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Kinetics of Uni-univalent Ion Exchange in Aqueous Solution using Strongly Acidic Cation Exchanger Ceralite IR-120

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ABSTRACT

The kinetics of the uni-univalent ion exchange reactions

$$X_{(R)} + Y_{(aq)} \rightleftharpoons Y_{(R)} + X_{(aq)}$$

Where $X = H^+$ and $Y = K^+$, Na^+ and Li^+ in the strongly acidic cation exchanger ceralite IR-120 has been studied at four temperatures. The rate constants, energy of activation, entropy of activation and enthalpy of reaction have been determined. The overall reaction was found to be second order. The ion exchange reaction was spontaneous, and the efficiency of the ion exchange resin was quantitatively determined. The effect of ionic size of the hydrated ions on the kinetics of the ion exchange reactions has been investigated.

Key words: *Ion-exchange, Uni-univalent Kinetics, Cation-exchanger, Order of reaction.*

1. INTRODUCTION

The ion exchange resin is capable of exchanging its ion with other similar ions present in solution [1,2]. This property has been of considerable utility in research and industry. The exchangeability of a resin depends upon factors such as exchange capacity of a resin, nature of resin, nature of the ion in the resin, nature of the ion to be exchanged, its concentration and temperature [3-6]. This is of considerable use not only in assessing an ion exchange resin for its utility in a stipulated ion exchange process quantitatively, l but also in assessing its efficiency in several ion exchange processes involving environmental studies [7-11]. The literature survey reveals that most of the work has been carried out on ion-exchange equilibria [12-14]. In view of this, the present study on kinetics of the following ion exchange reaction-

$$X_{(R)} + Y_{(aq)} \rightleftharpoons Y_{(R)} + X_{(aq)} \ldots. \quad (1)$$

Where $X = H^+$ and $Y = K^+$, Na^+ and Li^+ in a typical cation exchanger ceralite IR-120 has been undertaken.

The study has been carried out at four different temperatures and rate constants, energy of activation, entropy of activation and enthalpy of the reaction have been determined.

The ions are selected such that the ionic size of the hydrated ions follows the order $K^+ < Na^+ < Li^+$. The extent of exchange increases with decrease in size of the hydrated cation. In the present study, the rate constants of these ion exchange reactions have been correlated with the ionic size of the hydrated ions [15].

2. EXPERIMENTAL

2.1. Ion-exchange Resin

Commercial strongly acidic cation-exchange resin, ceralite IR-120 was supplied by chemical Drug House, New Delhi. The main properties of the ion-exchange resin used in this work are listed in Table 1.

Table 1: Specifications of cation-exchange resin.

Physical properties	Ceralite IR-120
Colour	Yellow brown
Particle size	22 mesh
Water content	45-50%
Standard ionic form	H^+
Ion-exchange capacity	7.0 meq/g
pH range	0-14
Cross linking	8%

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2.2. Conditioning of the Resin, Ceralite IR-120

To ensure that the resin was completely in the hydrogen form, adequate amount of resin was placed in a glass column and was eluted with 500 ml 2 M HCl solution at the rate of 1 cm^3 min. After complete elution with hydrochloric acid solution, the resin was washed with conductivity water until the washing was free from hydrogen. The washed resin was then air dried and used for ion-exchange studies.

2.3. Determination of the Resin Capacity

Five grams of the resin and 250 cm^3 conductivity water had been taken in a glass column. Using a separating funnel, 250 cm^3 of 0.25 M sodium sulphate solution was passed through the column at the rate of 2 cm^3 min^{-1}. The effluent was titrated with standard 0.1 N sodium hydroxide using phenolphthalein indicator. The resin capacity was determined using the formula:

$$\frac{a \times V}{W}$$

Where, "a" is the normality of NaOH solution, V is the volume of NaOH solution in cm^3 and W is the weight of the resin in grams. This formula gave the resin capacity in milli equivalent g^{-1}.

Using the above formula, the resin capacity of ceralite IR-120 was found to be 7.088 milli equivalent g^{-1}.

2.4. Preparation of Solutions

Analytical research grade chemicals lithium carbonate, sodium chloride and potassium chloride were used to prepare solutions for ion-exchange study. 100 ppm stock solutions of lithium, sodium and potassium were prepared in conductivity water from the above salts.

