

# Study on preferential selectivity of nuclear grade resin Indion-223 towards some bivalent ions

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## ABSTRACT

In the present paper attempts are made to understand the selectivity of nuclear grade cation exchange resin Indion-223 in H<sup>+</sup> form towards Ca<sup>2+</sup> and Mg<sup>2+</sup> bivalent ions in the solution based on thermodynamic concept. It was observed that with rise in temperature the equilibrium constant *K* values for H<sup>+</sup>/Ca<sup>2+</sup> uni-bivalent ion exchange reactions increases from 0.000397 to 0.000639. Similarly for H<sup>+</sup>/Mg<sup>2+</sup> uni-bivalent ion exchange reactions the equilibrium constant *K* values increases from 0.000177 to 0.000333. The increase in equilibrium constant values with rise in temperature indicate endothermic ion exchange reactions having the enthalpy change values of 38.92 and 51.46 kJ/ mol respectively. The difference in *K* values and enthalpy values were used to predict the selectivity behaviour of the resin towards the Ca<sup>2+</sup> and Mg<sup>2+</sup> bivalent ions in the solution. The thermodynamic concept of the present study can be applied to understand the selectivity behaviour of different nuclear as well as non-nuclear grade resins towards wide range of ionic species present in the exchanging liquid medium.

**Keywords:** bivalent exchange reactions; nuclear grade resins; cation exchange; reaction thermodynamics; enthalpy change; ionic selectivity; equilibrium constant; Indion-223

## 1. INTRODUCTION

Since their development, synthetic organic ion exchange resins are mainly used for water treatment, for instance in the preparation of demineralized water. Ion exchange resins are also having many industrial applications like purification and separations. As far as nuclear industry is concerned, one specific application is the purification of coolant and / or moderator in nuclear reactors. Particularly for CANDU- type reactors, heavy water is used as a moderator, and it is kept in high purity conditions by ion exchange resins in a purification loop. The resins remove both radiological and non-radiological impurities [1]. In nuclear power plants these resins are widely applied in- primary coolant (water) purification, treatment of primary effluents and fuel storage pond water, steam generator blow-down demineralization, for treatments of liquid waste and drainage water, purification of boric acid for recycling, condensate polishing (for nuclear power plants with boiling water reactors) [2-

6]. Inorganic ion exchangers often have the advantage of a much greater selectivity than organic resins for certain radiologically important species, such as caesium and strontium. These inorganic materials may also prove to have advantages with respect to immobilization and final disposal when compared with organic ion exchangers. However, in nuclear power plant operations the currently available inorganic exchangers cannot entirely replace conventional organic ion exchange resins, especially in high purity water applications or in operations in which the system chemistry must be controlled through the maintenance of dissolved species such as lithium ions or boric acid [7].

These organic ion exchange resins are very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid and have proved to be reliable and effective for the control of both the chemistry and radiochemistry of water coolant systems at nuclear power plants and also for processing some liquid radioactive waste [7]. As a result organic ion exchange resins are developed extensively [8-11] and various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy in various technological applications [5,6,12,13]. Development and synthesis of new organic ion exchange resins is usually followed by their characterization [14-37]. 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 [38-76].

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 [77-83]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed [84]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase [38-41,85-111]. Attempts were also made to study the temperature effect on anion exchange systems [38-41,100-111] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems [85-99]. Therefore, in the present investigation, thermodynamics study of uni-bivalent ion exchange reactions was made to predict the selectivity behaviour of strongly acidic gel type nuclear grade cation exchange resin Indion-223 towards some divalent ions in the solution.

## 2. MATERIALS AND METHODS

**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.

**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.

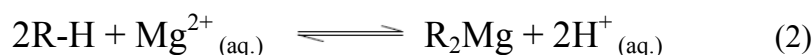
All Chemicals used were of analytical reagent (AR) grade. Distilled deionised water was used throughout the experiments for solution preparation.

**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<sup>+</sup> form having styrene divinyl benzene cross-linking. The resin was having

-SO<sub>3</sub><sup>-</sup> 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<sup>+</sup> 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<sup>+</sup> ions. The resins in H<sup>+</sup> form were air dried over P<sub>2</sub>O<sub>5</sub> and used for further studies.

The ion exchange resins in H<sup>+</sup> form were equilibrated separately with Ca<sup>2+</sup> and Mg<sup>2+</sup> 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<sup>+</sup> 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<sup>+</sup> ions exchanged in the solution and Ca<sup>2+</sup> and Mg<sup>2+</sup> 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-bivalent ion exchange reactions were calculated.

