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# Study of Ion Exchange Equilibria of Uni-Univalent ions on Duolite A-113

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The exchange capacity of an ion exchange resin has been of considerable utility in scientific research and industry. The exchange capacity depends upon several factors like capacity, nature, concentration and temperature etc. It will be therefore useful in qualitative assessment of an ion exchange resin for its utility in a stipulated process and also in assessing its efficiency in several ion exchange process. The present work is an attempt to study an ion exchange equilibria on an exchange Duolite A-113.

## INTRODUCTION

Many investigations[1–4] on uni-univalent ion exchange equilibria with cation exchange resin is earlier studied, but very few studies were carried out on an ion exchange resins. Also a study on enthalpy and entropy were done by Glueckauf *et al*[5] According to them equilibrium constant of reaction can be calculated by knowing the activity coefficient of ions in the solution as well as in resin. Hence the study of various exchange reaction has been carried out in Duolite A 113 in two parts.

In the first part equilibrium constant for the ion exchange reaction,

$$\text{R-Cl} + I^-_{(aq)} \rightleftharpoons \text{R-I} + Cl^-_{(aq)} \text{ was studied.}$$

In the second part equilibrium constant for the ion exchange reaction,

$$\text{R-Cl} + Br^-_{(aq)} \rightleftharpoons \text{R-Br} + Cl^-_{(aq)} \text{ was studied.}$$

To study these reactions, known amount of ion exchange resin in the chloride form was allowed to attain equilibrium with KBr/KI solutions of different concentration at a specific temperature. From the titration readings the equilibrium constant of the chloride and iodide/bromide ions in the solution as well as on the resin are determined. From this the amount of ion exchange and equilibrium constant is evaluated. Similar experiments were carried out at various temperatures and the enthalpy of the reaction was calculated.

## EXPERIMENTAL

The resin Duolite A-113 when originally received from the manufacturer was in chloride form. But in order to ensure that it is completely in chloride form, it is conditioned with 10% potassium chloride at a rate of 1 mL per minute. It is then dried and used for further experiments.

A litre of potassium iodide (0.1M) and distilled water was kept in a thermostat at 25°C. From the stock solution 10, 15, 20, 25, 30 and 40 mL of potassium iodide and 40, 35, 30, 25, 20, and 10 mL of distilled water was transferred to six 100 mL glass bottles. In each bottle 0.5 g of resin was added and kept in a thermostat at 25°C for 4 h to attain equilibrium. After 4 h solution from each bottle was analysed by potentiometric titirations for chloride and iodide ions with silver nitrate solution. From the result equilibrium constant K was determined. Similarly experiments were carried out at different temperatures (25 to 45°C) and the enthalpy of reaction was evaluated.

Similar experiments were carried out for the reaction

$$\text{R-Cl} + \text{Br}^-_{(aq)} \rightleftharpoons \text{R-Br} + \text{Cl}^-_{(aq)}$$

## RESULTS AND DISCUSSIONS

The equilibrium constant under study is given by the expression

$$K = \frac{C_{R\text{-}X} C_{Cl^-}}{(A - C_{R\text{-}X}) C_{X^-}}$$

where K = equilibrium constant $X^- = I^-/Br^-$ ions

A = Resin capacity

$C_{R\text{-}X}$, $C_{Cl^-}$ and $C_{X^-}$ are experimentally determined where,

$C_{R\text{-}X}$ = Amount of $I^-/Br^-$ exchanged in the resin.

$C_{Cl^-}$ = Concentration of $Cl^-$ ion exchanged.

$C_{X^-}$ = Concentration of $I^-/Br^-$.

In the above equation there are two unknowns K and A by substituting values of $C_{R\text{-}X}$, $C_{Cl^-}$ and $C_{X^-}$ several simultaneous equations are obtained. By solving these equations the values of K and A are determined. The average value of A was found to be 1.27 ± 0.02 milli-equivalents per 0.5 g of resin. Similarly the equilibrium constant constant K is also calculated and was found to be 11.4 and 2.5 (Table 1 and 3)

The mean value of K at various temperatures is presented in Table 2 and Table 4. From these results the enthalpy of the ion exchange reaction is evaluated to be 17.2 kJ/mole and 36.6 kJ/mole.

