

Comparative Study on Bromide and Iodide Ion-Isotopic Exchange Reactions Using Strongly Basic Anion Exchange Resin Duolite A-113

R. S. Lokhande,^a P. U. Singare,^{*,b} and M. H. Dole^a

^aDepartment of Chemistry, University of Mumbai, Vidyantagri, Santacruz, Mumbai-400098, India

^bDepartment of Chemistry, Bhavan's College, Munshi Nagar, Andheri, Mumbai 400 058, India

Received: June 16, 2006; In Final Form: September 4, 2006

Kinetics of ion-isotopic exchange reaction was studied using industrial grade ion exchange resin Duolite A-113. The radioactive isotopes ¹³¹I and ⁸²Br were used to trace the ion-isotopic exchange reaction. The experiments were performed in the temperature range of 26.0 °C to 43.0 °C and the concentration of external ionic solution varying from 0.005 M to 0.100 M. For bromide ion-isotopic exchange reaction, the calculated values of specific reaction rate, initial rate of bromide ion exchange, and amount of bromide ions exchanged were obtained higher than that for iodide ion-isotopic exchange reaction under identical experimental conditions. The observed variation in the results for two ion-isotopic exchange reactions was due to the difference in the ionic size of bromide and iodide ions.

1. Introduction

There are number of liquid processes and waste streams at nuclear power plants, fuel reprocessing plants, and nuclear research centers that require treatment for removal of radioactive contaminants. One of the most common treatment methods for such aqueous streams is the use of ion exchange, which is a well developed technique that has been employed for many years in nuclear industries. The ion exchange process is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid. Efforts to develop new ion exchangers for specific applications are continuing. In spite of their advanced stage of development, various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy of their application in radioactive waste management. The selection of an appropriate ion exchange material for the liquid radioactive waste treatment is possible on the basis of information provided by the manufacturer. However since the selection of the appropriate ion exchange material depends on the needs of the system, it is expected that the data obtained from the actual experimental trials will prove to be more helpful. Generally the selected ion exchange materials must be compatible with the chemical nature of the waste such as pH, type of ionic species present as well as the operating parameters notably temperature. Also while designing an ion exchange processing system it is desirable to have an adequate knowledge of the rate at which the reaction occur. From the reaction rate information it is possible to decide the required contact time, which will further influence the physical size of the radioactive waste processing plant. Although there are different alternative methods available to know the reaction rate, but radioactive isotopic technique is expected to be the most appropriate method as it offers several advantages such as high detection sensitivity, capability of in-situ detection, and physico-chemical compatibility with the material under study. Therefore in the present investigation attempts were made to study the rate of bromide and iodide ion-isotopic exchange reactions by application of radiotracer technique using strongly basic anion exchange resin Duolite A-113 under various operational parameters.

Research works on radiochemical applications,¹ characteriza-

tion of ion exchangers,²⁻⁴ their exchange properties in various aqueous and organic medium,⁵⁻⁷ ion exchange equilibrium,⁸⁻¹⁷ and ion exchange reaction kinetics¹⁸⁻²⁷ were performed extensively. However not much work was carried out to study the kinetics of ion-isotopic exchange reaction²⁸⁻³¹ using these ion exchangers. In the present investigation attempts were made to standardize the parameters affecting the ion-isotopic exchange reaction kinetics by application of tracer technique. The results of the present investigation will be useful to set the operational process parameters for the efficient industrial application of this ion exchanger. The same radioactive tracer technique can be applied for the characterization of other industrial grade ion exchange resins so as to decide about their selection for the specific industrial application.

2. Experimental

2.1. Conditioning of ion exchange resin. Duolite A-113 as supplied by the manufacturer (Auchtel Products Ltd., Mumbai, India) is a strongly basic anion exchanger in chloride form having quaternary ammonium N⁺(CH₃)₃ functional group containing 8% styrene divinylbenzene of 20–50 mesh size. For the present investigation the resins were converted into iodide and bromide form by using 10% potassium iodide and 10% potassium bromide solution respectively by adjusting the flow rate as 1 mL / min. The resins were then washed with double distilled water, until the washings were free from iodide/bromide ions as tested by AgNO₃ solution. These resins in bromide and iodide form were then dried separately over P₂O₅ in desiccators at room temperature.

