Asian Journal of Chemistry Vol. 13, No. 1 (2001), 8–12

Study on Variation of Equilibrium Constants as a Function of Ionic Size in Some Uni-Univalent Ion Exchange Systems

R.S. LOKHANDE* and P.U. SINGARE
Department of Chemistry, University of Mumbai
Vidyanagari, Santacruz, Mumbai-400 098, India

Ion exchangers in chloride form were equilibriated with potassium iodide and potassium bromide solutions of different concentrations and at different temperatures from 30–45°C. The equilibrium constant (K) values for both exchange reaction were observed to increase with increase in temperature. However the equilibrium constant (K) for Cl^-/Br^- exchange at 30°C was 1.16 which was less than 16.70 for Cl^-/I^- exchange at the same temperature which was due to difference in ionic size of iodide (2.20 Å) and bromide (1.96 Å) ion exchanged.

INTRODUCTION

Various attempts have been made to describe and predict quantitatively the ion exchange equilibria[1–3]. More rigorous calculations were made by including the activity coefficients of the counter ions in solution and resin phases to compute the thermodynamic equilibrium constant[4–14]. While extensive studies on ion exchange equilibrium involving uni-univalent cations have been made[1,2,15] using different types of resins,[16–20] very few attempts have been made to study uni-univalent anion exchange equilibria[21–24].

The present study explains the variation of equilibrium constant (K) for Cl^-/I^- and Cl^-/Br^- ion exchange systems using ion exchange resin Amberlite IRA-400 a strongly basic anion exchanger.

EXPERIMENTAL

A known weight (0.5 g) of ion exchange resins in chloride form were equilibriated with potassium iodide solution of five different concentrations ranging from 0.099 M to 0.037 M in five different stoppered reagent bottles at constant temperature of 30°C (±0.1°C) for 4 h. From the kinetic study[25] using the same ion exchange resin, it has been observed that this duration was adequate for equilibrium to be attained. After 4 h the solution in each bottle was analysed for the chloride and iodide ion concentration potentiometrically with standard silver nitrate solution. From this results the equilibrium constant (K) for the ion exchange reaction

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

was determined. The equilibrium constants for the above system are thus determined at various temperatures ranging from 30–45°C.

Similarly by using potassium bromide solution of five different concentrations from 0.019 M to 0.042 M, the equilibrium constants (K) for the ion exchange reaction

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.) \quad (2)$$

are determined in the same temperature range.

The exchange capacity[26] was experimentally determined by using 0.25 N $NaNO_3$ solution.

RESULTS AND DISCUSSION

In the study of uni-univalent ion exchange equilibria (eqns. 1 and 2), from a knowledge of the initial and equilibrium concentrations of Br^- and I^- in solution, the decrease in the concentration of the latter was noted. Since it was an exchange between uni-univalent ions an equal concentration of Cl^- would be now present in the solution due to the exchange. The concentration of the Cl^- was experimentally determined and was compared with the decrese in the concentration of Br^- and I^- in solution and in all the experiments these two quantities are found to be satisfactorily equal within the limits of ±0.0002 moles per litre (Table-1, 3). The amount of Br^- and I^- ion in milliequivalents which has exchanged on to the resin was calculated from the observed decrease in concentration of Br^- and I^- ions in solution. This gives $C_{R—Br}$ and $C_{R—I}$.

TABLE-1
EQUILIBRIUM CONCENTRATION OF CHLORIDE AND IODIDE ION IN THE SOLUTION AND IN THE RESIN PHASE FOR THE ION EXCHANGE REACTION

$$R—Cl + I^-(aq.) \rightleftharpoons R—I + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of iodide ion solution = 50 mL
Temperature = 35°C
Exchange capacity = 2.18 meq/0.5 g of resin

Systems	Initial conc. of iodine ion (M)	Final conc. 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/0.5 g $C_{R—I}$
1	0.0094	0.00013	0.00927	0.0094	0.4630
2	0.0197	0.00070	0.01900	0.0192	0.9500
3	0.0244	0.00130	0.02310	0.0234	1.1550
4	0.0310	0.00250	0.02850	0.0283	1.4250
5	0.0371	0.00470	0.03240	0.0326	1.6200

The equation for the equilibrium constant would be given by

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

for experimental determined exchange capacity 'A'; the C_{R-Cl} at equilibrium would be $(A-C_{R-X})$. Therefore the modified equation for the equilibrium constant would be given by

$$K = \frac{C_{R-X} \cdot C_{Cl^-}}{A-C_{R-X} \cdot C_{X^-}} \quad (4)$$

where X represents the exchangeable Br^-/I^- ions.

