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

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ABSTRACT

In the present paper the uni-univalent and uni-bivalent ion exchange reactions were investigated using nuclear grade anion exchange resin Indion-223 in H$^+$ form. For both H$^+$/K$^+$ uni-univalet ion exchange reactions and H$^+$/Mg^{2+} uni-bivalet ion exchange reactions, the equilibrium constant K values increases from 0.01710 to 0.02374 and from 0.000177 to 0.000333 respectively as the reaction temperature rises from 35.0 °C to 45.0 °C. The increase in K values with temperature suggest endothermic ion exchange reactions having the enthalpy change values of 22.72 and 51.46 kJ/ mol respectively. The results of such studies will help in selection of suitable ion exchange resins in order to bring about efficient separation of different ionic species present in the waste water effluents released from nuclear as well as chemical process industries.

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

1. INTRODUCTION

Commercial organic based resins are synthesized having wide range of applications in chemical, nuclear, pharmaceutical, food industry, etc. [1]. The synthetic resins are not only used for purifying water, but also for various other applications including separation of some rare earth elements. By taking advantage of the fact that, under certain conditions, ion exchange media has a greater affinity for certain ionic species than for others, a separation of these species can be made [2,3]. The ion exchange resins are used in a number of chemical decontamination or cleaning processes and in nuclear industries for removal of radionuclide [3-8]. Highly specific nuclear grade ion exchange resins are readily available for radionuclide which is common in the nuclear industry [3-8]. The nuclear grade 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. Efforts 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 their performance in various technological applications [9-17]. However, 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 [18-41]. 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 [3,18-39]. 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 [42-48]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed [49]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase [50-73]. Attempts were also made to study the temperature effect on anion exchange systems [65-73] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems [50-64]. Therefore, in the present investigation, attempts were made to understand the thermodynamics of uni-univalent and uni-bivalent ion exchange reactions using the 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.
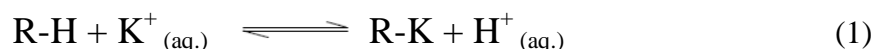
2. 3. Potentiometer

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

$$\text{R-H} + \text{K}^+_{\text{(aq.)}} \rightleftharpoons \text{R-K} + \text{H}^+_{\text{(aq.)}} \tag{1}$$

$$2\text{R-H} + \text{Mg}^{2+}_{\text{(aq.)}} \rightleftharpoons \text{R}_2\text{Mg} + 2\text{H}^+_{\text{(aq.)}} \tag{2}$$

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

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

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).
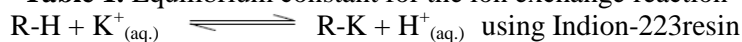
Similar K values are calculated for the reaction 1 performed at different temperatures (Table 2). From the slope of the graph of log K against 1/T (in Kelvin) the enthalpy change of the ion exchange reaction 1 was calculated (Figure 1). The equilibrium constant K values for the reactions were found to increase with rise in temperature indicating endothermic ion exchange reactions having the enthalpy change value of 22.72 kJ/ mol (Table 3). The equilibrium constants for the ion exchange reaction 2 were calculated by the equation

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

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

The apparent equilibrium constants ($K_{app.}$) calculated by the equation (4) were plotted versus the equilibrium concentrations of the Mg^{2+} ions in the solution (Figure 2). Lower the equilibrium concentration of the Mg^{2+} ion, lower would be its concentration in the resin and in the limiting case of zero equilibrium concentration of the Mg^{2+} ion in the solution, the resin would be in its standard state.
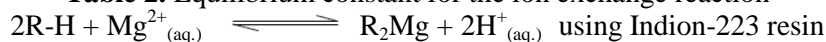
Table 1. Equilibrium constant for the ion exchange reaction
R-H + K$^+_{(aq.)}$ $\rightleftharpoons$ R-K + H$^+_{(aq.)}$ using Indion-223resin
Amount of the ion exchange resin in H$^+$ form = 0.500 g, Ion exchange capacity = 2.91meq./0.5 g.
Temperature = 35.0 °C.

