RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.3 (2009), 645-648
ISSN: 0974-1496
CODEN: RJCABP

THERMODYNAMICS OF UNI-UNIVALENT ION EXCHANGE REACTIONS USING STRONGLY ACIDIC CATION EXCHANGE RESIN TULSION T-46

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Abstract
The study on thermodynamics of ion exchange equilibrium for uni-univalent H^+ / Na^+ and H^+ / K^+ reaction systems was carried out using strongly acidic cation exchange resin Tulsion T-46. The equilibrium constant **K** calculated for uni-univalent ion exchange reaction systems were observed to increase with rise in temperature indicating the endothermic ion exchange reactions having the enthalpy values 4.19 and 3.80 kJ /mol respectively.
Key words: Ion exchange equilibrium; Equilibrium constant; Enthalpy; Endothermic reaction; Tulsion T-46.

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 were 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 Tulsion T-46 as supplied by the manufacturer (Thermax Ltd., Pune) was a strongly acidic cation exchange resin in Li^+ 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 [25-29].

0.500g of ion exchange resins in H^+ form was equilibrated with Na^+ ion solution of different concentrations in the range of 0.01 to 0.04M at a constant temperature of 30.0 ^{0}C for 4 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 4 h the different Na^+ ion solutions in equilibrium with ion exchange resins were analysed for their H^+ ion concentration by titration with standard 0.1N NaOH solution. From the results the equilibrium constant ***K*** for the reaction

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

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 40.0 ^{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

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

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

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

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

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 2).Similar values of ***K*** were calculated for both H^+ / Na^+ and H^+ / K^+ systems for different temperatures (Table 3). 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]. 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 3), 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 3), indicate that the resins in H^+ form are having more affinity for larger ionic size K^+ ions as compared to that for Na^+ ions 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.

Table- 1: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion T-46

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

Amount of the ion exchange resin in H^+ form = 0.500 g; Ion exchange capacity = 2.84meq./ g; Volume of Na^+ ion solution = 75.0 mL; Temperature =35.0 ^{0}C

System	Initial conc. of Na^+ ion (M)	Final conc. of Na^+ ions (M) C_{Na^+}	Change in Na^+ ion conc.	Conc. of H^+ ions exchanged (M) C_{H^+}	Amount of Na^+ ions exchanged on the resin meq./ 0.5 g C_{RNa}	Equilibrium constant ***K***
1	0.010	0.0039	0.0061	0.0061	0.307	0.20
2	0.020	0.0099	0.0101	0.0101	0.506	0.23
3	0.025	0.0137	0.0113	0.0113	0.567	0.21
4	0.030	0.0176	0.0124	0.0124	0.620	0.20
5	0.040	0.0263	0.0137	0.0137	0.685	0.17

Average equilibrium constant (***K***) = 0.20

Table- 2: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion T-46

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

Amount of the ion exchange resin in H^+ form = 0.500 g; Ion exchange capacity = 2.84meq./g; Volume of K^+ ion solution =75.0 mL; Temperature =35.0 ^{0}C

System	Initial conc. of K^+ ions (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	0.0036	0.0064	0.0064	0.320	0.23
2	0.020	0.0095	0.0105	0.0105	0.527	0.25
3	0.025	0.0133	0.0117	0.0117	0.587	0.23
4	0.030	0.0169	0.0131	0.0131	0.653	0.23
5	0.040	0.0256	0.0144	0.0144	0.720	0.19

Average equilibrium constant (***K***) = 0.23

Table -3: Effect of temperature on equilibrium constant for Uni-Univalent ion exchange reaction using ion exchange resin Tulsion T-46

Amount of the ion exchange resin in H^+ form = 0.500 g; Ion exchange capacity = 1.50 meq./0.500g; Volume of Na^+ / K^+ ion solution = 100.0 mL

Temp. ^{O}C	Equilibrium Constant (***K***) for the reactions	
	$R\text{-}H + Na^{+}_{(aq.)} \rightleftharpoons R\text{-}Na + H^{+}_{(aq.)}$	$R\text{-}H + K^{+}_{(aq.)} \rightleftharpoons R\text{-}K + H^{+}_{(aq.)}$
30.0	0.17	0.21
35.0	0.20	0.23
40.0	0.22	0.24
Enthalpy (kJ/mol)	4.19	3.80

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(Received: 17 February 2009 Accepted: 20 February 2009 RJC-331)