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# STUDIES OF SOME UNI-UNIVALENT ION EXCHANGE REACTION SYSTEMS USING STRONGLY BASIC ANION EXCHANGE RESIN DUOLITE 101-D

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**ABSTRACT**
**The selectivity behaviour of ion exchange resin Duolite 101-D in chloride form for inorganic anions like iodide and bromide ions was predicted on the basis of thermodynamic data. The equilibrium constant *K* calculated for uni-univalent ion exchange reaction systems were observed to decrease with rise in temperature indicating the exothermic exchange reactions having the enthalpy values -12.77 and -24.64 kJ/mol respectively. The low enthalpy and higher *K* values for iodide ion exchange reaction indicates more affinity of the resin for iodide ions as compared to that for bromide ions also in the solution.**
**Keywords:** *Ion exchange equilibrium; Equilibrium constant; Enthalpy; Exothermic reactions; Anion exchange; Duolite 101-D.*

## INTRODUCTION

There are number of liquid processes waste streams at chemical processing, nuclear power plants, nuclear fuel reprocessing plants and nuclear research centers that require treatment for removal of various contaminants. One of the most common treatment methods for such aqueous streams is the use of ion exchange, which is a well developed technique that has been employed for many years in chemical as well as nuclear industries. While designing an ion exchange liquid waste processing system it is desirable to have an adequate knowledge about the distribution coefficient values and the selectivity behaviour of these ion exchange resin towards different ions present in liquid waste. Generally the selected ion exchange materials must be compatible with the chemical nature of the waste such as type and concentration of ionic species present as well as the operating parameters notably temperature. Considerable work was done by previous researchers to study the properties of the ion exchange resins, to generate thermodynamic data related to various uni-univalent and heterovalent ion exchange systems[1-7]. Recently theories explaining ion exchange equilibrium between the resin phase and solution were also developed[8]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase[9-31]. Attempts were also made to study the equilibrium of cation exchange systems[9-23]. However very little work was carried out to study the temperature effect on anion exchange systems[12, 24-31] for computing the thermodynamic equilibrium constants. Therefore in the present investigation attempts were made to study the thermodynamics of uni-univalent anion exchange equilibrium, the results of which will be of considerable use in explaining the selectivity of ion exchanger for various univalent ions in solution.

## EXPERIMENTAL

The ion exchange resin Duolite 101-D as supplied by the manufacturer (Auchtel Products Ltd., Mumbai) was a strongly basic anion exchange resin in chloride form of 16-50 mesh size.

**Table-1: Equilibrium constant for the uni-univalent ion exchange reactions using ion exchange resin Duolite 101-D.** Amount of the ion exchange resin in chloride form = 0.500g, Ion exchange capacity =1.5 meq./0.500g, Volume of external ionic solution =50.0mL

| Reaction 1 | | | | | Reaction 2 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Temperature =35.0 $^{0}$C** | | | | | | | | | |
| **Initial conc. of iodide ion solution (M)** | **Final conc. of $I^-$ ions ( M ) $C_{I^-}$** | **Conc. of $Cl^-$ ions exchanged ( M ) $C_{Cl^-}$** | **Amount of $I^-$ ions exchanged on the resin meq./ 0.5 g $C_{RI}$** | **Equilibrium constant K** | **Initial Conc. of bromide ion solution (M)** | **Final conc. of $Br^-$ ions ( M ) $C_{Br^-}$** | **Conc. of $Cl^-$ ions exchanged ( M ) $C_{Cl^-}$** | **Amount of $Br^-$ ions exchanged on the resin meq./ 0.5 g $C_{RBr}$** | **Equilibrium constant K** |
| 0.010 | 0.00040 | 0.00955 | 0.4800 | 10.23 | 0.010 | 0.00090 | 0.00907 | 0.4550 | 4.00 |
| 0.020 | 0.00160 | 0.01835 | 0.9190 | 15.48 | 0.020 | 0.00325 | 0.01672 | 0.8375 | 5.65 |
| 0.025 | 0.00250 | 0.02242 | 1.1250 | 21.24 | 0.025 | 0.00460 | 0.02036 | 1.0200 | 7.78 |
| 0.030 | 0.00425 | 0.02571 | 1.2875 | 24.92 | 0.030 | 0.00600 | 0.02395 | 1.2000 | 11.97 |
| 0.040 | 0.01030 | 0.02968 | 1.4850 | 37.21 | 0.040 | 0.01050 | 0.02946 | 1.4750 | 33.11 |
| **Average equilibrium constant (*K*) =21.82** | | | | | **Average equilibrium constant (*K*) = 12.50** | | | | |

| Temperature $^{O}$C | 30.0 | 35.0 | 40.0 | 45.0 | Enthalpy (kJ/mol) | 30.0 | 35.0 | 40.0 | 45.0 | Enthalpy (kJ/mol) |
|---|---|---|---|---|---|---|---|---|---|---|
| Equilibrium Constant (*K*) | 29.28 | 21.82 | 18.03 | 16.01 | -12.77 | 14.54 | 12.50 | 11.35 | 9.88 | -24.64 |

For the present investigation, the resin grains of 30-40 mesh size were used. The conditioning of the resins in chloride form was done by usual methods using 10% potassium chloride solution[25-28].