A typical experimental results at 35°C to calculate the equilibrium constant (using eq. 4) are shown in Tables-1–4.

TABLE-2
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION

$$R-Cl + I^-(aq.) \rightleftharpoons R-I + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of iodide ion solution = 50 mL
Temperature = 35°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

Systems	1	2	3	4	5
Equilibrium Constant (K)	19.5	20.9	20.3	21.2	20.3

Average value of K = 20.5

TABLE-3
EQUILIBRIUM CONCENTRATION OF CHLORIDE AND BROMIDE ION IN THE SOLUTION AND IN THE RESIN PHASE FOR THE ION EXCHANGE REACTION

$$R-Cl + Br^-(aq.) \rightleftharpoons R-Br + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of bromide ion solution = 50 mL
Temperature = 35°C
Exchange capacity = 2.18 meq/0.5 g of resin

Systems	Initial conc. of bromide ion (M)	Final conc. of bromide ion (M) C_{Br^-}	Change in bromide ion concentration (M)	Concentration of chloride ion exchanged (M) C_{Cl^-}	Amount of bromide ion exchanged in the resin meq/0.5 g C_{R-Br}
1	0.0194	0.0049	0.0145	0.0148	0.725
2	0.0296	0.0102	0.0194	0.0196	0.970
3	0.0323	0.0118	0.0205	0.0206	1.025
4	0.0371	0.0148	0.0223	0.0224	1.115
5	0.0422	0.0177	0.0245	0.0243	1.225

TABLE-4
EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of bromide ion solution = 50 mL
Temperature = 35°C
Exchange capacity (A) = 2.18 meq/0.5 g of resin

Systems	1	2	3	4	5
Equilibrium constant (K)	1.50	1.53	1.55	1.57	1.76

Average value of K = 1.58

Bonner and Pruett[27] studies the temperature effect on uni-univalent exchanges involving some divalent ions. In all divalent exchanges the equilibrium constant decreases with increasing temperature resulting in exothermic reactions. However, in the present investigation, the equilibrium constant (K) increases with increase in temperature (Table 5 and 6) indicating the endothermic ion exchange reaction with enthalpy values of 45.91 kJ/mole for Cl^-/Br^- exchange and 19.13 kJ/mole for Cl^-/I^- exchange, details regarding the calculations of enthalpy are given in our previous papers[28–31].

TABLE-5
VARIATION OF EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT DIFFERENT TEMPERATURE

$$R—Cl + I^-(aq.) \rightleftharpoons R—I + Cl^-(aq.)$$

Amount of ion exchange resin = 0.5 g
Volume of iodide ion solution = 50 mL

Temperature (°C)	30	35	40	45
Equilibrium constant (K)	16.7	20.5	23.6	26.5

Enthalpy of ion exchange reaction = 19.13 kJ/mole

TABLE-6
VARIATION OF EQUILIBRIUM CONSTANT FOR THE ION EXCHANGE REACTION AT DIFFERENT TEMPERATURE

$$R—Cl + Br^-(aq.) \rightleftharpoons R—Br + Cl^-(aq.)$$

Temperature (°C)	30	35	40	45
Equilibrium constant (K)	1.16	1.58	2.25	2.95

Enthalpy of ion exchange reaction = 45.91 kJ/mole

Since the need of solvation of crystallographically smaller Cl^- ion (1.84 Å) is stronger[32], it will preferentially go in to the dilute solution phase forcing relatively larger I^- ion (2.20 Å)[33] and Br^- ion (1.96 Å)[33] in the more poorly solvated concentrated exchanger phase (represented by eqns. 1 and 2). Also the relative selectivity34 of strongly basic polystyrene resin with about 8% DVB for Br^- ion is 2.80 and for I^- ion is 8.70, thereby giving higher value of K for Cl^-/I^- exchange as compared to that of Cl^-/Br^- exchange (Tables 5 and 6).

