ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Study of iodide ion exchange reactions involving nuclear and non-nuclear grade anion exchange resins.

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ABSTRACT

In the present research study attempts were made to understand the iodide selectivity behavior of anion exchange resin Indion GS-300 (nuclear grade) and Indion FFIP (non-nuclear grade). The thermodynamic concept was applied to envisage the selectivity behavior of ion exchange resins. During the ion exchange reactions, it was observed that as the temperature was raised from 30.0^{o}C to 45.0^{o}C, the equilibrium constant *(K)* values decreased from 1.942 x10^{-2} to 0.322 x 10^{-2} for Indion GS-300 resin and from 3.112 x10^{-2} to 0.675 x10^{-2} for Indion FF IP resin. The decrease in *K* values with rise in temperature indicated exothermic ion exchange reactions having negative enthalpy values using Indion GS-300 (-97.36 kJ/mol) and Indion FFIP (-93.39 kJ/mol) ion exchange resins. The negative enthalpy values indicate that the iodide ion exchange reaction is thermodynamically feasible using both the resins. The high *K* value obtained for Indion FF IP as compared to Indion GS-300 resin indicate that the iodide ion exchange reaction will proceed more rapidly in forward direction when performed using Indion FF IP resins. However, the low enthalpy value obtained for the reaction using Indion GS-300 resin indicated their greater selectivity for the iodide ions as compared to Indion FFIP resins under identical experimental conditions. The observed trend in selectivity of the resins towards iodide ions in solution is attributed to the difference in moisture content of the two resins.

Keywords: equilibrium constant, anion exchange, Indion GS-300, Indion FF IP, enthalpy, selectivity.

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INTRODUCTION

A process in which the moveable ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups which is within the solid matrix is termed as 'Ion Exchange'. Ion exchangers are either cation exchangers, exchanging positively charged ions or anion exchangers, exchanging negatively charged ions. In a solution, when these ion exchange resins are placed they reach an equilibrium state between the ions in the solution and the ions on the resin. From this state of equilibrium, the selectivity coefficients that is the equilibrium constants is defined based on the ratios of ions in solution vs. ions on the resin. Thus, the measurement of the resins preference for the ion defines the selectivity coefficient of the resin. The higher the selectivity coefficient, the higher the preference for the ion [1]. Variables relating to the resin are the exchange capacity; degree of cross-linking determining the permeability of the resin, swelling potential, and the access of the exchange sites to the ion; the effective exchange affinity; and particle size of the resin which controls accessibility to the exchange ions [2]. Moreover, the insolubility of the resin phase is a significant functional aspect of the resin that makes them environmentally attuned and thus they have been used in water softening, removing toxic metals from water bodies, wastewater treatment, hydrometallurgy, sensors, chromatography and biomolecular separations. Having explained on the variety of applications of the ion exchange resin, thus forming one of the most significant scientific developments of the 20th century [3]. Munday and Eaves were the first to suggest removal of acids and bases from petroleum fractions, using ion exchange resins [4]. The experience gained has also led to more widespread applications in research as well as practical use [5]. Almost all the resins are produced by polymerizing styrene in presence of divinylbenzene [6].Thus, the ion exchange resins produced commercially in various formulations and with diverse 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 advance the efficiency and economy aspects of their application [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 liquid waste becomes difficult in presence of chemically similar ionic species. In the present investigation, attempt was made to understand the difference in iodide ion selectivity of resins Indion GS-300 and Indion FFIP in chloride form. The present technique can be applied to understand the selectivity behavior of different anion exchange resins towards series of anions in the exchanging medium.

EXPERIMENTAL

The ion exchange resin IndionGS-300 and Indion FFIP as supplied by the manufacturer (Ion exchange India Limited, Mumbai) were the anion exchangers in the OH^- form. The details regarding the various physico-chemical properties of the 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	Polystyrene	$-N^+R_3$	0.3-1.2	51.9%	0-14	60	1.40
Indion FF IP	Styrene DVB	$-N^+R_3$	0.3-1.2	48.0%	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 removed 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 using sodium nitrate and titrating the eluent against standard silver nitrate solution was followed [11]. Ion exchange resins (0.500g) in chloride form were equilibrated with iodide ion solution of different concentrations at 35.0°C for 3 h when the following reaction takes place:

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

From various research studies conducted by experts; it was observed that the duration of the 3 h was adequate to attain the ion exchange equilibrium [12-19]. After 3 h, the equilibrated solutions were analyzed potentiometrically for their chloride and iodide 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 30.0°C.Similar *K* values were measured for different temperatures ranging from 30.0°C to 45.0°C. A semi-micro burette having an accuracy of 0.02 mL was used for potentiometric titrations against standard $AgNO_3$, in the entire study. The titration readings were accurate to ±0.02 mL and the magnitude of the titre values; the average equilibrium constants testified in the experiment was accurate to ±3 %.

