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Study on Effect of Ionic Charge on Ion Exchange Equilibria Involving Uni-Univalent and Uni-Bivalent Ion Exchange Systems

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The equilibrium constant (K) for uni-univalent Cl^-/Br^- and uni-bivalent Cl^-/SO_4^{2-} exchange systems is studied at different temperatures from 30–45°C, using different concentrations of bromide and sulphate ions. The K values for both the exchange reactions increases with increase in temperature indicating the endothermic ion exchange reaction having enthalpy values of 45.91 kJ/mole and 11.5 kJ/mole respectively. The equilibrium constant (K) for Cl^-/Br^- ion exchange is 1.16 at 30°C which is lower than 20 at 30°C for Cl^-/SO_4^{2-} exchange, which is due to the difference in ionic charge of the exchangeable counter ions.

INTRODUCTION

Ion exchangers are of great importance in rapid chemical analysis. The present large, and year by year increasing, literature on ion exchangers, shows the great importance of these substances. Furthermore, not only the fields of application are increasing but new ion exchange products afford new opportunities for both chemists and analysts[1]. The knowledge of important physical and chemical properties[2] of ion exchangers is a complementary part of resin characterisation study. The property that involves stability of ion exchangers is of great significance in most instances and it generally decides the selection of an exchanger in any particular exchange process. Extensive study on ion exchange equilibria involving uni-univalent[3–9] and uni-bivalent cation exchange systems[10–13], using different types of resins[14–17] has been done, but very few attempts have been made to study the equilibrium for anion exchanger systems[18–21]. Among the previous investigators, in their study to calculate the equilibrium constants, only few[22–27] have emphasized on the activity coefficients of the ions in resin phase in uni-bivalent exchange system.

The ion exchange resin Amberlite IRA-400 used in the present investigation finds a variety of industrial applications in decolourising sugar syrup, as a desilicizer[28]. It is expected that the present investigation on equilibrium study of ion exchange reaction will help in quantitative evaluation of ion exchangers for assessing its efficiency in several ion exchange processes.

EXPERIMENTAL

In an attempt to study the ion exchange equilibria involving Cl^-/Br^- uni-univalent ions, the ion exchange resin (0.5 g) in ehloride form was equilibrated with 50 mL of potassium bromide solution of five different concentrations from 0.019 M to 0.042 M in different stoppered bottles in a constant temperature water bath maintained at 30°C (± 0.1°C) for 4 h. From the kinetic study using the same ion exchange resin, which was reported earlier[29], it has been found that this duration is adequate for equilibrium to be attained. After 4 h the solution in each bottle was analysed for the chloride and bromide ion concentration potentiometrically with standard silver nitrate solution. From these results, the equilibrium constant (K) for the ion exchange reaction

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.) \quad (1)$$

was determined. The study was extended further to understand equilibrium constant (K) for the ion exchange reaction (1) up to 45°C.

The study on equilibrium constant was carried further for Cl^-/SO_4^{2-} uni-bivalent exchange system, in which the ion exchanger (0.5 g) in chloride form was equilibriated with sulphate ion solution of seven different concentrations from 0.01 M to 0.05 M in the same temperature range of 30 to 45°C. The ion exchange reaction at equilibrium is represented by

$$2R—Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.) \quad (2)$$

The concentration of the chloride ion in the solution at equilibrium was estimated potentiometrically as explained earlier. From this the amount of sulphate ion that has exchanged on to the resin was estimated, since it was known that one mole of sulphate ion replaces two moles of chloride ions. Because the initial concentration of sulphate ion and the amount of it which has exchanged on to the resin were known, the concentration of sulphate ions in the solution at equilibrium was calculated. Further from the known resin capacity and the amount of sulphate ions replacing the chloride ions on the resin, the amount of chloride ions remaining in the resin was calculated. Having thus known the concentration of chloride ions and sulphate ions in the solution and the amount of chloride ions and sulphate ions in the resin at equilibrium, the apparent equilibrium constant $K_{app.}$ was calculated.

The exchange capacity was experimentally determined according to standard proccedure[41] and was calculated to be 2.18 meq/0.5 g of ion exchange resin in chloride form.

