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# STUDY OF KINETICS OF THE OXALATE ION EXCHANGE EQUILIBRIA IN ION EXCHANGE RESIN THERMAX A27

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**ABSTRACT**

The equilibrium constant in the standard state $K_{std}$ for the uni-bivalent ion exchange between the resin (R) and the aqueous solution (aq)

$$2X^{-}_{(R)} + Y^{2-}_{(aq)} \rightleftharpoons 2X^{-}_{(aq)} + Y^{2-}_{(R)} ,$$

where $X^{-} = Cl^{-}$ and $Y^{2-} = C_2O_4^{2-}$, have been determined in anion exchange resin Thermax A27 with due regards to mean activity coefficients of ions both in the solution and in the resin. For this purpose the apparent equilibrium constants, $K_{app}$, for various equilibrium concentrations of the bivalent ion, $C_2O_4^{2-}$, in the solution have been calculated from the expression.

$$K_{app} = \frac{[C_{Y^{2-}(R)}]\ [C_{X^{-}(aq)}\ \gamma_{\pm(aq)}]^2}{[C_{X^{-}(R)}]^2\ [C_{Y^{2-}(aq)}\ \gamma_{\pm(aq)}]}$$

where the 'C's are the concentrations of the ions and $\gamma_{\pm(aq)}$ is the mean activity coefficient of the ions in the solution. From this, the equilibrium constant in the standard state, $K_{std}$, is determined by a graphical method. The resin in its purely univalent anion form is chosen as the standard state. From $K_{std}$, for various temperature the enthalpy change for the ion exchange reaction has been evaluated.

**Key Words: Thermax A27, Oxalate ion, Exchange Equilibrium.**

## INTRODUCTION

In ion exchange reactions, the precise determination of the equilibrium constant in uni-bivalent in exchange has been found to be very difficult because of the lack of data on the activity coefficients of the ions in the ion exchange resin. The unavailability of these important data is a 'missing link' in the theory or ion exchange equilibrium[1]. Many workers[2-5] attempted the determination of such equilibrium constants but they all ignored the activity coefficients. Under such circumstances

the best that can be done is to evaluate the equilibrium constant from experimental data or some logical basis. In present study we have evaluated the equilibrium constant for uni-bivalent ion exchange and the mean activity coefficient of the ions in the resin, $\gamma_{\pm(R)}$ on the basis of a certain chosen standard state for the two ion exchange reactions. Further, the enthalpy changes for these reactions have also been determined. As a typical case, the following reaction has been studied in the strongly basic anion exchanger Thermax A27.

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

where (R) and (aq) represent the ion exchange resin and aqueous solution, respectively.

**EXPERIMENTAL**

The ion exchange resin supplied by manufacturer was in the chloride form and it was conditioned[6] to remove impurities. The resin was eluted with 5% KCl followed by water to ensure that it was completely in chloride form. The resin in bromide form was obtained by eluting chloride form of the resin with ammonium bromide solution.

In a typical equilibrium study, 0.5g of the resin in chloride form was mixed with 100cm$^3$ of 0.01M oxalic acid solution in narrow mouthed reagent bottle and stoppered. Preliminary trials showed that the equilibrium was reached in about 24 hours. Therefore the bottle was kept shaken for three hours and then kept for 24 hours in thermostat. The concentration of chloride ions in solution was estimated by potentiometric titration with standard silver nitrate solution after 24 hours. From this the amount of oxalate ions exchanged into 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 and amount of it which has exchanged into resin were known, the concentration of oxalate in the solution at equilibrium was calculated.

Further, from the known resin capacity 1.45 milliequivalent per 0.5g and the amount of oxalate ion replacing the chloride ion in resin, the amount of chloride ion remaining in resin was calculated.

Having thus known the concentration of chloride ion and oxalate ion in solution and the amount of chloride ion and oxalate ion in the resin at equilibrium, the apparent equilibrium constant $K_{app}$, was calculated.

The same experiment was repeated with various concentration of the oxalate ion in the range of 0.006M to 0.050M and each time apparent equilibrium constant was calculated (Ref. Table-1).

The equilibrium constant were determined at various temperature in the range of 20°C to 40°C and the $K_{std}$ at these temperatures were evaluated. From the plot of $K_{std}$ versus 1/T, the enthalpy changes of the ion exchange reaction were determined. (Ref. Table-2)

**RESULTS AND DISCUSSION**

The equilibrium constant for the ion exchange reaction can be represented by the expression

$$K = \frac{[a_{Y^{2-}(R)}]\ [a_{X^{-}(aq)}]^2}{[a_{X^{-}(R)}]^2\ [a_{Y^{2-}(aq)}]}$$

where the 'a's are the activities of the ions and $X^-$ = $Cl^-$ and $Y^{2-}$ = $C_2O_4^{2-}$. Here the activities of the $X^-$ and $Y^-$ in the aqueous solutions are obtained from their respective concentrations and activity coefficient derived from Debye-Huckel limiting law[7]. As regards the activities of the two ions in the resin are concerned, the situation is different. Ordinarily the activity should be obtained as a product of the concentration and the activity coefficient. In lieu of the concentration of the ions in the resin, their

respective amount in milliequivalent can be used. On this basis, the equilibrium constant would be given by the expression

$$K = \frac{(C_{R2Y}.\gamma_{R2Y})\ (C_X.\ \gamma_X)^2}{(C_{RX}.\ \gamma_{RX})^2\ (C_Y.\ \gamma_Y)}$$

