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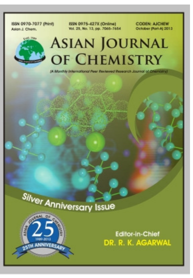

Chiral Recognition of Lysine by Cyclodextrin Intercalated Layered Double Hydroxides

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The chiral sorption of racemic lysine by carboxymethyl-α-cyclodextrin intercalated layered double hydroxides has been studied. It was found that L-lysine was preferentially adsorbed by carboxymethyl-α-cyclodextrin intercalated layered double hydroxides. Furthermore, the intraparticle diffusion model was successfully validated in this work. Intraparticle effective diffusivities (D_{eff}) of lysine in carboxymethyl-α-cyclodextrin intercalated layered double hydroxides macroparticle were determined from the homogeneous Fickian diffusion model. Moreover, the crystallites diffusivity (D_c) and pore diffusivity (D_p) for the parallel diffusion model were determined.

Key Words: Layered double hydroxides, Adsorption, Parallel diffusion, Chiral.

INTRODUCTION

Cyclodextrins (CD) are among the most remarkable macrocyclic molecules, with important theoretical and practical impacts in chemistry. Cyclodextrins are produced on a multitonne scale and widely used in chemical, pharmaceutical, food and other technologies as enzyme mimics, enantioselective catalysts, drug carriers[1-3]. Another important field of application of cyclodextrins is separation science. At present, cyclodextrins have been used as chiral selectors in gas chromatography (GC), high-performance liquid chromatography (HPLC), supercritical fluid chromatography (SFC), capillary electrophoresis (CE), capillary electrochromatography (CEC) and most recently in lab-on-chip enantioseparations[4-6].

Layered double hydroxides (LDHs) are a large class of host materials, which can be described by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}A^{n-}_{x/n}.yH_2O$. M(II) and $M(II)^I$ are divalent and trivalent metals, respectively; A^{n-} is the interlayer guest anion. Layered double hydroxides hold special importance as a rare anion exchangeable layered host in materials chemistry as well as afford multi-functionality such as for adsorbents, catalysts, solid state nanoreactors, molecular sieves, polymer composites, bioactive materials and pharmaceuticals[7-11].

In recent years, the immobilization of cyclodextrins with layered double hydroxides has attracted much attention. Modified cyclodextrins have been used as a "guest" molecule incorporating into layered hosts[12-14]. In our previous work, we have shown that when the internal surfaces of the layered double hydroxides are functionalized by anchoring anionic cyclodextrin cavities, neutral racemic guest molecule can be enantioselectively included within it[15,16].

Lysine (Lys) is an α-amino acid with the chemical formula $HO_2CCH(NH_2)(CH_2)_4NH_2$, which is an essential amino acid for humans[17,18]. Furthermore, L-Lysine is a necessary building block for all protein in the body, which plays a major role in calcium absorption, building muscle protein, recovering from surgery or sports injuries. Limited studies suggest that a high-Lysine diet or L-Lysine monochloride supplements may have a moderating effect on blood pressure and the incidence of stroke.

In this study, the enantioselective adsorption of racemic lysine by CMCD-LDHs has been investigated. Compared with other adsorbents which have been used for chiral separation of Lys, CMCD-LDHs are easy and inexpensive to prepare and environmentally friendly. The adsorption isotherms of enantioselective as well as non-enantioselective adsorption of Lys by CMCD-LDHs have been studied by using a batch method. Moreover, the parallel diffusion model is successfully validated in this work. Intraparticle effective diffusivities (D_{eff}) of Lys in CMCD-LDHs macroparticle were determined from the homogeneous Fickian diffusion model, increasing with the increase of Lys bulk phase concentration (C_0), which indicates the existence of parallel diffusion (crystallites diffusion and pore diffusion). Therefore, a detailed understanding of the adsorption behaviour of Lys on carboxymethyl-α-cyclodextrin (CMCD) functionalized layered double hydroxides should facilitate the application of such inorganic layered materials as chiral stationary phases (CSPs) for chromatographic columns.

