Comparative Study of Duolite A-378 and Duolite A-143 Anion Exchange Resins by Application of $^{131}$I and $^{82}$Br as a Tracer Isotopes

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Abstract In the present study radioactive tracer isotopes $^{131}$I and $^{82}$Br are applied to study the kinetics of iodide and bromide ion-isotopic exchange reactions in two anion exchange resins Duolite A-378 and Duolite A-143. The study is performed by varying the experimental parameters like temperature and concentration of exchanging medium to understand the effect of above parameters on exchange reaction rate (min$^{-1}$), amount of ions exchanged (mmol), percentage of ions exchanged and distribution coefficient. For both the ion-isotopic exchange reactions it is common observation that the exchange reaction rate increases with increase in concentration and decreases with rise in temperature of exchanging medium. Also there exists a strong positive co-relationship between amount of ions exchanged and concentration of ionic solution, while a strong negative co-relationship exists between amounts of ions exchanged and temperature of exchanging medium. Comparing the values of reaction rate (min$^{-1}$), amount of ions exchanged (mmol); percentage of ions exchanged and distribution coefficient calculated for the two resins, it is observed that Duolite A-378 resins show superior performance than Duolite A-143 resins under identical operational parameters.

Keywords Duolite A-378, Duolite A-143, Reaction Kinetics, Radioactive Isotopes, Tracer Applications, Distribution Coefficient, Ion-Isotopic Exchange Reactions, Reaction Rate

1. Introduction

Radio isotopes hold a central place in atomic energy programme as the major non-power application of nuclear industry [1]. Radio isotope as a tracers offer several advantages in radiochemical investigation such as high detection sensitivity, capability of in-situ detection, limited memory effects and physico-chemical compatibility with the material under study. The fundamental principle in radiochemical investigations is that the chemical properties of a radio isotope of an element are almost the same as those of the other stable/radioactive isotopes of the element. When radio isotope is present in a chemical form identical to that of the bulk of the element in a chemical process, then any reaction the element undergoes can be directly traced by monitoring the radio isotope. Radiochemical work involves two main steps first is the sampling of chemical species to be studied and second is quantitative determination of the radiation emitted by the radio isotope in the sample [1]. In radiotracer study, a short lived radio isotope in a physico-chemical form similar to that of the process material is used to trace the material under study. The radio isotopes in suitable physical and chemical forms are introduced in systems under study. By monitoring the radioactivity both continuously or after sampling (depending on the nature of study), the movement, adsorption, retention etc. of the tracer and in turn, of the bulk matter under investigation, can be followed. The tracer concentration recorded at various locations also helps to draw information about the dynamic behaviour of the system under study. The radio isotopes preferred for such studies are gamma emitters having half-life compatible with the duration of studies. The strength of radioactivity used varies depending on the nature of application.

Radiotracer methodology is described extensively in the literature [2-6]. Applications of radiotracers in chemical research cover the studies of reaction mechanism, kinetics, exchange processes and analytical applications such as radiometric titrations, solubility product estimation, isotope dilution analysis and autoradiography. The radio isotopes have proved as a tool to study many problems in chemical, biological and medicinal fields. Radiotracers have helped in identification of leaks in buried pipelines and dams. Process parameters such as mixing efficiency, residence time, flow rate, material inventory and silt movement in harbours are studied using radio isotopes[1]. The efficiency of several devices in a wastewater treatment plant (primary and secondary clarifiers, aeration tank) is investigated by means
of radiotracers[7]. Radio isotopes play an important role in a variety of fields such as health-care, agriculture, industry, hydrology, life sciences, pollution control and research. The radio isotopes have also proved a tool to study many problems in chemical, biological and medicinal fields.

Considering the above wide use of radioactive isotopes in various industrial and technical applications, in the present investigation, they are applied to assess the performance of industrial grade anion exchange resins Duolite A-378 and Duolite A-143 under different operational parameters like temperature and ionic concentrations. It is expected that the tracer technique used here can also be used for characterization of other organic ion exchange resins which are synthesized for their specific technical applications [8-10]. The present technique can also be extended further to standardize the operational parameters so as to bring about the most efficient performance of those resins in their specific industrial applications.

2. Experimental

2.1. Conditioning of Ion Exchange Resins

Ion exchange resin Duolite A-378 is a weak base anion exchange resin in OH- form having -N+R2 functional group, while Duolite A-143 is a strongly basic anion exchange resin in Cl- form having -N0R2 functional group (supplied by Auchtel Product Ltd., Mumbai, India). Details regarding the properties of the resins used are given in Table 1. These resins were converted separately to the iodide / bromide form by treatment with 10 % KI / KBr solution in a conditioning column which is adjusted at 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

The radioisotope 131I and 82Br used in the present experimental work was obtained from Board of Radiation and Isotope Technology (BRIT), Mumbai. Details regarding the isotopes used in the present experimental work are given in Table 2.

