

Ion-exchange reaction thermodynamics to study the selectivity behaviour of nuclear and non-nuclear grade anion exchange resins

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ABSTRACT

In the present investigation, attempts were made to understand the difference in bromide ion selectivity of the two closely related anion exchange resins Auchlite ARA-9366 and Auchlite A-378 in chloride form. The selectivity difference was predicted based on the thermodynamic equilibrium constants and enthalpy values of Cl^-/Br^- ion exchange reactions performed by using the two resins. During Cl^-/Br^- exchange reactions, with rise in temperature from 30.0 °C to 45.0 °C, the equilibrium constant (K) values were observed to decrease from 8.15×10^{-2} to 6.06×10^{-2} for Auchlite ARA-9366 resins and from 2.16×10^{-2} to 1.10×10^{-2} for Auchlite A-378 resins. The decrease in K values with rise in temperature, indicate exothermic ion exchange reactions having enthalpy values of -36.14 and -18.38 kJ/mol respectively. The high K and low enthalpy values obtained for Auchlite ARA-9366 resins indicate their greater selectivity for the bromide ions in the solution as compared to Auchlite A-378 resins.

Keywords: ionic selectivity; uni-univalent exchange; thermodynamic equilibrium constant; enthalpy; nuclear grade ion exchange resin; Auchlite ARA-9366; Auchlite A-378

1. INTRODUCTION

Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electro statically bound to the functional groups contained within a solid matrix. When the functional groups are negatively charged the exchange will involve cations and when they are positively charged they involve anions. In recent times various aspects of ion exchange technology are being studied in many countries to improve its efficiency and economy in its applications in chemical, nuclear, pharmaceutical, food industry, etc. [1]. Also number of organic ion exchange resins which are more superior than the selective inorganic ion exchangers has been developed over a much longer period of time are now becoming available in commercial quantities so as to meet the requirements of the nuclear industry. When used in nuclear industries these organic ion exchange resins very effectively transfer

the radioactive content of a large volume of liquid into a small volume of solid and hence are applied for cleaning and decontamination processes and also for removal of radionuclide [2-6]. As a result these organic ion exchange resins have proved to be reliable and effective for the control of both the chemistry and radiochemistry of water coolant systems at nuclear power plants and also for processing some liquid radioactive waste [7]. In number of cases, for specific physical and chemical reasons, organic resins cannot be replaced by commercially available inorganic ion exchangers and organic ion exchange resins continued to be used globally [7].

Extensive work is done on development and characterization of new ion exchange resins so as to improve the performance of those resins in various technical applications [8-13]. By taking advantage of the fact that, under certain conditions, ion exchange media has a greater affinity for certain ionic species than for others, a separation of these species can be made [7,14]. However presence of chemically similar ionic species in the liquid waste will create difficulty in selection of suitable ion exchange media. If low cost general ion exchange media are used, large volumes may be required, leading to larger volumes of waste to treat and dispose of. Higher cost ion specific exchangers may be a better choice, especially when the extra cost of the media is more than offset by the reduction in the total cost for the treatment and subsequent storage and/or disposal of the spent media.

Therefore, in the present investigation, based on the thermodynamic equilibrium constants attempts was made to understand the difference in bromide ion selectivity of the two closely related anion exchange resins Auchlite ARA-9366 and Auchlite A-378 in chloride form. It is expected that the present technique can be applied further to understand the selectivity behaviour of series of anion exchange resins towards different uni and multivalent ions in the solution. The experimental data generated from such studies will be useful in selection of suitable resin for various technical applications.

2. EXPERIMENTAL

The ion exchange resin Auchlite ARA-9366 and Auchlite A-378 as supplied by the manufacturer (Auchtel Products Ltd., Mumbai, India) were the anion exchange resins in hydroxide form. The details regarding various physico-chemical properties of the two ion exchange resins are 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) |
|--------------------|-------------|---------------------|-------------------------|----------------------|--------------|------------------------------------|
| Auchlite ARA-9366 | polystyrene | quaternary ammonium | 0.3-1.0 | 50 | 0-14 | 60.0 |
| Auchlite A-378 | polystyrene | tertiary ammonium | 0.3-1.2 | 48 | 0-7 | 60.0 |

For present investigation, the resin grains of 30-40 mesh size were used. The soluble impurities of the resin were removed by repeated Soxhlet extraction using water and occasionally with distilled methanol to remove non-polymerized organic impurities. In order to convert the resins in chloride form, they were conditioned with 10 % potassium chloride solution in a conditioning column. The resins were washed with distilled deionised water until the washings were free from chloride ions.

The resins in chloride form were air dried over P₂O₅ and used for further studies. The exchange capacity of ion exchange resins was experimentally determined by the standard method [15] using sodium nitrate and titrating against standard silver nitrate solution. Ion exchange resins (0.500 g) in chloride form were equilibrated with bromide ion solution of different concentrations at a constant temperature of 30.0 °C for 3 h. From the results of kinetics study reported earlier [16-36]; it was observed that this duration was adequate to attain the ion exchange equilibrium.

