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Mechanism of Isotopic Exchange for $Cs^+/{}^*Cs^+$, $Sr^{2+}/{}^*Sr^{2+}$, and $Co^{2+}/{}^*Co^{2+}$ on Cerium(IV) and Tin(IV) Antimonates Particles

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Self-diffusion coefficients ($\overline{D}$) for Cs^+, Sr^{2+}, and Co^{2+} ions in cerium(IV) antimonate and tin(IV) antimonate have been investigated under conditions of particle diffusion and the limited batch technique for these ions in solutions of different acidity. The effect of heat treatment on the rate of isotopic exchange reactions on both materials was also studied. Values for the diffusion coefficients, activation energy, and entropy of activation have been evaluated. The data obtained have been compared with those reported for other organic and inorganic exchangers, which give some information regarding the mechanism of ion exchange on the surface of the ion exchange materials.

Kinetic studies are helpful in understanding the reaction mechanism which a particular system undergoes on the basis of the reaction rate. A measurement of the isotopic exchange rate of cations between ion exchangers and solutions provides fundamental data which are useful for elucidating ion exchange kinetics.[1,2] Such studies on inorganic ion exchange materials so far have been useful in drawing some important conclusions regarding their ion-exchange behavior and potential uses under different conditions.[1,2]

The authors undertook radiochemical experiments to measure the rate of the isotopic exchange of Na^+, Cs^+, and Cl^- in hydrous ceria.[3—5] The self diffusion of Sr^{2+} in hydrous ceria and zirconia were also studied.[6] In addition, self diffusion of Co^{2+} in tin(IV) antimonate was also investigated.[7] Such studies on synthetic inorganic ion exchangers are generally lacking.[1] Further investigations, therefore, should be carried out for a variety of other double salts of polybasic acids in order to understand the ion exchange kinetics of this kind of material.

This paper deals with the rates of the isotopic exchange of Cs^+, Sr^{2+}, and Co^{2+} ions in tin(IV) and cerium(IV) antimonates and the thermodynamic parameters for the exchange are calculated. The results may throw some light on the structure of cerium(IV) and tin(IV) antimonates or generally of double salts as ion exchange materials.

Experimental

All chemicals were of A.R. grade and were used without further purification.

Preparation of Cerium(IV) and Tin(IV) Antimonates. Cerium(IV) antimonate and tin(IV) antimonate were prepared as reported earlier.[7—9]

Self Diffusion Experiments. Kinetic experiments were preformed under particle diffusion control conditions.[2] Both materials, cerium(IV) antimonate and tin(IV) antimonate, heated at 50, 200, and 400 °C were saturated with a $M(NO_3)_x + HNO_3$ solution ($M = Cs^+$, Sr^{2+}, and Co^{2+}) and tagged with respective radioactive elements ($M = {}^{134}Cs$, ${}^{85}Sr$, and ${}^{60}Co$). Each solution had a total metal ion concentration of 0.1 $mol\,dm^{-3}$ and various nitric acid concentrations. The radioactive solid was then put in contact with the same solution used in saturation, except that the solution did not contain the radioactive isotope. Isotopic exchange then occurs, which was followed with time until equilibrium was attained. Since the samples were saturated with solutions of various acidity, isotopic exchange was measured at various loadings of the exchangers. The effect of temperature (30, 45, and 60±1 °C) on the isotopic exchange rates was also studied for the samples heated at 50, 200, and 400 °C in 0.1 $mol\,dm^{-3}$ metal solutions. All the experiments were done at a V/m ratio of 100 $cm^3\,g^{-1}$ (where V is the solution volume, cm^3, and m is the weight of the exchanger, g).

The experiments were performed as before[6,10,11] to follow the rate of exchange with time. The degree of exchange was followed by counting the activity of both solution and solid. The results agreed to ±3% for all reaction times.

The apparent capacity of different cerium(IV) and tin(IV) antimonate samples was determined at different equilibrium pH values by the isotopic dilution method. In these experiments, the solid saturated with inactive metals (Cs^+, Sr^{2+}, and Co^{2+}) is equilibrated with same solution used in its saturation but containing radioactive metals (${}^{134}Cs$, ${}^{85}Sr$, and ${}^{60}Co$, respectively). The capacity is calculated from the distribution of activity between the solution and solid (Table 1).

Analysis. ${}^{134}Cs$, ${}^{85}Sr$, and ${}^{60}Co$, purchased from Amersham, were counted by a NaI(Tl) Scintillation detector connected to an ORTEC assembly.

