Characteristic Signal Behaviors for Water-in-Oil and Oil-in-Water Emulsions Measured by Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometry

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INTRODUCTION

An emulsion is a system whereby one liquid is dispersed into another liquid as small droplets.1 Emulsions are utilized for many types of products such as inks, cosmetics, foods, and medicines. Emulsions are classified according to their phase condition. For example, a water-in-oil (W/O) emulsion describes water droplets dispersed in an oil phase, whereas an oil-in-water (O/W) emulsion refers to oil droplets dispersed in a water phase. In the case of an emulsion where a nonionic surfactant is used as a disperser, the phase condition changes from W/O to O/W or O/W to W/O by changing the water volume fraction (\(f_w\)). The phase inversion arising from varying \(f_w\) is called catastrophic inversion, and the method for preparing an emulsion via the phase inversion process is called phase inversion emulsification.2–4

In phase inversion emulsification, slight differences in the preparation conditions have an effect on the change in the phase inversion behavior, which also affects changes in the properties of the resultant emulsions. Therefore, it is important to evaluate the phase inversion behavior of emulsions arising from changes to the value of \(f_w\). At present, electrical conductivity measurement is mainly used to explain the phase inversion behavior of an emulsion.5–7 In general, to provide electrical conductivity to an emulsion, an electrolyte such as sodium chloride (NaCl) must be added. Electrolytes enhance the interfacial forces between the water and oil phases.8 As a result, electrolytes tend to suppress coalescence and Ostwald ripening. In this manner, the addition of an electrolyte might have an effect on any change in the behavior of phase inversion. In other words, the original condition of an emulsion cannot be directly evaluated.

We have reported a method for the direct analysis of an emulsion without pretreatment using resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS).8–14 REMPI has superior spectroscopic selectivity and produces fewer contaminants,15–20 and TOFMS is easy to clean because of the simple structure,21–23 even when there is contamination. These advantages make REMPI-TOFMS suitable for the measurement of an emulsion where the concentrations of the constituents are inherently high.

When REMPI-TOFMS is applied to the online measurement of an emulsion, a series of mass spectra is obtained.

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When measuring an O/W emulsion, the concentration of an oil component often increases instantaneously at the ionization region because of the existence of oil droplets in the emulsion. When the wavelength of the laser pulses for REMPI is adjusted to the absorption wavelength of an oil component, strong peaks appear in the mass spectrum. By plotting the peak areas of an oil component as the vertical axis and the time as the horizontal axis, a time profile of the component is obtained. When measuring an O/W emulsion, positive spikes are detected.

By applying REMPI-TOFMS, it is possible to evaluate the phase inversion of an emulsion that arises from changing the value of \( f_w \). In a previous study, we demonstrated the evaluation of an emulsion where phase inversion had occurred via a temperature change. In that report, a capillary column was used for sample introduction, and when the temperature of the column was low (40 °C), several positive spikes were detected. This indicated that the emulsion was surely an O/W emulsion. By contrast, no positive spikes were found when the sample introduction outlet was heated to 80 °C. These results suggested the shrinkage or even disappearance of oil droplets following phase inversion via a temperature change. If negative spikes can be detected, this indicates the presence of water droplets, i.e., it is a W/O emulsion. In that study, however, no negative spikes were found because the intensity of the base signals on the time profile was insufficient to produce negative signals.

As mentioned previously, using a nonionic surfactant as a disperser, phase inversion of an emulsion occurs by changing the \( f_w \). Therefore, the signal behavior on the time profile was expected to change when the \( f_w \) was changed; specifically, negative signals are detected when measuring a W/O emulsion, and those signals become positive when phase inversion changes the emulsion to an O/W. Such changes offer detailed information concerning the local composition of an emulsion before and after phase inversion.

In the present study, the signal behavior for two types of emulsions, W/O and O/W, was studied via online monitoring using REMPI-TOFMS. First, the phase type of the emulsions prepared by phase inversion emulsification was confirmed using an optical microscope, an electrical conductivity meter, and a viscometer. Then, REMPI-TOFMS was applied to directly measure emulsions with different values of \( f_w \) and the signal behaviors that suggest a phase inversion from W/O to O/W were discussed.

### EXPERIMENTAL SECTION

**Reagents.** Sorbitan monooleate (Span 80, CAS no. 1338-43-8, hydrophilic-lipophilic balance (HLB) = 4.3) and poly(oxyethylene) sorbitan monolaurate (Tween 20, CAS no. 9005-64-5, HLB = 16.7) were used as nonionic surfactants. Cyclohexane (CAS no. 110-82-7, density 0.779 g/cm³) was used to represent an oil phase. Toluene (CAS no. 108-88-3, density 0.867 g/cm³) was used as a detection component for the water and cyclohexane. The HLB of all emulsions was set at 8.0, and the concentration of the sum of the two surfactants was set at 1.0 g/kg (denominator is the sum of the weight of water and oil).

