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Kinetics of Exchange of Cs^+, Co^{2+} and Sr^{2+} on Synthetic Hydrous Titanium Oxides

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Abstract: In the present work, a study of the kinetics of adsorption of Cs^+, Co^{2+}, and Sr^{2+} on four hydrous titanium oxides, prepared in different media, and designated as Ti-I, Ti-II, Ti-III, and Ti-IV, was carried out. In the aqueous medium, the internal diffusion coefficients, D_i for Cs^+ were found to be equal to 3.7×10^{-9}, 3.7×10^{-9}, 2.3×10^{-9}, and $1.5 - 10^{-9}$ cm^2/s, in Ti-I, Ti-II, Ti-III, and Ti-IV, respectively. For Co^{2+} and Sr^{2+}, these values are equal to 0.96×10^{-9} and 0.64×10^{-9} cm^2/s, respectively for Ti-IV. In Ti-IV, D_i for all ions generally increases on adding methanol or propanol. This is probably due to greater dehydration, leading to faster ion diffusion, and, hence, to a decrease of ion mobility due to stronger interaction with the surface. In all media in Ti-IV, the order: $D_i(Cs^+) > D_i(Co^{2+}) \geq D_i(Sr^{2+})$ was found which is due to a stronger interaction of the bivalent ions with the exchange sites.

Keywords: Inorganic ion exchanges, hydrous oxides, hydrous titanium oxide, kinetics, diffusion coefficient, mixed solvents

INTRODUCTION

Ion exchangers play an important role in atomic energy processing in the separation of fission products. More attention is paid to inorganic ion exchangers due to their resistance to radiation damage. The removal of cesium activity is one of the main goals in the management of liquid waste effluents. Cesium ion is absorbed by many hydrous oxides: hydrous zirconia (1–3) manganese oxide (4), and hydrous titanium oxide (5, 6). Cobalt is a

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heavy metal, which represents an environmental pollutant in both the inactive and radioactive states. Strontium is one of the important elements to be separated from radioactive liquid waste. The behavior of sodium titanate for strontium was investigated by Heinonen et al. (7). Mikahail (8), found that the adsorption of both cesium and cobalt by MnO_2 follows the Freundlich adsorption isotherm. Tracer cobalt can be removed from highly concentrated saline solutions; the distribution coefficients K_d of the radionuclides Cs^+, Sr^{2+}, and Co^{2+} are equal to 4245, 675, and 821 ml/g, respectively.

Kinetics has an important role in the mechanism of ion exchange. However, kinetic studies in nonaqueous and mixed solvents are rather limited and are almost exclusively concerned with ion exchange resins. For inorganic exchangers, Huang, et al. (9) found that $t_{1/2}$ for exchange of K^+ and Ag^+ on the Na^+ form of Linde 13 X zeolite increases in the presence of methanol and ethanol due to a decrease in the mobility of the ions and in the fractional pore volume of the exchanger with solvent uptake.

In hydroxide solutions of Li^+, Na^+, and K^+ on hydrous stannic oxide, the inter-diffusion coefficient D_i decreases in the order propanol > ethanol > methanol (10–12). This indicates that, on going from one alcohol to another, the decrease of ion size is a dominant factor. A considerable replacement of the more retarding OH^- coion in the oxide by Cl^- enhances alkali ion diffusivity. The order of D_i for Li^+ is the same as in the purely hydroxide solutions. With Na^+, this order is primarily the reverse (methanol > ethanol > propanol).

The self-diffusion coefficient of Na^+ (D_i) in hydrous stannic oxide in aqueous and alcoholic solution at different Na^+—capacities displays the expected decrease with capacity, which seems to be much less at relatively high capacities. There is apparently almost no effect with the addition of methanol on D_i, whereas a decrease of D_i, which disappears in relatively high capacity, occurs with the addition of propanol (13).

The self-diffusion coefficients (D_i) of Na^+ generally increase with alcohol concentration. The effect of alcohol addition on ion-solvent interactions is counteracted by the effect of ion—ion interactions in the exchanger, leading to an increase of D_i. The addition of NaCl to the external solution enhances Na^+ diffusivity due to weaker interaction with Cl^- coion inside the oxide pores, or due to the addition of NaCl decreasing the sorption of alcohol by the oxide (14, 15).

