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Study of Temperature Effect on Uni-Univalent/Bivalent Ion Exchange Reaction

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Ion exchange equilibrium constant (K) for Cl^-/Br^- and $Cl^-/C_2O_4^{2-}$ systems was studied at different temperatures from 30 to 45°C. For both uni-univalent and uni-bivalent exchange systems, the value of K increases with rise in temperature, *i.e.*, from 1.16 at 30°C to 2.95 at 45°C for Cl^-/Br^- system and 19.5 at 30°C to 30.0 at 45°C for $Cl^-/C_2O_4^{2-}$ system indicating the endothermic ion exchange reaction. The difference in K values at the same temperature for the two systems was related to the ionic charge of exchangeable ions in the solution.

INTRODUCTION

Ion exchange materials of different origin, composition and structure often have very different properties. In order to use ion exchangers properly in laboratory work, it is important to know thoroughly their properties and behaviour. It is then easier to choose the most suitable resin for a certain analytical work. The present large, and year by year increasing, literature on ion exchangers shows the great importance of these substances; furthermore, not only the field of applications is increasing but new ion exchange products afford new opportunities for both chemists and analysts[1]. From the wide range of applications of these ion exchangers, it was thought to have a detailed study on the ion exchange equilibria at different temperatures, which will not only help in qualitative evaluation of ion exchangers, but also will be useful in assessing its efficiency in several ion exchange processes.

A number of investigators[2–4] carried out very 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 phases to compute the thermodynamic equilibrium constant[5–17]. Extensive study on ion exchange equilibria involving uni-univalent[18–24] and uni-bivalent[25–28] cation exchange systems using different types of resin[21, 29–32], but very few attempts have been made to study the equilibrium for anion exchange systems[33–37]. Among the previous investigators in their study to calculate the equilibrium constants only few[15, 16, 38] 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 constants in

Cl^-/Br^- and $Cl^-/C_2O_4^{2-}$ 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^-/Br^- uni-univalent ion exchange reaction, the ion exchange resin (0.500 g) in chloride form was equilibrated with 50 mL of potassium bromide solution of five different concentrations from 0.019 M to 0.042 M in different stoppered bottles kept 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 resin, which was reported earlier[39], 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 bromide ion concentration potentiometrically with standard silver nitrate solution. From these results the equilibrium constant (K) for the ion exchange reaction

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.) \qquad (1)$$

was determined. The same experimental work was carried out to understand the equilibrium constant (K) for the ion exchange reaction (1) up to 45°C.

In the second set of experiments 0.5 g of ion exchange resin in chloride form was equilibriated with 100 mL of oxalate ion solution of seven different concentrations varying from 0.01 M to 0.05 M at 30°C. The uni-bivalent ion exchange reaction can be represented as:

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

After 4 h the concentration of the chloride ions in the solution was estimated potentiometrically using standard silver nitrate solution. From this the amount of oxalate ions that has exchanged on to the resin was estimated, since it is known that one mole of oxalate ion replaces two moles of chloride ions. Because the initial concentration of oxalate ions in the solution and the amount of it which has exchanged on to the resin are known, the concentration of oxalate ions 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 (as determined above) the amount of chloride ions remaining on the resin was calculated. Having thus known the concentrations of chloride and oxalate ions in the solution as well as in the resin phase at equilibrium, the apparent equilibrium constant $K_{app.}$ was calculated. The experiment was repeated at different temperatures up to 45°C.

The exchange capacity was experimentally determined according to the standard procedure[40] and was calculated to be 2.18 meq/0.5 g of resin.

RESULTS AND DISCUSSION

In the study of Cl^-/Br^- uni-univalent exchange, from the knowledge of initial and equilibrium concentration of bromide ion, the decrease in the concentration of the latter was noted. Since it is 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 the chloride ions was experimentally determined and was compared with the decrease in concentration of bromide ions and in all the experiments, these two quantities are found to be satisfactorily equal within the limits of ± 0.0002 moles/litre (Table-1). The amount of bromide ions in milli-equivalents which had exchanged on to the resin was calculated from the observed decrease in the concentration of bromide ions in solution. This gives $C_{R—Br}$.

TABLE-1
EQUILIBRIUM CONCENTRATION OF CHLORIDE AND BROMIDE IONS IN THE SOLUTION AND IN THE RESIN PHASE FOR THE ION EXCHANGE REACTION

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$$

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

System	Initial conc. of bromide ions (M)	Final conc. of bromide ions (M) C_{Br^-}	Change in bromide ion concentration (M)	Concentration of chloride ion exchanged (M) C_{Cl^-}	Amount of bromide ion exchanged on the resin meq/ 0.5 g $C_{R—Br}$
1	0.0196	0.0033	0.0163	0.0161	0.815
2	0.0292	0.0073	0.0219	0.0215	1.095
3	0.0326	0.0092	0.0234	0.0236	1.170
4	0.0376	0.0120	0.0256	0.0254	1.280
5	0.0424	0.0153	0.0271	0.0273	1.355

