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ION EXCHANGE EQUILIBRIUM STUDY USING STRONGLY ACIDIC CATION EXCHANGE RESINS DUOLITE ARC 9353

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ABSTRACT

The study on thermodynamics of ion exchange equilibrium for uni-univalent H^+ / Na^+, H^+ / K^+ reaction systems were carried out using strongly acidic cation exchange resin Duolite ARC 9353. For both the uni-univalent ion exchange reaction systems, the equilibrium constant *K*' were calculated by taking in to account the mole fraction of ions in the resin phase. The equilibrium constant values calculated for uni-univalent cation exchange reaction systems were observed to increase with rise in temperature. The enthalpy values calculated were 6.80 and 6.20 kJ/mol respectively indicating the endothermic ion exchange reactions. On the basis of enthalpy values the preferential selectivity of ion exchange resins in H^+ form for different univalent ions in aqueous solution is predicted.

Keywords: I*on exchange equilibrium; equilibrium constant; ionic selectivity; enthalpy; endothermic reactions; Duolite ARC 9353.*

INTRODUCTION

Extensive 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 [1-7]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed [8.] A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase [9-31]. Attempts were also made to study the temperature effect on anion exchange systems [12, 24-31] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems [9-23.] Therefore in the present investigation attempts were made to study the thermodynamics of uni-univalent cation exchange equilibrium, the results of which will be of considerable use in explaining the selectivity of ion exchanger for various bivalent ions in solution.

EXPERIMENTAL

The ion exchange resin Duolite ARC 9353 as supplied by the manufacturer (Auchtel Products, Ltd., Mumbai) was a strongly acidic cation exchange resins in H^+ form of 16-50 mesh size. For present investigation, the resin grains of 30-40 mesh size were used. The conditioning of the resins was done by usual methods [25-28]. 0.500g of ion exchange resins in H^+ form was equilibrated with Na^+ ion solution of different concentrations at a constant temperature of 30.0 ^{0}C for 3 h. From the results of kinetics study reported earlier [32-43]; it was observed that this duration was adequate to attain the ion exchange equilibrium. After 3 h the different Na^+ ion solutions in equilibrium with ion exchange resins were analysed for their H^+ ion concentration by potentiometric titration with standard 0.1N NaOH solution. From the results the equilibrium constant ***K*** for the reaction

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

was determined at 30.0 ^{0}C. The equilibrium constants ***K*** for the above H^+/Na^+ system was determined for different temperatures in the range of 30.0 ^{0}C to 45.0 ^{0}C. Similar study was also carried out for H^+/K^+ system in the same temperature range, to study the equilibrium constant ***K*** for the reaction

$$\textbf{R-H} + \textbf{K}^+_{(aq.)} \rightleftharpoons \textbf{R-K} + \textbf{H}^+_{(aq.)} \qquad (2)$$

The sodium and potassium ion solutions used in the entire experimental work, where prepared by dissolving potassium and sodium chloride salts (Analytical grade) in distilled deionised water. In the present study, a semi-micro burette having an accuracy of 0.05 mL was used in the titrations and the titration readings were accurate to ± 0.05 mL. Considering the magnitude of the titer values, the average equilibrium constants reported in the experiment are accurate to ± 3 %.

RESULTS AND DISCUSSION

The equilibrium constants for the uni-univalent ion exchange reactions (1 and 2) would be given by the expression

$$K = \frac{C_{RX} . C_{H^+}}{(A - C_{RX}) . C_{X^+}} \qquad (3)$$

where A is the ion exchange capacity of the resin, x^+ represents Na^+ or K^+ ions. For different concentrations of x^+ ions in solution at a given temperature, ***K*** values was calculated from which average value of ***K*** for that set of experiment was calculated (Tables 1 and 3).Similar values of ***K*** were calculated for both H^+/K^+ and H^+/Na^+ systems for different temperatures (Table 5). Earlier researchers have expressed the concentration of ions in the solution in terms of molality and concentration of ions in resin in terms of mole fraction[23]. In view of above, the experimental results obtained in the present study have been substituted in the following equation by Bonner et.al [16, 20] and the equilibrium constant ***K***' was calculated (Tables 2 and 4).

$$K' = \frac{[N_{X^+}]\,[m_{H^+}]}{[N_{H^+}]\,[m_{x^+}]} \qquad (4)$$

Where;

N_X^+ = mole fraction of K^+ or Na^+ ions exchanged on the resin
m_H^+ = molality of H^+ ions exchanged in the solution
N_H^+ = mole fraction of H^+ ions remained on the resin
m_x^+ = molality of K^+ or Na^+ ions remained in the solution at equilibrium.

