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Ion exchange equilibrium study using strongly basic anion exchange resin Indion-102

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ABSTRACT

The thermodynamic study was carried to predict the selectivity behaviour of anion exchange resin Indion-102 in chloride form for iodide and bromide ions in solution. The equilibrium constant K values for the ion exchange reactions were calculated at different temperatures from which the enthalpy values were obtained. The equilibrium constant ***K*** calculated for Cl^-/I^- and Cl^-/Br^- uni-univalent ion exchange reaction systems were observed to decrease with rise in temperature indicating the endothermic exchange reactions having enthalpy values 3.86 and 6.36 kJ /mol respectively.

Key words: Ion exchange equilibrium; equilibrium constant; ionic selectivity; enthalpy; endothermic reactions; anion exchange; Indion-102.

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 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 Indion-102 as supplied by the manufacturer (Ion Exchange India Ltd., Mumbai) was a strongly basic anion exchange resin in OH^- 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].

Ion exchange resins in Cl^- form (0.500g), was equilibrated with I^- ion solution of different concentrations at a constant temperature of 35^0 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 I^- ion solutions in equilibrium with ion exchange resins were analysed for their Cl^- and I^- ion concentration by potentiometric titration with standard 0.1N $AgNO_3$ solution. From the results the equilibrium constant ***K*** for the reaction

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

was determined at 35.0 °C. The equilibrium constants ***K*** for the above Cl^- / I^- system was determined for different temperatures up to 45.0°C.

Similar study was also carried out for Cl^- / Br^- system in the same temperature range, to study the equilibrium constant *K* for the reaction

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

The chloride, bromide and iodide ion solutions used in the entire experimental work were 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

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

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. Similar values of *K* were calculated for both Cl^-/I^- and Cl^-/Br^- systems for different temperatures (Table 1). 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).

$$K' = \frac{[N_{X^-}]\,[m_{Cl^-}]}{[N_{Cl^-}]\,[m_{x^-}]} \quad ...(4)$$

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). Such *K'* values were calculated for different temperatures and the values were in good agreement with *K* values calculated by equation 3 (Tables 1 and 2). 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 from the slope of the graph log *K* against 1 / T [25-28]. In the present investigation, for the uni-univalent exchange reactions the value of equilibrium constant decreases with rise in temperature giving positive enthalpy values (Tables 1 and 2), indicating the endothermic ion exchange reactions. The low enthalpy and higher *K* values for

Table 1: Equilibrium constant for the uni-univalent ion exchange reactions using ion exchange resin Indion - 102 Amount of the ion exchange resin in chloride form = 0.500g, Ion exchange capacity =2.72 meq./0.500g, Volume of external ionic solution = 50.0mL

Reaction 1					Reaction 2				
Temperature =35.0 ^{0}C									
Initial conc. of iodide ion solution (M)	**Final conc. of I^- ions (M) C_{I}^-**	**Conc. of Cl^- ions exchanged in the solution (M) C_{Cl}^-**	**Amount of I^- ions exchanged on the resin meq./ 0.5 gC_{RI}**	**Equilibrium constant K**	**Initial Conc. of bromide ion solution (M)**	**Final conc. of Br^- ions (M) C_{Br}^-**	**Conc. of Cl^- ions exchanged in the solution (M) C_{Cl}^-**	**Amount of Br^- ions exchanged on the resin meq./ 0.5 g C_{RBr}**	**Equilibrium constant K**
0.02	0.0056	0.0140	0.36000	0.381	0.02	0.0092	0.0116	0.2700	0.134
0.03	0.0104	0.0184	0.49000	0.389	0.03	0.0174	0.0132	0.3150	0.099
0.04	0.0198	0.0182	0.52000	0.217	0.04	0.0270	0.0130	0.3250	0.065
0.05	0.0258	0.0214	0.60500	0.237	0.05	0.0358	0.0136	0.3550	0.057
Average equilibrium constant (*K*) = 0.306					**Average equilibrium constant (*K*) = 0.090**				
Temperature $^{\circ}$C Enthalpy(kJ/mol)		35.0	40.0	45.0	Enthalpy(kJ/mol)		35.0	40.0	45.0
Equilibrium Constant (*K*)		0.306	0.216	0.174	3.86	0.090	0.088	0.082	6.36

Table 2. Equilibrium constant for the uni-univalent ion exchange reactions using ion exchange resin Indion – 102 calculated by Bonner et.al. Equation

Amount of the ion exchange resin in chloride form = 0.500g, Ion exchange capacity = 2.72 meq./0.500g, Volume of external ionic solution = 50.0mL

Reaction 1					Reaction 2				
Temperature =35.0 ^{0}C									
Initial conc. of iodide ion solution (M)	**Final conc. of I^- ions (M) C_{I^-}**	**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'**	**Initial Conc. of bromide ion solution (M)**	**Final conc. of Br^- ions (M) C_{Br^-}**	**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'**
0.02	0.0056	0.132	0.868	0.380	0.02	0.0092	0.099	0.901	0.139
0.03	0.0104	0.180	0.820	0.388	0.03	0.0174	0.116	0.884	0.100
0.04	0.0198	0.191	0.809	0.217	0.04	0.0270	0.119	0.881	0.065
0.05	0.0258	0.222	0.778	0.235	0.05	0.0358	0.131	0.869	0.057
Average equilibrium constant (*K*) = 0.305					**Average equilibrium constant (*K*) = 0.090**				
Temperature $^{\circ}$C Enthalpy(kJ/mol)		35.0	40.0	45.0	Enthalpy(kJ/mol)		35.0	40.0	45.0
Equilibrium Constant (*K'*)		0.305	0.217	0.173	3.86	0.090	0.088	0.081	6.36

Cl^- / I^- exchange as compared to that for Cl^- / Br^- exchange (Tables 1 and 2), 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.

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.

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