2.5. Procedure

A solution of 25 ppm of the elements Li, Na and K were prepared from stock solutions.

In a typical study, 100 cm^3 of 25 ppm lithium ion solution was taken in the stoppered bottle and was kept in a thermostat to attain the temperature 25.8°C. The 0.500 g of ion-exchange resin was then transferred into the stoppered bottle. The bottle was stoppered, well shaken and kept in thermostat 25.8°C. The solution was then analyzed for lithium ion at intervals of 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 min. The concentration of lithium ion was determined by Elico flame photometer. From the concentration of Li^+ in the solution, the rate constant "k" was determined for the reaction (1) at temperature 25.8°C.

The determination of rate constant "k" was carried out at various temperatures, i.e., at 13.8°C, 21.8°C and 27.8°C to determine the energy of activation.

Further, the energy of activation was used to determine the entropy of the reaction and the enthalpy of the reaction. Similar kinetic studies were also carried out with the ions Na^+ and K^+ in aqueous solution.

3. RESULTS AND DISCUSSION

In the present study, the kinetics of the ion-exchange reaction

$$X_{(R)} + Y_{(aq)} \rightleftharpoons Y_{(R)} + X_{(aq)}$$

Where X = H^+ and y = K^+, Na^+ and Li^+

has been studied in the strongly acidic cation exchanger ceralite IR-120.

3.1. Accuracy of the Results

The concentrations of the exchanging ions, i.e., K^+, Na^+ and Li^+ ions have been determined by Elico flame photometer. Considering the accuracy in the intensity measurements, the results obtained have an error of ± 3% (Table 2 and Figure 1).

3.2. Determination of Concentrations

As the exchange proceeds, the concentration of exchanging ions in aqueous solution decreases; rapidly. At 25.8°C more than 95% concentration decreased in about 25 min and thereafter it remained almost constant.

The concentrations of the ions exchanged in the resin were determined by the working curve method. Since it was a uni-univalent exchange, whatever concentrations of ions in aqueous solutions were exchanged, an equivalent amount of H^+ ions came out in the solution. The amounts of H^+ ions remained in the resin were determined from the knowledge of the resin capacity. Since ion-exchange resin is a solid, the concentrations of the ions in the resin could not be conveniently expressed in the conventional units of moles per liter. Therefore, these concentrations were expressed as milli equivalents of the ions per 0.500 g of the resin.

3.3. Order of the Reaction

The data obtained were fitted in the kinetic equations for the first order, second order, and third order reactions:

Rate = k [y] ..... (1)

Rate = k [x] [y]..... (2)

Rate = k [H^+] [x] [y]..... (3)

When the data were fitted in the first order rate equation, log (a-x) versus time plot yielded a curve rather than a straight line, indicating that the reaction

was not of the first order. Similarly, the possibility of third order reaction was also ruled out (Tables 3 and 3a, Figures 2 and 3). In fact, the plot log (a-x)/(b-x) versus time yielded a straight line indicating that the exchange reaction was of second order [16]. It also indicated that the exchange process was dependent on the concentrations of ions present in the solution as well as present in the resin. From the slope of this line, rate constant was evaluated. The rate constants at various temperatures were used to determine the energy of activation.

Similar experiments were carried out for all the exchange reactions and the rate constant, energy of activation, entropy of activation and enthalpy of the reactions were determined (Tables 4 and 5).

3.4. Effect of Ionic Size of Hydrated Ions on the Kinetics Study

Under identical conditions, the effect of ionic size of hydrated ions on the rate constants of the ion-exchange reactions has been studied.