Since in the present study the solution was dilute, the molality and molarity of the ions in the solution were almost the same, with negligible error. Therefore the molality of the ions can be easily replaced by molarity. The equilibrium constant ***K***' was calculated by equation 4 and the average value of ***K***' is reported (Table 2, and Table 4).Such ***K***' values were calculated for different temperatures and the values were in good agreement with ***K*** values calculated by equation 3 (Table 5).This justifies that the choice of units for the concentration in the present study is insignificant. The enthalpy value for the ion exchange reactions 1 and 2 were calculated by plotting the graph of log ***K*** against 1/T [25, 27]. Bonner and Pruett [16] studied the temperature effect on uni-univalent exchanges involving some bivalent ions. In all bivalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. However in the present investigation, the equilibrium constant values increases with rise in temperature (Table 5), giving positive values of enthalpy, indicating the endothermic ion exchange reactions. The low enthalpy and higher ***K*** values for H^+ / K^+ exchange as compared to that for H^+ / Na^+ exchange(Table 5), indicate that the resins in H^+ form are having more affinity for larger ionic size K^+ ions in solution as compared to that for Na^+ ions also in the solution.

CONCLUSION

Efforts to develop new ion exchangers for specific applications are continuing. In spite of their advanced stage of development, various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy in various technical applications. The selection of an appropriate ion exchange material is possible on the basis of information provided by the manufacturer. However, it is expected that the data obtained from the actual experimental trials will prove to be more helpful. The thermodynamic data obtained in the present experimental work will be useful to understand the selectivity behaviour of ion exchange resins for various ions in solution thereby helping in characterization of resins.

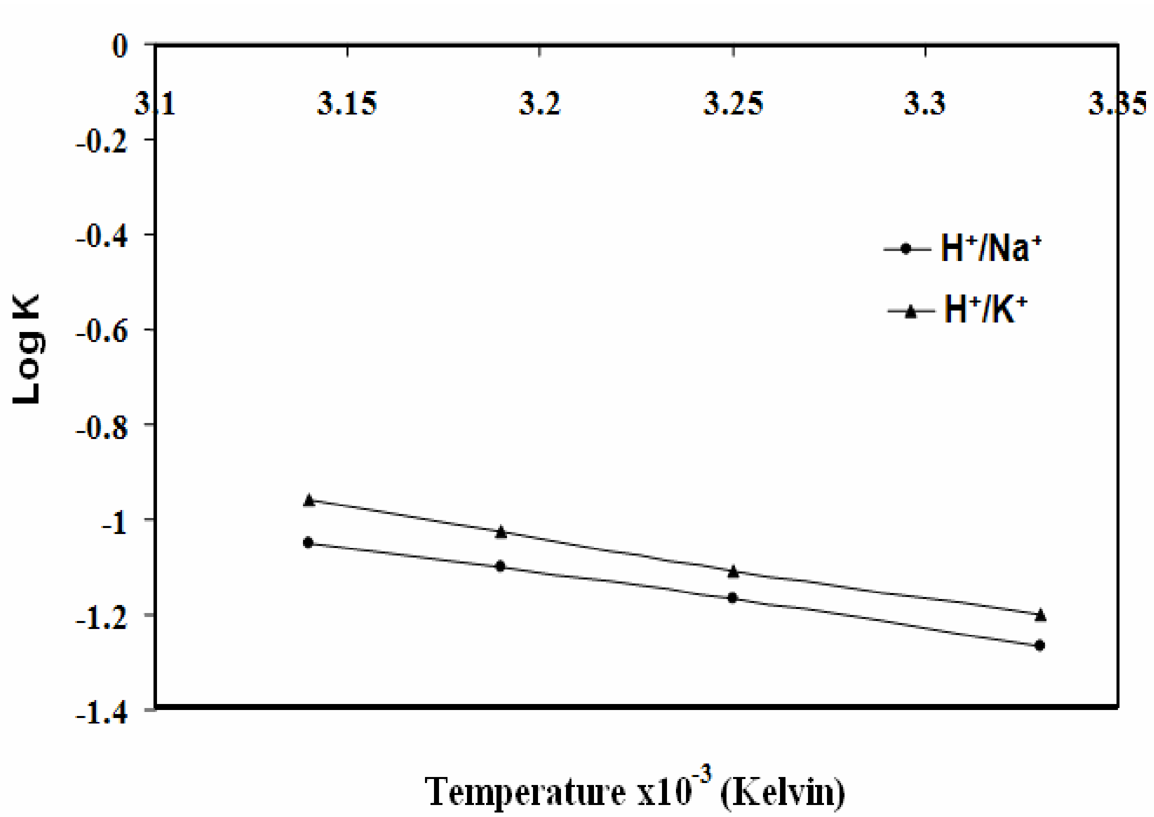

Fig.-1: Variation of Equilibrium Constant with Temperature for Uni-Univalent Ion Exchange Reactions using ion exchange resin Duolite ARC 9353.

