Nondestructive Radioactive Tracer Technique in Characterization of Anion Exchange Resins Purolite NRW-8000 and Duolite A-368

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ABSTRACT

Radioactive tracer isotopes $^{131}$I and $^{82}$Br were used to characterize anion exchange resins Purolite NRW-8000 and Duolite A-368 by application of nondestructive technique. The resin characterization was based on their performance during iodide and bromide ion-isotopic exchange reactions. It was observed that during the iodide ion-isotopic exchange reaction at a constant temperature of 40.0 °C, as the concentration of labeled iodide ion solution increases from 0.001 mol/L to 0.004 mol/L, the percentage of iodide ions exchanged increases from 62.10 % to 68.10 % using Purolite NRW-8000 resins and from 44.20 % to 46.80 % using Duolite A-368 resins. Also at a constant temperature of 40.0 °C, 1.000 g of ion exchange resins and 0.003 mol/L labeled iodide ion solution, 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 calculated as 0.260, 0.500, 0.130 and 11.8 respectively for Purolite NRW-8000 resin, which was higher than the respective values of 0.130, 0.345, 0.045 and 6.7 as that obtained for Duolite A-368 resins. The similar trend was observed for the two resins during bromide ion-isotopic exchange reaction. From the overall results it appears that under identical experimental conditions, Purolite NRW-8000 resins show superior performance over Duolite A-368 resins. It is expected here that the present nondestructive technique can be extended further for characterization of different industrial grade ion exchange resins, which will help in their selection for specific industrial application.

Keywords: ion exchange resin; anion exchange; Purolite NRW-8000; Duolite A-368; radio tracer isotopes; $^{131}$I, $^{82}$Br; characterization; isotopic exchange

1. INTRODUCTION

A large number of natural and synthetic inorganic and organic ion exchangers has been developed and is in use today. Inorganic ion exchangers often have the advantage of a much greater selectivity than organic resins for certain radiologically important species, such as caesium and strontium. These inorganic materials may also prove to have advantages with respect to immobilization and final disposal when compared with organic ion exchangers. However, in nuclear power plant operations the currently available inorganic exchangers cannot entirely replace conventional organic ion exchange resins, especially in high purity
water applications or in operations in which the system chemistry must be controlled through the maintenance of dissolved species such as lithium ions or boric acid [1]. As a result organic ion exchange resins are the wave of the present research and are considered as the material of next generation. 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. Efforts to develop new organic ion exchange resins for specific applications are continuing [2-7].

Novel composites using combinations of existing and new ion exchangers are also being investigated. Therefore development of new organic ion exchange materials for specific industrial and technological applications is a biggest challenge to present day researchers. Development of ion exchange resins is usually followed by characterization to understand the performance of those resins in various technological applications [5-11]. Although number of techniques are available for the characterization of ion exchange resins [12-14], but the radiotracer technique offer several advantages such as high detection sensitivity, capability of in-situ detection, limited memory effects and physico-chemical compatibility with the material under study [15,16]. As a result radioisotopes have become useful tool and almost every branch of industry which uses them [15,16] and radiotracer methodology is described extensively in the literature [17-23]. Considering the extensive application of radioactive tracer technique, in the present investigation, attempts are made to apply the same technique to study the kinetics of ion-isotopic exchange reactions in Purolite NRW-8000 (nuclear grade) and Duolite A-368 (non-nuclear grade) anion exchange resins. It is expected that the kinetics data obtained here will not only be used in characterization of these resins but also in standardization of the process parameters for their efficient industrial application.

2. EXPERIMENTAL

2.1. Conditioning of ion exchange resins

Purolite NRW-8000 is a type I strong base, quaternary ammonium, nuclear grade anion exchange resins in hydroxide form (supplied by Purolite International India Private Limited, Pune, India) while Duolite A-368 is a weak base anion exchange resin both in hydroxide form (supplied by Auchtel Products Ltd., Mumbai, India). Details regarding the properties of the resins used are given in Table 1.

