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NOTE

Study on Equilibrium Constant of Ion Exchange Reaction involving Cl^-/I^- Uni-Univalent Ion Exchange System in the Strongly Basic Anion Exchanger Amberlite IRA-400

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A known amount of ion exchange resin in chloride form was allowed to reach equilibrium with potassium iodide solution of five different concentrations at a specified temperature. The equilibrium concentrations of the chloride and iodide ions in the solution as well as in the resin phase are determined. From these measurements the equilibrium constant (k) and enthalpy of ion exchange reaction were calculated.

The property of ion exchange resin to exchange one type of ion with another has been of considerable utility in scientific research and industry. For a qualitative evaluation of an ion exchange resin, it is of importance to study the equilibrium for the ion exchange process. Recently many theories have been developed for equilibria between the ion exchangers and solution.[1, 2] They are in good aggreement with experimental results. Many investigators[3–5] have carried out studies on uni-univalent and uni-bivalent[6, 7] ion exchange systems, but mostly with cation exchange resin. In view of this, the present study of ion exchange equilibria in a typical strongly basic anion exchanger Amberlite IRA-400 is undertaken to study the temperature effect on ion exchange equilibrium constant (k) and also to evaluate the enthalpy of an ion exchange reaction.

(a) *Determination of exchange capacity*: About 100.0 mL of 0.25 N $NaNO_3$ at 2 mL/min was passed through a column containing 0.500 g of anion exchange resin (chloride form). The eluent was collected in 250 mL measuring flask and diluted up to the mark. 25.0 mL of diluted solution was pipetted out in a conical flask and titrated against 0.01 N standard silver nitrate solution.

$$\text{Exchange capacity (A)} = \frac{0.01 \times 10 \times \text{B.R.}}{0.500}$$

(b) *Conditioning of resin in chloride form*: The resin Amberlite IRA-400 when originally received from the manufacturer was already in the chloride form. However, in order to ensure that it was completely in this form, the resins were conditioned in a column with 10% potassium chloride solution. The resins were washed with distilled water until the washings were free from chloride ions. The resins were then air-dried and used for further study.

(c) *Equilibrium Study*: The potassium iodide solution (50.0 mL) of five different concentrations ranging from 0.009 M to 0.037 M were prepared in different stoppered bottles. Into each of the bottles 500 gm of the air-dried resins in chloride form were transferred. The bottles were stoppered, well shaken and kept in a thermostat at 30°C for 4 h, which was sufficient time for the equilibrium to be attained.

The solution in each bottle was analysed for chloride and iodide concentrations by potentiometric tritration with standard silver nitrate solution (0.1 N). From these results the equilibrium constant for the reaction was determined.

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

A typical set of result is presented in Table-1.

TABLE-1
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION
$R\text{—}Cl + I^-(aq.) \rightleftharpoons R\text{—}I + Cl^-(aq.)$ IN AMBERLITE IRA—400 at 30°C

Amount of the Ion Exchange Resin	0.500 g
Volume of the iodide ion solution	50.0 cm^3
Exchange capacity	2.18 meq/0.500 g of resin in Cl^- form

Initial conc. of iodide ion (M)	Final conc. of iodide ion (M) (C_{I^-})	Change in iodide ion conc. (M)	Conc. of chloride ion exchanged (M) (C_{Cl^-})	Amount of iodide ion exchanged in the resin (meq/0.5 g)	Equilibrium constant (k)
0.0091	0.00015	0.0089	0.0092	0.447	15.8
0.0193	0.00080	0.0185	0.0183	0.925	16.7
0.0245	0.00150	0.0230	0.0232	1.150	17.3
0.0313	0.00310	0.0282	0.0280	1.410	16.3
0.0378	0.00550	0.0323	0.0325	1.615	16.9

Average value of equilibrium constant = 16.6.

Similarly the equilibrium constants for the above system were determined at various temperatures in the range from 30° to 45°C to evaluate the enthalpy of the ion exchange reaction.

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

From the knowledge of the initial and the equilibrium concentrations of iodide ion, the decrease in the concentraion of the latter is noted. Since it is an exchange between uni-univalent ions an equal concentration of chloride ion would be now present in the solution due to exchange (Table-1). The concentration of the chloride ion is experimentally determined and is compared with decrease in the concentration of iodide ion and in all the experiments these two quantites are found to be satisfactorily equal within the limits of ±0.0002 moles per litre.

The amount of iodide ion in miliequivalents which has exchanged into the resin is calculated from the observed decrease in the concentration of iodide ion in solution. This gives $C_{R\text{—}I}$. From the knowledge of exchange capacity (A), the amount of iodide ion exchanged on the resin ($C_{R\text{—}I}$). final concentration of iodide ion (C_{I^-}) and amount of chloride ion exchanged in solution (C_{Cl^-}), the equilibrium constant is calculated by

$$k = \frac{C_{R-I} \cdot C_{Cl^-}}{(A - C_{R-I}) \cdot C_{I^-}} \qquad (2)$$

Similar values of k are obtained for different temperatues ranging from 30C to 45°C. It is observed that with rise in temperature, the ion exchange reaction rate increases thereby increasing equilibrium constant (k) to increase from 16.7 at 30°C to 26.5 at 45°C (Table-2). The graph of log k against 1/T is plotted which gives a straight line with negative slope (Fig. 1), from which enthalpy of ion exchange reaction[1] is calculated to be 19.1 kJ/mole.

TABLE-2
DEPENDENCE OF EQUILIBRIUM CONSTANT FOR THE REACTION ON TEMPERATURE $R-Cl + I^-(aq.) \rightleftharpoons R-I + Cl^-(aq.)$

Amount of ion exchange resin = 0.500 g
Volume of iodide ion in solution = 50 c.c.

Temperature °C	30.0	35.0	40.0	45.0
Equilibrium constant (k)	16.6	20.4	23.4	26.5

Slope of the plot log k versus 1/T = –1000
Enthalpy of the reaction = 19.13 kJ/mole

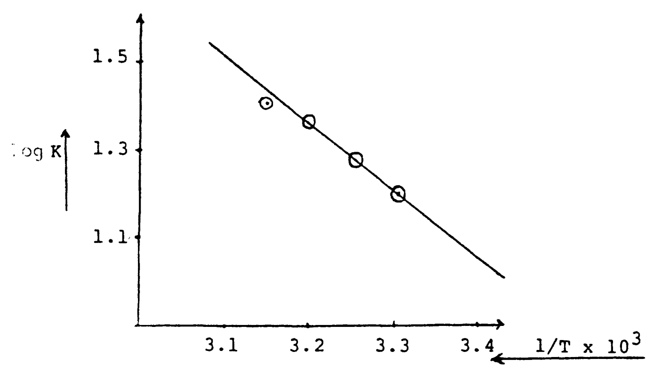

Fig. 1 Variation of equilibrium constant for the reaction $R-Cl + I^-(aq.) \rightleftharpoons R-I + Cl^-(aq.)$ with temperature

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