RESULTS AND DISCUSSION

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

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

(B-

where, *A* symbolizes the ion exchange capacity of the resin. At a fixed temperature, *K* values were measured for different iodide 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). It was observed that the *K* values for the ion exchange reaction (1) using Indion FF IP were higher as compared to the values obtained for the same reaction using Indion GS-300 resin. The high *K* value obtained for Indion FF IP as compared to Indion GS-300 resin indicate that the iodide ion exchange reaction will proceed more rapidly in forward direction when performed using Indion FF IP resins. The enthalpy values for the ion exchange reaction (1) using the two resins was calculated from the slope of the graph log *K* against 1/T (in Kelv in) (Figures1 and 2). The enthalpy values of the ion exchange reaction 1 for the two resins are presented in Table 4.

Table 2.Equilibrium constant for the ion exchange reaction (1) using Indion GS-300 resin
Amount of the ion exchange resin in chloride form = 0.500 g,
Ion exchange capacity = 2.00 meq./0.5 g, Temperature = 30.0°C.

System	Initial concentration of iodide ion (M)	Final concentration of iodide ions (M)C_{I^-}	Change in iodide ion concentration	Concentration of chloride ions exchanged in the solution (M)C_{Cl^-}	Amount of iodide ions exchanged on the resin meq./0.5 g C_{RI}	Equilibrium constant *(K)* x10^{-2}
1	0.100	0.078	0.022	0.022	1.100	0.210
2	0.200	0.186	0.014	0.014	0.700	0.140
3	0.300	0.294	0.006	0.006	0.300	0.031
4	0.400	0.372	0.030	0.030	1.500	3.348
5	0.500	0.468	0.032	0.032	1.600	5.990
Average *K*						**1.942**

Table 3. Equilibrium constant for the ion exchange reaction (1) using Indion FF IP resin
Amount of the ion exchange resin in chloride form = 0.500 g,
Ion exchange capacity = 2.50 meq./0.5 g, Temperature = 30.0°C

System	Initial concentration of iodide ion (M)	Final concentration of iodide ions (M)C_{I^-}	Change in iodide ion concentration	Concentration of chloride ions exchanged in the solution (M) C_{Cl^-}	Amount of iodide ions exchanged on the resin meq./0.5 g C_{RI}	Equilibrium constant *(K)* x10^{-2}
1	0.100	0.084	0.020	0.020	1.000	0.112
2	0.200	0.175	0.030	0.030	1.500	0.788
3	0.300	0.278	0.022	0.022	1.100	0.481
4	0.400	0.354	0.040	0.040	2.000	5.664
5	0.500	0.453	0.047	0.047	2.000	8.516
Average *K*						**3.112**

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]. The results of our study also revealed the same fact giving enthalpy values of -97.36 kJ/mol for Indion GS-300 and -93.39 kJ/mol for Indion FFIP ion exchange resins.

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

Resin	**Indion GS-300**				**Indion FFIP**			
Temperature(°C)	30.0	35.0	40.0	45.0	30.0	35.0	40.0	45.0
Equilibrium Constant *(K)* x10^{-2}	1.942	0.668	0.352	0.322	3.112	2.442	0.721	0.675
Enthalpy *(H)*(kJ/mol)	**-97.36**				**-93.39**			

The low enthalpy value for the ion exchange reaction (1) obtained by using Indion GS-300 resins indicates that the reaction is thermodynamically more feasible as compared to Indion FF IP resins. Previous study reported low enthalpy value for the similar ion exchange reaction system using Auchlite ARA-9366 (-47.87 kJ/mol) as compared to Auchlite A-378 (-39.51 kJ/mol) indicating higher selectivity of Auchlite ARA-9366 towards the iodide ions in the solution which is attributed to difference in moisture content of the two resins. The results of present study also indicate that the moisture content of the resin greatly impact their selectivity behavior. From the results of present study it was observed that ion exchange reaction (1) using Indion GS-300 resin proceed with relatively low enthalpy (-97.36 kJ/mol) as compared to the enthalpy value of -93.39 kJ/mol obtained by using Indion FF IP resins. The low enthalpy value obtained by using Indion GS-300 indicate its high selectivity towards iodide ions in the solution as compared to Indion FF IP resins under similar experimental conditions which is also attributed to the difference in moisture content (Table 5).

