Periodic Expansion-contraction Motion of Photoabsorbing Organic Droplets during Laser Photophoretic Migration in Water

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Laser photophoretic behavior of 2-benzylpyridine droplets including Co(III)-pyridylazo complex as a photoabsorber was examined in water by irradiating cw Ar^+ ion laser. We have made a new observation like a ''breathing'' motion that the droplets repeated the expansion and the sudden contraction during laser photophoretic migration. The period of the motion decreased with increasing the Co complex concentration in the droplet and also with increasing the laser power. The origin of the motion is the water vaporization in the droplet by photothermal conversion.

Separation and characterization of micrometer-sized particles in liquids are important subjects in current analytical chemistry, colloidal chemistry, environmental chemistry, and biological technology. Various kinds of external fields such as a gravitational field, an electric field, a magnetic field etc. have been utilized for migrating particles. Recently, we have proposed a laser-photophoresis of particles, which is a new technique to migrate and to characterize particles in liquid, using a scattering force of laser light.[1,2] This new method could characterize a single microdroplet in liquid by its size and its refractive index.

For colorless and optically transparent particles, it has been elucidated that laser photophoretic velocity is governed by both the refractive index and the radius of the particle, and is predictable by using Mie scattering theory. In the case of photoabsorbing particles, however, the photophoretic behavior is still ambiguous. In the previous study,[3] 2-benzylpyridine droplets including molybdenum blue as a photoabsorber was examined and it was found that the droplets smaller than 1.5 μm in radius with high absorptivity (absorption coefficient of $26\,cm^{-1}$) migrated in the opposite direction against the laser irradiation (negative photophoresis). In this study, laser photophoretic behavior of more photoabsorptive organic droplets (absorption coefficient of 75 to $275\,cm^{-1}$) in water was examined. Anomalous photophoretic phenomenon was observed that the droplets repeated the expansion and the sudden contraction during laser photophoretic migration.

The photophoretic behavior of the organic droplet was observed on a Raman scattering microscope apparatus (Photon Design). A laser beam of a cw Ar^+ ion laser (Spectra-Physics, Stabilite 2017, 514.5 nm) horizontally irradiated droplets suspended in water in a quartz square cell (Polymicro Technologies Inc.; $(0.1\,mm)^2 \times 50\,mm$ length). The power of the laser was set at 28 to 110 mW, and the radius was 33.3 μm at the sample position. The photophoretic behavior of the droplets was observed vertically by using a microscope with a CCD video system and recorded on a digital video recorder (SONY, DCR-TRV30). A Jasco V-570 spectrophotometer was used to measure the absorptivity of the sample solution and to determine the water content in the organic phase. All experiments were performed in a thermostated room at 25 ± 1 °C.

Chemicals used were $Co(NO_3)_2{\cdot}6H_2O$, Na_2SO_4 (Wako Pure Chemicals), 4-(2-pyridinylazo)-1,3-benzenediol (PAR, Dojindo Laboratories), *N*,*N*-dimethyl-*N*-tetradecylbenzenemethanaminium (zephiramine, Dojindo Laboratories), 2-morpholino-ethanesulfonic acid monohydrate (MES, Dojindo Laboratories), and 2-benzylpyridine (Tokyo Kasei). Water was purified by a Millipore Gradient-A10 system.

Co(III)-PAR complex was used as a photoabsorbing compound because of its high absorption coefficient at the laser wavelength. It was extracted with zephiramine into 2-benzylpyridine[4,5] in the conditions of aqueous phase; $7.0 \times 10^{-3}\,mol\,dm^{-3}$ $Co(NO_3)_2$, $3.4 \times 10^{-1}\,mol\,dm^{-3}$ zephiramine, and $4.5 \times 10^{-2}\,mol\,dm^{-3}$ Na_2SO_4 and organic phase; certain concentration of PAR. Na_2SO_4 was added in order to extract Co-PAR complex completely as $Co(PAR)_2{}^+$-(zephiramine)$^-$ into the organic phase. The pH value of the solution was adjusted to 6.0 with MES buffer. After 60 min of shaking, the deep red complex was completely extracted into the organic phase. Co(II) changed into Co(III) by air oxidation in this procedure.[5]

Sample emulsions were prepared by injecting 0.5 μL of the organic phase in 1 mL of the aqueous phase after the extraction equilibrium. The radius of the organic droplet was in the range of 1 μm to 6 μm. 2-Benzylpyridine was chosen as organic solvent because of the high extractability of Co(III)-PAR complex, the high boiling point (276 °C), and the density close to unity.

Figure 1 is an example of the photograph for the photophoretic migration behavior of Co(III)-PAR complex /2-benzylpyridine droplet in water. The photograph is a composite of eight photographs captured every 1/2 s during the migration. The absorbance of the organic phase was 75 for 1 cm path length at 514.5 nm. On irradiation, the droplet started to migrate in the

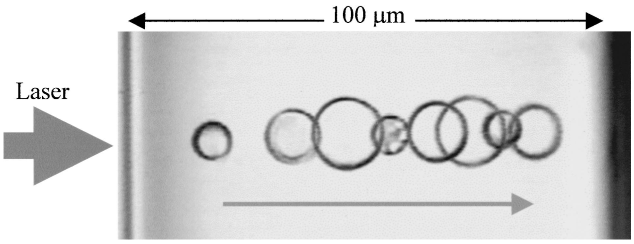

Figure 1. Photophoretic behavior of 2-benzylpyridine droplets including Co(III)-PAR complex in water media. Laser beam (514.5 nm) irradiates the droplet from the left side of the picture and the migration direction of the droplet is indicated by an arrow. The power and the radius of the laser at the sample position were 50 mW and 33 μm, respectively. The photograph is a composite of eight photographs captured every 1/2 second during the laser irradiation.

direction of the laser propagation (indicated by an arrow), and then began to expand. In this case, the expansion of the droplet continued for about 1.2 s and then the expanded droplet suddenly contracted to the initial size. The motion of expansion and contraction cycle was repeated as long as the laser irradiation continued. This is curious behavior we have never observed. In the case of the droplets prepared without Co(III)-PAR complex, the droplet migrated in the direction of laser propagation without any change in radius or shape. The origin of the expansion of the droplet was considered to be the heat production inside the droplet by the photothermal conversion and some subsequent phase transition.

