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Study of H^+/ Mg^{2+} and H^+ / Ca^{2+} ion exchange reaction systems using cation exchange resin amberlite IR-120

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ABSTRACT

The study on thermodynamics of ion exchange equilibrium for uni-bivalent H^+ / Mg^{2+} and H^+ / Ca^{2+} reaction systems was carried out using ion exchange resin Amberlite IR-120.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. The *K* values calculated for H^+/Mg^{2+} and H^+/Ca^{2+}reaction systems were observed to increase with rise in temperature, indicating the endothermic exchange reactions having enthalpy values of 38.8 and 20.6 kJ /mol respectively.

Key words: Ion exchange equilibrium, Equilibrium constant, Enthalpy, Endothermic reactions, Amberlite IR-120.

INTRODUCTION

Extensive work was done by previous researchers to study the properties of the ion exchange resins, to generate thermodynamic data related to various uni-univalent and heterovalent ion exchange systems[1-7]. Recently theories explaining ion exchange equilibrium between the resin phase and solution was also developed[8]. A number of researchers carried out equilibrium studies, extending over a wide range of composition of solution and resin phase[9-31]. Attempts were also made to study the temperature effect on anion exchange systems[12,24-33] for computing the thermodynamic equilibrium constants. However very little work was carried out to study the equilibrium of cation exchange systems[9-23]. Therefore in the present investigation attempts were made to study the thermodynamics of uni-bivalent cation exchange equilibrium, the results of which will be of considerable use in explaining the selectivity of ion exchanger for various bivalent ions in solution.

EXPERIMENTAL

The ion exchange resin Amberlite IR-120 as supplied by the manufacturer (Rohm and Hass Co.,USA) was a strongly acidic cation exchange resins in H^+ form containing 8% S-DVB of 16-50 mesh size. For present investigation, the resin grains of 30-40 mesh size were used. The conditioning of the resins was done by usual methods [25-28].

Ion exchange resins in H^+ form weighing 0.500g was equilibrated with Mg^{2+} ion solution of different concentrations at a constant temperature of 30.0 ° C for 4 h. From the results of kinetics study reported earlier[34-45] ; it was observed that this duration was adequate to attain the ion exchange equilibrium. After 4 h the different Mg^{2+} ion solutions in equilibrium with ion exchange resins were analyzed for their H^+ ion concentration by

potentiometric titration with standard 0.1N NaOH solution. From the results the equilibrium constant ***K*** for the reaction

$$2RH + Mg^{2+}_{(aq.)} \rightleftharpoons R_2Mg + 2H^+_{(aq.)} \quad ...(1)$$

was determined at 30.0°C. The equilibrium constants ***K*** for the above H^+ / Mg^{2+} system was determined for different temperatures in the range of 30.0 °C to 45.0 °C.

Similar study was also carried out for H^+ / Ca^{2+} system in the same temperature range, to study the equilibrium constant ***K*** for the reaction

$$2RH + Ca^{2+}_{(aq.)} \rightleftharpoons R_2Ca + 2H^+_{(aq.)} \quad ...(2)$$

The Mg^{2+} and Ca^{2+} ion solutions used in the entire experimental work, where prepared by dissolving magnesium and calcium sulfate salts (Analytical grade) in distilled deionised water. In the present study, a semi-micro burette having an accuracy of 0.05 mL was used in the titrations and the titration readings were accurate to ± 0.05 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-bivalent ion exchange reactions (1 and 2) would be given by the expression

$$K = \frac{(\alpha_{R2Y})(\alpha_{X^+})^2_{aq.}}{(\alpha_{RX})^2(\alpha_{Y^{2+}})_{aq.}} \quad ...(3)$$

where γ is the activities of various species, X = H^+ ion and Y = Mg^{2+} or Ca^{2+} ions. In the above expression, the activities of X and Y in the aqueous solution are obtained from their respective concentrations and activity coefficients derived from Debye Huckel limiting law. As regards the activities of the two ions in the resin are concerned, the situation is different. Ordinarily the activity should be obtained as a product of concentration and the activity coefficient. In lieu of the concentration of the ions in the resin, their respective amounts in milliequivalents can be used, as shown by the satisfactory results obtained for the equilibrium constant of uni-univalent exchange reactions. On this basis, the equilibrium constant would be given by the expression

$$K = \frac{(C_{R2Y}.\gamma_{R2Y})(C_{X^+}.\gamma_{X^+})^2}{(C_{RX}.\gamma_{RX})^2(C_{Y^{2+}}.\gamma_{Y^{2+}})} \quad ...(4)$$

here γ is the activity coefficient of ions in the solution at equilibrium.

