福井大学審査
学位論文 [博士 (工学)]

Spontaneous emulsification
at the water|oil interface

（油水界面におけるエマルションの自発的生成）

平成二十三年九月

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Abstract

The aim of this thesis is to know whether W/O emulsions and/or O/W emulsions can form spontaneously near the oil-water interface, when an oil phase comes in quiescent contact with a water phase without any surfactant. The size distributions and number densities of the emulsions were determined by use of an optical microscope and a dynamic light scattering (DLS) instrument. The molar concentrations of the emulsions were determined by use of UV spectra and cyclic voltammetry with a help of deliberately dissolved ferrocene. A redox prove was used for researching electrochemical properties of emulsions.

This thesis has five chapters. Chapter 1 is devoted to introduction of the history of liquid-liquid interface, and properties of emulsions. The experimental procedures are described in chapter 2. The following chapters are devoted to the spontaneously formed water-in-oil emulsions (chapter 3), and the spontaneously formed oil-in-water emulsions (chapter 4). The conclusion is given in chapter 5.

Chapter 3 was devoted to self-emulsification on the water | o-nitrophenyl octyl ether (NPOE) interface. The water droplets formed spontaneously at the interface on the oil phase side when the oil contained tetraalkylammonium chloride without surfactant. The droplets less than some micrometers in diameter gathered at the interface abundantly. The number density of the water droplets was proportional to the concentration of the tetraalkylammonium chloride, and decreased with an increase in length of the alkyl chains. Thus the salt should facilitate the formation of the droplets as a surfactant. The water droplets took Brownian motion at the interface on the oil phase side. The applied voltage varied the direction of the motion and speed of the droplets.

Chapter 4 was devoted to properties of nitrobenzene droplets formed in water. The
size distributions of the NB droplets in the water phase were determined by use of DLS. The concentrations of NB in the spontaneously separated supernatant and in the centrifuged supernatant were determined by use of UV spectra. The former was 1.7 times as large as the latter, which suggested the presence of NB droplets. The diffusion coefficient and number density of the O/W emulsions was determined by use of deliberately dissolved ferrocene as a redox probe in the oil-water mixed solutions. The stability of O/W emulsions was explained.
Acknowledgments

This work was finished at Department of Applied Physics Graduate school of Engineering, University of Fukui under the supervision of Professor Koichi Aoki from October 2008.

First of all, I wish to express my most sincere appreciation and gratitude to my supervisor Professor Koichi Aoki, without his conscientious guidance, selflessly help and warm encouragement; I am not able to fulfill this dissertation.

This work was also carried out under the direction of Associated Professor Jingyuan Chen, I also would like to give my thanks to her invaluable advice and help in the submission of this dissertation and daily lives.

I am also thankful to Dr. Nishiumi Toyohiko, for the valuable suggestions and helpful discussion during this work.

I owe thanks to many Aoki group members who have helped with this work. Thanks also give all members of Aoki’ group.

Above all, I wish to acknowledge from the depth of my heart the untiring sacrifices made by my parents to achieve the highest degree in the field of education.

Sincerely yours:

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2011-05-12
Chapter 1

Introduction

1.1 Liquid-liquid interface

No matter exists on earth without having interfaces. With the origin of life and the emergence of organic compounds, the liquid-liquid interfaces came into play [1]. A mixture of water and hydrophobic oil takes either a phase-separated state or an emulsion [2]. The former is thermodynamically stable [3], whereas the latter is formed dynamically [4–6].

Emulsions are necessarily generated when phase-separated states are mixed vigorously. The type of emulsion formed is determined by the interactions between two liquids. The free energy gap between the two phases is relaxed with mutual dissolution and formation of oil droplets in water (O/W) or water droplets in oil (W/O) [7]. Surfactants facilitate formation of emulsions because they decrease surface tension so that generation of droplets does not enhance the interfacial energy [8]. The O/W emulsions are formed with hydrophilic surfactants and the W/O emulsions with lipophilic surfactants. This is known as Bancroft’s rule [9, 10]. It has important consequences for the choice of surfactants to obtain emulsions with desired properties. Bancroft’s rule is very powerful; for example, a change in surfactant hydrophilicity/ lipophilicity can result in a transition from one emulsion type to another [11], i.e. an inversion from W/O to O/W takes place, or vice versa [12].

Emulsions sometimes are formed spontaneously even at quiescent contact, depending on conditions [13–16]. Emulsions have been found to coexist with phase-separated states for a long time [17] even without including surfactant at a quiescent contact [18]. This fact indicates that a stable mixture should take either a phase-separation or an emulsion, but does both of them.
1.2 Investigation of liquid-liquid interface

Processes at the interface between two immiscible liquids are of not only fundamental interest but also industrial interest. Interfaces between immiscible liquids are ubiquitous in nature e.g. in heterogeneous structures involving lipid membranes. Model systems have been proposed and studied in order to quantify and simulate processes such as ion partitioning or facilitated ion transfer. On the other hand, concept on liquid|liquid interface based systems has been proposed to solve technical problems in phase transfer catalysis, in efficient energy conversion, for sensing, and for drug or gene delivery.

