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Comparative Study on Uni-Univalent and Uni-Bivalent Ion Exchange Reaction as a Function of Ionic Charge

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Determination of equilibrium constant of Cl^-/I^- and $Cl^-/C_2O_4^{2-}$ ion exchange reaction was carried out in the temperature range of 30–45°C, by varying the concentration of iodide and oxalate ion solution. It was observed that under identical conditions of temperature 30°C, using 0.5 g of ion exchange resin (in chloride form), the equilibrium constant (K) for Cl^-/I^- exchange was 16.7 which was lesser than 19.5 for $Cl^-/C_2O_4^{2-}$ exchange. Also for both uni-univalent and uni-bivalent exchange, value of K increases with increase in temperature, indicating the endothermic ion exchange reaction with enthalpy values of 19.13 kJ/mole and 12.2 kJ/mole respectively.

INTRODUCTION

Ion exchangers which are an integral part of many chemical industries also find wide range of applications in modern sophisticated laboratories. For a quantitative evaluation of ion exchange resins it is of importance to study the equilibrium for the ion exchange reaction, which will be useful in assessing its efficiency in several ion exchange processes.

Extensive studies on ion exchange equilibria involving uni-univalent[1–7] and uni-bivalent cation exchange systems[8–11] using different types of resins[4, 12–15], but very few attempts have been made to study the equilibrium for anion exchange system[16–18]. Among the previous investigators in their study to calculate the equilibrium constants, only few[19–21] have emphasized on the activity coefficients of the ions in resin phase in uni-bivalent exchange systems. The present investigation was therefore carried out to calculate the equilibrium constants in Cl^-/I^- uni-univalent system and $Cl^-/C_2O_4^{2-}$ uni-bivalent system using strongly basic anion exchanger AMBERLITE IRA-400 giving due regard to the activity coefficients of the ions both in the solution as well as in the resin phase.

EXPERIMENTAL

A known weight (0.5 g) of ion exchange resins in chloride form were equilibrated with potassium iodide solutions of five different concentrations ranging from 0.009 M to 0.037 M in five different stoppered bottles at constant temperature in a water bath maintained at 30°C (± 0.1°C) for 4h. From the kinetic study using the same ion exchange resin, which was reported earlier[22], it has been found that this duration was adequate for equilibrium to be attained. After 4 h the solutions in each bottle were analysed for the chloride and iodide concentration potentiometrically with standard silver nitrate solution. From these results, the equilibrium constant (K) for the ion exchange reaction

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

was determined. The equilibrium constant for the above exchange reaction were determined at various temperatures in the range of 30–45°C.

In the second set of experiment 0.5 g of ion exchange resins in chloride form were equilibrated with 100 mL of oxalate ion solution of seven different concentrations varying from 0.010 M to 0.050 M at 30°C. The uni-bivalent ion exchange reaction can be represented as:

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

After 4 h the concentration of the chloride ion in the solution was estimated potentiometrically using standard silver nitrate solution. From this the amount of oxalate ion that has exchanged on to the resin was estimated, since it was known that one mole of oxalate ion replaces two moles of chloride ions. Because the initial concentration of oxalate ion in the solution and the amount of it which has exchanged on to the resin were known, the concentration of oxalate ions in the solution at equilibrium was calculated. Further from the known resin capacity and the amount of oxalate ion replacing the chloride ions on the resin (as determined above), the amount of chloride ions remaining on the resin was calculated. Having thus known the concentration of chloride and oxalate ions in the solution as well as on the resin phase at equilibrium, the apparent equilibrium constant $K_{app.}$ was calculated. The experiment was repeated at different temperatures up to 45°C.

The exchange capacity was experimentally determined according to standard proccedure[23] and was calculated to be 2.18 meq/0.5 g of resins in chloride form.

RESULTS AND DISCUSSION

In the study of Cl^-/I^- uni-univalent exchange, from the knowledge of initial and equilibrium concentration of iodide ion, the decrease in the concentration of the latter was noted. Since it was an exchange between uni-univalent ions an equal concentration of chloride ion would be now present in the solution due to the exchange. The concentration of the chloride ion was experimentally determined and was compared with the decrease in concentration of iodide ion and in all the experiments, the two quantities were found to be satisfactorily equal within the limits of ± 0.0002 moles/litre (Table-1). The amount of iodide ion in milliequivalents which has exchanged on to the resin was calculated from the observed decrease in the concentration of iodide ion in solution. This gives C_{R-I}.

TABLE-1
EQUILIBRIUM CONCENTRATION OF CHLORIDE AND IODIDE IONS IN THE SOLUTION AND IN THE RESIN PHASE FOR THE ION EXCHANGE REACTION

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

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

System	Initial conc. of iodide ions (M)	Final conc. of iodide ions (M) C_{I^-}	Change in iodide ion concentration (M)	Concentration of chloride ion exchanged (M) C_{Cl^-}	Amount of iodide ion exchanged on the resin (meq/ 0.5 g) $C_{R—I}$
1	0.0096	0.00012	0.0095	0.0096	0.474
2	0.0199	0.00060	0.0193	0.0195	0.965
3	0.0245	0.00120	0.0233	0.0236	1.165
4	0.0310	0.00230	0.0287	0.0285	1.435
5	0.0371	0.00440	0.0327	0.0328	1.635

The equation for the equilibrium constant would be given by

$$K = \frac{C_{R—I} \cdot C_{Cl^-}}{C_{R—Cl} \cdot C_{I^-}} \tag{3}$$

For experimental determined exchange capacity 'A'[24] the $C_{R—Cl}$ at equilibrium would be $(A—C_{R—I})$. Therefore the modified equation for the equilibrium constant would be given by

$$K = \frac{C_{R—I} \cdot C_{Cl^-}}{(A—C_{R—I}) \cdot C_{I^-}} \tag{4}$$

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

TABLE-2
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION

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

Amount of ion exchange resin = 0.5 g
Volume of iodide 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)	22.2	25.6	22.6	23.5	22.4

