NON DESTRUCTIVE APPLICATION OF RADIOACTIVE TRACER TECHNIQUE FOR CHARACTERIZATION OF INDUSTRIAL GRADE ANION EXCHANGE RESINS INDION GS-300 AND INDION-860

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Received June 11, 2013
Accepted for Publication September 11, 2013

1. INTRODUCTION

The overall goal of radioactive waste management is to deal with radioactive waste in a manner that protects both human health and the environment now and in the future, without imposing an undue burden on future generations [1]. Waste management includes the handling, pretreatment, treatment, conditioning, storage, transportation, and disposal of conditioned radioactive waste, as well as the release and discharge of decontaminated materials [2]. As far as the liquid radioactive waste management is concerned, ion exchange is the most appropriate and efficient method which is widely accepted for the treatment of a variety of low and intermediate level liquid waste streams [3]. With respect to economy and efficacy, the ion exchange process stands between the other two major liquid waste treatment processes of chemical precipitation and evaporation [4]. Nowadays, highly specific nuclear grade ion exchange resins are most predominantly used in nuclear industries [5-9]. The major factors responsible for their use are high capacity, wide applicability, wide versatility, and low relative cost, which make them superior over some synthetic inorganic media. In spite of extensive work done in the development of new organic ion exchange resins so as to match the requirements of industries, different aspects of ion exchange technologies are still studied continuously so as to improve the performance of those resins in various technical applications [10-15]. Generally the selected ion exchange materials must be compatible with the chemical nature of the liquid waste, such as its pH, type of ionic species present, as well as the operating parameters, in particular temperature. Therefore it is essential to have adequate knowledge regarding the physical and chemical properties of the resins for a proper selection, which forms the complementary part of any resin characterization study.

Although there are many alternative methods available for the characterization of ion exchange resins [16-21], the radioactive tracer isotopic technique is one of the sensitive analytical techniques [22, 23]. By monitoring the radioactivity continuously, the migration of the tracer, and in turn of the bulk matter under investigation, can be followed. As a result, radioisotopes have become a useful
tool and almost every branch of industry which uses them [22, 23] and the radiotracer methodology is described extensively in the scientific literature [24-26]. Considering the extensive technological application of radioactive tracers, in the present investigation, attempts are made to apply the same technique to study the kinetics of ion-isotopic exchange reactions in Indion GS-300 (nuclear grade) and Indion-860 (non-nuclear grade) anion exchange resins. The kinetics data so obtained was further used to characterize the two resins.

2. EXPERIMENTAL

2.1 Conditioning of Ion Exchange Resins

Indion GS-300 is a strong base cross linked polystyrene type I resin having quaternary ammonium \(-N'(CH₃)₃\) functional group. Indion-860 is a weak base macroporous cross linked polystyrene tertiary ammonium \(-N'(CH₃)₂\) functional group. Both resins in the chloride form were supplied by Ion Exchange India Ltd., Mumbai, India. Details regarding the properties of the resins used are given in Table 1. These resins were converted separately into iodide/bromide form by treatment with 10 % KI / KBr 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 2.

### Table 1. Properties of Ion Exchange Resins

<table>
<thead>
<tr>
<th>Ion exchange resin</th>
<th>Particle Size (nm)</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>Indion GS-300</td>
<td>0.3-1.2</td>
<td>54</td>
<td>0-14</td>
<td>60</td>
<td>1.20</td>
</tr>
<tr>
<td>Indion-860</td>
<td>0.3-1.2</td>
<td>52</td>
<td>0-7</td>
<td>60</td>
<td>1.40</td>
</tr>
</tbody>
</table>

### Table 2. Properties of \(^{131}\)I and \(^{82}\)Br Tracer Isotopes [22]

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Half-life</th>
<th>Radioactivity / mCi</th>
<th>(\gamma) energy / MeV</th>
<th>Chemical form</th>
<th>Physical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{131})I</td>
<td>8.04 d</td>
<td>5</td>
<td>0.36</td>
<td>Iodide(^\ast)</td>
<td>Aqueous</td>
</tr>
<tr>
<td>(^{82})Br</td>
<td>36 h</td>
<td>5</td>
<td>0.55</td>
<td>Bromide(^\ast\ast)</td>
<td>Aqueous</td>
</tr>
</tbody>
</table>

