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# STUDIES IN ION EXCHANGE EQUILIBRIUM USING SOME ANION EXCHANGE RESINS

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## ABSTRACT

The study on thermodynamics of anion exchange equilibrium for $Cl^-$ / $I^-$ and $Cl^-$ / $Br^-$ uni-univalent reaction systems were carried out by using four different anion exchange resins in chloride form. The equilibrium constants (K) were calculated for these systems at different temperatures by using Bonner et al. equation by taking in to account the mole fraction of ions in the resin phase. The K values were observed to increase with rise in temperature, indicating the endothermic ion exchange reactions. From the values of equilibrium constants at different temperatures, enthalpies for the above reaction systems were also calculated. The selectivity of different ion exchangers in chloride form towards $I^-$ and $Br^-$ ions were predicted on the basis of enthalpy values.

**Key words:** Ion exchange equilibrium, Equilibrium constant, Ionic selectivity, Enthalpy, Endothermic reactions, Duolite A – 162, Duolite A -113, Duolite A – 116, Duolite A - 102D.

## INTRODUCTION

Extensive work has been done by previous researchers on the properties of the ion exchange resins[1–3], to generate thermodynamic data[4–7] related to various uni-univalent and heterovalent ion exchange systems. Recently, theories explaining ion exchange equilibrium[8] between the resin phase and solution were also developed. A number of researchers have carried out equilibrium studies[9–31], extending over a wide range of composition of solution and resin phase. Attempts were also made to study the temperature effect on cation exchange systems for computing the thermodynamic equilibrium constants[9–23]. However, very little work was carried out to study the equilibrium of anion exchange systems[12, 24–29]. Therefore, in the present investigation, attempts have been made

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to study the anion exchange equilibrium, and to predict the selectivity of anion exchangers for monovalent ions on the basis of the thermodynamic data.

## EXPERIMENTAL

All the ion exchange resins as supplied by the manufacturer (Auchtel Products Ltd., India) were strongly basic quaternary ammonium $–N\text{-}(CH_3)^+$ anion exchangers in chloride form (Table 1). The exchange capacities of different ion exchange resins was experimentally determined by the standard method[32] using sodium nitrate and titrating against standard silver nitrate solution. 0.500 g of ion exchange resins in chloride form were equilibrated separately with 50 mL iodide and bromide ion solutions of different concentrations at a constant temperature of $30.0^0$C for 4h. From the results of kinetics study reported earlier [33–40]; it was observed that this duration was adequate to attain the ion exchange equilibrium. After 4 h, the different iodide / bromide ion solutions in equilibrium with ion exchange resins in chloride form were analyzed for their chloride and iodide / bromide ion concentrations by potentiometric titration with standard silver nitrate solution. From the results, the equilibrium constants K for the reactions were determined at $30.0^0$C. The equilibrium constants for the above $Cl^-$ / $I^-$ and $Cl^-$ /$Br^-$systems were determined for different temperatures in the range of $30.0^0$C to $40.0^0$C.

$$\text{R-Cl} + I^-\text{(aq.)} \rightleftharpoons \text{R-I} + Cl^-\text{(aq.)} \quad ...(1)$$

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

**Table 1. Physico-chemical properties of ion exchange resin**

| Resins | Type | Functional Groups | Exchange capacity (eq/L) | % Moisture content | Max. temp. ($^0$C) | Specific gravity |
|---|---|---|---|---|---|---|
| Duolite A - 162 | Polystyrene Macroporous resin in chloride form | Quaternary ammonium Type-2 | 1.15 | 48-53 | 75 | 1.10 |
| Duolite A -113 | Polystyrene true gel resin in chloride form | Quaternary ammonium Type-1 | 1.30 | 50-55 | 100 | 1.07 |