The study of uni-univalent ion exchange equilibrium was performed by equilibrating 0.500 g of ion exchange resins in chloride form with iodide and bromide ion solution in the temperature range of 30.0$^0$C to 45.0$^0$C for 3 h.

From the results of kinetics study reported earlier it was observed that this duration was adequate to attain the ion exchange equilibrium[32-43]. After 3 h the concentration of chloride ions exchanged in the solution; iodide and bromide ions left in the solution was estimated by potentiometric titration against standard 0.1 N $AgNO_3$ solutions. From the results the equilibrium constant ***K*** for the following reactions was calculated.

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

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

The chloride, bromide and iodide ion solutions used in the entire experimental work where prepared by dissolving their respective analytical grade potassium salts in distilled deionised water. In the present study, a semi-micro burette having an accuracy of 0.05 mL was used in the titrations and the titration readings were accurate to ± 0.05 mL. Considering the magnitude of the titer values, the average equilibrium constants reported in the experiment are accurate to ± 3%.

## RESULTS AND DISCUSSION

Therefore the equilibrium constants for the reactions (1 and 2) can be given by the expression-

$$K = \frac{C_{RX} \cdot C_{Cl^-}}{(A - C_{RX}) \cdot C_{X^-}} \quad (3)$$

where A is the ion exchange capacity of the resin, $X^-$ represents $I^-$ or $Br^-$ ions.

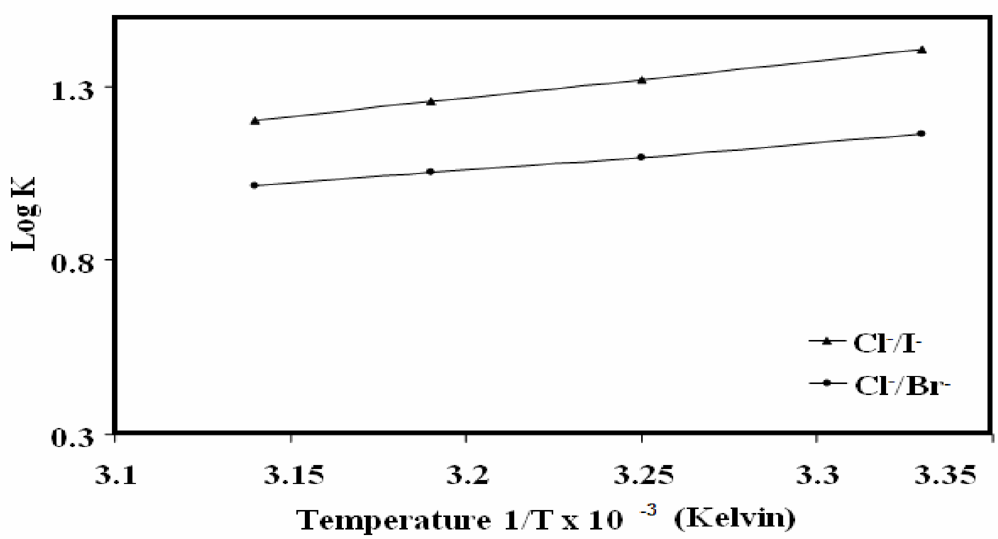


**Fig.-1**: Variation of Equilibrium Constant with Temperature for Uni-Univalent Ion Exchange Reactions using ion exchange resin Duolite101-D.

Amount of the ion exchange resin in $Cl^-$ form = 0.500 g; Ion exchange capacity =1.5 meq. / 0.500g; Volume of $I^-$ / $Br^-$ ion solution = 100.0 mL; Temperature range = 30.0 $^0$C-45.0 $^0$C

For different concentrations of $X^-$ ions in solution at a given temperature, ***K*** values were calculated from which average value of ***K*** for that set of experiment was calculated (Table-1). Similar values of ***K*** were calculated for $Cl^-/I^-$ and $Cl^-/Br^-$ systems for different temperatures (Table-1). The enthalpy value for the ion exchange reactions 1 and 2 were calculated by plotting the graph of log ***K*** against 1/T (Figure 1). Bonner and Pruett[16] studied the temperature effect on uni-univalent exchanges involving some bivalent ions. In all bivalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. Similarly in the present investigation, for the uni-univalent exchange reactions the value of equilibrium constant decreases with rise in temperature giving negative enthalpy values (Table-1), indicating the exothermic ion exchange reactions. The low enthalpy and higher ***K*** values for $Cl^-$ / $I^-$ exchange as compared to that for $Cl^-$ / $Br^-$ exchange (Table-1), indicate that the resins in $Cl^-$ form are having more affinity for $I^-$ ions in solution as compared to that for $Br^-$ ions also in the solution.

## CONCLUSION

Various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy of ion exchangers in various technical applications. The selection of an appropriate ion exchange material for the specific industrial and research application is possible on the basis of information provided by the manufacturer. However, it is expected that the data obtained from the actual experimental trials will prove to be more helpful. The thermodynamic data obtained in the present experimental work will be useful to understand the selectivity behaviour of ion exchange resins for various ions in solution thereby helping in characterization of resins.

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