Kinetics of ion exchange in binary and ternary systems using strongly acidic cation exchanger: Part 1—The mechanisms of ion exchange processes and diffusion coefficients in binary systems

Song Yinjie & Zhao Aimin*

Department of Modern Physics, Lanzhou University, Lanzhou, 730000, Gansu Province, P R China

The three-necked flask technique has been employed to study the kinetics of ion exchange in the binary systems of $H^+ - Na^+$, $H^+ - UO_2^{2+}$ and $Na^+ - UO_2^{2+}$. The kinetic curves are obtained with changing concentration of bulk solution, rate of stirring, temperature and resin radius. The mechanisms of ion exchange in binary systems have been reported, and the diffusion coefficients for all counter ions in the systems are obtained.

As ion exchange became established as a tool in laboratory and in industry, it was studied chiefly by practical chemists interested in effects and performance rather than mechanisms and kinetics[1]. But interest in ion-exchange operations in industry is increasing as their field of application expands. Industrial ion-exchange equipment is in most cases empirically designed, due to the absence of available information about ion exchange mechanisms[2]. Therefore, it would be very interesting to establish a method of investigation on the kinetics of both ion exchange and adsorption.

Actually, the studies on the kinetics of ion exchange have been made recently, and most of the theoretical treatments was restricted to exchanges of two given counter-ion species[3-6] and even to isotopic ion exchange reactions[7,8] because binary systems may be considered as the most traditional objects of investigations in the field of ion exchange. Also the studies on the mechanisms of isotopic ion exchange reactions can provide some novel knowledge of the microscopic behaviours of various transport phenomena.

Ion exchange involves, as a rule, a solid (sometimes liquid) ion exchanger and a liquid solution. The process of ions in solution exchanged with those in the resin is a heterogeneous reaction between solid and liquid phases. There are a number of sequential processes that determine the rate of reaction: (i) diffusion of ions through the liquid film surrounding the particle, (ii) diffusion of ions through the polymetric matrix of the resin and (iii) chemical reaction of the counter ions with the functional groups attached to the matrix. One of these steps usually offers much greater resistance than the others, so it can be considered as the slowest step and determines the overall rate of ion exchange briefly. Although there are only a few cases in which the rate of ion exchange is controlled by chemical reaction[9], the chemical-reaction-retarded diffusion mechanism in dilute solution has been developed[10], and verified experimentally that this is a more likely situation in ion exchange processes.

The Nernst-Planck equation (NPE), taking into account the effect of electric field in an electrode solution, is still the dominant theory, and the solutions under the film and particle diffusion controlling are summarized[11] in Eqs (1) and (2)

$$FUN = (1 - a\overline{X}_B^\infty) Ln(1 - F_{(t)}) - (1 - a\overline{X}_B^\infty - ab)$$

$$\times Ln\left(1 - \frac{F_{(t)}}{1 + b/\overline{X}_B^\infty}\right) = -gt \qquad \ldots (1)$$

$$F_{(r)} = [1 - \exp[\Pi^2(f_{1(\alpha)}\tau + f_{2(\alpha)}\tau^2 + f_{3(\alpha)}\tau^3)]]^{1/2}$$
$$\ldots (2)$$

Materials and Methods

The three-necked flask technique[12] was employed to study the kinetics in these systems. The 001×7 strongly acidic cation exchanger made in Shanghai Resin Factory was used, and treated in order to obtain spherical exchangers.

Procedure for determining the ion exchange rates in binary systems was as follows. The time was measured as soon as certain weight of resin was injected into the bulk solution which had been thermostatted and stirred adequately. Then, at regular time intervals, 1.0 ml of solution was with-

drawn by an auto-micro-pipette, and the UO_2^{2+} concentration of the sample was obtained by spectrophotometric analysis with Arsenazo III. The concentration of H^+ ion was derermined by means of a hydrogen ion-selective electrode. Since the total volume of the solution decreased with periodical withdrawal of samples during the experiments, the concentration obtained was corrected[13]. In addition, since the value of pH is strictly proportional to H^+ ion activity which is affected by Na^+ or UO_2^{2+} ions and thus the electrode response is to some extent dependent on the Na^+ or UO_2^{2+} concentrations, calibrations were made in corresponding mixed solutions in order to relate the values of pH to the actual H^+ concentration.

