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Effect of Ionic Size on Equilibrium Constant of Some Uni-Bivalent Ion Exchange Reactions

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Ion exchange resins in chloride and iodide form were equilibriated with oxalate ion solution of seven different concentrations from 0.010 M to 0.050 M, in temperature range of 30 to 45°C. The difference in the ionic size of exchangeable Cl^- and I^- ions on the resin results in variation of equilibrium constant (K) values, *i.e.*, for $Cl^-/C_2O_4^{2-}$ exchange value of K at 30°C was calculated to be 19.5, while for $I^-/C_2O_4^{2-}$ exchange the value of K was calculated to be 0.260 for same temperature. For both uni-bivalent exchanges the equilibrium constant (K) values increases with increase in temperature, indicating the endothermic ion exchange reaction having enthalpy of 12.2 kJ/mole for $Cl^-/C_2O_4^{2-}$ exchange and 14.5 kJ/mole for $I^-/C_2O_4^{2-}$ exchange.

INTRODUCTION

Ion exchange materials of different origin, composition and structure often have different properties. The knowledge of important physical and chemical properties[1] of ion exchanger is a complementary part of resin characterisation study. The property that involves stability of ion exchangers is of great significance[2] in most instance and it generally decides the selection of an exchangers for any particular exchange process.

A number of investigators[3–5] carried out equilibrium studies extending over a wide range of composition of solution and resin. More rigorous calculations were made by including the activity coefficients of the counter ions in solution and resin phases to compute the thermodynamic equilibrium constant[6–18]. Extensive study is available 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 anion, Andreev and Kuznetsov[41] showed that the absorbability of the anion 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, 42, 43] have emphasized on the activity coefficients of the ions in resin phase in uni-bivalent exchange systems.

The ion exchange resin Amberlite IRA-400 which was used in present investigation has opened new fields of applications for ion exchange process[44]. They have been widely employed for adsorption and fractionation of acids, biochemical and pharmaceutical uses and also in catalysis of organic synthesis. Considering the wide range of industrial and research applications, it was expected that the study carried out in present investigation may be helpful in characterisation and upgradation of ion exchange resins.

EXPERIMENTAL

The study on ion exchange equilibria involving $Cl^-/C_2O_4^{2-}$ uni-bivalent ion exchange reaction was carried out by equilibriating the ion exchange resin (0.5 g) in chloride form with 100 mL of oxalate ion solution of seven different concentrations from 0.010 M to 0.050 M for 4 h at constant temperature of 30°C (±0.1°C). The temperature was properly controlled by using constant temperature water bath having automatic on-off control system. From the results of our previous investigations[45] using the same ion exchangers it was observed that the duration of 4 h was sufficient for the exchange reaction to reach the equilibrium. The ion exchange reaction at equilibrium may be represented as:

$$2R\text{—}Cl + C_2O_4^{2-}(aq.) \rightleftharpoons R_2C_2O_4 + 2Cl^-(aq.) \qquad (1)$$

The concentration of the chloride ions in the solution at equilibrium was estimated potentiometrically with standard silver nitrate solution. From this the amount of oxalate ions 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. From the initial concentration of oxalate ion and the amount of it which has exchanged on to the resin are known, the concentration of oxalate ion in the solution at equilibrium was calculated. Further from the known resin capacity and the amount of oxalate ions replacing the chloride ions on the resin, the amount of chloride ions remaining on the resin was calculated. Thus the concentration of chloride ions and oxalate ions in the solution and the amount of chloride ions and oxalate ions on the resin at equilibrium, the apparent equilibrium constant K_{app} was calculated. The same set of experiment was performed up to 45°C.

In order to study the $I^-/C_2O_4^{2-}$ ion exchange reaction, the ion exchange resin Amberlite IRA-400 a strongly basic anion exchangers in chloride form was converted into iodide form by using 10% potassium iodide solution in a conditioning column. The conditioned resins were then air dried and known weight (0.5 g) of resins in iodide form were equilibriated with 100 mL of oxalate ion solution of seven different concentrations from 0.010 M to 0.050 M at 30°C. The ion exchange reaction at equilibrium may be represented as

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

The experimental sets were repeated up to temperature of 45°C as explained earlier.

The exchange capacity of anion exchanger was experimentally determined according to the standard procedures[46] and is calculated to be 2.18 meq/0.5 g of resin.

RESULTS AND DISCUSSION

In the study of $Cl^-/C_2O_4^{2-}$ uni-bivalent exchanges from the knowledge of equilibrium concentration of oxalate ($C_{C_2O_4^{2-}}$) ions and chloride (C_{Cl^-}) ions in the solution and from the exchange capacity of the resin, the amount of chloride (C_{RCl}) and oxalate ($C_{R_2C_2O_4}$) 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 Huckles 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 on the resin phase, the apparent equilibrium constant $K_{app.}$ for reaction represented by equation (1) may be calculated from the expression

$$K_{app.} = \frac{(C_{R_2C_2O_4}) \cdot (C_{Cl^-})^2}{(C_{RCl})^2 \cdot (C_{C_2O_4^{2-}})} \cdot \frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})} \qquad (3)$$

Similarly the apparent equilibrium constant $K_{app.}$ for $I^-/C_2O_4^{2-}$ ion exchange reaction represented by equation (2) may be 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 bivalent ions in solution when extrapolated back to zero bivalent ion concentration gives equilibrium constant in the standard state $K_{std.}$. (Fig. 1, 2). The ratio of $K_{std.}/K_{app.}$ will give the ratio of activity coefficients of both the ions in resin phase. A typical results are presented in Tables-1, 3. The equilibrium constants in standard state $K_{std.}$ calculated at different temperatures from 30 to 45°C are presented in Tables-2 and 4. The choice of standard state over the apparent state for equilibrium constant was already justified in our previous work[42, 43].

