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THERMODYNAMICS OF ION EXCHANGE EQUILIBRIUM FOR SOME UNI-UNIVALENT AND DIVALENT REACTION SYSTEMS USING STRONGLY BASIC ANION EXCHANGE RESIN INDION FF-IP

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ABSTRACT. The study on thermodynamics of ion exchange equilibrium for uni-univalent Cl^-/I^-, Cl^-/Br^-, and uni-divalent Cl^-/SO_4^{2-}, $Cl^-/C_2O_4^{2-}$ reaction systems was carried out using ion exchange resin Indion FF-IP. The equilibrium constant K was calculated by taking into account the activity coefficient of ions both in solution as well as in the resin phase. For uni-univalent ion exchange reaction systems, the equilibrium constant K' were also calculated by considering mole fraction of ions in the resin phase. The K values calculated for uni-univalent and uni-divalent anion exchange reaction systems were observed to increase with rise in temperature, indicating the endothermic exchange reactions having enthalpy values of 22.45, 28.57, 17.84, 15.97 kJ/mol, respectively.

KEY WORDS: Ion exchange equilibrium, Equilibrium constant in standard state, Apparent equilibrium constant, Enthalpy, Endothermic reaction

INTRODUCTION

Extensive work was done by previous researchers to study the properties of the ion exchange resins [1-3], to generate thermodynamic data [4-7] related to various uni-univalent and heterovalent ion exchange systems. Recently theories explaining ion exchange equilibrium [8] between the resin phase and solution was also developed. A number of researchers carried out equilibrium studies [9-30], extending over a wide range of composition of solution and resin phase. Attempts were also made to study the temperature effect on cation exchange systems for computing the thermodynamic equilibrium constants [9-23]. However very little work was carried out to study the equilibrium of anion exchange systems [12] and [24-30]. Therefore in the present investigation attempts were made to study the temperature effect on uni-univalent and uni-divalent anion exchange reaction equilibrium, the result of which will be of considerable use in qualitatively assessing an ion exchange resin for its utility in a stipulated exchange process.

EXPERIMENTAL

Conditioning of ion exchange resin

The ion exchange resin Indion FF-IP as supplied by the manufacturer was a strongly basic quaternary ammonium $-N-(CH_3)_3{}^+$ anion exchanger in chloride form containing 8 % S-DVB of 20-50 mesh size. For present investigation, the resin grains of 30-40 mesh size were used. The resin was conditioned and air dried by usual methods [33, 34].

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Method

Study of uni-univalent ion exchange equilibrium. Ion exchange resin (0.500 g) in chloride form was equilibrated with iodide/bromide ion solution of different concentrations in a temperature range of 30.0 ^{0}C to 45.0 ^{0}C for 4 h. From the results of kinetics study reported earlier [31, 32]; it was observed that this duration was adequate to attain the ion exchange equilibrium. After 4 h the different iodide ion solutions in equilibrium with ion exchange resins in chloride form were analysed for their chloride and iodide/bromide ion concentrations by potentiometric titration with standard silver nitrate solution. From the results the equilibrium constant K for the following reactions was calculated.

$$\text{R-Cl} + \text{I}^-_{(aq)} \leftrightarrows \text{R-I} + \text{Cl}^-_{(aq)} \qquad (1)$$

$$\text{R-Cl} + \text{Br}^-_{(aq)} \leftrightarrows \text{R- Br} + \text{Cl}^-_{(aq)} \qquad (2)$$

Similar study was carried out by equilibrating 0.500 g of ion exchange resins in chloride form with sulfate and oxalate ion solution of known different initial concentrations, in the temperature range of 30.0 ^{0}C to 45.0 ^{0}C to calculate the apparent equilibrium constant K_{app} for the Cl^-/SO_4^{2-} and $Cl^-/C_2O_4^{2-}$ systems. The ion exchange reactions can be represented as

$$2\text{R-Cl} + SO_4^{2-}{}_{(aq)} \leftrightarrows R_2SO_4 + 2Cl^-_{(aq)} \qquad (3)$$

$$2\text{R-Cl} + C_2O_4^{2-}{}_{(aq)} \leftrightarrows R_2C_2O_4 + 2Cl^-_{(aq)} \qquad (4)$$

The iodide, bromide, sulfate and oxalate ion solutions used in the entire experimental work, were prepared by dissolving their corresponding potassium salts (Analytical grade) in distilled deionised water. In the present study, a semi-micro burette having an accuracy of 0.02 mL was used in the titrations against silver nitrate solution. The titration readings were accurate to ± 0.02 mL. Considering the magnitude of the titer values, the average equilibrium constants reported in the experiment are accurate to ± 3 %.

