

# Dynamic Adsorption Behaviors Between $\text{Cu}^{2+}$ Ion and Water-Insoluble Amphoteric Starch in Aqueous Solutions

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**ABSTRACT:** Dynamic adsorption behavior between  $\text{Cu}^{2+}$  ion and water-insoluble amphoteric starch was investigated. The sorption process occurs in two stages: external mass transport occurs in the early stage and intraparticle diffusion occurs in the long-term stage. The diffusion rate of  $\text{Cu}^{2+}$  ion in both stages is concentration dependent. In the external mass-transport process, the diffusion coefficient ( $D_1$ ) increases with increasing initial concentration in the low- ( $1 \times 10^{-3}$ – $4 \times 10^{-3}M$ ) and high-concentration regions ( $6 \times 10^{-3}$ – $10 \times 10^{-3}M$ ). The values of adsorption activation energy ( $k_{a1}$ ) in the low- and high-concentration regions are 15.46–24.67 and  $-1.80$  to  $-11.57$  kJ/mol, respectively. In the intraparticle diffusion process, the diffusion coefficient ( $D_2$ ) increases with increasing initial concentration in the low-concentration region ( $1 \times 10^{-3}$ – $2 \times 10^{-3}M$ ) and decreases with increasing initial concentration in the high-concentration region ( $4 \times 10^{-3}$ – $10 \times 10^{-3}M$ ). The  $k_{a2}$  values in the low- and high-concentration regions are 9.96–15.30 and  $-15.53$  to  $-10.71$  kJ/mol, respectively. These results indicate that the diffusion process is endothermic in the low-concentration region and is exothermic in the high-concentration region for both stages. The external mass-transport process is more concentration dependent than the intraparticle diffusion process in the high-concentration region, and the dependence of concentration for both processes is about equal in the low-concentration region. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2849–2855, 2001

**Key words:** dynamic adsorption behaviors; water-insoluble; amphoteric starch; metal ion; diffusion

## INTRODUCTION

Many low-cost agricultural by-products are capable of adsorption, chelation, or ion-exchange with heavy metal ions. The use of peanut skins,<sup>1,2</sup> onion skins,<sup>3</sup> wool,<sup>4–7</sup> and cotton<sup>8</sup> for the adsorption of toxic heavy metal ions have been effective. Starch is a low-cost polymer that can be highly crosslinked with epichlorohydrin or other agents to make it water-insoluble. Chemical modification of the crosslinked starch with various reactive

monomers yields ionomer products that can be used to remove heavy metal ions from wastewater.<sup>9</sup> Xanthation of a crosslinked starch yields insoluble starch xanthate that was shown to effectively remove heavy metal cations from wastewater.<sup>10,11</sup> Insoluble starch products containing tertiary amine or quaternary ammonium compounds were shown to remove heavy metal anions from wastewater effectively.<sup>12</sup>

Recently, we have indicated that water-insoluble amphoteric starches, containing the phosphate or sulfonate anionic group and the quaternary ammonium or tertiary amine cationic group, can simultaneously remove heavy metal ions and phenol organic compounds from aqueous solution

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effectively.<sup>13-16</sup> The  $\text{Cl}^-$  of the tertiary amine group and the  $\text{Na}^+$  of the sodium phosphate group are used to exchange  $\text{CrO}_4^{2-}$  and  $\text{Pb}^{2+}$  ions, respectively, and the tertiary amine group is used to adsorb phenol. The functional groups used for adsorption and exchange processes are independent.<sup>16</sup>

Within the context of solute adsorption onto an amphoteric polymer, the adsorption process consists of three steps: (1) the solute from the bulk solution diffuses through a liquid film surrounding the particle surface; then, (2) the solute diffuses through the particle to the adsorption active site; and finally, (3) the solute adsorbs on the active site. Establishment of the rate-limiting step assumes that step 3 is rapid and hence not considered in any kinetic analysis. Consequently, the two rate-limiting steps are considered to be the external mass-transport process (the first step) and the intraparticle diffusion process (the second step). The external mass-transport process was found to be rate controlling for only the initial few minutes of adsorption. The initial rapid rate of solute uptake quickly slowed down and the intraparticle diffusion became rate controlling.

