Anomalous Laser Photophoretic Behavior of Photo-Absorbing Organic Droplets in Water

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Laser photophoretic behavior of 2-benzylpyridine droplets including molybdenum blue as a photo-absorber was examined in water by irradiating with a cw Nd:YAG laser (1064 nm). The photophoretic velocity of the droplet decreased with increasing its absorptivity. The droplets smaller than 1.5 μm in radius with high absorptivity migrated in the opposite direction against the laser irradiation. This is the first observation of the negative photophoresis in liquid media.

Separation and characterization of micrometer-sized particles in liquids are important subjects in current analytical chemistry, colloid chemistry, environmental chemistry, and biological technology. Recently, we have proposed a laser-photophoresis of particles, which is a new technique to migrate and to characterize particles in liquid, using the scattering force of laser light.[1,2] This new method could characterize a single micro-droplet in liquid by the size, the refractive index, and the viscosity of the medium. For optically transparent particles, it has been elucidated that laser photophoretic velocity is governed by their refractive index and their radius of the particle. And the photophoretic efficiency of the particle is predictable from light scattering theory such as ray-optics theory and Mie scattering theory. In this study, the laser photophoretic behavior of photo-absorbing organic droplets in water was examined by irradiating with an Nd:YAG laser.

The photophoretic velocity of the organic droplet in water was measured on the apparatus shown in elsewhere.[1,2] Briefly, a laser beam of 1064 nm from a diode laser pumped cw Nd:YAG laser (ADLAS, DPY321) was slightly focused by a lens (f = 50 mm) and irradiated droplets suspended in water in a quartz square cell (Polymicro Technologies Inc.; $(0.1\ \mathrm{mm})^2 \times$ ca. 50 mm long). The convergence angle of the laser beam was 0.03°, and the radius of the laser beam was 33 μm at the position of the optical cell. The power of the laser beam was set at 315 mW. The photophoretic behavior of the droplets was observed by using a microscope (Nikon, Labophot YF) with a CCD video-system (Olympus, OV100) and recorded on an S-VHS video recorder (Mitsubishi, HV-S66). All experiments were performed in a thermostated room at 25 ± 1 °C.

Molybdenum blue was used as photo-absorbing compound[3] and was extracted in 2-benzylpyridine. An aqueous solution of molybdenum blue was prepared as follows. First, 76 mg of 12-molybdophosphoric acid was dissolved in 10 cm^3 water and 20 cm^3 of 0.01 mol dm^{-3} nitrous acid was added. Then, 57 mg of L-ascorbic acid was added to the solution and the solution was diluted to 50 cm^3 with 0.01 mol dm^{-3} nitric acid. The solution was then mixed with a certain volume of 2-benzylpyridine and molybdenum blue was completely extracted to 2-benzylpyridine phase.

Sample emulsions were prepared by injecting 2 μL of 2-benzylpyridine into 5 cm^3 of Millipore-Q water (18 MΩ cm) saturated with 2-benzylpyridine under sonication. The radius of the organic droplet in water was in the range of 0.5 μm to 3 μm. 2-Benzylpyridine was chosen because of the high extractability of molybdenum blue, the high boiling point (276 °C), and the density close to unity.

Figure 1 shows the example of the photographs for the photophoretic migration of molybdenum blue/2-benzylpyridine droplets in water. The concentration of molybdenum blue in the organic droplets was 0.7 mol dm^{-3} reduced to Mo concentration. This concentration corresponds to the absorbance of 26 for 1 cm path length (corresponds to extinction coefficient of 5.1×10^{-4}) at the laser wavelength. The photographs in Figure 1 were captured every one second during the laser irradiation. It was observed that some droplets migrated in the same direction as the laser propagation (positive photophoresis), while other droplets

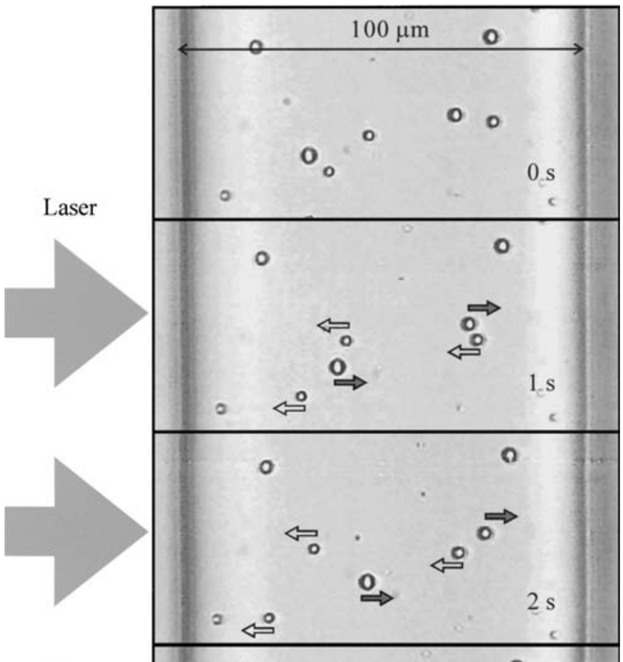

Figure 1. Photophoretic behavior of 2-benzylpyridine droplets including Mo Blue in water media. Laser beam (1064 nm) irradiates the droplet from the left side of the pictures and the migration directions of the droplets are indicated by arrows. The power and the radius of the laser were 315 mW and 67 μm, respectively. Pictures were taken every 1 s during the irradiation.

migrated in the opposite direction (negative photophoresis) as indicated by arrows. The negative photophoresis is curious phenomenon which we have never observed. In our knowledge, this is the first observation of the negative photophoresis in liquid media.