2.2. Radioactive Tracer Isotopes. Details regarding the isotopes used in the present experimental work are given in Table 1.

TABLE 1: Properties of ¹³¹I and ⁸²Br tracer isotopes (Ref. 32)

Isotopes	Half-life	Radioactivity / mCi	γ energy / MeV	Chemical form	Physical form
¹³¹ I	8.04 d	5	0.36	Iodide*	Aqueous
⁸² Br	36 h	5	0.55	Bromide**	Aqueous

* Sodium iodide in dilute sodium sulphite.

** Ammonium bromide in dilute ammonium hydroxide.

*Corresponding author. E-mail: pravinsingare@vsnl.net

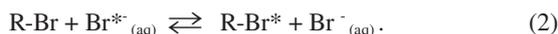
2.3. Study on kinetics of iodide ion-isotopic exchange reaction. In a stoppered bottle 200 mL of 0.005 M iodide ion solution was labeled with diluted ^{131}I radioactive solution using a micro syringe, such that 1.0 mL of labeled solution has a radioactivity of around 15,000 cpm (counts per minute) when measured with γ -ray spectrometer having NaI (Tl) scintillation detector. Since only about 50–100 μL of the radioactive iodide ion solution was required for labeling the iodide ion solution, the iodide ion concentration will remain unchanged, which was further confirmed by potentiometer titration against AgNO_3 solution. The above labeled iodide ion solution of known initial activity was kept in a thermostat adjusted to 26.0 °C. The swelled and conditioned dry ion exchange resins in iodide form weighing exactly 1.000 g were transferred quickly into this labeled iodide ion solution which was vigorously stirred by using mechanical stirrer and the activity in cpm of 1.0 mL of solution was measured. The activity in cpm so measured represents initial activity at zero time. The solution was transferred back to the same bottle containing labeled iodide ion solution after measuring activity. The iodide ion-isotopic exchange reaction can be represented as:



Here R-I represents ion exchange resin in iodide form; $\text{I}^*_{(\text{aq})}$ represents aqueous iodide ion solution labeled with ^{131}I radio-tracer isotope.

The activity of solution was measured at a fixed interval of every 2.0 min. To know the activity exchanged at infinite time, the activity was measured after three hours. The activity measured at various time intervals was corrected for background counts. Due to the rapid iodide ion-isotopic exchange reaction taking place, the activity of solution decreases rapidly initially and then due to the slow exchange reaction the activity of the solution decreases slowly and finally remains nearly constant. Similar experiments were carried out with labeled iodide ion solution of various concentration in the range of 0.005 M to 0.100 M in the temperature range of 26.0 °C to 43.0 °C keeping amount of ion exchange resin in iodide form 1.000 g constant. The experiment was also performed by using different amount of ion exchange resin in iodide form in range of 1.000 g–5.000 g by using 0.005 M labeled iodide ion solution at a constant temperature of 26.0 °C.

2.4. Study on kinetics of bromide ion-isotopic exchange reaction. The experiment was performed in similar way as explained above by using labeled bromide ion solution of different concentrations in the temperature range 26.0 °C to 43.0 °C by using ion exchange resin in bromide form varying from 1.000 g to 5.000 g. Labeling the bromide ion solution was done by using dilute solution of radioactive ^{82}Br tracer isotope in the similar manner as explained above. The bromide ion-isotopic exchange reaction taking place can be represented as:



Here R-Br represents ion exchange resin in bromide form and $\text{Br}^*_{(\text{aq})}$ represents aqueous bromide ion solution labeled with ^{82}Br radiotracer isotope.