The K values obtained by the above equation are fairly concordant as mentioned earlier. This is inspite of the initial $I^-$ ion concentration or the initial $Br^-$ ion concentration. These variations would have readily revealed effects of activity coefficient on the equilibrium constant. Therefore the assumptions made that the activity coefficient ratio of the ions in the solution as well as in resin is unity, seems to be valid in the above exchange equilibrium.

TABLE-1
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT 25°C

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)}$$

Amount of the ion exchange resin : 0.5 g
Volume of iodide ion solution : 50 $cm^3$

| System | Initial Concentration of $I^-$ ion per M | Final Concentration of $I^-$ ion per M $C_{I^-}$ | Change in $I^-$ ion Concentration per M | Concentration of $Cl^-$ ion exchanged per M $C_{Cl^-}$ | Amount of $I^-$ ion exchange in the resin meq 0.5 g $C_{R-I}$ | Equilibrium Constant K |
|---|---|---|---|---|---|---|
| 1. | 0.0203 | 0.0031 | 0.0172 | 0.0172 | 0.0860 | 11.5 |
| 2. | 0.0343 | 0.0123 | 0.0220 | 0.0220 | 1.1000 | 11.6 |
| 3. | 0.0421 | 0.0191 | 0.0230 | 0.0230 | 1.1500 | 11.3 |
| 4. | 0.0597 | 0.0357 | 0.0240 | 0.0240 | 1.2000 | 11.5 |
| 5. | 0.0665 | 0.0423 | 0.0242 | 0.0242 | 1.2100 | 11.4<br>Average<br>K = 11.4 |

TABLE-2
DEPENDENCE OF EQUILIBRIUM CONSTANT FOR THE REACTION AT DIFFERENT TEMPERATURES

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)}$$

Amount of ion exchange Resin : 0.5 g
Volume of iodide ion solution : 50 $cm^3$

| Temperature(°C) | 25 | 30 | 35 | 40 | 45 |
|---|---|---|---|---|---|
| Equilibrium Constant K | 11.4 | 13.1 | 15.6 | 17.3 | 19.3 |

Enthalpy of the Reaction E = slope × −2.303 × R, *where R is gas constant*

$$E = -900 \times -2.303 \times 1.987$$
$$= 4118.45 \text{ cal/mole}$$
$$= 4118.45 \times 4.18 \text{ J/mole}$$
$$= 17215.12 \text{ J/mole}$$
$$= 17.21 \text{ kJ/mole}$$

TABLE-3
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT 25°C

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)}$$

Amount of the ion exchange resin : 0.5 g
Volume of bromide ion solution : 50 $cm^3$

| System | Initial Concentration of $I^-$ ion per M | Final Concentration of $I^-$ ion per M $C_{Br^-}$ | Change in $I^-$ ion Concentration per M | Concentration of $Cl^-$ ion exchanged per M $C_{Cl^-}$ | Amount of $I^-$ ion exchange in the resin meq 0.5 g $C_{R-Br}$ | Equilibrium Constant K |
|---|---|---|---|---|---|---|
| 1. | 0.0035 | 0.0046 | 0.0110 | 0.0110 | 0.350 | 2.5 |
| 2. | 0.0039 | 0.0180 | 0.0145 | 0.0145 | 0.525 | 2.6 |
| 3. | 0.0065 | 0.0230 | 0.0166 | 0.0166 | 0.630 | 2.4 |
| 4. | 0.0074 | 0.0258 | 0.0184 | 0.0184 | 0.670 | 2.7 |
| 5. | 0.0067 | 0.0292 | 0.0195 | 0.0195 | 0.725 | 2.7 |
| | | | | | | Average K = 2.5 |

TABLE-4
DEPENDENCE OF EQUILIBRIUM CONSTANT FOR THE REACTION AT DIFFERENT TEMPERATURES

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)}$$

Amount of ion exchange Resin : 0.5 g
Volume of bromide ion solution : 50 $cm^3$

| Temperature(°C) | 25 | 30 | 35 | 40 | 45 |
|---|---|---|---|---|---|
| Equilibrium Constant K | 2.58 | 3.65 | 4.26 | 4.72 | 5.90 |

Enthalpy of the Reaction E = slope × −2.303 × R *where R is gas constant*

$$E = -1916.6 \times -2.303 \times 1.987$$
$$= 8770.47 \text{ cal/mole}$$
$$= 8770.47 \times 4.18 \text{ J/mole}$$
$$= 36660.56 \text{ J/mole}$$
$$= 36.6 \text{ kJ/mole}$$

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