2.3. Study on kinetics of Iodide Ion-Iodide Exchange Reaction

In a stoppered bottle 250 mL (V) of 0.001 M iodide ion solution was labeled with diluted 131I 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 labelling the solution, its concentration will remain unchanged, which was further confirmed by potentiometer titration against AgNO3 solution. The above labeled solution of known initial activity (Ai) was kept in a thermostat adjusted to 30.0 °C. The swelled and conditioned dry ion exchange resins in iodide form weighing exactly 1.000 g (m) were transferred quickly into this labeled solution which was vigorously stirred by using mechanical stirrer and the activity in cpm of 1.0 mL of solution was measured. The solution was transferred back to the same bottle containing labeled solution after measuring activity. The iodide ion-iodide exchange reaction can be represented as:

\[ \text{R-I} + I^-_{(aq)} \rightleftharpoons \text{R-I}^* + I^-_{(aq)} \]  (1)

Here R-I represents ion exchange resin in iodide form; I^-_{(aq)} represents aqueous iodide ion solution labeled with 131I radiotracer isotope.

The activity of solution was measured at a fixed interval of 2.0 min. The final activity (Af) of the solution was also measured after 3h which was sufficient time to attain the equilibrium [12-26]. The activity measured at various time intervals was corrected for background counts.

Similar experiments were carried out by equilibrating separately 1.000 g of ion exchange resin in iodide form with labeled iodide ion solution of four different concentrations ranging up to 0.004 M at a constant temperature of 30.0 °C. The same experimental sets were repeated for higher temperatures up to 45.0°C.

### Table 1. Properties of ion exchange resins

<table>
<thead>
<tr>
<th>Ion exchange resin</th>
<th>Matrix</th>
<th>Particle Size (mm)</th>
<th>Moisture content (%)</th>
<th>Operating pH</th>
<th>Maximum operating Temperature (°C)</th>
<th>Total exchange capacity (meq/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duolite A-378</td>
<td>Crosslinked polystyrene</td>
<td>0.3-1.2</td>
<td>48-52</td>
<td>0-7</td>
<td>60</td>
<td>1.30</td>
</tr>
<tr>
<td>Duolite A-143</td>
<td>Crosslinked polystyrene</td>
<td>0.3-1.2</td>
<td>62-67</td>
<td>0-14</td>
<td>100</td>
<td>1.00</td>
</tr>
</tbody>
</table>

### Table 2. Properties of 131I and 82Br tracer isotopes [11]

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Half-life</th>
<th>Radioactivity / mCi</th>
<th>γ-energy / MeV</th>
<th>Chemical form</th>
<th>Physical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>131I</td>
<td>8.04 d</td>
<td>5</td>
<td>0.36</td>
<td>Iodide*</td>
<td>Aqueous</td>
</tr>
<tr>
<td>82Br</td>
<td>36 h</td>
<td>5</td>
<td>0.55</td>
<td>Bromide**</td>
<td>Aqueous</td>
</tr>
</tbody>
</table>

* Sodium iodide in dilute sodium sulphite  ** Ammonium bromide in dilute ammonium hydroxide
Table 3. Concentration effect on Ion-Isotopic Exchange Reactions Amount of ion exchange resin = 1.000 g, Volume of labeled ionic solution = 250 mL, Temperature = 30.0°C

<table>
<thead>
<tr>
<th>Concentration of Ionic Solution (M)</th>
<th>Amount of Ions in 200 mL Solution (mmol)</th>
<th>Specific Reaction Rate of Rapid Process (mmol/min)</th>
<th>Initial Rate of Iodide Ion Exchange (mmol/min)</th>
<th>Log Kd</th>
<th>Amount of Iodide Ion Exchanged (mmol)</th>
<th>Specific Reaction Rate of Rapid Process (mmol/min)</th>
<th>Initial Rate of Bromide Ion Exchange (mmol/min)</th>
<th>Log Kd</th>
<th>Amount of Bromide Ion Exchanged (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.250</td>
<td>0.210</td>
<td>0.140</td>
<td>0.029</td>
<td>13.6</td>
<td>0.178</td>
<td>0.129</td>
<td>0.023</td>
<td>13.1</td>
</tr>
<tr>
<td>0.002</td>
<td>0.500</td>
<td>0.218</td>
<td>0.293</td>
<td>0.064</td>
<td>14.8</td>
<td>0.195</td>
<td>0.263</td>
<td>0.051</td>
<td>14.3</td>
</tr>
<tr>
<td>0.003</td>
<td>0.750</td>
<td>0.227</td>
<td>0.454</td>
<td>0.103</td>
<td>15.7</td>
<td>0.213</td>
<td>0.428</td>
<td>0.091</td>
<td>15.2</td>
</tr>
<tr>
<td>0.004</td>
<td>1.000</td>
<td>0.233</td>
<td>0.614</td>
<td>0.143</td>
<td>17.0</td>
<td>0.225</td>
<td>0.602</td>
<td>0.135</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 4. Temperature effect on Ion-Isotopic Exchange Reactions Amount of ion exchange resin = 1.000 g, Concentration of labeled exchangeable ionic solution = 0.001 M, Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.250 mmol