Voltammetry at the interface of two immiscible electrolyte solutions (ITIES) is now a well-studied area [19–22]. Some sensitive amperometric detection techniques [23–26] have been developed on the substantial knowledge, which has created the field of electrochemistry at the ITIES [27–29]. Most of these investigations only focused on the study of an ionophore-mediated organic phase since ionophore could be more selective to extract ions from aqueous to organic phases. The principle of an electrochemical ion-transfer reaction for an ion from aqueous to organic phases is to provide the ion with the Gibbs energy of transfer required by polarising the interface. The main contribution of the ionophore is to lower the Gibbs energy of transfer of ions [30].

Thermodynamic and kinetic transfer functions of ionic species from water to organic solvents are of considerable interest because of their importance in the theory of ion extraction [31], phase-transfer catalysis [32] and ion-selective electrodes [33]. Their measurements can also be of relevance to biological transport phenomena. Physiological effects of drugs correlate with the drug partition coefficient between water and oil phases [34]. Ion transfer to polar organic solvents of low miscibility with water can be investigated most conveniently by electrochemical methods, which are based on the polarization of ITIES [35, 36]. Systematic thermodynamic and kinetic studies have been focused on the water|nitrobenzene (NB) and water|1,2-dichloroethane
(DCE) interfaces, though some thermodynamic data have also been reported for ion transfer from water to chloroform [37], acetophenone [38], nitroethane [39], benzonitrile [40], o-nitrotoluene [41] and o-nitrophenyl octyl ether to-NPOE) [42].

1.3 The significance of the study on emulsions

Microdroplets are quite ubiquitous in chemical systems [43]. Formation and properties of these liquid vesicles are important in emulsion formation, liquid phase separations, and phase transfer catalysis. Microdroplets containing redox active groups can be electrochemically reduced or oxidised as emulsion components [44, 45] or deposited on the electrode surface [46–48].

The process of an emulsion solution separating into the two phases, called demulsification, is significant in industrial processes, especially at the petroleum industry for separating water-in-crude oil dispersions. Demulsification of water-in-oil emulsions has been carried out by means of applications of voltages [49 - 59], filtration [60], heat treatment owing to change in viscosity [61], gravitational sedimentation [62], addition of surfactants [63], and pH adjustment [50]. The electrical demulsification has been thought to have energetically highest efficiency [59].

1.4. In this study

Before investigating effects of droplets formation on ion transfer voltammograms, we should know size distribution of droplets and their number concentrations, which may depend on solution conditions. Qualitative detection of droplets has been challenged by voltammetry when redox species was added to emulsions [64–68]. In order to determine concentrations of droplets, voltammetric currents should be related quantitatively with concentrations of droplets, droplet size and redox concentrations. From the electrochemical viewpoint, oil droplets containing redox species resemble suspended redox latex particles such as hydrogen ion in polystyrene latex [69], polyaniline-coated
polystyrene [70–72], ferrocenyl derivatives on polystyrene [73,74], and polyacrylic acid–polystyrene latex [75]. Redox latex particles react at electrodes by releasing redox moieties [69,73], propagating redox reactions in the latex particles [70–72], letting redox moieties diffuse in the latex particles [74] or contacting the spherical surface with electrodes [75,76]. In contrast, droplets including redox species cannot react at an electrode until they are adsorbed. They often change their geometry and sometimes coalesce [66]. A common feature is diffusion of latex particles and droplets caused by electrode reactions. This report is devoted to measurements of size distribution and the amount of nitrobenzene droplets in aqueous solution by use of DLS and UV-spectroscopy. Voltammetry is made in droplet-dispersed aqueous solutions including ferrocene as a redox marker. Combination of the DLS data with the voltammetric data evaluates the number concentration of the droplets.

The aim of this thesis is to know whether W/O emulsions and/or O/W emulsions can form spontaneously near the oil-water interface, when an oil phase come in quiescent contact with a water phase without any surfactant. The size distribution of droplets and their number concentrations were obtained.
2.1 Chemicals

2-Nitrophenyloctyl ether (NPOE) (Wako) was used as received for an oil phase. Tetramethylammonium chloride (Wako), tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl) were used as received.

Nitrobenzene (Wako) was refined by adsorbing impurities with active alumina of 300 mesh, and filtering them. Ferrocene (Wako) was used after sublimation. Sodium perchlorate and tetrabutylammonium perchlorate (Nakalai Tesque. Inc) were used for supporting electrolyte as received, respectively, in aqueous solution and NB solution.

2.2 Apparatus

The optical microscope was a video microscope, VH-5000 (Keyence, Osaka). Incident light was emitted from the lens toward the sample and was reflected at a mirror located under the oil|water sample. A potentiostat, HECS-1112 (Fuso, Kawasaki) was used.

