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Study on thermodynamic feasibility of uni-univalent ion exchange reactions using nuclear grade anion exchange resin Indion GS-300

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ABSTRACT

The present study deals with the thermodynamics of ion exchange reactions using nuclear grade anion exchange resin Indion GS-300. The ion exchange reactions were performed by separately equilibrating the resin in chloride form with iodide and bromide ion solution of different concentrations at varying temperature. Based on the equilibrium constant (K) values obtained at different temperatures, the enthalpy values for the two ion exchange reactions were calculated. For Cl^-/I^- ion exchange reaction, the K values were observed to decrease with rise in temperature giving negative enthalpy value (-97.36 kJ/mol) thereby indicating exothermic ion exchange reaction; while for Cl^-/Br^- ion exchange reaction reverse trend was observed having enthalpy value of 67.66 kJ/mol. Based on the enthalpy values it can be predicted that under identical experimental conditions, by using Indion GS-300 resins, the Cl^-/I^- ion exchange reaction is thermodynamically more feasible as compared to Cl^-/Br^- ion exchange reaction.

Keywords: Thermodynamics; reaction feasibility; anion exchange reaction; enthalpy; Indion GS-300.

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INTRODUCTION

Over several decades, ion exchange technology has received growing attention in various industries like chemical, petrochemical, food, power and pharmaceutical industries. This technology is generally used to purify solutions by removing the dissolved ions by electrostatic sorption into ion exchange materials of various forms. In this process, either the removed ions are replaced with equivalent number of other ions of the same charge in the solution or particular ions are selectively separated. Thus, selective removal of ionic contamination and complete deionization, can be very well distinguished [1]. Thus, the ion exchange process is widely used for purification, separation and decontamination of aqueous and other ionic solutions [2]. The removing of acids and bases from petroleum fractions, using ion exchange resins was first suggested by Munday and Eaves [3]. 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 [4]. Most of the resins are produced by polymerizing styrene in presence of divinylbenzene [5]. Thus, the ion exchange resins produced commercially in various formulations and with different characteristics have a wide range of application. Thus forming one of the most significant scientific development of the 20th century [6]. Having known the benefits, research to develop new ion exchangers for specific applications and to enhance the productivity and making it low-cost of their application in various technological applications is a continuous endeavor [7-10]. Further delving deeper into the subject, it was learned that ion exchange media has a greater affinity under certain conditions, for certain ionic species than for others. Thus, separation of these species becomes easy; ironically selection of the desired ion exchange media becomes difficult in presence of chemically similar ionic species in the liquid waste. The present study was therefore performed to understand the thermodynamic feasibility of the bromide and iodide ion exchange separation reactions. The experimental technique can be extended further for series of ions in the solution. It is expected that the results of such study will help in understanding the selectivity behavior of the resins towards different ions in the solution.

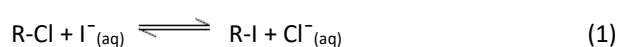
EXPERIMENTAL

The ion exchange resin Indion GS-300 as supplied by the manufacturer (Ion exchange India Ltd., Mumbai) were the anion exchangers in the OH⁻ form. The details regarding the various physico-chemical properties of the ion exchange resin has been presented in 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	51.9	0-14	60	1.40

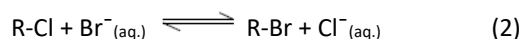
For the present investigation, the resin grains of 30-40 mesh size were used. The soluble impurities of the resins were separated by repeated soxhlet extraction using water. Moreover, distilled methanol was used occasionally to remove non-polymerized organic impurities. The resin was conditioned with 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 free from Cl⁻ ions. The resin in the chloride form was air dried over P₂O₅ in desiccators. For determining the exchange capacity of the resins, standard method using sodium nitrate and titrating against standard silver nitrate solution was used [11]. Ion exchange resin which was 0.500g in chloride form was equilibrated with iodide ion solution of different concentrations for 3h at a constant temperature of 30°C, when the following reaction takes place:



From the results of previous studies it was observed that the time duration of 3h was adequate to attain the ion exchange equilibrium [12-19]. After 3h, the iodide ion solutions in equilibrium with the resins were analyzed for their chloride and iodide ion concentrations by potentiometric titration with standard 0.03

N AgNO₃ solutions. From the knowledge of ion exchange capacity; chloride and iodide ions in the solution; the amount of iodide and chloride ions on the resin, the *K* value for the reaction (1) at 30°C was determined. Similar *K* values were determined for the above ion exchange reaction at different temperatures extending up to 45°C.

The above experimental procedure was further extended by equilibrating the ion exchange resins in chloride form with bromide ion solution of different concentrations when the following ion exchange reaction takes place:



The ion exchange reaction (2) was performed at different temperatures as mentioned above for 3h. From the knowledge of ion exchange capacity; amount of chloride ions exchanged in the solution and amount of bromide ions left in the solution; amount of bromide ions exchanged on the resin, the *K* values for the ion exchange reaction (2) was calculated for different temperatures.