Figure 2 shows the dependence of the photophoretic velocity of pure 2-benzylpyridine and molybdenum blue/2-benzylpyridine droplets upon the radius of the droplet. In the case of the droplets of pure 2-benzylpyridine, the photophoretic velocity was always positive and was proportional to the radius of the droplet. This relation is similar to the particles which are transparent for the irradiated laser wavelength.[1] While in the case of molybdenum blue/2-benzylpyridine droplets, the velocity for the smaller droplets ($r < 1.5\,\mu$m) was negative and that of the larger droplets ($r > 1.5\,\mu$m) was positive. And also in this case the velocity seems to be linearly depends upon the radius of the droplet. The difference in the velocity between the transparent droplets and the photo-absorbing droplets seems to become larger as the radius of the droplet decreases.

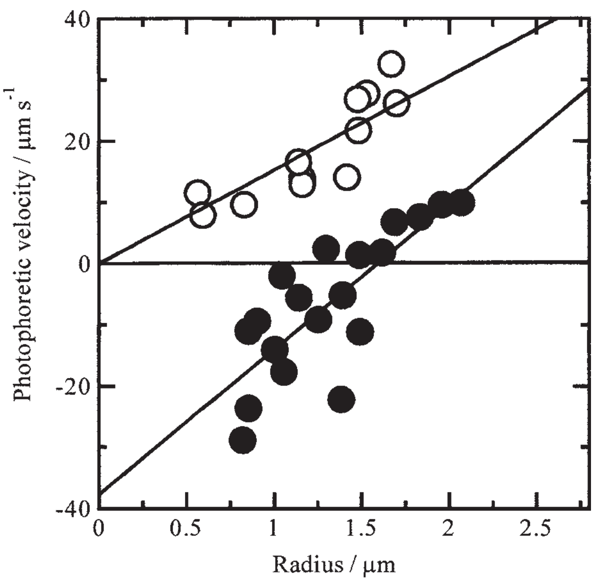

Figure 2. Dependence of the photophoretic velocity of liquid droplets upon the radius of the droplets for 2-benzylpyridine (open circle) and 2-benzylpyridine including 0.7 M Mo Blue (closed circle).

The negative photophoresis with parallel light beam can be explained by neither the ray-optics nor the Mie scattering theory, because light pressure always gives rise to positive photophoresis, that is, the particle has to move along the propagation direction of the incident light. Therefore, the origin of the negative photophoresis observed in this study is thought to be due to the photo-thermal effect induced by laser irradiation. It is well-known that a small particle located in temperature gradient experiences a force and the particle moves in the direction of lower temperature. This phenomenon is called thermophoresis and has been studied theoretically and experimentally on the particles in gas media.[4–6] But only one systematic study has been done on the thermophoresis of the particle in liquid media.[7]

In our case, it is assumed that the unequal heat generation on the laser irradiation between the back side and the front side of the droplet produces temperature gradient in the water around the droplet, and the temperature gradient causes the thermophresis. If the heat generation on the irradiated side is less than that on the opposite side, the droplet migrates to the inverse direction against the radiation pressure. The origin of the unequal heating on the droplet is thought to be due to the lens effect of the droplet itself. Although water slightly absorbs light at 1064 nm, the optical density is much smaller than that of molybdenum blue/2-benzylpyridine droplet and the effect of the heat generation in water for the negative photophoresis is thought to be negligible. The origin of the negative photophoresis is therefore due to the inhomogeneous heat production inside the droplet. In the case of spheres in vacuum, it has been theoretically predicted that the temperature distribution generates inside the irradiated sphere and the distribution depends upon both the absorptivity and the size of the sphere.[8] But in our system, the droplet is in the water media and the estimation of the temperature gradient is difficult due to the complexity of the system. As mentioned above, the negative photophoresis is remarkable for the smaller droplets. This fact indicates that the temperature gradient is larger for the smaller droplet because the thermophoretic velocity in liquid is independent of the particle size and is proportional to the temperature gradient.[7] The detailed analysis on the dependence of photophoretic velocity on the irradiated laser power, the radius of the droplet, the absorptivity of the droplet, is now in progress.

The results obtained in this study are important to understand the photophoretic forces that can be applied for separation and characterization of micrometer-sized particles in liquid. The negative photophoresis in liquid media is applicable to the separation of micrometer-sized particles in liquid media by their absorptivity.

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