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ION EXCHANGE EQUILIBRIUM STUDY USING STRONGLY BASIC ANION EXCHANGE RESIN TULSION A-33

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ABSTRACT

The selectivity behaviour of ion exchange resin Tulsion A-33 for inorganic anions like iodide and bromide ions was predicted on the basis of thermodynamic data. The equilibrium constant **K** for Cl^-/I^- and Cl^-/Br^- uni-univalent ion exchange reactions was calculated by taking in to account the mole fraction of ions in the resin phase. The values of **K** were observed to decrease with rise in temperature indicating the exothermic ion exchange reactions having enthalpy values -8.43 and -15.30 kJ/mol respectively. The higher **K** values for iodide ion exchange reaction indicate more affinity of the resin for iodide ions as compared to that for bromide ions also in the solution.

Key Words: Ion exchange equilibrium; equilibrium constant; ionic selectivity; enthalpy; exothermic reactions; anion exchange; Tulsion A-33.

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 equilibrium of cation exchange systems [9-23.] However very little work was carried out to study the temperature effect on anion exchange systems [12, 24-31] for computing the thermodynamic equilibrium constants. Therefore in the present investigation attempts were made to study the thermodynamics of uni-univalent anion 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 A-33 as supplied by the manufacturer (Thermax Ltd., Pune) was a strongly basic anion exchange resin in hydroxide form of 16-50 mesh size. For present investigation, the resin grains of 30-40 mesh size were used. The conditioning of the resins in chloride form was done by usual methods using 10% potassium chloride solution [25-28].

The study of uni-univalent ion exchange equilibrium was performed by equilibrating 0.500 g of ion exchange resins in Cl^- form separately with I^- and Br^- ions solution in the temperature range of 30.0 ^{0}C

to 45.0 ^{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 equilibrium [32-43]. After 3 h the concentration of Cl^- exchanged in to the solution and I^- / Br^- ions left in the solution was estimated by potentiometric titration against standard 0.1 N $AgNO_3$ solutions. From the results the equilibrium constant ***K*** for the following reactions was calculated.

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

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

The chloride, bromide and iodide ion solutions used in the entire experimental work, where prepared by dissolving their respective analytical grade potassium salts 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

$$\boldsymbol{K} = \frac{C_{RX} \cdot C_{Cl^-}}{(A - C_{RX}).\, C_{X^-}} \quad (3)$$

here A is the ion exchange capacity of the resin, x^- represents I^- or Br^- 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 (Table 1, and 3).Similar values of ***K*** were calculated for both Cl^-/I^- and Cl^-/Br^- 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 (Table 2, and 4).

$$\boldsymbol{K}' = \frac{[N_X\text{-}]\,[m_{Cl}\text{-}]}{[N_{Cl}\text{-}]\,[m_x\text{-}]} \quad (4)$$

here N_X^- = mole fraction of I^- or Br^- ions exchanged on the resin

m_{Cl}^- = molality of Cl^- ions exchanged in the solution

N_{Cl}^- = mole fraction of Cl^- ions remained on the resin

m_x^- = molality of I^- or Br^- 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 (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. Similarly in the present investigation, for the uni-univalent exchange reactions the value of equilibrium constant decreases with rise in temperature giving negative enthalpy values (Table 5), indicating the exothermic ion exchange reactions. The low enthalpy and higher ***K*** values for Cl^-/I^- exchange as compared to that for Cl^-/Br^- exchange (Table 5), indicate that the resins in Cl^- form are having more affinity for I^- ions in solution as compared to that for Br^- ions also in the solution.

