Distribution of Zinc Tetraphenylporphine in Single Melamine-Resin/Toluene Microcapsules Studied by Laser Trapping-Microspectroscopy

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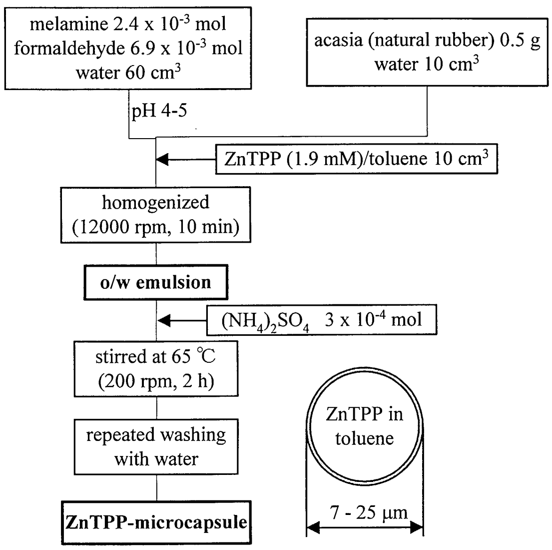
Absorption microspectroscopy has been conducted to study chemical properties of single melamine-resin microcapsules containing a zinc tetraphenylporphine (ZnTPP)/toluene solution. Although absorbance of ZnTPP in the capsule increased with increasing the capsule diameter, its tendency was much smaller than that expected from a homogeneous distribution of ZnTPP in the inner toluene solution. The results were discussed in terms of a distribution of ZnTPP in both the melamine-resin and toluene phases.

Microencapsulation is a method of wrapping small amounts of an arbitrary compound in a spherical polymeric resin wall. This provides an effective means to protect core substances and/or to control their gradual release, so that capsules have been widely used in drugs, printings, and foods[1] as well as in liquid/liquid extraction.[2] In spite of the importance of the capsules, a study on the chemical/physical properties has been so far studied for a number of capsules by particle-unresolved methods, and rarely explored to analyze individuals owing to technical difficulties to manipulate single particles. One example for single capsule measurements is the report by Koshioka et al. on the basis of time-resolved fluorescence microspectroscopy, by which the concentration of pyrene dissolved in an inner toluene solution, surrounded by a melamine-resin wall, has been shown to be different between the capsules.[3] Although the results are quite interesting and involve characteristic chemical behavior of microcapsules, further detailed work has not been reported. In order to obtain a direct evidence of a concentration distribution in and/or between capsules, absorption spectroscopy is clearly superior to fluorometry. Therefore, we explored direct measurements of a solute concentration in individual microcapsules by a laser trapping-microspectroscopy technique.[4] In this letter, we report an inhomogeneous distribution of zinc tetraphenylporphine (ZnTPP) in single melamine-resin/toluene microcapsules in water.



Scheme 1. Preparation of melamine-resin microcapsules containing a ZnTPP/toluene solution.

Melamine-resin microcapsules containing a ZnTPP (1.9 mM (10^{-3} mol dm^{-3}))/toluene solution were prepared by the reported procedures (Scheme 1)[3] and, were redispersed in a toluene-saturated aqueous solution as a sample. A single ZnTPP/toluene microcapsule (diameter (d) = 7 ~ 25 μm) was optically trapped by a focused 1064 nm laser beam under an optical microscope and absorption spectroscopy was conducted by the reported system.[4] A typical example of the absorption spectrum is shown in Figure 1, in which the Soret and Q bands of ZnTPP can be seen at maximum wavelengths of 424 and 550 nm, respectively. The spectrum agreed very well with that observed for a homogeneous ZnTPP toluene solution.

When ZnTPP is solubilized exclusively in the toluene phase and d corresponds to the optical path length for absorption measurements, the absorbance of the Soret band should be 1.9 as calculated from d (18.5 μm), the molar absorptivity of ZnTPP ($\varepsilon = 5.4 \times 10^5$ cm^{-1} M^{-1} at 424 nm), and the concentration of

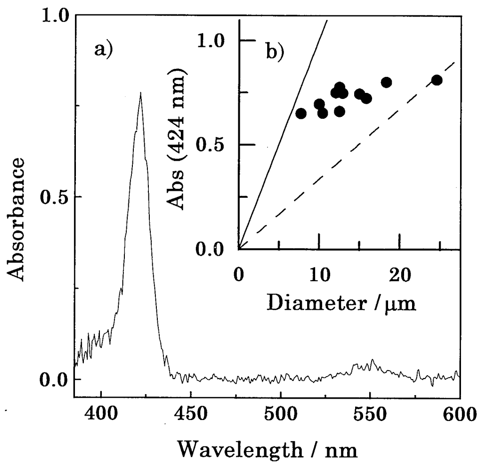


Figure 1. a) Absorption spectrum of a single microcapsule containing a ZnTPP/toluene solution (d = 18.5 μm). b) A capsule diameter dependence of the absorbance of ZnTPP (●). A solid line and a broken curve represent diameter dependencies of the absorbance when ZnTPP is assumed to be distributed exclusively in the toluene solution and in the resin phase, respectively (see also the text).

