



ION EXCHANGE EQUILIBRIUM STUDIES USING STRONGLY ACIDIC CATION EXCHANGE RESINS DUOLITE ARC 9351

P.U.Singare*¹, R.S.Lokhande² and M.G.Patil³

¹ Department of Chemistry, Bhavan's College, Andheri, Mumbai - 58

² Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz, Mumbai-98

³ Department of Chemistry, VIVA College, M.B.Estate, Virar (West), Mumbai-4013030

*E-mail: pravinsingare@vsnl.net

ABSTRACT

The thermodynamic study was carried to predict the selectivity behaviour of ion exchange resin Duolite ARC 9351 for inorganic cations like sodium and potassium. The equilibrium constant K values for the ion exchange reactions were calculated at different temperatures from which the enthalpy values were obtained. The K values calculated for H^+/Na^+ and H^+/K^+ were observed to increase with rise in temperature, indicating endothermic ion exchange reactions having enthalpy values of 9.30 and 7.41 kJ/mol respectively. 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.

Key Words: Ion exchange equilibrium; equilibrium constant; ionic selectivity; enthalpy; endothermic reactions; Duolite ARC 9351.

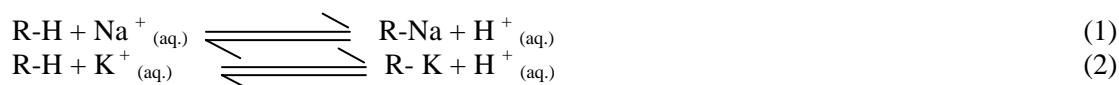
INTRODUCTION

Ion exchange is one of the most common techniques that have been employed for many years in chemical process industries and effluent treatment plant. The ion exchange process is very effective at transferring the content of a large volume of industrial effluent into a small volume of solid. Extensive work was done by previous researchers to study the concentration and temperature effect in various uni-univalent and heterovalent ion exchange systems¹⁻⁷. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed⁸. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase⁹⁻³¹. 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 systems⁹⁻²³. 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 9351 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 methods²⁵⁻²⁸.

The study of uni-univalent ion exchange equilibrium was performed by equilibrating 0.500 g of ion exchange resins in H^+ form with sodium and potassium ion solution in the temperature range of 30.0 °C to 45.0 °C for 3 h. From the results of kinetics study reported earlier it was observed that this duration was adequate to attain the ion exchange equilibrium³²⁻⁴³. After 3 h the concentration of H^+ ions exchanged in to the solution was estimated by potentiometric titration against standard 0.1 N NaOH solutions. From the results the equilibrium constant K for the following reactions was calculated.



The sodium and potassium ion solutions used in the entire experimental work, were 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 $\pm 3\%$.

Results and Discussion

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

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

here 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 were 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 fraction²³. 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).

$$K' = \frac{[N_{x^+}] [m_{\text{H}^+}]}{[N_{\text{H}^+}] [m_{x^+}]} \quad (4)$$

here 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.

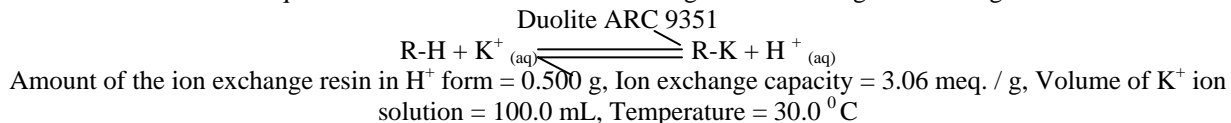
Since in the present study the solution was dilute, the molality and molarity of the ions in the solution were almost the same, with negligible error. Therefore the molality of the ions can be easily replaced by molarity. The equilibrium constant K' was calculated by equation 4 and the average value of K' is reported (Tables 2, and 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 $1/T$ (Figure 1). Bonner and Pruett¹⁶ 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 K increases with rise in temperature (Table 5), 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

Various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy of ion exchangers in various technical applications. The selection of an appropriate ion exchange material for the specific industrial and research application 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.

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



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 in the solution (M) C _{H⁺}	Amount of K ⁺ ions exchanged on the resin meq./ 0.5 g C _{RK}	Equilibrium constant K
1	0.01	0.0068	0.0032	0.0032	0.160	0.0259
2	0.02	0.0137	0.0063	0.0063	0.315	0.0528
3	0.025	0.0178	0.0073	0.0073	0.363	0.0549
4	0.03	0.0220	0.0080	0.0080	0.400	0.0547
5	0.04	0.0307	0.0093	0.0093	0.463	0.0536

Average equilibrium constant (**K**) = 0.048

Table-2: Equilibrium constant for the ion exchange reaction

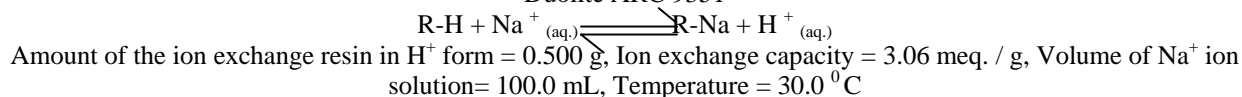
$$\text{R-H} + \text{K}^+_{(\text{aq})} \rightleftharpoons \text{R-K} + \text{H}^+_{(\text{aq})}$$
 using ion exchange resin
 Duolite ARC 9351 calculated by Bonner et.al. equation