<table>
<thead>
<tr>
<th>Ion exchange resin</th>
<th>Matrix</th>
<th>Functional Group</th>
<th>Mean 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>Purolite NRW-8000</td>
<td>Gel polystyrene crosslinked with divinyl benzene</td>
<td>-N+R&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.57</td>
<td>55</td>
<td>0-14</td>
<td>60</td>
<td>1.3</td>
</tr>
<tr>
<td>Duolite A-368</td>
<td>Crosslinked Polystyrene</td>
<td>-N+R&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.3-1.2</td>
<td>46</td>
<td>0-7</td>
<td>60</td>
<td>1.70</td>
</tr>
</tbody>
</table>

These resins were converted separately in to 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, India. Details regarding the isotopes used in the present experimental work are given in Table 2.

Table 2. Properties of ¹³¹I and ⁸₂Br tracer isotopes [15].

<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.

2. 3. Study on kinetics of iodide ion-isotopic exchange reaction

In a stoppered bottle 250 mL (V) of 0.001 mol/L 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 labeling 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-isotopic exchange reaction can be represented as:

$$R-I + I^{*-\text{(aq.)}} \rightleftharpoons R-I^{*} + I^{-\text{(aq.)}}$$  \hspace{1cm} (1)

here R-I represents ion exchange resin in iodide form; I^{*-\text{(aq.)}} represents aqueous iodide ion solution labeled with ¹³¹I radiotracer isotope. The activity of solution was measured at a fixed interval of every 2.0 min.

The final activity (Aᵢ) of the solution was also measured after 3 h which was sufficient time to attain the equilibrium [7-11]. 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 mol/L at a constant temperature of 30.0 °C. The same experimental sets were repeated for higher temperatures up to 45.0 °C.

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 labeling of bromide ion solution was done by using $^{82}\text{Br}$ 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:

$$\text{R-Br} + \text{Br}^{*\text{aq.}} \rightleftharpoons \text{R-Br}^* + \text{Br}^{-\text{aq.}} \quad (2)$$

here R-Br represents ion exchange resin in bromide form; Br$^{*\text{aq.}}$ represents aqueous bromide ion solution labeled with $^{82}\text{Br}$ radiotracer isotope.

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

Amount of ion exchange resin = 1.000 g, Concentration of labeled exchangeable ionic solution = 0.003 mol/L, Volume of labeled ionic solution = 250 mL, Temperature = 40.0 °C
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 = 40.0 °C.

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 = 0.003 mol/L, Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.750 mmol.
Figure 4. Correlation between concentration of iodide ion solution and amount of iodide ion exchanged. Amount of ion exchange resin = 1.000 g, Volume of labeled ionic solution = 250 mL, Temperature = 40.0 °C. Correlation coefficient (r) for Purolite NRW-8000 = 0.9999. Correlation coefficient (r) for Duolite A-368 = 0.9999.

Figure 5. Correlation between concentration of bromide ion solution and amount of bromide ion exchanged. Amount of ion exchange resin = 1.000 g, Volume of labeled ionic solution = 250 mL, Temperature = 40.0 °C. Correlation coefficient (r) for Purolite NRW-8000 = 1.0000. Correlation coefficient (r) for Duolite A-368 = 0.9985.
Figure 6. Correlation between Temperature of exchanging medium and amount of iodide ion exchanged. Amount of ion exchange resin = 1.000 g, Concentration of labeled exchangeable ionic solution = 0.003 mol/L, Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.750 mmol. Correlation coefficient (r) for Purolite NRW-8000 = -0.9779. Correlation coefficient (r) for Duolite A-368 = -0.9886.

Figure 7. Correlation between Temperature of exchanging medium and amount of bromide ion exchanged. Amount of ion exchange resin = 1.000 g, Concentration of labeled exchangeable ionic solution = 0.003 mol/L, Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.750 mmol. Correlation coefficient (r) for Purolite NRW-8000 = -0.9933. Correlation coefficient (r) for Duolite A-368 = -0.9896.
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 = 40.0 °C.