Cont…

| Resins | Type | Functional Groups | Exchange capacity (eq/L) | % Moisture content | Max. temp. ($^0C$) | Specific gravity |
|---|---|---|---|---|---|---|
| Duolite A - 116 | Polystyrene true gel resin in chloride form | Quaternary ammonium Type-2 | 1.30 | 47-53 | 75 | 1.10 |
| Duolite A - 102D | Polystyrene homoporous resin in chloride form | Quaternary ammonium Type-2 | 1.30 | 47-52 | 75 | 1.10 |

## RESULTS AND DISCUSSION

Earlier researchers[23] have expressed the concentration of ions in the solution in terms of molality and concentration of ions in resin in terms of mole fraction. In view of above, the experimental results obtained in the present study have been substituted in the following equation by Bonner et al.[16, 20] and the equilibrium constant K was calculated.

$$k = \frac{[N_{x^-}]\,[m_{Cl^-}]}{[N_{Cl^-}]\,[m_{x^-}]} \qquad \ldots(3)$$

Where $N_{X^-}$ = Mole fraction of $I^-$ or $Br^-$ ions exchanged on the resin

$m_{Cl^-}$ = Molality of $Cl^-$ ions exchanged in the solution

$N_{Cl^-}$ = Mole fraction of $Cl^-$ ions remained on the resin

$m_{x^-}$ = Molality of $I^-$ or $Br^-$ ions in the solution at equilibrium

Since in the present study, the solution was dilute, the molality and molarity of the ions in the solution were almost the same, with negligible error. Therefore, the molality of the ions can be easily replaced by molarity. The equilibrium constants K at a constant temperature calculated by eq. (3) are reported in Tables 2 and 3. Similarly, K values are also calculated at different temperatures (Table 4).The graph of log K was plotted against temperature (in Kelvin), which gives a straight line with a negative slope (Fig. 1, 2) from which, enthalpy of the ion exchange reactions 1 and 2 was calculated (Table 4).

**Table 2. Equilibrium constant for the ion exchange reaction**

$R-Cl + I^- (aq.) \rightleftharpoons R\text{-}I + Cl^- (aq.)$ in Duolite A-102D calculated by Bonner et al. equation

Amount of the ion exchange resin in chloride form = 0.500 g | Ion exchange capacity = 1.2 meq. / 0.5 g

Volume of iodide ion solution = 50.0 mL | Temperature = 30.0 ºC

| Initial conc. of iodide ions in solution (M) | Final conc. of iodide ions in solution (M) $m_{I^-}$ | Change in conc. of iodide ions in solution (M) | Conc. of chloride ions exchanged in solution (M) $m_{Cl^-}$ | Amount of iodide ions exchanged on the resin $C_{RI}$ | Amount of chloride ions remained on the resin $C_{RCl}$ | Mole fraction of iodide ions exchanged on the resin $N_{I^-}$ | Mole fraction of chloride ions remained on the resin $N_{Cl^-}$ | Equilibrium constant K |
|---|---|---|---|---|---|---|---|---|
| 0.020 | 0.003 | 0.017 | 0.017 | 0.850 | 0.350 | 0.708 | 0.292 | 13.680 |
| 0.030 | 0.009 | 0.021 | 0.021 | 1.030 | 0.170 | 0.858 | 0.142 | 13.280 |
| 0.040 | 0.018 | 0.022 | 0.022 | 1.100 | 0.100 | 0.917 | 0.083 | 13.380 |
| 0.050 | 0.027 | 0.023 | 0.023 | 1.130 | 0.070 | 0.942 | 0.058 | 13.260 |
| 0.060 | 0.037 | 0.023 | 0.023 | 1.145 | 0.055 | 0.954 | 0.046 | 12.960 |
| 0.080 | 0.057 | 0.023 | 0.024 | 1.165 | 0.035 | 0.971 | 0.029 | 13.800 |