EXPERIMENTAL

All chemicals including $Zn(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, NaOH, $NaNO_3$, methanol, chloroactic acid, α-cyclodextrin and

Lysine were of analytical grade. They were purchased from the Beijing Chemical Plant Limited.

Synthesis of carboxymethyl-α-cyclodextrin (CMCD) (3.7): CMCD was synthesized according to the procedure described in the literature[19] with some modifications. In brief, α-cyclodextrin (29.3 g) and NaOH (35.2 g) were dissolved in 200 mL of water and monochloroacetic acid (37.8 g) was added with gentle stirring. The mixture was heated at 80 ºC for 3 h. The solution was then cooled in an ice bath and the pH was adjusted to 6.0 with concentrated hydrochloric acid. Methanol was gradually added into the solution with stirring to obtain CMCD precipitation. The average number of carboxylate groups (3.7) per CMCD was calculated using ^{1}H NMR[20].

Synthesis of CMCD-LDHs: The precursor $Zn_{0.67}Al_{0.33}(OH)_2(NO_3)_{0.33}.yH_2O$ (NO_3-LDHs) was synthesized by a procedure similar to that of described prebviously[14,16]. Under N_2 atmosphere through the conventional route, a solution of $Zn(NO_3)_2\cdot 6H_2O$ (1.2×10^{-1} mol) and $Al(NO_3)_3\cdot 9H_2O$ (6.0×10^{-2} mol) in deionized water (2.0×10^{-4} m^3) was added dropwise over 2 h to a solution of NaOH (3.1×10^{-1} mol) and $NaNO_3$ (2.1×10^{-1} mol) in water (1.0×10^{-4} m^3). The mixture was held at 343 K for 24 h. The precipitates were separated by centrifugation, washed with water and dried at 343 K for 20 h.

The CMCD-LDHs was obtained by the method of ion exchange. A solution of CMCD (5×10^{-3} kg) in deionized water (5×10^{-5} m^3) was added to a suspension of NO_3-LDHs (1×10^{-2} kg) in water (1×10^{-4} m^3) and the solution pH was kept 6 by adding 1×10^2 mol/m^3 NaOH solution or 1×10^2 mol/m^3 HCl solution during reaction. The mixture was heated at 333 K under a nitrogen atmosphere for 48 h. The product was washed extensively with deionized water, centrifuged and dried at 343 K for 20 h.

As Ca^{2+} cannot be adsorbed on LDHs layers, the void fraction of the CMCD-LDHs, ε, was obtained by dissolving the CMCD-LDHs whose pore was filled with $CaCl_2$ solution in HNO_3 solution (1×10^2 mol/m^3). The concentration of Ca^{2+} in the filtrate was determined by ICP. The value of ε was calculated according to eqn. 1, where C_{Ca} is the concentration of Ca^{2+} filled in the pore (mol/m^3); W and θ are the weight of the wet CMCD-LDHs particles (kg) and the apparent density (kg of wet CMCD-LDHs m^{-3}), respectively; $C_{f,Ca}$ and V_f are the concentration of Lys in the filtrate (mol/m^3) and the volume of the filtrate (m^3), respectively. The experimental physical properties of CMCD-LDHs are listed in Table-1.

$$\varepsilon = \frac{C_{f,Ca} V_f}{(W/\theta) C_{Ca}} \qquad (1)$$

Sorption experiments: Lysine sorption experiments were carried out using a batch method. Both the effects of contact time and Lys concentration on the adsorption were investigated, the effect of contact time was used to determine kinetic model of Lys sorption and equilibrium time. 4×10^{-4} kg of CMCD-LDHs and 3×10^{-5} m^3 of Lys solutions (typically ranging from 0.0 to 2.28×10^2 mol/m^3) were added to 5.0×10^{-5} m^3 Erlenmeyer stopper flasks. After capped and vigorously shaken by hand, the flasks were place in a water bath at 303 K and gently shaken for specific time period or until adsorption equilibrium. After the suspensions were filtered, the e.e. % of the solutions were measured using a digital polarimeter. Moreover, the Lys concentrations were determined by the method of ninhydrin colorinetry at 570 nm. The amount of Lys adsorbed by the CMCD-LDHs was calculated by the difference between the initial ($C_{a,0}$) and equilibrium concentrations ($C_{a,e}$), per kilogram of LDHs adsorbent:

$$Q_e = \frac{(C_{a,0} - C_{a,e})}{m} \times V$$

TABLE-1
EXPERIMENTAL PHYSICAL PROPERTIES OF CMCD-LDHS

Chemical composition of CMCD-LDHs	$Zn_{0.67}Al_{0.33}(OH)_2(CMCD(3.7))_{0.057}(NO_3)_{0.12}\cdot 0.8H_2O$
Particle diameter (m)	2.37×10^{-4}
True density (kg of dry CMCD-LDHs m^{-3})	1.93×10^{3}
Apparent density (kg of wet CMCD-LDHs m^{-3})	1.18×10^{3}
The void fraction of CMCD-LDHs macroparticles (-)	0.302

Characterization: X-Ray diffraction pattern of the samples were obtained using a Shimadzu XRD-6000 diffractometer with CuK_α radiation (40 kV and 30 mA) at a scanning rate of 5º min^{-1}. Elemental analysis was performed with a Shimadzu ICP-7500 instrument. The C, H and N contents were determined using an Elementarvario elemental analysis instrument. An UV-visible spectrophotometer (Shimadzu UV-2501PC) was employed to measure the absorbance spectra of compounds in the 200-700 nm wavelength range. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter, which was used to determine e.e.% of the solutions after the adsorption experiment.

Theory: A single LDHs macroparticle is an agglomerate of spherical crystallites and the LDHs crystallites consist of LDHs layers and anions between the sheets. In the adsorption, the adsorbate molecules diffuse into pores and are adsorbed on the crystallites walls and also diffuse into the interlayer of LDHs crystallites and are adsorbed there[16]. In order to simplify calculation, the LDHs crystallites are considered as microspheres, which can adsorb Lys at the surface. Meanwhile, Lys molecules can diffuse from one adsorption site to the next adsorption site and also diffuse between the nearby crystallites. A macroparticle of LDHs is made up of lots of these crystallites micropheres.

In this experimental study, the intraparticle diffusion of Lys in CMCD-LDHs was analyzed based on a parallel transport[21,22] by Lys diffused in the crystallites (hereafter called crystallites diffusion) and the liquid-phase diffusion inside the network structure between crystallites (hereafter called pore diffusion). The following assumptions apply:

Crystallites and pore diffusions occur in parallel inside the CMCD-LDHs macroparticles. Crystallites and pore diffusives are constant throughout the adsorption process. The void fraction of CMCD-LDHs macroparticle is constant throughout the adsorption process. The liquid-phase concentration of Lys inside the particle is in local equilibrium with the concentration of the adsorbed lysine in the LDHs crystallites. The bulk phase concentration of lysine is constant during the adsorption process.

The parallel diffusion model for this system can be written as follows:

$$\varepsilon\frac{\partial C}{\partial t}+(1-\varepsilon)\frac{\partial q}{\partial t}=D_p\varepsilon\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial C}{\partial r})$$

$$+D_c(1-\varepsilon)\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial q}{\partial r}) \quad (2)$$

where C (mol/m^3) represents liquid-phase concentration of lysine inside the macroparticle and q (mol/m^3 wet LDHs) corresponds to solid-phase concentration of Lys on the surface of the crystallites micropheres. r (m) means radial dimension of an adsorbent particle. Symbol ε denotes the void ratio of LDHs macroparticles. D_c and D_p (m^2/s) are the effective diffusivities in the crystallites and in the pore, respectively. Using the dimensionless variables, eqn. 2 is transformed into eqn. 3

$$\frac{\partial X}{\partial \tau_p}+\alpha\frac{\partial Y}{\partial \tau_p}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial X}{\partial \xi}\right)+\beta\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial Y}{\partial \xi}\right) \quad (3)$$

where $X = C/C_e$, $Y = q/q_e$, $\tau_p = D_pt/r_0^2$, $\xi = r/r_0$, $\alpha=\frac{(1-\varepsilon)q_e}{\varepsilon C_e}$,

