3456 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3456—3459 (1975) [Vol. 48, No. 12

Kinetics of Ion Exchange in the Chelating Resin Dowex A-1

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(Received April 1, 1975)

The kinetics of ion exchanges of Ag^+, Zn^{2+} and Cr^{3+} at extremely low concentrations on the chelating resin Dowex A-1 has been studied by means of finite volume method. The rate of exchanges for both Ag^+ and Zn^{2+} is dependent on the ionic strength, particle size of the resin and reaction temperature. At higher ionic strength (0.1—0.05) the kinetics is controlled by particle diffusion, whereas at lower ionic one (0.01—0.001) film diffusion is predominant. The apparent activation energy obtained is 3.84 kcal/mol for Ag^+ and 3.91 kcal/mol for Zn^{2+}. The exchange rate of Cr^{3+} obeys a first-order rate equation independent of the ionic strength and particle size of the resin. The apparent activation energy is 15.5 kcal/mol. These results support the view that the rate-determining step of this reaction is chelate formation reaction.

It has long been established that the ion exchange reaction in the synthetic cation exchange resin is controlled either by film or by particle diffusion.[1] Since the chelating resin with iminodiacetic acid as the functional group was prepared by Moris *et al.*,[2] increasing interest has been paid to the kinetic behavior of the resin. Upon studying the exchange kinetics of a series of cations such as Na^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+} and Cu^{2+} in Dowex A-1, Turse and Rieman[3] concluded that the rate-determining step is particle diffusion for cations which do not form chelate with the functional group, while in the case of cations which chelate with it the slowest step is a second-order chemical reaction. However, Schwartz *et al.*[4] reported that ion exchanges of Na^+, Co^{2+} and Zn^{2+} in this resin are controlled by particle diffusion. Varon and Rieman[5] reinvestigate this problem and concluded that the slowest step is particle diffusion. The authors found that exchanges of Ce^{3+} and Pu^{4+} in Dowex A-1 are controlled by a first-order chemical reaction.[6,7]

In this paper, an attempt was made to establish the kinetic behavior of this resin and to elucidate the possibility of the chemical reaction, *i.e.* chelate formation reaction between the metal ion and the functional group, being the rate-determining step with the use of Ag^+, Zn^{2+} and Cr^{3+} at extremely low concentrations.

Experimental

Materials. Dowex A-1 (crosslinked polystyrene matrix with iminodiacetic acid as the functional group, DVB content; *ca.* 1%, Dow Chemical) was used. The resin was treated with 2 M NaOH and 2 M HNO_3 three times in a column. After conversion into the sodium form, the resin was washed with distilled water until the effluent came to have the same composition as that of the influent. By subjecting the resin to the wet elutriation method, resin beads of a constant particle size were obtained. The mean particle radius was determined microscopically with a calibrated eye piece ocular. The quantity of iminodiacetic acid per unit weight of the resin was determinated by putting 300 mg of the resin (in the hydrogen form) into contact with 100 ml of 0.1 M NaOH in a 200 ml flask. When ion exchange equilibrium was reached, the supernatant solution was filtered, and free hydroxide was titrated with 0.1 M HCl. The capaicty obtained was 2.29±0.24 mM/g resin. Radionuclides used were $^{51}CrCl_3$(8.8×10^4 mCi/g Cr), $^{65}ZnCl_2$ (7.4×10^2 mCi/g Zn), and $^{110m}AgNO_3$(1.2×10^3 mCi/g Ag) from the Radiochemical Centre, Amersham. The radiochemical purity of these nuclides was confirmed by γ-ray spectrometer using a Ge(Li) detector, no other peaks greater than 0.1% of the expected predominant peak being observed. Cr(III) was separately purified from Cr(VI) by adsorbing Cr(III) onto the cation exchanger(Dowex 50W×8), then desorbing it from the resin by eluting with 0.5 M HNO_3. The chemical form of Zn^{2+} was converted into the nitrate by the ion exchange method. Reagent grade chemicals were used without further purification.

Procedure. The batch method was used throughout the work. A three-necked flask containing 300 mg of the resin and 400 ml of the solution adjusted to pH 4.5 and to prescribed ionic strength ($NaNO_3$), was submerged in the thermostatically controlled water bath. From the requirement in the heterogeneous reaction system, the whole reaction system was vigorously stirred (400 rpm). This rotation speed was high enough to neglect the effect of agitation on the rate of exchange reaction. After thermal equilibrium was attained, a fixed volume of the solution containing a radionuclide was added to the reaction system to initiate the reaction. At each preset time interval, 100 μl of the solution was pipetted out for measurement of radioactivity. Even though the volume of reaction system decreased gradually owing to the fact that a definite volume of it has to be removed at preset time intervals, no correction was made for this decrease since the amount of the solution taken out was negligibly small as compared with that of the reaction system.

