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Exchange Kinetics of Rubidium and Caesium Ions on Pyridinium Tungstoarsenate Exchanger

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The Kinetics of exchange of Rb^+ and Cs^+ has been investigated on pyridinium tungstoarsenate ion exchanger using limited bath technique. The exchange rate was studied as a function of concentration, temperature and particle size of exchanger to determine the slowest step. It was found that Rb^+ exchange is particle diffusion controlled whereas Cs^+ exchange shows dual behaviour at low concentration level. However, at higher concentrations, particle diffusion controls Cs^+ exchange but the rate is concentration dependent. This anomalous behaviour has been explained by assuming that Cs^+ exchange approaches closely to a chemical reaction. Thermodynamic parameters of exchange such as effective diffusion coefficient (D), activation energy (E_a) and entropy of activation (ΔS^*) were calculated. The D and E_a values were found in the same order as that of ionic size, ΔS^* value being positive for Cs^+ exchange and negative for Rb^+ exchange. A negative ΔS^* value is usual but a positive value for Cs^+ exchange might be due to dehydration of the cation while passing through the channels of the exchanger. This explanation is in line with that of interaction energy for the exchange of Cs^+ on pyridinium tungstoarsenate.

The study of the kinetics of ion exchange process is important since it provides information on the mechanism of the rate controlling process, reactions accompanying the ion exchange, as well as internal physical structure of the exchanger and the extent of hydration of exchanging ion.

Systematic kinetic studies on ion exchangers were started by Nachod and Wood,[1,2] the earliest theory being developed by Boyd *et al.*[3] The kinetics of cation exchange in organic resins[4-6] and synthetic zeolites[7-9] has been studied in length. However, little information is available on other inorganic ion exchangers. Of synthetic inorganic ion exchangers, kinetic studies on hydrated oxides of thorium,[10] titanium[11] and zirconium,[12] zirconium phosphate,[13] hydrated alumina,[14] tantalum arsenate[15] and zirconium antimonate[16] have been reported.

Heteropolyacid salts form well defined crystalline inorganic ion exchangers.[17] They show high affinity for Tl^+, Cs^+, and Rb^+ and are used for ^{137}Cs separation in nuclear waste. However, no kinetic studies, necessary for ion exchange mechanism, seem to have been carried out on these exchangers.

Malik and coworkers[18] reported on the ion exchange properties of pyridinium tungstoarsenate, a new heteropolyacid salt, showing its selectivity for Rb^+ and Cs^+ amongst alkali metal ions. In order to explain their results they assumed the dehydration of Cs^+ during the course of exchange. In the present communication, we report on the kinetic studies of exchange of Rb^+ and Cs^+ on pyridinium tungstoarsenate (PWA). Effective diffusion coefficient, activation energy, and entropy of activation have been calculated, the results confirming the assumption that Cs^+ becomes dehydrated before undergoing exchange.

Experimental

Reagents and Materials. All the reagents used were of AR grade. The exchanger, pyridinium tungstoarsenate ($(C_5H_5NH)_3W_{12}AsO_{40}$) was prepared by the method reported.[18]

Apparatus. A unicam SP 500 spectrophotometer was used for the estimation of pyridine. A Leitz Wetzler microscope, Germany, model 12.5 X was used for the determination of the particle size of exchanger.

Kinetic Measurements. Limited bath technique[19] was used to study the exchange rate. PWA was ground and sieved to the desired mesh size (-50 to $+100$, -100 to $+200$). Solutions of Rb^+ and Cs^+ were thermostated at the required temperature in stoppered pyrex boiling tubes containing pyridinium nitrate and nitric acid,[18] the total volume in each tube being made 10 cm^3. The final concentrations of pyridinium nitrate and nitric acid were 0.001 mol dm^{-3} and 0.01 mol dm^{-3}, respectively, while that of the cation were varied from 0.05—0.2 mol dm^{-3} (for Rb^+) and 0.05—0.3 mol dm^{-3} (for Cs^+).

A weighed amount (0.1 g) of the exchanger of desired mesh size was added to these tubes which were thoroughly shaken, mechanically. After appropriate intervals of time the contents of the tubes were filtered with Whatman No. 1 filter paper, the extent of exchange being measured by determining pyridinium cations released spectrophotometrically at 256 nm. The exchange between Rb^+/Cs^+ and pyridinium cation is stoichiometric.[18] Experiments were conducted at 300.5, 305.5, 310.5, 315.5, and 320.5 ± 0.1 K.

