

Study on Kinetics of Self-diffusion Reaction by Application of ^{82}Br as a Radioactive Tracer Isotope

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The kinetics of ion-isotopic self-diffusion reaction was studied by using radioactive ^{82}Br as a tracer isotope as to study the effect of exchangeable ion concentration in the exchanger phase and that in solution. The effect of exchangeable ion concentration in the exchanger phase was studied by varying the amount of labelled ion exchange resins from 0.250 to 0.750 g, using fixed ionic concentration of 0.01 M bromide ions in solution at a constant temperature of 27°C. The effect of ionic concentrations in solution was studied by varying the concentration of bromide ions in solution from 0.0025 to 0.02 M and by keeping the exchangeable ion concentration on the exchanger phase constant (0.5 g of labelled ion exchange resins), at 27°C.

Key Words: Kinetics, Self-diffusion, Trace isotope.

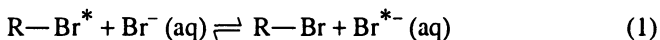
INTRODUCTION

Radioisotope tracers offer several advantages¹ such as high detection sensitivity, capability of *in situ* detection, limited memory effect and physico-chemical compatibility with the materials under study. New technologies² can be developed by using tracers for balancing of elements, new catalysts and plasma reactor characterization. In the present investigation the radio isotope ^{82}Br has been successfully applied as a tracer to study the kinetics of ion-isotopic self-diffusion reaction using ion exchange resins Amberlite IRA-400, a strongly basic anion exchanger.

The study on ionic diffusion mechanism by previous investigators³⁻¹² reveals that film diffusion or particle diffusion mechanism operates under different conditions of self diffusion reaction, thereby affecting the reaction rate. Extensive study was carried out by previous investigators on various parameters affecting the reaction rate like temperature¹³⁻¹⁷, particle size¹³, degree of cross-linking^{13, 17, 18}, nature of exchangeable species¹⁹⁻²¹, composition of pore liquid^{19, 22}, nature of functional group²³, swelling and mesh width of an exchange^{22, 24-25}, concentration of external solution²⁶. The present investigation on ion-isotopic self-diffusion reaction is of great significance as the results may be helpful in understanding various optimum parameters under which the ion exchangers can be used effectively and efficiently for various industrial and technological applications.

EXPERIMENTAL

The ion exchange resin Amberlite IRA-400, a strongly basic anion exchanger, originally in chloride form. For the present investigation, it was converted into bromide form (using 10% potassium bromide solution) and labelled with radioactive ^{82}Br as a tracer isotope, to study the kinetics of ion-isotopic self-diffusion reaction.



Here Br^* represents radioactive ^{82}Br tracer isotope.

A. Labelling of ion exchange resins: For converting the ion exchange resins to radioactive form, the ion exchangers were placed in diluted radioactive ^{82}Br solution of known initial activity in counts per min (as measured on gamma ray spectrometer) for 2 h under continuous and uniform stirring. From the results of previous investigation¹⁶ it was observed that the duration of 2 h was sufficient for equilibrium to be attained. After 2 h the activity of the solution was again measured; the decrease in the activity corresponds to the activity exchanged on to the resin surface. The resins were then air-dried and preserved for further study.

B. Effect of bromide ion concentration in solution: Known weight of 0.5 g ion exchange resins labelled with ^{82}Br isotope of known initial activity were placed in stoppered reagent bottles containing potassium bromide solution in the concentration range of 0.0025 to 0.02 M at a constant temperature of 27°C under uniform mechanical stirring. The temperature was maintained constant by $\pm 0.1^\circ\text{C}$ using constant temperature insurf water bath. The activity in counts per min (CPM) of 1.0 mL solution was measured at a fixed interval of every minute, after 30 min activity, was measured for longer interval of every 10 min up to 90 min, which will give the activity exchanged at infinite time.

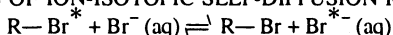
C. Effect of ionic concentration in the exchanger phase: In the present investigation, the experimental set was performed in the similar way as explained above, but by varying the amount of ion exchange resins (thereby increasing the bromide ion concentration in the exchanger phase) from 0.250 to 0.750 g at a constant temperature of 27°C, using fixed bromide ion concentration of 0.01 M.

RESULTS AND DISCUSSION

The kinetics of ion-isotopic self-diffusion reaction (1) as represented graphically in Fig. 1 was studied. It was observed that during the initial stage of self-diffusion reaction, due to the rapid self-diffusion process, the activity of the solution increases sharply and then remains nearly constant due to the slow diffusion reaction. Comparing the specific reaction rate (min^{-1}) for slow and rapid self-diffusion reaction for any particular concentration of bromide ion solution and for fixed temperature as well as for same amount of ion exchange resin, it was observed that rapid self-diffusion reaction contributes mainly to the overall reaction rate.

From the calculations of specific reaction rate (min⁻¹) of rapid self-diffusion reaction for different concentrations of bromide ion solution in the range of 0.0025–0.02 M at constant temperature of 27°C, it was observed that the specific reaction rate increases very slowly (remains nearly constant) even though the bromide ion concentration was varied to ten times (Table-1). In the second series of experiments as the amount of resin increases from 0.250 to 750 g, the number of exchangeable bromide ions on the exchanger phase increases, as a result of which even though for other parameters like temperature (27°C) and bromide ion concentration in solution (0.010 M), which are kept constant, there was a pronounced increase in the specific reaction rate of ion-isotopic self-diffusion reaction (Table-2).