External mass-transport processes during the adsorption of basic dyestuffs from aqueous solutions onto maize cob was studied.<sup>17</sup> It was found that the external mass-transfer coefficient ( $k_s$ ) varies linearly with agitation, the initial dye concentration, the particle size, and mass of the maize cob, according to the general equation  $k_s = X(\text{variable})^Y$ , where  $X$  and  $Y$  are constants. The intraparticle-diffusion process during the adsorption of dyestuffs from aqueous solutions onto fired clay or silica was also studied.<sup>18</sup> It was found that an intraparticle diffusion rate parameter ( $k$ ) could be defined to characterize intraparticle diffusion within the adsorption systems. The rate parameter was correlated for a number of system variables, namely, the initial dye concentration, the adsorbent mass, and particle size, using equations of the general form  $k = A(\text{variable})^B$ , where  $A$  and  $B$  are constants. The activation energy of adsorption for a basic dye on silica is 12.6–13.8 kJ/kg. The temperature dependence of the diffusion coefficient varies from  $9 \times 10^{-9} \text{ cm}^2/\text{s}$  at  $20^\circ\text{C}$  to  $10 \times 10^{-8} \text{ cm}^2/\text{s}$  at  $80^\circ\text{C}$ .<sup>19</sup> However, few investigations of the diffusion mechanism of the external mass-transport process, together with the intraparticle diffusion process during adsorption, have been reported in relevant literature. The mass-transport process for the adsorption of Cr(VI) onto water-insoluble cationic starch in

aqueous solutions was reported in our previous work.<sup>20</sup> The diffusion rate of  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  ions are concentration dependent on the external mass-transport and intraparticle-diffusion processes. The external mass-transport and intraparticle-diffusion processes are endothermic and exothermic, respectively.

This study examines the effects of the initial concentration and adsorption temperature on the external mass-transport and intraparticle-diffusion processes during the removal of  $\text{Cu}^{2+}$  ion with a highly water-insoluble amphoteric starch in aqueous systems. The mechanism and kinetic parameters of ion mass-transport process at  $30$ – $60^\circ\text{C}$  are also investigated.

## EXPERIMENTAL

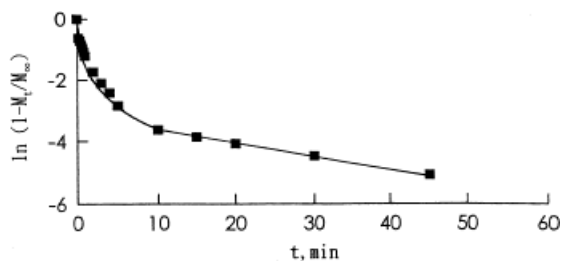
Industrial grade cornstarch powder was dried at  $105^\circ\text{C}$ . Epichlorohydrin and cupric nitrate (extra-pure grade from Merck Chemical Co., Darmstadt, Germany), and 2-chlorotriethylamine hydrochloride (extrapure grade from Aldrich Chemical Co., Milwaukee, WI) were used as received.

The procedures for preparing water-insoluble amphoteric starch have been described earlier.<sup>13-16</sup> The dynamic adsorption experiments of this study were a series of glass-stoppered Erlenmeyer flasks containing 1.0 g adsorbent and 100 mL cupric nitrate aqueous solution at the desired concentration and initial pH 4.0 in a shaking isothermal water bath. The desired concentrations were  $1 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $4 \times 10^{-3}$ ,  $6 \times 10^{-3}$ ,  $8 \times 10^{-3}$ , and  $1 \times 10^{-2} \text{ M}$ . One flask was removed at the desired adsorption time and the solution analyzed until the adsorption had reached equilibrium (about 1 h). The desired adsorption times were 0.167, 0.333, 0.5, 0.667, 0.833, 1, 2, 3, 4, 5, 10, 15, 20, 30, 45, and 60 min. The initial pH value of the cupric nitrate aqueous solution for adsorption was adjusted with 0.1N  $\text{HNO}_3$  and 0.1N  $\text{NaOH}$ . The concentration of  $\text{Cu}^{2+}$  ion in the solution before and after adsorption was analyzed by an atomic absorption spectrophotometer GBC Model AA-932 (GBC Scientific Equipment Co., Victoria, Australia)

## RESULTS AND DISCUSSION

The reaction process for preparing water-insoluble amphoteric starch can be proposed as the following scheme<sup>13-16,21</sup>:





**Figure 3** Plot of  $\ln[1 - (M_t/M_\infty)]$  versus  $t$  at the initial concentration  $10 \times 10^{-3}M$  and  $30^\circ\text{C}$ .

and

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln \frac{6}{\pi^2} + \left(\frac{-D\pi^2}{r^2}\right)t \quad (\text{as } t \rightarrow t_\infty) \quad (4)$$

A plot of  $M_t/M_\infty$  versus  $t^{1/2}$  and  $\ln[1 - (M_t/M_\infty)]$  versus  $t$  should correspond to a line, from which the diffusion coefficient for small and large times ( $D_1$  and  $D_2$ ) can be determined, respectively.

The activation energy  $E_d$  and preexponential factor  $D_0$  for diffusion were calculated by using the Arrhenius expression:

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \quad (5)$$

The constant  $D_0$  was obtained from the Eyring rate theory of diffusion<sup>24</sup>

$$D_0 = (e\lambda^2kt/h)\exp(\Delta S^*/R) \quad (6)$$

where  $\lambda$  is the jump length of a diffusate molecule and  $\Delta S^*$  is the entropy of activation for diffusion.

### Effect of Concentration

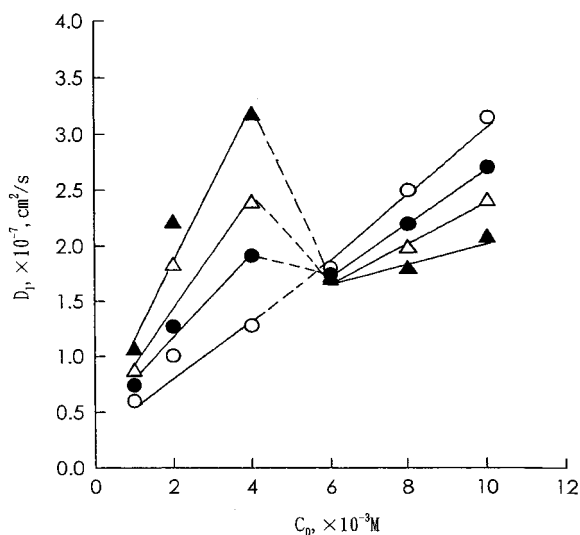
The variations of the concentration of  $\text{Cu}^{2+}$  ion with time during adsorption for the initial concentrations ( $10^{-3}$ - $10^{-2}M$ ) at the initial pH 4 and  $30^\circ\text{C}$  are shown in Figure 1. The concentration of  $\text{Cu}^{2+}$  ion sharply decreases with time in the early stage (0- to 1-min range), and then gradually decreases to reach an equilibrium value (approximately 60 min) for various initial concentrations. The plots of  $M_t/M_\infty$  versus  $t^{1/2}$  and  $\ln[1 - (M_t/M_\infty)]$  versus  $t$  calculated from the data in Figure 1 are shown in Figures 2 and 3 (only initial concentration  $10 \times 10^{-3}M$  is shown). In Figures 2 and 3, the  $\text{Cu}^{2+}$  ion sorption occurs in two stages (i.e., two linear regions with a relatively abrupt transition region between them). This can be attributed to the external mass-transport process in the early stage and the intraparticle diffusion process in the long-term stage. The diffusion coefficient  $D_1$  was calculated from the slope of the first straight line (the early stage, 0- to 1-min range) in an  $M_t/M_\infty$  versus  $t^{1/2}$  plot using eq. (3), and  $D_2$  from the slope of the second line (the long-term stage, 10- to 45-min range) in an  $\ln[1 - (M_t/M_\infty)]$  versus  $t$  plot using eq. (4). The least-squares method is used to estimate the slopes of the lines used to determine  $D_1$  and  $D_2$ , and the values of coefficient of correlation are larger than 0.980. The slopes of the lines are tested by regression analysis and the calculated two-sided  $p$  values are  $< 0.005$ . The low  $p$  values indicate the null hypothesis is not plausible and so the slope param-

