

# Thermodynamics of uni-univalent $H^+/K^+$ and uni-bivalent $H^+/Ca^{2+}$ ion exchange reactions using nuclear grade resin Indion-223

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## ABSTRACT

The present paper deals with the thermodynamic of uni-univalent and uni-bivalent ion exchange reactions using nuclear grade anion exchange resin Indion-223. It was observed that with rise in temperature the equilibrium constants  $K$  values for  $H^+/K^+$  uni-univalent ion exchange reaction increases from 0.01710 to 0.02374. Similarly for  $H^+/Ca^{2+}$  uni-bivalent ion exchange reaction the equilibrium constants  $K$  values increases from 0.000397 to 0.000639. The increase in  $K$  values with rise in temperature for both the reactions indicates its endothermic nature having the enthalpy change values of 22.72 and 38.92 kJ/ mol respectively. The technique used here can be extended further to standardise the process parameters in order to bring about the efficient separation of the desired ionic species from the solution.

**Keywords:** ion exchange; nuclear grade resins; cation exchangers; enthalpy change; standard equilibrium constant; Indion-223

## 1. INTRODUCTION

In the past decade inorganic ion exchange materials have emerged as an increasingly important replacement or complement for conventional organic ion exchange resins. However in number of cases, for specific physical and chemical reasons, organic resins cannot be replaced by inorganic ion exchangers and the use of synthetic organic ion exchange resins continued globally. The main advantages of synthetic organic ion exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. Organic ion exchange resins are used in a number of chemical decontamination or cleaning processes and in nuclear industries for removal of radionuclide [1-5]. In recent years, use of organic ion exchange resins as a heterogeneous catalyst in liquid phase reactions has greatly increased due to their advantages such as high activity, selectivity, reusability, ease of separation etc. Extensive work was done by previous researchers to synthesis various organic ion exchange resins for specific applications and their

characterization [6,7]. Efforts are also made to develop new organic ion exchangers for their specific applications in nuclear industries are continuing and various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy of their application in various technological applications [8,9]. For proper selection of ion exchange resin, it is essential to have adequate knowledge regarding their physical and chemical properties, which forms the complementary part of resin characterization study [10-55]. Generally the selected ion exchange materials must be compatible with the chemical nature of the liquid waste such as pH, type of ionic species present as well as the operating parameters, in particular temperature [10-55]. However, since the selection of the appropriate ion-exchange material depends on the needs of the system, it is expected that the data obtained from the actual experimental trials will prove to be more helpful. Hence in the present study attempt was made to understand the thermodynamic of uni-univalent and uni-bivalent ion exchange reaction using nuclear grade cation exchange resin Indion 223.

## 2. MATERIALS AND METHODS

### 2. 1. Glasswares

All apparatus used in the study were made up of Pyrex or Coming glass. Micro-burette of 0.02 mL accuracy was used for the entire experimental work.

### 2. 2. Analytical balance

For weighing the sample above 25 mg, analytical balance of 0.1 mg sensitivity was used. Metler balance was used for weighing the samples less than 25 mg.

### 2. 3. Potentiometer

Digital potentiometer of Equiptronics make having saturated calomel electrode as a reference electrode and platinum electrode in contact with quinhydrone as an indicator electrode was used in the experimental work.

All Chemicals used were of analytical reagent (AR) grade. Distilled deionised water was used throughout the experiments for solution preparation.

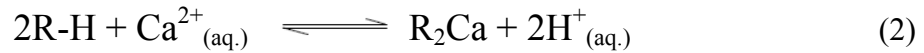
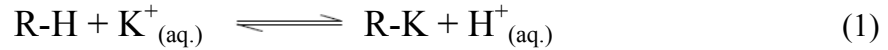
### 2. 4. Ion exchange Resin

The ion exchange resin Indion-223 as supplied by the manufacturer (Ion Exchange India Limited, Mumbai) was a strongly acidic gel type nuclear grade anion exchange resin in  $H^+$  form having styrene divinyl benzene cross-linking. The resin was having  $-SO_3^-$  functional group, having moisture content of 50-55 %. The operational pH range was 0-14 and maximum operating temperature was 120 °C.

The soluble non-polymerized organic impurities of the resin were removed by repeated Soxhlet extraction using distilled deionised water and occasionally with methanol. In order to ensure complete conversion of resins in  $H^+$  form, the resins were conditioned with 0.1 N HCl in a conditioning column. The resins were further washed with distilled deionised water until the washings were free from  $H^+$  ions. The resins in  $H^+$  form were air dried over  $P_2O_5$  and used for further studies.

