



Electrochemistry in bicontinuous microemulsions based on control of dynamic solution structures on electrode surfaces



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ABSTRACT

Bicontinuous microemulsions (BMEs, Winsor III), also called middle-phase microemulsions, are low-viscosity, isotropic, thermodynamically stable, and spontaneously formed mixtures of water, oil, and surfactants. They are unique solution media for electrochemistry. Here, we introduce the recent progress in the electrochemistry of BMEs from their fundamental aspects to their practical applications. Electrochemistry using BMEs has two irreplaceable properties: the coexistence of hydrophilic and lipophilic species with high self-diffusion coefficients; and the dynamic deformation of structures at an oil/water/electrode ternary interface, which is easily changed according to the property of the electrode surface. Electrochemical contact with the micro-saline and oil phases in a BME is alternately or simultaneously achieved by controlling the hydrophilicity and lipophilicity of the electrode surfaces. The selective electrochemical analysis of hydrophilic and lipophilic antioxidants in liquid foods without extraction demonstrated as the use of the unique ternary solution structures of BME on solid surfaces.

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1. Introduction

Emulsions, which consist of a mixture of two immiscible liquids, typically oil and water, have been widely used in a variety of major industrial fields, such as the pharmaceutical industry, cosmetics, paints and ink, and food products. One of a huge variety of emulsions, microemulsions (MEs) are thermodynamically stable, isotropic liquids that are stabilized by a surfactant, frequently in combination with a cosurfactant [1]. The characteristics, theories, and applications associated with MEs are some of the basic fundamentals of colloidal chemistry. Variations and systematic changes in the solution structure of MEs can be explained by a phase diagram in terms of the concentration and hydrophilic–lipophilic balance (HLB) of a surfactant system. Generally, an ME is considered to be a heterogeneous system of one immiscible liquid dispersed in another in the form of droplets: oil-in-water (O/W) or water-in-oil (W/O) dispersions. Except such closed-droplet phases, the structural variations of MEs include bicontinuous phases and liquid crystal phases.

In this article, we describe our recent progress in the electrochemistry of bicontinuous microemulsions (BME), from their fundamental aspects to their practical applications. We cover the assessment of the dynamic ternary structures of the water/oil/electrode interface in BME, which are easily changed according to the property of the electrode surface. We

also introduce the selective electrochemical analysis of hydrophilic and lipophilic antioxidants in liquid foods without extraction to demonstrate the use of the unique ternary solution structures of BME on solid surfaces.

2. Electrochemistry in bicontinuous microemulsions

BMEs, also called, Winsor III MEs and middle-phase MEs, are low-viscosity, isotropic, thermodynamically stable, and spontaneously formed mixtures of water, oil, and surfactants [1]. The dynamic morphology of an ME is generally determined by the HLB of the surfactants in the emulsion system, as shown in Fig. 1. When the hydrophilicity and lipophilicity of a surfactant are well balanced in an ME system, the ME frequently possesses a bicontinuous structure, in which the water and oil phases coexist on a microscopic scale. Generally, in an ME system stabilized by a neutral surfactant, it is not easy to produce a bicontinuous phase because the system is too sensitive to temperature; the solution structure of an ME system stabilized by an ionic surfactant is not sensitive to temperature, and MEs that include BMEs are usually controlled by the concentrations of salts (electrolytes) and cosurfactants.

Electrochemistry in emulsions or microemulsions has been widely researched [2]. A heterogeneous solution structure in emulsions has potential advantages over ordinary homogeneous electrolyte solutions as a unique electrolyte solution medium for electrochemical studies. Electrochemical and electrocatalytic reactions in emulsions with a heterogeneous solution structure involve many complex processes, including

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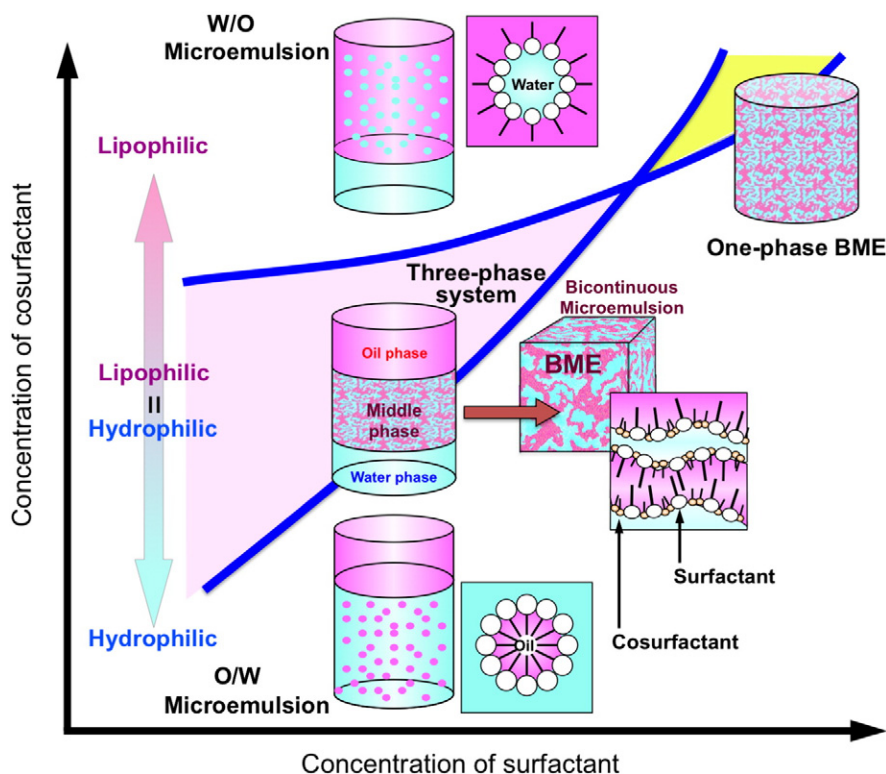