\(^\ast\) Sodium iodide in dilute sodium sulphite
\(^\ast\ast\) Ammonium bromide in dilute ammonium hydroxide

2.3 Study on Kinetics of Iodide Ion-isotopic Exchange Reaction

In a stoppered bottle 250 mL (1) of 0.001 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 a gamma-ray spectrometer having an NaI (TI) scintillation detector. Since only about 50–100 \(\mu\)L of the radioactive iodide ion solution was required for labeling the solution, its concentration remained nearly unchanged, which was further confirmed by potentiometer titration against the AgNO₃ solution. The above labeled solution of known initial activity (\(A_i\)) 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 a 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 the labeled solution after measuring its activity. The iodide ion-isotopic exchange reaction can be represented as:

\[
R-I + I^-_{(aq)} \leftrightarrow R-I^+ + I^-_{(aq)} \tag{1}
\]

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

The activity of solution was measured at a fixed interval of every 2.0 min. The final activity (\(A_f\)) of the solution was also measured after 3h which was sufficient time to attain equilibrium [27-31]. 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 the 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.

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 a labeled bromide ion solution in the same concentration and temperature range as above. The labeling of the bromide ion solution was done by using \(^{82}\)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:

\[
R-Br + Br^-_{(aq)} \leftrightarrow R-Br^+ + Br^-_{(aq)} \tag{2}
\]

Here R-Br represents ion exchange resin in bromide form; \(Br^-_{(aq)}\) represents aqueous bromide ion solution labeled with \(^{82}\)Br 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 the solution initially decreases rapidly, then due to the slow exchange the activity of the solution, it decreases slowly and finally remains nearly constant. The discrepancies in the graphical results represented in Figure 1 indicates that for both resins, the iodide ion-isotopic exchange reaction takes place at a faster rate as compared to the bromide ion-isotopic exchange reaction. These discrepancies are mainly related to the differences in the ionic size of the exchangeable ions in the solution. Preliminary studies show that the above exchange reactions are of first order [27-31]. Therefore a logarithm of activity when plotted against time gives a composite curve in which the activity initially decreases sharply and thereafter very slowly, making nearly a straight line (Figure 1). Evidently rapid and slow ion-isotopic exchange reactions were occurring simultaneously [27-31]. Now the straight line was extrapolated back to zero time. The extrapolated portion represents the contribution of the slow process to the total activity which now also includes rapid process. The activity due to the slow process was subtracted from the total activity at various time intervals. The difference gives the activity due to the rapid process only. From the activity exchanged due to the 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 the 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 (min⁻¹), the initial rate of ion exchanged (mmol/min) was calculated.

Because of the 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 in comparison with that of iodide ions. Hence under identical experimental conditions, the values of the specific reaction rate (min⁻¹), amount of ion exchanged (mmol), and initial rate of ion exchange (mmol/min) are calculated to be lower for the bromide ion-isotopic exchange reaction than that for the 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, with temperature remaining constant at 40.0 ºC, the values of the specific reaction rate increases with the increase in ionic concentration from 0.001M to 0.004M (Table 3).

However, at a constant ionic concentration of 0.003 M, the specific reaction rate was observed to decrease with rise in temperature from 30.0 ºC to 45.0 ºC, as shown in Table 4. Thus in the case of Indion GS-300 at 40.0 ºC, when the ionic concentration increases from 0.001M to 0.004M, the specific reaction rate values for the iodide ion-isotopic exchange increases from 0.317 to 0.337 min⁻¹, while for the bromide ion-isotopic exchange the values increases from 0.248 to 0.268 min⁻¹. Similarly in the case of Indion-860, under identical experimental conditions, the values for the iodide ion-isotopic exchange increases from 0.162 to 0.189 min⁻¹, while for the bromide ion-isotopic exchange the values increases from 0.108 to 0.134 min⁻¹. However when the concentration of ionic solution is kept constant at 0.003 M and the temperature is raised from 30.0 ºC to 45.0 ºC, in the case of Indion GS-300, the specific reaction rate values for the iodide ion-isotopic exchange decrease from 0.346 to 0.323 min⁻¹, while for the bromide ion-isotopic exchange the values decrease from 0.275 to 0.255 min⁻¹. Similarly in the case of Indion-860, under identical experimental conditions, the specific reaction rate values for the iodide ion-isotopic exchange decrease from 0.198 to 0.171 min⁻¹, while for the bromide ion-isotopic exchange the values decrease from 0.143 to 0.118 min⁻¹. From the results, it appears that iodide ions exchange at a faster rate as compared to that of bromide ions, which was related to the extent of solvation as shown in Tables 3 and 4.