Two silver wires, 0.05 mm in diameter, coated with silver chloride were fixed on a slide glass (27×76×1.2 mm³) parallel each other. A 4 mM KCl aqueous solution was dropped on one silver wire, whereas an oil drop was mounted on the other silver wire. Two droplets were covered with the other slide glass plate so that two phases came in contact each other. The oil-water included glass plates were folded with polyethylene film in order to keep from evaporation of water and oil. The evaporation disturbed the interface hydrodynamically during the observation. This primitive structure of the cell was found to the best of several trial cells.

A clear part of the oil-water boundary was searched by an xyz-positioner immediately after forming the boundary on the glass. When a sharp and quiescent boundary was found, a movie through a zoom lens was recorded. Thus, the recorded boundary
displayed images 10-30 s after formation of the boundary.

A potentiostat, HECS-1112 (Fuso, Kawasaki) was used for cyclic voltammetry. Glassy carbon electrode 3 mm in diameter was purchased (BAS, Tokyo). The reference and the counter electrodes were Ag/AgCl (3 M KCl, M = mol dm\(^{-3}\)) and platinum wire, respectively.

The size distribution was determined by a dynamic light scattering (DLS) instrument (Malvern Zetasizer Nano-ZS, UK). The UV-spectrometer was V-570 (JASCO, Tokyo). A centrifuge was SRX-201 (Tomy, Tokyo), which kept temperature of samples at 4 °C.
Chapter 3

Spontaneous emulsification at oil-water interface
by tetraalkylammonium chloride

3.1. Alm

When an oil phase comes in contact with a water phase, the free energy gap between the two phases is relaxed with mutual dissolution and/or formation of oil droplets in water and water droplets in oil [77], called emulsions. A history of these phenomena has been overviewed [78]. Since application of potential to the interface varies surface tension, as is known as an electrocapillarity [79,80], it should alter the relaxation kinetics of the contacting surface. It frequently causes macroscopic fluctuations [81-85] such as drastic convection yielding large currents [86, 87], spiked currents [88], and formation of emulsions and flow [89]. Similar behavior has been classically observed at mercury electrodes called polarographic maximum currents [90]. These studies may be complicated by emulsification very close to the interface.

Electrochemical studies on emulsions have directed to controllable enhancement of reactivity, exemplified by solvent extraction [91, 92], acoustic cavitation [93], electrochemical coloring [94], mimic blood [95], inversion of emulsions [96], separation of emulsions by conducting polymers [97], and activated reactions [98, 99]. These studies are orientated to applications, but have not dealt with mechanisms or conditions of emulsification. Basic work on emulsification has recently been made for long term contact of oil with water without electrochemical viewpoints [100]. We are here concerned with exploring possibilities of emulsification under conventional conditions of ion-transfer experiments.
3.2. Instruments

Fig. 3.1. Illustrations of (A) top and (B) side views of the cell structure for observing the oil-water interface.

Figure 3.1 A shows an illustration of the top view of the cell. Two silver wires, 0.05 mm in diameter, coated with silver chloride were fixed on a slide glass (27×76×1.2 mm³) parallel each other. A 4 mM KCl aqueous solution was dropped on one silver wire, whereas an oil drop was mounted on the other silver wire. Two droplets were covered with the other slide glass plate so that two phases came in contact each other. The oil-water included glass plates were folded with polyethylene film in order to keep from evaporation of water and oil. The evaporation disturbed the interface hydrodynamically during the observation. This primitive structure of the cell was found to the best of several trial cells.

A clear part of the oil-water boundary was searched by an xyz-positioner immediately after forming the boundary on the glass. When a sharp and quiescent boundary was
found, a movie through a zoom lens was recorded. Thus, the recorded boundary displayed images 10-30 s after formation of the boundary.

3.3. Results and Discussion

The oil-water interface on the glass was often not perpendicular to the glass surface (Fig. 3.1 B) because of difference in surface energies at oil-glass and water-glass boundaries although the glass surface was treated with silane at several degrees. Consequently the interface was prone to look a broad band in the view of the microscope rather than a line, depending on focus depth. We used only the video with sharp boundaries for quantitative analysis.

Figure 3.2. shows a photograph of the oil-water interface ca. 1 min after the oil phase including 4 mM tetraethylammonium chloride (TEACl) came in contact with the aqueous phase. Spheres were arranged closely not only at the interface on the oil side but also in the oil phase, whereas no spheres were found in the aqueous phase. The spheres should be aqueous droplets which might contain smaller oil droplets as emulsion [101].