EXPERIMENTAL

Reagents, Radioactive Isotopes, and Counting Techniques

All the reagents used were of the analytical grade and distilled water, was used in all preparations. Carrier free chloride solutions of cesium-134, cobalt-60, and strontium-90 were purchased from the Amersham Radiochemical

Center. The γ- activity of the isotopes used was measured using a scintillation probe provided with a NaI (T1) crystal. The scintillation head is connected to a scalar type Rotemeter SR7 made in England. The γ-activity of solutions and/or solid was measured.

Preparation of Hydrous Titanium Oxides

Hydrous titanium oxide gels (hydrous titania or titanic acid) are designated as Ti-I, Ti-II, Ti-III, and Ti-IV. The first three samples (Ti-I, Ti-II, and Ti-III) were prepared as previously described (16), by adding liquid $TiCl_4$ (150 cm^3) to 450 cm^3 of distilled water, followed by adding 2.5 M NaOH dropwise with vigorous stirring. The pH of the solution was adjusted to 4, 7, and 9, respectively. The precipitate was filtered and washed several times with distilled water until it was free of chloride ions and the washings were neutral. The released Cl^- ions were determined as AgCl and was found that each 1g of Ti-I, Ti-II, Ti-III, and Ti-IV contain 0.042, 0.039, 0.03, and 0.031 meq of Cl^- ions. These values of Cl^-ions constitute a very small fraction of the anion exchange capacity. The product was dried at 50°C.

The Ti-IV sample was prepared as described by Abe (17) where the liquid $TiCl_4$ (60 cm^3) was added dropwise to 3 L of distilled water, followed by adding 5 M NH_4OH solution with vigorous stirring to adjust the pH of the solution to 7. Ammonium ions were removed by repeated washing with 0.1 M HCl by centrifugation until free of NH_4^+. The precipitate was washed with distilled water until it was free of Cl^- ions, then was filtered and dried at 50°C for 4 weeks.

The semitransparent gels formed (Ti-I, Ti-II, Ti-III, and Ti-IV) were allowed to break, into different particle sizes, in hot water (80°C). Subsequently, the solid was filtered, redried, sieved to different sizes, and stored over saturated NH_4Cl.

Physicochemical Properties of the Prepared Hydrous Titanium Oxide Samples

The physicochemical properties of the different prepared samples were studied by Ayoub et al. (16), using a scanning electron microscope, SEM, porous texture evaluation, BET method, X-ray diffraction, XRD, infrared analysis, IR, and thermal analysis (TGA and DTA). The microscopic studies have shown that Ti-III has seemingly a higher porosity than Ti-I and Ti-II. Ti-IV seem to be similar to Ti-III but with a rather more porous texture. This is in general agreement with the results of the porous texture evaluation. The latter study gave surface area S_{BET} values of 216, 202, 280, and 272 m^2/g for Ti-I, Ti-II, Ti-III, and Ti-IV, respectively. The micropore volume is equal, respectively, to 0.061, 0.062, 0.081, and 0.089 cm^3/g.

The mesopore volume is 0.149, 0.17, 0.111, and 0.087 cm^3/g and the total pore volume is 0.210, 0.232, 0.192, and 0.176 cm^3/g, respectively.

X-ray diffraction analysis has indicated that all the samples are microcrystalline or very weakly crystalline. The change of the method of preparation, seems to give rise to minor change in the structure of the oxide. The data obtained (16), for the d-spacing corresponding to the observed peaks together with their relative intensities (I/I°) were compared with data from JCPDS—ICDD (Joint Venture Committee of Powder Diffraction System—International Center for Diffraction Data) and found that the investigated samples belong to the anatase type. The ignition loss was found to be 18.4, 18.5, 30.7, and 34.8% for Ti-I, Ti-II, Ti-III, and Ti-IV, respectively (16). This gives rise to the empirical formulae $TiO_2 . 0.82\ H_2O$, $TiO_2 . 0.83\ H_2O$, $TiO_2 . 1.36\ H_2O$, and $TiO_2 . 1.54\ H_2O$, respectively.

Kinetic Measurements and Techniques

The hydrous titania, acting as a H^+-form cation exchanger in basic solutions and as OH^--form anion exchanger in acid solutions, was used as such in the cation exchange kinetic experiments. 0.1 g of the original titania (the four samples) of a given particle diameter was weighed in clean dry vials. 25 ml of 0.01 M CsOH + 0.09 M CsCl and different volume percents of alcohol (30–60% methanol or propanol) were added to the titania samples and the vial was immediately shaken mechanically in a water thermostat at $25 \pm 1^\circ C$. At the desired time, portions of the supernatant solution, were withdrawn, centrifuged, and analyzed for the release of H^+ by titration with standard acid. Also, the solution and/or solid were radiometricly counted. The time of the liquid sample withdrawal was less than 15 seconds and, therefore, the% reaction could be followed at reaction times of as low as to 2 minutes. Duplicates and triplicates of the kinetic experiments were done and the maximum differences observed were within 3%.

