

## Kinetics of ion exchange in binary and ternary systems using strongly acidic cation exchanger: Part 2—Kinetic behaviour and diffusion coefficients in ternary system

Zhao Aimin\* & Song Yinjie

Department of Modern Physics, Lanzhou University, Lanzhou, 730 000, Gansu Province, P R China

Received 14 November 1995; revised 24 June 1996

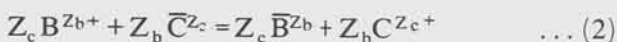
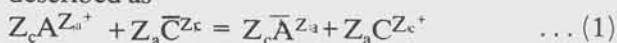
The three necked flask technique has been employed to study the kinetics of ion exchange in ternary system of  $H^+ - Na^+ - UO_2^{2+}$ . The kinetic curves have been obtained with changing the fraction of counter ions in bulk solution, the rate of stirring, temperature and resin radius. The particle diffusion coefficients in ternary system has been calculated by fitting the polar-coordination equation, and it has been found that they are of same order as that of corresponding binary systems and the sequence of them is  $\bar{D}_H > \bar{D}_{Na} > \bar{D}_{UO_2}$ . The selectivity coefficients are also reported, and the sequence of them is exactly opposite to that of particle diffusion coefficients.

In applications of ion exchange one of the problems of increasing interest is the treatment of dilute wastes, such as wash waters from metal pickling or plating operations. In order to use resinous exchangers for this purpose most effectively, it is necessary to learn the mechanisms of the ion exchange processes (particularly the rate-determining step) and to measure the fundamental constants governing the exchange, such as diffusion coefficient, selectivity coefficient and so on. With an understanding of the mechanisms and the values of the appropriate constants, it should be possible to design a suitable ion-exchange unit for any given purpose with a minimum of laboratory experiments<sup>1</sup>. But so far, only very few papers<sup>2</sup> report these values systematically, especially on multi-component systems due to the fact that the mathematical analysis of kinetics for such ion exchange reactions, as well as for the behaviours of ternary systems, is more complicated than that for corresponding binary systems<sup>2</sup>.

An investigation was undertaken in our laboratory to study the equilibria and kinetics of cation exchange in binary and ternary systems. Some diffusion coefficients have been reported according to isotopic ion exchange and moving boundary models<sup>3-5</sup>. Guided by previous work, the Nernst-Planck equation (NPE) was applied to experimental data in these systems, and the diffusion coefficients have been calculated. The present paper is a continuation of the previous work.

### Theory

Let us assume that the ions A and B are exchanged by an ion exchanger in C-form. These exchange reactions starting at time  $t=0$  can be described as



where the bars denote the ion exchanger phase, Z denotes electric charge of the counter ions.

Ion exchange in this system with three counter ions is a more complex phenomenon. The independent fluxes of the species cannot be expressed in terms of only one inter-diffusion coefficient. Thus the mathematical problem is one of solving three simultaneous differential equations, namely, the three Nernst-Planck equations, which include the influence of the concentration gradient arising during ion exchange processes due to the transport of counter ions with different mobilities, and each of them describing the particle diffusion flux of a given counter ion as an independent process.

$$J_i = -\bar{D}_i \left( \text{grad } \bar{C}_i + Z_i \bar{C}_i \frac{\mathfrak{R}}{RT} \text{grad } \varphi_i \right) \quad \dots (3)$$

where  $i=A, B$  or  $C$ ,  $J$  is diffusion flux in the particle of ion exchanger ( $\text{mol/l}^2 \text{ s}$ ),  $\bar{D}$  denotes particle diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $\bar{C}$  is concentration of counter ions in resin ( $\text{mol/l}$ ),  $\mathfrak{R}$  is Faraday con-

stant,  $R$  is gas constant,  $T$  is absolute temperature and  $\varphi$  is electro-potential gradient. The relation for the diffusion flux of the  $i$ th component is obtained through the combination of three Nernst-Planck equations with expressions presenting the conditions of electroneutrality and of total zero current of electric charges inside the particles

$$\sum_{i=1}^3 Z_i \bar{C}_i = -\omega \bar{C}_R = \text{constant} \quad \dots (4)$$

$$\sum_{i=1}^3 Z_i J_i = 0 \quad \dots (5)$$

where  $\omega$ ,  $\bar{C}_R$ , is electric charge and concentration of fixed ion, respectively.