Particle Size. The average particle radius of each sieved fraction was determined by measuring the diameter of about 100 beads on a micrometer microscope. Measurements were carried out on dry particles as well as on particles which had been immersed for 24 hours in an appropriate electrolyte solution (concentration 0.1 mol dm^{-3}). There was no significant difference between the size of dry and immersed particles.

Results and Discussion

According to the theory developed by Boyd *et al.*,[3] the following equation holds in particle diffusion controlled exchange:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2},$$

where F is the extent of exchange at time t, $B = \pi^2 D / r^2$, r is the average radius of the exchanger particle and D the effective diffusion coefficient. Thus the rate of particle diffusion controlled exchange should be dependent on r but independent of the concentration of exchanging ion; a plot of Bt *vs.* t (Reichenberg's test[20]) should be a straight line passing through origin.

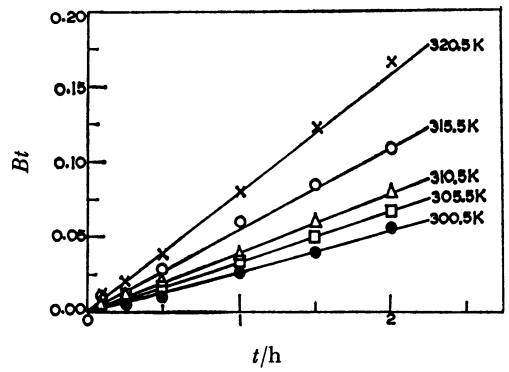

Fig. 1. Plots of *Bt vs. t* for Rb^+ exchange at different temperatures (r=0.0160 cm, concentration=0.1 mol dm^{-3}).

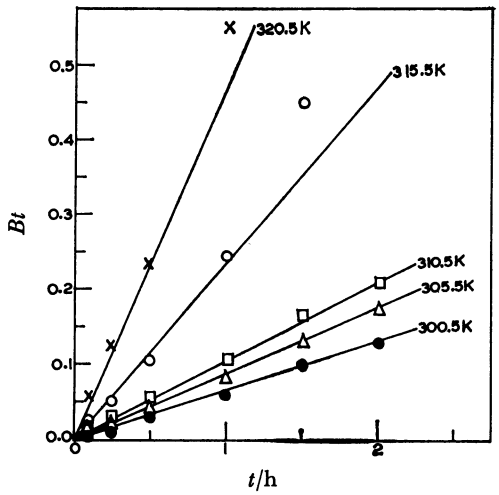

Fig. 2. Plots of *Bt vs. t* for Cs^+ exchange at different temperatures (r=0.0160 cm, concentration=0.1 mol dm^{-3}).

The kinetics of exchange of Rb^+ and Cs^+ on PWA was studied in the light of these considerations.

Figures 1 and 2 show the plots, *Bt vs. t*, for the exchange of Rb^+ and Cs^+ at different temperatures. These plots are linear, passing through origin, showing that the exchange is particle diffusion controlled. The plots of $-\log(1-F)$ *vs. t* (Mc Kay plots[21]) are nonlinear, supporting the above result. The effect of particle size of the exchanger shows that in both cases rate increases with decrease in particle radius. The rate of exchange of Rb^+ was found to be independent of concentration (Fig. 3), but not for Cs^+ exchange. Figure 4 shows *Bt vs. t* plots for Cs^+ exchange at four different concentrations. At concentration 0.05 mol dm^{-3}, the nonlinear behavior and fast uptake of Cs^+ shows that film diffusion also contributes to exchange.[3,22] At concentrations 0.1, 0.2, and 0.3 mol dm^{-3}, though the plots are linear (for 0.2 and 0.3 mol dm^{-3}, only initially) the rate is concentration dependent. Such an anomalous behavior was also reported.[23-25] Helfferich[26] showed theoretically that particle diffusion controlled exchange accompanied by ionic reactions (association, neutralization or complex formation) would exhibit such a behavior.