The particle diameter of the hydrous titania samples was measured after one week immersions in water, methyl alcohol, and propyl alcohol. No changes in particle diameters were observed due to immersion in these liquids, which shows that hydrous titania samples do not swell in either water or the alcoholic solutions.

The same technique was used in the kinetic measurements with hydrous titania samples and Co^{2+} and Sr^{2+}. 0.1 g of the solid of the given particle diameter was weighed in clean dry vials. 25 ml of 10^{-2} M $CoCl_2$ or $SrCl_2$ at pH 5.56 and 5.8 respectively, and different volumes of alcohol (30–60% methanol or propanol) were added as described above. Co-60 and Sr-90 tracers were added and the exchange rate was followed by measuring the γ-activity.

RESULTS AND DISCUSSION

Kinetics of Exchange of the Different Samples

The variation of Q_t/Q_e (Q_t is the % exchange at time t and Q_e is that at equilibrium) with time are given in Fig. 1 for the uptake of Cs^+ from 0.01 M CsOH + 0.09 M CsCl in aqueous medium (30% methanol, 60% methanol, 30% propanol, and 60% propanol solutions, not represented here for the sake of brevity), for the different titanium oxides and the particle sizes 170 μm and 370 μm; and in Figs. 2 and 3 for the uptake of Co^{2+} and Sr^{2+} from 0.01 M aqueous and alcoholic chloride solutions by Ti-IV of the same particle sizes. The values of Q_e in the different conditions are given in the respective figures.

Preliminary experiments have shown that at CsCl concentration of 0.05–0.09 M, the rate of approach to equilibrium of Cs^+ uptake in both the aqueous and alcoholic solutions was independent of Cs^+ concentration. This rate was, however, slower at 0.01 M CsCl. Figure 1 shows that Cs^+ uptake from 0.1 M Cs^+ (0.01 M CsOH + 0.09 M CsCl) solutions is largely enhanced when the particle size was decreased from 370 to 170 μm. The same effect was observed in the presence of different percent of methanol or propanol.

For Co^{2+} and Sr^{2+}, preliminary experiments have shown that the rate in both the aqueous and alcoholic solutions was independent of concentration in the concentration range 0.008–0.01 M of the chloride salt. Figures 2 and 3

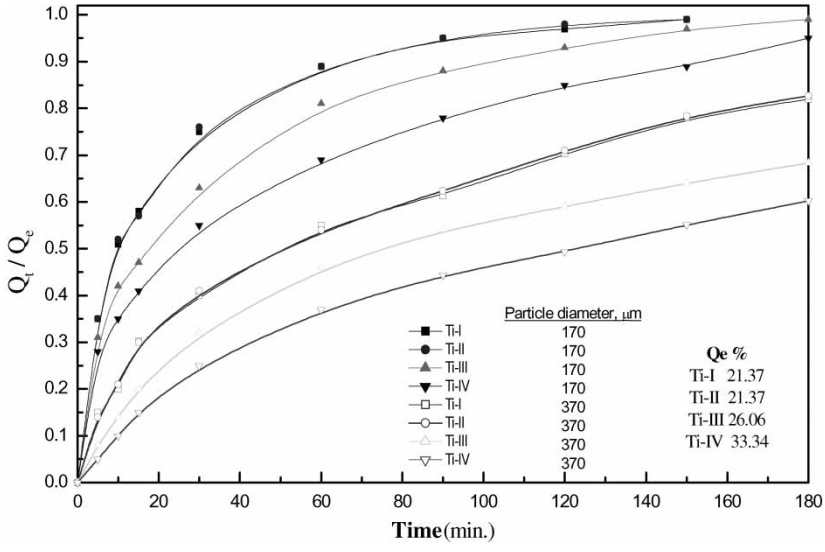

Figure 1. Variation of Q_t/Q_e with time for uptake of Cs^+ ion from aqueous (0.01 MCsOH + 0.09 M Cscl) solution by different particle sizes.

