Asian Journal of Chemistry Vol. 11, No. 3 (1999), 758–762

Study of Equilibrium Constants of Cl^-/Br^- Ion Exchange System Using 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 bromide ion solutions of five different concentrations from 0.019 M to 0.042 M at different temperatures ranging from 30°C to 45°C. Mole fraction of bromide ion exchanged in the resin (N_{Br^-}) and mole fraction of chloride ion remained in the resin (N_{Cl^-}) were calculated from which the equilibrium constant (K′) was calculated using Bonner *et al.* equation. From the knowledge of equilibrium constants at different temperatures, enthalpy of ion exchange reaction was obtained to be 45.91 KJoules/mole.

INTRODUCTION

Ion exchange resins are an integral part of many chemical industries and the utility of an ion exchange resin depends upon its capability of exchanging one type of ion with another. Therefore for a qualitative evaluation[1] of an ion exchange resin it is of importance to study the equilibrium of the ion exchange process. This will be of considerable use not only in qualitatively 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.

Bonner and coworkers[2–6] have reported the thermodynamic equilibrium constants for several univalent, divalent, univalent-di/trivalent cation exchange systems on 4% and 8% cross linked PSS type exchangers in aqueous medium. Hoegfeldt, Ekedahl and Sillen[7–9] have considered the exchange equilibria for multivalent ions. They have derived expressions for the resin phase activity coefficients, considering both equivalent fraction and mole fraction scales for the resin phase.

In the present study an attempt has been made to calculate equilibrium constant (K′) from the knowledge of mole fraction of the bromide ion exchanged in the resin (N_{Br^-}) and mole fraction of the chloride ion (N_{Cl^-}) remaining in the resin, using Bonner *et al.*[2–6] equation (4) at different temperatures from 30°C to 45°C at different concentrations from 0.019 M to 0.042 M using fixed amount of ion exchange resin (0.500 g).

EXPERIMENTAL

(a) *Determination of exchange capacity:* About 100 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 mL of diluted solution was pipetted in a conical flask and tirated 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) *Conversion of the resin into the 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. The resins were then air dried and used for further studies.

(c) *Equilibrium Study:* The potassium bromide solutions (50 mL) of different concentrations ranging from 0.019 M to 0.042 M were prepared in different stoppered bottles. Into each of the bottles 0.500 g of the air dried ion exchange resin in chloride form was transferred. The bottles were stoppered, well shaken and kept in a thermostat at 30°C for 4 h which was sufficient time for equilibrium to be attained.

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

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

was determined. A typical set of results are presented in Table-2 and Table-3. 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 ion exchange reaction (2).

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 silver nitrate solution. The titration readings are accurate to ± 0.02 cm^3. Considering the magnitudes of the titre values the average equilibrium constants reported here have an accuracy of ± 3%.

From a knowledge of the initial, the equilibrium 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 ion is experimentally determined and is compared with the decrease in the concentration of bromide ion and in all the experiments these two quantities are found to be satisfactorily equal within the limits of ± 0.0002 moles per litre. The amount of bromide ion in milliequivalents which has exchanged into the resin, *i.e.*, $C_{R—Br}$ is calculated from the observed decrease in concentration of bromide ion in the solution. Thus knowing the value of exchange capacity (A) of the resin, $C_{R—Br}$, C_{Cl^-} and C_{Br^-} the equilibrium constant (K) is calculated by

$$K = \frac{C_{R—Br} \cdot C_{Cl^-}}{(A - C_{R—Br}) \cdot C_{Br^-}} \quad (3)$$

Thus the equilibrium constants (K) are calculated for different concentrations from 0.019 M to 0.042 M, for fixed amount of ion exchange resin (0.500 g) and for fixed temperature 30°C and average value of K is calculated. Some experimental sets are carried out for different higher temperatures up to 45°C. It is observed that with increase in temperature, the rate of ion exchange reaction increases resulting in higher values of K; thus for 30.0°C the value of K is 1.16 which increases to 2.95 at 45°C (Table-1). From the graph of log K against 1/T (Fig. 1), enthalpy of the ion exchange reaction is calculated to be 45.91 KJoules/mole.

