Dissolution Kinetics and Mechanism of Powder Detergent in Water

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The dissolution process of powder detergent in deionized water was investigated systemically. The effects of percentage of sodium linear alkyl benzene sulfonate, particle size, solid/liquid ratio and dissolution temperature on the dissolution rate of powder detergent were investigated. The dissolution kinetics data was correlated by using heterogeneous dissolution models, which indicates that the dissolution process of powder detergent is in agreement with diffusion control model well. Based on the kinetics study, the mechanism of the dissolution process and roles sodium linear alkyl benzene sulfonate and sodium carbonate play in the dissolution were discussed.

Keywords: Powder detergent, Dissolution kinetics, Mechanism, Heterogeneous model.

INTRODUCTION

Powder detergents play important roles in our daily lives for personal, household surface and fabric care[1]. As average per capita income rises more and more consumers are able to have wider options about products not only based on necessity but also on lifestyle, image and perceived enhanced performance[2]. Powder detergents are considered as a typical "performance products", whose value depends on the consumers' acceptance. Among all the assessments, dissolution performance is absolutely a vital property of powder detergents[3,4].

Dissolution rate of powder detergents can be measured by UV/visible spectroscopy[5], rotating disks and laser particle seizer[6]. LeBlanc & Fogler[7] and Dabral *et al.*[8] surveyed the effects of particle size distribution on the dissolution rates, which revealed that a decrease in particle size would result in an increase in dissolution rate. Knight[9] indicated that the dissolution rates would decrease with increasing the density of a powder detergent. Martín and Martínez[10] discussed the effect of solubility on powder dissolution rate. They found that the key factor for solubility tends to be formulation and component interactions. In addition process conditions also play an important role. However, few papers refer to the mechanism of the powder detergent dissolution process.

In this paper, the dissolution kinetics of powder detergent in water was studied. A 'simplified' powder detergent with the composition of sodium linear alkyl benzene sulfonate (NaLAS) and sodium carbonate was used to investigate the effects of percentage of NaLAS, particle size, solid/liquid ratio

and temperature on the powders' dissolution performance. The dissolution kinetics of powder detergents in water was simulated by using heterogeneous dissolution models and mechanism of the dissolution process was discussed. This works is helpful for better understanding of the powder detergent's dissolution process and offering useful information for industrial design.

THEORY

According to the wide accepted hypothesis[11], the dissolution of a solid particle in liquid mainly includes two stages. The first stage is an interfacial reaction between the solid phase and the liquid phase, which results in the liberation of solute molecules from the solid phase (*i.e.*, solvation). The second stage is the transport of these molecules from the interface into the bulk solvent under the influence of diffusion and mixing. Thus, dissolution rates can be influenced by the chemical saturation state of the fluid with respect to the dissolving particles, degree of the particle aggregation, surface area, particle shape and particle size, *etc*.

The dissolution rate of solid in the solvent can be expressed by homogeneous and/or heterogeneous model[12]. It is visualized that a reactant liquid enters into the particle and reacts throughout the particle at all times. Thus, the solid reactant behaves as if it was dissolved. As a result, the rate of the reaction can be given in the same form as for a homogeneous reaction. In heterogeneous model, the reaction is considered to take place at the outer surface of the unreacted particle. The heterogeneous reaction model assumes that the rate may be controlled by

diffusion through a fluid film, by diffusion through the product (ash) layer, or by a surface chemical reaction.

Levenspiel[13] gives rate equations for each of the above control mechanisms. For spherical particles, the fractional conversion (X), as a function of the reaction time (t), is given by

$$\frac{t}{t^*} = 1 - (1-X)^{1/3} \qquad (1)$$

For surface chemical reaction control,

$$\frac{t}{t^*} = X \qquad (2)$$

For film diffusion control and

$$\frac{t}{t^*} = 1 - 3(1-X)^{2/3} + 2(1-X) \qquad (3)$$

For diffusion control through the product (ash) layer.