<table>
<thead>
<tr>
<th>Concentration of ionic solution (mol/L)</th>
<th>Amount of ions in 250 mL solution (mmol)</th>
<th>Specific reaction rate of rapid process (min⁻¹)</th>
<th>Amount of iodide ion exchanged (mmol)</th>
<th>Initial rate of iodide ion exchange (mmol/min)</th>
<th>Log Kd</th>
<th>Specific reaction rate of rapid process (min⁻¹)</th>
<th>Amount of bromide ion exchanged (mmol)</th>
<th>Initial rate of bromide ion exchange (mmol/min)</th>
<th>Log Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.250</td>
<td>0.234</td>
<td>0.155</td>
<td>0.036</td>
<td>9.8</td>
<td>0.106</td>
<td>0.012</td>
<td>5.8</td>
<td>0.195</td>
</tr>
<tr>
<td>0.002</td>
<td>0.500</td>
<td>0.247</td>
<td>0.321</td>
<td>0.079</td>
<td>11.1</td>
<td>0.118</td>
<td>0.027</td>
<td>6.2</td>
<td>0.204</td>
</tr>
<tr>
<td>0.003</td>
<td>0.750</td>
<td>0.260</td>
<td>0.500</td>
<td>0.130</td>
<td>11.8</td>
<td>0.130</td>
<td>0.045</td>
<td>6.7</td>
<td>0.216</td>
</tr>
<tr>
<td>0.004</td>
<td>1.000</td>
<td>0.275</td>
<td>0.681</td>
<td>0.187</td>
<td>12.5</td>
<td>0.144</td>
<td>0.067</td>
<td>7.1</td>
<td>0.232</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 = 0.003 mol/L,
Volume of labeled ionic solution = 250 mL, Amount of exchangeable ions in 250 mL labeled solution = 0.750 mmol.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Purolite NRW-8000</th>
<th>Duolite A-368</th>
<th>Purolite NRW-8000</th>
<th>Duolite A-368</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific reaction rate of rapid process min⁻¹</td>
<td>Amount of iodide ion exchanged (mmol)</td>
<td>Initial rate of iodide ion exchange (mmol/min)</td>
<td>Log Kd</td>
</tr>
<tr>
<td>30.0</td>
<td>0.280</td>
<td>0.515</td>
<td>0.144</td>
<td>13.0</td>
</tr>
<tr>
<td>35.0</td>
<td>0.271</td>
<td>0.504</td>
<td>0.137</td>
<td>12.6</td>
</tr>
<tr>
<td>40.0</td>
<td>0.260</td>
<td>0.500</td>
<td>0.130</td>
<td>11.8</td>
</tr>
<tr>
<td>45.0</td>
<td>0.249</td>
<td>0.485</td>
<td>0.121</td>
<td>11.4</td>
</tr>
</tbody>
</table>
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 [24-28]. 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 [24-28]. 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 of solution. From the amount of ions exchanged on the resin (mmol) and the specific reaction rates \( \text{min}^{-1} \), 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. Hence under identical experimental conditions, the values of specific reaction rate \( \text{min}^{-1} \), 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 the concentration of iodide and bromide ions in solution from 0.001 mol/L to 0.004 mol/L (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).

Thus in case of Purolite NRW-8000 at 40.0 °C when the concentration of iodide and bromide ions in solution increases from 0.001 mol/L to 0.004 mol/L, the specific reaction rate values for iodide ion-isotopic exchange increases from 0.234 to 0.275 \text{min}^{-1}, while for bromide ion-isotopic exchange the values increases from 0.195 to 0.232 \text{min}^{-1}. Similarly in case of Duolite A-368, under identical experimental conditions, the values for iodide ion-isotopic exchange increases from 0.106 to 0.144 \text{min}^{-1}, while for bromide ion-isotopic exchange the values increases from 0.090 to 0.118 \text{min}^{-1}. However when the concentration of iodide and bromide ions in solution is kept constant at 0.003 mol/L and temperature is raised from 30.0 °C to 45.0 °C, in case of Purolite NRW-8000 the specific reaction rate values for iodide ion-isotopic exchange decreases from 0.280 to 0.249 \text{min}^{-1}, while for bromide ion-isotopic exchange the values decreases from 0.240 to 0.208 \text{min}^{-1}.

