Study of Kinetics of the Uni-Univalent Ion Exchange Equilibrium in the Anion Exchanger Thermax A27

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The uni-univalent ion exchange equilibrium constants for the Cl^--I^- and CI^--Br^- exchange in the strongly basic anion exchange Thermax A27 have been determined. The equilibrium constants can be evaluated satisfactorily over by assuming that the ratios of the activity coefficients of ions in the resin and also in the solution are unity. A different method for determining the ion exchange resin capacity has been developed.

Key words: Thermax A27, Ion exchange, Equilibrium constant, resin capacity.

Introduction

The exchangeability of resin depends upon several factors such as the capacity and nature of the resin[1,2], the ion in the resin, the ion to be exchanged, concentration of ion[3] and temperature[4]. Therefore for quantitative evaluation of an ion exchange resin it is important to study the equilibrium for the ion exchange process. While many researchers[5-10] have studied uni-univalent ion exchange equilibria in cation exchange resins, very few[11-13] have studied anion exchange resins. In view of this, the present study of ion exchange equilibria in the following two systems in a typical anion exchanger,

$$R\text{-}Cl + I^-_{aq} \rightleftharpoons R\text{-}I + Cl^-_{aq} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$R\text{-}Cl + Br^-_{aq} \rightleftharpoons R\text{-}Br + Cl^-_{aq} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Thermax A27 is undertaken. It is strongly basic anion exchanger with a gel type bead structure. In this study the problem of proper unit for expressing the concentration of ions in the resin, the role of activity coefficients of the ions in the resin and the accurate determination of the resin capacity have been emphasized in determining the equilibrium constants for the ion exchange reactions.

Experimental

The ion exchange resin: The Thermax A27as received from the manufacturer is in the chloride form. The particle size of the resin is 16-50 mesh and the degree of cross linking is 5% of DVB. For the present study the resin grain of 30-40 mesh size only are used. Further, the exchanger is 'conditioned'[14] and ensured that it is completely in the chloride form by equilibrating with sodium chloride solution.

Equilibrium study: A liter each of potassium iodide solution (0.1M) and distilled water are kept in a thermostat at 25°C. The exact concentration of the potassium iodide is determined by careful potentiometric titration with standard silver nitrate.

From the stock solution, 5, 10, 15, 30 and 40 cm³ of the potassium iodide and 45, 40, 35, 20 and 10 cm³ of distilled water respectively are transferred to five 100cm³ reagent bottles.

Into each of the bottles 0.500g dry ion exchange resin, which has been swelled overnight with water, is transferred. The bottles are well shaken and kept in the thermostat at 25°C for four hours. From preliminary trials it has been found that this duration is adequate for the equilibrium to be attained.

The solution in each bottle is analyzed for chloride and iodide concentrations by potentiometric titration with standardized silver nitrate solution. From these results equilibrium constant for the reaction (1) is determined. A typical set of results is presented in table 1. The equilibrium constants are also determined at various temperatures in the range from 20.0°C to 40.0°C to evaluate the enthalpy of the reaction. Similar studies are also carried out for the reaction (2).

Results And Discussion

The equilibrium constant under study is given by the expression

$$K = \frac{C_{R\text{-}X}\,.C_{Cl^-}}{C_{R\text{-}Cl}\,.\,C_{X^-}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (i)$$

Since it is an exchange between uni-univalent ions, the decrease in the concentration of X^- and the concentration of C_{Cl^-} of Cl^- exchanged into the solution should be the same. Experimentally these two quantities are found to be equal within the limit of ± 0.002 M.

The amount of X^- ion in milliequivalents which has exchanged into the resin, $C_{R\text{-}X}$ is calculated from the observed decrease in concentration of X^- in the solution. Now in order to know the initial amount of Cl^- present in the resin in milliequivalents per 0.500g, this can either be known from the data supplied by the manufacturer or preferably determined from the experimental data. We have relied on the experimental data and evaluated the concentration of Cl^- in resin as described below.