In the present case, it seems that the Cs^+ is dehydrated[18] during the course of exchange, getting chemically associated to tungstoarsenate ion. The resulting compound forms a shell around the exchanger particle which prevents further entry of Cs^+ into the core. This would eliminate Donnan exclusion of the co-ions. If a sufficient number of counter ions pass through the shell, they should carry with them co-ions so as not to disturb electroneutrality.[26] The invasion of counter and co-ions should be concentration dependent. This may also be the reason why the *Bt vs. t* plots (Fig. 4) are a bit nonlinear towards the end. The assumption of Cs^+ becoming dehydrated while exchanging with pyridinium cation is further supported by the entropy data.

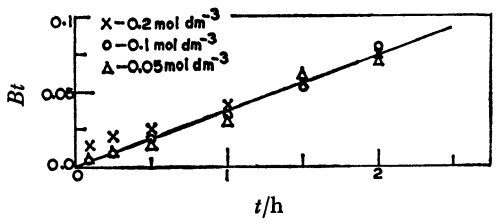

Fig. 3. Plots of *Bt vs. t* for Rb^+ exchange at different concentrations (r=0.0160 cm, T=310.5 K).

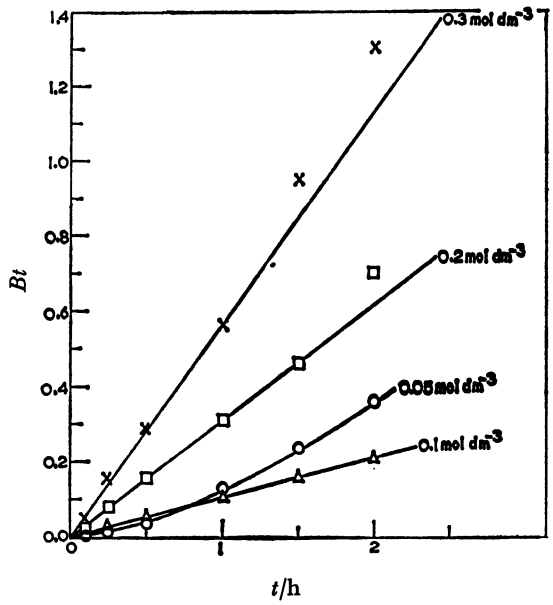

Fig. 4. Plots of *Bt vs. t* for Cs^+ exchange at different concentrations (r=0.0160 cm, T=310.5 K).

The exchange data at different temperatures (Figs. 1 and 2) have been used to calculate the values of effective diffusion coefficient (D), activation energy (E_a) and entropy of activation (ΔS^*). The D values computed from the B values are given in Table 1. They are in the order $Cs^+ > Rb^+$, in line with the order reported for alkali metal ions exchange on other exchangers.[12,27] The values are much lower than those reported on organic resins.[27,28] Nancollas and Paterson[10] inferred that crystallinity of the exchanger affects the D values such that more crystalline the exchanger, the lower the values. For PWA, a crystalline heteropolyacid salt, the D values of Rb^+ and Cs^+ exchange on it are very low.

Table 1. B values and effective diffusion coefficient D as a function of temperature (average particle radius of the exchanger = 0.0160 cm, concentration of Rb^+ and Cs^+ = 0.1 mol dm^{-3})

S. No.	Temp/K	Rb^+-exchange		Cs^+-exchange	
		B/s^{-1}	$D/m^2\ s^{-1}$	B/s^{-1}	$D/m^2\ s^{-1}$
1	300.5	0.75×10^{-5}	1.95×10^{-14}	1.81×10^{-5}	4.68×10^{-14}
2	305·5	0.97×10^{-5}	2.52×10^{-14}	2.64×10^{-5}	6.85×10^{-14}
3	310.5	1.11×10^{-5}	2.88×10^{-14}	2.92×10^{-5}	1.07×10^{-13}
4	315.5	1.53×10^{-5}	3.96×10^{-14}	6.67×10^{-5}	1.73×10^{-13}
5	320.5	2.22×10^{-5}	5.76×10^{-14}	13.19×10^{-5}	3.42×10^{-13}

