

Comparative study of uni-univalent H^+/Na^+ 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 ion exchange equilibrium studies of uni-univalent and uni-bivalent ion exchange reactions using nuclear grade anion exchange resin Indion-223 in H^+ form towards Na^+ and Ca^{2+} ions in the solution. It was observed that with rise in temperature the equilibrium constants K values for H^+/Na^+ uni-univalent ion exchange reaction increases from 0.01389 to 0.01855. 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 equilibrium constant values with rise in temperature indicate endothermic ion exchange reactions having the enthalpy change values of 25.55 and 38.92 kJ/mol respectively.

Keywords: ion exchange reactions; nuclear grade resins; cation exchange resins; enthalpy; equilibrium constant; Indion-223

1. INTRODUCTION

Ion exchange materials are insoluble polymeric substances containing loosely held ions which are exchanged with other ions in solutions when they come in contact with each other. These exchanges take place reversibly without any physical alteration to the ion exchange material. Nowadays, ion exchange resins are not only used for separation but also used as a catalyst. Efforts to develop new organic ion exchangers for specific applications are continuing [1,2] and various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy of their application in various technological applications [3-11]. The selection of an appropriate ion exchange material for treatment of liquid waste is possible on the basis of information provided by the manufacturer. 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. Further, 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 [12-35].

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 [36-42]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed [43]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase [44-70]. Attempts were also made to study the temperature effect on anion exchange systems [47,59-70] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems [44-58]. Therefore, in the present investigation, attempts were made to understand the ionic selectivity of the nuclear grade cation exchange resin Indion-223 based on the thermodynamic equilibrium constants.

2. MATERIALS AND METHODS

Glasswares: All apparatus used in the study were made up of Pyrex or Coming glass. Microburette of 0.02 mL accuracy was used for the entire experimental work.

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.

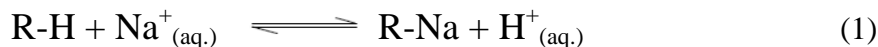
Potentiometer: Digital potentiometer of Equiptronics make having saturated calomel electrode as a reference electrode and platinum electrode in contact with quinhydrone as an indicator electrode was used in the experimental work.

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

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 Na^+ 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 Na^+ and Ca^{2+} ions exchanged on the resin; equilibrium constant (K) for the reactions



were calculated. From the K values obtained at different temperatures, the enthalpy change 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

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

here, R represent the resin phase; A is the ion exchange capacity of the resin; X represents Na^+ ions. For different concentrations of Na^+ 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).

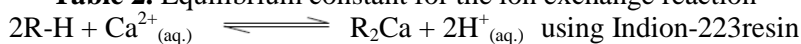
Table 1. Equilibrium constant for the ion exchange reaction
 $\text{R-H} + \text{Na}^+_{(\text{aq.})} \rightleftharpoons \text{R-Na} + \text{H}^+_{(\text{aq.})}$ using Indion-223resin
 Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 2.91 meq./0.5 g,
 Temperature = 35.0 °C.

System	Initial concentration of Na^+ ion (M)	Final concentration of Na^+ ions (M) C_{Na^+}	Change in Na^+ ion concentration	Concentration of H^+ ions exchanged (M) C_{H^+}	Amount of Na^+ ions exchanged on the resin meq./0.5 g C_{RNa}	Equilibrium constant $K \times 10^{-2}$
1	0.0100	0.0071	0.0029	0.0029	0.1427	2.057
2	0.0500	0.0444	0.0056	0.0056	0.2844	1.378
3	0.1000	0.0940	0.0060	0.0060	0.2997	0.732
Average K						1.389

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 for the ion exchange reaction 1 was calculated (Figure 1).

The equilibrium constant K values for the reactions are found to increase with rise in temperature indicating endothermic ion exchange reactions having the enthalpy change value of 25.55 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 = 3.02meq./0.5 g,
Temperature = 35.0 °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		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	0.006	0.007	2.42	0.300	0.1643	1.47	0.00039	1.0186
0.0500	0.008	0.046	2.22	0.400	0.3821	2.45	0.00028	1.4188
0.1000	0.008	0.096	2.22	0.400	0.5441	3.58	0.00019	2.0908

Equilibrium constant in the standard state (K_{std.}) = 0.000397

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

Reactions	1			2		
	Temperature (°C)	35.0	40.0	45.0	35.0	40.0
Equilibrium Constant (K _{std.})	0.01389	0.01624	0.01855	0.000397	0.000629	0.000639
Enthalpy Change ΔH ⁰ (kJ·mol ⁻¹)	25.55			38.92		

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

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

here, R represent the resin phase and Y = Ca²⁺ ions.

The apparent equilibrium constants (K_{app.}) calculated by the equation (4) were plotted versus the equilibrium concentrations of the Ca²⁺ ions in the solution (Figure 2). Lower the equilibrium concentration of the Ca²⁺ ion, lower would be its concentration in the resin and in the limiting case of zero equilibrium concentration of the Ca²⁺ ion in the solution, the resin would be in its standard state. Therefore on extrapolating the above curve to zero equilibrium concentration of Ca²⁺ ion in the solution, the equilibrium constant in the standard state, K_{std.} was obtained.