Fig. 3.2. Photograph of the oil-water interface when the oil phase contained 4 mM TEACl, where the oil phase is on the left side.
The aqueous droplets had diameter less than 5 μm in diameter. The smallest droplets were 1 μm in diameter, which was close to a detection limit of the microscope. The droplets away from the interface had Brownian motion, and were not aggregated. Those on the interface had no Brownian motion, and hence can be regarded as adsorbed droplets. Some of them had been coalescing into bigger droplets (three droplets almost at the center of Fig. 3. 2). When the oil phase did not contain TEACl, droplets were rarely found.

We expressed quantitatively the population of the droplets in terms of their density, which was evaluated by counting the number of droplets in a given area (e.g. 10 ×50 μm²) of flames of the microscope. The density, \( \langle r \rangle \), decreased with the distance, \( x \), from the interface in Fig. 3. 3., and was extinct for \( x > 200 \) μm. The distribution suggests diffusion of the droplets from the interface toward the oil bulk.

![Graph](image)

Fig. 3. 3. Density distribution of the number of aqueous droplets in the direction normal to the oil-water interface when the oil contained 4 M TEACl, where the density was evaluated by counting the number of droplets in the area 10×50 μm².

We obtained dependence of the density of the droplets on concentrations of TEACl. More droplets (in Fig. 3. 4.) were generated at higher concentration of the salt with a
linear relation. This observation implies that TEACl exhibits a feature of a surfactant. Plots at low concentrations of TEACl tend to be deviated upward from the proportionality to have a positive intercept (dashed line in Fig. 3. 4.). The intercept suggests possible formation of droplets without salt.

![Graph](image)

Fig. 3. 4. Variation of the number of aqueous droplets in the region 1500×30 μm² with the concentration of TEACl in the oil phase.

Tetraethylammonium ion takes a regular tetrahedron in a molecular form, and thus it cannot stride across the oil\water interface as a surfactant. A possible model of the function of the salt as a surfactant is such a coulombic attraction of chloride in water and ammonium cation in oil (Fig. 3. 5.) that both ions might form a ridged molecule like a surfactant. As a support of the model, we obtained dependence of the density on the length of alkyl chains, i.e., methyl showing 120 droplets per 1500 μm², ethyl showing 60, and butyl showing 10 for 4 mM salt concentration. With an increase in the length of the alkane chains, less amount of droplets were formed. Since the coulombic attraction decreases with an increase in the chains, the rigidity of the adsorbed salt is weakened and thus the surfactant ability is lost.
Fig. 3.5. Illustration of adsorbed TEACl at oil\water interface.

Voltage was applied potentiostatically between the KCl-included aqueous phase and the TEACl-included oil phase through two Ag|AgCl electrodes. According to the thermodynamic data, standard ion-transfer potentials of TEA\(^+\), K\(^+\) and Cl\(^-\) are -0.063, 0.241 and -0.395 V, respectively, in the nitrobenzene|water interface [81]. The application voltages, ±0.6 V, are the domain of giving rise to ion-transfer. When the voltage difference of the oil against the aqueous phase, \(\Delta \phi_{\text{W-O}}\), was more than 0.6 V, the droplets moved away from the interface. In contrast, the droplets gathered at the interface for \(\Delta \phi_{\text{W-O}} < 0.6\) V, and disappeared gradually from the interface by merging into the aqueous phase. These motions imply that the droplets should take negative charge. We shall estimate qualitatively the charge, \(q\), per droplet by the force balance of the electric force with the viscous friction force acting on the spherical droplet \(r\) in radius, i.e.,

\[
q\vec{E} = 6\pi \eta \vec{r} \nu
\]  

(1)

where the vector \(\vec{E}\) is the electric field, \(\eta\) is the viscosity of oil (12 mPa s [102]), and the vector \(\nu\) is the velocity of the moving droplet. It is assumed that the electric field is
uniform, 0.6 V / 6 mm (separation of the two electrodes). According to the model in Fig. 5, this value is due to chloride ions adsorbed on the surface of an aqueous droplet. It is equivalent to $4 \times 10^{20}$ mol ($2 \times 10^4$ ions), the surface density population being 190 ions $\mu$m$^2$, or the area occupied by a chloride ion on the surface being $(73 \text{ nm})^2$ or the surface concentration of $3 \times 10^{-14}$ mol cm$^2$. Since we have not taken into account a steep potential drop at the diffuse double layer of the oil–water interface, the value of $|q|$ must be underestimated and hence more chloride ions should be adsorbed on the surface.

The negatively charged droplets departed from the aqueous phase into the oil even under the open circuit conditions. Then, negative charge might be accumulated in oil phase. In order to keep electric charge neutral, anions should transfer from the oil to the aqueous phase or cations should transfer in the opposite direction. A possible transferring species for keeping the neutrality is chloride ion because chloride ion is involved in the both phases. Consequently, negatively charged droplets can transfer to the oil without any net current.
Chapter 4

Voltammetric determination of concentrations of ferrocene-included nitrobenzene droplets in water

4. 1. Alm

A mixture of water and hydrophobic oil takes either a phase-separated state or an emulsion [103]. The former is thermodynamically stable [104], whereas the latter is formed dynamically [105-107]. Emulsions are necessarily generated when phase-separated states are mixed vigorously. They sometimes are formed spontaneously even at quiescent contact, depending on conditions [108-111]. Emulsions have been found to coexist with phase-separated states for a long time [112] even without including surfactant at a quiescent contact [112]. This fact indicates that a stable mixture should take either a phase-separation or an emulsion, but does both of them. The coexistence has been theoretically supported by distributions of any size of droplets evaluated from statistical mechanics [114], as being in agreement with experimental results [112, 113].