$$J_i = \frac{[\bar{D}_i \bar{D}_j Z_j (Z_j \bar{C}_j \nabla \bar{C}_i - Z_i \bar{C}_i \nabla \bar{C}_j) + \bar{D}_i \bar{D}_k Z_k (Z_k \bar{C}_k \nabla \bar{C}_i - Z_i \bar{C}_i \nabla \bar{C}_k)]}{\sum_{i=1}^3 Z_i \bar{C}_i \bar{D}_i} \quad \dots (6)$$

A complicated second-order differential equation is obtained by substitution of Eq. (6) into the equation of continuity (i.e., Fick's second law<sup>7a</sup>) and by transformation to polar coordinates (for spherical particles of the ion exchanger):

$$\begin{aligned} \frac{\partial \bar{C}_i}{\partial t} = & \left\{ \bar{D}_i \bar{D}_j Z_j \left[ Z_j \left( \frac{\partial \bar{C}_j}{\partial t} Q - \bar{C}_j \frac{\partial Q}{\partial t} \right) \frac{\partial \bar{C}_i}{\partial t} \right. \right. \\ & - Z_i \left( \frac{\partial \bar{C}_i}{\partial t} Q - \bar{C}_i \frac{\partial Q}{\partial t} \right) \frac{\partial \bar{C}_j}{\partial t} \\ & + \bar{D}_i \bar{D}_k Z_k \left[ Z_k \left( \frac{\partial \bar{C}_k}{\partial t} Q - \bar{C}_k \frac{\partial Q}{\partial t} \right) \frac{\partial \bar{C}_i}{\partial t} \right. \\ & \left. \left. - Z_i \left( \frac{\partial \bar{C}_i}{\partial t} Q - \bar{C}_i \frac{\partial Q}{\partial t} \right) \frac{\partial \bar{C}_k}{\partial t} \right] \right\} / Q^2 \\ & + \left\{ \bar{D}_i \bar{D}_j Z_j \left[ Z_j \bar{C}_j \left( \frac{\partial^2 \bar{C}_i}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}_i}{\partial r} \right) \right. \right. \\ & - Z_i \bar{C}_i \left( \frac{\partial^2 \bar{C}_j}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}_j}{\partial r} \right) \\ & + \bar{D}_i \bar{D}_k Z_k \left[ Z_k \bar{C}_k \left( \frac{\partial^2 \bar{C}_i}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}_i}{\partial r} \right) \right. \\ & \left. \left. - Z_i \bar{C}_i \left( \frac{\partial^2 \bar{C}_k}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}_k}{\partial r} \right) \right] \right\} / Q \quad \dots (7) \end{aligned}$$

The total quantity  $q_{i(t)}$  of the components (A, B or C) in the resin at different time  $t$  were obtained experimentally. The two-dimension profiles of

concentration-time and concentration-radius of each component in the particle, related to the volume of the resin bead, at time  $t$  was evaluated by substitution of the  $q_{i(t)}$  values into

$$q_{i(t)} = \frac{3}{r_0} \int_0^{r_0} \bar{C}_{i(t,r)} r^2 dr \quad \dots (8)$$

where  $r_0$  is radius of spherical ion exchanger which is assumed to be equal to all particles (cm), and  $r$  denotes the distance from the particle centre,  $0 \leq r \leq r_0$  (cm). Plicka *et al.*<sup>8</sup> have verified the applicability of Nernst-Planck equation in the ternary system with strongly acidic cation exchanger QSTIONKS-08. In present paper, the particle diffusion coefficients  $D_{H^+}$ ,  $D_{Na^+}$  and  $D_{UO_2^{2+}}$  in the system of  $H^+ - Na^+ - UO_2^{2+}$  are calculated by fitting the data of the two-dimensional profiles using Eq. (7) under the following initial and boundary conditions:

$$t=0, \bar{C}_{i,r=0} = 0, \bar{C}_{i,r=r_0} = C^0$$

$$t>0, \bar{C}_{i,r=0} = \bar{C}_{i,r=r_0} / K, \bar{C}_{i,r=r_0} = C(t)$$

$$t=\infty, \bar{C}_{i,r=0} = \bar{C}_{i,r=r_0} = C^\infty$$

where  $K$  denotes distribution coefficient of counter ions. The selectivity coefficients of counter ions for ion exchanger are also obtained.

## Results and Discussion

The ion exchange kinetics in ternary system of  $H^+ - Na^+ - UO_2^{2+}$  were carried out at fixed solution composition  $\sum_{i=1}^3 Z_i C_i^0 = 0.04$  mol/l, in which the ion exchange processes were determined by particle diffusion, where  $C_i^0$  denotes initial molar concentration of  $i$ th counter ion in bulk solution, and at three radii of ion exchanger ( $r_0 = 0.045, 0.035$  and  $0.025 \pm 0.002$  cm), the temperature thermostatted at  $25.0 \pm 0.2^\circ\text{C}$ , the stirring speed of 800 rpm and various fractions of counter ions initially in bulk solution. A part of the findings is shown in Figs 1 to 4. As shown in Figs 1 to 3, (i) the rate of counter ions initially in bulk solution exchanging with those initially in resin-phase increased with increasing the ionic fractions of counter ions in bulk solution, i.e., with increasing concentration of individual counter ions in feed solution; (ii) in every  $\bar{X}_{Na} - t$  or  $\bar{X}_H - t$  curve,  $\bar{X}_{Na}$  or  $\bar{X}_H$  goes through a maximum, but  $\bar{X}_{UO_2}$  is always increased with increase in time; Helfferich<sup>7b</sup> predicted this phenomenon theoretically, but further experimental verification has rarely been reported; and (iii)  $\bar{X}_H - t$  curves always depend upon the ionic fraction of  $H^+$  ion in solution, while  $\bar{X}_{Na} - t$  curves be-

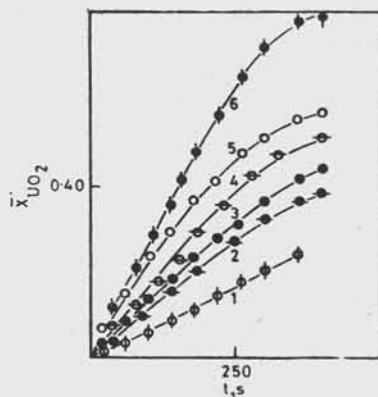


Fig. 1—The effect of the fraction of  $\text{UO}_2^{2+}$  ion in solution on  $\bar{X}_{\text{UO}_2}$  curves of  $\text{RNa}/(\text{UO}_2^{2+}, \text{H}^+)$  ion exchange  $X_{\text{UO}_2^{2+}} =$  (1) 0.2, (2) 0.3, (3) 0.4, (4) 0.5, (5) 0.6, (6) 0.7, respectively

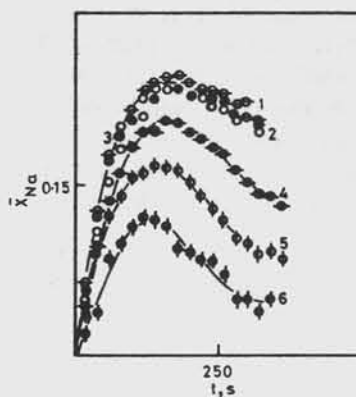


Fig. 3—The effect of the fraction of  $\text{Na}^+$  ion in solution on  $\bar{X}_{\text{Na}}$  curves of  $\text{RH}/(\text{UO}_2^{2+}, \text{Na}^+)$  ion exchange  $X_{\text{Na}^+} =$  (1) 0.8, (2) 0.7, (3) 0.6, (4) 0.5, (5) 0.4, (6) 0.3 respectively

