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STUDY OF $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ ION EXCHANGE EQUILIBRIA ON LEWITAT M500 CHELATING RESIN

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Thermodynamic equilibrium constants of $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ ion exchange reaction on the strongly basic anion - exchanger Lewitat M500 were determined different temperatures ranging from 25° - 45°C. It was found that the value of K is ≤I and increases with increasing in temperature and $K^{\bar{Br}}_{\bar{Cl}}$ is greater that $K^{\bar{I}}_{\bar{Cl}}$. The standard enthalpy ΔH^0, free energy ΔG^0 and entropy ΔS^0 changes were calculated. ΔH^0 of ion exchange reactions were obtained to be 20.43 KJ mol^{-1} for $\bar{I}/\bar{Cl}$ and 16.63 KJ mol^{-1} for $\bar{Br}/\bar{Cl}$.

Key words : Ion exchange equilibrium, Thermodynamic, Enthalpy (ΔH), Free energy (ΔG), Entropy (ΔS)

Introduction

Determination of equilibrium constants for the ion exchange processes is of importance for the development of theoretical treatment and optimization of e.g. analytical methods and industrial processes. This holds also for ion exchange systems like chelating resins. However, ion exchange equilibrium and kinetic data on chelate ion exchangers have been studied experimentally by several investigators (Leyden and Underwood 1964; Eger *et al* 1968; Szabadka 1982; Harju and perus 1987). Equilibrium constans can be found only for a few metal ions. Harju and perus (1987) have reported equilibrium constants for copper chelates with the Dowex A-1 resin Harju and Krook (1995) measured the equilibrium constants of the alkaline earth metal ion chelates with Dowex A-1 resin Yoshida *et al* (1986) presented equilibrium kinetic data of chelation of copper, cobalt and chromium on two typical Na-form chelate ion exchangers Dowex A-1 and UR-10. Bonner and Smith (1957) studied the effect of temperature on Na^+/H^+ exchangers. Lokhande and Singare (1998a) studied the temperature effect of I/SO_4^{2-} and $\bar{Cl}/\bar{I}$ ion exchange system in Amberlite IRA-400 and they pointed out that in dilute solutions the molality of ions in solution can be replaced by molarity in Bonner *et al* (1957) equation. In the present study attempt has been made to determine the equilibrium constants for the $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ exchangers on the strong basic anion exchangers Lewitat M500 chelating resin.

Experimental

The strongly basic tert-amine Lewitat M500 anion exchanger was already provided in the chloride form.

a) Determination of exchange capacity. About 20.0g of the resin in $\bar{Cl}$ form was transferred to a conical flask, covered with 100 ml of 0.25 M $Na\bar{NO}_3$ and left or 24 hours, then if filtered off and washed several times with distilled water until the washing is free from $\bar{Cl}$ ion, then the resin was air dried and used for further study.

0.5 g of each resin in NO_3 form was transferred into a conical flask and covered with 50 ml of 0.2 M NaCl and left for 24 hours, then filtered off, 20 ml of the filtrate was transferred into a small beaker and concentration of the chloride was determined by potentiometric titration with standard 0.1 M silver nitrate solution using digital pH-meter (pH 525-Germany).

b) Conditioning of the resin. The resin Lewitat M500 was already in the chloride form. However, In order to ensure that it was completely in this form the resin (about 10 g) was transferred into a beaker covered with 100 ml of 10% sodium chloride solution. The resin was filtered off, washed with distilled water until the washing is free from chloride and air-dried.

c) Equilibrium study of $\bar{I}/\bar{Cl}$ in lewitat M500. Stock solutions of 0.1 M potassium iodide and 0.1 M potassium bromide were prepared. By dilution method six samples of 50 ml of potassium iodide solution of different concentration ranging from 0.0084 M to 0.0312 M were prepared in different stopped bottles. Into each of the bottles 0.5 g of air-dried ion exchange resins in chloride form were transferred. The bottles were stoppered, well shaken and kept in a thermostat at 25±0.1°C for 4 hours, which was sufficient time for the equilibrium to be attained. The solution in each bottle was analysed for the chloride and iodide concentration 0.1 M silver nitrate solution. From these results the equilibrium constants for the reaction:

$$R\text{-}Cl + \bar{I}\,(aq) \leftrightarrow R\text{-}I + \bar{Cl}\,(aq)$$

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was determined. A typical set of results at 25°C are given in Table 1.

