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Study on Variation of Equilibrium Constant in Some Uni-Bivalent Ion Exchange Systems

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Ion exchange resins in chloride and iodide form were equilibriated with sulphate and oxalate ion solution of seven different concentrations varying from 0.010 M to 0.050 M respectively. The equilibrium study was carried in the temperature range of 30 to 45°C. For both Cl^-/SO_4^{2-} and $I^-/C_2O_4^{2-}$ uni-bivalent exchanges the value of equilibrium constant (K) increases with rise in temperature, indicating the endothermic ion exchange reaction. Also K value for Cl^-/SO_4^{2-} ion exchange reaction was observed to be greater than $I^-/C_2O_4^{2-}$ ion exchange reaction *i.e.*, at 30°C the K value of Cl^-/SO_4^{2-} ion exchange was calculated to be 20 while for $I^-/C_2O_4^{2-}$ ion exchange it was calculated to be 0.260 which was due to the difference in relative selectivity of ion exchange resin towards I^- and Cl^- ions.

INTRODUCTION

Ion exchangers which are the integral part of many chemical industries has also opened to the research workers whole new field of application for ion exchange process[1]. Furthermore not only the field of applications are increasing but new ion exchange products afford new opportunities for both chemists and analyst[2]. The ion exchange resin Amberlite IRA-400 has been widely employed for adsorption and fractionation of acids, biochemical and pharmaceutical uses and also in catalysis of organic synthesis[1]. In view of this, the study on ion exchange equilibria involving uni-bivalent exchange as carried out in present investigation will be of great significance in selection of an ion exchangers in various industrial and research applications, hence may prove to be a complementary part of resin characterisation study.

A number of investigators[3–5] carried out equilibrium studies extending over a wide range of composition of solution and resins. More rigorous calculations were made by including the activity coefficients of the counter ions in solution and resin phase to compute the thermodynamic equilibrium constant[6–18]. Extensive studies were carried out on ion exchange equilibria involving uni-univalent[19–27] and uni-bivalent[28–31] cation exchange systems using different types of resin[22, 32–35], but very few attempts have been made to study the equilibrium for anion exchange systems[36–40]. In their study to predict the selectivity of ion exchange materials towards a wide range of anions, Andreev and Kuznetsov[41] showed that the adsorbability of anions on an ion exchangers increases as it's affinity for water is decreased. Among the previous investigators in their study to calculate the equilibrium constants only few[16, 17, 39, 40, 42] have emphasized on the activity coefficients of the ions in resin phase in uni-bivalent systems. The present investigation was therefore been carried out to calculate the equilibrium constants in Cl^-/SO_4^{2-} and $I^-/C_2O_4^{2-}$ ion exchange systems giving due regard to the activity coefficients of the ions both in the solution as well as in the resin phase.

EXPERIMENTAL

The study on ion exchange equilibria involving Cl^-/SO_4^{2-} ions was carried out by using ion exchange resins in chloride form which were equilibriated with sulphate ion solution of seven different concentrations from 0.010 M to 0.050 M for 4 h. From the results of kinetic study using the same ion exchange resins which was reported earlier[43], it was observed that the duration of 4 h was adequate for the equilibrium to be attained. The ion exchange reaction at equilibrium may be represented as

$$2R{-}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.) \qquad (1)$$

After 4 h the concentration of the chloride ions in the solution at equilibrium was estimated potentiometrically. 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 ions replaces two moles of chloride ions. From the initial concentration of sulphate ions in the amount of it which has exchanged on to the resin are known, the concentration of sulphate ions in the solution at equilibrium was calculated. Further from the known resin capacity, the amount of sulphate ions replacing the chloride ions on the resin was calculated. Having thus known the concentrations of chloride and sulphate ions in the solution and the amount of chloride and sulphate ions on the resin at equilibrium, the apparent equilibrium constant $K_{app.}$ was calculated. The experimental set was carried in the temperature range of 30 to 45°C.

