Study of bromide ionic selectivity behavior of nuclear and non-nuclear grade anion exchange resins

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ABSTRACT

The study was performed to understand the bromide ion selectivity behavior of anion exchange resin Indion GS-300 (nuclear grade) and Indion FF IP (non-nuclear grade). The thermodynamic concept was applied to predict the selectivity behavior of ion exchange resins. The exchange reaction was performed by equilibrating ion exchange resins in chloride form with bromide ion solution. During the ion exchange reactions, it was observed that as the temperature was raised from 30.0°C to 45.0°C, the equilibrium constant *(K)* increased from 4.123×10^{-2} to 16.535×10^{-2} for Indion GS-300 resin and from 5.564×10^{-2} to 26.980×10^{-2} for Indion FF IP resin. The increase in *K* values with rise in temperature indicated endothermic ion exchange reactions having positive enthalpy values using Indion GS-300 (67.66 kJ/mol) and Indion FF IP (86.60 kJ/mol) ion exchange resins. The low enthalpy value obtained for Indion GS-300 resin indicated their greater selectivity for the bromide ions as compared to Indion FF IP resins under identical experimental conditions.
Keywords: Thermodynamics; equilibrium constant; ionic selectivity; enthalpy; exothermic reactions; Indion GS-300; Indion FF IP.

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INTRODUCTION

Ion exchangers, exchange either positively or negatively charged ions, hence termed as cation exchangers or anion exchangers respectively. These ion exchange resins reach an equilibrium state between the ions in the solution and the ions on the resin, when kept in a solution. From this equilibrium state, the selectivity coefficient that is the equilibrium constants can be defined based on the ratios of ions in solution vs. ions on the resin. These selectivity coefficients are a measurement of a resins preference for an ion. The higher the selectivity coefficient, the higher the preference for the ion. For example, a strong acid cation resin with 8% crosslink has a selectivity coefficient for sodium vs. hydrogen of 1.56, while the selectivity coefficient for calcium as against hydrogen is 4.06. As a result, calcium is selectively removed by the ion exchange over the sodium [1].Variables relating to the resin are the exchange capacity; degree of cross-linking, which determines the permeability of the resin, the swelling capability, and the access of the exchange sites to the ion; the effective exchange affinity; and the resin particle size, which controls approachability to the exchange ions [2]. Moreover, ion exchangers are of significance because of the insolubility of the resin phase. Upon coming in contact with the ion containing solution, the resin can be detached by filtration. This function of the resins makes them environmentally compatible and thus they have been used in water softening, removing toxic metals from water bodies, wastewater treatment, hydrometallurgy, sensors, biomolecular separations and so on [3]. Thus having elaborated on the applications, the ion exchange resins form on the most important scientific development of the 20th century [4]. Munday and Eaves were the first to suggest removal of acids and bases from petroleum fractions, using ion exchange resins [5]. Most of the resins are produced by polymerizing styrene in presence of divinylbenzene [6].Thus, the ion exchange resins produced commercially in various formulations and with different characteristics have a wide range of application in the industrial and engineering chemistry. Efforts are also being taken to develop new ion exchangers for specific applications and also studies are undertaken to improve the cost effectiveness of their application in various technological applications [7-10].Given the understanding, ion exchange media has a greater affinity under certain conditions, for certain ionic species than for others. Thus, separation of these species becomes easy. However, selection of the desired ion exchange media in the given liquid waste becomes tedious in presence of chemically similar ionic species. In the present investigation, attempt was made to understand the bromide ion selectivity of the anion exchange resins Indion GS-300 and Indion FF IP in chloride form. The present technique can be extended further to understand the selectivity behavior of series of anion exchange resins. Moreover, the experimental data generated from this study will be useful in selection of suitable resin for various technical applications.

EXPERIMENTAL

The ion exchange resin Indion GS-300 and Indion FF IP as supplied by the manufacturer (Ion exchange India Ltd., Mumbai) were the anion exchangers in the hydroxide form. The details regarding the various physico-chemical properties of the considered ion exchange resins are presented in the Table 1.

Table 1. Physico-chemical properties of anion exchange resins.