**Table I** The Values of  $D_1$  and  $D_2$  at Various Initial Concentrations and Temperatures

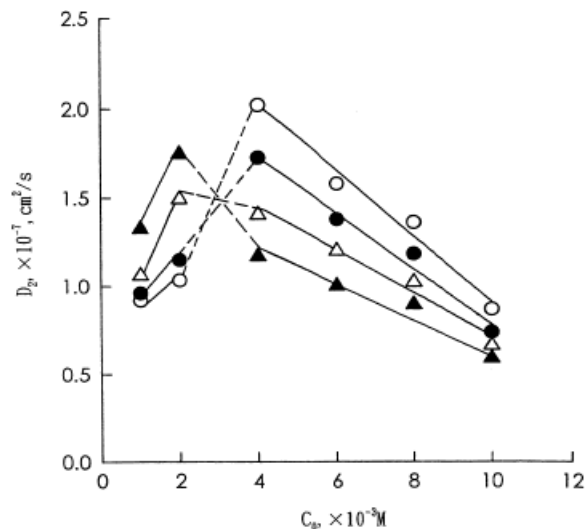
Diffusion Coefficient, $\times 10^{-7}$ (cm <sup>2</sup> /s)	Initial Concentration, $\times 10^{-3}$ (M)					
	1.0	2.0	4.0	6.0	8.0	10.0
$D_1$						
30°C	0.599	1.005	1.280	1.806	2.500	3.155
40°C	0.740	1.271	1.915	1.747	2.200	2.709
50°C	0.860	1.821	2.382	1.715	1.980	2.400
60°C	1.053	2.202	3.166	1.692	1.793	2.074
$D_2$						
30°C	0.919	1.035	2.024	1.580	1.363	0.870
40°C	0.961	1.151	1.727	1.379	1.185	0.740
50°C	1.061	1.493	1.405	1.200	1.021	0.663
60°C	1.326	1.746	1.169	1.000	0.893	0.590

eter is known to be nonzero. The calculated  $D_1$  and  $D_2$  values are listed in Table I. Therefore,  $D_1$  and  $D_2$  are regarded as the diffusion rate of  $\text{Cu}^{2+}$  ion in the external mass-transport and intraparticle-diffusion processes, respectively.

The  $D_1$  value increases from  $0.599 \times 10^{-7}$  to  $3.155 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  (5.26 times) as the initial concentration increases from  $10^{-3}$  to  $10^{-2} \text{ M}$  (Table I). The results indicate that the rate of ion diffusion in the external mass-transport process increases with increasing the initial concentration. The reason is that the rate of ion diffusion in the external mass-transport process is controlled by the ion diffusion in the aqueous solution, so the higher initial concentration has a higher concentration gradient. The  $D_2$  value increases from  $0.919 \times 10^{-7}$  to  $2.024 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  (2.20 times) as the initial concentration increases from  $10^{-3}$  to  $4 \times 10^{-3} \text{ M}$  and decreases from  $2.024 \times 10^{-7}$  to  $0.870 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  (0.42 times) as the initial concentration increases from  $4 \times 10^{-3}$  to  $10 \times 10^{-3} \text{ M}$  (Table I). The results indicate that the rate of ion diffusion in the intraparticle diffusion process increases and decreases with increasing the initial concentration in the low- ( $1 \times 10^{-3}$  to  $4 \times 10^{-3} \text{ M}$ ) and high-concentration regions ( $4 \times 10^{-3}$  to  $10 \times 10^{-3} \text{ M}$ ), respectively. The diffusion ion must pass through the adsorbed active sites located on the thin surface layer to empty active sites located on the deeper layer in the long-term stage. Thus, the rate of ion diffusion in the intraparticle diffusion process is controlled by



**Figure 4** The variation of  $D_1$  with initial concentration for various temperatures: (○) 30°C, (●) 40°C, (△) 50°C, (▲) 60°C.



**Figure 5** The variation of  $D_2$  with initial concentration for various temperatures: (○) 30°C, (●) 40°C, (△) 50°C, (▲) 60°C.

the ion diffusion within the adsorbent. The amount of adsorbed ion on the active sites located on the thin surface layer increases as the initial concentration increases in the early stage. The higher concentration gradient leads to the rate of ion diffusion within the adsorbent increasing. However, when the amount of adsorbed ion on the active sites in the early stage is over a certain level, the rate of ion diffusion within the adsorbent decreases with initial concentration increasing in the long-term stage. Thus, the value of  $D_2$  increases and decreases with initial concentration in the low- and high-concentration regions, respectively, and has a maximum at the initial concentration  $4 \times 10^{-3} \text{ M}$ . The ion diffusions in both processes are concentration dependent.