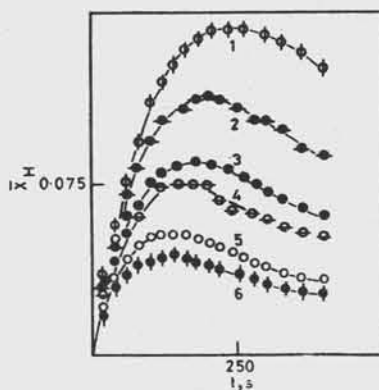


Fig. 2—The effect of the fraction of  $\text{H}^+$  ion in solution on  $\bar{X}_{\text{H}^+}$  curves of  $\text{RNa}/(\text{UO}_2^{2+}, \text{H}^+)$  ion exchange  $X_{\text{H}^+} =$  (1) 0.8, (2) 0.7, (3) 0.6, (4) 0.5, (5) 0.4, (6) 0.3, respectively

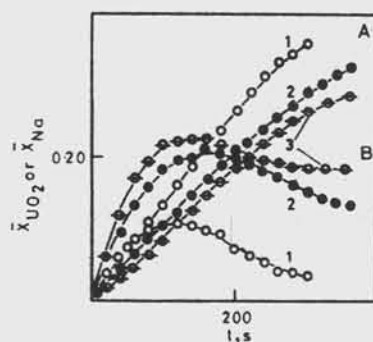


Fig. 4—The effect of resin radius on the rate of  $\text{RH}/(\text{UO}_2^{2+}, \text{Na}^+)$  ion exchange reaction A,  $\bar{X}_{\text{UO}_2}$ ,  $\bar{X}_{\text{Na}^+}$ ;  $r_0 =$  (1) 0.045, (2) 0.035, (3) 0.025

come almost identical when the fraction of  $\text{Na}^+$  ion in feed solution come to be 0.6, 0.7 and 0.8 at the isostatic composition of bulk solution. As can be seen from Fig. 4, it is the same as that found in binary system; the amount of counter ions (here  $\text{Na}^+$ ) exchanged to the resin phase per unit time increases with decrease in the radius of ion exchanger, but for that of  $\text{UO}_2^{2+}$ , the opposite is the case, which may be explained as follows: the counter ions of multi-component systems are competitors during the process of ion exchange; accelerating to one kind of counter ions may result in the resistance of their competitors in the system. Hence, it is possible to observe the finding in which the rate of ion exchange for some kinds of counter ions decreases with increase in agitation rate and even the temperature. The rate may be also reduced with decreasing the radius of ion exchanger.

In order to explain these results, the particle diffusion coefficient has been evaluated by numer-

ical calculation. The selectivity coefficient in ternary system was also obtained, and the results are summarized together in Table 1.

As can be seen in Table 1, (i) the sequence of particle diffusion coefficients of counter ions  $\text{H}^+$ ,  $\text{Na}^+$  and  $\text{UO}_2^{2+}$  is  $\bar{D}_{\text{H}} > \bar{D}_{\text{Na}} > \bar{D}_{\text{UO}_2}$ . In addition to a few cases, the numerical order of their value is basically  $10^{-6}$ ,  $10^{-7}$  and  $10^{-8}$ , respectively, namely, the particle diffusion coefficients of counter ions of ternary systems are of the same order as that of corresponding binary systems. It may be concluded that the values of diffusion coefficients obtained from the binary systems can be used approximately in ternary systems under certain conditions, such as the pre-experiment to evaluate the optimization of experimental conditions economically. (ii) The particle diffusion coefficients of counter ions initially in ion exchanger remain constant within experimental deviations during exchange processes at the isostatic composition of bulk solution, in spite of ionic fraction of other two counter ions initially in feed solution chang-

Table 1—Particle diffusion coefficient ( $cm^2/s$ ) and selectivity coefficient in  $H^+ - Na^+ - UO_2^{2+}$  ternary system