RESULTS AND DISCUSSION

The equilibrium constants for the uni-univalent ion exchange reactions (1 and 2) would be given by the expression

$$K = \frac{C_{RX} \cdot C_{Cl^-}}{(A - C_{RX}) \cdot C_{X^-}} \qquad (5)$$

where A is the ion exchange capacity of the resin, x^- represents I^- or Br^- ions.

For different concentrations of x^- ions in solution at a given temperature, K values were calculated from which average value of K for that set of experiment was calculated (Table 1 and Table 3). The enthalpy value for the ion exchange reactions 1 and 2 were calculated by plotting the graph of log K against 1/T (Figure 1). Earlier researchers [20] have expressed the concentration of ions in the solution in terms of molality and concentration of ions in resin in terms of mole fraction. In view of above, the experimental results obtained in the present study have been substituted in the following equation by Bonner *et al.* [13, 17] and the equilibrium constant K’ was calculated (Table 2 and Table 4).

$$K' = \frac{[N_{X}^{-}]\,[m_{Cl}^{-}]}{[N_{Cl}^{-}]\,[m_{x}^{-}]} \tag{6}$$

where N_X^- = mole fraction of I^- or Br^- ions exchanged on the resin, m_{Cl}^- = molality of Cl^- ions exchanged in the solution, N_{Cl}^- = mole fraction of Cl^- ions remained on the resin, and m_x^- = molality of I^- or Br^- ions remained in the solution at equilibrium.

Similar values of K and K' were calculated for both Cl^-/I^- and Cl^-/Br^- systems at different temperatures (Table 5).

The equilibrium constants for the uni-divalent ion exchange reactions (3 and 4) were calculated similarly as reported earlier [34]. The results of such calculations are presented in the Tables 6 and 7. The enthalpy for ion exchange reactions 3 and 4 was obtained by plotting a graph of log K_{std} against 1/T (Figure 2).

Table 1. Equilibrium constant (K) for the ion exchange reaction: $R\text{-}Cl + I^-_{aq} \leftrightarrows R\text{-}I + Cl^-_{aq}$ in Indion FF-IP.

System	C^0 (M)	C (M)	C^0- C (M)	C_{Cl}^- (M)	C_{R-I} meq./0.5 g	K
1	0.0206	0.0031	0.0175	0.0173	0.875	12.36
2	0.0346	0.0124	0.0222	0.0221	1.110	12.36
3	0.0425	0.0193	0.0232	0.0231	1.160	12.62
4	0.0598	0.0357	0.0241	0.0238	1.205	12.36
5	0.0668	0.0425	0.0243	0.0242	1.215	12.58

Amount of the ion exchange resin in chloride form = 0.500 g, ion exchange capacity = 1.27 meq./0.5 g, volume of iodide ion solution = 50.0 mL, temperature = 30.0 ^{0}C. C^0 and C are the initial and final concentration of iodide ions in solution, C_{cl}^- is the concentration of chloride ions exchanged in solution, C_{R-I} is the amount of iodide ions exchanged on the resin. Average equilibrium constant (K) = 12.46.

Table 2. Equilibrium constant (K') calculated by Bonner *et al.* [13, 17] equation for the ion exchange reaction: $R\text{-}Cl + I^-_{aq} \leftrightarrows R\text{-}I + Cl^-_{aq}$ in Indion FF-IP.