### 3. RESULTS AND DISCUSSION

The equilibrium constants for the ion exchange reactions 1 and 2 were calculated by the equation

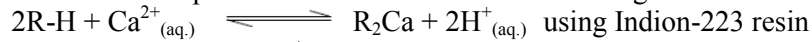
$$K_{app.} = \frac{(\text{CR}_2\text{Y} \cdot \gamma_{\text{R}_2\text{Y}}) (\text{C}_{\text{H}^+} \cdot \gamma_{\text{H}^+})^2}{(\text{CRH}\gamma_{\text{RH}})^2 (\text{CY}^{2+} \cdot \gamma_{\text{Y}^{2+}})} \quad (3)$$

here, R represent the resin phase and Y = Mg<sup>2+</sup> or Ca<sup>2+</sup> bivalent ions.

The apparent equilibrium constants (*K<sub>app.</sub>*) calculated by the equation (3) were plotted versus the equilibrium concentrations of the bivalent ions in the solution (Figure 1 and 2). Lower the equilibrium concentration of the bivalent ion, lower would be its concentration in the resin and in the limiting case of zero equilibrium concentration of the bivalent ion in the solution, the resin would be in its standard state. Therefore on extrapolating the above curve to zero equilibrium concentration of bivalent ion in the solution, the equilibrium constant in the standard state, *K<sub>std.</sub>* was obtained. Having thus obtained the equilibrium constant in the standard state, the activity coefficient ratio of ions  $\gamma_{\text{R}_2\text{Y}}/(\gamma_{\text{RH}})^2$  at any finite equilibrium concentration of bivalent ion in the solution was calculated as the ratio of *K<sub>std.</sub>*/*K<sub>app.</sub>* (Tables 1 and 2). From the slope of the graph of log *K<sub>std.</sub>* against 1/T (in Kelvin), the enthalpy change of the ion exchange reactions 1 and 2 were calculated (Figure 3). The equilibrium constant *K<sub>std.</sub>* values for the reactions 1 and 2 were found to increase with rise in temperature indicating

endothermic ion exchange reactions having the enthalpy change values of 38.92 and 51.46 kJ/mol respectively (Table 3). The low enthalpy and high equilibrium values for  $H^+/Ca^{2+}$  as compared to that obtained for  $H^+/Mg^{2+}$  exchange indicates preferential selectivity of the Indion-223 resins in  $H^+$  form towards  $Ca^{2+}$  ions than that towards  $Mg^{2+}$  ions when both of them are present in the same solution

**Table 1.** Equilibrium constant for the ion exchange reaction

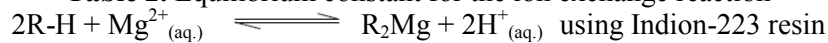


Amount of the ion exchange resin in  $H^+$  form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g,  
Temperature = 45.0 °C.

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	0.0065	2.33	0.3464	0.1629	1.465	0.00068	0.9396
0.0500	0.0082	0.0459	2.20	0.4133	0.3820	2.448	0.00031	2.0611
0.1000	0.0085	0.0958	2.17	0.4250	0.5439	3.934	0.00027	2.3664