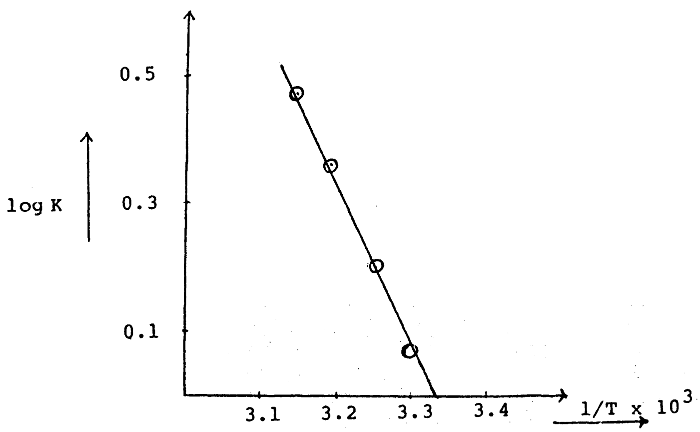

Fig. 1 Variation of equilibrium constant for the reaction $R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$ with temperature

TABLE-1
DEPENDENCE OF EQUILIBRIUM CONSTANT FOR THE REACTION $R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$ ON TEMPERATURE

Temperature (°C)	30	35	40	45
Equilibrium Constant (K)	1.16	1.59	2.25	2.95

Slope of the plot log K *vs.* 1/T = –2400
Enthalpy of the ion exchange reaction = 45.91 KJoules/mole

Earlier investigators of similar systems had expressed the concentration of ions in the solution in terms of molality and the concentration of ions in the resin in terms of mole fraction. In view of the above, the experimental results obtained in the present study have been substituted in the following equation by Bonner *et al.*[2–6], and the equilibrium constants are calculated.

$$K' = \frac{[N_{Br^-}][m_{Cl^-}]}{[N_{Cl^-}][m_{Br^-}]} \quad (4)$$

where N_{Br^-} = mole fraction of bromide ion in the resin

N_{Cl^-} = mole fraction of chloride ion in the resin

m_{Cl^-} = molality of chloride ion in the solution

m_{Br^-} = molality of bromide ion in the solution

Since in the present study the solutions used are dilute, the molality and the molarity of the ions in the solution are almost the same with negligible error. Therefore the molality of the ions can be easily replaced by molarity. The equilibrium constant (K) values calculated by equation (3) are in good agreement with K′ values obtained by Bonner *et al.* equation (4). This justifies that the choice of units for the concentrations in the present study is insignificant.

TABLE-2
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION
$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$
IN AMBERLITE IRA-400 CALCULATED BY EQUATION (3)

Amount of ion exchange resin = 0.500 g
Volume of the bromide ion solution = 50 cc
Exchange capacity = 2.18 meg/0.5 g of resin in chloride form
Temperature = 40°C

Initial conc. of bromide ion (M)	Final conc. of bromide ion (M) C_{Br^-}	Change in bromide ion conc. (M)	Conc. of chloride ion exchanged (M) C_{Cl^-}	Amount of bromide ion exchanged in the resin meq./0.5 g $C_{R—Br}$	Equilibrium constant (K)
0.0192	0.0037	0.0155	0.0153	0.775	2.28
0.0293	0.0085	0.0208	0.0210	1.040	2.23
0.0323	0.0102	0.0221	0.0233	1.105	2.25
0.0378	0.0136	0.0242	0.0245	1.210	2.23
0.0425	0.0166	0.0259	0.0258	1.295	2.27

Average value of K = 2.25

TABLE-3
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION
$R{-}Cl + Br^-(aq.) \rightleftharpoons R{-}Br + Cl^-(aq.)$
IN AMBERLITE IRA-400 CALCULATED BY EQUATION (4)

Amount of ion exchange resin = 0.500 g
Volume of the bromide ion solution = 50 cc
Exchange capacity = 2.18 meg./0.5g of resin in chloride form
Temperature = 40°C

Initial conc. of bromide ion (M)	Final conc. of bromide ion m_{Br}	Conc. of chloride ion exchanged in solution m_{Cl^-}	Mole fraction of the bromide ion exchanged in the N_{Br^-} resin	Mole fraction of chloride ion remained in the resin N_{Cl^-}	Equilibrium constant (K′)
0.0192	0.0037	0.0153	0.355	0.644	2.28
0.0293	0.0085	0.0210	0.477	0.523	2.25
0.0323	0.0102	0.0223	0.507	0.493	2.25
0.0378	0.0136	0.0245	0.555	0.445	2.25
0.0425	0.0166	0.0258	0.594	0.406	2.27

Average value of K′ = 2.26

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(*Received*: 17 November 1998; *Accepted*: 20 February 1999) AJC-1695