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

$$K_d = \left[\frac{(A_i - A_f)}{A_f}\right] \times \frac{V}{m} \quad (3)$$

Previous studies [32, 33] 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. [34] 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 reaction.
**Table 3.** Concentration Effect on Ion-Isotopic Exchange Reactions

<table>
<thead>
<tr>
<th>Concentration of ionic solution (M)</th>
<th>Amount of ions in 250 mL solution (mmol)</th>
<th>Specific reaction rate of rapid process (mmol/min)</th>
<th>Amount of iodide ion exchanged (mmol)</th>
<th>Initial rate of iodide ion exchange (mmol/min)</th>
<th>Log $K_d$</th>
<th>Specific reaction rate of rapid process (mmol/min)</th>
<th>Amount of bromide ion exchanged (mmol)</th>
<th>Initial rate of bromide ion exchange (mmol/min)</th>
<th>Log $K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.250</td>
<td>0.317</td>
<td>0.188</td>
<td>0.060</td>
<td>18.5</td>
<td>0.162</td>
<td>0.124</td>
<td>0.020</td>
<td>15.9</td>
</tr>
<tr>
<td>0.002</td>
<td>0.500</td>
<td>0.321</td>
<td>0.379</td>
<td>0.122</td>
<td>18.9</td>
<td>0.171</td>
<td>0.255</td>
<td>0.044</td>
<td>16.6</td>
</tr>
<tr>
<td>0.003</td>
<td>0.750</td>
<td>0.328</td>
<td>0.577</td>
<td>0.189</td>
<td>19.7</td>
<td>0.180</td>
<td>0.386</td>
<td>0.070</td>
<td>17.0</td>
</tr>
<tr>
<td>0.004</td>
<td>1.000</td>
<td>0.337</td>
<td>0.784</td>
<td>0.264</td>
<td>20.2</td>
<td>0.189</td>
<td>0.524</td>
<td>0.099</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Amount of ion exchange resin = 1.000 g / Volume of labeled ionic solution = 250 mL / Temperature = 40.0 °C

**Table 4.** Temperature Effect on Ion-Isotopic Exchange Reactions

<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>Initial rate of iodide ion exchange (mmol/min)</th>
<th>Log $K_d$</th>
<th>Specific reaction rate of rapid process (mmol/min)</th>
<th>Amount of bromide ion exchanged (mmol)</th>
<th>Initial rate of bromide ion exchange (mmol/min)</th>
<th>Log $K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>0.346</td>
<td>0.599</td>
<td>0.207</td>
<td>21.3</td>
<td>0.198</td>
<td>0.395</td>
<td>0.078</td>
<td>18.6</td>
</tr>
<tr>
<td>35.0</td>
<td>0.335</td>
<td>0.585</td>
<td>0.196</td>
<td>20.4</td>
<td>0.189</td>
<td>0.393</td>
<td>0.074</td>
<td>17.8</td>
</tr>
<tr>
<td>40.0</td>
<td>0.328</td>
<td>0.577</td>
<td>0.189</td>
<td>19.7</td>
<td>0.180</td>
<td>0.386</td>
<td>0.070</td>
<td>17.0</td>
</tr>
<tr>
<td>45.0</td>
<td>0.323</td>
<td>0.571</td>
<td>0.184</td>
<td>19.0</td>
<td>0.171</td>
<td>0.383</td>
<td>0.065</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Amount of ion exchange resin = 1.000 g / Concentration of labeled exchangeable ionic solution = 0.003M
Volume of labeled ionic solution = 250 mL / Amount of exchangeable ions in 250 mL labeled solution = 0.750 mmol
resin was studied by Shuji et al. [35]; where they observed that the values of $K_d$ increased with the fall in temperature. The present experimental results also indicate that the $K_d$ values for bromide and iodide ions increases with the increase in ionic concentration of the external solution, however with the rise in temperature, the $K_d$ values were found to decrease. Thus in the case of Indion GS-300 at 40.00°C when the ionic concentration increases from 0.001 M to 0.004 M, the log $K_d$ values for iodide ions increases from 18.5 to 20.2, while for bromide ions the values increase from 13.4 to 15.0. Similarly in the case of Indion-860, under identical experimental conditions, the log $K_d$ values for iodide ions increase from 15.9 to 17.7, while for bromide ions the values increase from 10.9 to 12.7. However when concentration of the ionic solution is kept constant at 0.003 M and the temperature is raised from 30.0°C to 45.0°C, in the case of Indion GS-300, the log $K_d$ values for iodide ions decrease from 21.3 to 19.0, while for bromide ions the values decrease from 15.7 to 14.2. Similarly in the case of Indion-860, under identical experimental conditions, the log $K_d$ values for iodide ions decrease from 18.6 to 16.3, while for bromide ions the values decrease from 13.1 to 11.6. It was also observed that the $K_d$ values for the iodide ion-isotopic exchange reaction were calculated to be higher than that of the bromide ion-isotopic exchange reaction as shown in Tables 3 and 4.