C^0 (M)	C (M)	C^0 – C (M)	m_{cl}^- (M)	C_{RI}	C_{R-Cl}	N_I^-	N_{Cl}^-	K'
0.0206	0.0031	0.0175	0.0173	0.875	0.395	0.689	0.311	12.36
0.0346	0.0124	0.0222	0.0221	1.110	0.160	0.874	0.126	12.36
0.0425	0.0193	0.0232	0.0231	1.160	0.110	0.913	0.087	12.62
0.0598	0.0357	0.0241	0.0238	1.205	0.065	0.949	0.051	12.36
0.0668	0.0425	0.0243	0.0242	1.215	0.055	0.957	0.043	12.58

See the footnote of Table 1. C^0 and C are the initial and final concentration of iodide ions, m_{Cl}^- is the concentration of chloride ions exchanged in solution, C_{R-I} is the amount of iodide ions exchanged on the resin, C_{R-Cl} is the amount of chloride ions remained on the resin, N_I^- is the mole fraction of iodide ions exchanged on the resin, N_{Cl}^- is the mole fraction of chloride ions remained on the resin. Average equilibrium constant (K') = 12.46.

Table 3. Equilibrium constant (K) for the ion exchange reaction $R\text{-}Cl + Br^-_{aq} \leftrightarrows R\text{-}Br + Cl^-_{aq}$ in Indion FF-IP.

System	C^0 (M)	C (M)	C^0 – C (M)	C_{Cl}^- (M)	C_{R-Br} meq./0.500 g	K
1	0.0150	0.0035	0.0115	0.0110	0.575	2.94
2	0.0220	0.0075	0.0145	0.0145	0.725	3.01
3	0.0295	0.0128	0.0167	0.0167	0.835	3.07
4	0.0359	0.0179	0.0180	0.0176	0.900	3.05
5	0.0420	0.0232	0.0188	0.0187	0.940	3.03

Amount of the ion exchange resin in chloride form = 0.500 g, ion exchange capacity = 1.19 meq./0.5 g, volume of bromide ion solution = 50.0 mL, temperature = 30.0 ^{0}C. C^0 and C are the initial and final concentration of bromide ions in solution, C_{cl}^- is the concentration of chloride ions exchanged in the solution, C_{R-Br} is the amount of bromide ions exchanged on the resin. Average equilibrium constant (K) = 3.02.

Table 4. Equilibrium constant (K') calculated by Bonner *et al.* [13, 17] equation for the ion exchange

reaction: R-Cl + Br^-_{aq} ⇆ R-Br + Cl^-_{aq} in Indion FF-IP.

C^0 (M)	C (M)	C^0- C (M)	m_{Cl}^- (M)	$C_{R\text{-}Br}$	$C_{R\text{-}Cl}$	N_{Br}^-	N_{Cl}^-	K'
0.0150	0.0035	0.0115	0.0110	0.575	0.615	0.483	0.517	2.94
0.0220	0.0075	0.0145	0.0145	0.725	0.465	0.609	0.391	3.01
0.0295	0.0128	0.0167	0.0167	0.835	0.355	0.702	0.298	3.07
0.0359	0.0179	0.0180	0.0176	0.900	0.290	0.756	0.244	3.05
0.0420	0.0232	0.0188	0.0187	0.940	0.250	0.790	0.210	3.03

See the footnote of Table 3. C^0 and C are the initial and final concentration of bromide ions in solution, m_{Cl}^- is the concentration of chloride ions exchanged in solution, $C_{R\text{-}Br}$ is the amount of bromide ions exchanged on the resin, $C_{R\text{-}Cl}$ is the amount of chloride ions remained on the resin, N_{Br}^- is the mole fraction of bromide ions exchanged on the resin, N_{Cl}^- is the mole fraction of chloride ions remained on the resin. Average equilibrium constant (K') = 3.02.