The exchange rate constant was found to be the highest for H^+-K^+ exchange and lowest for H^+-Li^+ exchange, and intermediate behavior was observed for H^+-Na^+ exchange. Thus, the rate constant values obtained for the above exchange reactions decreased with increase in the hydrated ionic size of ions. This is due to the operation of ion-dipole forces of the ion and solvent molecules. A certain number of water molecules in the immediate vicinity of the ion are trapped and immobilized. The ion and its water sheath become a single kinetic entity. Thus, the picture is of ions enveloped by a solvent sheath of oriented and immobilized water molecules. The sheath restricted the exchange between the ions [17]. Thicker the sheath of solvent molecules, slower was the exchange. Although the rate constants changed there

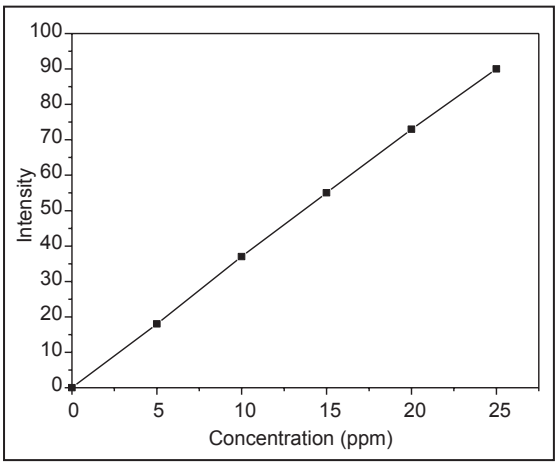

Figure 1: Calibration curve to determine the concentration of K+ ion in the solution at the temperature 25.8°C.

Table 2: Calibration curve to determine the concentration of K^+ in the solution at 25.8°C.

Concentration of K^+ (ppm)	5.0	10.0	15.0	20.0	25.0
% Intensity	18	37	55	73	90

Table 3: Kinetics of the uni-univalent ion-exchange reaction.

$R\text{-}H^+ + K^+_{aq} \leftrightarrow R\text{-}K^+ + H^+_{aq}$ in ceralite IR 120	
Amount of the ion-exchange resin	0.500 g
Vol. of the 25 ppm "K^+" ion solution	100 cm^3
Temperature	25.8°C
Hydrogen and potassium ion concentration in the resin and solution	
Initial concentration of hydrogen ion in the resin, a	3.554×10^{-3} N
Initial concentration of potassium ion in the solution, b	6.390×10^{-4} N
Conc. of potassium ion exchanged	×

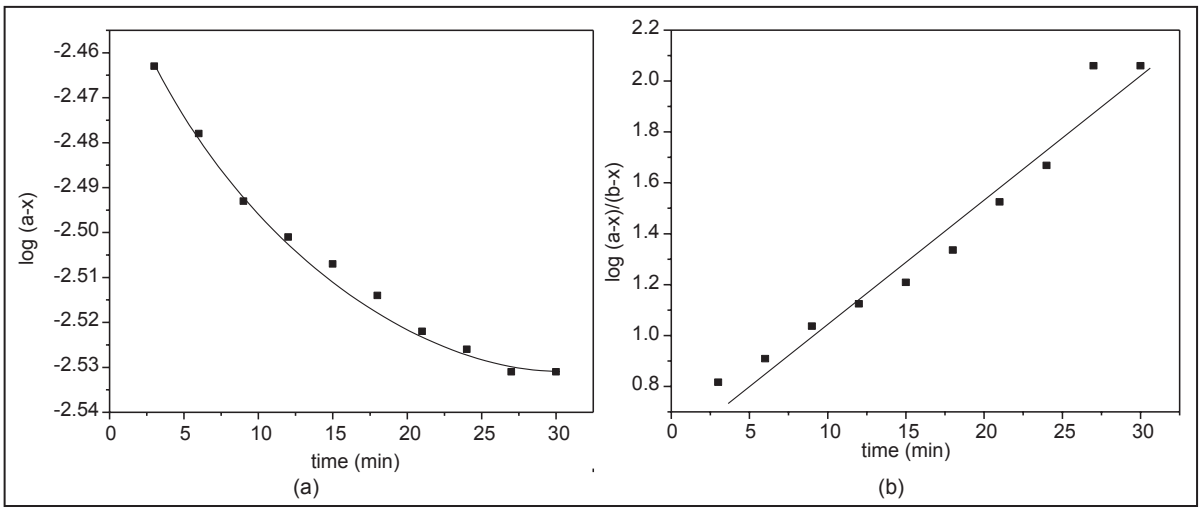

Figure 2: (a) Curve for first order kinetics of the uni-univalent ion exchange reaction at 25.8°C. (b) Curve for second order kinetics of the uni-univalent ion exchange reaction at 25.8°C.