Results and Discussion

The kinetics of ion exchange in binary systems of $H^+ - Na^+$, $H^+ - UO_2^{2+}$ and $Na^+ - UO_2^{2+}$, using strongly acidic cation exchange resin, were studied systematically with changing solution concentration, stirring speed, temperature and the radius of ion exchanger. The film and particle diffusion coefficients in the systems were calculated with the help of NPE.

The mechanisms of ion exchange processes

$H^+ - Na^+$ *binary system*—The rates of both forward ion exchange (RH/Na^+) and reverse ion exchange (RNa/H^+) were carried out at the stirring speed of 800 rpm, the resin bead radius, $r_0 = 0.045 \pm 0.002$ cm, the temperature thermostated $= 25.0 \pm 0.2°C$ and the concentrations of counter ions in bulk solution 0.002 to 0.5 mol/l. The results are substituted to solutions (1) and (2), and the statistical fittings are shown in Fig. 1. As can be seen in Fig. 1, solution (1) gives the best statis-
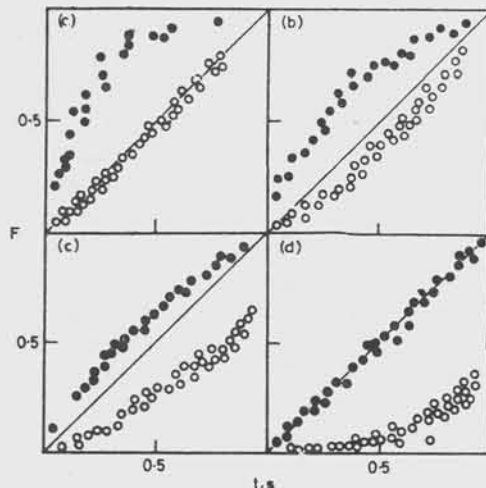
tical fitting to the experimental results at low concentration of counter ions in bulk solution, while the best statistical fitting is worked out by substitution of the findings at high concentration of that into solution (2).

It may be concluded from Fig. 1 that the rates of both forward and reverse ion exchange processes are controlled by film diffusion at low concentration and by particle diffusion at high concentration. As the concentration of the counter ions in solution increased, the mechanism of ion exchange in $H^+ - Na^+$ binary system changed from film diffusion controlling, through, mixed diffusion determining, to particle diffusion governing.

$Na^+ - UO_2^{2+}$ *binary system*—The rates of both foward exchange reaction (RNa/UO_2^{2+}) and reverse ion exchange (R_2UO_2/Na^+) were studied at the stirring speed of 800 rpm, temperature controlled $= 25.0 \pm 0.2°C$ and the radius of resin bead, $r_0 = 0.045 \pm 0.002$ cm. The rate curves obtained are shown in Figs 2 and 3. As shown in Figs 2 and 3, the rate of RNa/UO_2^{2+} increases with increase in concentration of $UO_2(NO_3)_2$ solution despite the three curves at concentrations of 0.05, 0.1 and 0.20 mol/l are almost identical. On the

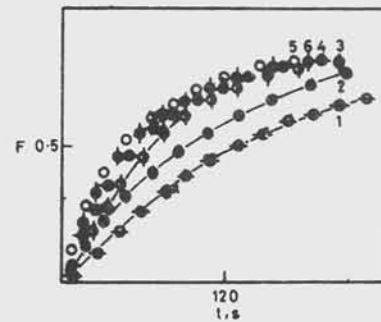Fig. 2—The effect of concentration of UO_2^{2+} in solution on the rate of RNa/UO_2^{2+} ion exchange 1, 0.001 mol/l; 2, 0.005 mol/l; 3, 0.01 mol/l; 4, 0.05 mol/l; 5, 0.10 mol/l; and 6, 0.20 mol/l