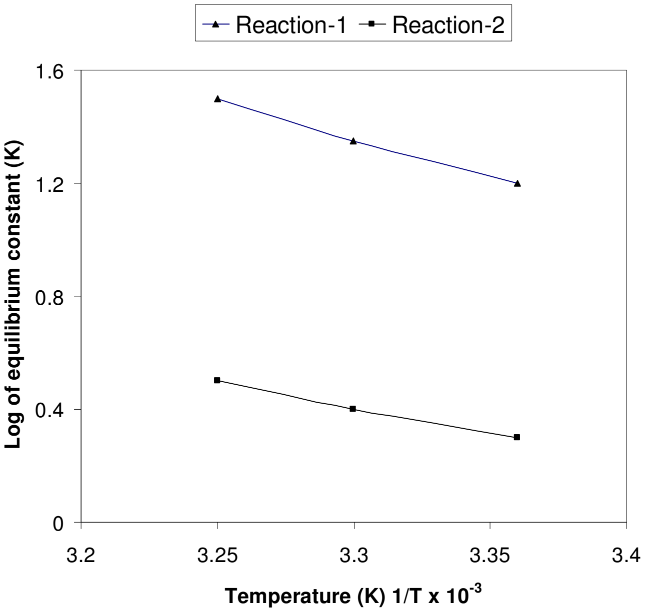

Figure 1. Effect of temperature on equilibrium constant (K) for uni-univalent ion exchange reaction systems using Indion FF-IP resins. (Amount of ion exchange resin in chloride form = 0.500 g, temperature range = 30.0 °C to 45.0 °C).

Table 5. Effect of temperature on equilibrium constant for uni-univalent ion exchange reactions in Indion FF-IP.

Temperature °C	Equilibrium constant for the ion			
	Reaction (1)		Reaction (2)	
	K	K'	K	K'
30.0	12.46	12.46	3.02	3.02
35.0	16.02	16.02	4.14	4.14
40.0	18.34	18.34	5.00	5.00
45.0	20.98	20.98	5.80	5.80
Enthalpy (kJ/mol)	22.45		28.57	

Table 6. Equilibrium constants for the uni-divalent ion exchange reaction

$2R\text{-}Cl + SO_4^{2-}{}_{aq} \leftrightarrows R_2SO_4 + 2Cl^-{}_{aq}$ in Indion FF-IP.

$C^0_{SO4}2-$ (M)	C_{cl}^- (M)	C_{SO4}^{2-} (M)	$C_{R\text{-}Cl}$	C_{R2SO4}	K_{app}	$K_{std.}/K_{app} = (\gamma_{R2SO4})/(\gamma_{RCl})^2$
0.007	0.0076	0.0022	0.54	0.380	34.1	1.06
0.008	0.0078	0.0026	0.52	0.390	32.3	1.12
0.009	0.0081	0.0035	0.49	0.405	28.4	1.27
0.010	0.0083	0.0042	0.47	0.415	26.5	1.36
0.015	0.0091	0.0085	0.39	0.455	23.7	1.53
0.020	0.0096	0.0118	0.34	0.486	20.8	1.74
0.030	0.0099	0.0152	0.31	0.495	19.3	1.88
0.050	0.0102	0.0348	0.28	0.510	9.6	3.78

Amount of the ion exchange resin in chloride form = 0.500 g, volume of the sulfate ion solution = 100 mL, temperature = 30.0 ^{0}C. $C^0{}_{SO4}{}^{2-}$ is the initial concentration of SO_4^{2-} ions in solution; C_{Cl}^- and C_{SO4}^{2-} are the equilibrium concentration of ions in solution; $C_{R\text{-}Cl}$ and C_{R2SO4} are the amount of ions on the resin in meq./0.500 g; K_{app} is the apparent equilibrium constant. The equilibrium constant in standard state (K_{std}) = 36.3.

Table 7. Equilibrium constant (K_{std}) for the uni-divalent ion exchange reaction
$2R\text{-}Cl + C_2O_4^{2-}{}_{aq} \leftrightarrows R_2C_2O_4 + 2Cl^-{}_{aq}$ in Indion FF-IP.

$C^0_{C2O4}{}^{2-}$ (M)	C_{Cl}^-	C_{C2O4}^{2-}	C_{RCl}	C_{R2C2O4}	K_{app}	$K_{std.}/K_{app} = (\gamma_{R2C2O4})/(\gamma_{RCl})^2$
0.007	0.0076	0.0025	0.54	0.380	29.8	1.10
0.008	0.0078	0.0030	0.52	0.390	27.7	1.19
0.009	0.0081	0.0038	0.49	0.405	25.9	1.27
0.010	0.0088	0.0092	0.42	0.440	18.4	1.79
0.015	0.0092	0.0140	0.38	0.460	12.3	2.68
0.020	0.0094	0.0210	0.36	0.470	10.1	3.26
0.030	0.0097	0.0260	0.33	0.480	8.3	3.97
0.050	0.0100	0.0350	0.30	0.500	7.2	4.58

Amount of the ion exchange resin in chloride form = 0.500 g, Volume of the oxalate ion solution = 100 mL, Temperature = 30.0 ^{0}C. $C^0{}_{C2O4}2-$ is the initial concentration of $C_2O_4^{2-}$ ions in solution; C_{cl}^- and $C_{C2O4}2-$ are the equilibrium concentration of ions in solution; $C_{R\text{-}Cl}$ and C_{R2C2O4} are the amount of ions on the resin in meq./0.500 g; K_{app} is the apparent equilibrium constant. The equilibrium constant in standard state (K_{std}) = 33.0.