RESULTS AND DISCUSSION

In the study of Cl^-/Br^- uni-univalent exchange, from the knowledge of initial and equilibrium concentration of bromide ions, the decrease in the concentration of the latter was noted. Since it is an exchange between uni-univalent ions an equal concentration of chloride ions would be now present in the solution due to the exchange. The concentration of the chloride ions was experimentally determined and was compared with the decrease in concentration of bromide ions and in all the experiments, these two quantities are found to be satisfactorily equal within the limits of ± 0.0002 moles/litre (Table-1). The amount of bromide ions in milliequivalents which has exchanged onto the resin was calculated from the observed decrease in the concentration of bromide ions in the solution. This gives the $C_{R—Br}$. From the experimentally determined resin capacity (A)[30, 31], the amount of bromide ions exchanged on the resin, ($C_{R—Br}$), and the amount of chloride ions C_{Cl^-} and bromide ions C_{Br^-} in the solution at equilibrium, the equilibrium constant (K) was calculated by the equation

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

TABLE-1

EQUILIBRIUM CONCENTRATION OF CHLORIDE AND BROMIDE IONS IN THE SOLUTION AND IN THE RESIN PHASE FOR THE ION EXCHANGE REACTION

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of bromide ion solution = 50 mL
Temperature = 40°C
Exchange capacity = 2.18 meq/0.5 g of resin

System	Initial conc. of bromide ions (M)	Final conc. of bromide ions (M) C_{Br^-}	Change in bromide ion concentration (M)	Concentration of chloride ion exchanged (M) C_{Cl^-}	Amount of bromide ion exchanged on the resin (meq/ 0.5 g) $C_{R—Br}$
1	0.0192	0.0037	0.0155	0.0153	0.775
2	0.0293	0.0085	0.0208	0.0210	1.040
3	0.0323	0.0102	0.0221	0.0223	1.105
4	0.0378	0.0136	0.0242	0.0245	1.210
5	0.0425	0.0166	0.0259	0.0258	1.295

Typical experimental results to calculate the equilibrium constant (K) at 40°C for Cl^-/Br^- uni-univalent exchange reaction are shown in Table-2. The equilibrium constants (K) values calculated at different temperatures from 30 to 45°C are presented in Table-3.

TABLE-2

EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of bromide ion solution = 50 mL
Temperature = 40°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

System	1	2	3	4	5
Equilibrium constant (K)	2.28	2.23	2.25	2.23	2.27

Average value of K = 2.25

TABLE-3
VARIATION OF EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT DIFFERENT TEMPERATURE

$R{-}Cl + Br^-(aq.) \rightleftharpoons R{-}Br + Cl^-(aq.)$

Amount of ion exchange resin = 0.5 g

Volume of bromide ion solution = 50 mL

Temperature (°C)	30	35	40	45
Equilibrium constant (K)	1.16	1.59	2.25	2.95

Enthalpy of ion exchange reaction = 45.91 kJ/mole

In the study of Cl^-/SO_4^{2-} uni-bivalent exchange, from the knowledge of equilibrium concentration of sulphate ion ($C_{SO_4^{2-}}$) and chloride ion (C_{Cl^-}) in solution as explained earlier and from the experimentally determined exchange capacity of the resin[24], the amount of chloride (C_{RCl}) and sulphate ($C_{R_2SO_4}$) ions on the resin phase can be calculated. The ratio of the activity coefficient of the ions on the resin phase was derived from the Debye Huckle's limiting law. Thus from the values of $C_{R_2SO_4}$, C_{RCl}, C_{Cl^-}, $C_{SO_4^{2-}}$ and the ratio of the activity coefficients of ions in the resin phase, the apparent equilibrium constant $K_{app.}$ is calculated from the expression.

$$K_{app.} = \frac{(C_{R_2SO_4}) \cdot (C_{Cl^-})^2}{(C_{RCl})^2 \cdot (C_{SO_4^{2-}})} \cdot \frac{(\gamma_{Cl^-})^2}{(\gamma_{SO_4^{2-}})} \qquad (4)$$