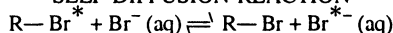
TABLE-1
EFFECT OF BROMIDE ION CONCENTRATION IN SOLUTION ON THE KINETICS OF ION-ISOTOPIC SELF-DIFFUSION REACTION



Amount of ion exchange resin = 0.500 g, Volume of bromide ion solution = 200 cm³
Temperature = 27°C

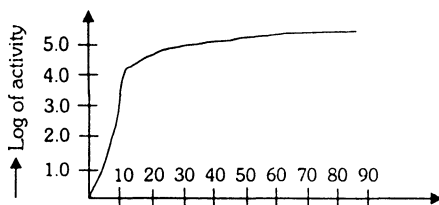
Concentration of bromide ions in solution (M)	0.0025	0.0050	0.0100	0.0200
Millimoles of bromide ions in 200 cm ³ solution	0.5000	1.0000	2.0000	4.0000
Specific reaction rate (min ⁻¹)	0.1120	0.1150	0.1170	0.1190

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



Concentration of bromide ion solution = 0.0100 M
Amount of bromide ions in 200 cm³ solution = 2.0 millimoles
Temperature = 27°C

Amount of ion exchange resins (g)	0.250	0.500	0.750
Specific reaction rate (min ⁻¹)	0.094	0.117	0.125



Concentration of bromide ion solution = 0.0100M
Amount of ion exchange resin = 0.500gm
Temperature = 27.0°C.

Fig. 1 Kinetics of ion-isotopic self-diffusion reaction
 $R-Br^* + Br^-(aq) \rightleftharpoons R-Br + Br^{*-}(aq)$

REFERENCES

1. D.D. Sood, In: Proceedings of the Conference on Applications of Radioisotopes and Radiation in Industrial Development, NAARRI, Mumbai, p. 46 (1998).
2. J.W. Leonhardt, In: Proceedings of the Conference on Applications of Radioisotopes and Radiation in Industrial Development, NAARRI, Mumbai, p. 73 (1998).
3. G.E. Boyd, A.W. Adamson and L.S. Myers (Jr.), *J. Am. Chem. Soc.*, **69**, 2836, (1947).
4. F. Helffrich and M.S. Plasset, *J. Chem. Phys.*, **28**, 418 (1958).
5. F. Helffrich, *J. Phys. Chem.*, **66**, 38 (1962); **67**, 1157 (1963).
6. D. Nandan, A.R. Gupta and J. Shankar, *J. Indian Chem. Soc.*, **10**, 931 (1972).
7. R. Kunin and R.J. Myers, *J. Am. Chem. Soc.*, **69**, 2874 (1974).
8. G. Dickel and A. Meyer, *Z. Electrochem.*, **57**, 901 (1953).
9. J. Harvie and G.H. Nancollas, *J. Inorg. Nucl. Chem.*, **30**, 273 (1968).
10. M.B. Hanley, S.C. Churms and E.C. Leisegang, *Chem. Commun.*, **2**, 78 (1967).
11. V. Talasek and J. Eliasek, *Collect. Czech. Chem. Commun.*, **36**, 77 (1971).
12. K. Bunzl, *J. Chromatogr.*, **102**, 169 (1974).
13. I. Madi and T. Varromagy, *Kem. Foly.*, **78**, 233 (1972).
14. B.A. Bolto and R.E. Warner, *Desalination*, **8**, 21 (1970).
15. H. Yoshida, K. Katao and Seiich Fuji Kawa, *Chem. Eng. Sci.*, **41**, 2525 (1986); *Chem. Abstr.*, **105** 197700u (1986).
16. R.S. Lokhande and P.U. Singare, *Asian J. Chem.*, **10**, 364, 630, 890, 894 (1998).
17. E.A. Chuveleva, P.P. Nazarov and K.V. Chmutov, *Russ. J. Phys. Chem.*, **46**, 1628 (1972).
18. S. Wilson and L. Lapidus, *Ind. Eng. Chem.*, **48**, 992 (1956).
19. G.E. Boyd and B.A. Soldano, *J. Am. Chem. Soc.*, **75**, 6091 (1953).
20. N.W. Rosenberg, J.H.B. George and W.D. Potter, *J. Electrochem. Soc.*, **104**, 111 (1957).
21. A.E. Lagos and J.A. Kitchener, *Trans. Faraday Soc.*, **56**, 1245 (1960).
22. B.A. Soldano, *Ann. N.Y. Acad. Sci.*, **57**, 116 (1953).
23. D.E. Conway, J.H.S. Green and D. Richtenberg, *Disc. Faraday Soc.*, **50**, 511 (1954).
24. K. Haagen, *Z. Electrochem.*, **57**, 178 (1953).
25. K.W. Pepper and D. Reichenberg, *Z. Electrochem.*, **57**, 183 (1953).
26. D. Richman and H.C. Thomas, *J. Phys. Chem.*, **60**, 237 (1956).

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