Table-1: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion A-33

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)}$$

Amount of the ion exchange resin in Cl^- form = 0.500 g; Ion exchange capacity = 1.5 meq. / 0.500g; Volume of I^- ion solution = 100.0 mL; Temperature =30.0 ^{0}C

System	Initial conc. of I^- ion (M)	Final conc. of I^- ions (M) C_{I^-}	Change in I^- ion conc.	Conc. of Cl^- ions exchanged (M) C_{Cl^-}	Amount of I^- ions exchanged on the resin meq./ 0.5 g C_{RI}	Equilibrium constant *K*
1	0.010	0.0003	0.0098	0.0097	0.488	18.74
2	0.020	0.0011	0.0189	0.0187	0.945	28.95
3	0.025	0.0020	0.0230	0.0210	1.150	34.50
4	0.030	0.0033	0.0268	0.0266	1.340	68.55

Average equilibrium constant (*K*) = 37.69

Table-2: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion A-33 calculated by Bonner et.al. equation

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)}$$

Amount of the ion exchange resin in Cl^- form = 0.500 g; Ion exchange capacity = 1.5 meq. / 0.500g; Volume of I^- ion solution = 100.0 mL; Temperature =30.0 ^{0}C

System	Initial conc. of I^- ions in solution (M)	Final conc. of I^- ions in solution (M) m_{I^-}	Conc. of Cl^- ions exchanged in solution (M) m_{Cl^-}	Mole fraction of I^- ions exchanged on the resin N_{I^-}	Mole fraction of Cl^- ions remained on the resin N_{Cl^-}	Equilibrium Constant *K'*
1	0.010	0.0003	0.0098	0.325	0.675	18.77
2	0.020	0.0011	0.0189	0.630	0.370	29.25
3	0.025	0.0020	0.0230	0.767	0.233	34.86
4	0.030	0.0033	0.0268	0.893	0.107	68.82

Average equilibrium constant (*K*') = 37.93

Table-3: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion A-33

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)}$$

Amount of the ion exchange resin in Cl^- form = 0.500 g; Ion exchange capacity = 1.5 meq. / 0.500g; Volume of Br^- ion solution =100.0 mL; Temperature =30.0 ^{0}C

System	Initial conc. of Br^- ion solution (M)	Final conc. of Br^- ion solution (M) C_{Br^-}	Change in Br^- ion conc. (M)	Conc. of Cl^- ion exchanged (M) C_{Cl^-}	Amount of Br^- ions exchanged on the resin meq./0.500g C_{RBr}	Equilibrium constant *K*
1	0.010	0.0008	0.0093	0.0092	0.463	5.49
2	0.020	0.0029	0.0171	0.0170	0.855	7.77
3	0.025	0.0043	0.0208	0.0207	1.038	10.95
4	0.030	0.0060	0.0240	0.0230	1.200	15.33

Average equilibrium constant (*K*) = 9.89

Table-4: Equilibrium constant for the ion exchange reaction using ion exchange resin Tulsion A-33 calculated by Bonner et.al. equation

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)}$$

Amount of the ion exchange resin in Cl^- form = 0.500 g; Ion exchange capacity = 1.5 meq. / 0.500g; Volume of Br^- ion solution =100.0 mL; Temperature =30.0 ^{0}C

System	Initial conc. of Br^- ions in solution (M)	Final conc. of Br^- ions in solution (M) m_{Br^-}	Conc. of Cl^- ions exchanged in solution (M) m_{Cl^-}	Mole fraction of Br^- ions exchanged on the resin N_{Br^-}	Mole fraction of Cl^- ions remained on the resin N_{Cl^-}	Equilibrium Constant *K*'
1	0.010	0.0008	0.0093	0.308	0.692	5.48
2	0.020	0.0029	0.0171	0.570	0.430	7.81
3	0.025	0.0043	0.0208	0.691	0.309	10.91
4	0.030	0.0060	0.0240	0.800	0.200	16.00

Average equilibrium constant (*K*') = 10.05

Table-5: Effect of temperature on equilibrium constant (*K)* for Uni-Univalent ion exchange reactions using ion exchange resin Tulsion A-33
Amount of the ion exchange resin in Cl^- form = 0.500 g, Volume of I^-/Br^- ion solution = 100.0 mL

Ion exchange reactions	Equilibrium constant of Ion exchange reaction	Temperature ^{o}C				Enthalpy of the Ion exchange reactions kJ/mol
		30.0	35.0	40.0	45.0	
$R\text{-}Cl + I^-_{(aq.)} \rightleftharpoons R\text{-}I + Cl^-_{(aq.)}$	*K*	37.69	27.25	22.59	20.93	-8.43
	K'	37.93	27.28	22.50	20.95	
$R\text{-}Cl + Br^-_{(aq.)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq.)}$	*K*	9.89	9.05	9.06	7.71	-15.30
	K'	10.05	9.02	9.11	7.68	

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.