Ion exchange Resin	Matrix	Functional group	Mean particle size (mm)	Moisture content (%)	Operating pH	Maximum operating temperature °C	Total exchange capacity meq/mL
Indion GS-300	Styrene DVB	$-N^+R_3$	0.3-1.2	47-55 %	0-14	60	1.40
Indion FF IP	Polystyrene	$-N^+R_3$	0.3-1.2	48-58%	0-14	60	1.33

The resin grains of 30-40 mesh size were used for the present investigation. The soluble impurities of the resins were separated by repeated soxhlet extraction using water. Moreover, distilled methanol was used occasionally to remove non-polymerized organic impurities. The resin was conditioned with 10% potassium chloride in a conditioning column so that complete conversion of the resin in chloride form takes place. Then the resins were washed with distilled deionized water until the washings were chloride free. The resin in the chloride form was air dried over P_2O_5. For determining the exchange capacity of the resins, standard method of eluting the resins with sodium nitrate solution and titrating the eluent against standard silver nitrate

solution was followed [11]. Ion exchange resins (0.500g) in chloride form were equilibrated with bromide ion solution of different concentrations at 35.0°C for 3h when the following reaction takes place:

$$R\text{-}Cl + Br^-_{(aq.)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq.)} \qquad (1)$$
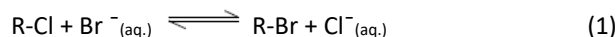
From the extensive research performed previously, it was observed that the time duration of 3h was adequate to attain the ion exchange equilibrium [12-19]. After 3h, the equilibrated solutions were analyzed potentiometrically for their chloride and bromide ion concentrations using standard 0.03 M $AgNO_3$ solution. From the results, the K values for the above ion exchange reaction were determined at 35.0°C.

Similar K values were measured for different temperatures ranging from 30.0°C to 45.0°C. For entire study, a semi-micro burette having an accuracy of 0.02 mL was used for potentiometric titrations against standard $AgNO_3$. The titration readings were accurate to ±0.02 mL and the magnitude of the titre values; the average equilibrium constants testified in the experiment were accurate to ±3 %.

3. RESULTS AND DISCUSSION

The observed equilibrium constants for reaction (1) can be written as

$$K = \frac{c_{R\text{-}Br} \cdot c_{Cl^-}}{(A - c_{R\text{-}Br}) \cdot c_{Br^-}} \qquad (2)$$

where, the ion exchange capacity of the resin is denoted by A. At a fixed temperature, K values were measured for different bromide concentrations, and the average K value for this set of experiments was calculated (Tables 2 and 3). Similarly, K values were calculated for the above reaction system at different temperatures (Table 4). Furthermore, the log K values were plotted against 1/T (in Kelvin), resulting in a linear graph (Figures 1and 2). The enthalpy of the ion exchange reaction 1 was calculated from the slope of this graph (Table 4).

Table 2. Equilibrium constant for the ion exchange reaction (1) using Indion GS-300 resin.

System	Initial concentration of bromide ion (M)	Final concentration of bromide ions (M) c_{Br^-}	Change in bromide ion concentration	Concentration of chloride ions exchanged in the solution (M) c_{Cl^-}	Amount of bromide ions exchanged on the resin meq./0.5 g c_{RBr}	Equilibrium constant (K) x10^{-2}
1	0.100	0.073	0.027	0.027	1.360	0.421
2	0.200	0.170	0.030	0.030	1.520	1.633
3	0.300	0.265	0.035	0.035	1.730	5.884
4	0.400	0.364	0.036	0.036	1.790	11.114
5	0.500	0.463	0.037	0.037	1.860	22.873
Average K						**8.384**

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.00 meq./0.5 g, Temperature = 35.0 °C.

Table 3. Equilibrium constant for the ion exchange reaction (1) using Indion FF IP resin.

| System	Initial concentration of bromide ion (M)	Final concentration of bromide ions (M) c_{Br^-}	Change in bromide ion concentration	Concentration of chloride ions exchanged in the solution (M) c_{Cl^-}	Amount of bromide ions exchanged on the resin meq./0.5 g c_{RBr}	Equilibrium constant (K) x10^{-2}
1	0.100	0.066	0.034	0.034	1.700	0.477
2	0.200	0.156	0.044	0.044	2.180	4.645
3	0.300	0.256	0.044	0.044	2.200	8.260
4	0.400	0.355	0.045	0.045	2.250	14.378
5	0.500	0.453	0.047	0.047	2.350	33.356
Average K						**12.223**

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.50 meq./0.5 g, Temperature = 35.0 °C.

Earlier researchers have investigated the effect of temperature on ion exchange equilibrium involving some divalent ions over the temperature range 0 to 97.5°C using the sulfonic acid type resins. In all divalent exchanges, the *K* values decreases with rise in temperature resulting in exothermic reactions [20]. However, in the present investigation, the equilibrium constant value has increased with rise in temperature giving positive enthalpy values indicating endothermic ion exchange reactions. The enthalpy values of Indion GS-300 and Indion FF IP was 67.66 and 86.60 kJ/mol respectively.