Results and Discussion

When the isotopic exchange rate is controlled by the diffusion of the ions in spherical particles of the exchangers immersed in a well-stirred solution of approximately infinite volume, the fraction attainment of equilibrium, $F(t)$, can be obtained by solving the following equation:[2]

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{oo} \frac{1}{n^2} \exp(-n_2Bt) \qquad (1)$$

Table 1. Capacity of Cs^+, Sr^{2+}, and Co^{2+} on Cerium(IV) Antimonate and Tin(IV) Antimonate at Different Heating Temperature at 30 °C

Exchange system		Capacity/mequiv g^{-1}					
		Tin(IV) antimonate			Cerium(IV) antimonate		
	pH[a)]	50 °C	200 °C	400 °C	50 °C	200 °C	400 °C
Cs^+	5.88	1.62	1.82	2.06	1.58	1.56	1.69
Sr^{2+}	2.93	0.34	0.31	0.38	0.36	0.33	0.37
Co^{2+}	5.37	0.50	0.51	0.56	0.49	0.42	0.52

a) Accuracy ±0.02.

and

$$B = \pi^2\overline{D}/r^2, \tag{2}$$

where, $\overline{D}$ is the self-diffusion coefficient of the ions in the exchanger, *r* refers to the particles, and n is an integer. When *F(t)* is less than about 0.4, Eq. 1 can be approximated to a simpler form:[12)]

$$F(t) = \frac{6}{r}(\overline{D}t/\pi)^{1/2} \tag{3}$$

The study of the effect of concentration on the rate of exchange for $Cs^+/^*Cs^+$ at 30 °C showed that at concentrations less than 8×10^{-3} mol dm^{-3}, the initial rate of exchange is proportional to $[Cs^+]$. At concentration $>8\times10^{-3}$ mol dm^{-3}, the rates are independent of the metal ion concentration. In $Co^{2+}/^*Co^{2+}$ and $Sr^{2+}/^*Sr^{2+}$ systems, the rates of exchange depend on the concentration for metal ion molarities lower than 10^{-3} mol dm^{-3}. At higher molarities (0.1 mol dm^{-3}) the rate of exchange is independent of the metal ion concentration (generally used in this work) of Cs^+, Sr^{2+}, and Co^{2+}. Hence, particle diffusion is the controlling mechanism and film diffusion can be excluded.[2)]

The plots of *Bt* vs. *t* for $Cs^+/^*Cs^+$ and $Sr^{2+}/^*Sr^{2+}$ exchanges on cerium(IV) and tin(IV) antimonates at different conditions show that straight lines passing through the origin are obtained, these are further proofs of a particle diffusion mechanism. The *Bt*–*t* plots were used instead of Eq. 2, because the fast rate of exchange reaction causes a decrease in the number of experimental points falling within the line of the validity of the equation $[F(t)\leq 0.4]$; due to a technical difficulty.

The effect of particle size on the rate of exchange was studied; straight lines passing through the origin are obtained in all cases, proving a particle diffusion control mechanism. The exchange rate increases with the decrease in particle size, which is in agreement with the fundamental conditions of particle diffusion.

Here, *Bt* values were calculated from the measured values of *F(t)* by using Eq. 4 derived by Reichenberg:[13)]

$$Bt = 2\pi - \frac{\pi^2}{3}F(t) - 2\pi[1 - 1/3\pi F(t)]^{1/2} \tag{4}$$

This equation gives a fairly good approximation in the region where *F(t)* is less than 0.85. Furthermore, Eq. 4 shows that the self diffusion coefficients of the metal ions studies are independent of the concentration in solution; the mechanism of the diffusion of these ions in the cerium(IV) antimonate and tin(IV) antimonate is considered to be unchanged by the composition of the material.

The average values of self-diffusion coefficients for Cs^+ and Sr^{2+} ions on tin(IV) antimonate samples heated at different temperatures at reaction temperature of 30 °C at different acidities are given in Table 2. Table 2 shows also that the values of $\overline{D}$ increases with increasing heating temperature. This can be related to the increase in the crystallinity of tin(IV) antimonate with an increase in heating temperature, as observed from the X-ray diffraction patterns of cerium(IV) antimonate and tin(IV) antimonate.[8)] By increasing treatment temperature, a gradual growth of cerium(IV) antimonate and tin(IV) antimonate particles is expected with possible increase in pore volume. Similar findings were obtained by others.[14,15)]