The concentration of toluene in each emulsion was 3.0 g/kg (the denominator is the sum of the weight of the water and oil). The \( f_w \) of the emulsions, or the water volume fraction of the sum of water and oil, was adjusted by changing the weight of the water and the cyclohexane. The HLB of all emulsions was set at 8.0, and the concentration of the sum of the two surfactants was set at 1.0 g/kg (denominator is the sum of the weight of water and oil).

The preparation procedures for an emulsion were as follows. First, a Span 80 solution, the solvent of which was a mixture of cyclohexane and toluene, was prepared in a 50 mL vial. Next, while stirring the solution with a magnetic stirrer at 1500 rpm, a Tween 20 aqueous solution was added dropwise at ca. 1.7 mL/s with a pipette until a predetermined \( f_w \) was reached. This solution was stirred for 30 min, and a measurable emulsion was obtained.

**Optical Microscope.** An optical microscope (ECLIPSE TE2000-U, Nikon, Tokyo, Japan) equipped with an objective lens (Plan Fluor, numerical aperture 0.45, magnification 20, Nikon) was applied to confirm the dispersion of the emulsions. Methyl orange was dissolved in a Tween 20 aqueous solution and was then used to distinguish between the water and oil phases as mentioned previously. The concentration of the methyl orange was adjusted to 1 wt % of the amount of water.

**Electrical Conductivity Meter and Viscometer.** Both the electrical conductivity and the viscosity of the emulsions were measured to confirm the behavior of the phase inversion. An electrical conductivity meter (CM-31P, TOA–DKK, Tokyo, Japan) equipped with an electrical conductivity cell (CT-58101B, TOA–DKK) was applied to measure the electrical conductivity. First, NaCl was dissolved in a Tween 20 aqueous solution to provide electrical conductivity to the emulsions, as mentioned previously. The concentration of NaCl was adjusted to 1 wt % of the amount of water. A viscometer (VM-100A-M, Sekonic, Tokyo, Japan) equipped with a probe (PR-110-L, Sekonic) was used to measure the viscosity.

**REMPI-TOFMS.** Figure 1 features a schematic diagram of the experimental apparatus. Details of the REMPI-TOFMS used in the present study are reported elsewhere. A pair of concentric capillaries was employed for the sample introduction. The inner and outer diameters of the inner capillary were 25 and 150 μm, and those of the outer capillary were 320 and 450 μm (deactivated, GL Sciences, Tokyo, Japan). The lengths of the inner and outer capillaries were 54 and 24 cm, respectively. The tip of the inner capillary column toward the TOFMS side was adjusted 2 mm inward from that of the outer capillary column. The temperature of the tip was set at 40 °C. The other end of the inner capillary column was inserted into the emulsion, which was stored in a vial. A pressure difference
caused the emulsion to flow through the inner capillary. The emulsion filled the vial container to a height of ca. 3 cm, and the sampling position was the center of the sample, i.e., ca. 1.5 cm from the bottom. Ambient air was flowed through the outer capillary column at a flow rate that was adjusted to 2 mL/min via the use of a flow meter. The inner and outer capillaries, and a stainless steel tube (outer diameter, 1/16 inch) for ambient air flow were connected with a union tee made of stainless steel (SS-100-3, Swagelok).

To monitor the flow of the emulsion through the inner capillary column, a microscopic system was constructed (G plan Apo; magnification 20; numerical aperture 0.28; Mitutoyo, Kanagawa, Japan), and the length between the microscopic observation point and the nozzle tip of the inner capillary column was set at 23 cm. A digital camera (DIGITAL SIGHT DS-U1, Nikon) was used to record the emulsion flow.

The fourth-harmonic emission of a Nd:YAG laser (GAIA II; wavelength, 266 nm; pulse width, 4 ns; repetition rate, 10 Hz, Rayture Systems, Tokyo, Japan) was employed for REMPI. The laser energy was adjusted to 20 μJ and the laser beam was focused via a plano-convex lens with a focal length of 200 mm. The distance between the tip of the outer capillary column and the ionization point was adjusted to 2 mm. A digitizer was used to record the ion signals (AP240; sampling rate, 1 GS/s; bandwidth, 1 GHz, Acqiris/Agilent Technologies, Tokyo, Japan). The recording was started simultaneously with the insertion of the inner capillary column into an emulsion. From a series of obtained mass spectra, a time profile for toluene was constructed by extracting the peak areas of both molecular ions (m/z 92) and fragment ions (m/z 91).