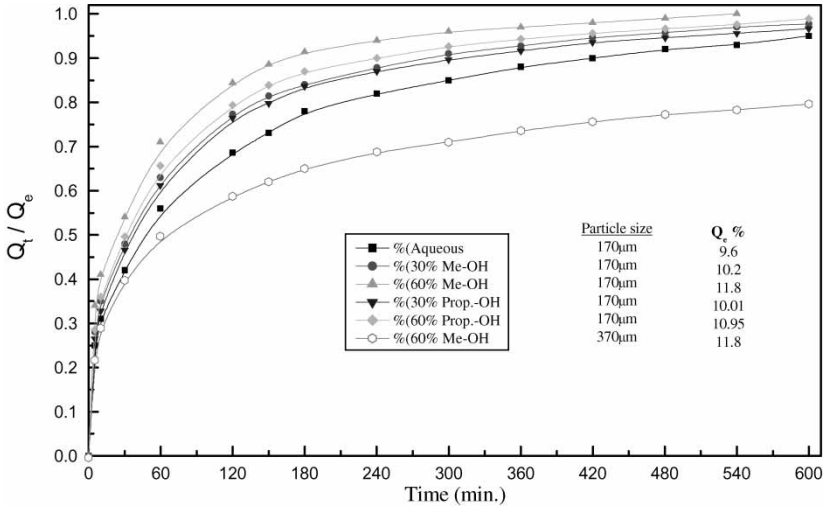

Figure 2. Variation of Q_t/Q_e with time for Co^{2+} ion uptake from aqueous and alcoholic 10^{-2} M $CoCl_2$ solutions on sample Ti-IV of different particle sizes.

show that, as in the case of Cs^+, Co^{2+}, and Sr^{2+} uptake is greatly enhanced by decreasing the particle size from 370 μm to 170 μm. Figures 1–3 show that in all cases, the addition of alcohol seems to enhance the exchange reaction of all the studied ions (Cs^+, Co^{2+}, and Sr^{2+}).

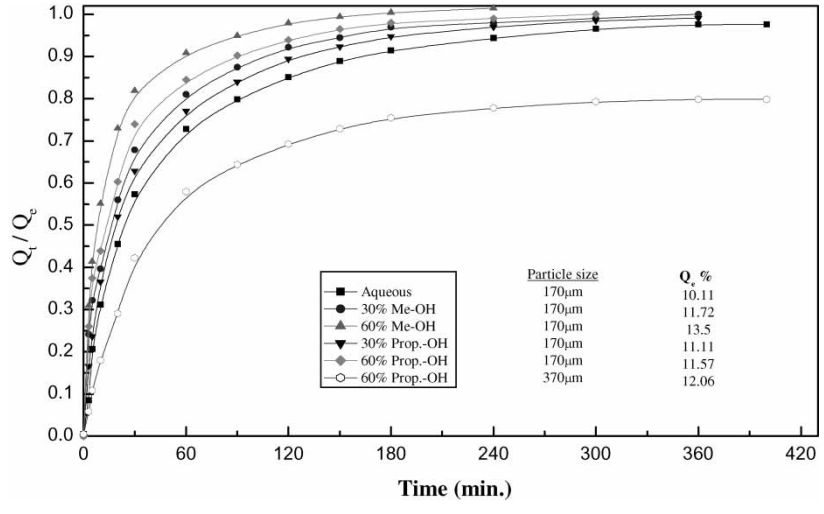

Figure 3. Variation of Q_t/Q_e with time for Sr^{2+} ion uptake from aqueous and alcoholic 10^{-2} M $SrCl_2$ solutions on sample Ti-IV of different particle sizes.

The fact that in the same experiments, the exchange rate of Cs^+, Co^{2+}, and Sr^{2+} by hydrous titania in the aqueous and alcoholic solutions is independent of electrolyte concentration and that it increases greatly with decrease of particle size points to a particle diffusion control mechanism in these solutions. At lower concentrations, as preliminary experiments have shown in the case of 0.01 M CsOH + 0.01 M CsCl solutions, the sorption rate depends on concentration.

The following equation may be used in case of particle diffusion control (18).

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

where, Q_t is the % exchange at time t, Q_e is that at equilibrium, $B = \pi^2 D_i/r^2$, D_i is the effective diffusion coefficient, r is the particle radius, n is an integer number. The equation applies when the exchanger is largely transformed from one cationic form to the other (19), which is the case in the present work.