After 3 h, the bromide ion solutions in equilibrium with ion exchange resins in chloride form were analyzed for their chloride and bromide ion concentrations by potentiometric titration with standard 0.1 M silver nitrate solution. From the results the equilibrium constant *K* for the reaction



was determined at 30.0 °C. The equilibrium constants *K* for the above Cl⁻/Br⁻ system was determined for different temperatures in the range of 30.0 °C to 45.0 °C.

In the present study, a semi-micro burette having an accuracy of 0.02 mL was used in the titrations against silver nitrate solution. The titration readings were accurate to ±0.02 mL. Considering the magnitude of the titre values, the average equilibrium constants reported in the experiment are accurate to ±3 %.

3. RESULTS AND DISCUSSION

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

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

where, *A* is the ion exchange capacity of the resin. For different concentrations of Br⁻ ions in solution at a given temperature, *K* values were calculated and an average *K* value for this set of experiments was found (Tables 2, 3). Similar *K* values were calculated for the Cl⁻/Br⁻ system at different temperatures (Table 4). The log *K* values were plotted against 1/*T* (in Kelvin), which gives a straight line graph (Figure 1) from the slope of this graph enthalpy of the ion exchange reaction 1 was calculated (Table 4).

Bonner and Pruett [37] studied the temperature effect on uni-univalent exchanges involving some divalent ions. In all divalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. Similar results were obtained in the present investigation for Auchlite ARA-9366 and Auchlite A-378 resins, during Cl⁻/Br⁻ uni-univalent ion exchange reactions having the enthalpy values of -36.14 and -18.38 kJ/mol respectively (Table 4).

These results obtained here are very much identical to the results of our previous research work performed on the same system using Duolite 101-D and Tulsion A-33 anion exchange resins in which the variation of K values with rise in temperature follow the same pattern indicating exothermic ion exchange reactions (Table 5) [38-41].

Table 2. Equilibrium constant for the ion exchange reaction (1) using Auchlite ARA-9366 resin. Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.3meq./0.5 g, Temperature = 30.0 °C.

| System | Initial conc. of bromide ion (M) | Final conc. of bromide ions (M) C_{Br^-} | Change in bromide ion conc. | Conc. of Cl^- ions exchanged (M) C_{Cl^-} | Amount of bromide ions exchanged on the resin meq./0.5 g C_{RBr} | Equilibrium constant K |
|-----------|----------------------------------|--|-----------------------------|---|--|------------------------|
| 1 | 0.0094 | 0.0034 | 0.0060 | 0.0060 | 0.30 | 0.2647 |
| 2 | 0.0224 | 0.0152 | 0.0072 | 0.0072 | 0.36 | 0.0879 |
| 3 | 0.0476 | 0.0392 | 0.0084 | 0.0084 | 0.42 | 0.0479 |
| 4 | 0.0726 | 0.0694 | 0.0032 | 0.0032 | 0.16 | 0.0034 |
| 5 | 0.0968 | 0.0930 | 0.0038 | 0.0038 | 0.19 | 0.0037 |
| Average K | | | | | | 0.0815 |

Table 3. Equilibrium constant for the ion exchange reaction (1) using Auchlite A-378 resin. Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 0.74meq./0.5 g, Temperature = 30.0 °C.

| System | Initial conc. of bromide ion (M) | Final conc. of bromide ions (M) C_{Br^-} | Change in bromide ion conc. | Conc. of Cl^- ions exchanged (M) C_{Cl^-} | Amount of bromide ions exchanged on the resin meq./0.5 g C_{RBr} | Equilibrium constant K |
|-----------|----------------------------------|--|-----------------------------|---|--|------------------------|
| 1 | 0.0096 | 0.0072 | 0.0024 | 0.0024 | 0.12 | 0.0645 |
| 2 | 0.0248 | 0.0228 | 0.0020 | 0.0020 | 0.10 | 0.0137 |
| 3 | 0.0490 | 0.0470 | 0.0020 | 0.0020 | 0.10 | 0.0066 |
| 4 | 0.0726 | 0.0710 | 0.0016 | 0.0016 | 0.08 | 0.0027 |
| 5 | 0.1060 | 0.0986 | 0.0074 | 0.0020 | 0.37 | 0.0203 |
| Average K | | | | | | 0.0216 |

Table 4. Thermodynamics of ion exchange reaction $R-Cl + Br^-_{(aq.)} \leftrightarrow R-Br + Cl^-_{(aq.)}$

| Resins | Auchlite ARA-9366 | | | | Auchlite A-378 | | | |
|---|-------------------|------|------|------|----------------|------|------|------|
| Temperature (°C) | 30.0 | 35.0 | 40.0 | 45.0 | 30.0 | 35.0 | 40.0 | 45.0 |
| Equilibrium Constant (<i>K</i>) x10 ⁻² | 8.15 | 6.66 | 6.46 | 6.06 | 2.16 | 1.68 | 1.17 | 1.10 |
| Enthalpy (kJ/mol) | -36.14 | | | | -18.38 | | | |