EXPERIMENTAL

Sodium carbonate (99.5 % in mass fraction) was purchased from KeWei Chemical Reagent Co. Ltd (Tianjin, China). Sodium linear alkyl benzene sulfonate (NaLAS) paste (78 % in mass fraction) was obtained from Procter & Gamble Technology (Beijing) Co., Lid. Distilled deionized water was used in all experiments.

In this work, weighted NaLAS paste and sodium carbonate were mixed by a food mixer and then the wet agglomerates were dried, grounded and sieved by an auto sieve machine (AS20, Retsch, Germany) to obtain laundry detergent powders with graded sizes. Particles within 350-420, 420-590, 590-710 and 710-840 μm were collected.

Dissolution rate measurement: The absorbance standard curve of NaLAS solutions was drawn by using a UV/visible spectrophotometer (TU-1901, Persee, China) with NaLAS concentration of 0, 0.05, 0.1, 0.2, 0.4 and 0.6 mg/mL. The detecting wavelength used in the experiments was 224 nm. As shown in Fig. 1, a good linear relationship was obtained between UV absorbance and NaLAS concentration; the correlation coefficient of the line is up to 0.99.

The dissolution process was carried out in a 600 mL glass reactor equipped with a stirrer motor for mixing, a thermostat (501A, Shanghai Instrument Factory Co., Ltd, China) for controlling the temperature in the reactor and a conductivity meter (DDB-303A, Shanghai Precision Instrument Co., Ltd, China) for recording the variety of conductivity. In each run, the reactor containing 500 mL deionized water was heated to a set temperature and then a given amount of the detergent powder was added with stirring maintained. The aliquots of the solution were withdrawn periodically by syringe and filtered through a 0.45 μm filters (Millipore, America). The concentration of dissolved NaLAS was determined by using UV/visible spectrophotometer and the standard curve shown in Fig. 1.

Experimental design: The per cent of NaLAS, particle size distribution, solid/liquid ratio and dissolution temperature were considered as the parameters that maybe affect the dissolution rate. The ranges of parameters are given in Table-1. The results were plotted as a function of conversion amount (X) of dissolved NaLAS in the solution/amount of NaLAS in the (original sample) *versus* time.
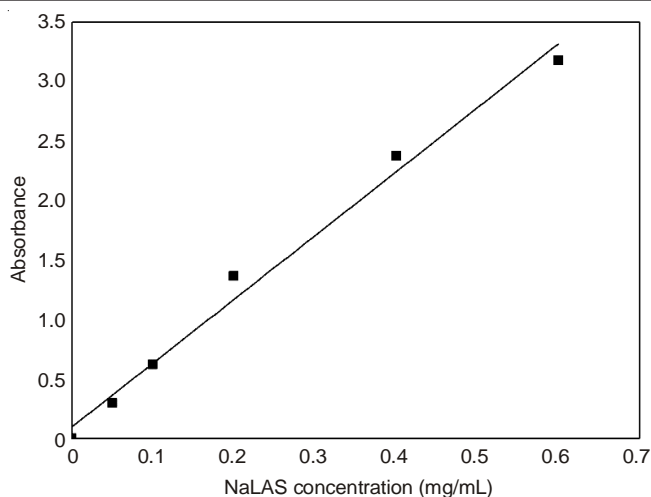

Fig. 1. Standard calibration curve of NaLAS in water

TABLE-1
PARAMETERS AND THEIR RANGES
USED IN THE EXPERIMENTS

Parameters	Values
NaLAS concentration (%)	21, 26, 42, 60, 70
Particle size (μm)	350-420, 420-590, 590-710, 710-840
Solid/liquid ratio (mg/mL)	0.4, 0.8, 1.2, 1.6
Temperature (°C)	25, 30, 35, 40