The radioactivity of the sample was determined with a conventional scintillation counter combined with NaI(Tl) detector.

The molar concentration of each metal ion was determined by the measured radioactivity obtained with a 2π-proportional counter and the specific activity of the corresponding radionuclide.

Results and Discussion

Kinetic Equation. Since the concentration of the adsorbing ion is extremely low, the changes in composition of the resin and the external solution remain insignificant. In such a system the conventional rate law for an isotope exchange reaction is valid.[8] The kinetic equation[9] for an exchange reaction controlled by film diffusion under the conditions of finite volume is

$$U(t) = 1 - \exp\left(\frac{-3Dt(\bar{C}\bar{V}+VC)}{r\delta\bar{C}V}\right) \tag{1}$$

where $U(t)$ is the fractional attainment of equilibrium,

D the diffusion coefficient, r the radius of resin beads, δ the thickness of the film, C and $\bar{C}$ are the equilibrium concentrations in solution of volume V and in resin of volume $\bar{V}$, respectively.

Similarly for a particle diffusion controlled exchange with the finite volume condition, the kinetic equation is given by the Paterson' equation:[10)]

$$U(t) = 1 - \frac{2}{3w}\sum_{n=1}^{\infty}\frac{\exp(-S_n{}^2\tau)}{1+S_n{}^2/9w(w+1)} \tag{2}$$

where $w=\bar{C}\bar{V}/CV$, $\tau=D\ t/r^2$, S_n are the roots of equation: $S_n \cot S_n=1+S_n^2/3w$. Under the experimental conditions, the volume of the solution is significantly larger than that of the resin, hence this system may be taken as semi-finite. Equation (2) can be approximated by:[11,12)]

$$U(t) = \frac{6Q_0\sqrt{Dt}}{r(Q_0-Q_\infty)\sqrt{\pi}} \tag{3}$$

where Q_0 is the amount of functional group in the reaction system, Q_∞ is the amount of exchange at equilibrium. The deviation from the linearity between $U(t)$ and $t^{1/2}$ is less than 2%, if $U(t)$ does not exceed *ca.* 0.5.

For an exchange reaction controlled by a chemical reaction, the rate is expressed by a conventional rate equation for a chemical reaction instead of such equation as Eqs. (1), (2) and (3) derived from the Fick diffusion law. Taking into consideration the fact that the amount of functional group in the reaction system is significantly larger than that of exchanging ion, this reaction can be regarded as first-order with respect to the exchanging ion.[13)] The rate equation is

$$\log\left(\frac{Q_1}{Q_1-Q_t}\right) = kt/2.303 \tag{4}$$

where Q_1 is the initial amount of the exchanging ion, Q_t the amount of exchange at time t, and k the rate constant. It was assumed that the reaction in the chelating resin was controlled either by diffusion (film or particle) or by a pseudo-first-order chemical reaction.

Diffusion Controlled Kinetics. Equation (1) predicts that if the rate-determining step is film diffusion, $-\log[1-U(t)]$ is directly proportional to the reaction time, and inversely to the particle radius and the film thickness. The film thickness decreases with an increase in the ionic strength. Thus the rate of exchange reaction increases with increasing ionic strength.[14)] From Eq. (3), we see that $U(t)$ in the reaction controlled by particle diffusion is proportional to the square root of the time, and inversely to the particle radius.

The kinetics of exchanges of $Ag^+(1.5\times10^{-8}\ M)$ and $Zn^{2+}(1.6\times10^{-8}\ M)$ in the solution for Na^+ in the resin was studied as a function of the ionic strength. The results are given in Figs. 1 and 2 in which $U(t)$ is plotted against $t^{1/2}$. We see that at high ionic strength (0.1—0.05) a linear relationship is obtained for both ions, while at low ionic strength (0.01—0.001) no linearity is obtained in both cases. However, when the results are plotted in the form of $-\log[1-U(t)]$ *vs.* t, straight lines passing through the origin are obtained in both cases (Fig. 3). The rate of exchange increases with increasing ionic strength.

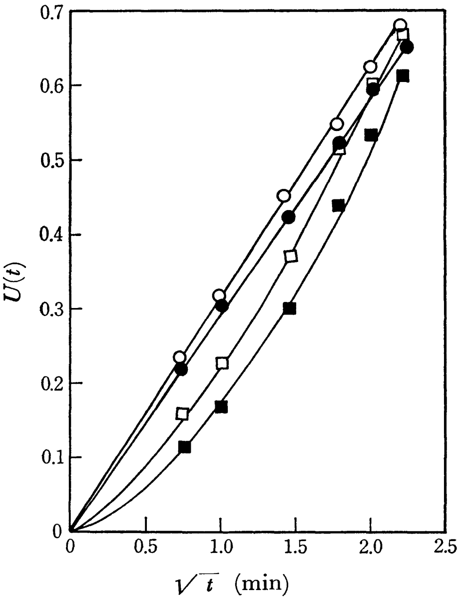

Fig. 1. Plots of $U(t)$ *vs.* $t^{1/2}$ for an ion exchange of Ag^+ on Dowex A-1 in the solutions of different ionic strength 25 °C (radius of the resin particle: 0.10 mm).
μ=○: 0.1, ●: 0.05, □: 0.01, ■: 0.001.