According to the above equation, if Bt, where $B = \pi^2 D_i/r^2$, is plotted against t, a straight line passing through the origin is obtained and D_i can be calculated from its slope; Bt is a mathematical function of Q_t/Q_e and it was calculated and tabulated by Reichenberg (20).

The plots of Bt versus t for Cs^+exchange on hydrous titania are given in Fig. 4 in aqueous solution, while those for different alcohols are given in Figs. 5–8. Figures 9 and 10 represent the plots for Co^{2+} and Sr^{2+} exchanges in different conditions (alcohols and particle sizes). Figures 4–10

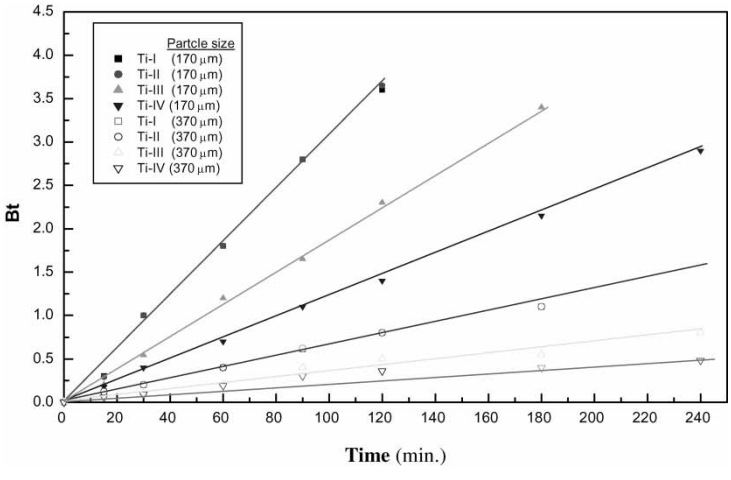

Figure 4. Plot of Bt against time for uptake of Cs^+ ion from aqueous (0.01 M CsoH + 0.09 M CsCl) solution by different samples of hydrous titanium oxides of different particle sizes.

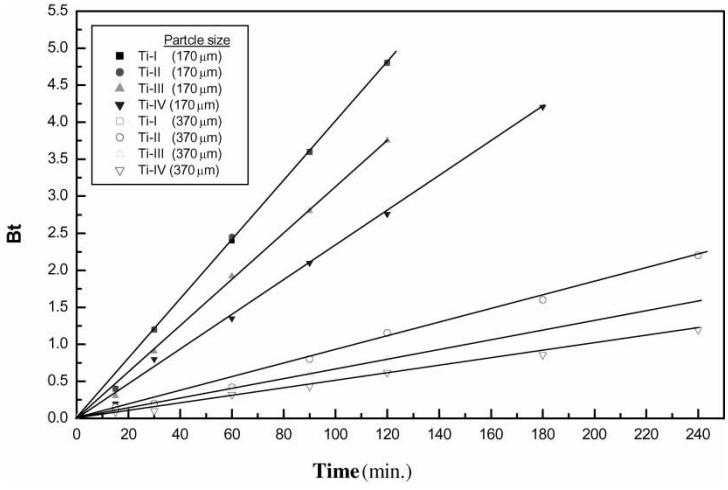

Figure 5. Plot of Bt against time for of Cs^+ ion from 30% methanol (0.01 M CsoH + 0.09 MCsCl) solution by different samples of hydrous trianium oxides particle sizes.

show that straight lines are obtained in all cases and for different conditions, which indicates that, under the given respective conditions, mono-and bivalent cation exchange on hydrous titania is particle diffusion controlled. Particle diffusion control at similar concentrations has been found also in case of