A model of ion transfer through oil|water interfaces is idealized to form a well-defined, flat, phase boundary [115-117]. Actual voltammograms deviate from ideal ones [118] at the following points; reactions of adsorbed species at the interface [119-121], electron transfer reactions at the interface [122-124], ion transfer in micro-volumes like droplets [125], and mixed potentials due to simultaneous transfer of cations and anions [126]. If droplets are involved in the other phase, they may alter properties of the bulk or the interface, exemplified by induction of convection [127] or fluctuations of currents [128, 129] due to local difference in surface tension of adsorbed droplets, and by variations of drop size [105, 106] due to compensation of the difference in pressure through Young-Laplace equation [130]. Revisit of the
model of oil|water interfaces may be required not only for microscopically flatness of the interface of the molecular dynamics [131, 132] but also for ion-penetration [133-139].

Before investigating effects of droplets formation on ion transfer voltammograms, we should know size distribution of droplets and their number concentrations, which may depend on solution conditions. Qualitative detection of droplets has been challenged by voltammetry when redox species was added to emulsions [140-144]. In order to determine concentrations of droplets, voltammetric currents should be related quantitatively with concentrations of droplets, droplet size and redox concentrations. From the electrochemical viewpoint, oil droplets containing redox species resemble suspended redox latex particles such as hydrogen ion in polystyrene latex [145], polyaniline-coated polystyrene [146-148], ferrocenyl derivatives on polystyrene [149,150], and polyacrylic acid-polystyrene latex [151]. Redox latex particles react at electrodes by releasing redox moieties [145, 149], propagating redox reactions in the latex particles [146-148], letting redox moieties diffuse in the latex particles [150] or contacting the spherical surface with electrodes [151, 152]. In contrast, droplets including redox species cannot react at an electrode until they adsorbed on the electrode. They often change their geometry and sometimes coalesce [142]. A common feature is diffusion of latex particles and droplets caused by electrode reactions. This chapter is devoted to measurements of size distribution and the amount of nitrobenzene droplets in aqueous solution by use of DLS and UV-spectroscopy. Voltammetry is made in droplet-dispersed aqueous solutions including ferrocene as a redox marker. Combination of the DLS data with the voltammetric data evaluates the number concentration of the droplets.

4.2. Instruments
Nitrobenzene (Wako) was refined by adsorbing impurities with active alumina of 300 mesh, and filtering them. Ferrocene (Wako) was used after sublimation.

The size distribution was determined by a dynamic light scattering (DLS) instrument (Malvern Zetasizer Nano-ZS, UK). The UV-spectrometer was V-570 (JASCO, Tokyo). A centrifuge was SRX-201 (Tomy, Tokyo), which kept temperature of samples at 4 °C.

4. 3. Results and Discussion

4. 3.1. Spontaneously formed nitrobenzene-in-water emulsions

It is not clear whether aliquots by addition of NB to the aqueous solution at concentrations less than the saturated concentration (14-17 mM [153]) might include NB droplets or not. A visual evidence of inclusion of droplets is generally turbidity of a solution, which is ascribed to light scattering by large droplets. The upper aqueous phase of the NB-water mixture was transparent by our eyes after vigorous mixing. A simple, quantitative measure of turbidity is a loss of transmittance of light by use of the UV-absorbance of NB. The absorbance may be expressed by $A = \varepsilon c = \varepsilon_d c_d + \varepsilon_s c_s$, where $c_s$, $c_d$ and $c$ are, respectively, number concentration of dissolved NB, that of droplets, and that of the added NB ($c = c_s + c_d$). Here, $\varepsilon$ is the absorption coefficient of the added NB, $\varepsilon_s$ is that of dissolved NB, and $\varepsilon_d$ is that of NB droplets depending on the turbidity. If $c_d$ and $c_s$ were to be proportional to $c$, the absorbance should be also proportional to $c$. The ratio $c_d/c$ is much smaller than $c_s/c$ for low concentrations because of few possibilities of coalescence for the growth of droplets. Then we predict that $A = \varepsilon_s c_s + \varepsilon_d c_d \approx \varepsilon_s c_s \rightarrow \varepsilon_s c$ for $c \rightarrow 0$ and that the relation of the absorbance with $c$ varies from non-proportionality to proportionality as $c$ tends to zero. In this prediction, we obtained the absorbance at 268 nm at various concentrations of NB-included water, and plotted it in Fig. 4. 1. The concentration
domain at which the absorbance was less than 2 was $c < 0.3$ mM, which is much lower than the saturated concentration. Proportionality was found for $c < 0.06$ mM, the slope of which gave the molar absorption coefficient, $1.0 \times 10^4$ M$^{-1}$. Deviation from the proportionality for $c > 0.08$ mM may be ascribed to light scattering by NB droplets. Since the errors of the absorbance for $0.7 < A < 2$ were less than 0.02, the appearance of the deviation was obvious. Consequently, 0.08 mM is a threshold concentration of formation of droplets from the optical viewpoint.

