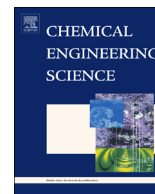




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The role of the solid-solution interface in the dissolution of benzoic acid



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HIGHLIGHTS

- Holographic interferometry was used to monitor the dissolution of benzoic acid.
- Limitations of existing dissolution theories in describing our results were shown.
- A physical model involving the solid-solution interface was developed.
- This model yields a new boundary condition which describes our results well.

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ABSTRACT

An experiment using holographic interferometry shows that the evolution of the concentration profile produced by the dissolution of a benzoic acid powder compact cannot be satisfactorily described by the traditional treatments of assuming fast solubility equilibrium at the solid surface or equating dissolution rate with the diffusion flux at the boundary. A physical model was developed which incorporates the solid-solution interface into the kinetic description of the dissolution process. This leads to a boundary condition in which the time-dependence of boundary concentration follows an exponential function. The resulting solution to the diffusion equation shows good agreement with experimental data.

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1. Introduction

The interface between a solid substance and its own solution is a transitional region between the bulk solid and the bulk solution. Its role in the dissolution process has largely been ignored due to the following reasons. First, it is believed by many that solubility equilibrium is rapidly established at the solid surface, so that the dissolution process is completely transport-controlled (Brunner, 1904; Nernst, 1904; Noyes and Whitney, 1897; Landau and Lifshitz, 1987). Second, some have suggested that the dissolution rate may simply be equated with the diffusion flux at the boundary under the tacit assumption that the boundary concentration (not necessarily equal to the equilibrium solubility as in the first case) is slow-varying with time, that is, in a “pseudo-steady-state”. In either case, the interface makes no appearance in the theoretical description. Although it is very difficult experimentally to probe

interfacial processes directly during dissolution, there are indirect ways of gauging their role. One such method is by monitoring the evolution of the concentration profile resulting from the dissolution of a solid in a static medium. This is governed by the diffusion equation:

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = D\nabla^2 c(\mathbf{r}, t) \quad (1)$$

The solution to Eq. (1) is dependent on the boundary condition. Therefore if interfacial processes do play a role in dissolution, it will be manifested in the boundary condition and, in turn, the final solution. The present investigation used holographic laser interferometry (HLI) to monitor concentration profiles produced by the dissolution from a flat surface of a benzoic acid powder compact. The results were compared with solutions yielded by the two approaches mentioned above, and finally with a solution yielded by a new type of boundary condition derived from our kinetic model which involves the solid-liquid interface as an intermediate phase in the dissolution process.

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2. Experimental section

Crystalline benzoic acid (Fisher®, 99.5%) was used as received. The compact was prepared by compressing benzoic acid powder on a hydraulic press with a pressure of 60 kN. It was then shaped into a 10 mm × 10 mm × 3 mm block and fitted snugly into the bottom of an optical cell (10 mm × 10 mm × 50 mm) to prevent natural convection due to density differences. Pure water (~ 5 mL) was used as the dissolution medium. The temperature of the cell was maintained at 20(± 0.5)°C with a thermostat throughout the dissolution experiment (4 h).

HII is a non-invasive technique based on the linear dependency of refractive index on concentration in dilute solutions. It has become a method of choice for visualizing real-time concentration distributions in static fluid systems (Colombani and Bert, 2007; Fernández-Sempere et al., 2004; Kaunisto et al., 2011; Marucci et al. 2006). The present experimental system is shown in

Fig. 1. The entire setup was located on a vibration-damping optical table covered with a closed shelter. The laser source was a 457.8 nm CW TEM₀₀ Ar⁺ (U.S., Spectra-Physics Inc., Model 177-G12) with a coherence length of 4.6 cm. During the experiment, the light beam was divided into a reference beam and an object beam by a beam splitter. The reference beam was passed through a variable attenuator which controlled the beam intensity as the hologram was being recorded and reproduced. Both beams were expanded and spatially filtered by a system comprised of a microscope objective, a pinhole and a convergent lens. During the dissolution experiment, the object beam was passed through the optical cell containing the benzoic acid tablet and water, after which it was allowed to interfere with the reference beam on a holographic plate (optical resist). The plate was later chemically processed in the dark with a film holder processor. During the processing, the plate was kept in its original position to avoid alterations due to plate shifting.

The key to holographic imaging resides in the capability of the hologram to keep a memory of the initial (t_0) phase of the object, or in this case, pure water. This allows the phase difference $\Delta\varphi$ of the object between times t_0 and t to be visualized through $N = \Delta\varphi / 2\pi$ interference fringes. A CCD camera (Nikon® DS-U2, Japan), focused on the external surface of the cell fitted with a ruler, was used to visualize and record interferograms. Recorded images were displayed on a computer equipped with image acquisition software. The evolution of the concentration profile $c(x, t)$ was obtained by monitoring the space-time evolution of the phase $\Delta\varphi = 2\pi L \Delta n / \lambda$ (L : cell path length).