RESULTS AND DISCUSSION

Effects of particle size and kinetics correlation: In a dissolution process of solid particles, the dissolution rate is directly proportional to interfacial surface area. Therefore, a decrease in particle size will usually result in an increase in dissolution rate. In this work, particles with the ranges of 350-420, 420-590, 590-710 and 710-840 μm were used to find the effects of the sizes on the dissolution rate of powder detergent. The results are shown in Fig. 2. It is clear that a smaller particle size sample has a higher dissolution rate, which trend is consistent with the former researches[14,15]. This result also illustrates that the 'simplified' powder detergent used in this paper has the similar dissolution performance with reported literature.
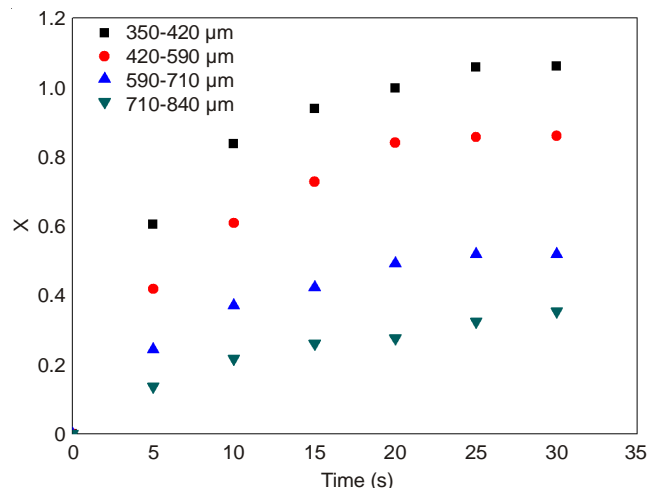

Fig. 2. Effect of particle size on the dissolution rate

The dissolution of powder detergent is a generally solid-liquid reaction process. Solid is considered to be a heterogeneous dissolution process. In this work, heterogeneous dissolution models as formula (1) to (3) were used to fit the data shown in Fig. 2. As shown in Fig. 3, the plot of $1-3(1-x)^{2/3} + 2(1-x)$ *versus* dissolution time is found to be linear, which indicates that the diffusion control model can appropriately represent the dissolution process of powder detergent.
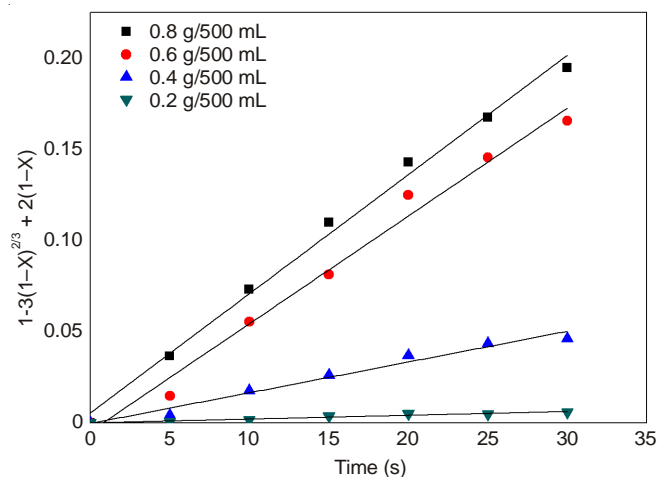

Fig. 3. Fit experimental data with product-layer diffusion model for different particle sizes.

During such a dissolution process, the dissolution rate is determined by the ions' diffusion rate throw the boundary layer. As shown in Fig. 4, when detergent powders are put into water, water molecules continue to penetrate and diffuse to the surface of the undissolved core and as well CO_3^{2-}, Na^+ and LAS diffuse to the body solution. Consequently, the particle' volume gradually decreases until completely dissolved. For NaLAS, due to be a surfactant, the dissolved LAS molecules will directional arrange on the solid surface, thus form an ionization film as shown in Fig. 4b. Such an ionization film will arrest the ions' diffusion and eventually reduce the dissolution rate of the particles.

Difference between NaLAS and Na₂CO₃: Sodium carbonate and NaLAS are two main compositions in powder detergents. In this work, the dissolution difference between NaLAS and sodium carbonate was investigated. In the experiments, conductivity meter and UV spectrophotometer were used to monitor the dissolution processes of Na_2CO_3 and NaLAS respectively.

