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Kinetics of the Forward and Reverse Na(I)-H(I) and K(I)-H(I) Exchanges on Antimony(V) Arsenatophosphate Cation Exchanger

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Kinetic studies have been made on antimony(V) arsenatophosphate cation exchanger, for the forward and reverse Na(I)–H(I) and K(I)–H(I) exchange processes. On the basis of such studies the self diffusion coefficients, energies of activation, and entropies of activation have been evaluated.

Kinetic studies are helpful in understanding the reaction mechanism undergoing in a particular system on the basis of the reaction rate. Such studies[1,2] on inorganic ion-exchange materials so far have been useful in drawing some important conclusions regarding their ion-exchange behavior and potential use under different conditions. Antimony(V) arsenatophosphate is a reasonably stable cation exchanger and has a promising ion-exchange behavior as our earlier observations indicate.[3] It is important to know the kinetics of the ion-exchange process going on in this material during its functioning so that its practical utility may be explored more clearly. The following pages summarize such a study for the Na(I)–H(I) and K(I)–H(I) exchanges in both the forward and reverse directions. The results have been compared with those of the antimony(V) silicate prepared earlier[1] in these laboratories.

Experimental

Reagents and Apparatus: Antimony(V) pentachloride was obtained from Fluka, Switzerland. All other reagents and chemicals were of Anala R grade. For the equilibrium studies a water bath incubator shaker with a temperature variation of ±0.5 °C was used. A flame photometer by Systronics India was used for the quantitative determination of Na(I) and K(I) in solutions.

Synthesis of Antimony(V) Arsenatophosphate: It was synthesized as reported earlier[3] and its ion-exchange capacity was found to be 2.2 mequiv g^{-1}.

Kinetic Experiment: The material was finely ground and sieved in order to obtain particles of mean radii 121 μm (52—72 mesh) used in the present study. Twenty ml of 0.05 M (1 M=1 mol dm^{-3}) NaCl or KCl solutions was shaken with the exchanger (0.2 g) at various temperatures (20, 30, 45, 60 °C) for different time intervals and the supernatant liquid was analyzed for the Na(I) and K(I) ions by flame photometry. In the reverse process the exchanger was taken in the metal form and shaken with 20 ml of 0.1 M HNO_3. The supernatant liquid was titrated against standard NaOH solution to find out the amount of the H(I) ions adsorbed on the exchanger, the range of error in the determination being ±1%. Five replicates were used for each determination. Under the conditions of particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium $U_{(\tau)}$ is expressed as

$$U_{(\tau)} = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}}. \qquad (1)$$

Results and Discussion

As verified experimentally (Fig. 1) the kinetic studies point out that the ion-exchange process on antimony(V) arsenatophosphate is controlled by the particle diffusion mechanism when the metal ion concentration is $\geqslant 0.05$ M. For the H(I) ions, however, this limit is $\geqslant 0.1$ M. This difference in the concentration limits is perhaps due to the different degrees of ionization of an acid and its salt. In the first case the exchanger behaves as an acid because of its H^+ form while in the second case it behaves as a salt as it was taken in the Na^+/K^+ forms. Below these concentrations the film diffusion is more prominent.

A plot of $U_{(\tau)}$ versus t (Fig. 2) indicates that the fractional attainment of equilibrium is faster at a higher temperature. In this regard the exchanger behaves in the similar way as antimony(V) silicate studied earlier.[1]

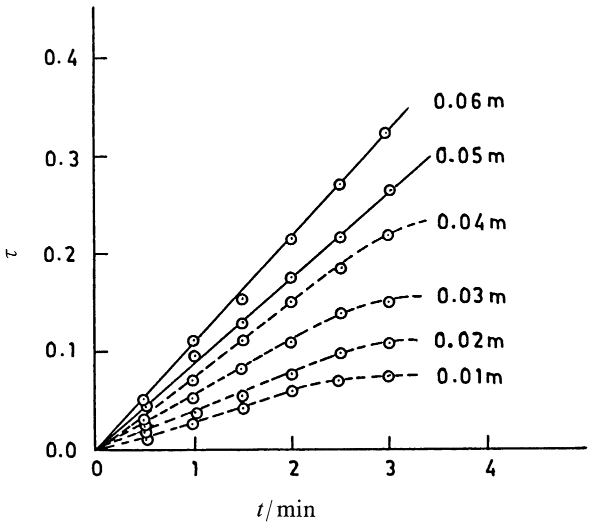

Fig. 1. Plots of τ vs. t for Na(I)–H(I) exchange using different solution concentration at 30 °C on antimony(V) arsenatophosphate.

