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Adsorption Equilibrium and Kinetics of Tetrahydrofuran + Water Solution Mixture on Zeolite 4A

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The adsorption of tetrahydrofuran + water solution mixture on zeolite 4A was carried out in a batch system. The equilibrium behavior was shown to fit a Langmuir isotherm. A surface diffusion model coupled with the Langmuir isotherm equation was used to interpret the observed experimental adsorption kinetic curves with different initial concentrations, temperatures, and particle sizes. The surface diffusivity (D_s) can be extracted. The surface diffusivity was 1.64×10^{-10} $m^2 \cdot s^{-1}$ at 298.15 K, $C_0 = 5.800$ %, $d_p = (2.92$ to $3.43)$ mm, and increased as temperature and initial concentration increased, while it was independent of particles size. The preexponential factor (D_{so}) was 7.75×10^{-7} $m^2 \cdot s^{-1}$, and the activation energy (E) was also extracted.

Introduction

Tetrahydrofuran (THF) is a fine organic solvent, an important organic raw material, and the precursor of polymers. Due to its proton-accepting nature, it is used as a solvent in many chemical industries. It is fully miscible with water. Many chemical and pharmaceutical industries encounter problem in separating THF from aqueous waste streams since their mixture form azeotropes at lower compositions of water (mass fraction is 5.800 % at 337.15 K).

Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role in a number of natural and industrial systems. Adsorption equilibrium and kinetics data are important in the design of separation processes and simulate the adsorption processes. This paper studies the adsorption equilibrium and adsorption kinetics of the tetrahydrofuran + water solution mixture on zeolite 4A.

Experimental Section

Materials and Analysis. Zeolite 4A was obtained from ShangHai Chemical Reagent Plant (Shanghai, China). Table 1 shows the properties of zeolite 4A. Prior to its use, the molecular sieve was crushed and screened to a series of particle sizes and then washed thoroughly in distilled water to remove fines. Before the measurement, the adsorbent was activated at 623.15 K in an electronic furnace 8 h and then kept in a vacuum vessel for use.

Tetrahydrofuran was obtained from Shuanglin Chemical Reagent Plant (Hangzhou, China), was a reagent grade chemical with purity higher than 99 %, and was used without further purification. A series of solutions were prepared using distilled water. Their concentrations were analyzed by gas chromatography.

Equilibrium. The equilibrium adsorption of the THF + water solution mixture at 298.15 K was performed as follows: A set of solutions of consecutively increasing concentrations was prepared and brought into contact with known masses of zeolite in conical flasks. These conical flasks were then capped and placed in an incubator shaker at a pre-settled temperature with an uncertainty of ± 0.01 K and shaken under 100 rpm. After adsorption reached equilibrium, the liquid concentrations were analyzed by gas chromatography.

Table 1. Characteristics of Zeolite 4A Adsorbent

adsorbent	zeolite 4A
form	sphere
pellet density/$g \cdot cm^{-3}$	0.66
average pore radius/Å	4
heat of adsorption/ $kJ \cdot kg^{-1}$(H_2O)	4200
BET surface area/$m^2 \cdot g^{-1}$ (N_2)	28.09

Kinetic. Kinetic studies were carried out in a 250 mL stirred tank. The tank was equipped with a two-bladed impeller and a thermometer, which had an uncertainty of ± 0.01 K. The volume of the solution was about 100 mL. The tank was kept in a thermostated bath, and the impeller was rotated at about 350 rpm, where the resistance at the particle surface was negligibly small, and 3 μL samples of solution were withdrawn from the bulk solution at specified time intervals. This was repeated until the constant concentration at equilibrium was achieved. These concentration measurements were performed by gas chromatography. An electrical balance with an uncertainty of ± 10 μg was used, and the uncertainty of the timer was ± 0.1 s. In this work, the estimated uncertainty of the concentration measurement was less than 0.1 %.