The ion exchange resins Amberlite IRA-400 as supplied by manufacturer in chloride form, were converted into iodide form in a conditioning column by passing a 10% potassium iodide solution. The resins thus converted into iodide form were air dried and used for further study of $I^-/C_2O_4^{2-}$ ion exchange reaction. In the experimental work the resins in iodide form were equilibriated with oxalate ion solutions of seven different concentrations from 0.010 M to 0.050 M. The ion exchange reaction at equilibrium may be represented as

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

The study was carried similarly to that explained earlier in the temperature range of 30 to 45°C. The exchange capacity was experimentally determined according to the standard procedure[44] 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^-/SO_4^{2-} uni-bivalent exchange, from the knowledge of equilibrium concentration of sulphate ions ($C_{SO_4^{2-}}$) and chloride ions (C_{Cl^-}) in solution as explained earlier and from the experimental determined exchange capacity of the resin, 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 in 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 from the ratio of the activity coefficients of ions on the resin phase, the apparent equilibrium constant $K_{app.}$ are calculated from the expression

$$K_{app.} = \frac{(C_{R_2SO_4}) \cdot (C_{Cl^-})^2}{(C_{RCl})^2 \cdot (C_{SO_4^{2-}})} \cdot \frac{(\gamma_{Cl^-})^2}{(\gamma_{SO_4^{2-}})} \qquad (3)$$

Similarly for $I^-/C_2O_4^{2-}$ uni-bivalent exchange the apparent equilibrium constant $K_{app.}$ are calculated from the expression

$$K_{app.} = \frac{(C_{R_2C_2O_4}) \cdot (C_{I^-})^2}{(C_{RI})^2 \cdot (C_{C_2O_4^{2-}})} \cdot \frac{(\gamma_{I^-})^2}{(\gamma_{C_2O_4^{2-}})} \qquad (4)$$

The graph of $K_{app.}$ versus equilibrium concentration of the bivalent ion in solution was plotted (Fig. 1 and 2) which was extrapolated back to zero bivalent 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 uni-univalent and bivalent ions on resin phase. A typical results are presented in Tables 1 and 3. The choice of standard state over the apparent state for the equilibrium constant was already justified in our previous work[39, 42]. The equilibrium constants in standard state thus obtained at various temperatures from 30°C to 45°C are presented in Tables 2 and 4.

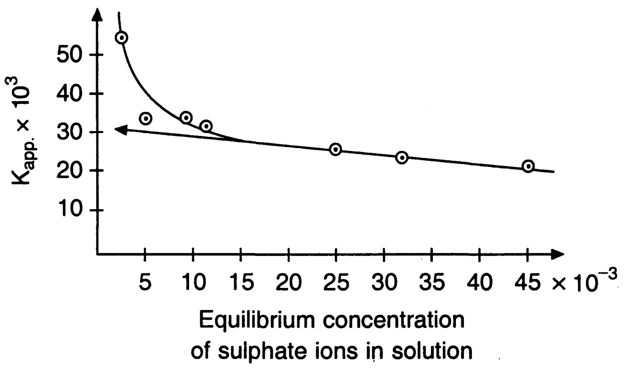

Fig. 1. Variation of apparent equilibrium constant with concentration of sulphate ions in solution at equilibrium for ion exchange reaction

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

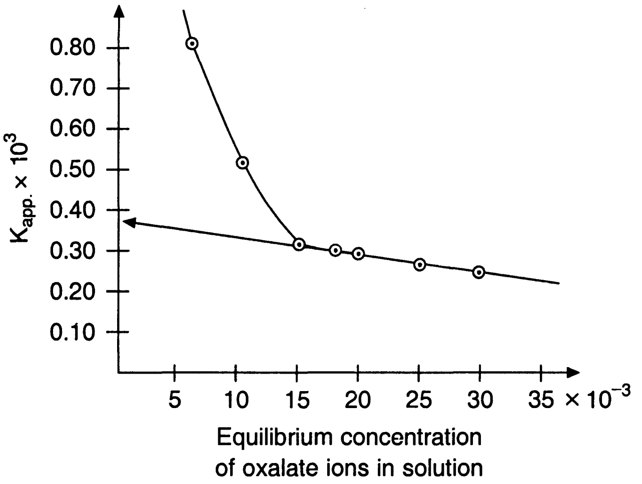

Fig. 2. Variation of apparent equilibrium constant with concentration of oxalate ions in solution at equilibrium for ion exchange reaction

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

TABLE-1

EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

Amount of ion exchange resin = 0.5 g
Volume of sulphate ion solution = 100 mL
Temperature = 45°C
Exchange capacity = 2.18 meq/0.5 g of resin