Similar set of experiments was repeated at different temperatures namely, 30°C, 35°C and 45°C to calculate the equilibrium constants.

d) Equilibrium study of $\bar{Br}/\bar{Cl}$ in lewitat M500. The equilibrium constants for the reaction:

$$R\text{-} Cl + \bar{Br}\,(aq) \leftrightarrow R\text{-}Br + \bar{Cl}\,(aq)$$

was determined using the same procedure mentioned above. The obtained results of $\bar{Br}/\bar{Cl}$ in Lewitat M500 at 25°C at 25°C are given in Table (2). Each series of experiments was carried out in duplicate and the results were reproducible to within ± 2%.

Results and Discussion

The equilibrium constants for the studied exchange reactions have been calculated by substituting the experimental results obtained in the following equation suggested by Lokhande and Singare (1998b).

$$K = \frac{C_{R\text{-}I} \cdot C_{Cl^-}}{C_{R\text{-}Cl} \cdot C_{I}} \quad \text{for } \bar{I}/\bar{Cl} \text{ ion-exchange reaction}$$

$$K = \frac{C_{R\text{-}Br} \cdot C_{Cl^-}}{C_{R\text{-}Cl} \cdot C_{Br^-}} \quad \text{for } \bar{Br}/\bar{Cl} \text{ ion-exchange reaction}$$

where,

$C_{R\text{-}I}$ and $C_{R\text{-}Br}$ are the amounts of iodide and bromide ions in mmoles/0.50 g resin, which have exchanged into the resins.

C_{Cl}- is the concentration of chloride ion which has exchanged in the solution. It is determined experimentally and compared with the decrease in the concentration of iodide or bromide ion in solution phase.

C_I- and C_{Br}- are the equilibrium concentration of idodde and bromide ions in the solution.

$C_{R\text{-}Cl}$ is the amount of chloride ion in mmole/0.5 g resin which is remained in the resin phase at equilibrium and calculated by (A-$C_{R\text{-}I}$) and (A-$C_{R\text{-}Br}$) for $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ respectively, where,

'A' is the exchange capacity of the resin which was found to be 2.835 mmol/0.50 g resin.

The equilibrium data obtained for $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ exchanges on Lewitat M500 at temperature of 25°, 30°, 35°, 40°. and 45°C are presented in Fig. 1 and given in Tables (4 & 5).

The plot of InK versus for $\bar{I}/\bar{Cl}$ and $\bar{Br}/\bar{Cl}$ exchange processes is shown in Fig. 1, whereas the enthalpy of the ion exchange reactions was calculated from the slope of the obtained straight lines with the aid of the equation:

$$\text{In}\,K = \frac{-\Delta H^\circ}{R}\,\frac{1}{T} + const$$

the free energy of the ion exchange was calculated from the values of thermodynamic equilibrium constant, K, using the general relation

$$\Delta G^\circ = -RT\,\text{In}\,K$$

and the entropy changes from the values obtained for ΔH° and ΔG° using the expression:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

The thermodynamic data obtained are given in Table (4 & 5).

Table 1

Equilibrium constant for $\bar{I}/\bar{Cl}$ ion-exchange reaction at 250°C

Init.Conc. $\bar{I}$ (M)	Final Conc. $\bar{I}$ (M) C_I-	Change in $\bar{I}$ Conc. (M)	Conc. of $\bar{Cl}$ exch. (M) $C_{\bar{Cl}}$	Amount of $\bar{I}$ exch. in resin mmol/0.50g $C_{R\text{-}I}$	Amount of $\bar{Cl}$ rem. In resin mmol/0.50g $C_{R\text{-}Cl}$	Equilibrium constant K
0.0084	0.00163	0.00677	0.00655	0.3385	2.4965	0.545
0.0132	0.00355	0.00965	0.00899	0.4825	2.3525	0.519
0.0176	0.00570	0.01190	0.01167	0.5950	2.2400	0.544
0.0220	0.00846	0.01354	0.01457	0.6770	2.1580	0.540
0.0264	0.01114	0.01526	0.01615	0.7630	2.0720	0.534
0.0312	0.01390	0.0173	0.01812	0.8650	1.9700	0.572
				Average value of K = 0.542		

Exchange capacity (A), 2.835 m mol/0.50 g resin in $\bar{Cl}$ - form.