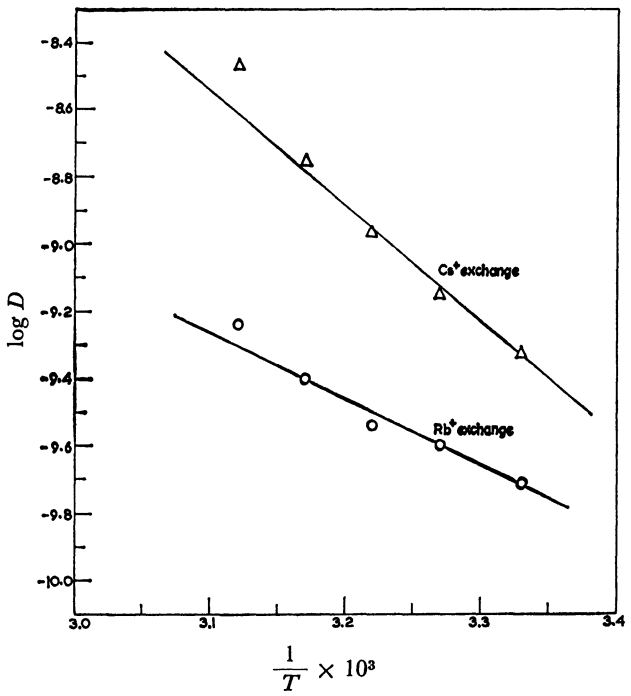

Fig. 5. Plots of $\log D$ *vs.* $1/T$.

The linearity of $\log D$ *vs.* $1/T$ plots (Fig. 5) indicates the validity of the Arrhenius equation

$$D = D_0 \exp(-E_a/RT),$$

which is used to calculate E_a values. The activation energy of a cation diffusion process reflects the ease with which cations can pass through exchanger particles. Freeman and Stamirs[29] observed an increase in E_a with increase in ion size of the alkaline earth metal ions. The increase is explained in terms of an increase in the strength of bonding to two crystallographically separated sites for the large, more polarizable cations. Similar findings were also observed for monovalent cations on analcite[30] and for alkaline earth metal ions on tantalum arsenate.[15] Our results (Table 2) which show that E_a for Cs^+ exchange is higher as compared to that of Rb^+ are in agreement with the increasing ion size.[15,29,30] In the present case the E_a values are higher as compared to the values 20—40 kJ mol^{-1} obtained for the exchange of hydrogen by monovalent ions on strong cation exchangers.[4,5] This may be due to low swelling of the exchanger. Similar findings were obtained by Heitner-Wirguin and Markovits.[19]

Table 2. D_0 values and thermodynamic parameters for Rb^+/Py^+ and Cs^+/Py^+ exchange on PWA exchanger

S. No.	System	$D_0/m^2\ s^{-1}$	E_a/kJ mol^{-1}	ΔS^*/J $mol^{-1}\ K^{-1}$
1	Rb^+/py^+	3.1×10^{-8}	35.7	−40.2
2	Cs^+/Py^+	3.4×10^{-2}	68.4	+75.7

Py^+ = pyridinium ion

The Arrhenius equation was also used to calculate D_0 which in turn is used to obtain ΔS^* by means of the following equation proposed by Barrer *et al.*[31]

$$D_0 = 2.72\, d^2k\, T/h \exp(\Delta S^*/R)$$

where k is Boltzmann constant, h Planck constant, d the distance between adjacent exchanging sites in the exchanger, and T is 273 K. For the calculation of ΔS^*, the value of d has usually been assumed to be equal to 5×10^{-8} cm.[15,16,32] We have also used the same value for ΔS^* calculation (Table 2). The entropy change normally depends on the extent of hydration of the exchangeable and exchanging ions along with any change in water structure around ions that may occur when they pass through the channels of exchanger particles. In general, negative values of ΔS^* have been reported.[15,16,29] ΔS^* for Rb^+ exchange in our case is negative whereas a positive value is obtained for Cs^+ exchange.

The positive value for Cs^+ exchange is unusual but not exceptional, being accounted for on the basis of disordering of water structure[32] around exchanging cations or their dehydration[33] during exchange. In our case, it appears that hydrated Cs^+ cation becomes dehydrated before exchanging with pyridinium ions of the exchanger. The explanation is in line with the one given by Malik, Srivastava and Satish[18] to explain higher interaction energy value for Cs^+ exchange on PWA which we utilized to explain the dependence of Cs^+ exchange rate on concentration.

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