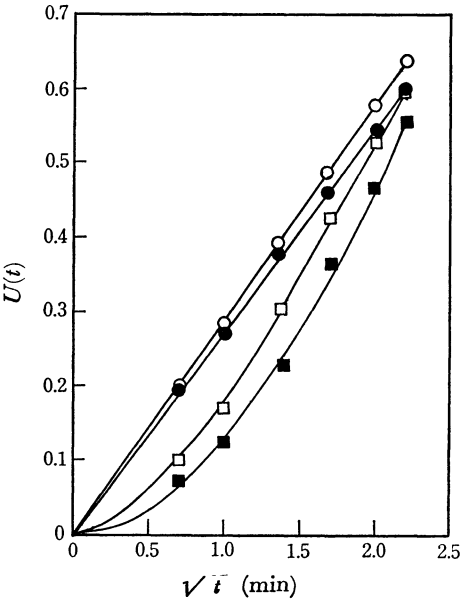

Fig. 2. Plots of $U(t)$ *vs.* $t^{1/2}$ for an ion exchange of Zn^{2+} on Dowex A-1 in the solutions of different ionic strength 25 °C (radius of the resin particle: 0.10 mm).
μ=○: 0.1, ●: 0.05, □: 0.01, ■: 0.001.

A small ionic strength effect can also be observed in the case of high ionic strength, *i.e.*, an increasing rate of exchange with an increase in the ionic strength (Figs. 1 and 2). The rate of exchange controlled by particle diffusion should also increase along with ionic strength, provided that the resin volume remains unchanged. According to Nikolaev's loose quasi-crystal model,[15,16)] freely moving ions, cations and gegenions

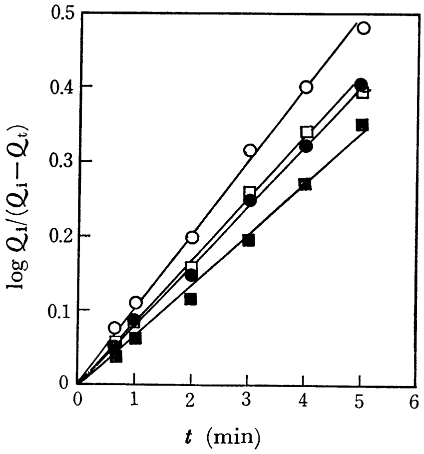

Fig. 3. Plots of $\log Q_i/(Q_i-Q_t)$ *vs.* t for ion exchanges of Ag^+ and Zn^{2+} on Dowex A-1 in the solutions of lower ionic strength, 25 °C (radius of the resin particle: 0.10 mm)
○: Ag^+, $\mu=0.01$; ●: Ag^+, $\mu=0.001$.
□: Zn^{2+}, $\mu=0.01$; ■: Zn^{2+} $\mu=0.001$.

present in the resin phase distort and diminish the depth of the potential well. The rate of diffusion of the ion which oscillates in a potential well a near the functional group, thus increases with an increase in ionic strength.

The rate-determining step of exchanges for both Ag^+ and Zn^{2+} changes from film to particle diffusion with increasing ionic strength. This may be explained as follows. In a range of lower ionic strength, the rate of diffusion through film is retarded by the Donnan exclusion, becoming significantly slow as compared with that of particle diffusion. With increasing ionic strength the Donnan potential and the film thickness might be sufficiently reduced to make the rate of diffusion through film by far greater than that of particle diffusion.

Table 1 shows the effect of the particle radius on the rate of exchange. In the cases of Ag^+ and Zn^{2+}, the half time of equilibrium increases with an increase in particle size. It seems that the effect of increasing particle radius on the exchange rate is nearly as large as that expected from Eq. (1) under the condition of low ionic strength, and from Eq. (3) under the condition of high ionic strength, within the over-all experimental error of *ca.* 10%.

Thus it could be concluded that the rates of exchange for both Ag^+ and Zn^{2+} are governed by film diffusion at a low ionic strength, and by particle diffusion at a high ionic strength.