![Graph](image)

Fig. 4. 1. Concentration variation of UV-absorbance on the left axis and diameters of droplets of NB-included aqueous solutions on the right axis.

The presence of NB droplets was examined with size distributions of droplets by DLS. The scattering light relative intensity vs. the diameter, $2r$, showed a peak, like in Fig. 4. 2. The appearance of one peak suggests narrow size distribution of diameter, which corresponds to formation of droplets with a certain diameter. The diameters of the droplets were plotted on the right axis against NB concentrations in Fig. 4. 1. The diameter ranged from 0.2 to 0.6 μm, regardless of the concentrations,
implying that specifically sized droplets are formed under quasi-equilibrium conditions. The formation of the specifically sized droplets is supported by the theory of the size distribution of droplets in emulsions by use of statistical mechanics [114]. The presence of droplets at concentrations less than 0.08 mM seems inconsistent with the result of UV absorbance. However, the DLS result demonstrates only the presence of the droplets but does not provide any information on amounts of droplets. The concentration of droplets may be much smaller than $c_b$ for $c < 0.08$ mM.

![Size distribution graph](image)

Fig. 4. 2. Size distributions of NB droplets in the upper water phase of the emulsion (v/v % of water to NB is 20/1) (a), centrifuged supernatant (b) and water droplets in NB phase (c), obtained by DLS.

Nitrobenzene was mixed with water at the volume ratio of 1:1 in an ultrasonicated bath. The mixture, which was retained quiescent for a few hours, showed clear two-phase separation. The upper aqueous phase was sampled for determining concentration of NB by UV. Since the absorbance was over 3, the supernatant was
dissolved by 200 times with water. The concentration of NB was 15.5 mM by use of the absorption coefficient obtained in Fig. 4. 1., independent of the mixing procedures or volume ratios of water and NB. When the supernatant was centrifuged at $4.7 \times 10^4 \text{ g}$ in 5 minutes, the concentration of NB was decreased to 9.3 mM, which did not decrease with further centrifugation periods. Since centrifugation generally removes dispersed particles or droplets, the difference in the concentrations, 6.2 mM, should correspond to the NB droplets. Both the quiescently formed supernatant and the centrifuged supernatant exhibited size distributions of droplets in Fig. 4. 2a and 2b, respectively, the diameters of which were ca. 0.5 µm and 0.15 µm. The centrifugation spun down large droplets. The centrifugal force at the acceleration, $a$, acting on an oil droplet with radius, $r$, in water is given by $(4\pi/3)r^3(d_o-d_w)a$, where $d_o$ and $d_w$ are densities of NB and water, respectively. When the droplet moves at a constant velocity, $u$, by the centrifugal force, the frictional force, $6\pi \eta ru$, acts on the droplet. Balance of both the forces yields $u = 2r^2(d_o-d_w)a/9\eta$. Values of $u$ at $2r = 0.5$ and 0.15 µm are 0.14 and 0.013 cm s$^{-1}$ for $a = 4.7 \times 10^4 \text{ g}$, respectively. The 5 min's centrifugation should move droplets by 42 and 3.8 cm, respectively. The latter value is large enough for separating oil droplets in 10 cm cell height. The inseparability of 0.15 µm droplets may be ascribed to the Brownian dispersion.

In contrast to the NB droplets, the oil phase in contact with water contained visible water droplets. The diameters ranged from 1 to 5 µm, as were consistent with values in the previous report [113]. The DLS data (Fig. 4. 2c) showed diameters close to those by the optical microscope. The diameter of water droplets larger than that of NB droplets may be related with much larger solubility of water in NB (3 M [154]) than the solubility of NB in water (0.015 M).