Equilibrium constant in the standard state ( $K_{std.}$ ) = 0.000639

**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 = 45.0 °C.

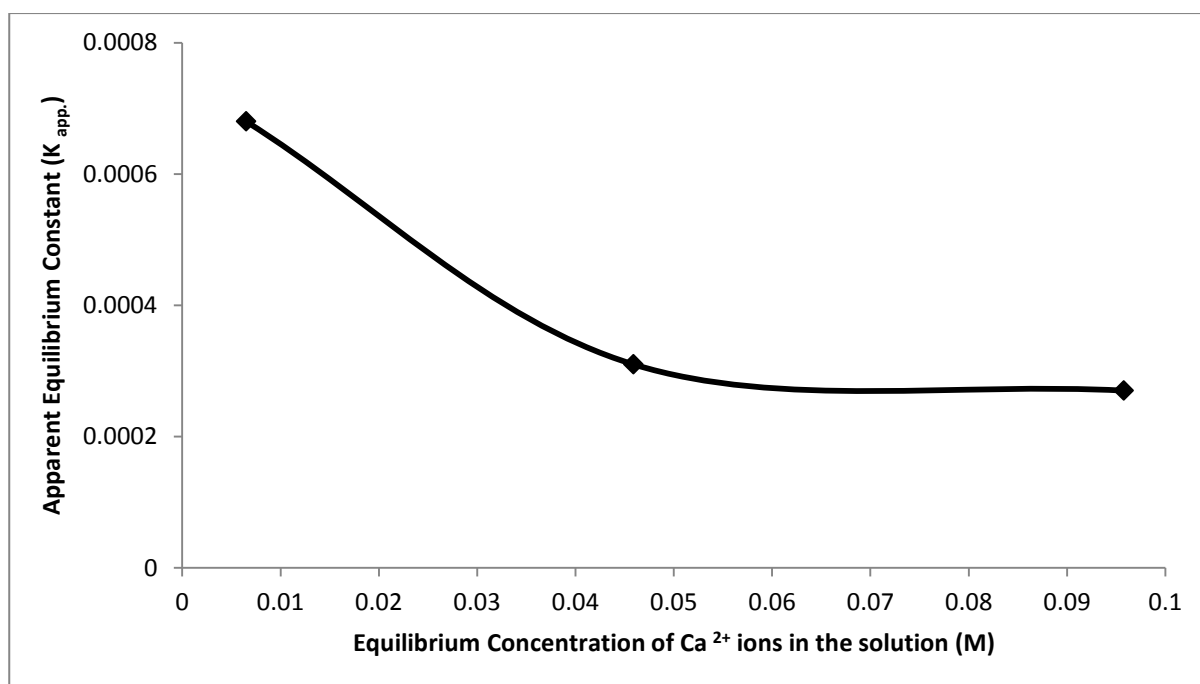
Initial Concentration of $Mg^{2+}$ ions in solution (M)	Equilibrium concentration in solution		Amount of the ions in the resin meq./0.500 g		$\sqrt{\text{Ionic Strength}}$	$\frac{(\gamma_{H^+})^2}{\gamma_{Mg^{2+}}}$	Apparent Equilibrium Constant $K_{app.}$	$\frac{(\gamma_{R_2Mg})}{(\gamma_{RH})^2} = \frac{K_{std.}}{K_{app.}}$
	$H^+$ (M)	$Mg^{2+}$ (M)	$H^+$	$Mg^{2+}$				
0.0100	0.0058	0.0071	2.44	0.289	0.165	1.47	0.00034	0.979
0.0500	0.0074	0.0463	2.28	0.370	0.382	2.45	0.00021	1.585
0.1000	0.0077	0.0961	2.25	0.387	0.544	3.58	0.00017	1.957

Equilibrium constant in the standard state ( $K_{std.}$ ) = 0.000333

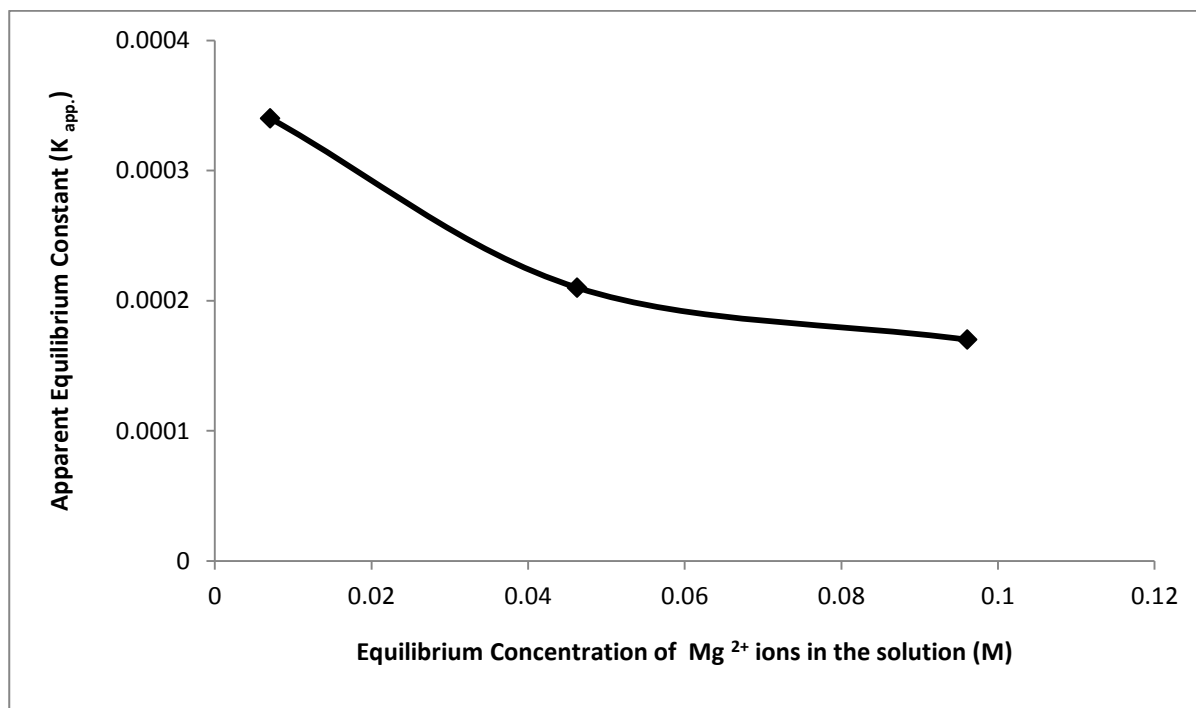
**Table 3.** Thermodynamics of ion exchange reactions using Indion-223 resin