Table 5. Comparison of thermodynamic equilibrium data of ion exchange reaction $R-Cl + Br^-_{(aq.)} \leftrightarrow R-Br + Cl^-_{(aq.)}$ using different ion exchange resins.

| Ion Exchange Resins | Temperature Range (°C) | Equilibrium Constant <i>K</i> range | Enthalpy (kJ/mol) | References |
|---------------------|-------------------------|-------------------------------------|-------------------|------------|
| Tulsion A-33 | 30-45 | 9.88-7.71 | -15.30 | [38,39] |
| Duolite 101-D | 30-45 | 14.54-9.88 | -24.64 | [40,41] |
| Auchlite ARA-9366 | 30-45 | 8.15-6.06 | -36.14 | This Study |
| Auchlite A-378 | 30-45 | 2.16-1.10 | -18.38 | This Study |

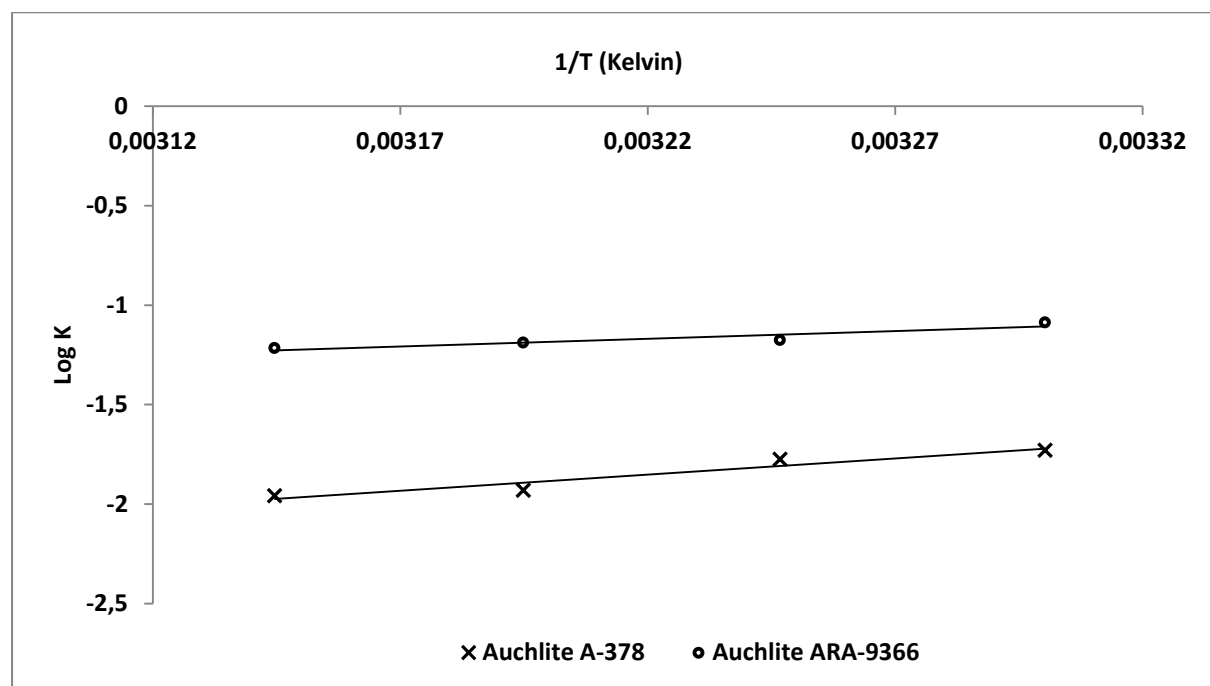


Figure 1. Effect of temperature on equilibrium constant of ion exchange reactions $R-Cl + Br^- \leftrightarrow R-Br + Cl^-$ performed by using Auchlite ARA-9366 and Auchlite A-378 resins.

The equilibrium constants K for uni-univalent ion exchange reaction (1) increases in the order Auchlite A-378 < Auchlite ARA-9366. Therefore, the selectivity of these ion exchange resins in chloride form towards Br^- ions increases in the same order. Similarly, the enthalpy values for the reaction (1) increases in the order Auchlite ARA-9366 < Auchlite A-378. The high K and low enthalpy values obtained for Auchlite ARA-9366 indicates their superior performance in terms of selectivity towards bromide ions in solution as compared to Auchlite A-378, when both of the resins are present in chloride form.

4. CONCLUSION

The experimental method used in the present study can be extended further for different ion exchange resins in order to understand their selectivity behaviour towards wide range of ionic species. The results of such studies will help in selection of suitable ion exchange resins in order to bring about efficient separation of different ionic species present in the waste water effluents released from nuclear as well as chemical process industries.

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