Amount of the ion exchange resin in H+ form = 0.500 g; Ion exchange capacity = 1.50 meq. / 0.5g; Volume of Na+ / K+ ion solution = 100.0 mL; Temperature range = 30.0^0C-45.0^0C

Table-1: Equilibrium constant for the ion exchange reaction using ion exchange resin Duolite ARC 9353

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

Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 1.50 meq. / 0.500g, Volume of K^+ ion solution = 100.0 mL, Temperature = 30.0^{0}C

System	Initial conc. of K^+ ion (M)	Final conc. of K^+ ions (M) C_{K^+}	Change in K^+ ion conc.	Conc. of H^+ ions exchanged (M) C_{H^+}	Amount of K^+ ions exchanged on the resin meq./ 0.5 g C_{RK}	Equilibrium constant *K*
1	0.010	0.0062	0.0039	0.0039	0.1925	0.047
2	0.020	0.0128	0.0073	0.0073	0.3625	0.086
3	0.025	0.0170	0.0081	0.0081	0.4025	0.081
4	0.030	0.0217	0.0084	0.0084	0.4175	0.069
5	0.040	0.0304	0.0096	0.0096	0.4800	0.067

Average equilibrium constant (***K***) = 0.070

Table-2: Equilibrium constant for the ion exchange reaction

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

using ion exchange resin Duolite ARC 9353 calculated by Bonner et.al. Equation
Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 1.50meq. / 0.500g, Volume of K^+ ion solution = 100.0 mL, Temperature = 30.0^{0}C

System	Initial conc. of K^+ ions in solution (M)	Final conc. of K^+ ions in solution (M) m_{K^+}	Conc. of H^+ ions exchanged in solution (M) m_{H^+}	Mole fraction of K^+ ions exchanged on the resin N_{K^+}	Mole fraction of H^+ ions remained on the resin N_{H^+}	Equilibrium Constant *K'*
1	0.010	0.0062	0.0039	0.07	0.93	0.047
2	0.020	0.0128	0.0073	0.13	0.87	0.085
3	0.025	0.0170	0.0081	0.15	0.85	0.081
4	0.030	0.0217	0.0084	0.15	0.85	0.068
5	0.040	0.0304	0.0096	0.18	0.82	0.069

Average equilibrium constant (***K'***) = 0.070

Table-3: Equilibrium constant for the ion exchange reaction

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

Using ion exchange resin Duolite ARC 9353. Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 1.50 meq. / 0.500g, Volume of Na^+ ion solution= 100.0 mL, Temperature = 30.0^0C

System	Initial conc. of Na^+ ion solution (M)	Final conc. of Na^+ ion solution (M) C_{Na^+}	Change in Na^+ ion conc. (M)	Conc. of H^+ ion exchanged (M) C_{H^+}	Amount of Na^+ ions exchanged on the resin meq./0.500g C_{RNa}	Equilibrium constant *K*
1	0.010	0.0068	0.0033	0.0033	0.162	0.030
2	0.020	0.0140	0.0061	0.0061	0.302	0.053
3	0.025	0.0176	0.0074	0.0074	0.370	0.065
4	0.030	0.0221	0.0079	0.0079	0.395	0.059
5	0.040	0.0308	0.0092	0.0092	0.460	0.060

Average equilibrium constant (***K***) = 0.053

Table- 4: Equilibrium constant for the ion exchange reaction

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

using ion exchange resin Duolite ARC 9353 calculated by Bonner et.al. equation
Amount of the ion exchange resin in H^+ form = 0.500 g, Ion exchange capacity = 1.50 meq. / 0.500g, Volume of Na^+ ion solution= 100.0 mL, Temperature = 30.0^0C

System	Initial conc. of Na^+ ions in solution (M)	Final conc. of Na^+ ions in solution (M) m_{Na^+}	Conc. of H^+ ions exchanged in solution (M) m_{H^+}	Mole fraction of Na^+ ions exchanged on the resin N_{Na^+}	Mole fraction of H^+ ions remained on the resin N_{H^+}	Equilibrium Constant *K'*
1	0.010	0.0068	0.0033	0.059	0.941	0.030
2	0.020	0.0140	0.0061	0.110	0.890	0.053
3	0.025	0.0176	0.0074	0.135	0.865	0.065
4	0.030	0.0221	0.0079	0.144	0.856	0.059
5	0.040	0.0308	0.0092	0.167	0.833	0.060

Average equilibrium constant (***K'***) = 0.053

Table -5: Effect of temperature on equilibrium constant for Uni-Univalent ion exchange reactions using ion exchange resin Duolite ARC 9353

Amount of the ion exchange resin in H^+ form = 0.500 g, Volume of K^+ / Na^+ ion solution = 100.0 mL

Ion exchange reactions	**Equilibrium constant of Ion exchange reaction**	**Temperature °C**				**Enthalpy of the Ion exchange reactions kJ/mol**
		30.0	35.0	40.0	45.0	
$R\text{-}H + K^+_{(aq.)} \rightleftharpoons R\text{-}K + H^+_{(aq.)}$	***K***	0.070	0.078	0.094	0.110	6.20
	K'	0.070	0.079	0.094	0.111	
$R\text{-}H + Na^+_{(aq.)} \rightleftharpoons R\text{-}Na + H^+_{(aq.)}$	***K***	0.053	0.071	0.080	0.085	6.80
	K'	0.053	0.073	0.081	0.086	

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Few tragedies can be more extensive than the stunting of life, few injustices deeper than the denial of an opportunity to strive or even to hope, by a limit imposed from without, but falsely identified as lying within.

-Stephen Jay Gould