$K_{UO_2^{2+}/Na^+}$ $\pm 0.6$	RH/( $UO_2^{2+}, Na^+$ )			$\Sigma_{i=1}^n Z_i C_i^0 = 0.040 \text{ mol/l}$					RNa/( $UO_2^{2+}, H^+$ )			$K_{UO_2^{2+}/H^+}$ $\pm 7$
	$10^6 \bar{D}_H$	$10^7 \bar{D}_{Na}$	$10^8 \bar{D}_{UO_2}$	$X_{UO_2}$	$X_{Na(H)}$	$r_0(\text{cm})$ $\pm 0.002$	rpm	temp ( $^\circ\text{C}$ )	$10^6 \bar{D}_H$	$10^7 \bar{D}_{Na}$	$10^8 \bar{D}_{UO_2}$	
26.9	2.9	8.4	.78	.2	.8	.045	800	25.0	5.4	4.0	41	130
34.4	2.9	7.0	.86	.3	.7	.045	800	25.0	4.9	3.6	50	279
41.0	3.0	5.4	.99	.4	.6	.045	800	25.0	2.1	3.7	65	348
45.4	3.0	3.6	1.1	.5	.5	.045	800	25.0	1.8	3.8	81	463
62.0	3.1	2.6	1.3	.6	.4	.045	800	25.0	1.0	3.9	92	1253
64.2	3.0	1.8	1.5	.7	.3	.045	800	25.0	.82	3.7	1.0	2831
11.7	4.5	4.8	1.3	.5	.5	.035	800	25.0	3.8	5.8	1.1	345
6.4	6.0	8.0	2.2	.5	.5	.025	800	25.0	7.2	9.0	1.8	270
45.9	3.2	3.6	1.0	.5	.5	.045	600	25.0	1.6	3.7	80	462
40.4	3.0	3.5	1.1	.5	.5	.045	1000	25.0	2.0	3.8	82	454
60.9	4.5	5.4	1.3	.5	.5	.045	800	35.0	3.0	5.4	1.2	409
37.1	6.0	7.0	1.6	.5	.5	.045	800	45.0	5.9	6.8	1.7	386

ing. It may be concluded that the particle diffusion coefficients of ions initially in ion exchanger are directly related with the total concentration of bulk solution, rather than the concentration of individual ions initially in feed solution. (iii) The particle diffusion coefficients of counter ions initially in both solution and resin increase with the rise in temperature and with decrease in the radius of ion exchanger, while they remain unaffected by the stirring speed. This conclusion is identical with that of binary systems. (iv) When the ionic fraction of  $UO_2^{2+}$  changes from 0.20 to 0.70, the  $\bar{D}_H$  decreases about 6.6 times for RNa/( $UO_2^{2+}, H^+$ ), while  $\bar{D}_{Na}$  decreases about 4.7 times for RH/( $UO_2^{2+}, Na^+$ ), but the  $\bar{D}_{UO_2}$  increases about only 2 times for both RNa/( $UO_2^{2+}, H^+$ ) and RH/( $UO_2^{2+}, Na^+$ ). It can be said that for more mobile counter ions, many changes may be obtained easily with changing experimental conditions. The same can be said of the effect of resin radius and temperature on particle diffusion coefficients. (v) The selectivity coefficients, which denote relative selectivities of counter ions for ion exchanger used,  $K_{UO_2^{2+}/H^+} > K_{UO_2^{2+}/Na^+} \gg 1$ . This means that the sequence of relative selectivities of counter ions  $H^+, Na^+$  and  $UO_2^{2+}$  for ion exchanger is  $H^+ < Na^+ \ll UO_2^{2+}$ . It is exactly opposite to that of diffusion coefficient.  $K_{UO_2^{2+}/H^+}$  and  $K_{UO_2^{2+}/Na^+}$  always increase with increase in the ionic fraction of  $UO_2^{2+}$  ions in bulk solution, and abruptly increase at the  $X_{UO_2}$  of about 0.6 or 0.7. It can be also seen from Table 1, the effect of experimental conditions on the selectivity coefficients is very complex, particularly that of temperature.