$\beta=\frac{(1-\varepsilon)q_eD_c}{\varepsilon C_eD_p}=\alpha\frac{D_c}{D_p}$ and q_e (mol/m^3 wet LDHs) is the concentration of Lys on the adsorption sites, in equilibrium with the concentration of Lys in the bulk solution C_e (mol/m^3). r_0 (m) is radius of an adsorbent particle. The first and second terms of the right-hand side of eqn. 3 represent the contributions of pore diffusion and crystallites diffusion, respectively. In this parallel diffusion model, α and β are the most important parameters. According to the definition, α means a distribution coefficient, while β is the ratio of the rate of crystallites diffusion to that of pore diffusion. The degree of the contributions of crystallites and pore diffusions should be evaluated from the value of β. There are two limiting cases to consider here: when $\beta\to 0$ ($\varepsilon D_pC_e >> (1-\varepsilon)D_cq_e$; pore diffusion control) and when $\beta\to\infty$ ($\varepsilon D_pC_e << (1-\varepsilon)D_cq_e$; crystallites diffusion control). When $\beta\to 0$, the second term of the right hand side of eqn. 3 becomes zero and the equation for the pore diffusion control is obtained (eqn. 4). However, when $\beta\to\infty$, the second term of eqn. 3 becomes infinite consequently, the equation cannot be solved directly. Therefore, eqn. 3 is transformed into eqn. 5:

$$\frac{\partial X}{\partial \tau_p}+\alpha\frac{\partial Y}{\partial \tau_p}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial X}{\partial \xi}\right) \quad (4)$$

$$\frac{1}{\alpha}\frac{\partial X}{\partial \tau_c}+\frac{\partial Y}{\partial \tau_c}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial Y}{\partial \xi}\right) \quad (5)$$

When $\alpha\to\infty$, the concentration of Lys adsorbed in the crystallites is substantially larger than that of in the pore. In this case, pore diffusion is negligible and the crystallites diffusion is the rate-controlling step. This is confirmed by substituting $\alpha\to\infty$ into eqn. 3. Dividing both sides of eqn. 3 by α and using the definition of β = α (D_c/D_P), the terms related to the concentration of Lys in the pore disappear and the following equation is obtained

$$\frac{\partial Y}{\partial \tau_c}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial Y}{\partial \xi}\right)$$

$$\text{(crystallites diffusion control, } \alpha\to\infty\text{)} \quad (6)$$

when $\alpha\to 0$, the concentration of Lys in the pore is much larger than in the crystallites. In this case, pore diffusion is the rate-controlling step and the terms relate to the concentration in the crystallites disappear and the eqn. 7 is obtained

$$\frac{\partial X}{\partial \tau_p}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial X}{\partial \xi}\right)$$

$$\text{(pore diffusion control, } \alpha\to 0\text{)} \quad (7)$$

Equilibrium as described by the equilibrium isotherms holds at the interface between the liquid and solid phases. In this case the model uses the Freundlich isotherm (eqn. 8).

$$q = kC^{1/n} \quad (8)$$

Using the dimensionless variables, eqn. 8 is transformed into eqn. 9

$$Y = k'X^{1/n} \qquad \text{where } \left(k'=\frac{kC_e^{1/n}}{q_e}\right) \quad (9)$$

Using eqns. 9, 3 and 5 are transformed into eqns. 10 and 11, respectively, as follows:

$$\left\{\alpha+\frac{nY^{n-1}}{k'^n}\right\}\frac{\partial Y}{\partial \tau_p}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left\{\xi^2\frac{nY^{n-1}}{k'^n}\frac{\partial Y}{\partial \xi}\right\}$$

$$+\frac{\beta}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial Y}{\partial \xi}\right) \quad (10)$$

$$\left\{1+\frac{nY^{n-1}}{\alpha k'^n}\right\}\frac{\partial Y}{\partial \tau_c}=\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial Y}{\partial \xi}\right) \quad (11)$$

