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

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ABSTRACT

In the present investigation the uni-univalent and uni-bivalent ion exchange reactions were studied using nuclear grade anion exchange resin Indion-223 in H$^+$ form. It was observed that for H$^+$/Na$^+$ uni-univalet ion exchange reaction, with rise in temperature the equilibrium constants *K* values increases from 0.01389 to 0.01855. Similarly increase in *K* values was observed from 0.000177 to 0.000333 for H$^+$/Mg^{2+} uni-bivalet ion exchange reaction. The increase in equilibrium constant values with rise in temperature indicate endothermic ion exchange reactions having the enthalpy change values of 25.55 and 51.46 kJ/ mol respectively. It is expected that the present study 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.

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

1. INTRODUCTION

There are number of liquid processes waste streams at chemical processing, nuclear power plants, nuclear fuel reprocessing plants and nuclear research centres that requires 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. Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electro statically bound to the functional groups contained within a solid matrix. When the functional groups are negatively charged the exchange will involve cations and when they are positively charged they involve anions.

In recent times various aspects of ion exchange technology are being studied in many countries to improve its efficiency and economy in its applications in chemical, nuclear, pharmaceutical, food industry, etc. [1]. Also number of organic ion exchange resins which are more superior than the selective inorganic ion exchangers has been developed over a much longer period of time are now becoming available in commercial quantities so as to meet the requirements of the nuclear industry.

When used in nuclear industries these organic ion exchange resins very effectively transfer the radioactive content of a large volume of liquid into a small volume of solid and hence are applied for cleaning and decontamination processes and also for removal of radionuclide [2-6]. As a result these organic ion exchange resins 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]. 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 [8-13]. 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 [14-34].

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 [35-41]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed [42]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase [43-69]. Attempts were also made to study the temperature effect on anion exchange systems [58-70] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems [43-57]. 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. Glassware's

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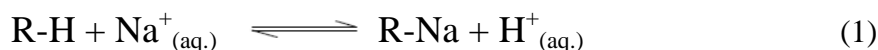
All Chemicals used were of analytical reagent (AR) grade. Distilled deionised water was used throughout the experiments for solution preparation.

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

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

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

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 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).

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 reaction were found to increase with rise in temperature indicating endothermic ion exchange reaction having the enthalpy change value of 25.55 kJ/ mol (Table 3).

Table 1. Equilibrium constant for the ion exchange reaction

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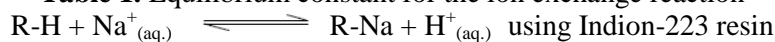
Amount of the ion exchange resin in H$^+$ form = 0.500 g, Ion exchange capacity = 2.91 meq./0.5 g, Temperature = 40.0 °C.

System	Initial concentration of 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 x 10^{-2}
1	0.0100	0.0069	0.0031	0.0031	0.1548	2.519
2	0.0500	0.0441	0.0059	0.0059	0.2996	1.542
3	0.1000	0.0938	0.0064	0.0062	0.3164	0.811
Average K						1.624

Table 2. Equilibrium constant for the ion exchange reaction
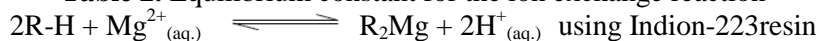
2R-H + Mg$^{2+}_{(aq.)}$ $\rightleftharpoons$ R$_2$Mg + 2H$^+_{(aq.)}$ using Indion-223 resin

Amount of the ion exchange resin in H$^+$ form = 0.500 g, Ion exchange capacity = 3.02 meq./0.5 g, Temperature = 40.0 °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$^+$ (M)	Mg^{2+} (M)	H$^+$	Mg^{2+}				
0.0100	0.0054	0.0073	2.48	0.271	0.165	1.47	0.00026	0.984
0.0500	0.0070	0.0465	2.32	0.352	0.383	2.45	0.00017	1.505
0.1000	0.0074	0.0963	2.28	0.369	0.544	3.58	0.00014	1.827

Equilibrium constant in the standard state (K$_{std.}$) = 0.000256

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	0.01389	0.01624	0.01855	0.000177	0.000256	0.000333
Enthalpy Change ΔH^o (kJ.mol^{-1})	25.55			51.46		

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.