The decrease of $\overline{D}$ of Cs^+ and Sr^{2+} ions with the increase of their capacities (Table 2) on tin(IV) antimonate is due to the increase of the strength of electrostatic interactions of the counter ions with the exchange sites. The latter increase is due to both the increase of site density (capacity) and the decrease of site acidity; both results lead to an increase of field strength of the exchange sites.[16,17)] A decrease of $\overline{D}$ with capacity was observed for the diffusion of Cl^- in hydrous ceria and zirconia and also for the diffusion of Na^+ and Cs^+ in hydrous zirconia.[11)]

The data in Table 1 show that the ion exchange capacity for Cs^+, Sr^{2+}, and Co^{2+} ions on cerium(IV) antimonate and tin(IV) antimonate heated at 200 °C are slightly decreased and no drastic change occurs in the surface structure and X-ray diffraction patterns, because of the loss of the free water. At 400 °C, it seems that the capacities generally largely increase. Thus the increase in adsorption ability can be explained in terms of the increasing electrostatic force on the adjacent sites by increasing the electron density on the field of sites in the heated sample, due to shrinkage of the distance between adjacent sites. On heating at 600 °C, strongly bonded water is removed and the capacity simultaneously decreases. No ion-exchange behaviour can be observed in tin(IV) antimonate and cerium(IV) antimonate heated at 700 °C.[7)]

The author found that the ideality of the ion exchange is the main mechanism for sorption of the investigated cations on both materials,[7,11)] the selectivity order was $Cs^+>Co^{2+}>Sr^{2+}$ for tin(IV) antimonate and $Sr^{2+}>Co^{2+}>Cs^+$ for cerium(IV) antimonate and its affinity for the monovalent ions is much smaller than that for the polyvalents. The fact that the self-diffusion coefficient of monovalent Cs^+ is higher than those of Sr^{2+} and Co^{2+}, suggests that this may be due to the specific electrostatic interaction of polyvalent cations with the fixed exchanged sites in the exchanger. However, the higher diffusion shown by Co^{2+} as compared to Sr^{2+} may be due to the smaller ionic radius of the former ion.

The $\overline{D}$ for cerium(IV) antimonate is in the order

$$Sr^{2+} > Co^{2+} > Cs^+$$

This may be due to the increase of the negativity of the

Table 2. $\overline{D}$ Values for $Cs^+/^*Cs^+$ and $Sr^{2+}/^*Sr^{2+}$ Exchange on Tin(IV) Antimonate at Various Heating Temperature and Capacities at 30 °C

Exchange system	Particle diameter mm	Heating temperature °C	Concentration mol dm^{-3}	pH$^{a)}$	Capacity mequiv g^{-1}	$\overline{D}$ 10^{-8}cm^2 s^{-1}
$Cs^+/^*Cs^+$	0.2±0.02	50	5×10^{-3}	—	—	0.87
		50	8×10^{-3}	—	—	1.59
		50	0.1	5.88	1.82	1.62
		200		5.88	1.72	3.46
		400		5.88	2.06	4.34
		50	0.1	3.21	1.76	1.23
		200		3.21	1.70	3.69
		400		3.21	1.93	5.69
		50	0.1	1.50	1.57	3.63
		200		1.50	1.50	3.82
		400		1.50	1.74	8.25
$Sr^{2+}/^*Sr^{2+}$	0.2±0.02	50	10^3	—	—	2.07
		50	5×10^{-3}	—	—	2.18
		50	0.1	2.93	0.34	2.20
		200		2.93	0.31	5.50
		400		2.93	0.38	10.21
		50	0.1	2.78	0.36	9.17
		200		2.78	0.33	12.10
		400		2.78	0.37	16.50
		50	0.1	1.02	0.30	11.55
		200		1.02	0.22	13.86
		400		1.02	0.29	16.58

a) Accuracy ±0.02.

entropy of activation, in the same trend where the mobility of the ions decreases with increasing the negativity of the entropy of activation.

The effect of reaction temperature on the isotopic exchange rates was studied for the samples heated at 50, 200, and 400 °C in 0.1 mol dm^{-3} metal ion solutions. It was found that the rate of exchange reactions increased with rising reaction temperature. The self diffusion coefficient values of Cs^+, Sr^{2+}, and Co^{2+} ions at reaction temperatures of 30, 45, and 60 °C are summarized in Tables 3 and 4. When $\log \overline{D}$ was plotted against $1/T$ (Fig. 1), straight lines were obtained, enabling the estimation of the energy of activation (E_a) and the pre-exponential constant (D_o) in the Arrhenius equation

$$\overline{D} = D_o \exp(-E_a/Rt) \qquad (5)$$

The entropy of activation (ΔS^*) can then be calculated from D_o by substituting the equation proposed by Barrer et al.[18)]

$$D_o = 2.72(kTd^2/h)\exp(\Delta S^*/R) \qquad (6)$$

where,

"k" is the Boltzmann constant, T=273 K, d is the average distance between successive positions in the process of diffusion, which is taken as equal to 5 Å, and h is Planck's constant.