**RESULTS AND DISCUSSION**

**Appearance and Microscopic Images of Emulsions.**

All emulsions prepared for the measurement of electrical conductivity, viscosity, and REMPI-TOFMS, the values for the $w$ of which were 0.005–0.995, were marked by white turbidity. Among these, the emulsion at $w = 0.005$ showed very low turbidity, while the others demonstrated much higher levels.

Figure 2 shows the microscopic images of emulsions prepared via phase inversion emulsification. The dispersed phases were colored for emulsions at $w = 0.005$ and 0.3, as shown in Figure 2a,b. Methyl orange is hydrophilic, which proves that both of these were W/O emulsions. Of course, the colored region obtained from $w = 0.3$ was larger than that obtained from $w = 0.005$. On the other hand, the continuous phase of the emulsion at $w = 0.995$ (Figure 2c) seemed to have color, which suggested it was an O/W emulsion. O/W emulsions with rather small oil droplets are reported to have been generated by applying a phase inversion emulsification method. Although such small oil droplets could not be clearly confirmed via an optical microscope in the present study, a phase inversion from W/O to O/W probably occurred when the $w$ of the emulsion was increased.

**Electrical Conductivity and Viscosity.** Figure 3 shows the relationship between electrical conductivity and viscosity in terms of the $w$ of an emulsion prepared via phase inversion emulsification. All data were obtained 5 min after the preparation of each emulsion.

As demonstrated in Figure 3, the electrical conductivity was rapidly increased at $w$ values between 0.955 and 0.96. Electrolytes generally exist in a water phase, and therefore, the electrical conductivity of an O/W emulsion is much higher than that of a W/O emulsion. In this manner, the phase inversion is easily confirmed by measuring the electrical conductivity. With the addition of an electrolyte, however, the possibility that the phase inversion behavior of an emulsion could be changed must be taken into account.

Viscosity values were increased with an increase in $w$. The highest viscosity occurred at $w = 0.955$, which was followed by a sudden decrease at $w = 0.96$. Tyrone et al. reported that a sudden drop in the emulsion viscosity indicated the completion of phase inversion. In the present study, therefore, the phase inversion of the emulsion was finished at $w = 0.96$. Unfortunately, emulsions with high viscosities are considered difficult to measure using the present REMPI-TOFMS because of problems in passing the emulsion through the inner capillary column. Therefore, in the following section, emulsions at $w =$...
0.005, 0.3, and 0.995 were measured via REMPI-TOFMS; the viscosities of these were 0.88, 1.12, and 1.15 mPa·s, respectively.

REMPI-TOFMS. Next, emulsions prepared by phase inversion emulsification were measured via REMPI-TOFMS. Figure 4 shows the result of emulsion measurements at \( f_w = 0.005 \) and 0.3, i.e., both were W/O emulsions.

Figure 4. Bright-field images of W/O emulsions flowing through an inner capillary column and time profiles of the peak areas of toluene in each W/O emulsion. (Left) \( f_w = 0.005 \), (Right) \( f_w = 0.3 \). (a) Bright-field images; the times obtained by a microscopic system are 120 and 60 s after starting the recording. (b) Time profiles of the peak areas of toluene. (c) Enlarged views of each of the time profiles shown above. Signals with intensities of almost zero are indicated either by arrows or dashed arrows (see text).

Figure 4a shows examples of the microscopic images of emulsions flowed through an inner capillary column for sample introduction. Each image was taken 120 and 60 s after the insertion of a capillary into the corresponding emulsions. It is noteworthy that an emulsion observed by the microscopic system further flowed through the capillary and finally reached the TOFMS inlet after several tens of seconds to a few minutes. These observations confirmed that various sizes of water droplets had passed through the capillary. Compared with an emulsion at \( f_w = 0.005 \), water droplets formed an aggregate at \( f_w = 0.3 \), and the aggregation occupied a certain length in terms of the flowing direction. Aggregates were considered to be generated as a lot of droplets flowed through the capillary column due to the differences in the line velocity among the droplets. Similar phenomena have been reported previously.\(^\text{10}\) The formation of aggregates would be suppressed to some extent by shortening the inner capillary column, but the length was set as short as possible in the present study due to the configuration of the device.

Figure 4b shows the time profiles of the peak areas for toluene in each emulsion; each of the enlargement profiles appear in Figure 4c. As shown in Figure 4b, at \( f_w = 0.005 \), no, or very few, signals were confirmed for the first 70 s because the emulsion had not yet fully reached the nozzle to allow sample introduction. After that, a constant base signal was confirmed with an intensity of 280. The constant signal intensity suggested that the emulsion sample was being continuously introduced; toluene that existed in a continuous phase was detected where the concentration was almost constant.