In this expression, the concentrations of ions in the resin phase in terms of their amounts in milliequivalents are known while their individual activity coefficients i.e. γ_{R2Y} and γ_{RX} are not known. Indeed, it appears that there is no way for evaluating them individually. In case of uni-univalent exchange reactions, they could be ignored because they where likely to be of the same magnitude (being for univalent ions) and in the expression for equilibrium their ratio is nearly one. In the present case for uni-bivalent exchange however, the activity coefficients can not be ignored because in the expression for the equilibrium constant they appear as $\gamma_{R2Y} / (\gamma_{RX})^2$. Since γ_{R2Y} and γ_{RX} are likely to vary with the concentration of the ions Y and X in the resin, the above mentioned quantity is also likely to vary with the concentrations of the ions in the resin. This is confirmed from the fact that the equilibrium constant as calculated from the expression

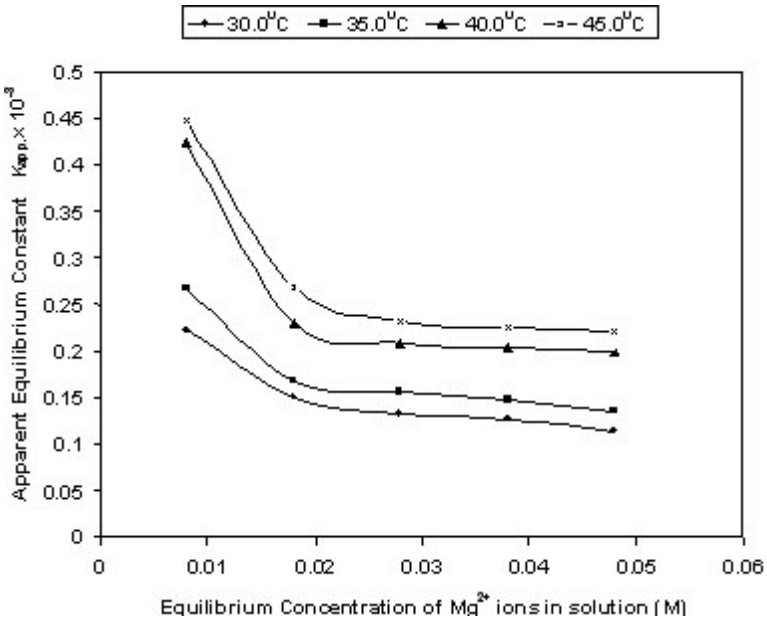
$$K_{app.} = \frac{(C_{R2Y})(C_{X^+})^2(\gamma_{X^+})^2}{(C_{RX})^2(C_{Y^{2+}})(\gamma_{Y^{2+}})} \quad ...(5)$$

varies with the concentration of the ions in the resin (Table 1).

In absence of any method to determine the activity coefficients of the ions in the resin individually the best that can be done is to attempt to determine the quantity $\gamma_{R2Y} / (\gamma_{RX})^2$ and to determine the true equilibrium constant. In ionic equilibrium it is conventional to regard zero concentration as the standard state when the mean activity coefficient becomes unity.In the present situation however, such standard state can not be chosen for the ions in the resin because the ion exchange resin will

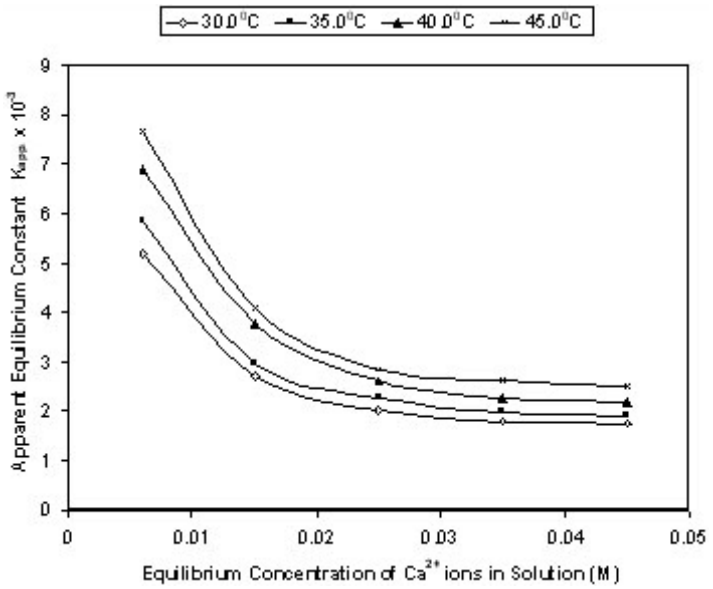
Table 1. Equilibrium constant for the uni-bivalent ion exchange reactions in Amberlite IR-120
Amount of ion exchange resin in H^+ form = 0.500g, Volume of exchangeable ion solution = 50.0 mL, Exchange capacity = 3.1 meq. /g