Figure 2 shows an example of the time course of the radius of the droplet during the laser irradiation. On irradiation, the radius of the droplet immediately increased in size and after 1 s induction time it began to grow. It can be seen that the radius of the droplet grows to about 2 times of its initial radius and suddenly contracted to nearly the initial radius. The maximum volume of the expanded droplet was more than 8 times as large as the initial volume of the droplet. It is impossible that the droplet expands so large with only the thermal expansion of liquid, and also the sudden contraction cannot be explained by the shrinking of the liquid phase. Therefore, the expansion of the droplet is considered to be due to the vaporization of water included in the droplet. In fact, the generation of small bubbles in the droplet was observed in the initial stage of the expansion and also the grown droplet had a hollow in its inside and the shell structure of the expanded droplet could be seen with the microscope.

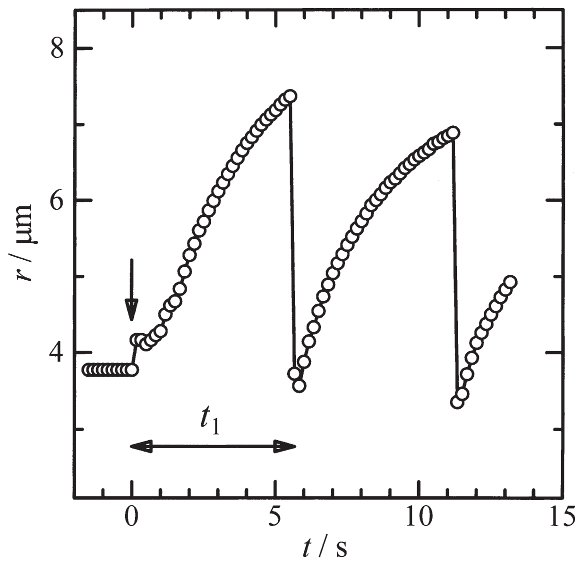

Figure 2. Time course of the radius of the Co(III)-PAR/ 2-benzylpyridine droplet during the photophoretic migration. The power and the radius of the laser were 50 mW and 33 μm, respectively.

The content of water in the organic phase was determined to be 54 ± 3 vol% by measuring the absorption band of water at 1450 nm. The high water content is resulted from the salting-out effect of Na_2SO_4 and excess amount of zephiramine, owing to the formation of w/o microemulsion in the organic phase. The high water content is an essential condition for the expansion of the droplet, because without Na_2SO_4 and excess amount of zephiramine, the content of water in the organic phase was less than 5 vol% and the expansion of the droplet was never observed. This fact also supports the hypothesis that the expansion of the droplet is due to the vaporization of water included in the droplet.

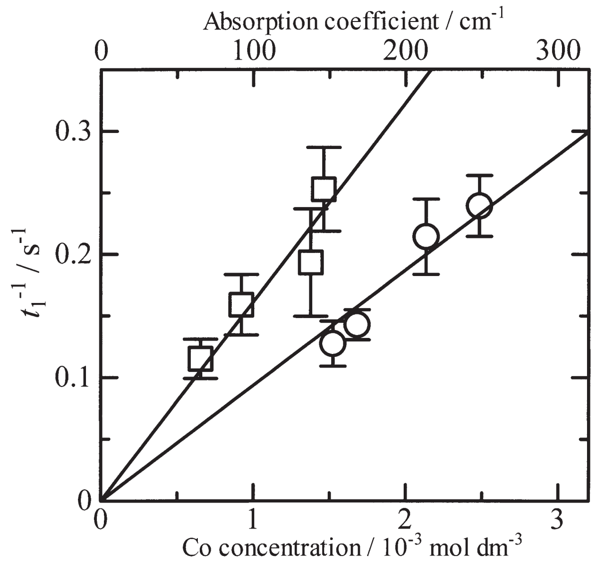

Figure 3. Dependence of the reciprocal period of the first expansion motion upon the extinction coefficient of Co(III)-PAR/2-benzylpyridine droplet at a laser power of 28 mW(○) and 50 mW(□).

The relation between the reciprocal period of the first expansion, t_1^{-1}, and the concentration of Co complex of the droplet is shown in Figure 3. It is clear that at a constant laser power, the reciprocal period of the motion is proportional to the concentration of Co complex in the droplet. It should be noted that the period of the motion was independent of the initial radius of the droplet in the range of 1 to 6 μm examined in the present study.

As indicated above, the origin of the expansion and sudden contraction motion of the droplet is considered to be due to the heat production and the vaporization of water in the droplet caused by the photothermal conversion. The analysis on the details of the mechanism for the motion as well as microscopic temperature measurement on the laser irradiated droplet is now in progress.

The results obtained in this study are important to understand the photophoretic behavior accompanied with photothermal conversion. The phenomenon of the expansion-contraction motion during laser photophoretic migration of organic droplet might be used as a new principle for the signal transducer and is applicable to characterize the photoabsorbing property of micrometer-sized droplets in liquid media.

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