Mathematical Model

The mathematical model described in the present work is founded on the following assumptions:[1,2]

(i) Adsorbent particles are spherical of radius R.

(ii) The pore structure inside the particle is uniform.

(iii) The mass transfer resistance at the particle surface is negligible.

(iv) The rate of adsorption is much faster than the rate of diffusion, and hence local equilibrium is maintained between the adsorbate in the pore space and that on the pore walls.

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With the above assumptions, the basic equations are represented in the following:

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{1}$$

Initial and boundary conditions are as follows:

$$t = 0 \text{ for } q = 0, \quad 0 \le r < R \tag{2}$$

$$t = 0 \text{ for } q = q_0 \quad r = R \tag{3}$$

$$(\partial q/\partial r) = 0 \text{ for } r = 0 \quad t > 0 \tag{4}$$

$$\partial q/\partial t = -3\frac{W}{VR}\left(\frac{\partial q}{\partial c}\right)D_s\left(\frac{\partial q}{\partial r}\right) \text{ for } r = R \quad t > 0 \tag{5}$$

where t is the time, R is the radius of the sphere, r is the distance from the core, q is the amount of water adsorbed at point r, c is the concentration (the mass fraction of water) at point r within particle, W is the amount of the adsorbent, V is the amount of the solution, and D_s is the surface diffusivity.

The equilibrium curves for the Langmuir isotherm are represented by the following equation:

$$q = \frac{q_m kC}{(1 + kC)} \tag{6}$$

where q_m and k are isotherm parameters, C is the concentration (the mass fraction of water) in liquid-phase, and q is the equilibrium amount adsorbed at C.

The set of partial differential equations was solved by the orthogonal collocation method (OCM)[3]. The mathematical algorithm was written in Fortran and implemented in a computer program. The objective function to minimize was the root mean square (RMS) of the normalized residuals:[4]

$$\text{RMS} = 100 \times \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(1 - \frac{C_{\text{cal},i}}{C_{\text{exp},i}}\right)^2} \tag{7}$$

where N is the number of experimental points, $C_{\text{exp},i}$ and $C_{\text{cal},i}$ are the experimental and calculated liquid-phase concentrations, respectively.

Results and Discussion

Equilibrium Isotherm. Equilibrium behavior of an adsorption system is an essential requirement for modeling of system kinetics. A clear review of the various equilibrium isotherms and their applications is in the literature.[5] The isotherm equations used in this study were the Langmuir and the Freundlich equations. The mathematical form of each model is as follows:

$$\text{Langmuir: } q = \frac{q_m kC}{(1 + kC)} \tag{6}$$

$$\text{Freundlich: } q = aC^b \tag{8}$$

where a and b are Freundlich isotherm parameters. The amount adsorbed of THF + H_2O system adsorption on 4A molecular sieve (see Table 2) was calculated by mass balance according to the following equation:

$$q = \frac{V}{W}\frac{C_0 - C}{1 - C} \tag{9}$$

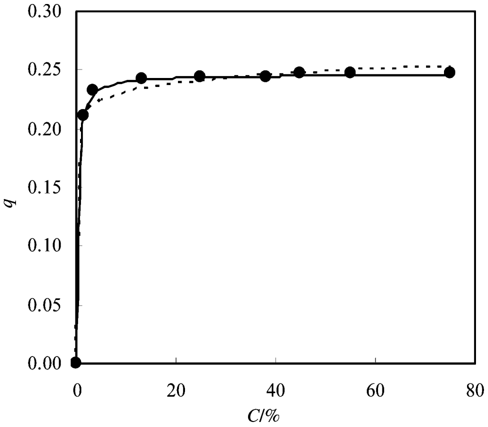

Figure 1. Adsorption isotherm of THF + water solution mixture on zeolite 4A at 298.15 K; ●, experimental data; —, Langmuir model; - - -, Freundlich model.

