

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

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Ion exchange resins Amberlite IRA-400 in chloride and iodide form were equilibrated respectively with oxalate and sulphate ion solution of seven different concentrations from 0.010 M to 0.050 M in the temperature range of 30 to 45°C. The equilibrium constant (K) values calculated for both $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ and $\text{I}^-/\text{SO}_4^{2-}$ uni-bivalent exchange increases with increase in temperature. The K value at 30°C for $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ ion exchange was calculated to be 19.5 which was higher than 0.250 for $\text{I}^-/\text{SO}_4^{2-}$ exchange at same temperature. The variation in values of K was due to the difference in ionic size of exchangeable oxalate and sulphate ions in solution.

INTRODUCTION

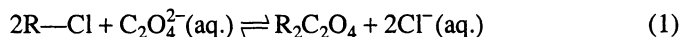
Ion exchangers which are the integral part of many chemical industries has also opened to the research workers whole new field of application for ion exchange process¹. Furthermore not only the field of applications are increasing but new ion exchange products afford new opportunities for both chemists and analyst². 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 synthesis¹. 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 carefully 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 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 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 Kuznetsov⁴¹ showed that the adsorbability of anions on an ion exchangers increases as its

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 exchange systems. The present investigation was therefore been carried out to calculate the equilibrium constants in $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ and $\text{I}^-/\text{SO}_4^{2-}$ ion exchange systems giving due regard to the activity coefficients of the ions both in the solution as well as in the resin phase.

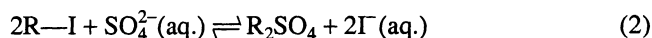
EXPERIMENTAL

The study of ion exchange equilibria involving $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ ion exchange reaction was carried out by using ion exchange resin in chloride form which were equilibrated with oxalate 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 earlier⁴³, 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



After 4 h, the concentration of the chloride ion in the solution at equilibrium was estimated potentiometrically. 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. From the initial concentration of oxalate ion in 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, the amount of oxalate ions replacing the chloride ions on the resin was calculated. Thus the concentrations of chloride and oxalate ions in the solution and the amount of chloride and oxalate 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 $\text{I}^-/\text{SO}_4^{2-}$ ion exchange reaction. In the experimental work the resins in iodide form were equilibrated with sulphate ion solutions of seven different concentrations from 0.010 M to 0.050 M. The ion exchange reaction at equilibrium may be represented as



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 procedure⁴⁴ 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 $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ uni-bivalent exchange, from the knowledge of equilibrium concentration of oxalate ions ($\text{C}_{\text{C}_2\text{O}_4^{2-}}$) and chloride ions (C_{Cl^-}) solution as explained earlier and from the experimental determined exchange capacity of the resin, the amount of chloride (C_{RCl}) and oxalate ($\text{C}_{\text{R}_2\text{C}_2\text{O}_4}$) 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 Huckle's limiting law. Thus from the values of $\text{C}_{\text{R}_2\text{C}_2\text{O}_4}$, C_{RCl} , C_{Cl^-} , $\text{C}_{\text{C}_2\text{O}_4^{2-}}$ and from the ratio of the activity coefficients of ions in the resin phase, the apparent equilibrium constant K_{app} are calculated from the expression

$$\text{K}_{\text{app}} = \frac{(\text{C}_{\text{R}_2\text{C}_2\text{O}_4}) \cdot (\text{C}_{\text{Cl}^-})^2}{(\text{C}_{\text{RCl}})^2 \cdot (\text{C}_{\text{C}_2\text{O}_4^{2-}})} \cdot \frac{(\gamma_{\text{Cl}^-})^2}{(\gamma_{\text{C}_2\text{O}_4^{2-}})} \quad (3)$$

Similarly for $\text{I}^-/\text{SO}_4^{2-}$ uni-bivalent exchange the apparent equilibrium constant K_{app} are calculated from the expression

$$\text{K}_{\text{app}} = \frac{(\text{C}_{\text{R}_2\text{SO}_4}) \cdot (\text{C}_{\text{I}^-})^2}{(\text{C}_{\text{RI}})^2 \cdot (\text{C}_{\text{SO}_4^{2-}})} \cdot \frac{(\gamma_{\text{I}^-})^2}{(\gamma_{\text{SO}_4^{2-}})} \quad (4)$$

The graph of K_{app} versus equilibrium concentration of the bivalent ion in solution was plotted (Figs. 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 $\text{K}_{\text{std}}/\text{K}_{\text{app}}$ 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^{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.