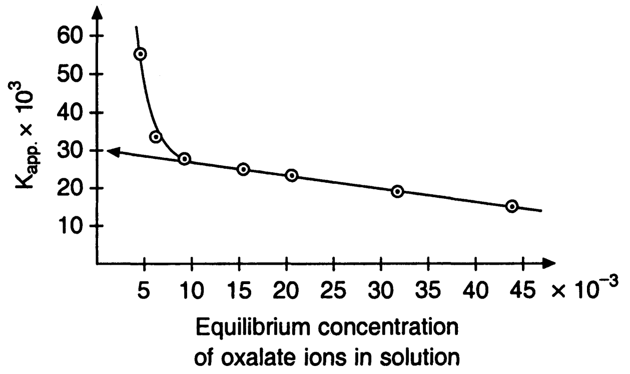

Fig. 1. Variation of apparent equilibrium constant with concentration of sulphate ions in solution at equilibrium for ion exchange reaction

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

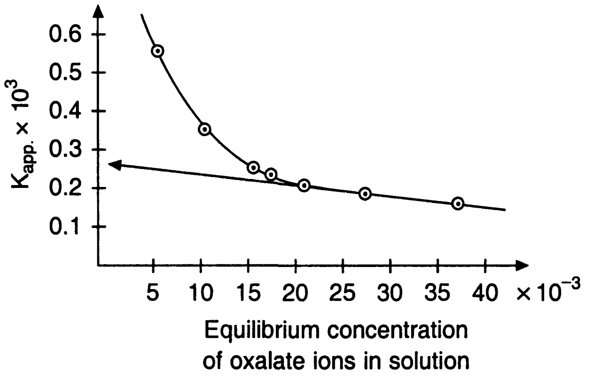

Fig. 2. Variation of apparent equilibrium constant with concentration of oxalate ions in solution at equilibrium for ion exchange reaction

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

TABLE-1

EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

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		$(\text{Ionic strength})^{1/2}$	$\frac{(\gamma_{I^-})^2}{(\gamma_{C_2O_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RI})^2} = K_{std.}/K_{app.}$
	I^-	$C_2O_4^{2-}$	I^-	$C_2O_4^{2-}$				
0.010	0.0064	0.0070	1.545	0.320	0.165	0.679	0.529	0.491
0.015	0.0065	0.0104	1.535	0.325	0.194	0.634	0.354	0.734
0.020	0.0067	0.0165	1.515	0.335	0.237	0.574	0.227	1.145
0.025	0.0068	0.0188	1.500	0.340	0.248	0.570	0.212	1.226
0.030	0.0069	0.0201	1.495	0.345	0.259	0.545	0.199	1.306
0.040	0.0071	0.0280	1.470	0.355	0.302	0.517	0.153	1.700
0.045	0.0074	0.0370	1.445	0.370	0.344	0.446	0.117	2.220

Equilibrium constant in standard state $K_{std.} = 0.260$

Bonner and Pruett[20], 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 reactions. However in the present investigation, the values of equilibrium constant (K) for both uni-bivalent exchanges increases with increase in temperature (Tables 2

AND 4), indicating the endothermic ion exchange reactions with enthalpy values of 12.2 kJ/mole for $Cl^-/C_2O_4^{2-}$ exchange and 14.5 kJ/mole for $I^-/C_2O_4^{2-}$ exchange.

TABLE-2

VARIATION OF THE 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 = 14.54 kJ/mole

Since the need of solvation of crystallographically smaller Cl^- ion (1.84 Å) is stronger[47] and due to very low relative selectivity[48] for ion exchange resins, the chloride ions on the ion exchanger will readily get exchanged into dilute solution phase giving higher value of K for $Cl^-/C_2O_4^{2-}$ exchanges represented by equation (1) (Table-2). As the iodide ion have larger ionic size (2.20 Å)[49], the need of solvation is less and it will have relative selectivity[48] high for ion exchange resins, so it will not readily get exchanged into dilute solution phase (as compared to Cl^-) thereby giving relatively lower value of K for $I^-/C_2O_4^{2-}$ exchanges represented by equation (2) (Table-4).

TABLE-3

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 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		$(\text{Ionic strength})^{1/2}$	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RCl})^2} = K_{std.}/K_{app.}$
	Cl^-	$C_2O_4^{2-}$	Cl^-	$C_2O_4^{2-}$				
0.010	0.0143	0.0033	0.755	0.715	0.156	0.694	55.4	0.612
0.015	0.0156	0.0056	0.625	0.780	0.180	0.372	32.3	1.049
0.020	0.0173	0.0098	0.455	0.865	0.216	0.233	29.8	1.138
0.025	0.0178	0.0155	0.400	0.890	0.254	0.225	25.6	1.324
0.030	0.0181	0.0220	0.375	0.905	0.290	0.223	21.4	1.584
0.040	0.0190	0.0329	0.280	0.950	0.343	0.154	20.5	1.654
0.050	0.0198	0.0447	0.205	0.990	0.392	0.099	19.1	1.775

Equilibrium constant in standard state $K_{std.} = 30$.

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

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

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

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