Average value of K = 23.3

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

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

Amount of ion exchange resin = 0.500 g
Volume of iodide ion solution = 50.0 mL

Temperature (°C)	30	35	40	45
Equilibrium constant (K)	16.7	20.5	23.3	26.5

Enthalpy of ion exchange reaction = 19.13 kJ/mole

In the study of $Cl^-/C_2O_4^{2-}$ uni-bivalent exchange from the knowledge of equilibrium concentration of oxalate ($C_{C_2O_4^{2-}}$) ion and chloride (C_{Cl^-}) ion in the solution (explained in the experimental part) and from the exchange capacity of the resin[18], the amount of chloride ($C_{R{-}Cl}$) and oxalate ($C_{R_2C_2O_4}$) ions on the resin phase can be calculated. The ratio of the activity coefficient of the ions in the resin phase was derived from the Debye Huckle's limiting law. Thus from the values of $C_{R_2C_2O_4}$, C_{RCl}, C_{Cl^-}, $C_{C_2O_4^{2-}}$ and the ratio of the activity coefficients of ions in the resin phase, the apparent equilibrium constant $K_{app.}$ where calculated from the expression

$$K_{app.} = \frac{C_{R_2C_2O_4} \cdot (C_{Cl^-})^2}{(C_{RCl})^2 \cdot (C_{C_2O_4^{2-}})} \cdot \frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})} \qquad (5)$$

The graph of $K_{app.}$ *vs.* equilibrium concentration of oxalate ion in solution when extrapolated back to zero oxalate ion concentration, gives equilibrium constant in standard state $K_{std.}$ (Fig. 1). 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 equilibrium constants in standard state $K_{std.}$ calculated at different temperatures from 30–45°C are represented in Table-5. The choice of standard state over the apparent state for equilibrium constant was already justified in our previous work[24].

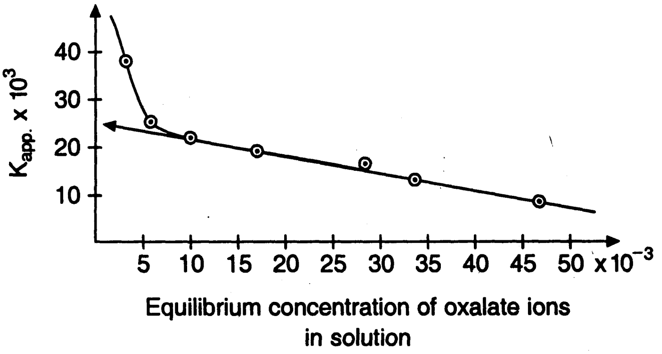

Fig. 1 Variation of apparent equilibrium constant with concentration of oxalate ion in solution at equilibrium

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

TABLE-4

EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

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

Initial conc. of oxalate ion in solution (M)	Equilibrium conc. in solution (M)		Amout of the ions on the resin meq/0.500g		(Ionic strength)$^{1/2}$	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RCl})^2} = K_{std.}/K_{app.}$
	Cl^-	$C_2O_4^{2-}$	Cl^-	$C_2O_4^{2-}$				
0.010	0.0139	0.0037	0.795	0.695	0.158	0.690	39.6	0.452
0.015	0.0146	0.0060	0.725	0.730	0.180	0.555	27.4	0.653
0.020	0.0154	0.0113	0.645	0.770	0.222	0.594	23.1	0.775
0.025	0.0160	0.0170	0.580	0.800	0.259	0.584	20.9	0.856
0.030	0.0170	0.0271	0.485	0.850	0.313	0.481	18.5	0.968
0.040	0.0176	0.0341	0.420	0.880	0.346	0.316	14.3	1.252
0.050	0.0183	0.0459	0.355	0.915	0.395	0.172	9.5	1.946

Equilibrium constant in standard state $K_{std.} = 26.0$

TABLE-5

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

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

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

Temperature (°C)	30	35	40	45
$K_{std.}$	19.5	26.0	28.5	30.0

Enthalpy of ion exchange reaction = 12.2 kJ/mole

Bonner and pruett[25], studied the temperature effect on uni-univalent exchanges involving some divalent ions. In all divalent exchanges, the equilibrium constant decreases with increasing temperature, resulting in an exothermic reaction. However, in the present investigation, the values of equilibrium constants (K) increase from 16.7 at 30°C to 26.5 at 45°C for Cl^-/I^- exchanges (Table-3) and from 19.5 at 30°C to 30.0 at 45°C for $Cl^-/C_2O_4^{2-}$ exchanges (Table-5), indicating the endothermic ion exchange reaction[24, 26], with enthalpy values of 19.13 kJ/mole and 12.2 kJ/mole.

When ion exchangers in chloride form are equilibrated with iodide and oxalate ions in solution, there exists a Donnan potential difference between the ion exchanger and dilute soultions. The force with which the potential acts on an ion is proportional to the ionic charge[27–33] thereby forcing the counter ions of higher valence ($C_2O_4^{2-}$) on the resin phase. Bonheffer[34] has suggested the term 'electroselectivity' for the electrostatic preference for the ion of higher valence. This phenomenon of electroselectivity and Donnan potential was responsible for the preferential affinity of the ion exchange resins towards the oxalate ions than that of iodide ions in solution.

The explains the higher values of equilibrium constant (K) for $Cl^-/C_2O_4^{2-}$ exchange as compared to that of Cl^-/I^- exchange (Tables 3, 5).

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