Table 4. Thermodynamics of ion exchange reaction (1) using nuclear and non-nuclear grade ion exchange resins.

Resin	Indion GS-300				Indion FF IP			
Temperature (°C)	30.0	35.0	40.0	45.0	30.0	35.0	40.0	45.0
Equilibrium Constant (K) x10^{-2}	4.123	8.384	8.770	16.535	5.564	12.223	23.067	26.980
Enthalpy (kJ/mol)	67.66				86.60			

From the results of our study, it was observed that with rise in temperature, the *K* values increases for both the resins (Table 4). The increase in *K* values with rise in temperature indicated endothermic ion exchange reactions having positive enthalpy values of 67.66 kJ/mol for Indion GS-300 and 86.60 kJ/mol for Indion FF IP ion exchange resins. The low enthalpy value for reaction (1) also indicates that the ion exchange reaction is thermodynamically more feasible using Indion GS-300 resins. Based on the low enthalpy value, it can be predicted that the Indion GS-300 resin is having higher selectivity for bromide ions in the solution as compared to that of Indion FF IP resins under identical experimental conditions.
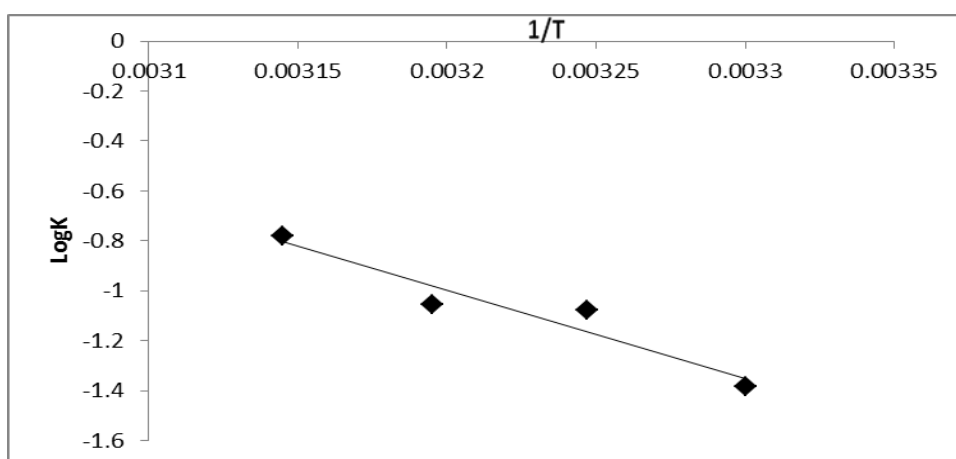
Figure 1. Effect of temperature on equilibrium constant of ion exchange reaction (1) performed by using Indion GS-300 resin.
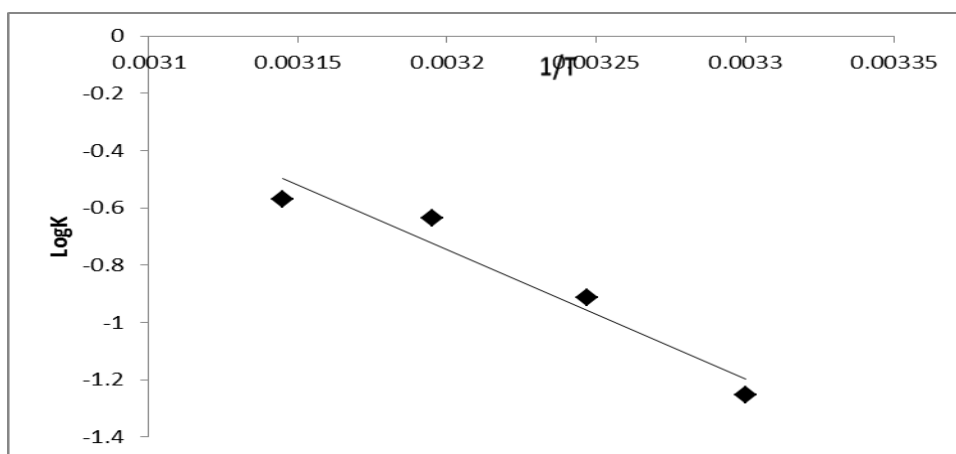
Figure 2. Effect of temperature on equilibrium constant of ion exchange reaction (1) performed by using Indion FF IP resin.

CONCLUSION

The selectivity behavior of different ion exchange resins towards other ionic species can be studied with the help of the experimental methodology adopted in this research study. The inferences drawn from the research study will also assist in selecting suitable ion exchange resins, so that effective parting of different ionic species present in both, the industrial as well nuclear waste can be undertaken.

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