Reaction 1							Reaction 2						
Temperature = 30.0°C													
Initial conc. of Mg^{2+} ions in solution (M)	Equilibrium conc. in solution (M)		Amount of the ions on the resin meq./ 0.500 g		Apparent Equilibrium Constant $K_{app}\times10^{-3}$	$\frac{K_{std.}}{K_{app.}} = \frac{(\gamma_{R_2Mg})}{(\gamma_{RH})^2}$	Initial conc. of Ca^{2+} ions in solution (M)	Equilibrium conc. in soluiton (M)		Amount of the ions on the resin meq. /0.500 g		Appa-rent Equili-brium Constant $K_{app}\times10^{-3}$	$\frac{K_{std.}}{K_{app.}} = \frac{(\gamma_{R_2Ca})}{(\gamma_{RH})^2}$
	C_{H^+}	$C_{Mg^{2+}}$	C_{RH}	$C\,R_2M$				C_{H^+}	$C_{Ca^{2+}}$	C_{RH}	$C\,R_2Ca$	$K_{app}\times10^{-3}$	
0.01	0.0039	0.0081	2.079	0.195	0.222	1.216	0.01	0.0085	0.0058	1.619	0.425	5.193	1.001
0.02	0.0042	0.0179	2.049	0.210	0.156	1.731	0.02	0.0088	0.0156	1.589	0.440	2.714	1.916
0.03	0.0044	0.0278	2.029	0.220	0.137	1.971	0.03	0.0090	0.0251	1.569	0.450	2.528	2.057
0.04	0.0046	0.0377	2.009	0.230	0.126	2.140	0.04	0.0092	0.0354	1.549	0.460	1.798	2.892
0.05	0.0049	0.0476	1.979	0.245	0.314	2.010	0.05	0.0095	0.0453	1.519	0.475	1.751	2.969
Equilibrium constant in standard state ($K_{std.}$) = 0.27×10^{-3}							Equilibrium constant in standard state ($K_{std.}$) = 5.20×10^{-3}						
Temperature ^{O}C		30.0	35.0	40.0	45.0	Enthalpy (kJ/ mol)		30.0	35.0	40.0	45.0	Enthalpy (kJ/ mol)	
$K_{std.}$ x 10^{-3}		0.27	0.33	0.50	0.55	38.8		5.20	5.80	6.90	7.60	20.6	



Amount of the ion exchange resin in H^+ form = 0.500g, Volume of exchangeable ion solution = 50.0 mL, Temperature Range = 30.0°C – 45.0°C

Fig. 1: Variation of apparent equilibrium constant with equilibrium concentration of mg $^{2+}$ Ions in solution for the ion exchange reaction (1) using ion exchange resin amberlite IR-120