3. Results and analysis

Fig. 2 shows several real-time interferograms recorded during the dissolution (the experiment was duplicated which yielded interferograms that almost coincided with those taken at the same

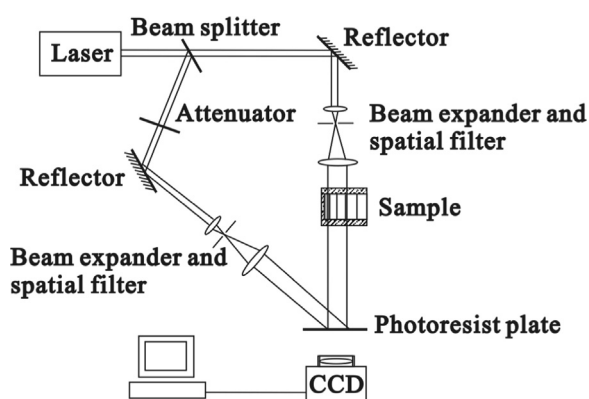


Fig. 1. Experimental setup.

time points from the first run). The determination of concentration profiles from fringe patterns has been discussed in detail elsewhere (Colombani and Bert, 2007; Kaunisto et al., 2011). In this study, the distribution of light intensity along the cell was determined using the image processing functions in MATLAB®. The error bars represent uncertainties caused by small degrees of fringe unevenness.

Superimposing all interferograms from 0–200 min showed negligible shifting in the position of the compact surface, due to the slow rate of dissolution. At the end of the experiment, the fringe pattern extended to approximately 1 cm above the surface of the compact, far from the water-air interface (~ 5 cm from the compact surface). These facts allow us to treat the system as a semi-infinite medium with a fixed boundary. Since the number of fringes ceased to increase after ~ 75 min, the concentration corresponding to the maximum number of fringes was taken to be the equilibrium solubility C_S (3.22 mg/mL, 20 °C; Ghosh, et al., 1991), which was used to normalize all concentration profiles $c(x, t)$. The simulation of theoretical concentration profiles was performed on MATLAB®, with diffusion coefficient $D = 0.0546 \text{ mm}^2 / \text{min}$ (Delgado, 2007).

The evolution of the concentration profile $c(x, t)$ for the system is governed by the one-dimensional diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

The traditional approaches mentioned in the introduction result in different solutions to Eq. (2). The first approach assumes rapid solubility equilibrium at the surface, leading to the simple boundary condition

$$c(0, t) = C_S \quad (3)$$

The solution is given by (Crank, 1975)

$$\frac{c(x, t)}{C_S} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (4)$$

which has a single parameter D . Fig. 3 (a) and (b) show plots of Eq. (4) at several distances (measured from the compact surface) and times, respectively. It is obvious that Eq. (4) vastly overestimates the concentration profile in the first hour. Deviations of this magnitude cannot be attributed to uncertainties in the literature diffusivity value, since varying D by ± 10% shows little improvement in the fits (not shown in Fig. 3 due to limited space).

The second approach equates dissolution rate with the diffusion flux at the boundary, leading to the boundary condition (Kaunisto et al., 2011)

$$K(C_S - c(0, t)) = -D \left. \frac{\partial c}{\partial x} \right|_0 \quad (5)$$

where C_S is solubility, K is commonly referred to as the dissolution rate constant and the subscript 0 denotes “value at the boundary”. The solution under this boundary condition is given by (Crank, 1975)

$$\frac{c(x, t)}{C_S} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - e^{-Kx + \frac{K^2}{D}t} \text{erfc}\left(\frac{x}{2\sqrt{Dt}} + K\sqrt{\frac{t}{D}}\right) \quad (6)$$

which has an additional parameter K besides the diffusivity. The best possible fits were obtained with K in the range of 0.09–0.11 mm/min. Fig. 4 (a) and (b) show plots of Eq. (6) at several distances (measured from the compact surface) and times, respectively, with $K = 0.105 \text{ mm/min}$. The dashed plots are the results of varying the value of D by ± 10%. It can be seen that this approach produces better overall agreement with experimental data. Still, deviations at small distances (< 1.5 mm) and after 30 min are quite significant, which cannot be addressed by adjusting the D -value within a reasonable range.

Given experimental uncertainties and the simplification involved in treating the system as one-dimensional, these results do not completely rule out Eq. (5) as a suitable boundary condition.

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