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Study of Uni-Bivalent Ion Exchange Equilibria in Cl^-/SO_4^{2-} System using Strongly Basic Anion Exchanger Amberlite IRA-400

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Ion exchanger in chloride form was allowed to reach equilibrium with sulphate ion solution of seven different concentrarions from 0.010 M to 0.050 M and the equilibrium concentration of the chloride and sulphate ions in the solution was determined. From the knowledge of ion exchange capacity of the resin, the amounts of the chloride and sulphate ions in the resin phase were calculated. From these results, the apparent equilibrium constants ($K_{app.}$) for the system, the ratio of the activity co-efficients of ions in the resin phase and hence the standard equilibrium constant ($K_{std.}$) were calculated. The value of $K_{std.}$ increases from 20 at 30°C to 31 at 45°C, indicating the endothermic ion exchange reaction. From the knowledge of standard equilibrium constants at different temperatures, enthalpy of ion exchange reaction was calculated to be 11.5 kJ/mole.

INTRODUCTION

Ion exchangers are the integral part of many chemical industries and the efficiency of an ion exchange resin depends on the capability of these resins to exchange one type of ion with another.[1] For a qualitative evaluation of an ion exchange resin it is of importance to study the equilibrium for the ion exchange process. This will be of considerable use not only in quantitatively assessing an ion exchange resin for its utility in a stipulated ion exchange process but also in assessing its efficiency in several ion exchange processes.[2]

Bonner *et al.*[3] studied the temperature effect on the ion exchange equilibrium for Ca^{2+}, Mg^{2+} and Cu^{2+} ions. Starobinets *et al.*[4] further studied the effect of temperature on the bivalent-univalent exchange system, *i.e.*, alkaline earths and transition metals with H^+. Bonner and Pruett[5] studied the temperature effect of NH_4^+/H^+ and Tl^+/H^+ exchanges, involving some bivalent ions, *i.e.*, Cu^{2+}/Zn^{2+}, Cu^{2+}/Mg^{2+}, Ca^{2+}/Cu^{2+}, Pb^{2+}/Ca^{2+} and Mg^{2+}/H^+ exchanges. In all bivalent exchanges, equilibrium constant decreases with increasing temperature resulting in exothermic ion exchange reaction.

Earlier studies regarding the activity coefficient of ions in uni-bivalent systems in resins are scanty and none of them has proposed any method to determine the activity coefficients of the ions in the resin. The present study has therefore been carriedout for determination of equilibrium for Cl^-/SO_4^{2-} uni-bivalent systems using a typical strongly basic anion exchange resin Amberlite IRA-400 giving due regard to the activity coefficients of the ions both in the solution as well as in the ion exchange resin.

EXPERIMENTAL

(a) *Determination of exchange capacity (A)*: About 100.0 mL of 0.25 N $NaNO_3$ at 2 mL/min was passed through a column containing 0.5 g of anion exchange resin in chloride form. The eluent was collected in a 250 mL measuring flask and diluted up to the mark. 25.0 mL of the diluted solution was pipetted out in a conical flask and titrated against 0.01 N standard silver nitrate solution.

$$\text{Exchange capacity (A)} = \frac{0.01 \times 10 \times \text{B.R.}}{0.5} \qquad (1)$$

(b) *Conditioning of ion exchange resin*: The ion exchange resin, as supplied by the manufacturer in the chloride form, was ensured to be completely in that form by eluting it with 10% potassium chloride solution. The resins were washed with distilled water until the washings are free from chloride ions. The resins were then air-dried and used for further study.