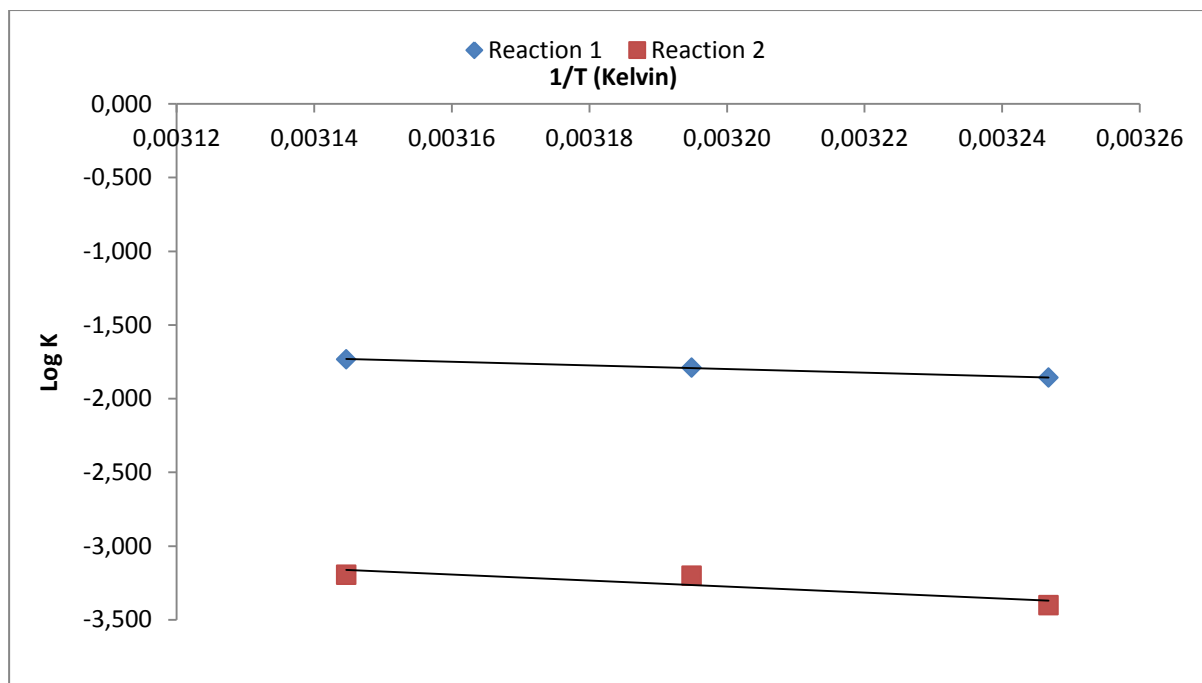


Figure 1. Variation of equilibrium constant with temperature of uni-univalent and uni-bivalent ion exchange reactions performed by using Indion-223 resins.

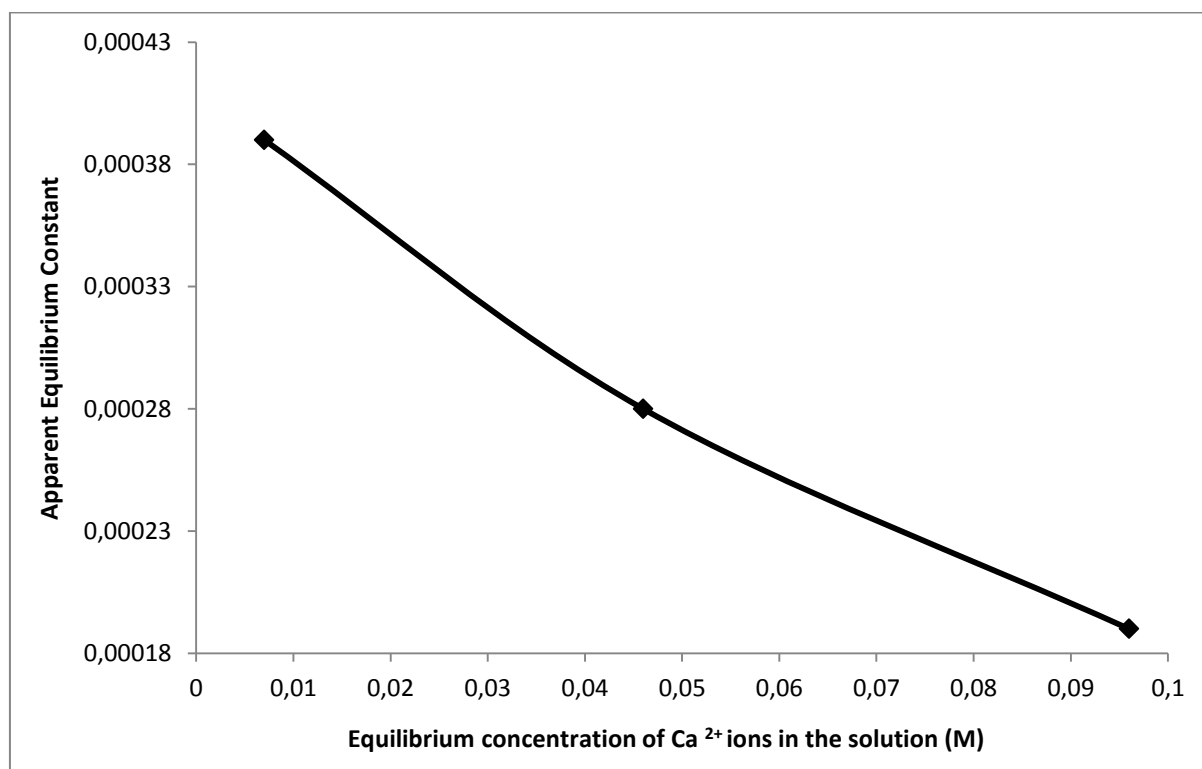


Figure 2. Variation of apparent equilibrium constant with equilibrium concentration of Ca²⁺ ions in solution for the ion exchange reaction (2) using ion exchange resin Indion-223. Amount of the ion exchange resin in H⁺ form = 0.500 g, Ion exchange capacity = 3.02meq./0.5 g, Temperature = 35.0 °C.

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 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 for 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).

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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