#### Effect of Temperature

The  $D_1$  and  $D_2$  values of various initial concentrations for adsorption temperatures ranging from 30 to 60°C are shown in Figures 4 and 5 and Table I. In Figure 4, the relationship of  $D_1$  with initial concentration can be divided into three regions for four adsorption temperatures. The  $D_1$  increases with initial concentration in low- ( $1 \times 10^{-3}$ – $4 \times 10^{-3} \text{ M}$ ) and high-concentration regions ( $6 \times 10^{-3}$ – $10 \times 10^{-3} \text{ M}$ ) and decreases with initial concentration in the middle concentration region ( $4 \times 10^{-3}$ – $6 \times 10^{-3} \text{ M}$ ) except at 30°C. The  $D_1$  values increase and decrease about 1.76–2.47 and 0.94–0.66 times over the low- and high-con-



**Table II** The Values of  $E_d$  and  $D_0$  at Various Initial Concentrations

	Initial Concentration, $\times 10^{-3}$ (M)					
	1.0	2.0	4.0	6.0	8.0	10.0
$E_{d,1}$ (kJ/mol)	15.46	22.76	24.67	-1.80	-9.26	-11.57
$D_{0,1}$ (cm <sup>2</sup> /s)	$2.78 \times 10^{-5}$	$8.35 \times 10^{-4}$	$2.36 \times 10^{-5}$	$8.79 \times 10^{-8}$	$6.30 \times 10^{-9}$	$3.19 \times 10^{-9}$
$E_{d,2}$ (kJ/mol)	9.96	15.30	-15.53	-12.65	-11.89	-10.71
$D_{0,2}$ (cm <sup>2</sup> /s)	$4.59 \times 10^{-6}$	$4.37 \times 10^{-5}$	$4.31 \times 10^{-10}$	$1.06 \times 10^{-9}$	$1.22 \times 10^{-9}$	$1.23 \times 10^{-9}$

centration regions, respectively, as the temperature increases from 30 to 60°C. This is because the thickness of the boundary layer surrounding the adsorbent decreases with increasing temperature,<sup>25</sup> so the mass-transfer resistance of adsorbate in the boundary layer decreases. This temperature effect leads the rate of ion diffusion in the external mass-transport process increasing. The interaction between the ions increases as the initial concentration increases, so the disturbance of ion diffusion in the boundary layer increases. This concentration effect leads to the rate of ion diffusion decreasing. Thus, the temperature effect is predominantly in the low-concentration region and the concentration effect is predominantly in the high-concentration region; the diffusion rate of ions in the external mass-transport process is affected by temperature and concentration predominantly in the low- and high-concentration regions, respectively.

In Figure 5, the relationship of  $D_2$  with initial concentration can also be divided into three regions for four adsorption temperatures. The  $D_2$  increases with initial concentration in the low-concentration region ( $1 \times 10^{-3}$ – $2 \times 10^{-3}M$ ), decreases with initial concentration in the high-concentration region ( $4 \times 10^{-3}$ – $10 \times 10^{-3}M$ ), and increases and decreases with initial concentration at 30–40°C and 50–60°C, respectively, in the middle-concentration region ( $2 \times 10^{-3}$ – $4 \times 10^{-3}M$ ). The  $D_2$  values increase and decrease about 1.44–1.69 and 0.53–0.68 over the low- and high-concentration regions, respectively, as the temperature increases from 30 to 60°C. As the amount of adsorbed ion on the active site increases to a certain level in the early stage, it leads to a decrease in the mobility of diffusion ions to pass through for adsorption in the long-term stage. The concentration effect leads to the rate of ion diffusion decreasing. Thus, the diffusion rate of ions in the intraparticle diffusion process decreases with increasing initial concentra-

tion in the high-concentration region. The diffusion rate of ions in the intraparticle diffusion process is affected by temperature and concentration predominantly in the low- and high-concentration regions, respectively.