(c) *Equilibrium study*: The potassium sulphate solutions (100.0 mL) of seven different concentrations ranging from 0.010 M to 0.050 M were prepared in different reagent bottles, to which exactly 0.500 g of resin in chloride form was added. The mixture was well stoppered and kept in a thermostat at 30°C for 4 h which was sufficient for the mixture to attain equilibrium. The concentration of the chloride ion in the solution was estimated by potentiometric titration with standard silver nitrate solution. From this the amount of sulphate ion that had exchanged into the resin was estimated, since it was known that one mole of sulphate ion replaces two moles of chloride ion. Because the initial concentration of sulphate ion and the amount of it which had exchanged into the resin were known, the concentration of sulphate ion was calculated. Furthre from the known resin capacity of 2.18 milliequivalent per 0.500 g the amount of chloride ion remaining in the resin was calculated. Having thus known the concentrations of chloride and sulphate ion both in the solution and in the resin phase at equilibrium and the activity coefficients of both ions in solution (calculated by Debye Hückel limiting law), apparent equilibrium constant K_{app} was calculated. Similar sets of experiments were performed at different temperatures from 30°C to 45°C. From the knowledge of equilibrium constant at different temperatures, enthalpy of ion exchange reaction was calculated.

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

RESULTS AND DISCUSSION

In the present study a semi-microburette having an accuracy of 0.02 cm^3 has been used in the titrations with standard silver nitrate solution. The titration readings are accurate up to ± 0.02 cm^3. Considering the magnitudes of the titre values the average equilibrium constants reported here have an accuracy of ±3%.

From the knowledge of equilibrium concentrations of sulphate ion $C_{SO_4^{2-}}$ and that of chloride ion C_{Cl^-} in solution which is experimentally determined and from the exchange capacity of the resin, the amounts of the chloride (C_{RCl}) and sulphate ion ($C_{R_2SO_4}$) in the resin phase can be determined. The ratio of the activity coefficients of ions in the resin phase was calculated from Debye-Hückel limiting law. Thus from the values of $C_{R_2SO_4}$, C_{RCl}, C_{Cl^-}, $C_{SO_4^{2-}}$ and the ratio of the activity coefficient of ions in the resin phase, the apparent equilibrium constant (K_{app}) is calculated from the expression

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

The graph of apparent equilibrium constant K_{app} versus equilibrium concentration of sulphate ion in solution is plotted (Fig. 1) which is extrapolated back to zero sulphate ion concentration to give equilibrium constat in standard state (K_{std}). The ratio of $\frac{K_{std}}{K_{app}}$ will give the ratio of activity coefficients of the ions in resin phase. A typical set of results in present in Table-1. The values of K_{std} are obtained for different temperatures from 30°C (Table-2). The value of $K_{std.}$ is observed to increase with temperature, *i.e.*, for 30°C, value of K_{std} is 20.0 which increases to 31 at 45°C, indicating the endothermic ion exchange reaction.

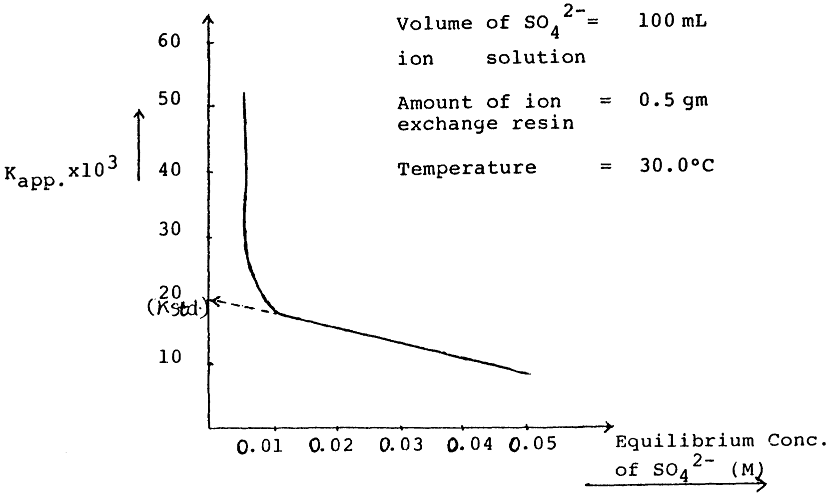

Fig. 1 Variation of K_{app} for the exchange reaction $2R\text{–}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$ with equilibrium conc. of sulphate ion in the solution.

