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STUDIES OF UNI-UNIVALENT ION EXCHANGE REACTIONS USING STRONGLY ACIDIC CATION EXCHANGE RESIN DUOILTE ARC 9353

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ABSTRACT

The selectivity behaviour of ion exchange resin Duolite ARC 9353 for inorganic cations like sodium and potassium was predicted on the basis of thermodynamic data. The equilibrium constant K values calculated for uni-univalent ion exchange reaction systems were observed to increase with rise in temperature, indicating endothermic ion exchange reactions. From the equilibrium constant K values calculated at different temperatures the enthalpy values were calculated. The low enthalpy and higher **K** values for K^+ ion exchange reaction indicates more affinity of the resin for potassium ions as compared to that for sodium ions also in the solution.

Key words: Ion exchange equilibrium; Equilibrium constant; Enthalpy; Endothermic reaction; Duolite ARC 9353.

INTRODUCTION

There are number of liquid processes waste streams at chemical processing, nuclear power plants, nuclear fuel reprocessing plants and nuclear research centers 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. 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. 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. 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 [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 univalent 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 analyzed for their H^+ ion concentration by potentiometric titration with standard 0.1N NaOH solution. From the results the equilibrium constant ***K*** for the reaction

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

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 by equilibrating ion exchange resins in H^+ form with K^+ ion solution of different concentrations in the same temperature range, to study the equilibrium constant ***K*** for the reaction

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

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

Therefore the equilibrium constants for the reactions (1 and 2) can be given by the expression-

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

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 (Table 1).Similar values of ***K*** were calculated for both H^+/Na^+ and H^+/K^+ systems for different temperatures (Table 1). 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 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, for the uni-univalent exchange reactions the value of equilibrium constant increases with rise in temperature giving positive enthalpy values (Table 1), 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 1) 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.

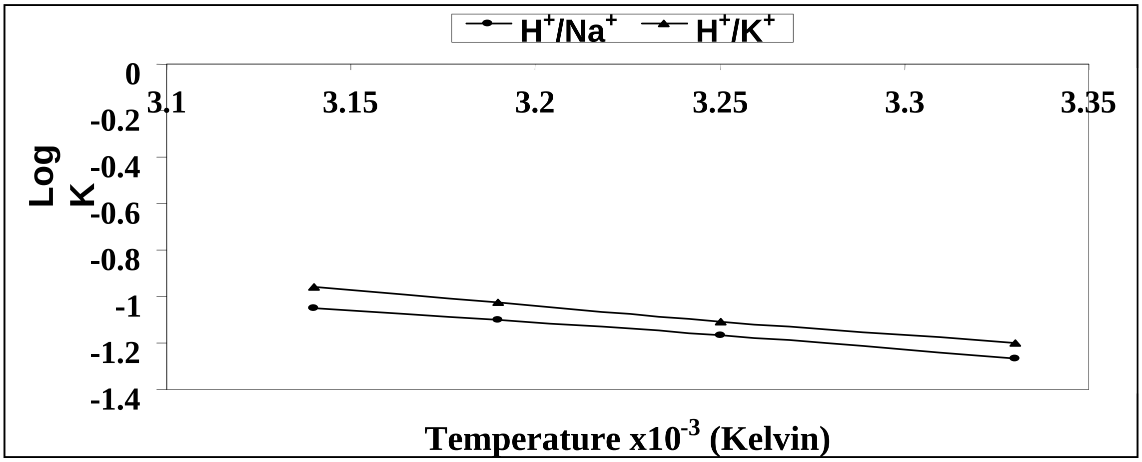

Fig.-1: Variation of Equilibrium Constant with Temperature for Uni-Univalent Ion Exchange Reactions for ion exchange resin Duolite ARC 9353

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

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Table-1: Equilibrium constant for the uni-univalent ion exchange reactions using ion exchange resin Duolite ARC-9353
Amount of the ion exchange resin in H^+ form = 0.500g, Ion exchange capacity =1.50 meq./0.500g, Volume of external ionic solution=100.0mL,

Reaction 1					*Reaction 2*				
Temperature =35.0 ^{0}C									
Initial conc. of Na^+ ion solution (M)	Final conc. of Na^+ ions (M) C_{Na^+}	Conc. of H^+ ions exchanged in solution (M) C_{H^+}	Amount of Na^+ ions exchanged on the resin meq./ 0.5 g C_{RNa}	Equilibrium constant K	Initial Conc. of K^+ ion solution (M)	Final conc. of K^+ ions (M) C_{K^+}	Conc. of H^+ ions exchanged in solution (M) C_{H^+}	Amount of K^+ ions exchanged on the resin meq./ 0.5 g C_{RK}	Equilibrium constant K
0.010	0.00595	0.00405	0.202	0.054	0.010	0.00595	0.00405	0.2025	0.054
0.020	0.0124	0.00760	0.380	0.098	0.020	0.01155	0.00845	0.4225	0.091
0.025	0.0168	0.00820	0.410	0.085	0.025	0.01635	0.00865	0.4325	0.099
0.030	0.0211	0.00885	0.442	0.069	0.030	0.02130	0.00870	0.435	0.078
0.040	0.0306	0.00940	0.470	0.048	0.040	0.03025	0.00975	0.4875	0.069
Average equilibrium constant (*K*) =0.071					Average equilibrium constant (*K*) = 0.078				

Temperature ^{O}C	30.0	35.0	40.0	45.0	Enthalpy (kJ/mol)	30.0	35.0	40.0	45.0	Enthalpy (kJ/mol)
Equilibrium Constant (*K*)	0.053	0.071	0.080	0.085	6.80	0.070	0.078	0.094	0.110	6.20

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