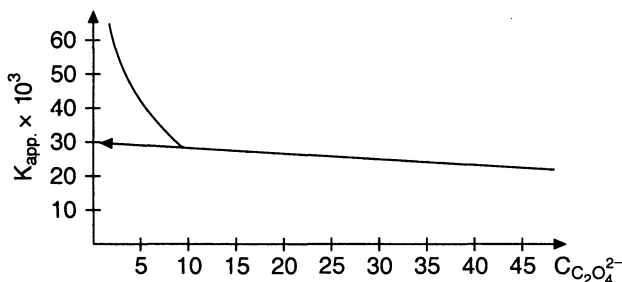
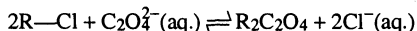


Fig. 1. Variation of apparent equilibrium constant with concentration of oxalate ion in solution at equilibrium for ion exchange reaction



Bonner and pruet²⁰, 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 reactions. However, in the present study, the 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 12.2 kJ/mole and 12.5 kJ/mole respectively.

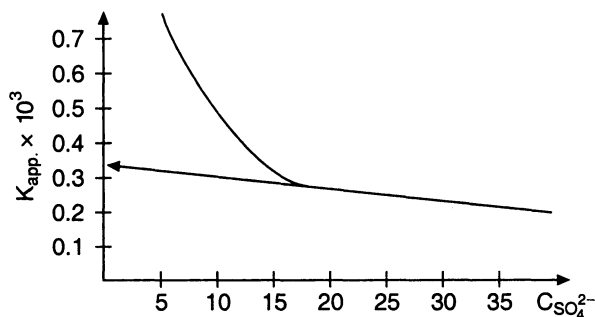


Fig. 2. Variation of apparent equilibrium constant with concentration of sulphate ion in solution at equilibrium for ion exchange reaction

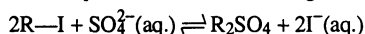
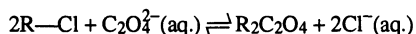


TABLE-1
EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

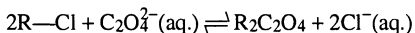


Amount of ion exchange resin	= 0.5 g
Volume of oxalate ion solution	= 100 mL
Temperature	= 45°C
Exchange capacity	= 2.18 meq/0.5 g of resin

Initial conc. of oxalate ion in solution (M)	Equilibrium conc. in on solution (M)		Amount of the ions on the resin meq/0.5 g		(Ionic strength) ^{1/2}	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})^2} \times 10^3$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RCl})^2} = K_{std.}/K_{app.}$
	Cl ⁻	C ₂ O ₄ ²⁻	Cl ⁻	C ₂ O 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
0.045	0.0198	0.0447	0.205	0.990	0.392	0.399	19.1	1.775

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

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



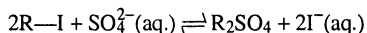
Amount of ion exchange resin = 0.5 g

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

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



Amount of ion exchange resin = 0.5 g

Volume of SO_4^{2-} 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
0.050	0.0082	0.0300	1.365	0.410	0.284	0.514	0.254	1.300

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

Bonhoeffer⁴⁵ 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 preferred⁴⁶⁻⁵². This combined effect of electroselectivity and Donnan potential was responsible for affinity of ion exchangers towards bivalent ($C_2O_4^{2-}$ and SO_4^{2-}) ions in the solution and hence $Cl^-/C_2O_4^{2-}$ and I^-/SO_4^{2-} ion exchange reactions (equations 1 and 2) will proceed in forward direction. However oxalate ions due to the larger ionic size will have less tendency to undergo solvation⁵³ and will form a strong covalent bonds⁴¹ with the electrophilic centre of the resin as compared to that of smaller ionic size sulphate ions which have strong tendency to undergo solvation. Therefore ion exchanger

will have higher affinity for oxalate ions of smaller solvated volume than that for larger solvated volume sulphate ions. Hence $\text{I}^-/\text{SO}_4^{2-}$ exchange reaction will proceed at relative slower rate giving lower value of K (Table-4) and $\text{Cl}^-/\text{C}_2\text{O}_4^{2-}$ ion exchange reaction proceed at relative faster rate giving higher value of equilibrium constant K (Table-2).

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

$$2\text{R}-\text{I} + \text{SO}_4^{2-}(\text{aq.}) \rightleftharpoons \text{R}_2\text{SO}_4 + 2\text{I}^-(\text{aq.})$$

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

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

Enthalpy of ion exchange reaction = 12.51 kJ/mole

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