Interestingly, until 200 s, negative signals were detected against the base signal. These signals suggested that the concentration of toluene instantaneously decreased when water droplets were introduced from the tip of the capillary column. The intensities of several negative signals were almost zero, as indicated by the arrows in Figure 4c, and at that moment, almost no toluene existed. As Figure 4a confirms, large water droplets sometimes filled the capillary column. Therefore, we assumed that such water droplets provided the negative signals with an intensity of zero. The negative signals disappeared 200 s after the recording. This was probably due to the effect of the creaming of this emulsion. With respect to the W/O emulsions prepared in the present study, water droplets should be sedimented because of the relationship between the densities of water and oil (mainly cyclohexane). Therefore, the number of large water droplets was decreased at the time of sampling, i.e., the center of the sample in terms of height. Incidentally, the creaming of the emulsion could not be confirmed by the naked eye.

In the case of a W/O emulsion at \( f_w = 0.3 \), as shown in Figure 4b, the signal was found ca. 200 s after the recording. A greater amount of time was required for the sample to reach the tip of the capillary by comparison with a W/O emulsion at \( f_w = 0.005 \). This could have been because the viscosity of the emulsion at \( f_w = 0.3 \) was slightly higher than that of an emulsion at \( f_w = 0.005 \), and/or because of an aggregation of water droplets. Though difficult to confirm, it seemed that the base peak gradually increased with time at \( f_w = 0.3 \). This could have been the effect of creaming, and therefore the average concentration of toluene at the sampling point was gradually increased; we were able to confirm the creaming behavior of the corresponding sample using only the naked eye.

Also, the intensities of the negative signals were almost zero at measurement times from 200 to 320 s. Interestingly, the number of plots for negative signals differed between \( f_w = 0.005 \) and 0.3. At \( f_w = 0.005 \), negative signals consisted of a single plot, i.e., they were all negative spikes, as shown in Figure 4c. At \( f_w = 0.3 \), however, negative peaks formed by multiple plots were observed, and these are indicated by the dashed arrows. These results indicated a difference in the length of the water phase with respect to the axis of the sample flow. As shown in Figure 4a, at \( f_w = 0.3 \) aggregates of water droplets were formed during passage through the capillary column, which brought about an increase in the length of time for the existence of water against a flowing direction. As a result, these aggregates could produce wider negative peaks. The negative peaks with an intensity of zero disappeared ca. 320 s after the recording. This could also have been due to the effect of the emulsion creaming. By checking the video recording, we roughly confirmed a decrease in the number of water droplets and their aggregates that had passed through the capillary column with time.
The value of $f_w$ obtained by a microscopic system is 0.995. (a) Bright-field image; the time obtained by a microscopic system is 261 s. (b) Time profile of the peak area of toluene.

Figure 5 shows the results of the measurement for the emulsion at $f_w = 0.995$, i.e., an O/W emulsion. In Figure 5a, many small oil droplets were aggregated and large aggregates passed through the capillary column. On the time profile of the peak area for toluene, as shown in Figure 5b, several positive signals were detected, and these were composed of multiple plots. This is acceptable based on the results of the formation of the aggregates of oil droplets. If the number of droplets would have decreased, individual droplets and/or small aggregates should have passed through the capillary column and positive spikes composed of a single plot would have been observed. In fact, we reported positive spikes by measuring the O/W emulsion.10,11 This marks the first report of signals changing from negative to positive as the emulsion type changed from W/O to O/W.

CONCLUSIONS

The signal behaviors obtained from W/O and O/W emulsions prepared using phase inversion emulsification were studied via REMPI-TOFMS. In the case of W/O emulsions, negative signals against the base signal line appeared, which indicated an instantaneous decrease in the concentration of toluene due to the existence of water droplets. Negative spikes appeared at $f_w = 0.005$, while positive signals composed of multiple plots were observed at $f_w = 0.3$ arising from the aggregates of water droplets. By contrast, O/W emulsions returned positive signals consisting of multiple plots arising from the aggregates of oil droplets. As a result, the present study marks the first reported recognition of both negative and positive signals being emitted according to the phase of the emulsion, i.e., W/O or O/W. The phase inversion behavior of emulsions containing multiple oil components will be studied in the future, that is, even if several oil components are present in an emulsion, REMPI-TOFMS has a potential to reveal the partition conditions of each oil component, which cannot be provided by general analytical methods such as electrical conductivity and viscosity measurements. REMPI-TOFMS can be applied to an online mass analysis of emulsions without pretreatment, and therefore, it can be a powerful tool for the evaluation of a local composition of emulsions before and after the occurrence of phase inversion.

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Notes
The authors declare no competing financial interest.

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