Guided by the values of particle diffusion coefficients and selectivity coefficients listed in

Table 1, the experimental results shown in Figs 1 to 4 can be explained as follows. Although the kinetics of ion exchange in the systems with more than two competing counter ions are more complex in theoretical treatment than that in binary systems, the basic concept in binary systems can be essentially applied to multi-component systems approximately. The most important factors are still the relative mobilities of counter ions and their relative affinities for ion exchangers. In our system, the sequence of relative mobilities of three given counter ions, expressed by particle diffusion coefficient, is  $\bar{D}_H > \bar{D}_{Na} \gg \bar{D}_{UO_2}$ , and that of relative affinities for ion exchanger used, shown in selectivity coefficients  $K_{UO_2^{2+}/Na^+}$  and  $K_{UO_2^{2+}/H^+}$ , is  $UO_2^{2+} \gg Na^+ > H^+$ . The effect of relative affinities is essentially same as it is in systems with only two counter ions i.e., the counter ion which is preferred by ion exchanger is taken up at higher rate and released at lower rate than its competitors. The effect of relative mobilities will be illustrated carefully. For ion exchange RH/( $UO_2^{2+}, Na^+$ ), initially,  $Na^+$  will rapidly replace  $H^+$  ion in the resin and uptake of  $UO_2^{2+}$  will lag far behind due to the fact that the  $Na^+$  ion is much more mobile than  $UO_2^{2+}$ , but later, because  $UO_2^{2+}$  is more preferred by the ion exchanger used than  $Na^+$ , it will follow, partly replacing the  $Na^+$  ions that were taken in the earlier stages. Thus the concentration of  $Na^+$  ion in the resin goes through a maximum. The same can be said of ion exchange RNa/( $UO_2^{2+}, H^+$ ). Certainly, for two or more counter ions initially in solution, if their mobilities in the resin (particle diffusion controlled exchange) or in the solution (film diffusion controlled exchange) are

about equal, these species will be taken up at approximately equal rate, and multi-component system can be reduced to binary system. This situation may be found in ion exchange reaction  $R_2UO_2/(Na^+, H^+)$  under certain conditions.

To conclude the ion exchange in ternary system of  $H^+ - Na^+ - UO_2^{2+}$  is more complicated than that in binary systems, but the most important factors which affect the rate of ion exchange are still the relative mobilities of counter ions and their affinities for ion exchanger used. Some complexities in the industrial applications arise from the interaction of counter ions in the system, and so novel findings may be continuously observed in the field of multi-component systems. The values of particle diffusion coefficients of counter ions in this system are of same order as that of corresponding binary systems. It is reasonable that the experimental phenomena in ternary systems may be predicted approximately under certain conditions by the rules obtained in corresponding binary systems. The description of kinetics of ion exchange

in ternary systems was based upon three Nernst-Planck equations, each of them describing the particle diffusion flux of a given counter ion as an independent process. In turn, this description can be approximately applied, for all practical purpose, to the systems in which exchanging counter ions were affected with each other.

### References

- 1 Selke W A, *Chem Eng Progress*, 46 (1950) 509.
- 2 Oscar Bricio, Jose Coca & Herminio Sastre, *Solvent Extr Ion Exch*, 10 (1992) 381.
- 3 Tao Zuyi, Zhao Aimin, Tong Wengong, Xiao Rong & Chen Xingqu, *J radioanal nucl Chem*, 116 (1987) 35.
- 4 Zhao Aimin, Tao Zuyi, Tong Wengong & Chen Xingqu, *J radional nucl Chem*, 116 (1987) 49.
- 5 Song Yinjie, Yang Qingdong & Zhao Aimin, *J nucl Radiochem*, (in Chinese), 17 (1995) 91.
- 6 Sing Yinjie & Zhao Aimin, *Indian J Chem*, 35 (1996).
- 7 Helfferich F G, *Ion exchange* (McGraw-Hill, New York) (1962)(a) p 275; (b) pp 250-322.
- 8 Plicka J, Stamberg K, Cabicar J & Gosman A, *J radional nucl Chem*, 102 (1986) 525.