It can be seen from Fig. 5 that both the concentration of NaLAS and Na_2CO_3 increase with time, while the dissolution rate of Na_2CO_3 is faster than NaLAS. Different solubility of NaLAS and Na_2CO_3 in deionized water lead to this phenomenon, (S NaLAS = 20 g/L, S Na_2CO_3 = 33 g/L), Na_2CO_3 is easier dissolving in deionized water. So the dissolution rate of Na_2CO_3 is faster than NaLAS. This result is consistent with the conclusion higher solubility leads higher dissolution rate[6].

Sodium linear alkyl benzene sulfonate is an important anionic surfactant used in laundry detergents. As for powder detergents it is usually the main active ingredient. The content of NaLAS will hereby affect the dissolution performance of the powder detergents. Five NaLAS content levels (21, 26,
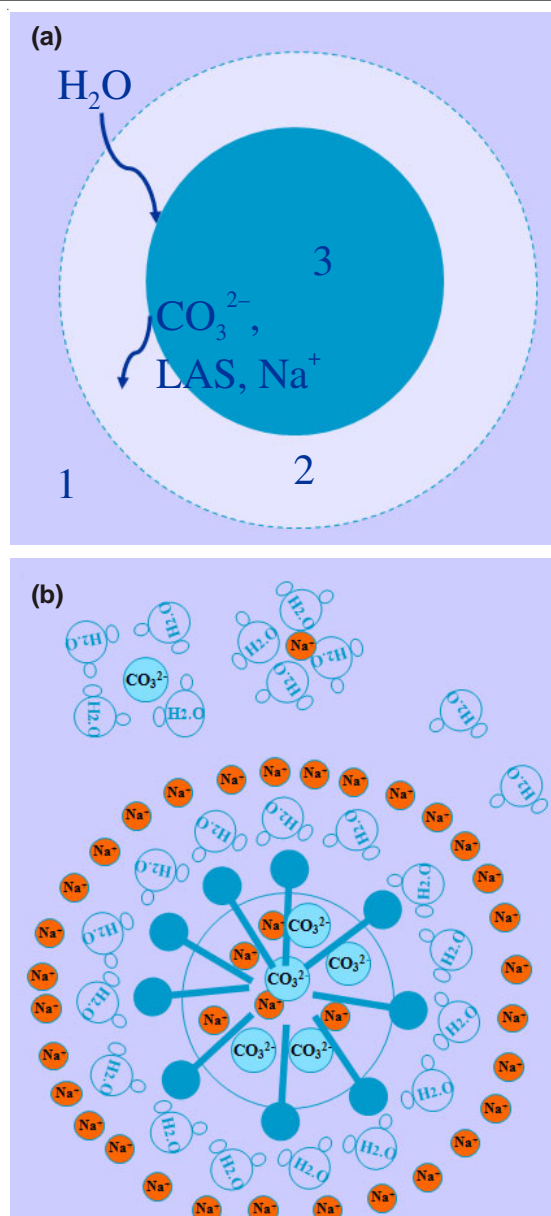

Fig. 4. (a) Detergent powder dissolving process schematic diagram: 1: water; 2: boundary layer; 3: particle; (b) Detergent powder dissolved in water and ionization schematic diagram
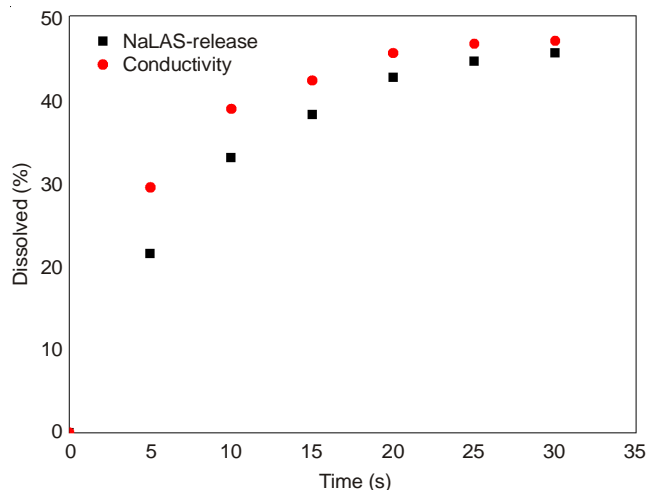

Fig. 5. NaLAS release and Na_2CO_3 conductivity curve of powder detergent (50 % NaLAS)

42, 60 and 70 %) were chosen in this work to investigate the effect on the dissolution rate of the powders. In each experiment, the particle size was fixed to 590-710 μm, the solid/liquid ratio of 0.8 mg/mL, the temperature of 25 °C and the stirring speed was 200 rpm.