### 3.2 Comparative Study of Anion Exchange Resins

From Table 3 and 4, it is observed that for the iodide ion-isotopic exchange reaction by using the Indion GS-300 resin, the values of the specific reaction rate (min⁻¹), the amount of iodide ion exchanged (mmol), the initial rate of iodide ion exchange (mmol/min), and the log $K_d$ were 0.328, 0.577, 0.189 and 19.7 respectively. The above values were higher than the respective values of 0.180, 0.386, 0.070 and 17.0 which were what was obtained by using the Indion-860 resins under identical experimental conditions of 40.0°C, 1.000 g of ion exchange resins, and 0.003 M labeled iodide ion solution. The identical trend was observed for the two resins during the bromide ion-isotopic exchange reaction.

From Table 3, it is observed that using Indion GS-300 resins, at a constant temperature of 40.0°C, as the concentration of the labeled iodide ion solution increases from 0.001 M to 0.004 M, the percentage of iodide ions exchanged increases from 75.16 % to 78.36 %. While using Indion-860 resins under identical experimental conditions, the percentage of iodide ions exchanged increases from 49.65 % to 52.36 %. Similarly in the case of the bromide ion-isotopic exchange reaction, the percentage of bromide ions exchanged increases from 63.95 % to 67.32 % using Indion GS-300 resin, while for Indion-860 resin it decreases from 45.20 % to 37.80 %. The effect of temperature on the percentage of ions exchanged is represented in Figure 3.

The overall results indicate that under identical experimental conditions, as compared to Indion-860 resins, Indion

![Fig. 2. Variation in Percentage Ions Exchanged with Concentration of Labeled Ionic Solution](image1)

![Fig. 3. Variation in Percentage Ions Exchanged with Temperature of Labeled Ionic Solution](image2)
GS-300 resins show a higher percentage of ions exchanged. Thus Indion GS-300 resins show superior performance compared to Indion-860 resins under identical operational parameters.

3.3 Statistical Correlations

The results of the present investigation show a strong positive linear co-relationship between the amount of ions exchanged and the concentration of ionic solution (Figures 4, 5). In the case of the iodide ion-isotopic exchange reactions, the values of the correlation coefficient \( r \) were calculated as 0.9998 and 0.9999 for Indion GS-300 and Indion-860 resins respectively, while for the bromide ion-isotopic exchange reactions, the respective values of \( r \) were calculated as 0.9998 and 0.9993 for the two resins.

There also exist a strong negative co-relationship between the amount of ions exchanged and the temperature of the exchanging medium (Figures 6, 7). In the case of the iodide ion-isotopic exchange reactions, the values of \( r \) were calculated as -0.9807 and -0.9775 respectively for the two resins, while in the case of the bromide ion-isotopic exchange reactions, the respective values were calculated as -0.9898 and -0.9995.
4. CONCLUSION

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

ACKNOWLEDGEMENT

The author is thankful to Professor Dr. R.S. Lokhande (Retired) for his valuable help and support by providing the required facilities so as to conduct the experimental work in the Radiochemistry Laboratory, Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai -58.

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