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 x 10^{-2}
1	0.0100	0.0068	0.0032	0.0032	0.1577	2.650
2	0.0500	0.0437	0.0063	0.0063	0.3150	1.749
3	0.1000	0.0940	0.0060	0.0060	0.3000	0.732
Average K						1.710

Table 2. Equilibrium constant for the ion exchange reaction
2R-H + Mg$^{2+}_{(aq.)}$ $\rightleftharpoons$ R$_2$Mg + 2H$^+_{(aq.)}$ using Indion-223 resin
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 Mg^{2+} ions in solution (M)	Equilibrium concentration in solution		Amount of the ions in the resin meq./0.500 g		$\sqrt{}$ Ionic Strength	$\dfrac{(\gamma_{H^+})^2}{\gamma_{Mg^{2+}}}$	Apparent Equilibrium Constant $K_{app.}$	$\dfrac{(\gamma_{R_2Mg})}{(\gamma_{RH})^2} = \dfrac{K_{std.}}{K_{app.}}$
	H$^+$	Mg^{2+}	H$^+$	Mg^{2+}				
0.0100	0.0049	0.0076	2.53	0.245	0.166	1.48	0.00018	0.986
0.0500	0.0067	0.0466	2.35	0.333	0.383	2.45	0.00014	1.267
0.1000	0.0071	0.0964	2.31	0.356	0.544	3.59	0.00013	1.365

Equilibrium constant in the standard state (K$_{std.}$) = 0.000177

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

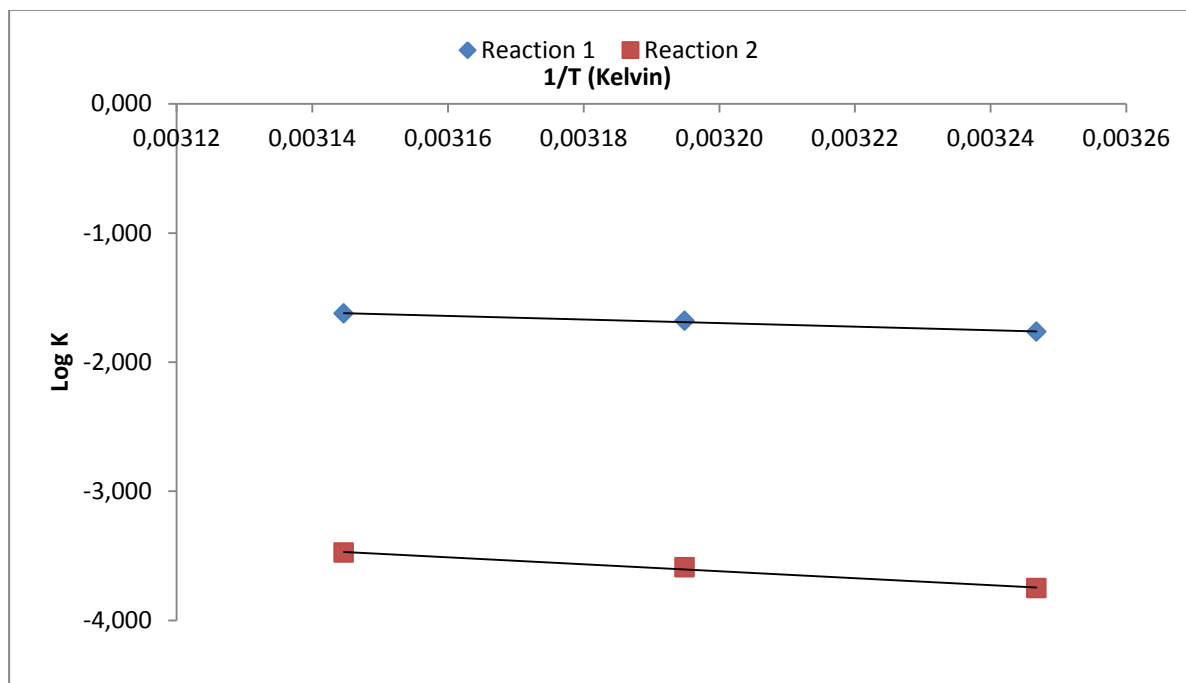| Reactions	1			2		
Temperature (°C)	35.0	40.0	45.0	35.0	40.0	45.0
Equilibrium Constant	0.01710	0.02080	0.02374	0.000177	0.000256	0.000333
Enthalpy Change ΔH^o (kJ·mol^{-1})	22.72			51.46		