For the entire experiment, a semi-micro burette having an accuracy of 0.02 mL was used for titrations against silver nitrate solution. The titration readings were accurate to ±0.02 mL and the magnitude of the titre values and the average *K* values reported were accurate to ±3 %.

RESULTS AND DISCUSSION

The equilibrium constants for reaction (1) and (2) can be written as

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

where, *A* is the ion exchange capacity of the resin and X⁻ represents I⁻ and Br⁻ ions in solution at a given temperature, *K* values were calculated and an average *K* value for this set of experiments was found as mentioned in Tables 2 and 3. Similarly, *K* values were calculated for the Cl⁻/I⁻ and Cl⁻/Br⁻ system at different temperatures as described in Table 4. Furthermore, the log *K* values were plotted against 1/*T* (in Kelvin), resulting in a straight line graph (Figures 1 and 2), from the slope of this graph enthalpy of the ion exchange reactions (1) and (2) was calculated as shown in Table 4.

The effect of temperature on ion exchange equilibrium involving some divalent ions over the temperature range 0°C to 97.5°C using the sulfonic acid type resins have been studied by many researchers. In all divalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions [20]. Similar trend was observed in the present study while investigating reaction (1), in which the *K* values decreases from 1.942x10⁻² at 30.0°C to 0.322x10⁻² at 45.0°C having enthalpy value of -97.36 kJ/mol indicating exothermic ion exchange reaction (Table 4). However, exactly opposite trend was observed during the investigation of reaction (2), in which the *K* values where observed to increase from 4.123x10⁻² to 16.535x10⁻², when the equilibration temperature was raised from 30.0°C to 45.0°C, indicating endothermic ion exchange reaction having the enthalpy value of 67.66 kJ/mol (Table 4).

The higher *K* values for reaction (2) in comparison to reaction (1) at different temperatures indicates that at any given temperature, the reaction (2) will proceed in forward direction much rapidly in comparison to reaction (1). The negative enthalpy value for reaction (1) and positive enthalpy value for reaction (2) suggest that the reaction (1) is thermodynamically more feasible. It also suggest that the Indion GS-300 resins are having higher affinity and hence higher selectivity towards the iodide ions than bromide ions when both of the ions are present in the same solution.

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

System	Initial concentration of iodide ions (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) $\times 10^{-2}$
1	0.100	0.081	0.020	0.020	1.000	0.162
2	0.200	0.180	0.023	0.023	1.000	0.360
3	0.300	0.288	0.012	0.012	0.600	0.148
4	0.400	0.390	0.010	0.010	0.500	0.130
5	0.500	0.480	0.020	0.020	1.000	0.960
Average K						0.352

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.00 meq./0.5 g, Temperature = 40.0°C

Table 3. Equilibrium constant for the ion exchange reaction (2) using Indion GS-300 resin.

System	Initial concentration of bromide ions (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) $\times 10^{-2}$
1	0.100	0.070	0.030	0.030	1.520	0.670
2	0.200	0.168	0.032	0.032	1.585	2.038
3	0.300	0.268	0.032	0.032	1.620	3.696
4	0.400	0.365	0.036	0.036	1.775	10.208
5	0.500	0.462	0.038	0.038	1.880	27.238
Average K						8.770

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.00 meq./0.5 g, Temperature = 40.0°C

Table 4. Thermodynamics of ion exchange reactions using Indion GS-300 ion exchange resin.

Reaction	1				2			
	30.0	35.0	40.0	45.0	30.0	35.0	40.0	45.0
Temperature (°C)	30.0	35.0	40.0	45.0	30.0	35.0	40.0	45.0
Equilibrium Constant (K) $\times 10^{-2}$	1.942	0.668	0.352	0.322	4.123	8.384	8.770	16.535
Enthalpy (kJ/mol)	-97.36				67.66			

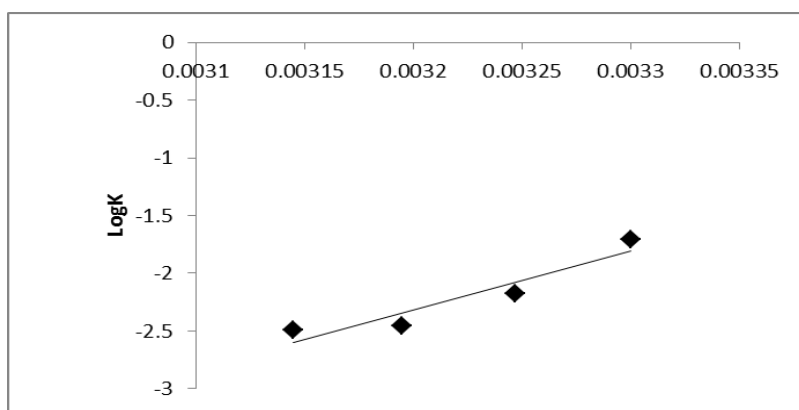


Figure 1. Effect of temperature on equilibrium constant of uni-univalent ion exchange reaction (1) performed by using Indion GS-300 resin.