REFERENCES

1. F. Helffrich, Ion Exchange, McGraw-Hill, New York (1962).
2. Y. Marcus and A.S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Interscience, London (1969).
3. K. Dorfner (Ed.), Ion Exchanger, Walter de Gruyter, Berlin (1991).
4. E. Glueckauf, *Proc. Roy. Soc. (London)*, **A214,** 207 (1952).
5. J.F. Duncan, *Proc. Roy. Soc. (London)*, **A214,** 344 (1952).
6. J. Kielland, *J. Soc. Chem. Ind. (London)*, **54,** 232T (1935).
7. A.P. Vanselow, *J. Am. Chem. Soc.*, **54,** 1307 (1932).
8. G.E. Boyd and G.E. Myers, *J. Phys. Chem.*, **60,** 521 (1956).
9. W.J. Argersinger and A.W. Davidson, *J. Phys. Chem.*, **56,** 92 (1952).
10. E. Ekedahl, E. Hogfeldt and L.G. Sillen, *Acta Chem. Scand.*, **4,** 556 (1950).
11. E. Hogfeldt, *Arkiv. Kemi.*, **5,** 147 (1952).
12. G.L. Gaines (Jr.) and H.C. Thomas, *J. Chem. Phys.*, **21,** 714 (1953).
13. W.J. Argersinger (Jr.), A.W. Davidson and O.D. Bonner, *Trans. Kansas. Acad. Sci.*, **53,** 404 (1950).
14. A.W. Davidson and W.J. Arjersinger (Jr.), *Ann. N.Y. Acad. Sci.*, **57,** 105 (1953).
15. O.D. Bonner, *J. Phys. Chem.*, **58,** 318 (1954).
16. O.D. Bonner and W.H. Payne, *J. Phys. Chem.*, **58,** 183 (1954).
17. O.D. Bonner, *J. Phys. Chem.*, **59,** 719 (1955).
18. S. Lindenbaum, C.F. Jumper and G.E. Boyd, *J. Phys. Chem.*, **63,** 1924 (1959).
19. G.E. Boyd, F. Vaslow and S. Lindenbaum, *J. Phys. Chem.*, **68,** 590 (1964).
20. A. Schwarz and G.E. Boud, *J. Phys. Chem.*, **69,** 4208 (1965).
21. K.A. Kraus, R.J. Raridon and D.L. Holcomb, *Chromatogr. J.*, **3,** 178 (1960).
22. K.A. Kraus and R.J. Raridon, *J. Phys. Chem.*, **63,** 1901 (1959).
23. R.S. Lokhande and P.U. Singare, *Asian J. Chem.*, **10,** 898 (1998).
24. ———, *Oriental J. Chem.*, **14,** 247 (1998).
25. ———, *Asian J. Chem.*, **10,** 364, 630, 890, 894 (1998).
26. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's Textbook of Quantitiative Chemical Analysis, 5th Edn., p. 208 (1989).
27. O.D. Bonner and R.R. Pruett, *J. Phys. Chem.*, **63,** 1420 (1959).
28. R.S. Lokhande and P.U. Singare, *Asian J. Chem.*, **10,** 1026 (1998).
29. ———, *Oriental J. Chem.*, **14,** 303 (1998).
30. ———, *J. Chem. Env. Research*, **7,** 129 (1998).
31. ———, *Asian J. Chem.*, **11,** 758 (1999).
32. R.M. Diamond and D.C. Whitney, Ion Exchange, Vol. 1, Chapter 8, Marcel-Dekker (1996).
33. J.D. Lee, Concise Inorganic Chemistry, 5th Edn., Chapman and Hall Ltd. (1966).
34. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th Edn., p. 191 (1989).

(*Received:* 25 March 2000; *Accepted:* 3 August 2000) AJC-2121