Table 2
Equilibrium constant for Br^-/Cl^- ion-exchange reaction at 250°C

Init.Conc. Br^- (M)	Final Conc. Br^- (M) C_{Br^-}	Change in Br Conc. (M)	Conc. of Cl^- exch. (M) C_{Cl^-}	Amount of Br^- exch. in resin mmol/0.50g $C_{R\text{-}Br}$	Amount of Cl^- rem. In resin mmol/0.50g $C_{R\text{-}Cl}$	Equilibrium constant K
0.0084	0.00133	0.00707	0.00699	0.3535	2.4815	0.749
0.0132	0.00315	0.01004	0.01102	0.5020	2.3330	0.750
0.0176	0.00503	0.01257	0.01334	0.6285	2.2065	0.755
0.0220	0.00730	0.01470	0.01545	0.7350	2.1000	0.741
0.0264	0.00967	0.01673	0.01723	0.8365	2.9985	0.746
0.0312	0.01199	0.01921	0.01755	0.9605	1.8745	0.750
					Average value of K = 0.749	

Exchange capacity (A), 2.835 m mol/0.50 g resin in Cl^- - form.

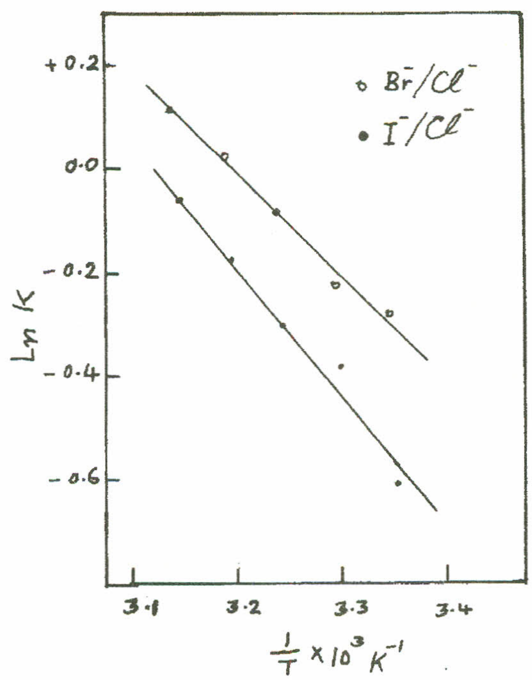

Fig 1. Dependence of InK on for I^-/Cl^- and Br^-/Cl^- ion exchange reactions of Lewitat M500.

Table 3
Thermodynamic parameters for I^-/Cl^- ion-exchange reaction on Lewitat M500 at different temperatures

Temperature °C	Equilibrium Constant, K	ΔH°J/mol	ΔG°J/mol	ΔS°J/mol K
25°	0.542	20427	1517.5	63.5
30°	0.680	20427	971.5	64.2
35°	0.736	20427	784.9	63.8
40°	0.834	20427	472.4	63.8
45°	0.936	20427	174.9	63.7

Table 4
Thermodynamic parameters for Br^-/Cl^- ion-exchange reaction on Lewitat M500 at different temperatures

Temperature °C	Equilibrium Constant, K	ΔH°J/mol	ΔG°J/mol	ΔS°J/mol K
25°	0.749	16628	716.1	53.4
30°	0.795	16628	577.9	53.0
35°	0.909	16628	244.3	53.2
40°	0.018	16628	-46.4	53.3
45°	0.120	16628	-299.6	53.2

It follows primarily from our results that the selectivity of strongly basic anion-exchange resins for I^- and Br^- ions increases with increasing of temperatures. The equilibrium constants are ≤1 over the entire range of temperatures and also increase with increasing temperature. Positive values of ΔH° and ΔS° were thus obtained. This indicates that I^-/Cl^- and Br^-/Cl^- ions exchanges is endothermic and heat is absorbed, i.e., the exchanger has a greater preference for Cl^- rather than I^- or Br^- ions that controlled by increase of enthaply. The positive ΔG° and ΔS° values also indicate lesser order produced in the forward reaction during the ion-exchange process and stronger binding of Cl^- ions at the exchanger surface than I^- or Br^- ions. Therefore the ion-exchange process processed at a state of balance so long heat is drawn into the system.

The greater values of ΔH°, ΔG° and ΔS° obtained for I^-/Cl^- exchange reaction compared with those obtained for Br^-/Cl^- system may be attributed to the difference in size of the exchanged anion. It seems that the Br^- is more easily exchanged with Cl^- on the strongly basic anion-exchanger than I^- ion.

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