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Ion Exchange Equilibria Involving uni-Univalent, uni-Bivalent Exchange Systems to Study Effect of Ionic Charge on Equilibrium Constant

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The ion exchange reactions for Cl^-/I^- and Cl^-/SO_4^{2-} systems were studied to determine the equilibrium constant (K) at different temperatures from 30.0° to 45°C. For Cl^-/SO_4^{2-} exchange, the value of K observed at 30°C was 20 which was higher than K value of 16.7 for Cl^-/I^- exchange at the same temperature. This difference in K values was due to the ionic charges of ions in solution.

INTRODUCTION

The knowledge of important physical and chemical properties of ion exchangers is a complementary part of resin characterisation study. The property that involves stability of an ion exchanger is of great significance in most instances and it generally decides the selection of an exchanger for any particular exchange process.

The ion exchange resin Amberlite IRA-400[1] as used in the present investigation, a strongly basic anion exchanger, has the high degree of basicity necessary to remove silica with a minimum leakage and other weakly ionised contaminants. Considering its wide range of industrial applications, the equilibrium study was carried out and it was expected that the study will be of considerable use in quantitatively assessing an ion exchange resin for its utility in a stipulated ion exchange process.

A number of investigators[2–4] carried out carefully equilibrium studies extending over a wide range of composition of solution and resin. More rigorous calculations were made by including the activity coefficient of the counter ions in solution and resin phases to compute the thermodynamic equilibrium constant[5–17]. There has been extensive study on ion exchange equilibria involving uni-univalent[18–24] and uni-bivalent[25–27] cation exchange systems using different types of resin[21, 28–31], but very few attempts have been made to study the equilibrium of anion exchange systems[32–36]. Among the previous investigators in their study to calculate the equilibrium constants only few[15, 16, 37] 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 constant in Cl^-/I^- and Cl^-/SO_4^{2-} ion exchange systems 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

In an attempt to study the ion exchange equilibria involving Cl^-/I^- uni-univalent system, the ion exchange resins (0.500 g) in chloride form were equilibrated with potassium iodide solution of five different concentrations from 0.009 M to 0.037 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 resins which was reported earlier[38], it has been found that this duration was adequate for the equilibrium to be attained. After 4 h the solution in each bottle was analysed for the chloride and iodide ion concentration potentiometrically with standard silver nitrate solution. From these results the equilibrium constant (K) for the ion exchange reaction

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

was determined. The study was extended further to calculate the equilibrium constant (K) for 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 exchange resins (0.500 g) in chloride form were equilibriated with sulphate ion solution (100.0 mL) of seven different concentrations from 0.010 M to 0.050 M in the same temperature range of 30° to 45°C. The ion exchange reaction at equilibrium can be represented as

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

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. From the initial concentration of sulphate ions and the amount of it which has exchanged on to the resin were known and the concentrtion 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 on the resin was calculated. Thus having known concentrations of chloride ions and sulphate ions in the solution and the amounts of chloride ions and sulphate ions on the resin at equilibrium, the apparent equilibrium constant K_{app} was calculated.

The exchange capacity was experimentally determined according to standard procedure[39] and was calculated to be 2.10 meq/0.5 g of ion exchange resin 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 ions would be now present in the solution due to the exchange. The concentration of chloride ions was experimentally determined and was compared with the decrease in concentration of iodide ions and in all experiments, these two quantities were found to be satisfactorily equal within the limits of ± 0.0002 moles/litre (Table-1). The amount of iodide ions in milliequivalents which has exchanged into the resin was calculated from the observed decrease in concentration of bromide ion in the solution. This gives C_{R-I}. From the experimentaly determined resin capacity (A), amount of iodide ion exchanged on the resin C_{R-I}, amount of chloride ion C_{Cl^-} and iodide ion C_{I^-} in the solution at equilibrium, the equilibrium constant (K) was calculated by the equation

$$K = \frac{C_{R-I} \cdot C_{Cl^-}}{(A - C_{R-I}) \cdot C_{I^-}} \qquad \ldots (3)$$

TABLE-1

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

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

Amount of ion exchange resin = 0.500 g
Volume of iodide ion solution = 50 mL
Temperature = 45°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

Systems	Initial Concentration of iodide ion (M)	Final Concentration of iodide ion (M) C_{I^-}	Change in iodide ion concentration (M)	Conc. of chloride ion exchanged (M) C_{Cl^-}	Amount of iodide ion exchanged on the resin meq/0.5 g C_{R-I}
1.	0.0098	0.00011	0.00969	0.0098	0.484
2.	0.0192	0.00050	0.01870	0.0192	0.935
3.	0.0248	0.00110	0.02370	0.0239	1.185
4.	0.0311	0.00220	0.02890	0.0290	1.445
5.	0.0371	0.00410	0.03300	0.0332	1.650

A typical experimental result to calculate equilibrium constant (K) for Cl^-/I^- exchange reaction at 45°C is shown in Table-2. The equilibrium constant (K) values calculated at different temperatures from 30° to 45°C are presented in Table-3.