Table 3a: Kinetics of the uni-univalent ion exchange reaction at 25.8°C.

Time (min)	Percentage of intensity	(b-x) $N\times10^{-4}$	(x) ppm	(a-x) $N\times10^{-3}$	Log (a-x)/(b-x)	Log (a-x)
03	74	5.2429	4.50	3.4389	0.8168	−2.4635
06	58	4.0920	9.00	3.3238	0.9096	−2.4783
09	42	2.9411	13.5	3.2087	1.0378	−2.4936
12	34	2.3657	15.7	3.1511	1.1245	−2.5015
15	27	1.9181	17.5	3.1065	1.2093	−2.5077
18	20	1.4066	19.5	3.0552	1.3368	−2.5149
21	13	0.8951	21.5	3.0041	1.5258	−2.5222
24	09	06393	22.5	29785	1.6682	−2.5260
27	04	0.2557	24.0	2.9401	2.0606	−2.5316
30	04	0.2557	24.0	2.901	2.066	−2.5316

Slope of the graph of log (a-x)/(b-x) versus time=0.04121 min^{-1}. Rate constant, 'k' = $\frac{2.303 \times slope}{a - b}$, k=32.5580 L mol^{-1} min^{-1}

Table 4: Determination of energy of activation (Ea) for the uni-uni valent ion exchange reaction.

Temperature, T (K)	298.8	294.8	290.8	286.8
$1/T\times10^{-3}$ (K^{-1})	3.3460	3.3926	3.4385	3.4864
Rate constant, "k"/ (L mol^{-1} min^{-1})	32.558	27.2883	23.3489	18.669
log k	1.5126	1.4359	1.3682	1.2711

Energy of activation for uni-univalent ion-exchange reaction, Ea=2.303×R×Slope, Ea=31.413 kJ per mole

Table 5: Energy of activation, entropy of activation and enthalpy of reaction for various exchange systems.

System	H^+-K^+	H^+-Na^+	H^+-Li^+
Energy of activation, Ea (kJ $mole^{-1}$)	31.413	28.395	26.327
Entropy of activation, ΔS (kJ $mole^{-1}$ k^{-1})	0.234	0.237	0.240
Enthalpy of reaction, ΔH (kJ $mole^{-1}$)	−4.837	−4.840	−4.843

Table 6: Variation of the rate constant with ionic size of hydrated ion at temperature 298.8 K.

System	H^+-K^+	H^+-Na^+	H^+-Li^+
Hydrated ionic size, pm	300	450	600
Rate constant, k (L $mole^{-1}$ min^{-1})	32.558	21.068	15.690

was no significant change in the energy of activation, entropy of activation and enthalpy of reaction (Table 6).

4. CONCLUSION

The present work portrays quantitatively, through kinetic investigation, subtelities of ion exchange reactions involving different univalent ions. The correlation of increased hydrated ionic size with the rate of ion exchange reactions is thereby revealed. The rate constant, the energy of activation, entropy of activation and enthalpy of the reaction for typical ion exchange reaction have been evaluated. The exchange rate constant was found to be inversely proportional to the ionic size of hydrated ions. These results that are quantitative in nature are of utility to separate these ions in a sample, in a preferential order with respect to the ionic size.

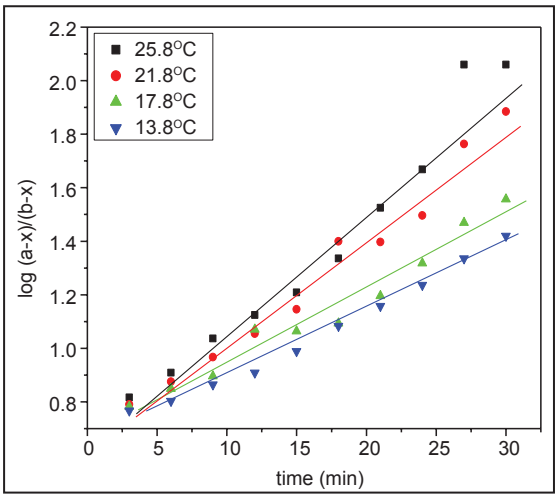

Figure 3: Curve for second order kinetics of the uni-univalent ion exchange reaction at various temperatures.

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***Bibliographical Sketch**

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