In this expression, the concentrations of ions in the resin in terms of their amounts in milliequivalent are known while their individual activity coefficient i.e. $\gamma_{RX}$ and $\gamma_{R2X}$ are not known. Indeed, it appears that there is no way of evaluating them individually. Also the activity coefficients cannot be ignored because in the expression for equilibrium constant they appears as $(\gamma_{R2Y})/(\gamma_{RX})^2$.

Since $\gamma_{R2Y}$ and $\gamma_{RX}$ are likely to vary with the concentration of the ions $X^-$and $Y^-$ in the resin, the above mentioned quantity is also likely to vary with the concentration of the ions in the resin. This is evident from the fact that the equilibrium constant as calculated from the expression.

$$K_{app} = \frac{(C_{R2Y})\ (C_X.\gamma_X)^2}{(C_{RX})^2\ (C_Y.\gamma_Y)}$$

various with concentration of the ions in the resin (Ref. Table 1 and Table 2).

In absence of any method to determine the activity coefficient of the ions in the resin individually the best that can be done is to attempt to determine the quantity $(\gamma_{R2Y})/(\gamma_{RX})^2$ and to determine the true equilibrium constant.

It is best to choose the ion exchange resin capacity in the univalent form or standard state and refer the resin at any other composition of the uni/bivalent ion to this stand state. Therefore the apparent equilibrium constants calculated by the above equation have been plotted versus the equilibrium concentrations of the oxalate ion in the solution. Extrapolating this curve to zero equilibrium concentration of $C_2O_4^{2-}$ ion in the solution, one obtains the equilibrium constant in solution, $K_{std}$.

Having thus obtained the equilibrium constant in the standard state one can obtain the activity coefficient ratio of ions $(\gamma_{R2Y})/(\gamma_{RX})^2$ at any finite equilibrium concentration of $C_2O_4^{2-}$ ion in the solution as the ratio of $K_{app}/K_{std}$. (Ref. Table-1)

By plotting log $K_{std}$ versus 1/T, one obtains a satisfactory straight line, from the slope of which the enthalpy change and the ion exchange reaction is determined. (Ref. Table-2)

**TABLE-1**

EQUILIBRIUM CONSTANT FOR THE UNI-BIVALENT ION EXCHANGE REACTION

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

Amount of the ion exchange resin : 0.500 g
Volume of the oxalate ion solution : 100 $cm^3$
Temperature : 25°C

| Initial concentration of $C_2O_4^{2-}$ ion in solution | Equilibrium concentration in solution / M | | Amount of ion in the resin meq/0.5 g | | $\sqrt{I}$ | $\gamma_{\pm\ aq}$ | $K_{app}$ | $\gamma_{\pm R}$ |
|---|---|---|---|---|---|---|---|---|
| | $Cl^-$ | $C_2O_4^{2-}$ | $Cl^-$ | $C_2O_4^{2-}$ | | | | |
| 0.006 | 0.0082 | 0.0019 | 0.450 | 0.410 | 0.118 | 0.758 | 35.8 | 0.743 |
| 0.008 | 0.0084 | 0.0038 | 0.430 | 0.420 | 0.141 | 0.719 | 21.1 | 0.437 |
| 0.010 | 0.0086 | 0.0057 | 0.410 | 0.430 | 0.160 | 0.688 | 16.5 | 0.342 |
| 0.015 | 0.0090 | 0.0105 | 0.370 | 0.450 | 0.201 | 0.624 | 12.7 | 0.263 |
| 0.020 | 0.0095 | 0.0156 | 0.390 | 0.475 | 0.237 | 0.574 | 9.1 | 0.189 |
| 0.030 | 0.0097 | 0.0255 | 0.370 | 0.485 | 0.293 | 0.503 | 6.5 | 0.135 |
| 0.050 | 0.0101 | 0.0452 | 0.330 | 0.505 | 0.382 | 0.408 | 5.3 | 0.109 |

**TABLE-2**

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

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

WITH TEMPERATURE

Amount of the ion exchange resin : 0.500 g

Volume of the oxalate ion solution : 100 $cm^3$

| Temperature / °C | 20.0 | 25.0 | 30.0 | 35.0 | 40.0 |
|---|---|---|---|---|---|
| $K_{std}$ | 33.4 | 48.2 | 59.1 | 64.3 | 75.5 |

Slope of the plot of log $K_{std}$ versus 1/T = - 1551.60

Enthalpy of the ion exchange reaction = 29.70 KJ $mole^{-1}$

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