ZnTPP in the mother solution before polymerization. Nonetheless, the observed value was only ≈0.8 as seen in Figure 1a. Analogous results have been obtained for the capsules with various d (7 ~ 25 μm) as a relationship between the absorbance at 424 nm and d is summarized in Figure 1b. The plot clearly demonstrates that, although the absorbance increases with the increase in d, the slope of the plot is much smaller than that expected from a homogeneous distribution of ZnTPP in the inner toluene solution (shown as a solid line). Furthermore, the intercept of the plot, extrapolated to $d = 0$, does not dissect the original point.

One possible reason for the results in Figure 1b will be partition of ZnTPP into the surrounding water phase. Nonetheless, the solubility of ZnTPP in water is extremely small and under the present conditions, actually, we could not confirm partition of ZnTPP across the toluene/melamine-resin/water interface even after several washing the capsules with toluene-saturated water. Distribution of ZnTPP to the resin wall may be another possible reason. In order to test such a possibility, we performed absorption spectroscopy on individual ZnTPP/toluene microdroplets in water, whose sample was essentially the same with that used for the capsule preparation, but before the polymerization (o/w emulsion in Scheme 1). For the emulsion, the absorbance of ZnTPP (424 nm) increased linearly with the droplet diameter and the slope of an absorbance - droplet diameter plot agreed very well with the product of the molar absorptivity and the concentration (1.9 mM) of ZnTPP. The results clearly indicate that the presence of a melamine-resin wall around the ZnTPP/toluene solution is responsible for the peculiar d dependence of the absorbance in Figure 1b. Also, the linear dependence between the absorbance and the droplet diameter proves that the results in Figure 1b are not ascribed to any optical effects on absorption measurements under a microscope.

When ZnTPP is distributed to both the toluene and resin phases (distribution coefficient ; K = [ZnTPP(resin)]/[ZnTPP (toluene)]), the absorbance of the dye (A) is given by eq.(1),

$$A = 2\varepsilon(r + K\theta)C_0 \bigg/ \left[\left\{\left(\frac{r+\theta}{r}\right)^3 - 1\right\}K + 1\right] \qquad (1)$$

where r, θ, and C_0 are the radius of the inner toluene droplet, the thickness of the melamine-resin wall, and the concentration of ZnTPP in the mother solution before the capsule preparation, respectively. Equation 1 is reduced to the Lambert-Beer's relation ($A = 2\varepsilon r C_0$) when ZnTPP is homogeneously distributed to the toluene solution ($K = 0$, solid line in Figure 1b as $d = 2r$). A broken curve in Figure 1b represents a d dependence of the absorbance under the assumptions that ZnTPP is distributed exclusively to the resin phase ($K \rightarrow \infty$) and θ is 100 nm. It is clear from Figure 1b that the observed data can be explained neither by a homogeneous distribution of the dye in the toluene solution nor that in the resin wall. Furthermore, a simulation of the d dependence of the absorbance, by varying the K and θ (10 ~ 100 nm) values based on eq. (1), did not reproduce the data in Figure 1b. Phenomenologically, the K value is suggested to be dependent on the capsule diameter, which leads to the d dependence of the absorbance. We suppose that distribution of ZnTPP between the resin and toluene phases competes with melamine-resin formation around a ZnTPP/toluene droplet. Since the formation of the resin wall is expected to be faster for smaller capsules, the amount of ZnTPP distributed to the resin phase will be lower and, thus, the K value approaches to 0 with decreasing in d. For larger capsules, on the contrary, the melamine-resin formation proceeds rather slowly so that the K value becomes larger as compared with those for smaller capsules. If this is the case, observed absorbance of ZnTPP approaches to that on the solid line or the broken curve in Figure 1b with decreasing or increasing in d, respectively. This is what observed experimentally.

Further detailed analyses are absolutely necessary to explain satisfactorily the present results. Nevertheless, the present study demonstrates the importance of direct measurements of individual microparticles. In particular, microcapsules possess an inhomogeneous solution/polymeric resin wall structure, so that measurements on a number of capsules do not warrant to give a correct information on properties of capsules, owing to a possibility of a distribution of a solute between the two phases as demonstrated in the present study. We think such effects should be considered, when microcapsules are used for controlled release of encapsulated compounds[1,5] or liquid/liquid extraction by an encapsulated solvent. Further studies are in progress and detailed analyses of the results will be reported in a separate publication.

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References

1 A. Kondo, *Microcapsule Process and Technology*, Marcel Dekker, New York (1979).
2 H. Watarai and S. Hatakeyame, *Anal. Sci.*, **7**, 487 (1991).
3 M. Koshioka, H. Misawa, K. Sasaki, N. Kitamura, and H. Masuhara, *J. Phys. Chem.*, **96**, 2909 (1992).
4 N. Kitamura, M. Hayashi, H.-B. Kim, and K. Nakatani, *Anal. Sci.*, **12**, 49 (1996).
5 K. Kono, T. Ohno, T. Kumei, and T. Takagishi, *J. Appl. Polym. Sci.*, **59**, 687 (1996).