Fig. 1—Statistical fittings of the experimental results of $H^+ - Na^+$ ion exchange reactions to Nernst-Planck equation O, to solution (1); ●, to solution (2); a, b, c, d − 0.002, 0.02, 0.10, 0.50 mol/l, respectively
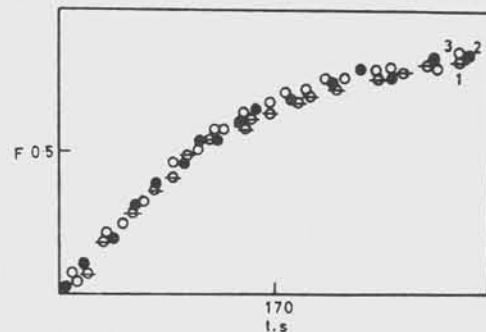

Fig. 3—The effect of concentration of Na^+ in solution on the rate of R_2UO_2/Na^+ ion exchange 1, 0.002 mol/l; 2, 0.05 mol/l; 3, 0.10 mol/l

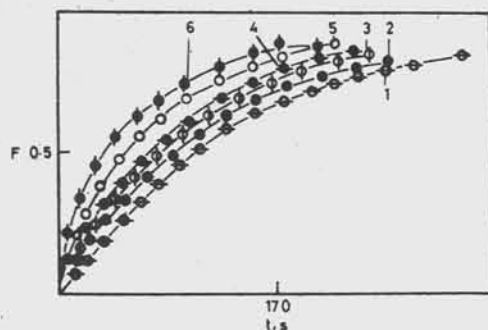Fig. 4—The effect of resin radius on the ion exchange rate in $Na^+ - UO_2^{2+}$ binary system R_2UO_2/Na^+, $r_0 = (1)$ 0.045, (2) 0.035, (3) 0.025 cm; RNa/UO_2^{2+}, $r_0 = (4)$ 0.045, (5) 0.035, (6) 0.025 cm

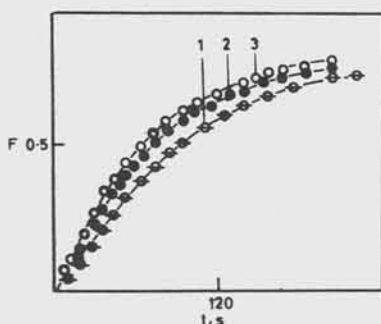Fig. 6—FUN--t curves of RH/UO_2^{2+} ion exchange in dilute solution (1), 0.001 mol/l; (2) 0.005 mol/l; (3) 0.01 mol/l; (4) 0.02 mol/l; (5) 0.05 mol/l

Fig. 5—The effect of stirring speed on the rate of RNa/UO_2^{2+} ion exchange (1) 600 rpm, (2) 800 rpm, (3) 1000 rpm

Fig. 7—Statistical fittings of the experimental results of RH/UO_2^{2+} at the concentration of UO_2^{2+} greater than 0.050 mol/l (O) and of R_2UO_2/H^+ at any concentration of HNO_3 (●) to solution (2)

contrary, the rate curves of reverse ion exchange at Na^+ concentrations of 0.002, 0.05 and 1.0 mol/l are coincided. The latter result does not fit with that of forward exchange RNa/UO_2^{2+} in the system and that of both forward and reverse exchange reactions in $H^+ - Na^+$ binary system.