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Specific Reaction Rate of Rapid Process (mmol/min)</th>
<th>Amount of Iodide Ion Exchanged (mmol)</th>
<th>Specific Reaction Rate of Rapid Process (mmol/min)</th>
<th>Amount of Bromide Ion Exchanged (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>0.210</td>
<td>0.140</td>
<td>0.029</td>
<td>13.6</td>
</tr>
<tr>
<td>35.0</td>
<td>0.200</td>
<td>0.133</td>
<td>0.027</td>
<td>13.1</td>
</tr>
<tr>
<td>40.0</td>
<td>0.187</td>
<td>0.131</td>
<td>0.024</td>
<td>12.7</td>
</tr>
<tr>
<td>45.0</td>
<td>0.170</td>
<td>0.127</td>
<td>0.022</td>
<td>12.1</td>
</tr>
</tbody>
</table>

2.4. Study on Kinetics of Bromide Ion-Isotopic Exchange Reaction

The experiment was also performed to study the kinetics of bromide ion-isotopic exchange reaction by equilibrating 1.000 g of ion exchange resin in bromide form with labeled bromide ion solution in the same concentration and temperature range as above. The labelling of bromide ion solution was done by using 82Br as a radioactive tracer isotope for which the same procedure as explained above...
was followed. The bromide ion-isotopic exchange reaction can be represented as:

\[ \text{R-Br} + \text{Br}^- \text{(aq.)} \rightarrow \text{R-Br}^- + \text{Br}^- \text{(aq.)} \]  

(2)

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

### 3. Results and Discussion

#### 3.1. Comparative Study of Ion-Isotopic Exchange Reactions

In the present investigation it was observed that due to the rapid ion-isotopic exchange reaction taking place, the activity of solution decreases rapidly initially, then due to the slow exchange the activity of the solution decreases slowly and finally remains nearly constant. Preliminary studies show that the above exchange reactions are of first order [27, 28]. Therefore logarithm of activity when plotted against time gives a composite curve in which the activity initially decreases sharply and thereafter very slowly giving nearly straight line (Figure 1), evidently rapid and slow ion-isotopic exchange reactions were occurring simultaneously [12-26]. 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. From the activity exchanged due to rapid process at various time intervals, the specific reaction rates (k) of rapid ion-isotopic exchange reaction were calculated. The amount of iodide / bromide ions exchanged (mmol) on the resin were obtained from the initial and final activity of solution and the amount of exchangeable ions in 250 mL solution. From the amount of ions exchanged on the resin (mmol) and the specific reaction rates (min\(^{-1}\)), the initial rate of ion exchanged (mmol/min) was calculated.

Because of larger solvated size of bromide ions as compared to that of iodide ions, it was observed that the exchange of bromide ions occurs at the slower rate than that of iodide ions [29]. Hence under identical experimental conditions, the values of specific reaction rate (min\(^{-1}\), amount of ion exchanged (mmol) and initial rate of ion exchange (mmol/min) are calculated to be lower for bromide ion-isotopic exchange reaction than that for iodide ion-isotopic exchange reaction as summarized in Tables 3 and 4. For both bromide and iodide ion-isotopic exchange reactions, under identical experimental conditions, the values of specific reaction rate increases with increase in concentration of ionic solution from 0.001M to 0.004M (Table 3). However, with rise in temperature from 30.0°C to 45.0°C, the specific reaction rate was observed to decrease (Table 4). From the results, it appears that iodide ions exchange at the faster rate as compared to that of bromide ions which was related to the extent of solvation (Tables 3 and 4).

![Figure 1. Kinetics of Ion-Isotopic Exchange Reactions](image)

From the knowledge of \(A_i, A_f\), volume of the exchangeable ionic solution (V) and mass of ion exchange resin (m), the \(K_d\) value was calculated by the equation

\[
K_d = \left[ \frac{A_i - A_f}{A_f} \right] \times \frac{V}{m}
\]  

(3)

Heumann et al. [30] in the study of chloride distribution coefficient on strongly basic anion exchange resin observed that the selectivity coefficient between halide ions increased at higher electrolyte concentrations. Adachi et al. [31] observed that the swelling pressure of the resin decreased at higher solute concentrations resulting in larger \(K_d\) values. The temperature dependence of \(K_d\) values on cation exchange resin was studied by Shuji et al. [32]; were they observed that the values of \(K_d\) increased with fall in temperature. The present experimental results also indicates that the \(K_d\) values for bromide and iodide ions increases with increase in ionic concentration of the external solution, however with rise in temperature the \(K_d\) values were found to decrease. It was also observed that the \(K_d\) values for iodide ion-isotopic reaction were calculated to be higher than that for bromide ion-isotopic reaction (Tables 3 and 4).