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 were found to increase with rise in temperature indicating endothermic ion exchange reactions having the enthalpy change value of 51.46 kJ/ mol (Table 3).
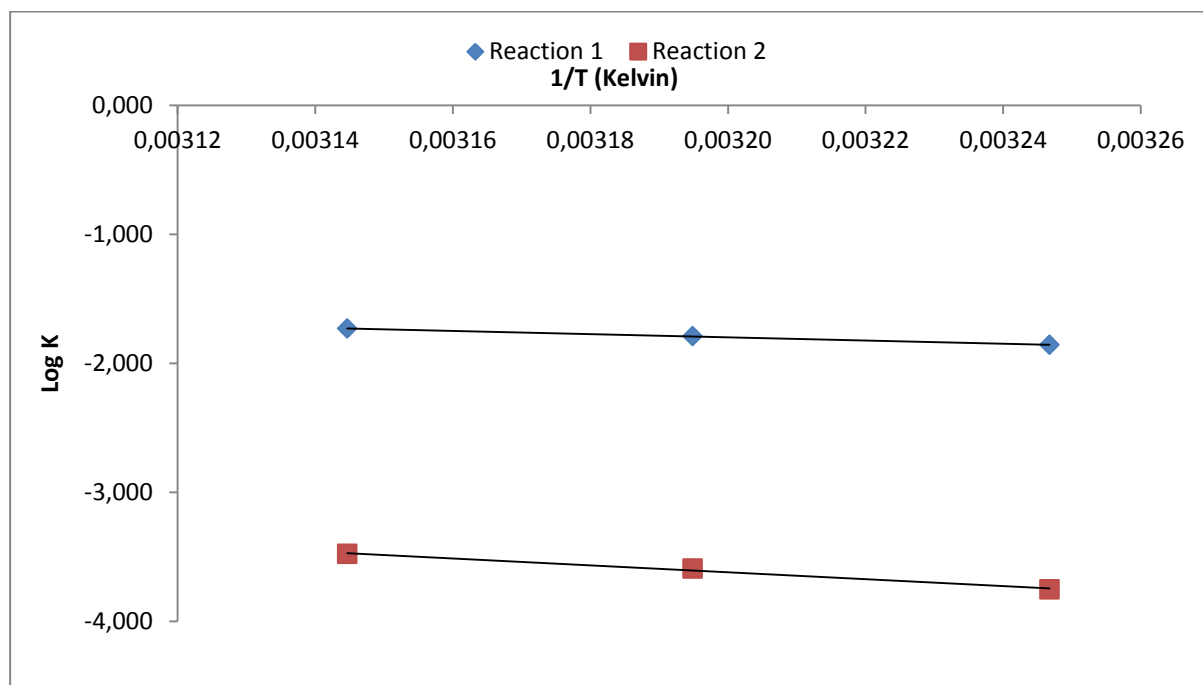

Figure 1. Variation of equilibrium constant with temperature of uni-univalent and uni-bivalent ion exchange reactions performed by using Indion-223 resins.
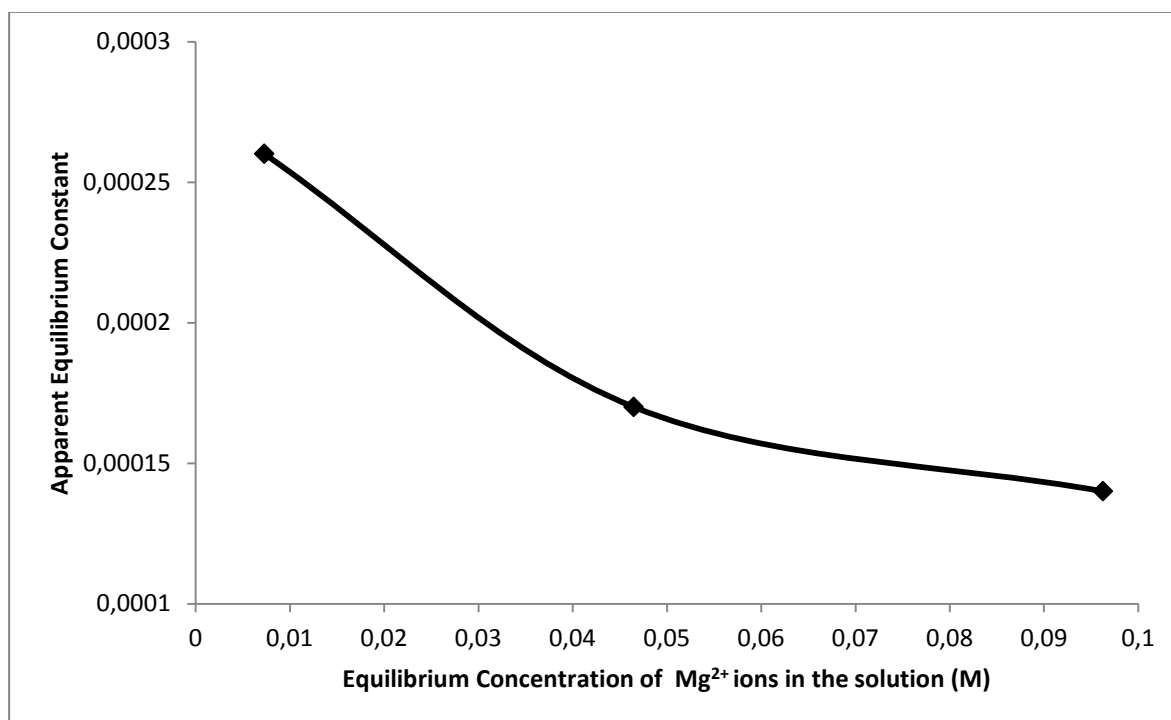
Figure 2. Variation of apparent equilibrium constant with equilibrium concentration of Mg^{2+} ions in solution for the ion exchange reaction (2) using ion exchange resin Indion-223.

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.

4. CONCLUSION

The experimental method used in the present study can be extended further for different ion exchange resins in order to understand their selectivity behaviour towards wide range of ionic species. 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.

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