Table 2. Date of Adsorption Equilibrium of THF + Water Solution Mixture on Zeolite 4A at 298.15 K

mass fraction of water C/%	amount of water adsorbed q/g·g^{-1}
1.34	0.211
3.30	0.232
13.33	0.242
24.97	0.244
37.93	0.245
45.00	0.247
55.00	0.247
75.00	0.247

Table 3. Effect of Temperature on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

T/K					
281.15		298.15		313.15	
t/min	C/%	t/min	C/%	t/min	C/%
0	5.800	0	5.800	0	5.800
4.5	4.888	2	4.900	3	4.787
7	4.446	6	4.285	8	3.888
12	4.026	9	3.916	15	3.347
16	3.824	16	3.529	22	3.024
23	3.460	21	3.247	28	2.842
35	3.014	27	2.988	34	2.700
49	2.680	33	2.788	42	2.557
60	2.308	39	2.759	50	2.500
70	2.222	49	2.581	54	2.421
80	2.115	60	2.274	61	2.399
		70	2.239	80	2.396

[a] d_p = (2.92 to 3.43) mm; C_0 = 5.800 %.

where C_0 is the initial liquid-phase concentration of water. The Langmuir isotherm selected for this work described the current date with high degree of accuracy over a wide concentration rage (see Figure 1). The estimated values of the parameter k = 3.778, q_m = 0.246, correlation efficients is 0.998.

Kinetics Study. The effects of temperature, initial concentration, and particle size on the adsorption kinetics of THF + water mixture on zeolite 4A were investigated (see Tables 3 to 5). Results of the surface diffusion model (SDM) application were presented in terms of the concentration decay curves, Figures 2 to 4 show a good agreement between experimental and calculated date.

Surface Diffusivity D_s. (a) Effect of Temperature. As shown in Table 6, the surface diffusivity D_s was increased as temperature increased. This could be attributed to the increase of the molecular energy with higher temperature. This is the case because[6]

$$D_s = D_{so}\exp(-E/RT) \tag{10}$$

Table 4. Effect of Initial Concentration on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

C_0					
5.800		12.795		32.059	
t/min	C/%	t/min	C/%	t/min	C/%
0	5.800	0	12.795	0	32.059
2	4.900	3	11.276	3	31.054
6	4.285	8	10.247	6	30.840
9	3.916	13	9.581	11	29.683
16	3.529	18	9.182	21	28.857
21	3.247	25	8.715	26	28.084
27	2.988	30	8.377	32	27.891
33	2.788	45	7.762	40	27.571
39	2.759	55	7.652	50	27.281
49	2.581	65	7.770	60	26.800
60	2.274	80	7.760	90	26.700
70	2.239				

[a] T = 298.15 K, d_p = (2.92 to 3.43) mm.

Table 5. Effect of Particle Size on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

d_p/mm					
2.92 to 3.43		1.80 to 2.40		1.20 to 1.80	
t/min	C/%	t/min	C/%	t/min	C/%
0	5.800	0	5.800	0	5.800
2	4.900	2	4.212	2	3.600
6	4.285	4	3.888	4	3.306
9	3.916	6	3.415	7	2.671
16	3.529	9	3.083	11	2.427
21	3.247	14	2.833	18	2.354
27	2.988	18	2.532	23	2.305
33	2.788	22	2.321	27	2.304
39	2.759	27	2.401	31	2.391
49	2.581	32	2.337	38	2.376
60	2.274	47	2.338	50	2.246
70	2.239	60	2.343	60	2.327

[a] T = 298.15 K, C_0 = 6.5000 %.