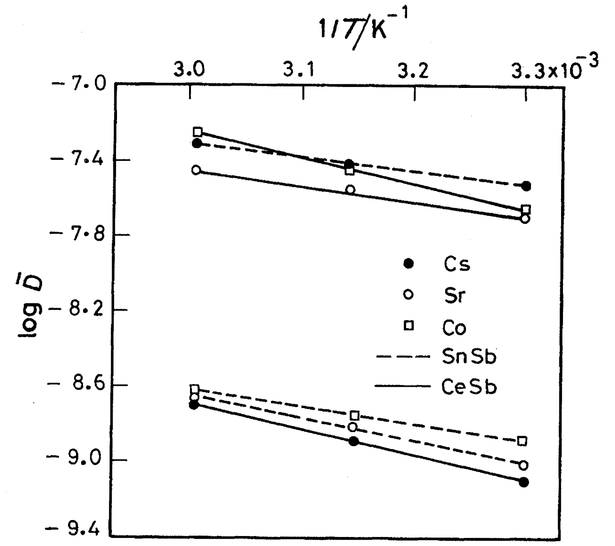

Fig. 1. Dependence of $\log \overline{D}$ on $1/T$ for isotopic exchange of Cs^+, Sr^{2+}, and Co^{2+} in cerium(IV) antimonate and tin(IV) antimonate dried at 50 °C.

The activation energy of the cation diffusion process reflects the ease with which cations can pass through the exchanger particles. The relatively small activation energy val-

Table 3. Self Diffusion Coefficients, Activation Energies, and Entropies of Activation of $\mathrm{Cs^+/^*Cs^+}$, $\mathrm{Sr^{2+}/^*Sr^{2+}}$, and $\mathrm{Co^{2+}/^*Co^{2+}}$ Exchange on Cerium(IV) Antimonate

Exchange system	Heating temp °C	$\bar{D}/10^{-9}$ cm^2 s^{-1}			D_o	E_a	ΔS^*
		30 °C	45 °C	60 °C	cm^2 s^{-1}	kJ mol^{-1}	J mol^{-1} k^{-1}
$\mathrm{Cs^+/^*Cs^+}$	50	0.76	1.34	1.99	1.31×10^{-5}	24.592	−66.39
	200	1.014	1.394	2.02	2.18×10^{-6}	19.333	−81.34
	400	1.394	1.902	2.515	1.25×10^{-6}	17.131	−85.96
$\mathrm{Sr^{2+}/^*Sr^{2+}}$	20	20.7	29.5	36.5	1.59×10^{-5}	16.753	−64.79
	200	23.9	40.7	69.0	3.19×10^{-4}	23.933	−39.89
	400	38.8	64.7	85.8	3.22×10^{-4}	22.737	−39.81
$\mathrm{Co^{2+}/^*Co^{2+}}$	50	22.43	36.23	55.21	2.99×10^{-4}	23.933	−40.42
	200	21.87	34.51	48.31	8.18×10^{-5}	20.729	−51.21
	400	25.90	46.61	86.20	8.21×10^{-3}	31.911	−12.89

Table 4. Self-Diffusion Coefficients, Activation Energies, and Entropies of Activation of $\mathrm{Cs^+/^*Cs^+}$, $\mathrm{Sr^{2+}/^*Sr^{2+}}$, and $\mathrm{Co^{2+}/^*Co^{2+}}$ Exchange on Tin(IV) Antimonate

Exchange system	Heating temp °C	$\bar{D}/10^{-9}$ cm^2 s^{-1}			D_o	E_a	ΔS^*
		30 °C	45 °C	60 °C	cm^2 s^{-1}	kJ mol^{-1}	J mol^{-1} k^{-1}
$\mathrm{Cs^+/^*Cs^+}$	50	32.32	41.20	50.11	5.39×10^{-6}	12.89	−73.82
	200	36.90	56.29	84.40	1.50×10^{-4}	20.94	−46.14
	400	53.30	82.40	121.60	4.46×10^{-4}	22.75	−37.11
$\mathrm{Sr^{2+}/^*Sr^{2+}}$	50	0.92	1.54	2.02	1.11×10^{-6}	17.87	−87.00
	200	1.20	1.82	2.47	3.20×10^{-6}	19.87	−78.15
	400	1.65	2.47	3.42	7.21×10^{-6}	21.11	−71.41
$\mathrm{Co^{2+}/^*Co^{2+}}$ a)	50	1.13	1.69	2.37	2.26×10^{-6}	19.15	−81.06
	200	2.25	3.76	5.63	1.16×10^{-4}	27.35	−48.24
	400	2.91	6.09	2.29	1.29×10^{-3}	32.74	−28.35

a) Ref. 7.