The effect of resin radius on the ion exchange rate in the system was studied under conditions of 800 rpm, 25.0 ± 0.2°C, 0.20 mol/l of UO_2^{2+} (for RNa/UO_2^{2+}) and 0.10 mol/l of Na^+ (for R_2UO_2/Na^+). The effect of stirring speed on the RNa/UO_2^{2+} ion exchange rate was carried out under the conditions of 25.0 ± 0.2°C, $r_0 = 0.045 \pm 0.002$ cm and concentration of $UO_2(NO_3)_2$ 0.005 mol/l. The results are shown in Figs 4 and 5. As shown in Figs 4 to 5, the rate of both forward and reverse ion exchange reactions increased with decrease in the radius of resin bead at high concentrations, and that of only fowrward ion exchange reaction increased with an increase in the stirring speed at low concentrations.

In short, the rate of forward ion exchange RNa/UO_2^{2+} is controlled by film diffusion at low concentration and by particle diffusion at high concentration, but the reverse ion exchange $R_2UO_2/$ Na^+ is always particle diffusion controlling in any HNO_3 solution.
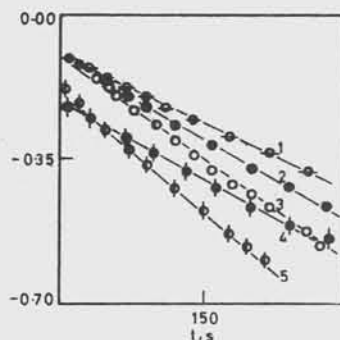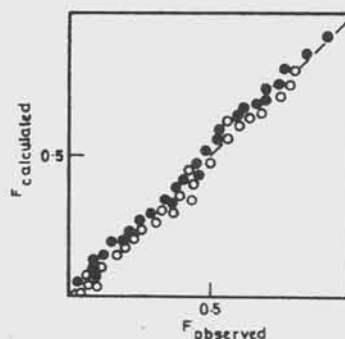
$H^+ - UO_2^{2+}$ binary system—The influence of concentration of counter ions in bulk solution on the rate of forward ion exchange RH/UO_2^{2+} was carried out at the stirring speed of 800 rpm, at 25.0 ± 0.2°C, the radius of resin bead, $r_0 = 0.045 \pm 0.002$ cm, $UO_2(NO_3)_2$ concentrations of 0.001, 0.005, 0.01, 0.05 and 0.10, 0.20, 0.50 mol/l. The rate of RH/UO_2^{2+} rapidly increases with increase in the solution concentration at low concentrations and is independent of it at high concentrations. The rate curves of reverse ion exchange, R_2UO_2/H^+, plotted in F versus t, are almost identical at the concentration range of 0.002 mol/l to 1.0 mol/l. This is the same conclusion as that reached in $UO_2(ClO_4)_2 - HClO_4$ system[12].

The experimental data observed in the system were substituted to the solutions (1) and (2), respectively, and found that only the experimental data of forward ion exchange at the concentrations of UO_2^{2+} in bulk solution less than or equal to 0.05 mol/l can be adequately applied to solution (1) (Fig. 6), and solution (2) gives better statistical

Table 1—Diffusion coefficients in $H^+ - Na^+$ ion exchange system (cm^2/s)