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

Table 5. Comparison of thermodynamic data of ion exchange reaction

Ion Exchange Resins	Temperature Range (°C)	% moisture content	Enthalpy (kJ/mol)	References
Auchlite ARA-9366	30-45	50.0	-47.87	[21]
Auchlite A-378	30-45	48.0	-39.51	[21]
Indion GS-300	30-45	51.9	-97.36	Present study
Indion FFIP	30-45	48.0	-93.39	Present study

CONCLUSION

Recent developments in resin technology and rationalized review of the literature have assisted in understanding and utilizing this technique efficiently. The experimental methodology adopted for this present research study can further be extended to different ion exchange resins to understand its selectivity behavior towards series of ionic species present in the exchanging medium. The results drawn from the research study can also be put to use for better selection of suitable ion exchange resin for the widespread technological applications.

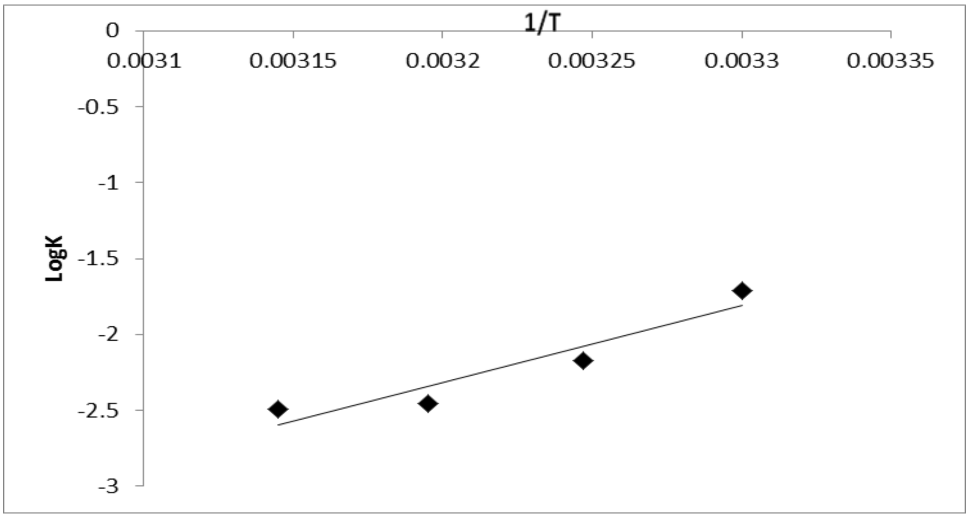

Figure 1. Effect of temperature on equilibrium constant of ion exchange reaction(1) performed by using Indion GS-300 resin.

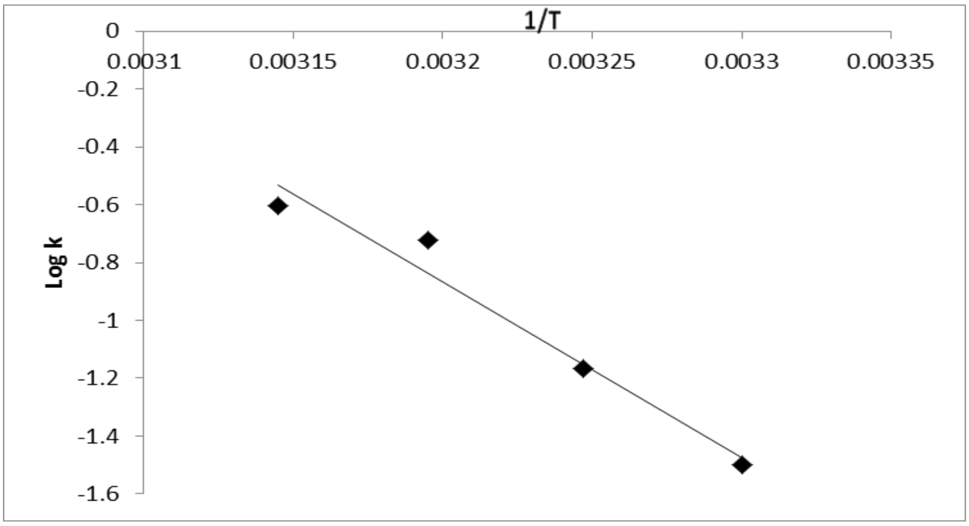

Figure 2.Effect of temperature on equilibrium constant of ion exchange reaction (1) performed by using Indion FFIP resin.

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