In equation (1) for the equilibrium constant, C_{Cl^-}, C_{X^-} and $C_{R\text{-}X}$ have been experimentally determined. If A is the initial $C_{R\text{-}Cl}$ i.e. resin capacity than $C_{R\text{-}Cl}$ at equilibrium would be ($A\text{-}C_{R\text{-}X}$).

Therefore, the equilibrium constant would be given by

$$K = \frac{C_{R\text{-}X} . C_{Cl^-}}{(A - C_{R\text{-}X})\, C_{X^-}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(ii)}$$

In this expression there are two unknowns namely, K and A. However by substituting for the values of $C_{R\text{-}X}$, C_{X^-} and C_{Cl^-} in the above expression from the experimental results of several systems studied, one obtains several simultaneous equations. By solving these simultaneous equations, one can obtain the values of K and A. It is found that the several values of A obtained in this way are in satisfactory agreement with each other. From the results, the average value of A is obtained to be 1.20 meq/0.5g of resin. This is in agreement with the value given by the manufacturer. Along with A values, several values of K are also obtained which are in satisfactory agreement among themselves. From these values, an average value of K for the reaction (1) at 25^oC is found to be 14.15 (Ref. Table 1).

Similar experimental results at various temperatures yield average values of A and K at those temperatures. It is significant that the values of A thus obtained at various temperatures are in satisfactory agreement with one another.

The average values of K at various temperatures are presented in Table 2. From these results the enthalpy for the ion exchange reaction (1) is evaluated to be 22.12 KJ Mole^{-1}.

Similar experiments are carried out for the ion exchange reaction (2). The equilibrium constant for the reaction at 25.0^oC is 2.97 and enthalpy change is 28.45 KJ Mole^{-1}.

The K values obtained by equation (i) are fairly concordant in spite of a wide variation in the initial X^- ion concentration which would have readily revealed any effect of activity coefficient on the equilibrium constant.

Therefore it appears that the activity coefficient ratios of the ions in solution as well as in resin are unity each, seems to be valid.

Several earlier investigaters[15] have preferred to express the concentration of ions in the solution in molality (m) and that in the resin in terms of mole fraction (M) for calculating the equilibrium constants. From the present experimental results when the equilibrium constants are calculated in this fashion, one obtains values which are indistinguishable from these obtained from equation (i). This also justifies that the choice of units for the concentrations in the present study is insignificant.

Table-1

Equilibrium constant for the ion exchange reaction

$R\text{-}Cl + I^-_{aq} \rightleftharpoons R\text{-}I + Cl^-_{aq}$ in Thermax A27.

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Amount of the ion exchange resin : 0.500 g

Volume of the Iodide ion solution : 50 cm^3

Temperature : 25°C

Chloride and Iodide ion concentration in the solution and in the resin at equilibrium.

System	Initial concentration of Iodide ion/M	Final concentration of Iodide ion/M C_{I^-}	Change in Iodide ion concentration / M	Concentration of Chloride ion exchanged / M C_{Cl^-}	Amount of Iodide ion exchanged in the resin meq/0.5g C_{R-I}
1	0.0095	0.00029	0.00921	0.00918	0.461
2	0.0190	0.00221	0.0168	0.01612	0.840
3	0.0285	0.0083	0.0202	0.0197	1.010
4	0.0570	0.0342	0.0228	0.0223	1.140
5	0.0765	0.0503	0.0262	0.0259	1.310

Table-2

Dependence of equilibrium constant for the reaction

$R\text{-}Cl + I^-_{aq} \rightleftharpoons R\text{-}I + Cl^-_{aq}$ on temperature

Amount of the ion exchange resin : 0.500 g

Volume of the Iodide ion solution : 50 cm^3

Temperature / °C	20.0	25.0	30.0	35.0	40.0
Equilibrium Constant K	10.2998	14.1556	15.0868	16.6319	19.5844

Slope of the plot log K versus 1/T = - 1155.44

Enthalpy of the reaction = 22.12 KJ $Mole^{-1}$

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