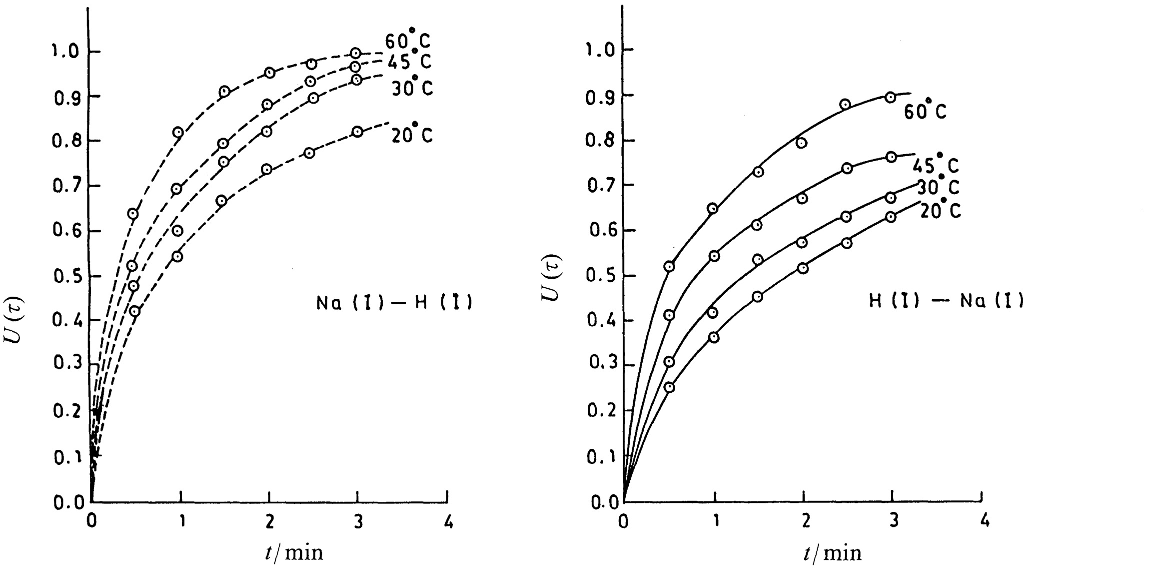

Fig. 2. Fractional attainment of equilibrium for Na(I)–H(I) and H(I)–Na(I) exchanges on antimony (V) arsenatophosphate.