4. 3. 2. Voltammograms of emulsions
Ferroocene was dissolved deliberately into 0.4 M NaClO₄ aqueous solution and 0.4 M tetrabutylammonium perchlorate NB solution with ultrasonication until solid of ferrocene was left in each solution. Each solution was centrifuged at $4.7 \times 10^4$ g to remove the solid ferrocene. The NB solution of 5 cm³ was mixed with the 95 cm³ aqueous solution in the ultrasonic bath to form a turbid emulsion. Voltammograms of the emulsion were obtained at the glassy carbon electrode 3 mm in diameter (Fig. 4. 3). Anodic and cathodic peaks were observed in the domains 0.45-0.50 and 0.25-0.30 V, respectively. The potential shift by scan rates is ascribed to the addition of NB droplets because of absence of the potential shift only for the aqueous solution. It may be caused by an increase in solution resistance of NB droplets or NB droplet film on the electrode. Plot of the anodic and the cathodic peak currents against the corresponding peak potentials fell on each line, as shown in Fig. 4. 3, according the technique of evaluating accurately a peak potential without IR-drop [155]. The slopes were approximately common, indicating that the potential shift with the scan rates should be caused by solution resistance. The difference between the cathodic and the anodic peak potentials for $I = 0$ was 80 mV, close to the diffusion-controlled reversible reaction. The cathodic peak potential is predicted to depend on solubility of ferricenium ion and ferrocene, and thus detailed discussion on 80 mV may be meaningless. The peak potentials (0.42, 0.34 V) extrapolated to $I = 0$ are closer to those of ferrocene in NB (0.47, 0.55 V [156]) than those in water (0.15, 0.23 V).

The anodic peak current, $I_p$, at the first scan was plotted against the square root of the potential sweep rate, $m$ in Fig. 4. 4a. The proportionality for $\nu < 0.1$ V s⁻¹ suggests the diffusion controlled process of the peak current. In contrast, the plot deviated to low values from the proportionality for $\nu > 0.3$ V s⁻¹. The diffusion-controlled current for $\nu > 0.3$ V s⁻¹ might be larger than 50 µA, according the proportional line in Fig. 4. 4. Then the IR-drop would be over 0.2 V from the extrapolated line to $I_p > 50$ µA in Fig. 4. 3. Such a large potential shift corresponds to net slower scan rate, and hence the peak currents for $\nu > 0.3$ V s⁻¹ in Fig. 4. 4 are
deviated from the proportional line.

Fig. 4. 3. Voltammograms of the O/W emulsion (volume fraction of the NB was 0.05) including saturated ferrocene and 0.4 M NaClO₄ in both phases at the glassy carbon electrode 3 mm in diameter at scan rate \( \nu = 80 \), (b) 50 and (c) 30 mV s⁻¹

The centrifuged supernatant, being the transparent aqueous phase, showed the voltammogram in Fig. 4. 5a, which was similar to the voltammograms in Fig. 4. 3 except for the potential shift. The anodic peak current was proportional to \( \nu^{1/2} \) (Fig. 4. 4(b)), indicating the diffusion control. The oxidation current should be provided by both ferrocene dissolved in water and ferrocene dissolved in NB droplets. In order to estimate an amount ratio of the two components, we carried out voltammetry of ferrocene-saturated aqueous solution including 0.4 M NaClO₄ (Fig. 4. 5(b)). The peak potentials of ferrocene in the centrifuged supernatant of the emulsion were the same as those in ferrocene-saturated aqueous solution. The peak current was diffusion-controlled from the proportionality of \( I \) vs. \( \nu^{1/2} \) (Fig. 4. 4(c)). The value of the slope of the proportionality was by 1/3.6 times of that for centrifuged supernatant. Therefore, the voltammetric current ratio of ferrocene dissolved in water to ferrocene in NB droplets is 1 : 2.6. This is not equivalent to the concentration ratio \( (c_1 : c_0) \) because voltammetric currents depend not only on the concentration but also on the diffusion coefficients of ferrocene and the droplets. The peak potentials of ferrocene in the centrifuged supernatant of the emulsion were the same as those in ferrocene-saturated aqueous solution. Thus the standard potential of the former, \( E^\circ(\text{centrifuge}) = \mu^\circ(\text{Fe}^\circ(\text{H}_2\text{O-NB})) - \mu^\circ(\text{Fc}(\text{H}_2\text{O-NB})) \), is close to that of the latter,
\[ E^\circ(\text{H}_2\text{O}) = \mu^\circ(\text{Fc}^+(\text{H}_2\text{O})) - \mu^\circ(\text{Fc}(\text{H}_2\text{O})) \], where \( \mu^\circ \) means the standard chemical potential in the state designated by the parentheses. The equality, \( E^\circ(\text{centrifug}) = E^\circ(\text{H}_2\text{O}) \), does not mean \( \mu^\circ(\text{Fc}^+(\text{H}_2\text{O}-\text{NB})) = \mu^\circ(\text{Fc}^+(\text{H}_2\text{O})) \), but NB contributes equally to the chemical potentials of Fc\(^+\) and Fc. In contrast, the standard potential in NB is given by \( E^\circ(\text{NB}) = \mu^\circ(\text{Fc}^+(\text{NB})) - \mu^\circ(\text{Fc}(\text{NB})) \). The experimental result was approximately \( E^\circ(\text{NB}) = E^\circ(\text{H}_2\text{O}) + 0.20 \text{ V} \). Since Fc is hydrophobic, \( \mu^\circ(\text{Fc}(\text{H}_2\text{O})) \) may be higher than \( \mu^\circ(\text{Fc}^+(\text{H}_2\text{O})) \), \( \mu^\circ(\text{Fc}^+(\text{NB})) \) and \( \mu^\circ(\text{Fc}(\text{NB})) \). This is an explanation of the potential shift of the midpeak value by 0.2 V.