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

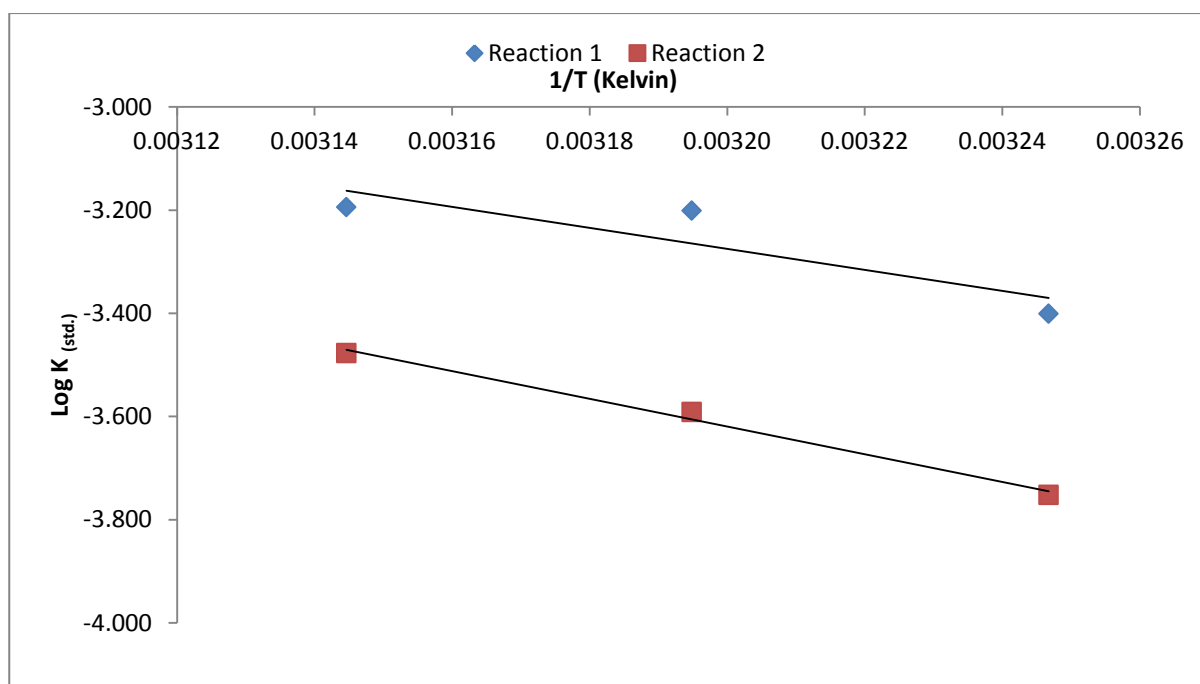
Reactions	1			2		
	Temperature (°C)	35.0	40.0	45.0	35.0	40.0
Equilibrium Constant ( $K_{std.}$ )	0.000397	0.000629	0.000639	0.000177	0.000256	0.000333
Enthalpy Change $\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	38.92			51.46		



**Figure 1.** Variation of apparent equilibrium constant with equilibrium concentration of Ca<sup>2+</sup> ions in solution for the ion exchange reaction (1) using ion exchange resin Indion-223. Amount of the ion exchange resin in H<sup>+</sup> form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g, Temperature = 45.0 °C.



**Figure 2.** Variation of apparent equilibrium constant with equilibrium concentration of Mg<sup>2+</sup> ions in solution for the ion exchange reaction (2) using ion exchange resin Indion-223. Amount of the ion exchange resin in H<sup>+</sup> form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g, Temperature = 45.0 °C.



**Figure 3.** Variation of equilibrium constant with temperature for uni-bivalent ion exchange reactions performed by using Indion-223 resins.

#### 4. CONCLUSION

From the results of present study, it appears that the experimental technique used here can be applied further to understand the ionic selectivity of different industrial grade ion exchange resins. It is expected that such studies will provide valuable information in order to decide about the selection of those resins for efficient separation of various ionic species present in the industrial waste water effluents.

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