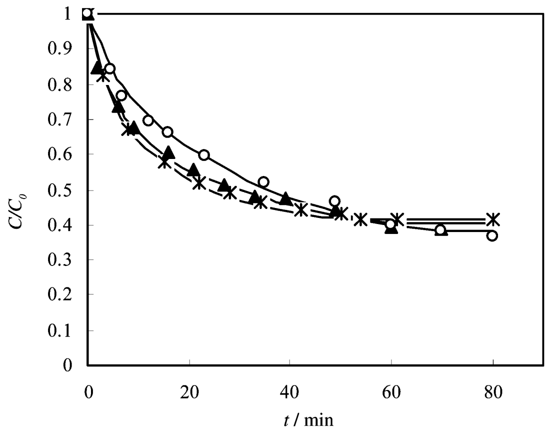

Figure 2. Application of the SDM to THF + water solution mixture on zeolite 4A in different temperatures; *, 313.15 K; ▲, 298.15 K; ○, 281.15 K.

where E is the activation energy, D_{so} is the pre-exponential factor, and T is the temperature. Using the date of Table 6, the ln D_s against 1/T (the values of E and D_{so} can be determined from the slope and intercept) values were 21072.66 $\text{J}\cdot\text{mol}^{-1}$ and 7.75×10^{-7} $\text{m}^2\cdot\text{s}^{-1}$ respectively. Then, the D_s at different temperature in this initial concentration and particle size could be determined (Figure 5).

(b) Effect of Initial Concentration. As shown in Table 7, the D_s values increased with initial concentration. Such tendency was also established in the literature[7] and attributed to the distribution of binding energy on surface. At low coverage, transport proceeds by the jumping of molecules between adjacent surface sites. At higher coverage, neighboring molecules interact and the process bears some similarity to liquid diffusion.[4] However, the variation in D_s is due to progressive filling of sites of decreasing energy.[8] In this work, E was correlated to initial concentration under the specified operating condition, and the results are presented in Figure 6. It can be

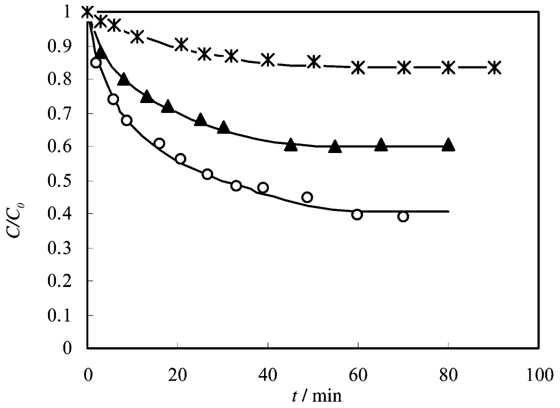

Figure 3. Application of the SDM to THF + water solution mixture on zeolite 4A with different initial concentrations: *, 32,059 %; ▲, 12.795 %; ○, 5.800 %.

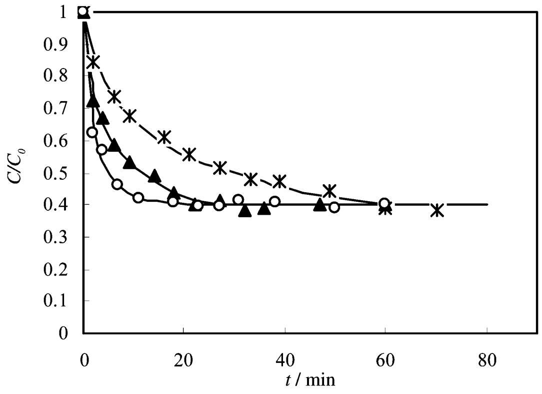

Figure 4. Application of the SDM to THF + water solution mixture on zeolite 4A with different particle sizes: *, 2.92 to 3.43 nm; ▲, 1.80 to 2.40 mm; ○, 1.20 to 1.80 mm.