Initial conc. of sulphate ion in solution (M)	Equilibrium conc. in solution (M)		Amount of the ions on the resin meq/0.5 g		(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	0.0144	0.0034	0.745	0.720	0.157	0.692	55.0	0.61
0.015	0.0157	0.0057	0.615	0.785	0.180	0.413	36.4	0.92
0.020	0.0174	0.0100	0.445	0.870	0.217	0.261	34.3	0.98
0.025	0.0176	0.0125	0.420	0.880	0.235	0.247	30.5	1.10
0.030	0.0180	0.0251	0.385	0.900	0.305	0.329	25.8	1.30
0.040	0.0187	0.0337	0.310	0.935	0.346	0.243	24.5	1.37
0.045	0.0199	0.0439	0.195	0.995	0.389	0.101	23.6	1.42

Equilibrium constant in standard state $K_{std.} = 31.0$

Bonner and Pruett[20], in their study of temperature effect on uni-univalent exchanges involving some bivalent ions observed that the equilibrium constant decreases with increasing temperatures resulting in an exothermic ion exchange reaction. However, in the present study, equilibrium constants for both uni-bivalent exchanges increases with increase in temperatures (Tables-2, 4), resulting in an endothermic ion exchange reaction with enthalpy values of 11.5 kJ/mole and 14.5 kJ/mole respectively.

TABLE-2
VARIATION OF EQUILIBRIUM CONSTANT IN THE STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION AT DIFFERENT TEMPERATURES

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

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

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

Enthalpy of ion exchange reaction = 11.5 kJ/mole

TABLE-3
EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

Amount of ion exchange resin = 0.5 g
Volume of oxalate ion solution = 100 mL
Temperature = 45°C
Exchange capacity = 2.18 meq/0.5 g of resin

Initial conc. of oxalate ion in solution (M)	Equilibrium conc. in solution (M)		Amount of the ions on the resin meq/0.5 g		(Ionic strength)$^{1/2}$	$\frac{(\gamma_{I^-})^2}{(\gamma_{C_2O_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RI})^2} = K_{std.}/K_{app.}$
	I^-	$C_2O_4^{2-}$	I^-	SO_4^{2-}				
0.010	0.0070	0.0065	1.485	0.350	0.163	0.682	0.809	0.439
0.015	0.0071	0.0100	1.475	0.355	0.193	0.636	0.523	0.679
0.020	0.0072	0.0159	1.465	0.360	0.234	0.578	0.317	1.120
0.025	0.0074	0.0175	1.440	0.370	0.245	0.561	0.314	1.131
0.030	0.0076	0.0192	1.425	0.380	0.255	0.550	0.310	1.145
0.040	0.0080	0.0245	1.380	0.400	0.285	0.516	0.283	1.254
0.050	0.0085	0.0308	1.335	0.425	0.318	0.474	0.268	1.325

Equilibrium constant in standard state $K_{std.} = 0.355$

Bonhoeffer[45] has suggested the term 'electroselectivity' for the electrostatic preference for the ions of higher valence. Also due to the Donnan potential difference existing between the ion exchanger and dilute solutions, the counter ion of higher valence is prefered[46–52]. This combined effect of electroselectivity and Donnan potential was responsible for affinity of ion exchangers towards bivalent (SO_4^{2-} and $C_2O_4^{2-}$) ions in the solution and hence Cl^-/SO_4^{2-} and

$I^-/C_2O_4^{2-}$ ion exchange reactions (equations 1 and 2) will proceed in forward direction. However compared to that of chloride ions, the relative selectivity[53] of ion exchangers towards iodide ions is more, hence $I^-/C_2O_4^{2-}$ ion exchange reaction (equation 2) will proceed comparatively slowly as that of Cl^-/SO_4^{2-} exchange reaction giving lower value of K for $I^-/C_2O_4^{2-}$ exchange (Table-4) than that for Cl^-/SO_4^{2-} exchange (Table-2).

TABLE-4
VARIATION OF EQUILIBRIUM CONSTANT IN THE STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION AT DIFFERENT TEMPERATURES

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

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

Temperature (°C)	30	35	40	45
$K_{std.}$	0.260	0.300	0.325	0.355

Enthalpy of ion exchange reaction = 14.5 kJ/mole

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