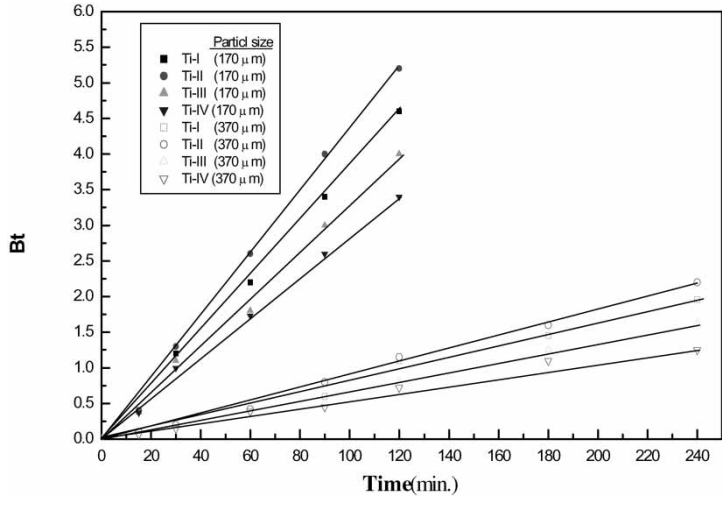

Figure 6. Plot of Bt against time for uptake of Cs^+ ion from 60% methanol (0.01 M CsOH + 0.09 M CsCl) solution by different samples of hydrous titanium oxides of different particle sizes.

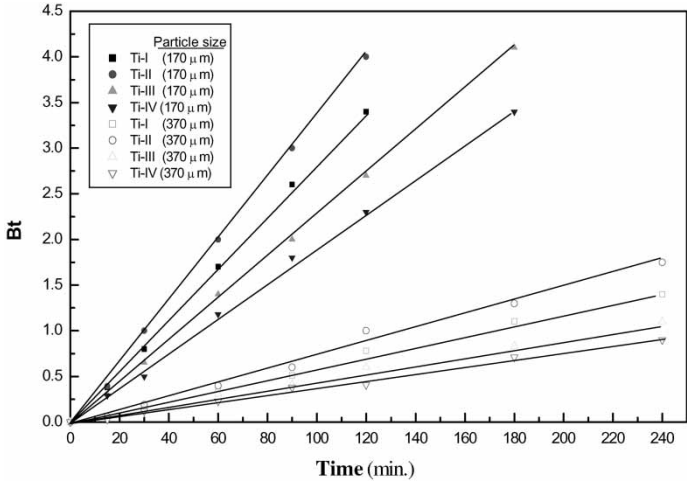

Figure 7. Plot of Bt against time for uptake of Cs^+ ion from 30% propanol (0.01 M CsOH + 0.09 M CsCl) solution by different samples of hydrous titanium oxides of different particle sizes.

thoria (21), titania (22), zirconia (1) and ceria (19). Also, Yacoub et al. (23) have been studying the kinetics of exchange with respect to Ni^{2+} ions and they found that a particle diffusion mechanism is partly or completely responsible for the rate of exchange. For strong acid organic resins (18), particle

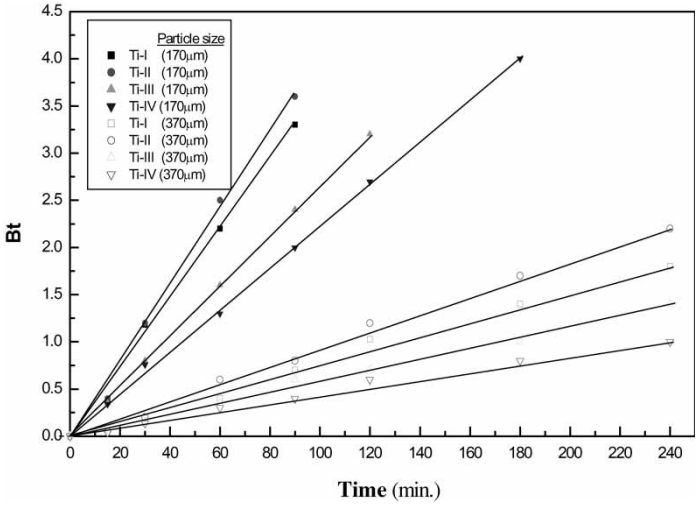

Figure 8. Plot of Bt against time for uptake of Cs^+ ion from 60% Propanol (0.01 M CsOH + 0.09 M CsCl) solution by different samples of hydrous titanium oxides of different particle sizes.