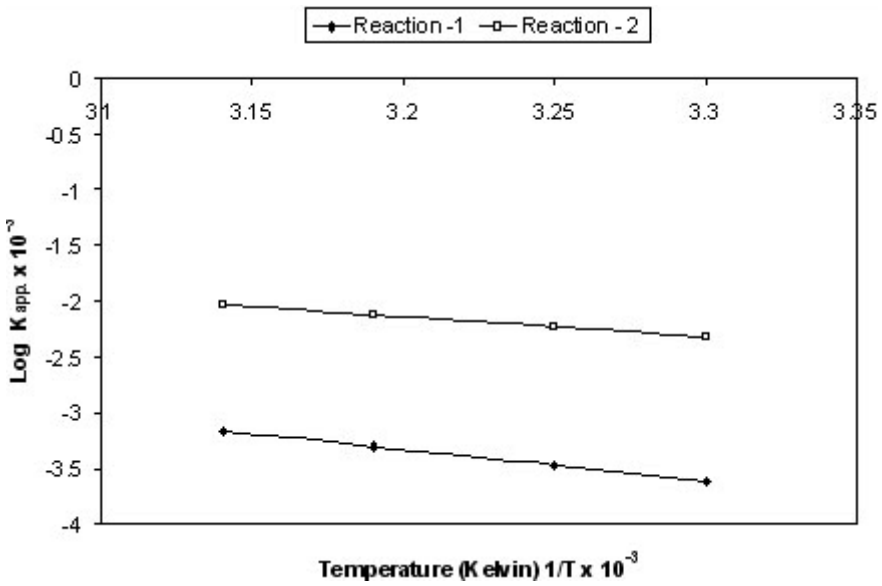


Amount of the ion exchange resin in H^+ form = 0.500g, Volume of exchangeable ion solution = 50.0 mL, Temperature Range = 30.0°C - 45.0°C

Fig. 2: Variation of apparent equilibrium constant with equilibrium concentration of ca^{2+} ions in solution for the ion exchange reaction (2) using ion exchange resin amberlite IR-120

always contains its capacity full of ions which can not be decreased.No doubt the ions in the resin might all be univalent or all be bivalent or partly univalent and partly bivalent. In any case the resin contain ions to its full capacity. However, when the resin is entirely in the H^+ form (univalent), its ionic strength will be much different from that when the resin is entirely in Mg^{2+} or Ca^{2+} (bivalent) form.Therefore it is expected that the quantity γ_{R2Y} / $(\gamma_{RX})^2$ will vary according to what extent the resin is in the univalent and bivalent ionic form.

In view of the above, it is found best to choose the ion exchange resin completely in univalent ionic form as the standard state and refer the resin at any other composition of the uni/bivalent ions to this standard state. Therefore the apparent equilibrium constants calculated by the equation 5 have been plotted versus the equilibrium concentrations of the bivalent ions in the solution (Figures 1 and 2). Lower the equilibrium concentration of the bivalent ion, lower would be its concentration in the resin and in the limiting case of zero equilibrium concentration of the bivalent ion in the solution, the resin would be in its standard state. Therefore on extrapolating the above curve to zero equilibrium concentration of bivalent ion in the solution, one obtains the equilibrium constant in the standard state, K_{std}. Having thus obtained the equilibrium constant in the standard state one can obtain the activity coefficient ratio of ions γ_{R2Y} / $(\gamma_{RX})^2$ at any finite equilibrium concentration of bivalent ion in the solution as the ratio of $K_{std.} / K_{app.}$ The results of such calculations are presented in the Table 1. It is significant that when the log $K_{app.}$ is plotted against 1 / T, different slopes and hence different values of enthalpy of ion exchange reaction are obtained. However, a satisfactory linear graph with definite slope was obtained when log $K_{std.}$ was plotted against 1 / T, giving a definite value of enthalpy for ion exchange reactions 1 and 2 (Fig. 3). This is an ample justification for the choice of standard state for equilibrium constant. Bonner and Pruett [16] studied the temperature effect on uni-univalent exchanges involving some bivalent ions. In all bivalent exchanges, the equilibrium constant decreases with rise in temperature resulting in exothermic reactions. However in the present investigation, for the uni-bivalent exchange reactions the value of equilibrium constant increases with rise in temperature giving positive enthalpy value (Table 1), indicating the endothermic ion exchange



Amount of the ion exchange resin in H^+ form = 0.500g, Temperature Range = 30.0^{0}C – 45.^{0}C

Fig. 3: Variation of equilibrium constant in standard state with temperature for the Ion exchange reactions (1) and (2) using ion exchange resin amberlite IR-120

reactions. The low enthalpy and higher *K* values for H^+ / Ca^{2+} exchange as compared to that for H^+ / Mg^{2+} exchange (Table 1), indicate that the resins in H^+ form are having more affinity for larger ionic size Ca^{2+} ions in solution as compared to that for Mg^{2+} ions also in the solution.

CONCLUSION

There are number of liquid processes waste streams at chemical processing, nuclear power plants, nuclear fuel reprocessing plants and nuclear research centers that requires treatment for removal of various contaminants. One of the most common treatment methods for such aqueous streams is the use of ion exchange, which is a well developed technique that has been employed for many years in chemical as well as nuclear industries. While designing an ion exchange liquid waste processing system it is desirable to have an adequate knowledge about the distribution coefficient values and the selectivity behaviour of these ion exchange resin towards different ions present in liquid waste. The thermodynamic data obtained in the present experimental work will be useful to understand the selectivity behaviour of ion exchange resins for various ions in solution thereby helping in characterization of resins.

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