As mentioned previously, eqn. 10 includes the expression of the pore diffusion control (β = 0). In addition, the following initial and boundary conditions apply

$$\text{(I.C.) } X = 0\ Y = 0 \text{ at } \tau_p = 0 \text{ or } \tau_c = 0 \quad (12)$$

$$\text{(B.C.) } \frac{\partial X}{\partial \xi}=0 \quad \frac{\partial Y}{\partial \xi}=0 \text{ at } \xi=0$$

$$X = 1\ Y = 1 \text{ at } \xi=1 \quad (13)$$

Given that, only the change in the total concentration of Lys in the particle Q_t (mol/m^3 wet LDHs) in eqn. 14, can be determined with time, while equilibrium adsorption capacity Q_e (mol/m^3 wet LDHs) in eqn. 15, can be obtained by adsorption at enough time.

$$Q_t=(1-\varepsilon)q+\varepsilon C=\frac{V(C_{a,0}-C_{a,t})}{V_{LDHs}} \quad (14)$$

$$Q_e=(1-\varepsilon)q_e+\varepsilon C_e=\frac{V(C_{a,0}-C_{a,e})}{V_{LDHs}} \quad (15)$$

where V and V_{LDHs} represent the solution volume and the wet LDHs volume. $C_{a,0}$, $C_{a,t}$ and $C_{a,e}$ represent the aqueous-phase Lys concentration at initial, at time t and at equilibrium, respectively.

Finally, the solution to the fractional attainment (F) of equilibrium under the initial and boundary conditions in eqns. 12 and 13, is given by eqn. 16[23]

$$F = \frac{Q_t}{Q_e} = \frac{3\int_0^{r_0} Q_t r^2 dr}{r_0^3 Q_e} = \frac{3[\alpha\int_0^1 Y\xi^2 d\xi + \int_0^1 X\xi^2 d\xi]}{\alpha+1}$$

$$= 1 - \sum_{n=1}^{\infty} \frac{6\omega(\omega+1)\exp(-D_{eff}\lambda_n^2 t/r^2)}{9+9\omega+\lambda_n^2\omega^2} \quad (16)$$

where the λ_n values are the nonzero roots of

$$\tan\lambda_n = \frac{3\lambda_n}{3+\omega\lambda_n^2} \quad (17)$$

And the parameter ω is expressed in terms of the final fractional uptake of solute by the LDHs macroparticles by the relation:

$$\frac{V_{LDHs}Q_e}{VC_{a,0}} = \frac{1}{1+\omega} \quad (18)$$

RESULTS AND DISCUSSION

Characterization of NO_3-LDHs and CMCD-LDHs: The CMCD intercalated LDHs powder (CMCD-LDHs) was obtained by an anion-exchange method. Fig. 1 displays the XRD patterns of the precursor NO_3-LDHs and the resulting composite CMCD-LDHs. In each case, the reflections can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of LDHs structures. The NO_3-LDHs precursor has an XRD pattern similar to that reported previously[16], with an interlayer spacing (d_{003}) of 0.890 nm. After intercalation of CMCD, the interlayer distance increased to 1.639 nm. The expanded interlayer distance is consistent with the intercalation of the organic anions within the gallery spaces of the LDHs. Since the thickness of the LDHs hydroxide basal layer is 0.480 nm, the gallery height is 1.159 nm.s