Table 8. Effect of temperature on equilibrium constant in standard state (K_{std}) for uni-divalent ion exchange reactions in Indion FF-IP.

Temperature ^{O}C	Equilibrium constant (K_{std})	
	Reaction (3)	Reaction (4)
30.0	36.3	33.0
35.0	40.0	36.3
40.0	45.0	40.0
45.0	52.5	45.5
Enthalpy (kJ/mol)	17.8	16.0

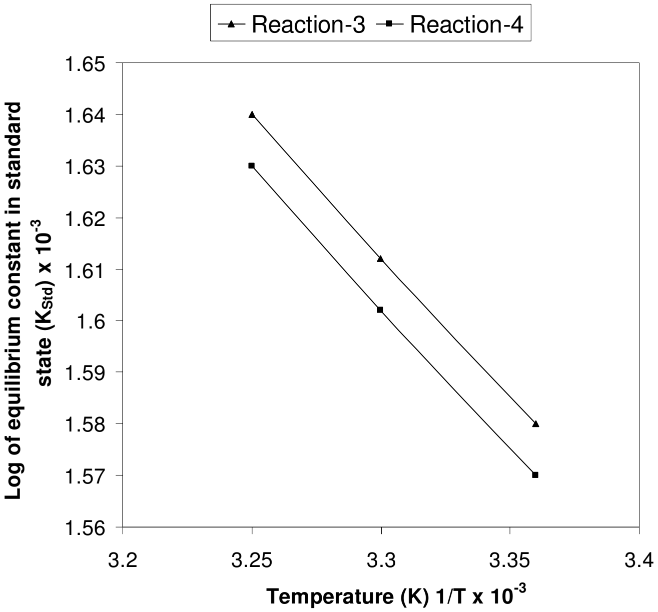

Figure 2. Effect of temperature on equilibrium constant in standard state (K_{std}) for uni-divalent ion exchange reaction systems using Indion FF-IP resins. (Amount of ion exchange resin in chloride form = 0.500 g, temperature range = 30.0 ^{0}C to 45.0 ^{0}C).

CONCLUSIONS

Bonner and Pruett [13] studied the temperature effect on uni-univalent exchanges involving some divalent ions. In all divalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. However in the present investigation, for both the uni-univalent and uni-divalent exchange reactions the value of equilibrium constant increases with rise in temperature giving positive enthalpy value (Tables 5, 8), indicating the endothermic ion exchange reactions. Hatsis *et al.* [29] in their study of the temperature dependence of retention of a wide range of inorganic anions, observed that temperature was ineffective at changing the selectivity of anions like sulphate and oxalate. They also observed that bromide ions were weakly retained indicating less selectivity while iodide ions were strongly retained indicating high selectivity. The results in the present investigation also indicates that the K values of Cl^-/SO_4^{2-}, and $Cl^-/C_2O_4^{2-}$ exchange are nearly same indicating their identical selectivity. Also the higher K values for Cl^-/I^- exchange as compared to that for Cl^-/Br^- exchange indicates that the selectivity of resin for iodide ion is more as compared to that for bromide ions.

Efforts to develop new ion exchangers for specific applications are continuing. In spite of their advanced stage of development, various aspects of ion exchange technologies have been continuously studied to improve the efficiency and economy in various technical applications. The selection of an appropriate ion exchange material is possible on the basis of information provided by the manufacturer. However, it is expected that the data obtained from the actual experimental trials will prove to be more helpful. Generally the selected ion exchange materials must be compatible with type of ionic species present as well as the operating parameters notably temperature. The thermodynamic data obtained in the present experimental work will decide the operational process parameters in order to bring about the efficient application of the ion exchange resins. The experimental technique used will be useful to understand the selectivity behaviour of ion exchange resins for various ions (of different ionic size and charge) in solution thereby helping in characterization of resins.

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