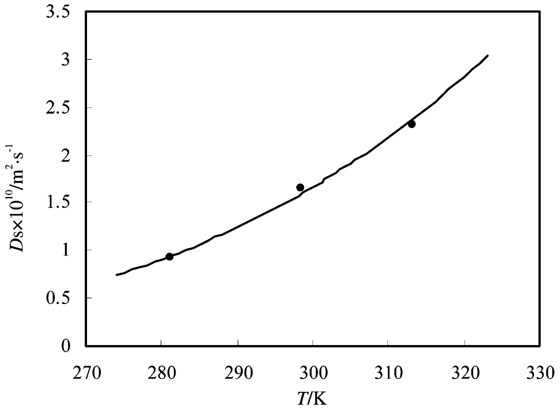

Figure 5. Surface diffusivity and temperature relationship for adsorption of THF + water solution mixture on zeolite 4A with C_0 = 5.800 %, d_p = (2.92 to 3.43) nm.

Table 6. Surface Diffusivity with Different Temperatures

T/K	C_0/%	d_p/mm	$D_s \times 10^{10}$/$\text{m}^2\cdot\text{s}^{-1}$	RMS/%
281.15	5.800	2.92 to 3.43	0.925	0.9
298.15	5.800	2.92 to 3.43	1.640	1.1
313.15	5.800	2.92 to 3.43	2.313	1.2

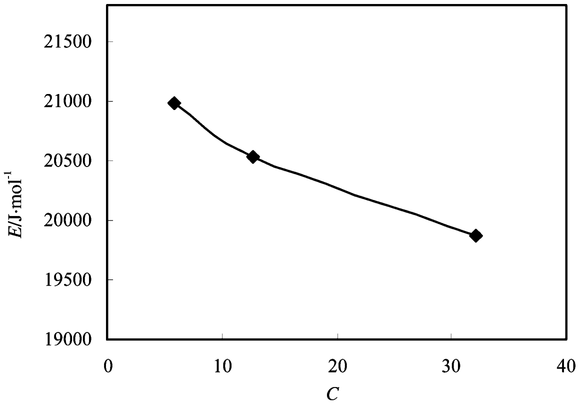

Figure 6. Activation energy and concentration relationship for adsorption of THF + water solution mixture on zeolite 4A at 298.15 K, $d_p = (2.92$ to $3.43)$ mm.

Table 7. Surface Diffusivity with Different Initial Concentrations

T/K	C_0/%	d_p/mm	$D_s \times 10^{10}$/m^2·s^{-1}	RMS/%
298.15	5.800	2.92 to 3.43	1.640	0.9
298.15	12.795	2.92 to 3.43	1.963	0.8
298.15	32.059	2.92 to 3.43	2.556	1.0

Table 8. Surface Diffusivity with Different Particle Sizes

T/K	C_0/%	d_p/mm	$D_s \times 10^{10}$/m^2·s^{-1}	RMS/%
298.15	5.800	2.92 to 3.43	1.640	0.9
298.15	5.800	1.80 to 2.40	1.640	0.8
298.15	5.800	1.20 to 1.80	1.640	1.1

seen that the activation energy decreased as initial concentration increased, so that the surface diffusivity D_s increased as increasing initial concentration.

(c) Effect of Particle Size. As shown in Table 8, in the present work, D_s was shown to be independent of particles size d_p. However, Figure 4 showed that the overall rate increased as the particle size decreased. This could because reducing the particle size would make the inner pore more accessible. But it would not change the internal structure of the particles and the overall adsorbent capacity.

Conclusion

The adsorption isotherm was fitted using Langmuir equation, and the adsorption kinetics data were fitted by the particle surface diffusion model and Langmuir equation.

The internal-particle surface diffusion coefficient (D_s) was solved. It was 1.64×10^{-10} m^2·s^{-1} at 298.15 K, $C_0 = 5.800$, $d_p = (2.92$ to $3.43)$ mm. The surface diffusion coefficient was a function of initial concentrations, temperatures, and particle sizes. D_s increased as temperature increased because of the increase of the molecular energy with higher temperature and increased as initial concentration increased because of the change of the distribution of binding energy on surface, while it was independent of particles size. The pre-exponential factor D_{so} was 7.75×10^{-7} m^2·s^{-1}, and the activation energy E was also extracted.

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