The equation for the equilibrium constant would be given by

$$K = \frac{C_{R—Br} \cdot C_{Cl^-}}{C_{R—Cl} \cdot C_{Br^-}} \tag{3}$$

If A is the experimental determined exchange capacity, then $C_{R—Cl}$ at equilibrium would be $(A—C_{R—Br})$. Therefore, the modified equation for the equilibrium constant would be given by

$$K = \frac{C_{R—Br} \cdot C_{Cl^-}}{(A—C_{R—Cl}) \cdot C_{Br^-}} \tag{4}$$

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

TABLE-2
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION

$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$

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

System	1	2	3	4	5
Equilibrium constant (K)	2.92	2.94	2.97	2.98	2.93

Average value of K = 2.95

TABLE-3
VARIATION OF EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT DIFFERENT TEMPERATURE

$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$

Amount of ion exchange resin = 0.5 g
Volume of iodide ion solution = 50 mL

Temperature (°C)	30	35	40	45
Equilibrium constant (K)	1.16	1.59	1.25	2.95

Enthalpy of ion exchange reaction = 45.91 kJ/mole

In the study of $Cl^-/C_2O_4^{2-}$ uni-bivalent exchange from the knowledge of equilibrium concentration of oxalate ($C_{C_2O_4^{2-}}$) ions and chloride (C_{Cl^-}) ions in the solution (explained in the experimental part) and from the exchange capacity of the resin[38], the amouot of chloride (C_{RCl}) and oxalate ($C_{R_2C_2O_4}$) ions in 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 $C_{R_2C_2O_4}$, C_{RCl}, C_{Cl^-}, $C_{C_2O_4^{2-}}$ and the ratio of the activity coefficients of ions in the resin phase, the apparent equilibrium constants $K_{app.}$ are calculated from the expression

$$K_{app.} = \frac{(C_{R_2C_2O_4}) \cdot (C_{Cl^-})^2}{(C_{RCl})^2 \cdot (C_{C_2O_4^{2-}})} \cdot \frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})} \tag{5}$$

The graph of $K_{app.}$ *vs.* equilibrium concentration of oxalate ions in solution when extrapolated back to zero oxalate ion concentration, gives equilibrium constant in the standard state $K_{std.}$ (Fig. 1). 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 equilibrium constants in standard state $K_{std.}$ calculated at different temperatures from 30 to 45°C are represented in Table-5. The choice of standard state over the apparent state for equilibrium constant was already justified in our previous work[38].

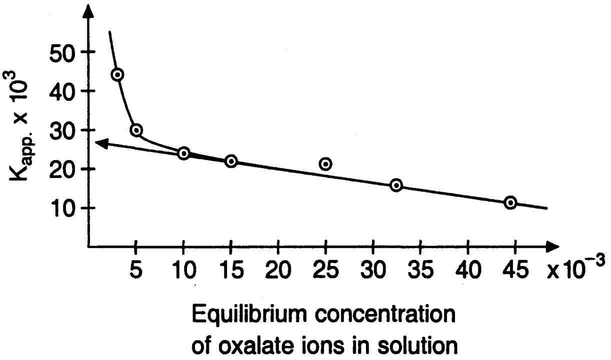

Fig. 1 Variation of apparent equilibrium constant with conc. of oxalate ions in solution at equilibrium

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

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

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

Amount of ion exchange resin = 0.5 g
Volume of oxalate ion solution = 100 mL
Temperature = 40°C
Exchange capacity (A) = 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)$^{1/2}$	$\frac{(\gamma_{Cl^-})^2}{(\gamma_{C_2O_4^{2-}})}$	$K_{app.} \times 10^3$	$\frac{(\gamma_{R_2C_2O_4})}{(\gamma_{RCl})^2} = K_{std.}/K_{app.}$
	Cl^-	$C_2O_4^{2-}$	Cl^-	$C_2O_4^{2-}$				
0.010	0.0141	0.0035	0.775	0.705	0.157	0.692	46.1	0.568
0.015	0.0152	0.0058	0.665	0.760	0.180	0.428	29.3	0.894
0.020	0.0164	0.0103	0.545	0.820	0.217	0.362	26.1	1.004
0.025	0.0170	0.0160	0.480	0.850	0.255	0.359	23.9	1.096
0.030	0.0176	0.0259	0.425	0.880	0.309	0.343	20.0	1.310
0.040	0.0185	0.0335	0.330	0.725	0.345	0.192	16.7	1.569
0.050	0.0194	0.0450	0.245	0.970	0.393	0.107	14.5	1.807

Equilibrium constant in standard state $K_{std.} = 28.5$

Bonner and Pruett[19] 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 reaction. However, in the present investigation, the values of equilibrium constants (K) for both uni-univalent and uni-bivalent exchanges increases with increase in temperature (Tables 3, 5) indicating the endothermic ion exchange reactions[38, 41] with enthalpy values of 45.91 kJ/mole and 12.2 kJ/mole, respectively.

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

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

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

When ion exchangers in chloride form are equilibrated with bromide and oxalate ions in solution, there exists a Donnan potential difference between the ion exchanger and dilute solutions. The force with which the potential acts on an ion is proportional to the ionic charge[42–48] thereby forcing the counter ion (oxalate ion) of higher valence onto the resin phase. Bonheffer[49] has suggested the term 'electroselectivity' for the electrostatic preference for the ions of higher valence. This phenomenon of 'electroselectivity' and Donnan potential was responsible for the preferential affinity of oxalate ion over that of bromide ion both in the solution for the resin phase. This explains the higher value of equilibrium constant (K) for $Cl^-/C_2O_4^{2-}$ exchange as compared to that for Cl^-/Br^- exchange (Tables 3, 5).

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