As can be seen from Fig. 6, dissolution rate increases with increasing NaLAS content. It has been revealed in Fig. 5 that the dissolution rate of Na_2CO_3 is faster than NaLAS. Then why higher content of Na_2CO_3 will lead to lower dissolution rate? It is a fact that one of the driven factors for NaLAS dissolution is the solution pH stronger electrostatic repulsion between molecules would result in a faster dissolution which can be obtained in high pH solution. Therefore, as for higher content NaLAS particles, the solubilization effect of Na_2CO_3 on NaLAS plays the dominated role, which leads to a faster dissolution.
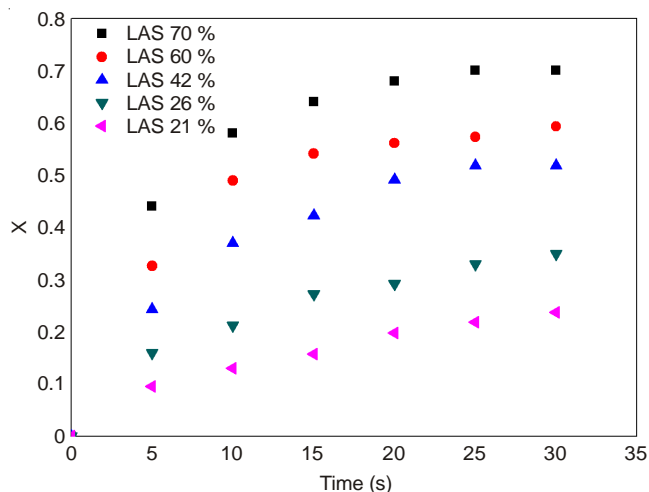

Fig. 6. Effect of NaLAS content on the dissolution rate

Effect of solid/liquid ratio and temperature: The kinetic experiments were performed at solid/liquid ratio 0.4, 0.8, 1.2, 1.6 mg/mL, respectively. The stirring speed is 200 rpm, the particle size is in the range of 590-710 μm and the reaction temperature is 25 °C. Fig. 7 shows that the dissolution rate increases with increased solid/liquid ratio. In the range of 0-1.6 mg/mL, the concentration of LAS increases with solid/liquid ratio increasing, which leads to an increase of the dissolution rate.
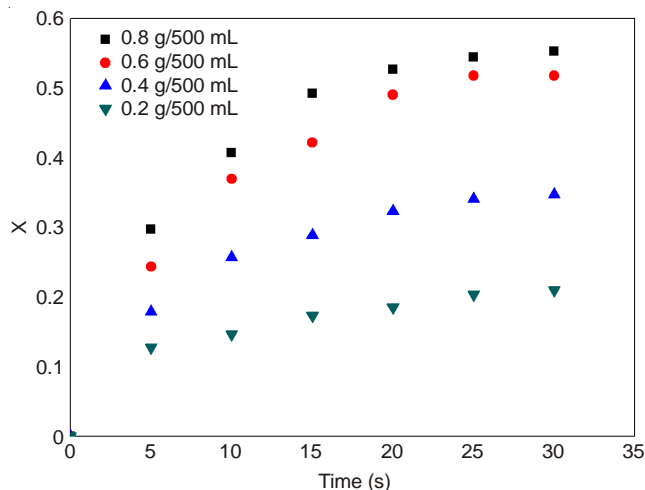