3. Results and Discussion

In the present investigation, it was observed that due to the rapid ion-isotopic exchange reactions the activity of solution goes on decreasing sharply with time and then further the activity remains nearly constant due to slow exchange reaction. Preliminary studies^{33,34} shows that reaction was of first order. Therefore logarithm of activity was plotted against time. This gives a composite curve in which the activity initially decreases sharply and thereafter very slowly (Figure 1), evidently rapid

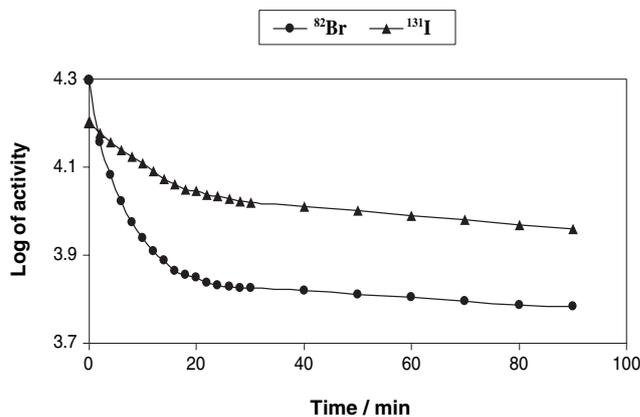


Figure 1. Kinetics of ion-isotopic exchange reactions using ion exchange resin Duolite A-113. 1.000 g of ion exchange resins in bromide and iodide form was equilibrated separately with 200 mL of 0.005 M (1 mmole) labeled bromide and iodide ion solutions respectively at a constant temperature of 26.0 °C for three hours. Activity of labeled iodide ion solution at complete equilibrium = 9120 cpm. Activity of labeled bromide ion solution at complete equilibrium = 6068 cpm.

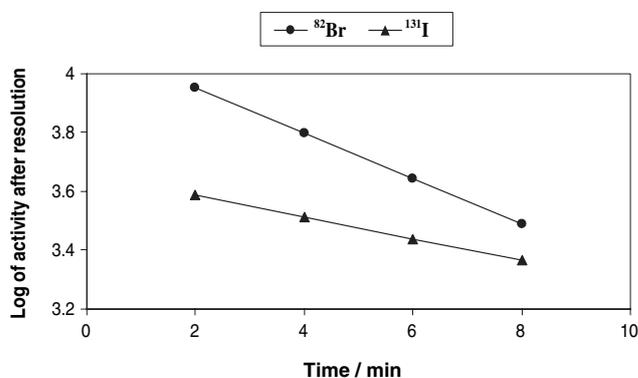


Figure 2. Variation of log activity after resolution with time for ion-isotopic exchange reactions using ion exchange resin Duolite A-113. See footnote of Figure 1.

and slow ion-isotopic exchange reactions were occurring simultaneously. The specific reaction rates for the rapid exchange reaction were obtained by resolving the composite curve in a manner similar to the determination of decay constants of radioactive isotopes in a mixture. The rapid ion-isotopic exchange reaction undergo completion in a short interval of time of about 15 to 20 min, however slow ion-isotopic exchange reaction continues over a much longer interval of time and the exchange reaction is assumed to reach the complete equilibrium after three hours. Hence the activity measured after three hours represents the activity of solution at complete equilibrium. At this later stage as the slow exchange process was the only reaction taking place, the log of activity due to slow process against time curve gives a straight line. Now the straight line was extrapolated back to zero time. The extrapolated portion represents the contribution of slow process to the total activity which now includes rapid process also. The activity due to slow process was subtracted from the total activity at various time intervals. The difference gives the activity due to rapid process only. The log of this activity after resolution was plotted against time which gives a straight line with negative slope (Figure 2). From the slope of this line the specific reaction rates (k) of rapid ion-isotopic exchange reaction were calculated. The amount of ions (Br^-/I^-) exchanged in mmol on the resin were obtained from the initial and final activity of solution and the amount of exchangeable ions in 200 mL of solution. From the amount of ions exchanged on the resin in mmol and the specific reaction rates (min^{-1}), the initial

TABLE 2: Effect of concentration on ion-isotopic exchange reactions using ion exchange resin Duolite A-113