Average equilibrium constant (K) = 13.39

**Table 3. Equilibrium constant for the ion exchange reaction**

$R-Cl + Br^{-}(aq.) \rightleftharpoons R-Br + Cl^{-}(aq.)$ in Duolite A-102D calculated by Bonner et al. equation

Amount of the ion exchange resin in chloride form = 0.500 g

Ion exchange capacity = 1.2 meq. / 0.5 g

Volume of bromide ion solution = 50.0 mL

Temperature = 30.0 ºC

| **Initial conc. of bromide ions in solution (M)** | **Final conc. of bromide ions in solution (M) $m_{Br^-}$** | **Change in conc. of bromide ions in solution ( M )** | **Conc. of chloride ions exchanged in solution ( M ) $m_{Cl^-}$** | **Amount of bromide ions exchanged on the resin $C_{RBr}$** | **Amount of chloride ions remained on the resin $C_{RCl}$** | **Mole fraction of bromide ions exchanged on the resin $N_{Br^-}$** | **Mole fraction of chloride ions remained on the resin $N_{Cl^-}$** | **Equilibrium constant K** |
|---|---|---|---|---|---|---|---|---|
| 0.020 | 0.003 | 0.017 | 0.017 | 0.850 | 0.350 | 0.708 | 0.292 | 13.680 |
| 0.030 | 0.009 | 0.021 | 0.021 | 1.030 | 0.170 | 0.858 | 0.142 | 13.280 |
| 0.040 | 0.018 | 0.022 | 0.022 | 1.100 | 0.100 | 0.917 | 0.083 | 13.380 |
| 0.050 | 0.027 | 0.023 | 0.023 | 1.130 | 0.070 | 0.942 | 0.058 | 13.260 |
| 0.060 | 0.037 | 0.023 | 0.023 | 1.145 | 0.055 | 0.954 | 0.046 | 12.960 |
| 0.080 | 0.057 | 0.023 | 0.024 | 1.165 | 0.035 | 0.971 | 0.029 | 13.800 |

Average equilibrium constant (K) = 13.39

**Table 4. Effect of temperature on equilibrium constant (K) of uni-univalent ion exchange reactions**

Amount of the ion exchange resin in chloride form = 0.500 g    Volume of iodide / bromide ion solution = 50.0 mL

| Ion exchange reactions | Ion exchange resins | Enthalpy of the ion exchange reactions (kJ/mol) | Temperature (°C) | | |
|---|---|---|---|---|---|
| | | | 30 | 35 | 40 |
| $R\text{-}Cl + I^- (aq.) \rightleftharpoons R\text{-}I + Cl^- (aq.)$ | Duolite A 162 | 28.69 | 6.82 | 8.80 | 9.10 |
| | Duolite A 102D | 17.20 | 13.39 | 14.47 | 15.61 |
| | Duolite A 113 | 14.90 | 13.90 | 15.60 | 17.30 |
| | Duolite A 116 | 13.70 | 14.48 | 15.88 | 17.40 |
| $R\text{-}Cl + Br^- (aq.) \rightleftharpoons R\text{-}Br + Cl^- (aq.)$ | Duolite A 162 | 38.40 | 2.32 | 3.16 | 4.29 |
| | Duolite A 102D | 36.00 | 3.23 | 4.01 | 4.60 |
| | Duolite A 113 | 32.60 | 3.64 | 4.26 | 4.72 |
| | Duolite A 116 | 31.60 | 3.86 | 4.52 | 4.90 |