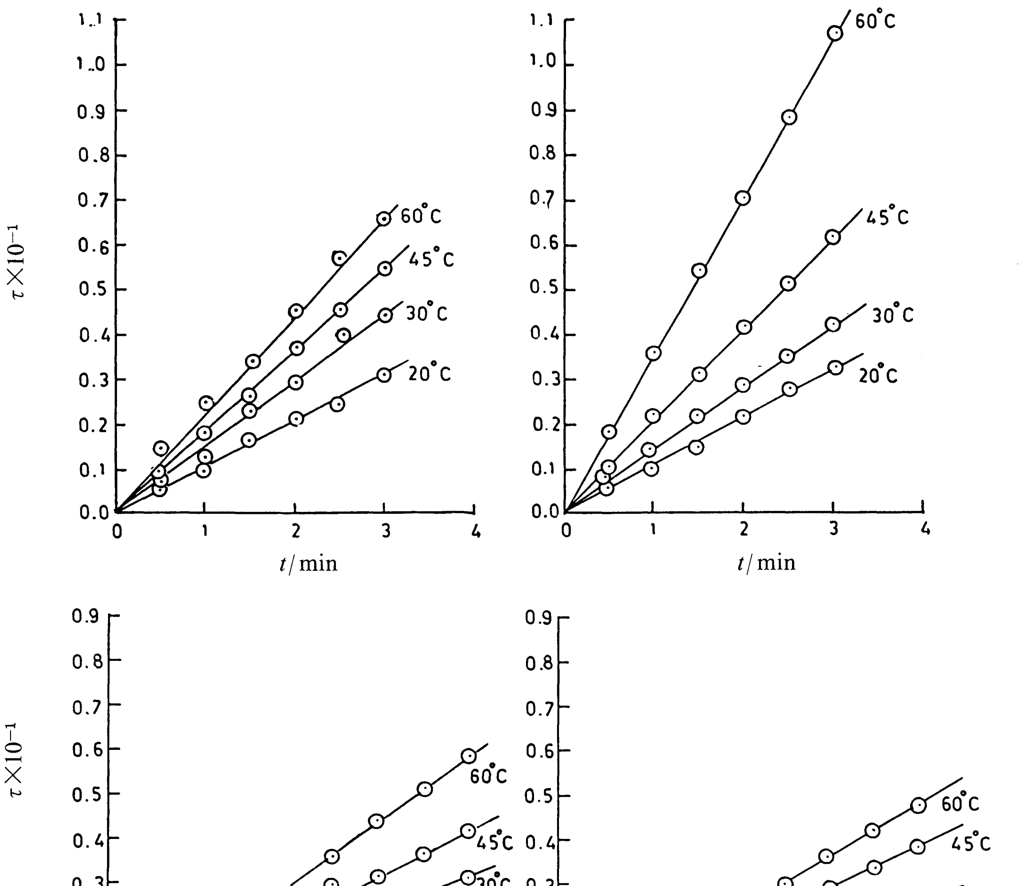

Fig. 3. Plots of τ versus time for foward and reverse metal(I)–H(I) & H(I)–metal(I) exchenges on antimony(V) arsenatophosphate at various temperatures.

The present system may be considered to follow the infinite solution volume condition because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases respectively while V and $\bar{V}$ are the volumes of these phases. The Nernst-Planck equation can be solved conveniently with some additional assumptions,[4-6] since inorganic ion exchangers do not swell significantly. As a result we obtain a coupled interdiffusion coefficient D_{AB}, the value of which depends on the relative concentrations of the counter ions 'A' and 'B' in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$ the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter ion initially present in the ion exchanger phase. The numerical results can be expressed[6] by the explicit approximation:

$$U_{(\tau)}=\{1-\exp[\lambda^2 f_1(\alpha)\tau+f_2(\alpha)\tau^2+f_3(\alpha)\tau^3]\}^{1/2} \tag{2}$$

where $\tau=\bar{D}_A\, t/r_0^2$, mobility ratio $\alpha=\bar{D}_A/\bar{D}_B$, r_0=particle radius and $\bar{D}_B$=the interdiffusion coefficient of the metal ion. Under the conditions $0.1 \leqslant \alpha \leqslant 10$ and $Z_A/Z_B=1$ which are fulfilled in the present case, the three coefficients $f_1(\alpha)$, $f_2(\alpha)$, and $f_3(\alpha)$ can be expressed as

$$f_1(\alpha)=-\frac{1}{0.570+0.430\alpha^{0.775}}$$

$$f_2(\alpha)=+\frac{1}{0.260+0.782\alpha}$$

$$f_3(\alpha)=-\frac{1}{0.165+0.177\alpha}$$

Each value of $U_{(\tau)}$ will have a corresponding value of τ as obtained earlier in these laboratories[7] by using Eq. 1. Plots of τ versus t at the four different temperatures (Fig. 3) for the forward and reverse M(I)-H(I) exchanges are shown at concentrations of 0.05 and 0.1 M respectively, which are straight lines passing through the origin, where M(I) stands for Na(I) or K(I) ions. This confirms that the phenomenon is controlled by the particle diffusion. Slopes (S) of such lines for all the four different temperatures are given in Table 1, which are related to $\bar{D}_A$ as follows:

$$S=\bar{D}_A/r_0^2 \tag{3}$$

The values of $\log \bar{D}_A$ obtained by this equation are plotted against $1/T$. Straight lines are obtained for Na(I), K(I) exchanges with H(I) and vice versa for reversible exchange, as shown in Fig. 4, justifying the validity of the Arrhenius equation.

$$\bar{D}_A=D_0\exp(-E_a/RT) \tag{4}$$

The D_0 was then obtained by extrapolating these curves, observing the intercept at the origin and taking the value of $\bar{D}_A$ at 273 K.