Concentration of external labeled ionic solution (M)	Amount of ions in 200 mL ionic solution (mmol)	R-Br + Br ^{*-} _(aq) ⇌ R-Br* + Br ⁻ _(aq)			R-I + I ^{*-} _(aq) ⇌ R-I* + I ⁻ _(aq)		
		Specific reaction rate (min ⁻¹)	Amount of bromide ions exchanged (mmol)	Initial rate of bromide ion exchange (mmol/min)	Specific reaction rate (min ⁻¹)	Amount of iodide ions exchanged (mmol)	Initial rate of iodide ion exchange (mmol/min)
0.005	1.0	0.177	0.743	0.132	0.112	0.528	0.059
0.010	2.0	0.175	1.210	0.212	0.110	0.762	0.084
0.020	4.0	0.173	2.347	0.406	0.113	1.550	0.175
0.100	20.0	0.180	10.68	1.923	0.111	5.117	0.568

1.000 g of ion exchange resins in bromide and iodide form was equilibrated separately with 200 mL of labeled bromide and iodide ion solution respectively of different concentrations at a constant temperature of 26.0 °C for three hours.

TABLE 3: Effect of amount of ion exchange resin on ion-isotopic exchange reactions using ion exchange resin Duolite A-113

Amount of ion exchange resin (g)	R-Br + Br ^{*-} _(aq) ⇌ R-Br* + Br ⁻ _(aq)			R-I + I ^{*-} _(aq) ⇌ R-I* + I ⁻ _(aq)		
	Specific reaction rate (min ⁻¹)	Amount of bromide ions exchanged (mmol)	Initial rate of bromide ion exchange (mmol/min)	Specific reaction rate (min ⁻¹)	Amount of iodide ions exchanged (mmol)	Initial rate of iodide ion exchange (mmol/min)
1	0.177	0.743	0.132	0.112	0.528	0.059
2	0.197	0.696	0.137	0.161	0.538	0.086
3	0.216	0.754	0.162	0.204	0.557	0.113
4	0.265	0.764	0.202	0.221	0.578	0.127
5	0.293	0.786	0.230	0.253	0.583	0.147

Different amount of ion exchange resins in bromide and iodide form was equilibrated separately with 200 mL of 0.005 M (1 mmol) labeled bromide and iodide ion solution respectively at a constant temperature of 26.0 °C for three hours.

TABLE 4: Effect of temperature on ion-isotopic exchange reactions using ion exchange resin Duolite A-113

Temperature °C	R-Br + Br ^{*-} _(aq) ⇌ R-Br* + Br _(aq)			R-I + I ^{*-} _(aq) ⇌ R-I* + I _(aq)		
	Specific reaction rate (min ⁻¹)	Amount of bromide ions exchanged (mmol)	Initial rate of bromide ion exchange (mmol/min)	Specific reaction rate (min ⁻¹)	Amount of iodide ions exchanged (mmol)	Initial rate of iodide ion exchange (mmol/min)
26.0	0.177	0.743	0.132	0.112	0.528	0.059
32.0	0.187	0.756	0.141	0.136	0.640	0.087
43.0	0.203	0.940	0.191	0.168	0.828	0.139

1.000 g of ion exchange resins in bromide and iodide form was equilibrated separately with 200 mL of 0.005 M (1 mmol) labeled bromide and iodide ion solutions respectively at various temperatures for three hours.

rate of (Br/I) ion exchanged in mmol/min was calculated.