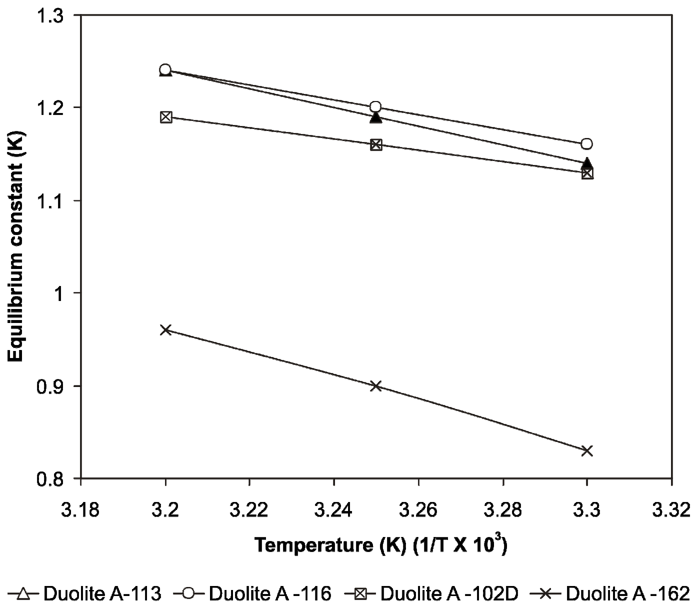


**Fig. 1: Variation of equilibrium constant with temperature for the ion exchange reaction (1) for strongly basic anion exchange resins**

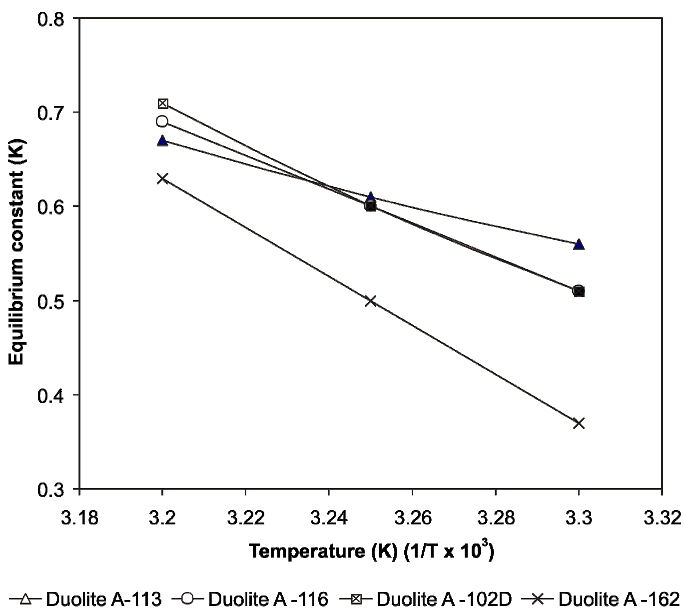


**Fig. 2 Variation of equilibrium constant with temperature for the ion exchange reaction (2) for strongly basic anion exchange resins**

# CONCLUSIONS

Bonner and Pruett [16] studied the temperature effect on uni-univalent exchanges involving some divalent ions. In all divalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. However, in the present investigation, the equilibrium constant K increases with rise in temperature (Table 4), indicating the endothermic ion exchange reactions[41]. From the results, it appears that for $Cl^-$ /$I^-$ exchange, the equilibrium constant (K) values are higher than that for $Cl^-$ / $Br^-$ exchange and the enthalpy of $Cl^-$ / $I^-$ exchange is low as compared to $Cl^-$ / $Br^-$ exchange reactions. This low enthalpy and higher K values for $Cl^-$ / $I^-$ is responsible for the preferential selectivity of resins in chloride form for iodide ions as compared to bromide ions in solution. The equilibrium constants K for uni-univalent ion exchange reactions (1) and (2) involving different ion exchange resins, increases in the order Duolite A 162 < Duolite A 102D < Duolite A–113 < Duolite A–116. Therefore, the selectivity of these ion exchange resins in chloride form towards $I^-$ and $Br^-$ ions increases in the same order. Similarly, the enthalpy values for the reactions (1) and (2), increases in the order Duolite A–116 < Duolite A–113 < Duolite A–102D < Duolite A 162. The high K and low enthalpy values indicate that Duolite A–116 ion exchange resins are more superior than Duolite A–162.

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