The entropy of activation (ΔS^*) is obtained by using Eq. 5,

$$D_0=2.72\, d^2\frac{kT}{h}\exp(\Delta S^*/R) \tag{5}$$

where k and h are the Boltzmann and Planck constants

Table 1. Slopes (S) of τ vs. t Plots for Forward and Reverse Exchanges of Na(I)-H(I) and K(I)-H(I) on Antimony(V) Arsenatophosphate Cation Exchanger

Migrating ion	Ion present on ion exchanger	$S\times10^{-4}$ (s^{-1})			
		20 °C	30 °C	45 °C	60 °C
Na(I)	H(I)	16.7	25.0	30.5	55.5
H(I)	Na(I)	17.5	22.9	34.5	58.3
K(I)	H(I)	9.5	13.3	18.5	25.0
H(I)	K(I)	8.3	11.5	16.6	20.0

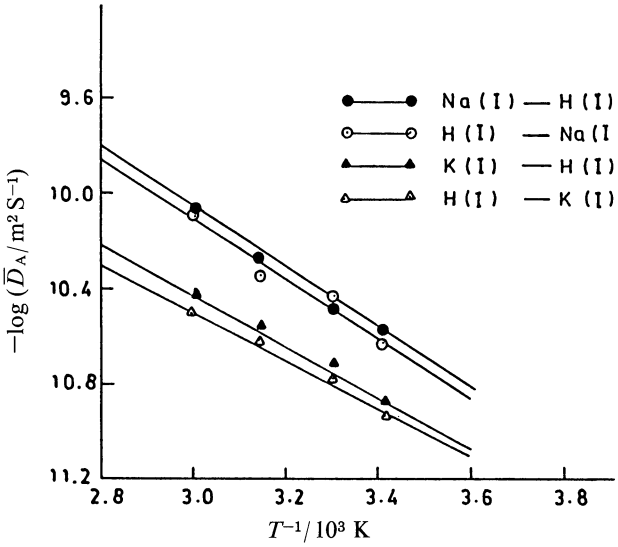

Fig. 4. Plots of $-\log \bar{D}_A$ versus $1/T$ for metal(I)-H(I) and H(I)-metal(I) exchanges on antimony (V) arsenatophosphate.

Table 2. Self Diffusion Coefficients, Energies of Activation, and Entropies of Activation for Forward and Reverse Exchanges of Na(I)-H(I) and K(I)-H(I) on Antimony(V) Arsenatophosphate Cation Exchanger

Migrating ion	Ion present on ion exchanger	Hydrated radii of the migrating ion	D_0	E_a	ΔS^*
		Å	m^2 s^{-1}	kJ mol^{-1}	J deg^{-1} mol^{-1}
Na(I)	H(I)	2.8	6.0×10^{-7}	10.8	−15.6
H(I)	Na(I)	—	5.7×10^{-7}	10.6	−16.1
K(I)	H(I)	2.3	2.3×10^{-8}	7.8	−42.7
H(I)	K(I)	—	1.1×10^{-9}	7.1	−49.0

respectively, d is the ionic jump distance taken[8] as 5 Å, R is the gas constant, and T is taken as 273 K. As the results show (Table 2), D_o, E_a, and ΔS^* values decrease with the decrease in hydrated radii of Na(I), K(I), and H(I). A decrease in ΔS^* values also indicates a greater order of exchange into the metallic form. A higher negative value of ΔS^* for the K(I)–H(I) exchange justifies the higher selectivity for K(I) than for Na(I) as indicated in our previous studies.[3] K_d value of K(I) is greater than that of Na(I) ions.

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References

1) K. G. Varshney, A. A. Khan, and S. Rani, *Colloidal Surf.-Act. Agents,* **25**, 131 (1987).

2) K. G. Varshney, A. A. Khan, and A. R Khan, *React. Kinet. Catal. Lett.,* **40**, No. 2, 319 (1989).

3) K. G. Varshney, A. A. Khan, and A. R. Khan, *Bull. Chem. Soc. Jpn.,* **61**, 3693 (1988).

4) W. Z. Nernst, *Phys. Chem.,* **2**, 613 (1888); **4**, 129 (1889).

5) M. Planck, *Ann. Phys. Chem.,* **39**, 161 (1890).

6) F. Helfferich, "Ion Exchange," McGrow Hill, New York (1962), Chap. 6.

7) K. G. Varshney, Ashfaq R. Khan, Anees Ahmad, and Khwaja Z. Alam, *Colloidal Surf.-Act. Agents,* **59**, 153 (1991).

8) R. M. Barrer, R. F. Bartholomow, and L. V. C. Rees, *J. Phys. Chem. Solids,* **12**, 21 (1961).