Because of smaller ionic size of bromide ions as compared to that of iodide ions, it was observed that the exchange of bromide ions occurs at the faster rate than that of iodide ions. Hence under identical experimental conditions, the specific reaction rate /min⁻¹, amount of ion exchanged in mmol and initial rate of ion exchange in mmol/min are calculated to be higher for bromide ion-isotopic exchange reaction than that of iodide ion-isotopic exchange reaction as summarized in Tables 2–4. For both bromide and iodide ion-isotopic exchange reaction under identical experimental conditions of temperature 26.0 °C, amount of ion exchange resin 1.000 g, the values of specific reaction rate remains nearly constant even though the concentration of external exchangeable ionic solution was varied twenty times i.e. from 0.005 M to 0.100 M as shown in Table 2. However when the concentration of ionic solution was

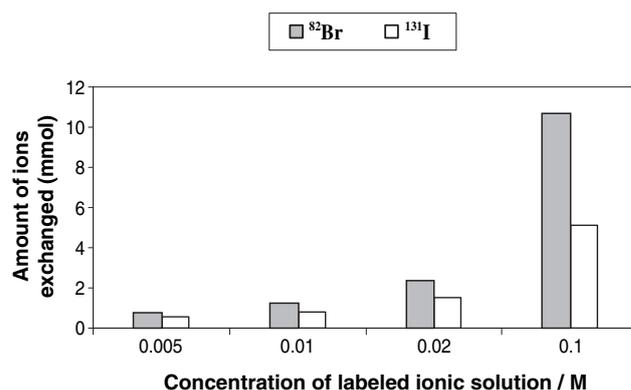


Figure 3. Effect of concentration on ion-isotopic exchange reactions using ion exchange resin Duolite A-113. See footnote of Table 2.

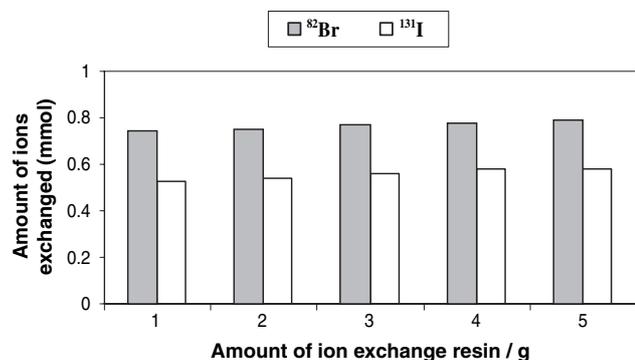


Figure 4. Effect of amount of ion exchange resin on ion-isotopic exchange reactions using ion exchange resin Duolite A-113. See footnote of Table 3.

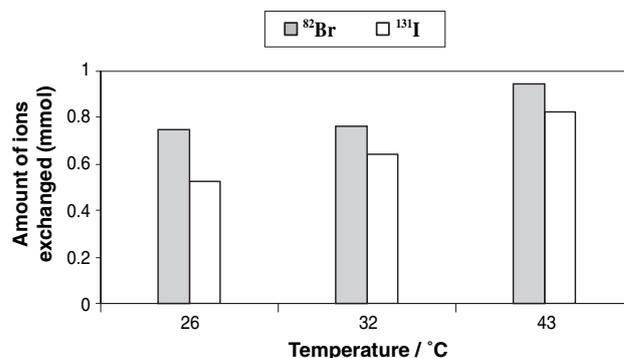


Figure 5. Effect of temperature on ion-isotopic exchange reactions using ion exchange resin Duolite A-113. See footnote of Table 4.

kept constant 0.005 M, the specific reaction rate increases sharply with rise in temperature from 26.0 °C to 43.0 °C as shown in Table 4. For 1.0 mmol of bromide ions in solution, the amount of bromide ions exchanged increases from 0.743 mmol at 26.0 °C to 0.940 mmol at 43.0 °C; while under the same experimental conditions the amount of iodide ions exchanged increases from 0.528 mmol to 0.828 mmol as shown in Table 4. From the results, it appears that bromide ions exchange at the faster rate as compared to that of iodide ions as shown in Figures 3–5 which was related to their ionic size.

