Asian Journal of Chemistry Vol. 13, No. 1 (2001), 43–49

Study on Ion Exchange Equilibria Involving I^-/SO_4^{2-} and $I^-/C_2O_4^{2-}$ Uni-Bivalent Ion Exchange Systems

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Ion exchange resins in iodide form were equilibriated with oxalate and sulphate ion solution of seven different concentrations in the range of 0.010 M to 0.050 M. The equilibrium constant (K) values are calculated in the temperature range of 30 to 45°C. The K value for $I^-/C_2O_4^{2-}$ exchange reaction at 30°C was calculated to be 0.260 which was observed to be greater than 0.250 for I^-/SO_4^{2-} exchange at same temperature which was due to the difference in ionic size of sulphate and oxalate ions in solution. The enthalpy of ion exchange reactions was calculated as 12.51 kJ/mole and 14.54 kJ/mole respectively indicating the endothermic ion exchange reaction.

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 fields of application are increasing but new ion exchange products afford new opportunities for both chemists and analysts[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 exchanger 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 solutions and resins. More rigorous calculations were made by indicating the activity coefficients of the counter ions in solution and resin phases 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 resins[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 exchanger increases as its affinity for water is decreased. Among the previous investigators in their study to calculate the equilibrium constants only few[16, 17, 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 I^-/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 I^-/SO_4^{2-} ion exchange reaction was carried out by using ion exchange resins in iodide form which were allowed to reach equilibrium 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 this duration of 4 h was adequate for the equilibrium to be attained. The ion exchange reaction at equilibrium may be represented as

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

After 4 h the concentration of the iodide ions in the solution at equilibrium was estimated potentiometrically. From this the amount of sulphate ions that has exchanged on to the resin was estimated, since it was known that one mole of sulphate ion replaces two moles of iodide ions. From the initial concentration of sulphate ions and 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 iodide ions on the resin, the amount of iodide ions remaining on the resin was calculated. Thus the concentration of iodide ions and sulphate ions in the solution and the amount of iodide ions and sulphate ions on the resin equilibrium, the apparent equilibrium constant $K_{app.}$ was calculated. The experimental set was carried in the temperature range of 30 to 45°C.

In the study of $I^-/C_2O_4^{2-}$ exchange reaction the ion exchange resins in iodide form were equilibriated with oxalate ion solution 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. The resins which were originally in chloride form were converted into iodide form using 10% potassium iodide solution in a conditioning column. The conditioned resins were then air dried and used for entire study.

RESULTS AND DISCUSSION

In the study of I^-/SO_4^{2-} uni-bivalent exchange, from the knowledge of equilibrium concentration of sulphate ions ($C_{SO_4^{2-}}$) and iodide ions (C_{I^-}) solution as explained earlier and from the experimental determined exchange capacity of the resin, the amount of iodide (C_{RI}) 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_{RI}, C_{I^-}, $C_{SO_4^{2-}}$ and from the ratio of the activity coefficients of ions in the resin phase, the apparent equilibrium constant $K_{app.}$ where calculated from the expression

$$K_{app.} = \frac{(C_{R_2SO_4}) \cdot (C_{I^-})^2}{(C_{RI})^2 \cdot (C_{SO_4^{2-}})} \cdot \frac{(\gamma_{I^-})^2}{(\gamma_{SO_4^{2-}})} \tag{3}$$

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

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

The graph of $K_{app.}$ versus equilibrium concentration of the bivalent ions in solution was plotted (Fig. 1, 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-valent and bivalent

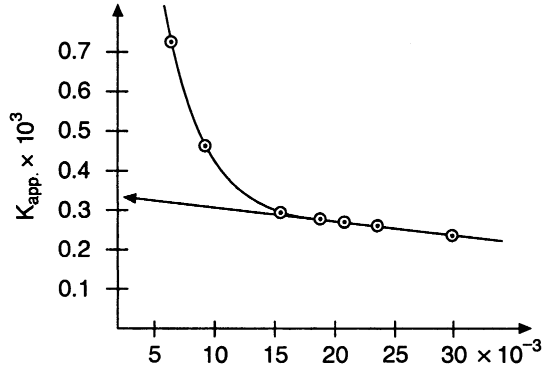

Fig. 1. Variation of apparent equilibrium constant with concentration of sulphate ions in solution at equilibrium for ion exchange reaction

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

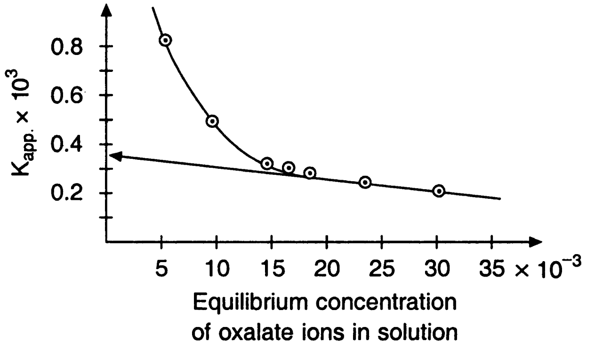

Fig. 2. Variation of apparent equilibrium constant with concentration of oxalate ions in solution at equilibrium for ion exchange reaction

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

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[40, 42]. The equilibrium constants in standard state thus obtained at various temperatures from 30 to 45°C are presented in Tables 2 and 4.

TABLE-1

EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

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)$^{1/2}$	$\frac{(\gamma_{I^-})^2}{(\gamma_{SO_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2SO_4})}{(\gamma_{RI})^2} = K_{std.}/K_{app.}$
	I^-	SO_4^{2-}	I^-	SO_4^{2-}				
0.010	0.0068	0.0067	1.505	0.340	0.164	0.681	0.718	0.460
0.015	0.0069	0.0099	1.495	0.345	0.191	0.639	0.473	0.698
0.020	0.0071	0.0160	1.475	0.355	0.235	0.576	0.296	1.115
0.025	0.0073	0.0180	1.450	0.365	0.248	0.564	0.290	1.138
0.030	0.0075	0.0197	1.435	0.375	0.258	0.546	0.284	1.162
0.040	0.0078	0.0242	1.400	0.390	0.283	0.540	0.270	1.220
0.045	0.0082	0.0300	1.365	0.410	0.284	0.514	0.254	1.300

Equilibrium constant in standard state $K_{std.} = 0.330$

TABLE-2

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

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

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

Temperature (°C)	30	35	40	45
$K_{std.}$	0.250	0.280	0.310	0.330

Enthalpy of ion exchange reaction = 12.51 kJ/mole

Bonner and Pruett[20], in their study of temperature effect on uni-univalent exchanges involving some divalent 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 increase with increase in temperature (Tables-2, 4), resulting in endothermic ion exchange reaction with enthalpy values of 12.51 kJ/mole and 14.54 kJ/mole respectively.

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

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

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 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^-	$C_2O_4^{2-}$				
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 ions of higher valence are preferred[46–52]. This combined effect of electroselectivity and Donnan potential was responsible for affinity of ion exchanger in iodide form towards sulphate and oxalate ions in solution, thereby I^-/SO_4^{2-} and $I^-/C_2O_4^{2-}$ ion exchange reactions (equations 1 and 2) will proceed in forward direction. However, for oxalate ion the need of solvation is low[53] and the affinity for the ion exchange resin is high as compared to sulphate ion, therefore $I^-/C_2O_4^{2-}$ ion exchange reaction will proceed relatively faster giving higher value of K (Table-4) relative to that of I^-/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

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

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 = 14.54 kJ/mole

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(*Received*: 25 March 2000; *Accepted*: 17 August 2000) AJC-2126