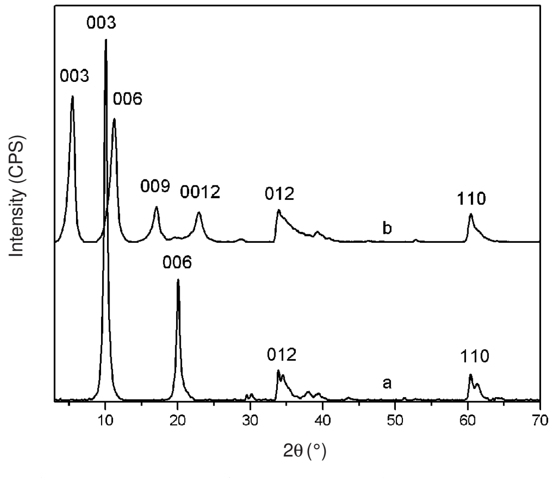

Fig. 1. XRD patterns of (a) NO_3-LDHs, (b) CMCD-LDHs

Taking into account the dimensions of the α-cyclodextrin molecule and the rule of charge balance, the CMCD anions can only adopt a monolayer arrangement with its cavity axis perpendicular to the LDHs layer and carboxymethyl groups on adjacent cyclodextrin molecules attached alternately to the upper and lower LDHs layer surfaces. This is similar to the arrangement reported in our previous paper[16].

Adsorption equilibrium: The optical rotations of the solution was used to determine e.e. % of the supernatants, by filtration after the adsorption experiment. The results indicate that L-Lys was adsorbed preferentially by CMCD-LDHs. It can be speculated that the adsorption of Lys by CMCD-LDHs includes two parts: the enantioselective adsorption (Q_s) resulting from the chiral reorganization of interlayer immobilized CMCD and the non-enantioselective adsorption (Q_{non-s}) produced by the surface of LDHs layers, which can be calculated by

$$Q_s = \frac{C_{a,t} \times V \times e.e.\%}{m} \quad (19)$$

$$Q_{non-s} = \frac{(C_{a,0} - C_{a,t}) \times V - C_{a,t} \times V \times e.e.\%}{m} \quad (20)$$

Thus the adsorption isotherms, including enantioselective adsorption, non-enantioselective adsorption and the total adsorption, were plotted and shown in Fig. 2.

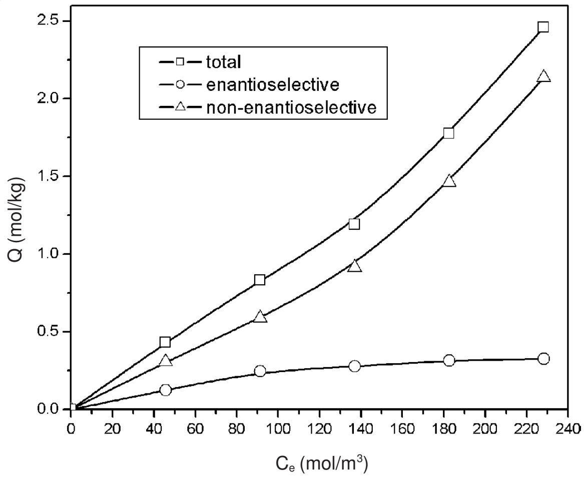

Fig. 2. The total, enantioselective and non-enantioselective adsorption isotherms of Lys by CMCD-LDHs at 303 K

According to the classification of IUPAC, the shape of its enantioselective isotherm can be considered as Type I. The enantioselective adsorptions by CMCD-LDHs have a maximum adsorption capacity, furthermore, in all the adsorption, the amount of enantioselective adsorption increases with the increase of temperature. The explanation for this behaviour is that the enantioselective adsorption is caused by the chiral inclusion of CMCD in the interlayer region of LDHs, which is an energy-needed process, so higher temperature is beneficial to chiral adsorption. Owing to the shape of the isotherms, the total sorption data were analyzed based on Freundlich equation.

Study on the diffusion kinetics: To determine the crystallites diffusivity D_c (m^2/s) and the pore diffusivity D_p (m/s) based on the parallel diffusion model, the intraparticle effective diffusivity D_{eff} (m/s) at 303 and 333 K for the homogeneous model was calculated. Assuming Fickian diffusion with a constant intraparticle effective diffusivity, the mass balance equation over the particle is given by the following equation

$$\frac{\partial Q}{\partial t} = D_{eff}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Q}{\partial r}\right) \qquad (21)$$

The initial (I.C.) and boundary conditions (B.C.) are given as follows

$$\text{(I.C.) } Q = 0 \text{ at } t = 0 \qquad (22)$$

$$\text{(B.C.) } \frac{\partial Q}{\partial r} = 0 \text{ at } r = 0$$

$$Q = Q_e \text{ at } r = r_0 \qquad (23)$$

In the adsorption experiments, the change of bulk concentration before and after adsorption is *ca.* 7 %, as a result the bulk concentration can be considered to be constant approximately during the adsorption process. This gives the above boundary condition at the surface of the adsorbent particle, *i.e.*, the adsorbent-phase concentration at the surface of the particle is constant.