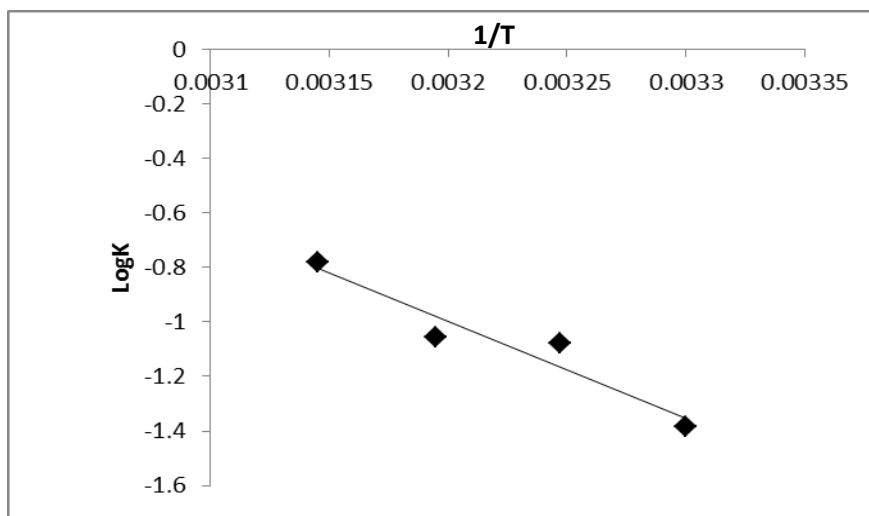


Figure 2. Effect of temperature on equilibrium constant of uni-univalent ion exchange reaction (2) performed by using Indion GS-300 resin.

CONCLUSION

A large number of commercial resins are available in the market, enabling enhancement of the custom designed ion exchange process for a defined application. Thus, the prerequisite for a system designed solution is thorough knowledge and understanding of the basic fundamentals and economics of ion exchange. This will ensure highly efficient and cost effective operations of using ion exchange technology. So, the present study value adds to the existing knowledge base of different ion exchange resins and its selectivity behavior towards various ranges of ionic species at varying temperatures.

REFERENCES

- [1] Nasef MM, Ujang Z. Introduction to Ion exchange process. In Inamuddin and Mhammad, L., (Eds.), *Ion Exchange Technology I: Theory and Materials*. Springer Netherlands, 2012 pp. 1-39.
- [2] Helfferich FG. *Ion Exchange*. McGraw-Hil, New York, 1962.
- [3] Jewell DM, Weber JH, Bungler JW, Plancher H, Latham DR, *Analytical Chemistry* 1972; 44: 1391-1398.
- [4] Guo X, Chang RK, Hussain MA. *Journal of Pharmaceutical Sciences* 2009; 98: 3886-3890.
- [5] Windsor B. *Resin Types and Production*
Available online:
http://www.soci.org/~media/Files/Conference%20Downloads/2012/IE%20Intro%20Water%20Sept%202012/Brian_Windsor_resin.ashx
Accessed on July 2016.
- [6] Alexandratos SD. *Industrial and Engineering Chemistry Research* 2008;48: 388-393.
- [7] Singare PU, Lokhande RS, Samant N. *Natural Science* 2009; 1: 124-128.
- [8] Singare PU, Patange AN. *International Letters of Chemistry, Physics and Astronomy* 2014; 25: 8-15.
- [9] Singare PU. *Nuclear Engineering and Technology* 2014; 46: 93-100.
- [10] Singare PU, Lokhande RS, Madyal RS. *Russian Journal of General Chemistry* 2010; 80: 527-532.
- [11] Jeffery GH, Bassett J, Mendham J, Denny RC. *Vogel's Textbook of Quantitative Chemical Analysis*, Longman Scientific & Technical, England, 5th Edition, 1989, pp.87.
- [12] Lokhande RS, Singare PU. *Chem. Environ. Research* 1998; 7: 129-132.
- [13] Lokhande RS, Singare PU, *Asian Journal of Chemistry* 1998; 10: 898-903.
- [14] Singare PU. *International Letters of Chemistry, Physics and Astronomy* 2013; 12: 1-13.
- [15] Lokhande RS, Singare PU. *Journal of Indian Council of Chemist* 2007; 24: 73-77.
- [16] Singare PU, Lokhande RS, Patil VV, Prabhavalkar TS, Tiwari SRD. *European Journal of Chemistry* 2010; 1:47-49.



- [17] Lokhande RS, Singare PU. Asian Journal Chemistry 2003; 15: 33-35.
- [18] Lokhande RS, Singare PU, Patil AB. Russian Journal of Physical Chemistry A 2007; 81: 2059-2063.
- [19] Lokhande RS, Singare PU, Kolte AR. Bulletin of Chemical Society of Ethiopia 2008; 22: 107-114.
- [20] Bonner OD, Pruett RR. The Journal of physical Chemistry 1959; 63: 1420-1425.