Similarly in case of Duolite A-368, under identical experimental conditions, the specific reaction rate values for iodide ion-isotopic exchange decreases from 0.154 to 0.121 \text{min}^{-1}, while for bromide ion-isotopic exchange the values decreases from 0.124 to 0.101 \text{min}^{-1}. 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). From the knowledge of \( A_i, A_b, V \), 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 = [(A_i - A_f) / A_f] x V / m $  \hspace{1cm} (3)

Previous studies [29,30] on halide ion distribution coefficient on strong and weak basic anion exchange resins indicate 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.

Thus in case of Purolite NRW-8000 at 40.0 °C when the concentration of iodide and bromide ions in solution increases from 0.001 mol/L to 0.004 mol/L, the log $K_d$ values for iodide ions increases from 9.8 to 12.5, while for bromide ions the values increases from 8.6 to 10.6. Similarly in case of Duolite A-368, under identical experimental conditions, the log $K_d$ values for iodide ions increases from 5.8 to 7.1, while for bromide ions the values increases from 2.5 to 4.1. However when the concentration of iodide and bromide ions in solution is kept constant at 0.003 mol/L and temperature is raised from 30.0 °C to 45.0 °C, in case of Purolite NRW-8000 the log $K_d$ values for iodide ions decreases from 13.0 to 11.4, while for bromide ions the values decreases from 11.0 to 9.5. Similarly in case of Duolite A-368, under identical experimental conditions, the log $K_d$ values for iodide ions decreases from 8.2 to 6.4, while for bromide ions the values decreases from 4.7 to 3.3. It was also observed that the $K_d$ values for iodide ion-isotopic exchange reaction were calculated to be higher than that for bromide ion-isotopic exchange 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 Purolite NRW-8000 resin, the values of specific reaction rate ($\text{min}^{-1}$), amount of iodide ion exchanged (mmol), initial rate of iodide ion exchange (mmol/min) and log $K_d$ were 0.260, 0.500, 0.130 and 11.8 respectively, which was higher than 0.130, 0.345, 0.045 and 6.7 respectively as that obtained by using Duolite A-368 resins under identical experimental conditions of 40.0 °C, 1.000 g of ion exchange resins and 0.003 mol/L 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 at a constant temperature of 40.0 °C, as the concentration of labeled iodide ion solution increases from 0.001 mol/L to 0.004 mol/L, the percentage of iodide ions exchanged increases from 62.10 % to 68.10 % using Purolite NRW-8000 resin and from 44.20 % to 46.80 % using Duolite A-368 resin. Similarly under identical experimental conditions of 40.0 °C, 1.000 g of ion exchange resins and 0.003 mol/L labeled iodide ion solution, the identical trend was observed for the two resins during bromide ion-isotopic exchange reaction.

From Table 4, it is observed that for 0.003 mol/L labeled iodide ion solution, as the temperature increases from 30.0 °C to 45.0 °C, the percentage of iodide ions exchanged decreases from 68.6 % to 64.60 % using Purolite NRW-8000 resin and from 47.70 % to 45.60 % using Duolite A-368 resin. Similarly under identical experimental conditions, in case of bromide ion-isotopic exchange reactions, the percentage of bromide ions exchanged decreases from 56.60 % to 51.20 % using Purolite NRW-8000 resin and from 42.90 % to
36.80% using Duolite A-368 resin. 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-368 resins, Purolite NRW-8000 resins shows higher percentage of ions exchanged. Thus Purolite NRW-8000 resins show superior performance over Duolite A-368 resins under identical operational parameters.

3.3. Statistical Correlations

The results of present investigation show a strong positive linear correlation 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 0.9998 and 0.9999 for Purolite NRW-8000 and Duolite A-368 resins respectively, while for bromide ion-isotopic exchange reaction, the values of $r$ was calculated as 1.0000 and 0.9985 respectively for the two resins.

There also exist a strong negative correlation 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 Purolite NRW-8000 and Duolite A-368 resins were -0.9779 and -0.9886 respectively. Similarly in case of bromide ion-isotopic exchange reactions the $r$ values calculated were -0.9933 and -0.9896 respectively for the two resins.

4. CONCLUSION

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 further for characterization of different nuclear as well as non-nuclear grade ion exchange resins.

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References


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