ues given in Tables 3 and 4 for the different cations suggest that the rate is particle diffusion controlled.[12,19—21] These values may be generally compared with those for highly cross-linked resins and many zeolites.[19,22] As mentioned above, the polyvalent cations are expected to interact electrostatically more strongly than $\mathrm{Cs^+}$ [$\mathrm{Sr^{2+}>Cs^+}$] with exchange sites. Besides, the hydration energy and hydrated volumes of $\mathrm{Cs^+}$ are expected to give a relatively low value of E_a for $\mathrm{Cs^+}$. Tables 3 and 4 show that cerium(IV) and tin(IV) antimonates (dried at 50 °C) have some narrow pores that offer relatively more considerable steric difficulties for $\mathrm{Cs^+}$ and $\mathrm{Co^{2+}}$ than for $\mathrm{Sr^{2+}}$. However, the difference in acidity is considerably larger for the materials heated at 50 and 200 °C, compared to those heated at 400 °C. Therefore, the generally higher mobility of all the ions studied in tin(IV) antimonate than in cerium(IV) antimonate (Tables 3 and 4) may be attributed to the differences in pore size and porosity.

The values of the activation energy given in Tables 3 and 4 for the cations studied would also indicate the presence of one or more narrow pores in tin(IV) antimonate and cerium(IV) antimonate heated at 200 and 400 °C which possess relatively more considerable steric difficulties for the mobility of the cations inside the particle. The fact that the mobility of $\mathrm{Cs^+}$, $\mathrm{Sr^{2+}}$, and $\mathrm{Co^{2+}}$ increase with the increase in heating temperature (Tables 3 and 4) could be explained, as has been already mentioned, on the basis of a gradual growth of SnSb particles with possible increase in pore volume.[14,23]

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 channel of the exchanger particles. In general, negative values of ΔS^* have been reported. The negative values for the entropy of activation suggest that, upon exchange of these cations, no significant structure change occur in the cerium(IV) and tin(IV) antimonates.[7] This is thermodynamically supported in Fig. 2, where the activation energy (E_a) was found to decrease with decreasing the entropy change of the system. Thus, the well ordered structure obtained for cerium(IV) antimonate and tin(IV) antimonate with increasing heating temperature from 50—400

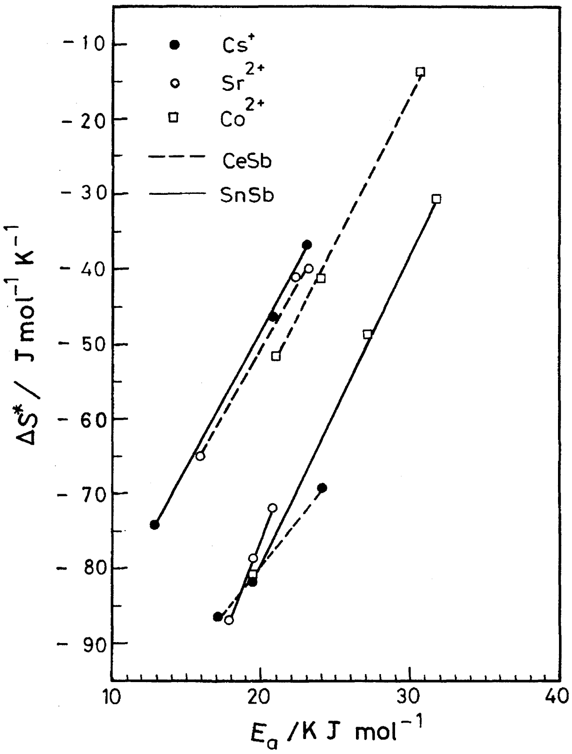

Fig. 2. Variation of ΔS^* vs. E_q for $Cs^+/^*Cs^+$, $Sr^{2+}/^*Sr^{2+}$, and $Co^{2+}/^*Co^{2+}$ exchange in tin(IV) antimonate and cerium(IV) antimonates.

°C is the main factor responsible for decrease of the activation energy of all the ions under investigation, as a result of the diffusion process in a well-ordered structure.[7]

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