The activation energy  $E_d$  and preexponential factor  $D_0$  of the early stage and long-term stage for various initial concentrations are shown in Table II. The  $E_d$  value of the early stage ( $E_{d,1}$ ) was calculated to be 15.46–24.67 kJ/mol over the low-concentration region, and it increases about 1.60 times as the initial concentration increases from  $1 \times 10^{-3}$  to  $4 \times 10^{-3}M$ . That was calculated to be -1.80 to -11.57 kJ/mol over the high-concentration region, and it decreases about 6.43 times as the initial concentration increases from  $6 \times 10^{-3}$  to  $10 \times 10^{-3}M$ . The  $E_d$  value of the long-term stage ( $E_{d,2}$ ) was calculated to be 9.96–15.30 kJ/mol over the low-concentration range and it increases about 1.54 times as the initial concentration increases from  $1 \times 10^{-3}$  to  $2 \times 10^{-3}M$ . The  $E_{d,2}$  was calculated to be -15.53 to -10.71 kJ/mol over the high-concentration region, and it increases about 0.69 times as the initial concentration increases from  $6 \times 10^{-3}$  to  $10 \times 10^{-3}M$ . The results indicate that the external mass-transport and intraparticle-diffusion processes are endothermic in the low-concentration region and exothermic in the high-concentration region. The increasing ratio of  $E_d$  is about equal for both stages in the low-concentration region, and the increasing ratio of the early stage is larger than the long-term stage in the high-concentration region. Thus, the external mass-transport process is more concentration dependent than the intraparticle-diffusion process in the high-concentration region, and the dependence of concentration for both processes is about equal in the low-concentration region.

The  $D_0$  value of the early stage is larger than that of the long-term stage over the initial concentration range (Table II). Since  $D_0$  increases

with the jump length of diffusion ions ( $\lambda$ ), the jump length of diffusion ions in the early stage is longer than that in the long-term stage. The jump length for the ion diffusion in the aqueous solution would be much longer than that within the adsorbent. Thus, the result confirms our assumption that the diffusion process in the early stage can be regarded as the external mass-transport process attributed to the ion diffusion in the aqueous solution, although the diffusion process in the long-term stage can be regarded as the intraparticle-diffusion process attributed to the ion diffusion within the adsorbent.

## CONCLUSION

The mass-transport process for the adsorption of  $\text{Cu}^{2+}$  ion onto water-insoluble amphoteric starch synthetic polymers in aqueous systems was investigated. The sorption process occurs in two stages: external mass transport occurs in the early stage and intraparticle diffusion occurs in the long-term stage. The diffusion rate of  $\text{Cu}^{2+}$  ion in both stages is concentration dependent. In the external mass-transport process, the diffusion coefficient ( $D_1$ ) increases with increasing initial concentration in the low- ( $1 \times 10^{-3}$ - $4 \times 10^{-3}M$ ) and high-concentration regions ( $6 \times 10^{-3}$ - $10 \times 10^{-3}M$ ) and decreases with increasing initial concentration in the middle-concentration region ( $4 \times 10^{-3}$ - $6 \times 10^{-3}M$ ) except at  $30^\circ\text{C}$ . The values of adsorption activation energy ( $k_{d1}$ ) in the low- and high-concentration regions are 15.46–24.67 and  $-1.80$  to  $-11.57$  kJ/mol, respectively. In the intraparticle diffusion process, the diffusion coefficient ( $D_2$ ) increases with increasing initial concentration in the low-concentration region ( $1 \times 10^{-3}$ - $2 \times 10^{-3}M$ ), decreases with increasing initial concentration in the high-concentration region ( $4 \times 10^{-3}$ - $10 \times 10^{-3}M$ ), and increases and decreases with initial concentration at  $30$ – $40$  and  $50$ – $60^\circ\text{C}$ , respectively, in the middle concentration region ( $2 \times 10^{-3}$ - $4 \times 10^{-3}M$ ). The  $k_{d2}$  values in the low- and high-concentration regions are 9.96–15.30 and  $-15.53$  to  $-10.71$  kJ/mol, respectively. For both stages, the diffusion process is endothermic in the low-concentration region and is exothermic in the high-concentration region. The  $D_1$  and  $D_2$  values increase and decrease with increasing temperature in the low- and high-concentration

regions, respectively. The external mass-transport process is more concentration dependent than the intraparticle-diffusion process in the high-concentration region, and the dependence of concentration for both processes is about equal in the low-concentration region.

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