RH/Na$^+$				r_0/cm ±0.002	rpm	temp./°C ±0.2	RNa/H$^+$			
C_{Na}^0	$D \times 10^5$	$\bar{D}_H \times 10^6$	$\bar{D}_{Na} \times 10^7$				C_H^0	$D \times 10^5$	$\bar{D}_H 10^6$	$\bar{D}_{Na} \times 10^7$
0.002	1.2	3.4	2.3	0.045	800	25.0	0.002	0.97	3.4	2.0
0.005	2.9	3.0	2.7	0.045	800	25.0	0.005	1.9	3.8	2.0
0.02	4.7	3.4	2.9	0.045	800	25.0	0.02	3.5	3.6	2.4
0.05	5.2	3.6	2.8	0.045	800	25.0	0.05	4.2	3.6	2.3
0.005	2.2	2.0	4.2	0.035	800	25.0	0.005	2.0	2.7	2.7
0.005	1.3	1.5	1.1	0.025	800	25.0	0.005	1.7	2.4	2.5
0.005	1.4	2.8	3.0	0.045	600	25.0	0.005	0.95	3.5	2.0
0.005	4.5	2.3	2.4	0.045	1000	25.0	0.005	3.4	3.8	2.0
0.005	4.6	3.9	3.5	0.045	800	35.0	0.005	2.7	4.5	2.5
0.005	6.6	5.4	5.0	0.045	800	45.0	0.005	3.5	5.3	3.1
0.10	5.5	4.0	4.2	0.045	800	25.0	0.10	4.5	4.2	3.7
0.20	5.4	5.8	7.0	0.045	800	25.0	0.20	4.4	5.8	6.5
0.50	5.5	7.5	8.4	0.045	800	25.0	0.50	4.5	7.2	8.0
0.20	5.2	7.4	8.2	0.035	800	25.0	0.20	4.4	7.4	7.8
0.20	5.5	9.1	9.9	0.025	800	25.0	0.20	4.5	9.0	9.4
0.20	5.4	5.9	6.9	0.045	600	25.0	0.20	4.3	5.9	6.4
0.20	5.3	6.0	7.0	0.045	1000	25.0	0.20	4.4	5.8	6.6
0.20	6.7	6.5	7.8	0.045	800	35.0	0.20	5.4	7.9	8.5
0.20	8.9	7.4	8.5	0.045	800	45.0	0.20	6.5	8.5	9.4

Table 2—Diffusion coefficients in $Na^+ - UO_2^{2+}$ ion exchange system (cm^2/s)

RNa/UO$_2^{2+}$				r_0/cm ±0.002	rpm	temp./°C ±0.2	R$_2$UO$_2$/Na$^+$			
$C_{UO_2}^0$	$D \times 10^5$	$\bar{D}_{Na} \times 10^7$	$\bar{D}_{UO_2} \times 10^8$				C_{Na}^0	$D \times 10^5$	$\bar{D}_{Na} \times 10^7$	$\bar{D}_{UO_2} \times 10^8$
0.001	3.0	2.1	1.5	0.045	800	25.0	0.002	3.2	3.0	3.2
0.005	5.1	2.7	5.1	0.045	800	25.0				
0.01	7.4	2.9	8.4	0.045	800	25.0				
0.05	80	3.4	9.7	0.045	800	25.0	0.05	3.1	2.9	3.2
0.005	4.8	2.8	5.0	0.035	800	25.0				
0.005	8.2	2.5	5.0	0.025	800	25.0				
0.005	2.9	2.9	5.4	0.045	600	25.0				
0.005	7.2	3.0	5.2	0.045	1000	25.0				
0.005	7.2	3.5	6.0	0.045	800	35.0				
0.005	8.4	4.4	6.9	0.045	800	45.0				
0.10	8.4	3.7	9.5	0.045	800	25.0	0.10	3.0	3.1	3.2
0.20	8.4	3.8	9.9	0.045	800	25.0	1.0	2.9	3.1	3.4
0.50	8.3	3.8	9.6	0.045	800	25.0				
0.20	8.4	4.7	12	0.035	800	25.0	0.10	3.3	4.2	4.5
0.20	8.2	5.8	13	0.025	800	25.0	0.10	3.0	5.4	5.4
0.20	8.1	3.7	9.5	0.045	600	25.0	0.10	2.8	3.0	3.2
0.20	8.5	3.8	9.6	0.045	1000	25.0	0.10	2.9	3.0	3.3
0.20	9.2	5.7	12	0.045	800	35.0	0.10	4.4	4.5	4.6
0.20	10	8.0	14	0.045	800	45.0	0.10	5.4	5.8	6.0

fittings to other experimental data in the system (Fig. 7).