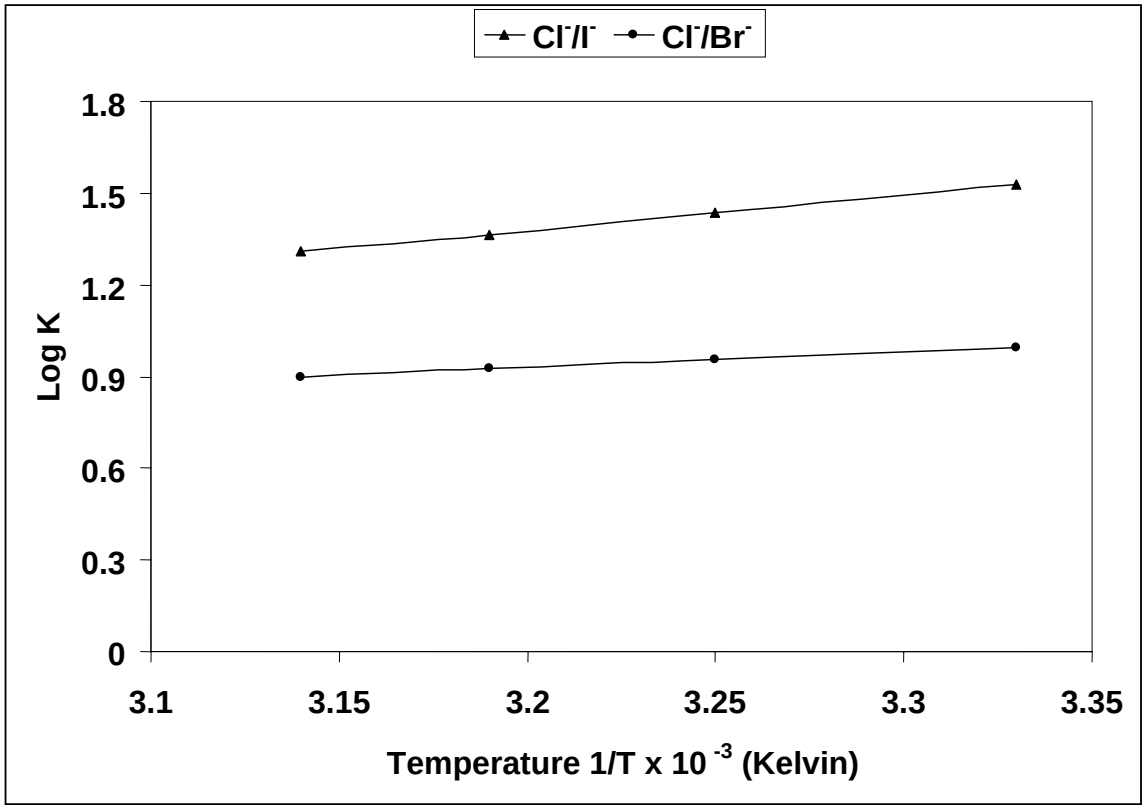

Fig.-1: Variation of Equilibrium Constant with Temperature for Uni-Univalent Ion Exchange Reactions using ion exchange resin Tulsion A-33

Amount of the ion exchange resin in Cl^- form = 0.500 g; Ion exchange capacity =1.5 meq. / 0.500g; Volume of I^-/Br^- ion solution = 100.0 mL; Temperature range = 30.0 ^{0}C-45.0 ^{0}C

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