The ion exchange resins in  $H^+$  form were equilibrated separately with  $K^+$  and  $Ca^{2+}$  ions solution of different but known concentrations in the temperature range of 35.0-45.0 °C for 3 h. After 3 h the concentration of  $H^+$  ions exchanged in the solution was determined

experimentally by potentiometric titration against standard 0.1 N NaOH solution. From the knowledge of amount of  $H^+$  ions exchanged in the solution and  $K^+$  and  $Ca^{2+}$  ions exchanged on the resin; equilibrium constants ( $K$ ) for the reactions



were calculated. From the  $K$  values obtained at different temperatures, the enthalpy values of the above uni-univalent and uni-bivalent ion exchange reactions were calculated.

### 3. RESULTS AND DISCUSSION

The equilibrium constants ( $K$ ) for reaction 1 were calculated by the equation

$$K = \frac{C_{R-X} \cdot C_{H^+}}{(A - C_{R-X}) \cdot C_{X^+}} \quad (3)$$

here, R represent the resin phase;  $A$  is the ion exchange capacity of the resin; X represents  $K^+$  ions.

For different concentrations of  $K^+$  ions in solution at a given temperature,  $K$  values were calculated and an average of  $K$  for this set of experiment was obtained (Table 1).

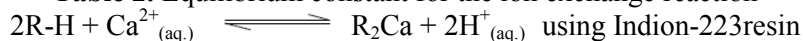
**Table 1.** Equilibrium constant for the ion exchange reaction  
 $R-H + K^+_{(aq)} \rightleftharpoons R-K + H^+_{(aq)}$  using Indion-223 resin  
 Amount of the ion exchange resin in  $H^+$  form = 0.500 g, Ion exchange capacity = 2.91 meq./0.5 g,  
 Temperature = 40.0 °C.

System	Initial concentration of $K^+$ ion (M)	Final concentration of $K^+$ ions (M) $C_{K^+}$	Change in $K^+$ ion concentration	Concentration of $H^+$ ions exchanged (M) $C_{H^+}$	Amount of $K^+$ ions exchanged on the resin meq./0.5 g $C_{RK}$	Equilibrium constant $K \cdot 10^{-2}$
1	0.0100	0.0063	0.0037	0.0037	0.1836	3.908
2	0.0500	0.0441	0.0059	0.0059	0.2972	1.518
3	0.1000	0.0937	0.0063	0.0063	0.3163	0.815
Average K						2.080

Similar  $K$  values were calculated for the reaction 1 performed at different temperatures (Table 2). From the slope of the graph of  $\log K$  against  $1/T$  (in Kelvin) the enthalpy change of the ion exchange reaction 1 was calculated (Figure 1). The equilibrium constant  $K$  values for

the reactions were found to increase with rise in temperature indicating endothermic ion exchange reactions having the enthalpy change value of 22.72 kJ/ mol (Table 3).

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



Amount of the ion exchange resin in  $H^+$  form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g,  
Temperature = 40.0 °C.

Initial Concentration of $Ca^{2+}$ ions in solution (M)	Equilibrium concentration in solution		Amount of the ions in the resin meq./0.500 g		$\sqrt{\text{Ionic Strength}}$	$\frac{(\gamma_{H^+})^2}{\gamma_{Ca^{2+}}}$	Apparent Equilibrium Constant $K_{app.}$	$\frac{(\gamma_{R_2Ca})}{(\gamma_{RH})^2} = \frac{K_{std.}}{K_{app.}}$
	$H^+$ (M)	$Ca^{2+}$ (M)	$H^+$	$Ca^{2+}$				
0.0100	0.0069	0.0066	2.33	0.345	0.1629	1.464	0.00067	0.939
0.0500	0.0082	0.0459	2.20	0.410	0.3821	2.451	0.00030	2.097
0.1000	0.0087	0.0956	2.15	0.436	0.5436	3.580	0.00026	2.420