The value of the intraparticle effective diffusivity (D_{eff}) was determined by fitting the experimental adsorption data with eqn. 16.

Initializing different values of D_{eff} until the best fit was obtained. As shown in Fig. 3, the experimental values were well correlated by eqn. 16. The experimental values of D_{eff} are listed in Table-2. D_{eff} increased with increasing bulk-phase Lys concentration, indicating an existence of a parallel transport by both crystallites and pore diffusions in the LDHs macroparticles.

The relationship between crystallites diffusivity, pore diffusivity and intraparticle effective diffusivity based on parallel diffusion model is given by the following equation, which is derived from the relation between the fluxes based on the parallel diffusion model and the Fickian model:

$$D_{eff}[(1-\varepsilon)+\varepsilon\frac{dC}{dq}] = (1-\varepsilon)D_c + \varepsilon D_p\frac{dC}{dq} \qquad (24)$$

Since, in our experimental method, the adsorption isotherm could be considered linear in the concentration range examined. By taking $dC/dq = C_e/q_e$ as an approximation, eqn. 24 is transformed into eqn. 25:

$$D_{eff}\left(1+\frac{1}{\alpha}\right) = D_c + D_p\frac{1}{\alpha} \qquad (25)$$

The value of the intercept of the line gives the crystallites diffusivity D_c and the slope of the line provides the pore diffusivity D_p, which are listed in Table-2. It can be seen that the values of D_{eff}, D_c and D_p increase continuously with temperature from 303-333 K, indicating that higher temperatures favour diffusion of Lys in LDHs.

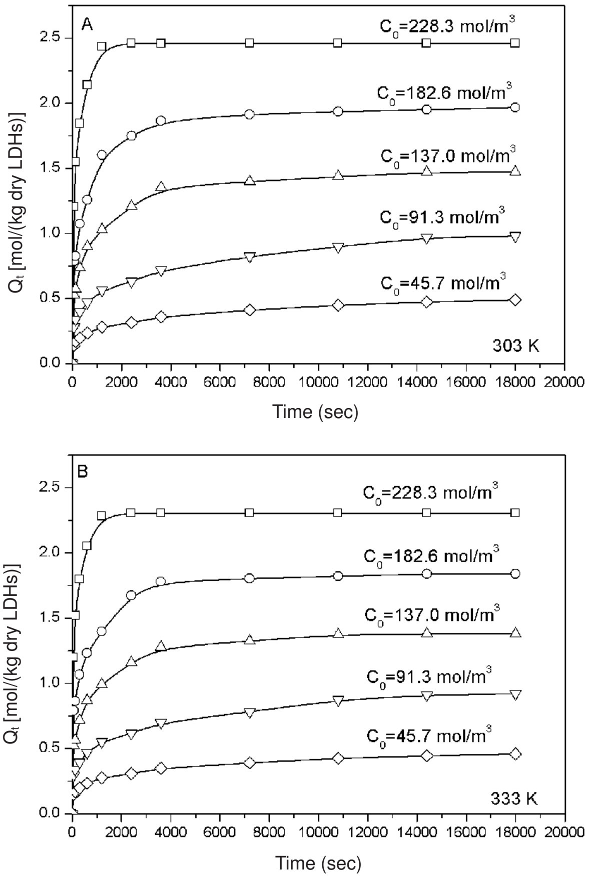

Fig. 3. Effect of concentration on the uptake curves for adsorption of Lys on CMCD-LDHs at (A) 303 K and (B) 333 K, respectively