Fig. 7. Solid/liquid ratio effect on the dissolution rate

The effect of the reaction temperature on the dissolution rate was also discussed. Reaction temperatures at 25, 30, 35, 40 °C were tested, the particle size is in the range of 590-710 μm, the solid/liquid ratio is 0.8 mg/mL and the stirring speed is 200 rpm. Fig. 8 shows that the dissolution rate increases with increasing temperature. This is because that higher temperatures will accelerate the ions movement, thus reducing the depth of the ionization film, which is beneficial for the dissolution process.
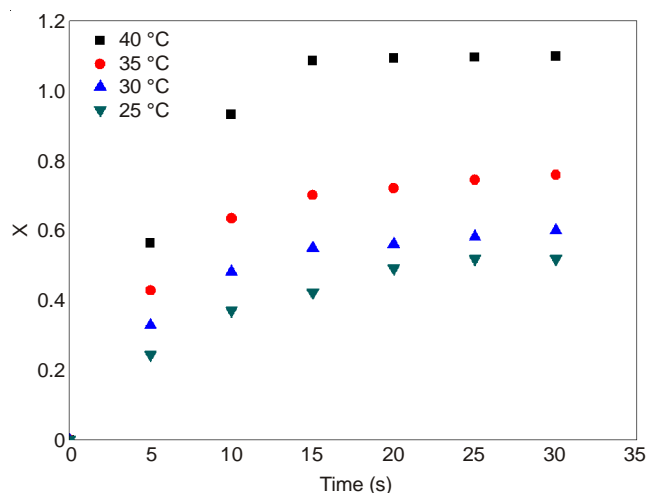

Fig. 8. Effect of temperature on the dissolution rate

Calculation of activation energy: To determine the activation energy of the dissolution reaction, an ln(k) *versus* 1/T plot was constructed (Fig. 9). The slope of this line gives the E/R value and the intercept is k_0. The values of E/R and k_0 were found to be 3953.3 and 10357.9. The E value is 32.867 kJ mol^{-1}.
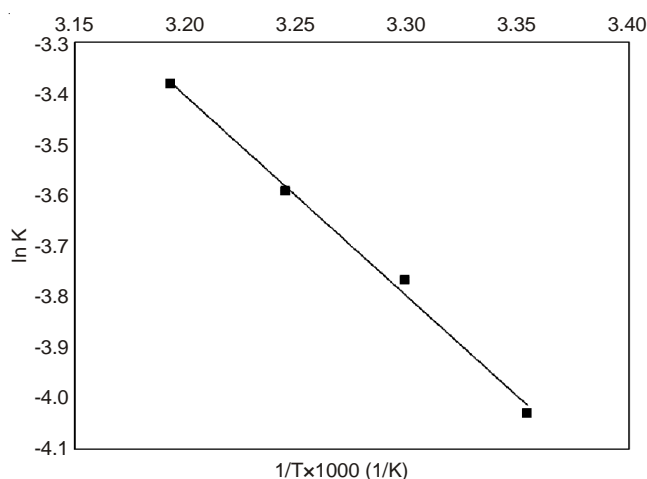

Fig. 9. Arrehenius plot for the dissolution process

Conclusions

In this paper, the dissolution kinetics and mechanism of powder detergent in deionized water was investigated. The main conclusions are as following:

• The dissolution rate increases with increasing NaLAS content, solid/liquid ratio, reaction temperature, while the dissolution rate decreases with increasing particle size.

• The diffusion control model in heterogeneous dissolution models can appropriately represent the dissolution process of powder detergent. The dissolution rate is determined by the ions' diffusion rate throwing the boundary layer. It is found that the surfacial ionization increases the difficulty of the ions diffusion. Sodium carbonate dissolves faster than NaLAS, while as for higher content NaLAS particles, the solubilization effect of Na_2CO_3 on NaLAS plays the dominated role, which leads to a faster dissolution.

• The activation energy of the dissolution reaction was calculated by using Arrehenius equation, which is 32.867 kJ mol^{-1}.

Nomenclature

E = Activation energy (kJ mol^{-1})

k = Dissolution rate

k_0 = Rate constant

R = 8.314 (J mol^{-1} K^{-1})

T = Temperature (K)

t = Reaction time (s)

t^* = Reaction time for complete conversion

X = Fractional conversion of NaLAS

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