Equilibrium constant in the standard state ( $K_{std}$ ) = 0.000629

**Table 3.** Thermodynamics of ion exchange reactions using Indion-223 resin.

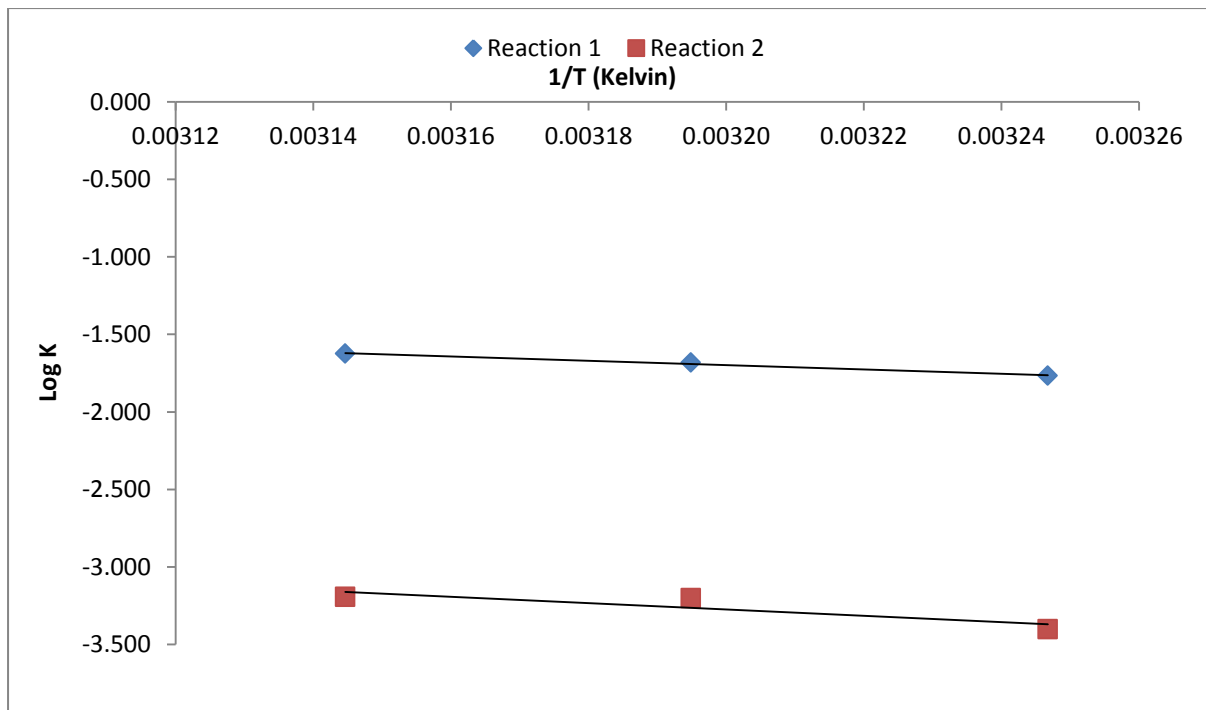
Reactions	1			2		
	Temperature (°C)	35.0	40.0	45.0	35.0	40.0
Equilibrium Constant	0.01710	0.02080	0.02374	0.000397	0.000629	0.000639
Enthalpy Change $\Delta H^0$ (kJ·mol <sup>-1</sup> )	22.72			38.92		

The equilibrium constants for the ion exchange reaction 2 were calculated by the equation