TABLE-1

EQUILIBRIUM CONSTANTS FOR THE UNI-BIVALENT ION EXCHANGE REACTION $2R{-}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$ IN AMBERLITE IRA-400

Amount of the ion exchange resin = 0.500 g
Volume of the sulphate ion solution = 100.0 mL
Exchange capacity = 2.18 meq/0.500 g of resin in chloride form
Temperature = 30°C

Initial conc. of sulphate ion in solution	Equilibrium conc. in solution (M)		Amounts of the ions in the resin meq./0.500 g		(Ionic strength)$^{1/2}$	$\frac{(Y_{Cl^-})^2}{(Y_{SO_4^{2-}})}$	Apparent equilibrium constant $(K_{app} \times 10^3)$	$\frac{Y_{R_2SO_4}}{(Y_{RCl})^2} = \frac{K_{std}}{K_{app}}$
	C_{Cl^-}	$C_{SO_4^{2-}}$	C_{RCl}	$C_{R_2SO_4}$				
0.010	0.0135	0.0042	0.835	0.675	0.161	0.686	28.0	0.54
0.015	0.0142	0.0069	0.765	0.710	0.187	0.645	22.8	0.66
0.020	0.0151	0.0121	0.675	0.755	0.227	0.587	18.3	0.82
0.025	0.0156	0.0189	0.620	0.780	0.269	0.577	15.1	1.00
0.030	0.0163	0.0283	0.555	0.815	0.318	0.474	11.7	1.28
0.040	0.0169	0.0350	0.490	0.845	0.349	0.366	10.5	1.43
0.050	0.0175	0.0485	0.435	0.875	0.404	0.329	9.7	1.55

Equilibrium constant in standard state $K_{std} = 20.0$

TABLE-2

VARIATION OF THE EQUILIBRIUM CONSTANT IN THE STANDARD STATE FOR THE UNI-BIVALENT ION EXCHANGE REACTION $2R{-}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$ WITH TEMPERATURE

Amount of ion exchange resin = 0.500 g
Volume of sulphate ion solution = 100.0 mL

Temperature °C	30.0	35.0	40.0	45.0
K_{std}	20.0	26.5	29.0	31.0

Slope of the plot log K_{std}. versus 1/t = –600
Enthalpy of the ion exchange reaction = 11.5 kJ/mole

It is significant that if log K_{app} versus 1/T is plotted, one does not get a satisfactory straight line. Further if the log K_{app} is plotted versus 1/T different curves having different slopes and hence different values for the enthalpy of the reaction are obtained. Among these different values, one cannot choose the standard value of the enthalpy of the reaction. Therefore the fact that one obtains a satisfactory straight line having a certain slope when log K_{std} is plotted versus 1/T (Fig. 2), giving a definite value of enthalpy of ion exchange reaction as 11.5 kJ/mole, is an ample justification for the choice of the standard state for the equilibrium constant.

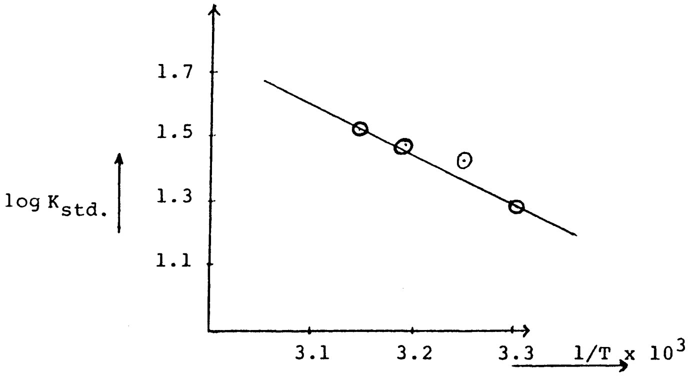

Fig. 2 Variation of $K_{std.}$ for the ion exchange reaction $2R{-}Cl + SO_4^{2-}(aq.) \rightleftharpoons R_2SO_4 + 2Cl^-(aq.)$ with temperature

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