References

- (1) C. V. King and S. Evans, *J. Phys. Chem.* **63**, 1816 (1959).
- (2) R. S. Lokhande, A. R. Kolte, and T. S. Prabhavalkar, *Asian J. Chem.* **11**, 1026 (1999).
- (3) R. S. Lokhande and S. R. Tiwari, *Asian J. Chem.* **12**, 97 (2000).
- (4) R. S. Lokhande and A. B. Patil, *Asian J. Chem.* **10**, 600 (1998).
- (5) R. P. Bhatnagar, A. Bhardwaj, and S. D. Bhardwaj, *Asian J. Chem.* **10**, 405, 409 (1998).
- (6) C. V. Bhat and J. Vardia, *Asian J. Chem.* **10**, 834 (1998).
- (7) G. E. Boyd, L. S. Myers, and A. W. Adamson, *J. Am. Chem. Soc.* **69**, 2849 (1947).
- (8) G. E. Boyd, J. Schubert, and A. W. Adamson, *J. Am. Chem. Soc.* **69**, 2818 (1947).
- (9) R. S. Lokhande and P. U. Singare, *Chem. Environ. Res.* **7** (1 & 2), 129; **7** (3 & 4), 283 (1998).
- (10) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **12**, 214, 990, 999, 1003 (2000).
- (11) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **11**, 758 (1999).
- (12) R. S. Lokhande and P. U. Singare, *Res. J. Chem. Environ.* **3** (3), 25 (1999).
- (13) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **10**, 898, 1026 (1998).
- (14) R. S. Lokhande and P. U. Singare, *Orient. J. Chem.* **14**, 247, 303 (1998).
- (15) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **13**, 8, 13, 20, 43, 50 (2001).
- (16) O. D. Bonner, G. Dickel, and H. Brummer, *Z. Phys. Chem. (Frankfurt)*, **25**, 81 (1960).
- (17) E. Ekedhal, E. Hogfeldt, and L. G. Sillen, *Acta. Chem. Scand.* **4**, 556, 828, 829 (1950).
- (18) F. Helfferich, *Ion exchange*, McGraw Hill (1962), p 250.
- (19) F. Helfferich, *J. Phys. Chem.* **66**, 39 (1962).
- (20) R. A. Blickenstaff, J. D. Wagner, and J. S. Dranoff, *J. Phys. Chem.* **71**, 1670 (1967).
- (21) Yu. P. Znamenskii, A. I. Kasperovich, and N. Y. Byekhon, *Rus. J. Phys. Chem.* **36**, 1060 (1962).
- (22) J. Inczedy, *Analytical applications of ion exchangers, 1st edition*, ed. I. Buzas, Oxford-Pregamon Press, (1966), p 40.
- (23) E. A. Chuveleva, P. P. Nazarov, and K. V. Chmutov, *Rus. J. Phys. Chem.* **46**, 1628 (1972).
- (24) B. A. Bolto, R. McNeill, R. Siudak, E. A. Swinton, R. E. Warner, D. E. Weiss, and D'wills, *J. Macromol Sci. Chem.* **4**, 1039 (1970).
- (25) B. A. Bolto and R. E. Warner, *Desalination* **8**, 21 (1970).
- (26) Yu. P. Znamenskii, A. I. Kasperovich, and N. V. Bychkov, *Rus. J. Phys. Chem.* **42**, 1586 (1968).
- (27) N. I. Gamayunov, *Rus. J. Phys. Chem.* **64**, 1787 (1990).
- (28) R. S. Lokhande and M. N. Ingale, *Asian J. Chem.* **11**, 1034 (1999).
- (29) G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Am. Chem. Soc.* **69**, 2836 (1947).
- (30) F. Helfferich and M. S. Plasset, *J. Chem. Phys.* **28**, 418 (1958).
- (31) Yu. P. Znamenskii, A. I. Kasperovich, and N. Y. Byekhov, *Rus. J. Phys. Chem.* **36**, 1060 (1962).
- (32) D. D. Sood, *Proc. Int. Conf. on Applications of Radioisotopes and Radiation in Industrial Development*, ed. D. D. Sood, A. V. R. Reddy, S. R. K. Iyer, S. Gangadharan, and G. Singh (B.A.R.C., India) 35–53 (1998).
- (33) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **15**, 33 (2003).
- (34) R. S. Lokhande and P. U. Singare, *Asian J. Chem.* **17**, 125 (2005).