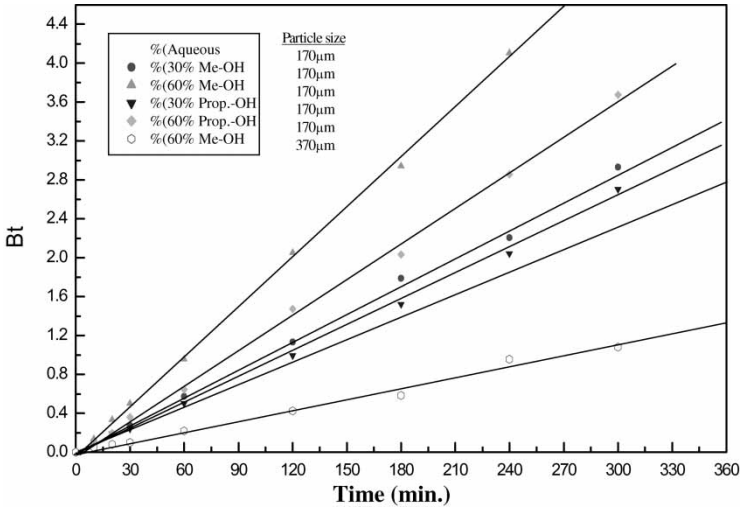

Figure 9. Plot of Bt against time for Co^{2+} ion uptake at 25°C from aqueous and alcoholic 10^{-2} M $CoCl_2$ solution on sample Ti-IV of different particle sizes.

diffusion control is the main mechanism at solution concentrations $\geq$0.1 M, while film diffusion control is the main mechanism at concentrations $\leq$0.003 M. At intermediate concentrations, both film and particle diffusion are rate controlling.

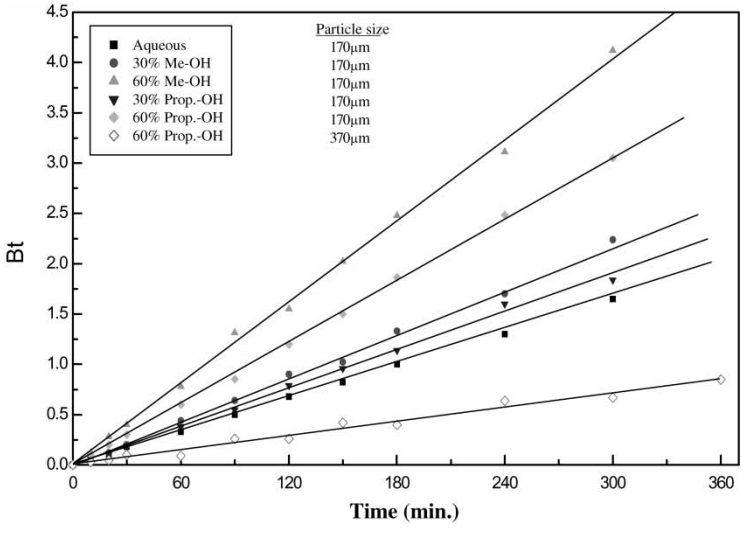

Figure 10. Plot of Bt with time for Sr^{2+} ion uptake at 25°C from aqueous and alcoholic 10^{-2} M $SrCl_2$ solution on sample Ti-IV of different particle sizes.

The values of the effective diffusion coefficients (D_i) of the Cs^+–H^+ systems, calculated from the data in the figures, are given for 25°C in Table 1, while those of Co^{2+}–H^+ and Sr^{2+}–H^+ systems are given at 25°C in Table 2 for the different media, and particle diameters. Tables 1 and 2 show that almost the same values of D_i are obtained for the different particle sizes. This is further proof of particle diffusion control where the rate of exchange, according to Equation (1), is proportional to $1/r^2$.

Tables 1 and 2 show a general increase of D_i of Cs^+, Co^{2+}, and Sr^{2+} on the addition of alcohol. Alcohol imbibition, which is deduced to occur in all cases, would lead to a decrease in D_i due to a stronger interaction of the

Table 1. Effective diffusion coefficients for Cs^+ ions in different hydrous titanium oxides in various media at 25°C ± 1°C

	$D_i \times 10^9$ cm^2/s	
	0.01 M CsOH + 0.09 M CsCl	
	Particle diameter	
Sample	170 μm	370 μm
Aqueous solution		
Ti-I	3.7	3.7
Ti-II	3.7	3.7
Ti-III	2.3	2.3
Ti-IV	1.5	1.5
30% Methanol		
Ti-I	4.9	4.9
Ti-II	4.9	4.9
Ti-III	3.8	3.9
Ti-IV	2.8	2.9
60% Methanol		
Ti-I	5.3	5.3
Ti-II	4.6	4.5
Ti-III	3.9	4.0
Ti-IV	3.5	3.6
30% Propanol		
Ti-I	4.2	4.2
Ti-II	3.5	3.5
Ti-III	2.8	2.8
Ti-IV	2.3	2.2
60% Propanol		
Ti-I	4.9	4.9
Ti-II	4.5	4.5
Ti-III	3.1	3.6
Ti-IV	2.7	2.6