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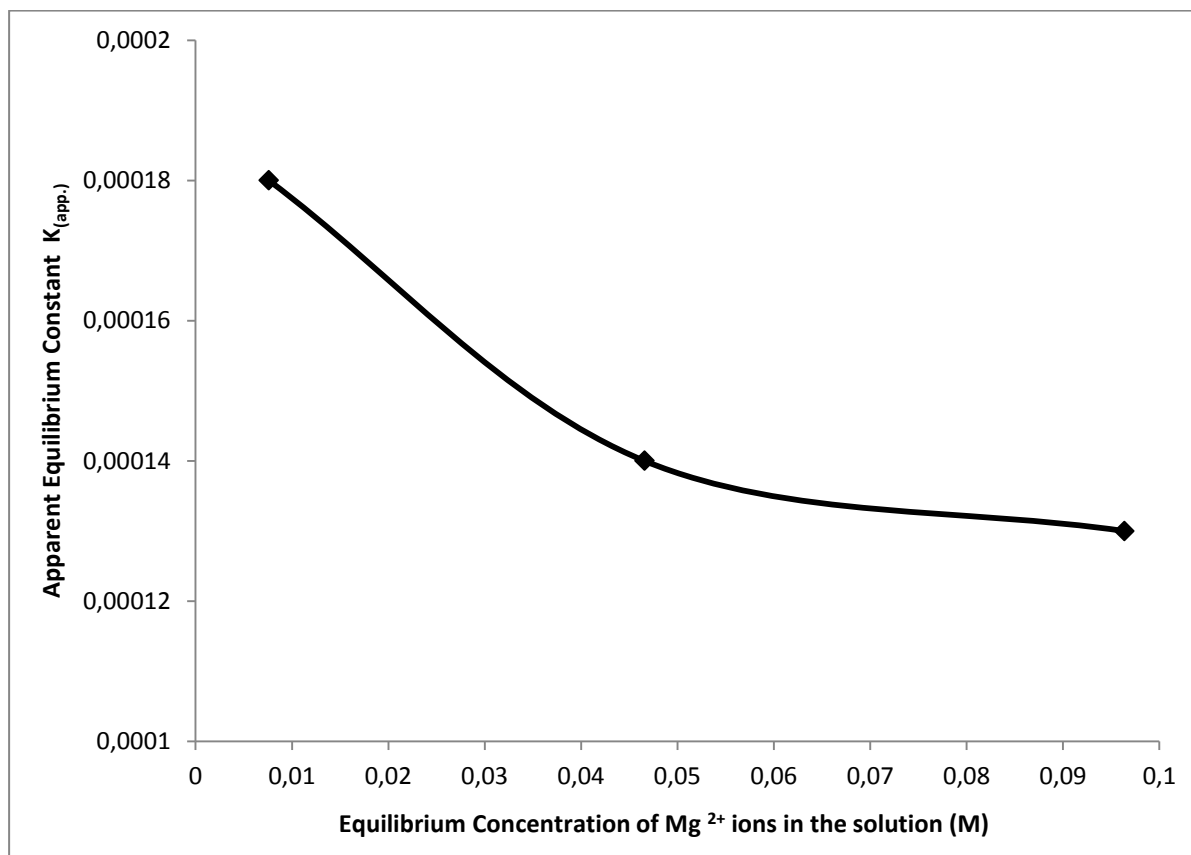

Figure 2. Variation of apparent equilibrium constant with equilibrium concentration of Mg^{2+} ions in solution for the ion exchange reaction (2) using ion exchange resin Indion-223.

Therefore on extrapolating the above curve to zero equilibrium concentration of Mg^{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 Mg^{2+} ion in the solution was calculated as the ratio of K_{std}/K_{app} (Tables 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 was found to increase with rise in temperature indicating endothermic ion exchange reaction having the enthalpy change value of 51.46 kJ/ mol (Table 3).

Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g, Temperature = 35.0 °C.

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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