Amount of the ion exchange resin in H⁺ form = 0.500 g, Ion exchange capacity = 3.06 meq. / g, Volume of K⁺ ion solution = 100.0 mL, Temperature = 30.0 °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	0.01	0.0068	0.0032	0.0523	0.9477	0.0259
2	0.02	0.0137	0.0063	0.1029	0.8971	0.0528
3	0.025	0.0178	0.0073	0.1185	0.8815	0.0549
4	0.03	0.0220	0.0080	0.1307	0.8693	0.0547
5	0.04	0.0307	0.0093	0.1511	0.8489	0.0536

Average equilibrium constant (**K'**) = 0.048

Table-3: Equilibrium constant for the ion exchange reaction using ion exchange resin
Duolite ARC 9351



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	0.0070	0.0031	0.0031	0.153	0.0230
2	0.020	0.0142	0.0058	0.0058	0.290	0.0428
3	0.025	0.0183	0.0068	0.0068	0.338	0.0458
4	0.030	0.0220	0.0081	0.0081	0.403	0.0555
5	0.040	0.0308	0.0092	0.0092	0.458	0.0521

Average equilibrium constant (**K**) = 0.044

Table-4: Equilibrium constant for the ion exchange reaction
R-H + Na⁺_(aq.) ⇌ R-Na + H⁺_(aq.) using ion exchange resin
Duolite ARC 9351 calculated by Bonner et.al. equation

Amount of the ion exchange resin in H⁺ form = 0.500 g, Ion exchange capacity = 3.06 meq. / g, Volume of Na⁺ ion solution = 100.0 mL, Temperature = 30.0 °C

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	0.0070	0.0031	0.0498	0.9502	0.0230
2	0.020	0.0142	0.0058	0.0947	0.9053	0.0427
3	0.025	0.0183	0.0068	0.1102	0.8890	0.0458
4	0.030	0.0220	0.0081	0.1315	0.8685	0.0555
5	0.040	0.0308	0.0092	0.1495	0.8505	0.0521

Average equilibrium constant (**K'**) = 0.044

Table-5: Effect of temperature on equilibrium constant (K) for Uni-Univalent ion exchange reactions using ion exchange resin Duolite ARC 9351

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	
$\text{R-H} + \text{K}^+_{(\text{aq.})} \rightleftharpoons \text{R-K} + \text{H}^+_{(\text{aq.})}$	K	0.048	0.053	0.060	0.066	7.41

	K'	0.048	0.052	0.061	0.065	
$R-H + Na^+_{(aq)} \rightleftharpoons R-Na + H^+_{(aq)}$	K	0.044	0.047	0.050	0.053	9.30
	K'	0.044	0.047	0.050	0.053	

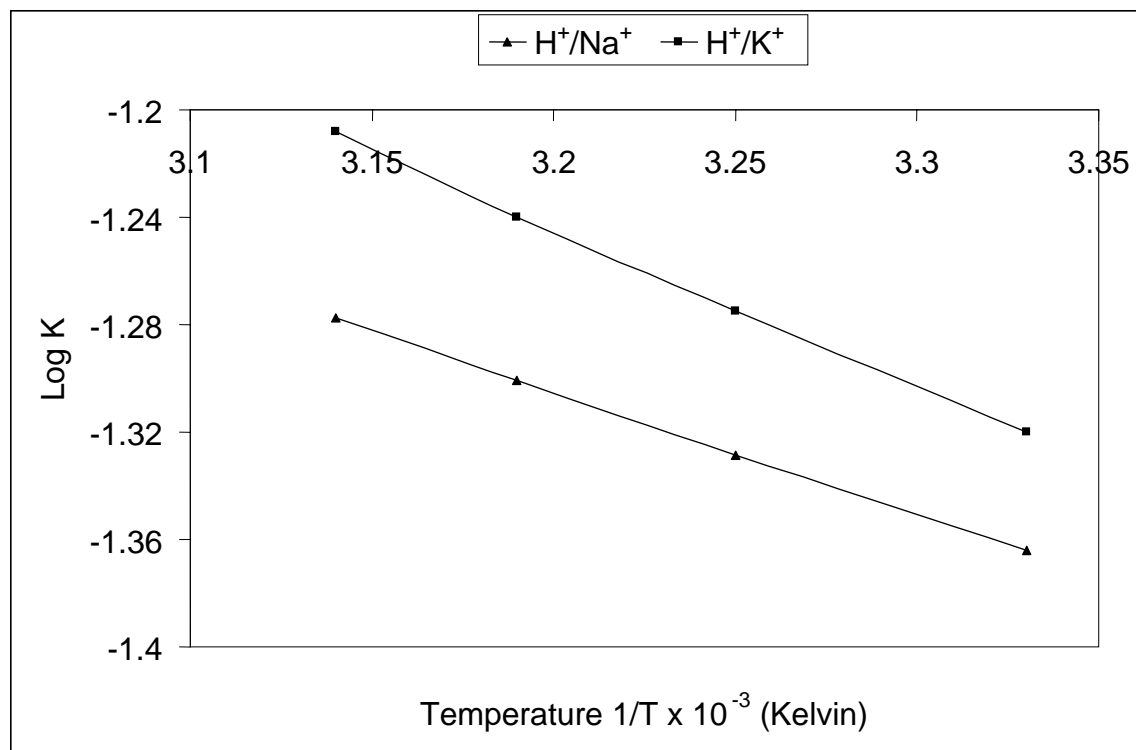


Fig.-1: Variation of Equilibrium Constant with Temperature for Uni-Univalent Ion Exchange Reactions using ion exchange resin Duolite ARC 9351

Amount of the ion exchange resin in H⁺ form = 0.500 g; Ion exchange capacity = 3.06 meq. / g; Volume of Na⁺ / K⁺ ion solution = 100.0 mL; Temperature range = 30.0 °C-45.0 °C

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