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, the amount of chloride (C_{RCl}) and sulphate ($C_{R_2SO_4}$) ions in the resin phase can be calculated. The ratio of the activity coefficient of the ions in the resin phase was derived from the Debye-Huckel's limiting law. Thus from the values of $C_{R_2SO_4}$, C_{RCl}, C_{Cl^-}, $C_{SO_4^{2-}}$ and from the ratio of the activity coefficient of ions in the resin phase, the apparent equilibrium constant K_{app} were calculated from the expression

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

TABLE-2
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION
$R—Cl + I^- (aq.) \rightleftharpoons R—I + Cl^- (aq.)$

Amount of ion exchange resin = 0.500 g
Volume of iodide ion solution = 50 mL
Temperature = 45°C
Exchange capacity = 2.18 meq/0.5 g of resin

Systems	1	2	3	4	5
Equilibrium constant (K)	25.4	28.6	26.0	25.5	25.2

Average value of K = 26.1

TABLE-3
VARIATION OF EQUILIBRIUM CONSTANT FOR THE REACTION
$R—Cl + I^- (aq.) \rightleftharpoons R—I + Cl^- (aq.)$
WITH TEMPERATURE

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	20.4	23.6	26.1

Enthalpy of ion exchange reaction = 19.13 kjoules/mole

The graph of K_{app} versus equilibrium concentration of the sulphate ion in solution was plotted (Fig. 1) which when extrapolated back to zero sulphate ion

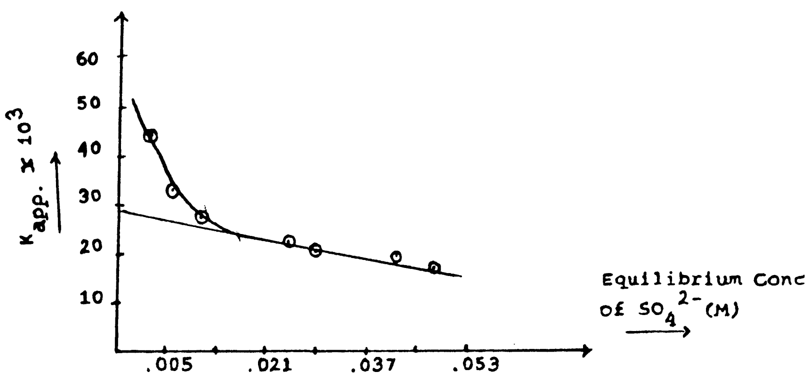

Fig. 1. Variation of apparents equilibrium constant with equilibrium concentration of sulphate ion in solution

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

concentration gives the 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 apparent state for the equilibrium constant was already justified in our previous work[35, 36]. The equilibrium constants thus obtained in the standard state at various temperatures from 30° to 45°C are presented in Table-5.

Bonner and Pruett[19] 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 constant increases for both uni-univalent and uni-bivalent exchange (Tables 3 and 5) indicating the endothermic ion exchange reactions with enthalpy values of 19.13 kjoules/mole and 11.5 kjoules/mole respectively.

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

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

Amount of ion exchange resin = 0.500 g
Volume of sulphate ion solution = 100 mL
Temperature = 40°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

Initial conc. of sulphate ion in solution (M)	Equilibrium conc. in on solution (M)		Amount of the ions on the resin (meq/0.5 g)		Ionic strength	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{SO_4^{2-}})}$	$K_{app} \times 10^3$	$\frac{(\gamma_{R_2SO_4})}{(\gamma_{RCl})^2} = K_{Std}/K_{app}$
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}				
0.010	0.0140	0.0037	0.785	0.700	0.158	0.690	42.0	0.71
0.015	0.0150	0.0060	0.685	0.750	0.181	0.542	32.5	0.92
0.020	0.0162	0.0104	0.565	0.810	0.218	0.465	29.4	1.02
0.025	0.0165	0.0140	0.530	0.825	0.242	0.459	26.2	1.14
0.030	0.0175	0.0260	0.435	0.875	0.309	0.432	23.5	1.30
0.040	0.0180	0.0342	0.380	0.900	0.347	0.340	20.1	1.49
0.050	0.0193	0.0450	0.255	0.965	0.393	0.140	17.2	1.74

Equilibrium constant in the standard state $K_{std} = 29.0$

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

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

Amount of ion exchange resin = 0.500 g
Volume of sulphate ion solution = 100.0 mL

Temperature (°C)	30	35	40	45
$K_{std.}$	20.0	26.5	29.0	31.0

Enthalpy of ion exchange reaction = 11.5 kjoules/mole

Bonhoeffer[40] has suggested the term 'electroselectivity' for the electrostatic preference of ions of higher valence. Also due to the Donnan potential difference existing between the ion exchanger and dilute solutions, the counter ions of higher valence were preferred[41–47]. This combined effect of electroselectivity and Donnan potential was responsible for preferential affinity of ion exchanger in chloride form towards sulphate ions in solution (equation 2), as compared to that of iodide ions also in solution (equation 1), giving higher value of K for Cl^-/SO_4^{2-} exchange (Table-5) than that for Cl^-/I^- exchange (Table-3).

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