The graph of $K_{app.}$ versus equilibrium concentration of sulphate ions in solution was plotted (Fig. 1) which was extrapolated back to zero sulphate ion concentration to give equilibrium constant in the standard state ($K_{std.}$). The ratio of $K_{std.}/K_{app.}$ will give the ratio of activity coefficients of both the ions in resin phase. A typical result is presented in Table-4. The choice of standard state over the

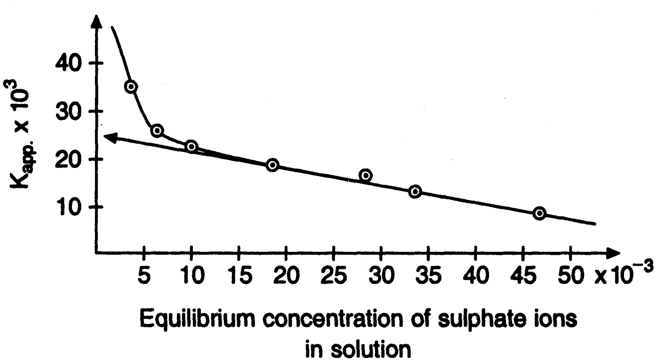

Fig. 1 Variation of apparent equilibrium constant with equilibrium concentration of sulphate ion in solution

$2R{-}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$

apparent state for the equilibrium constant was already justified in our previous work[24]. The equilibrium constants thus in the standard state at different temperatures from 30 to 45°C are presented in Table-5.

TABLE-4
EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

$$2R—Cl + C_2O_4^{2-}(aq.) \rightleftharpoons R_2C_2O_4 + 2Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of the sulphate ion solution = 100 mL
Temperature = 35°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

Initial conc. of sulphate ion in solution (M)	Equilibrium conc. in solution (M)		Amout of the ions on the resin (meq/0.5g)		(Ionic strength)$^{1/2}$	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{SO_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2SO_4})}{(\gamma_{RCl})^2} = K_{std.}/K_{app.}$
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}				
0.010	0.0138	0.0039	0.805	0.690	0.160	0.687	35.3	0.64
0.015	0.0145	0.0062	0.735	0.725	0.182	0.653	29.2	0.77
0.020	0.0155	0.0115	0.635	0.775	0.223	0.593	24.0	0.94
0.025	0.0160	0.0170	0.580	0.800	0.259	0.592	21.2	0.06
0.030	0.0168	0.0272	0.505	0.825	0.314	0.479	16.1	1.40
0.040	0.0173	0.0345	0.450	0.865	0.347	0.378	14.0	1.61
0.050	0.0182	0.0460	0.365	0.910	0.395	0.254	12.4	1.81

Equilibrium constant in standard state $K_{std.}$ = 26.5

TABLE-5
VARIATION OF THE EQUILIBRIUM CONSTANT IN THE STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION AT DIFFERENT TEMPERATURE

$$2R—Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of sulphate ion solution = 100 mL

Temperature (°C)	30	35	40	45
$K_{std.}$	20.5	26.5	29.0	31.0

Enthalpy of ion exchange reaction = 11.5 kJ/mole

Bonner and Pruett[32], in their study of temperature effect on uni-univalent exchanges involving some divalent ions observed that the equilibrium constant decreases with increasing temperature, resulting in an exothermic ion exchange reaction. However, in the present study the equilibrium constants increases from 1.16 at 30°C to 2.95 at 45°C for Cl^-/Br^- exchanges (Table-3) and from 20 at

30°C to 31 at 45°C for Cl^-/SO_4^{2-} exchanges (Table-5), indicating the endothermic ion exchange reactions, with enthalpy values of 45.91 kJ/mole[30, 31] and 11.5 kJ/mole[24] respectively.

Bonhoefer[33] has suggested the term 'electroselectivity' for the electrostatic preference for the ion of higher valence. Also due to Donnan potential difference existing between the ion exchanger and dilute solutions, the counter ions of higher valence are prefered[34–40]. This combined effect of electroselectivity and Donnan potential is responsible for preferential affinity of ion exchanger in chloride form towards the sulphate ions in solution (equation 2), as compared to that of bromide ions also in solution (equation 1), giving higher value of K for Cl^-/SO_4^{2-} exchange (Table-5), than that for Cl^-/Br^- exchange (Table-3).

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