concentration of labeled Br^{-} ion solution (M)	0.005	0.010	0.020	0.040	0.100
Millimoles of Br^{-} ions in 200 mL solution	1.000	2.000	4.000	8.000	20.000
Specific reaction rate (min^{-1})	0.150	0.152	0.154	0.157	0.159

TABLE-2
EFFECT OF AMOUNT OF RESIN ON KINETICS OF ION-ISOTOPIC SELF DIFFUSION REACTION



Concentration of Br^{-} ion in Solution = 0.0100 M,

Amount of Br^{-} ion in 200 mL solution = 2.0 millimoles, Temperature = 27°C

Amount of labeled ion exchange resins in bromide form (g)	0.7500	1.0000	1.2500
Specific reaction rate (min^{-1})	0.1250	0.153	0.1760

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