Conclusion

The CMCD-LDHs has been demonstrated to represent enantioselective adsorption for Lys, which suggests that CMCD-LDHs may have prospective application as the basis of a novel chiral separation system. The adsorption isotherms of enantioselective as well as non-enantioselective adsorption of Lys by CMCD-LDHs have been investigated and the enantioselective adsorptions have a maximum adsorption capacity. Moreover, the parallel transport of Lys by crystallites and pore diffusion in CMCD-LDHs macroparticle was investigated. The values of the intraparticle effective diffusivity (D_{eff})

TABLE-2
DETERMINED PARAMETERS AGAINST INITIAL CONCENTRATION

Temperature (K)	$C_{a,0}$ (mol/m^3)	$D_{eff} \times 10^{11}$ (m^2/s)	$D_c \times 10^{12}$ (m^2/s)	$D_p \times 10^{10}$ (m^2/s)	α (-)	β (-)
303	228.3	3.25	7.26	2.53	8.74	0.250
	182.6	2.91			10.2	0.293
	137.0	2.65			11.7	0.336
	91.3	2.53			12.6	0.362
	45.7	2.44			13.3	0.382
333	228.3	3.89	8.09	3.17	8.97	0.229
	182.6	3.43			10.8	0.275
	137.0	3.20			11.9	0.303
	91.3	3.06			12.7	0.324
	45.7	2.94			13.5	0.344

obtained from the homogeneous Fickian model increased with increasing bulk phase concentration for the whole rang of Lys concentration. The parallel diffusion model is successfully validated in this work.

Notation

C = liquid-phase concentration of Lys inside the macroparticle, mol/m^3
$C_{a,0}$ = initial aqueous-phase Lys concentration, mol/m^3
$C_{a,t}$ = aqueous-phase Lys concentration at time t, mol/m^3
$C_{a,e}$ = aqueous-phase Lys concentration at equilibrium, mol/m^3
C_{Ca} = the concentration of Ca^{2+} filled in the pore, mol/m^3
C_e = the equilibrium concentration of Lys in the pore, mol/m^3
$C_{f,Ca}$ = the concentrate of Ca^{2+} in the filtrate, mol/m^3
D_{eff} = intraparticle effective diffusivity, m^2/s
D_p = pore diffusivity, m^2/s
D_c = the effective diffusivity in the crystallites, m^2/s
F = fractional attainment of equilibrium
m = the mass of CMCD-LDHs, kg
q = solid-phase concentration of Lys on the surface of the crystallites micropheres, mol/m^3
q_e = the equilibrium concentration of Lys on the adsorption sites, mol/m^3
Q_e = the adsorption capacity at equilibrium, mol/kg
Q_t = $(= (1 - \varepsilon)q + \varepsilon C)$ total concentration of Lys in the particle, mol/m^3 wet LDHs
$Q_{s,e}$ = the enantioselectively sorption capacity at equilibrium, mol/kg
$Q_{non\text{-}s,e}$ = the non-enantioselectively sorption capacity at equilibrium, mol/kg
$Q_{total,e}$ = the total sorption capacity at equilibrium, mol/kg
Q_e = $(= (1 - \varepsilon)q_e + \varepsilon C_e)$ total concentration of Lys in the particle in equilibrium, mol/m^3 wet LDHs
r = radial dimension of an adsorbent particle, m
r_0 = radius of an adsorbent particle, m
t = time, s
V_f = the voloume of the fitrate, m^3
W = eight of the wet CMCD-LDHs particles, kg
X = $(= C/C_e)$ dimensionless constant
Y = $(= q/q_e))$ dimensionless constant

Greek letters

$$\alpha = \frac{(1-\varepsilon)q_e}{\varepsilon C_e}$$

$$\beta = \alpha\left(\frac{D_c}{D_p}\right)$$

ε = void ration of LDHs macroparticles
λ_n = the nonzero roots of Eq. 17

$$\xi = \frac{r}{r_0}$$

ω = final fractional uptake of solute by the LDHs macroparticles

$$\tau_p = \frac{D_p t}{r_0^2}$$

$$\tau_c = \frac{D_c t}{r_0^2}$$

θ = the apparent density, kg of wet CMCD-LDHs m^{-3}

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