Table 2. Effective diffusion coefficients of Co^{2+} and Sr^{2+} ions in hydrous titanium oxide(Ti-IV) in various media at 25°C ± 1°C

		$D_i \times 10^9$ cm^2/s	
		Particle diameter	
Ion	Media	170 μm	370 μm
Co^{2+}	Aqueous	0.93	0.98
	30% methanol	1.02	—
	60% methanol	2.20	2.26
	30% propanol	1.07	—
	60% propanol	1.45	1.51
Sr^{2+}	Aqueous	0.68	0.60
	30% methanol	0.85	—
	60% methanol	1.55	1.68
	30% propanol	0.78	—
	60% propanol	1.29	1.29

exchange ions with the exchanger matrix (24). The increase of D_i on adding alcohol may, therefore, be attributed to the increased dehydration of ions in the presence of the alcohols. This leads to smaller, and hence faster diffusing ions, a factor which outweighs the effect of a stronger interaction with the exchanger matrix.

For Ti-I, Table 1 shows that D_i of Cs^+ decreases in the order: 60% methanol >30% methanol >60% propanol >30% propanol >aqueous. For Ti-II, the order is 30% methanol ~ 60% methanol ~ 60% propanol >aqueous >30% propanol. For Ti-III, it is: 60% methanol >30% methanol >60% propanol >30% propanol >aqueous. For Ti-IV, it is: 60% methanol >30% methanol ~60% propanol >30% propanol >aqueous.

For Co^{2+}, the order of D_i in Ti-IV (Table 2) is almost: 60% methanol >60% propanol >30% propanol ~ 30% methanol >aqueous. For Sr^{2+}, it is: 60% methanol >60% propanol >30% methanol >30% propanol >aqueous (Table 2).

Thus, the order of the effect of alcohol on D_i is only slightly different for the different ions and different samples. Generally speaking, the effect of methanol on enhancement of ion mobility is greater than that of propanol. The increase in alcohol concentration generally leads to an increase in D_i.

It was deduced in the capacity study (16) that imbibition of propanol, having a lower dielectric constant than methanol, leads to a lower dielectric constant in the oxide. Therefore, inside the oxide, greater dehydration and, hence, a smaller size of diffusing ions is expected in case of propanol. This factor, which would have led to a higher D_i in case of propanol, is

Table 3. Surface characteristics of different hydrous titanium oxide samples

Sample	S_{BET} m^2/g	V_{mic} cm^3/g	V_{meso} cm^3/g	V_{tol} cm^3/g
Ti-I	216	0.061	0.149	0.210
Ti-II	202	0.062	0.17	0.232
Ti-III	280	0.081	0.111	0.192
Ti-IV	272	0.089	0.087	0.176

counteracted by the stronger interaction with the exchanger matrix in the case of this alcohol. The higher D_i with methanol, compared to propanol, would be due to the relatively higher effect of the latter alcohol in increasing the strength of interaction with the exchange sites. The generally higher ion mobility at a higher alcohol concentration can be attributed to a higher dehydration.

Comparing the results of D_i of Cs^+ in the different titania samples, the following order is generally observed: Ti-I$\geq$Ti-II$>$Ti-III$>$Ti-IV. This order may, at least partly, be interpreted on the basis of the amount of pores in the different samples. This amount may roughly be related to the micropore volume. The micropore volume decreases in the following order (Table 3): Ti-IV $>$Ti-III $>$Ti-II $\sim$ Ti-I. The more micropores in the samples the lower is D_i as the ions must pass through more of the narrow paths before exchange can occur.

Tables (1 and 2) show that in all media, D_i in Ti-IV has the following order for the different ions: $Cs^+ > Co^{2+} \geq Sr^{2+}$. The higher $D_i$for Cs^+, compared to Co^{2+} and Sr^{2+}, can be attributed to a stronger interaction of the bivalent ions with the exchange sites. The rather similar D_i for Co^{2+} and Sr^{2+} ions may be due to more dehydration of Co^{2+}, leading to higher mobility than Sr^{2+}, balancing it stronger interaction with the surface, which leads to the reverse effect.

Comparing the obtained results Table 1 and Table 2 with other published results (5, 15, 19, 25) indicate that the rate of ion exchange on hydrous titania is much lower than that on strong acid resins but comparable with that on weak-acid resins.

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