![Graph](image1.png)

**Fig. 4.4** Variations of anodic peak current of saturated ferrocene (a) in the emulsion, (b) in the supernatant, and (c) in water phase against square-roots of the scan rate.

![Graph](image2.png)

**Fig. 4.5** Voltammograms of ferrocene in the centrifuged supernatant of the emulsion including 0.4 M NaClO4 in aqueous phase and 0.4 M TBAP in NB (a) and
in ferrocene-saturated water (b) including 0.4 M NaClO₄ at the glassy carbon electrode 3 mm in diameter for \( v = 30 \text{ mV s}^{-1} \).

4.3.3. Evaluation of number concentration of NB droplets

Although the DLS measurement of the centrifuged supernatant showed uniform diameter 0.15 \( \mu \text{m} \) of NB droplets (Fig. 4.2. (b)), it did not provide the number concentration of droplets. We shall estimate the concentration by use of the voltammetric currents, combining them with the diameter of the droplets. When a particle contains \( m \) molecules of a redox species with one-electron transfer, the expression for the diffusion-controlled peak current is given by [157]

\[
I_p = 0.446 F A m c_d \sqrt{D v F^3 / R T}
\]  

(1)

where \( c_d \) is the bulk concentration of the particle (droplet) and \( D \) is the diffusion coefficient of the particle. Variable \( m \) corresponds to the number of ferrocene molecules per NB droplet.

The concentration of ferrocene in the droplet may be close to the saturated one, because the emulsion was generated under the ferrocene-saturated condition. From the UV-absorbance, the saturated concentration was 0.67 M. Consequently we estimate \( m \) to be 0.67 M \( \times (4\pi/3) r^3 / N A = 7.1 \times 10^5 \) for \( 2r = 0.15 \mu \text{m} \), where \( N A \) is the Avogadro constant. The diffusion coefficient of the droplet was estimated from the Stokes-Einstein equation \( (D = k_B T / 6\pi \eta r) \) for the viscosity of water, \( \eta = 0.89 \text{ mPa s} \). It was \( 3.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \). Since \( \beta \) in Eq.(2) is equal to 2.6 times the peak current in the supernatant, we evaluated the number concentration of the droplets \( (c_d) \) from Eq. (2) to be \( 1.1 \times 10^{14} \text{ dm}^{-3} \). If one droplet were to be regarded as a molecule, \( c_d \) might be \( 1.8 \times 10^{-10} \text{ M} \). This value is equivalent to the average distance, \( L = (c_d N A)^{1/3} = 2.1 \mu \text{m} \), between closest neighboring droplets. If a droplet moves in the distance by diffusion to coalesce, it takes \( L^2 / D = 1.3 \text{ s} \) for the travelling. This period is too long for droplets to collide with each other, resulting in the stable emulsion. If ferrocene in the centrifuged supernatant were not to be localized to NB droplets but were to be distributed uniformly at a molecular level, the average concentration might be \( m / N A L^3 = 0.13 \text{ mM} \). This value is by 40 times larger than the saturated concentration.
of ferrocene in water (0.003 mM evaluated from the slope of line (c) in Fig. 4. 5). NB facilitates apparently dissolution of ferrocene in water.
Chapter 5

Conclusions

When the oil phase makes a quiescent contact with water phase, W/O emulsions and/or O/W emulsions formed spontaneously near the oil-water interface without any surfactant. The droplets were accumulated on the interface and diffused toward the oil bulk. The size distributions of both W/O emulsions and O/W emulsions, less than some micrometers in diameter, were determined by optical microscope and DLS.

When water makes a contact with electrolyte-included NPOE, water droplets formed. The formation of the droplets was more active for higher concentrations of the tetraalkylammonium salt and for shorter length of the alkylammonium cations. The salts added in the oil phase should be responsible for the formation of the droplets as a surfactant. The potential-dependent motion of the water droplets indicated that the droplets were negatively charged.

Transparent NB-mixed water contained dissolved NB and NB droplets 0.15-0.5 μm in diameter for any mixing ratio, according to DLS. The molar and number concentrations of NB droplets were estimated by the voltammetric peak currents of added ferrocene in each phase. Voltammetric peak currents in the NB-mixed aqueous solutions were controlled by both diffusion of dissolved ferrocene molecules and that of ferrocene-included NB droplets. They depend on not only their concentrations but also their diffusion coefficients. The average distance between neighboring droplets was large enough for coalescence through diffusion of droplets.
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