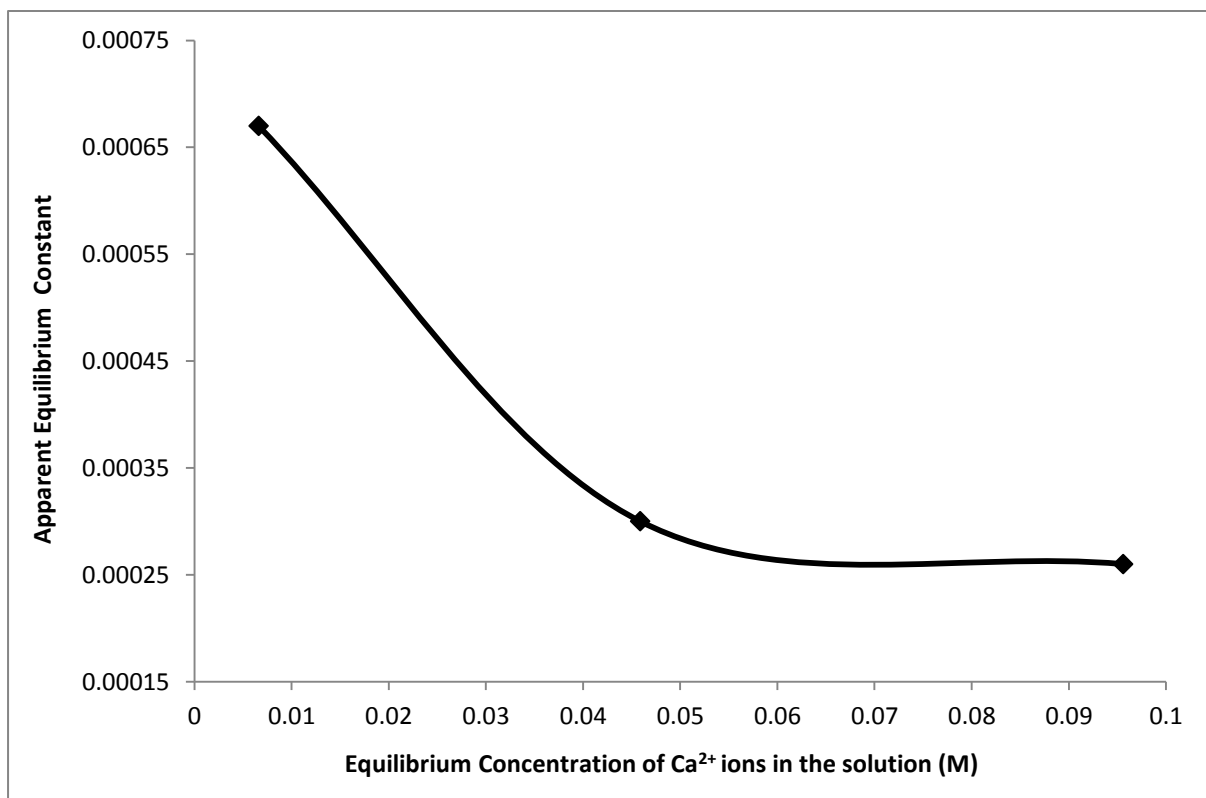
$$K_{app.} = \frac{(CR_2Y \cdot \gamma_{R_2Y}) (C_{H^+} \cdot \gamma_{H^+})^2}{(CRH\gamma_{RH})^2 (CY^{2+} \cdot \gamma_{Y^{2+}})} \quad (4)$$

here, R represent the resin phase and  $Y = Ca^{2+}$  ions.

The apparent equilibrium constants ( $K_{app.}$ ) calculated by the equation (4) were plotted versus the equilibrium concentrations of the  $Ca^{2+}$  ions in the solution (Figure 2). Lower the equilibrium concentration of the  $Ca^{2+}$  ion, lower would be its concentration in the resin and in the limiting case of zero equilibrium concentration of the  $Ca^{2+}$  ion in the solution, the resin would be in its standard state.



**Figure 1.** Variation of equilibrium constant with temperature of uni-univalent and uni-bivalent ion exchange reactions performed by using Indion-223 resins.



**Figure 2.** Variation of apparent equilibrium constant with equilibrium concentration of Ca<sup>2+</sup> ions in solution for the ion exchange reaction (2) using ion exchange resin Indion-223.

Therefore on extrapolating the above curve to zero equilibrium concentration of  $\text{Ca}^{2+}$  ion in the solution, the equilibrium constant in the standard state,  $K_{std}$  was obtained. Having thus obtained the equilibrium constant in the standard state, the activity coefficient ratio of ions  $\gamma_{R_2Y}/(\gamma_{RH})^2$  at any finite equilibrium concentration of  $\text{Ca}^{2+}$  ion in the solution was calculated as the ratio of  $K_{std}/K_{app}$  (Table 2). From the slope of the graph of  $\log K_{std}$  against  $1/T$  (in Kelvin), the enthalpy change of the ion exchange reaction 2 was calculated (Figure 1). The equilibrium constant  $K_{std}$  values for the reaction 2 were found to increase with rise in temperature indicating endothermic ion exchange reactions having the enthalpy change value of 38.92 kJ/mol (Table 3).

Amount of the ion exchange resin in  $\text{H}^+$  form = 0.500 g, Ion exchange capacity = 3.02meq./0.5 g, Temperature = 40.0 °C.

#### 4. CONCLUSION

Ion exchange technology is widely being used for separation of particular ionic species in presence of other. The selection of suitable ion exchange material is still more critical when the process involves separation of two or more chemically same ionic species in the solution. Under such critical conditions the present experimental technique will be useful in deciding about the selection of suitable ion exchange material. The technique used here can be extended further to standardise the process parameters in order to bring about the efficient separation of the desired ionic species from the solution.

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