Table 1. Effect of the radius of the resin particle (r) on the half time of equilibrium (τ)

Ion	$\mu(NaNO_3)$	r(mm)	τ(min)
Ag^+	0.1	0.10	2.6
Ag^+	0.1	0.13	4.2
Ag^+	0.001	0.10	3.3
Ag^+	0·001	0.13	4.3
Zn^{2+}	0.1	0.10	2.9
Zn^{2+}	0.1	0.13	4.7
Zn^{2+}	0.001	0.10	3.7
Zn^{2+}	0.001	0.13	4.7

Chemical Reaction Controlled Kinetics. The kinetics of exchange of $Cr^{3+}(1.5\times10^{-8}\,M)$ in the solution for Na^+ in the resin was studied, and the results are given in Table 2. It can be seen that the relationship between $\log[Q_i/(Q_i-Q_t)]$ or $-\log[1-U(t)]$ and t is linear corresponding to Eq. (4) or to Eq. (1), no linearity being obtained in $U(t)$-t relation. Each value of $\log[Q_i/Q_i-Q_t)]$ at the corresponding time does not so much differ from that of $-\log[1-U(t)]$ (Table 2). This makes it difficult to determine which mechanism is operating as the rate-determining step.

Table 2. Rate of an ion exchange of Cr^{3+} on Dowex A-1 (25 °C, $\mu=0.1$, radius of the resin particle; 0.10 mm)

t(min)	$U(t)$	$\log Q_i/(Q_i-Q_t)$	$-\log[1-U(t)]$
1.00	0.109	0.049	0.050
2.00	0.193	0.091	0.093
3.00	0.306	0.155	0.159
4.00	0.370	0.196	0.201
5.00	0.433	0.238	0.246
6.00	0.505	0.297	0.305

For the sake of clarification, the effects of the ionic strength (0.1—0.0001) and the particle radius (0.10—0.13 mm) on the rate of exchange reaction were examined. The rate of exchange is independent of both the particle radius and the ionic strength over the ranges investigated. If the exchange reaction is controlled by film diffusion, the rate should depend on these factors. Thus it might be concluded that the rate of exchange of Cr^{3+} in the resin should be controlled by a pseudo-first-order chemical reaction.

The effect of temperature on the rate of exchange can also be expected to afford a criterion of mechanism, since the activation energy for an exchange controlled by diffusion is supposed to be distinctly lower than that for the chelate formation reaction. This is

Table 3. Influence of the reaction temperature on the diffusion coefficient for exchanges of Ag^+ and Zn^{2+} (particle diffusion) and the rate constants for an exchange of Cr^{3+}, $\mu=0.1$, radius of the resin particle; 0.10 mm.

Ion	Temperature (°C)	$D(cm^2/s)$	$k(s^{-1})$	E_a(kcal/mol)
Ag^+	15	1.13×10^{-8}		3.84
	20	1.26×10^{-8}		
	25	1.41×10^{-8}		
	30	1.56×10^{-8}		
Zn^{2+}	15	9.39×10^{-9}		3.91
	20	1.07×10^{-8}		
	25	1.20×10^{-8}		
	30	1.34×10^{-8}		
Cr^{3+}	15		7.68×10^{-4}	15.5
	20		1.21×10^{-3}	
	25		1.88×10^{-3}	
	30		2.89×10^{-3}	

certainly the case with such metal ions as Ce^{3+} and Pu^{4+} adsorbed onto the Dowex A-1, where the apparent activation energy is about 14—20 kcal/mol, whereas that of most ions taking part in particle diffusion is about 4—6 kcal/mol. Table 3 shows the rate constant for an exchange of Cr^{3+} and the diffusion coefficient (particle diffusion) for exchanges of Ag^+ and Zn^{2+}, depending on the temperature, and the apparent activation energy obtained from the Arrhenius plots. The apparent activation energy for an exchange of Cr^{3+} is higher than that for exchanges of both Ag^+ and Zn^{2+} which are controlled by particle diffusion.

From the fact that Cr^{3+} is inert in the chelate formation reaction,[17] it is reasonable to suppose that the rate of chelate formation reaction between Cr^{3+} and iminodiacetate is sufficiently smaller than that of either film or particle diffusion.

The results also support the view that the rate-determining step of this reaction is chelate formation reaction.

Conclusion. The results of kinetic studies on Dowex A-1 given by various authours might be summarized as follows.

(1) The exchange reactions of univalent and divalent metal ions are controlled either by film or particle diffusion except for the cations which are inert in the chelate formation reaction such as Ni^{2+} and V^{2+}.

(2) The exchange reactions of multivalent and other ions which are inert in the chelate formation reaction are controlled by chemical reaction.

The kinetic behavior of Dowex A-1 is similar to that of Bio-Rex 63 (containing phosphonic acid as a functional group, Bio Rad Laboratories).[18]

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