The film and particle diffusion coefficients

The film and particle diffusion coefficients in binary systems have been evaluated by means of the Nernst-Planck equation, and the results are summarized, in Tables 1 to 3. First of all, the film diffusion coefficient increases with increasing the concentration of counter ions in bulk solution and the stirring speed, while the particle diffusion coefficient increases with decreasing the radius of ion exchanger, and is independent of the concentration of counter ions in feed solution and the stirr-

Table 3—Diffusion coefficients in $H^+ - UO_2^{2+}$ ion exchange system (cm²/s)

RH/UO_2^{2+}				r_0/cm ±0.002	rpm	temp./°C ±0.2	R_2UO_2/H^+			
$C^0_{UO_2}$	$D \times 10^5$	$\bar{D}_H \times 10^6$	$\bar{D}_{UO_2} \times 10^8$				C^0_H	$D \times 10^5$	$\bar{D}_H \times 10^6$	$\bar{D}_{UO_2} \times 10^8$
0.001	3.0	1.2	1.3	0.045	800	25.0	0.002	3.0	2.9	3.2
0.005	7.2	7.4	5.2	0.045	800	25.0				
0.01	12	8.5	9.9	0.045	800	25.0				
0.05	13	12.0	14	0.045	800	25.0	0.05	2.8	2.8	3.2
0.005	8.3	6.6	7.0	0.035	800	25.0				
0.005	5.8	3.4	4.8	0.025	800	25.0				
0.005	6.9	5.6	3.0	0.045	600	25.0				
0.005	8.4	7.8	7.0	0.045	1000	25.0				
0.005	7.3	8.7	9.6	0.045	800	35.0				
0.005	52	13	15	0.045	800	45.0				
0.10	12	12	16	0.045	800	25.0	0.10	2.9	3.0	3.2
0.20	12	11	15	0.045	800	25.0	1.0	2.7	3.1	3.0
0.50	13	11	14	0.045	800	25.0				
0.20	13	15	18	0.035	800	25.0	0.10	3.0	4.2	4.5
0.20	12	18	20	0.025	800	25.0	0.10	2.8	5.1	5.5
0.20	11	12	14	0.045	600	25.0	0.10	2.7	2.9	3.0
0.20	12	10	15	0.045	1000	25.0	0.10	2.7	3.0	3.1
0.20	15	14	17	0.045	800	35.0	0.10	4.2	4.4	4.8
0.20	17	16	18	0.045	800	45.0	0.10	5.4	6.0	6.4

ing speed. In addition, the film diffusion coefficient seems to decrease with decrease in the radius of resin bead. This novel phenomena is directly attributable to invalidity evaluation of the thickness of Nernst-Planck film, and has been explained thoroughly in our previous work[10]. Secondly, the numerical order of 10^{-5} cm²/s has been held by film diffusion coefficients except those in ion exchange reaction RH/UO_2^{2+}, and the particle diffusion coefficients of H^+, Na^+ and UO_2^{2+} are of the numerical order of 10^{-6}, 10^{-7} and 10^{-8} cm²/s, respectively, except those in ion exchange reaction RH/UO_2^{2+}. Finally, the effect of temperature on both film and particle diffusion coefficients can always be observed, and both diffusion coefficients increase with increase in temperature but to a different extent.

It can be concluded that in $H^+ - Na^+$ ion exchange system, it has been found that the ion exchange rate may be controlled by film diffusion at low concentration and by particle diffusion at high concentration for both forward and reverse ion exchange processes. To $Na^+ - UO_2^{2+}$ system, the same can only be said to forward ion exchange RNa/UO_2^{2+}, but reverse ion exchange R_2UO_2/Na^+ is always controlled by particle diffusion at various concentrations of H^+ ion in bulk solution. It is verified experimentally that the conclusion abstracted from $Na^+ - UO_2^{2+}$ system can be said of $H^+ - UO_2^{2+}$ system. The film diffusion coefficient increases with increase in concentration of counter ions in bulk solution, the stirring speed and temperature, while it is independent of radius of resin bead. The particle diffusion coefficient increases with decrease in the radius of ion exchanger and with increase in temperature, while it is independent of the concentration of counter ions in bulk solution, and of stirring speed.

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