#### 3.2. Comparative Study of Anion Exchange Resins

From the Table 3 and 4, it is observed that for iodide ion-isotopic exchange reaction by using Duolite A-378 resin, the values of specific reaction rate (min\(^{-1}\), amount of iodide ion exchanged (mmol), initial rate of iodide ion exchange (mmol/min) and log \(K_d\) were 0.210, 0.140, 0.023 and 13.6 respectively, which was higher than 0.178, 0.129, 0.023 and 13.1 respectively as that obtained by using Duolite A-143 resins under identical experimental conditions of 30.0°C, 1.000 g of ion exchange resins and 0.001 M labeled iodide ion solution. The identical trend was observed for the two resins during bromide ion-isotopic exchange reaction.

From Table 3, it is observed that using Duolite A-378
resins, at a constant temperature of 30.0 °C, as the concentration of labeled iodide ion solution increases 0.001 M to 0.004 M, the percentage of iodide ions exchanged increases from 56.1 % to 61.4 %. While using Duolite A-143 resins under identical experimental conditions the percentage of iodide ions exchanged increases from 51.4 % to 60.2 %. Similarly in case of bromide ion-isotopic exchange reaction, the percentage of bromide ions exchanged increases from 50.2 % to 52.6 % using Duolite A-378 resin, while for Duolite A-143 resin it increases from 43.7 % to 51.5 %. The effect of ionic concentration on percentage of ions exchanged is graphically represented in Figure 2.

![Figure 2](image_url)

**Figure 2.** Variation in Percentage Ions Exchanged with Concentration of Labeled Ionic Solution Amount of ion exchange resin = 1.000 g, Volume of labeled ionic solution = 250 mL, Temperature = 30.0°C

![Figure 3](image_url)

**Figure 3.** Variation in Percentage Ions Exchanged with Temperature of labeled Ionic Solution Amount of ion exchange resin = 1.000 g, Concentration of labeled exchangeable ionic solution = 0.001M, Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.250 mmol
From Table 4, it is observed that using Duolite A-378 resins, for 0.001 M labeled iodide ion solution, as the temperature increases 30.0°C to 45.0°C, the percentage of iodide ions exchanged decreases from 56.1% to 50.9%. While using Duolite A-143 resins under identical experimental conditions the percentage of iodide ions exchanged decreases from 51.4% to 50.2%. Similarly in case of bromide ion-isotopic exchange reaction, the percentage of bromide ions exchanged decreases from 50.2% to 44.3% using Duolite A-378 resin, while for Duolite A-143 resin it decreases from 43.7% to 41.1%. The effect of temperature on percentage of ions exchanged is graphically represented in Figure 3.

The overall results indicate that under identical experimental conditions, as compared to Duolite A-143 resins, Duolite A-378 resins shows higher percentage of ions exchanged. Thus Duolite A-378 resins show superior performance than Duolite A-143 resins under identical operational parameters.

3.3. Statistical Correlations

The results of present investigation show a strong positive linear co-relationship between amount of ions exchanged and concentration of ionic solution (Figures 4, 5). In case of iodide ion-isotopic exchange reaction, the values of correlation coefficient \(r\) were calculated as 0.9999 and 0.9983 for Duolite A-378 and Duolite A-143 resins respectively, while for bromide ion-isotopic exchange reaction, the respective values of \(r\) was calculated as 1.0000 and 0.9999.

There also exist a strong negative co-relationship between amount of ions exchanged and temperature of exchanging medium (Figures 6, 7). In case of iodide ion-isotopic exchange reactions the values of \(r\) calculated for Duolite A-378 and Duolite A-143 resins were -0.9732 and -0.8944 respectively. Similarly in case of bromide ion-isotopic exchange reactions the \(r\) values calculated were -0.8823 and -0.9759 respectively for both the resins.
4. Conclusions

The experimental work carried out in the present investigation will help to standardize the operational process parameters so as to improve the performance of selected ion exchange resins. The radioactive tracer technique used here can also be applied for characterization of different nuclear as well as non-nuclear grade ion exchange resins.

ACKNOWLEDGEMENTS

The author is thankful to Professor Dr. R.S. Lokhande for his valuable help and support in carrying out the experimental work in Radiochemistry Laboratory of Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai -58.

The author is extremely thankful to SAP Productions for developing and maintaining the manuscript template.

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