Fig. 1. Schematic representation of phase structures of microemulsions (MEs) governed by hydrophilic–lipophilic balance (HLB). The phase structures of MEs are controlled by salt (electrolyte) and cosurfactant concentrations.

the electrode interfacial processes “electron transfer” and “simple diffusion”, and the “phase partitioning” and “phase transfer” of reactants, intermediates, and products. Such complexity often leads to advantageous results and useful applications.

Mackay et al. were the first to suggest that electrochemical methods can be used to obtain information about the microstructure of microemulsions [1]. In 1990, the electrochemistry in BME solutions was reported. The authors observed changes in the microstructure of oil/water microemulsions (cetrimonium bromide (CTAB) + *n*-butanol/hexadecane/water system) including BMEs, which were identified electrochemically using glassy carbon (GC) electrodes in terms of the diffusion coefficients of the electroactive probes, such as ferrocene derivatives.

The use of probes of different hydrophobicity/hydrophilicity in different ME microenvironments has been investigated. The electrochemical reversibility of the probes is affected by the structure and appears to reflect the ease of mobility across the interphases. The apparent redox potential of the probes depends on the composition of the microemulsion [3]. Rusling et al. [4–14] reported the electrochemistry in BME solutions of didodecyldimethylammonium bromide (DDAB)/dodecane/water using a GC electrode for voltammetric reductions and oxidations of hexammine ruthenium (III) chloride, ferrocyanide, cob(II)alamin, and several polycyclic aromatic hydrocarbons. They reported that the electrochemical theory for homogeneous media was a good approximation, even in clear and conductive DDAB MEs. Electrochemically initiated bimolecular reactions in BMEs have also been reported [4]. The researchers demonstrated a kinetic advantage of bicontinuous over W/O MEs, possibly because of more efficient reactant mixing in the bicontinuous system, which has a larger interfacial area.

We have reported electrochemistry in BME media since 2002 [15]. Fig. 2 shows cyclic voltammograms (CVs) of ferrocene using an Au disk electrode in a series of MEs comprising toluene and saline stabilized by sodium dodecyl sulfate (SDS) with a cosurfactant. Lipophilic ferrocene was distributed only in a micro-oil in the ME. The solution structure of the ME was controlled by electrolyte concentration as the

result of the change of HLB. Because the hydrophilicity of SDS is stronger than its lipophilicity, SDS generally possesses an O/W droplet phase. However, the addition of a hydrophilic salt to an ME system induces a reduction of hydrophilicity of the surfactant system. Therefore, the solution structure was changed from an O/W phase via a BME phase to a W/O phase when the electrolyte concentration was increased.

In cases of low electrolyte concentration, small redox peaks were observed, indicating an O/W phase. The phase structures in the MEs are changed from the O/W phase via a BME until a W/O phase with the increasing of electrolyte concentration. The reversible redox peaks were observed in the MEs with the O/W phase and BME. Peak currents increased with the increasing electrolyte concentration, which was due to the increasing volume fraction of the ferrocene-containing oil in the ME. The peak currents were proportional to the square root of the scan rate, indicating a simple diffusion control, as we discuss in details later. Beyond the critical concentration for phase transition to the WO phase, electrochemistry in the ME was prohibited because of the lack of ionic conduction in the ME.

Normally, the redox potential is independent of electrolyte concentration in a homogeneous medium, although a certain amount of salt is necessary as an electrolyte. The shift of redox potential is related to the change of solution structure in MEs, but is not related to the change of ionic conductivity.

With the increasing electrolyte concentration, the redox potential was increased (shifted to positive) toward the redox potential measured in a homogeneous saline solution. The negative shift of redox potential of ferrocene in MEs against the standard redox potential measured in saline indicates that the ferrocenium cation is stabilized in MEs. The small potential shift in BME indicates that BME is closer to the water environment than O/W, although ferrocene is distributed in the oil phase. Conversely, the HLB is biased to the hydrophilic, ferrocene-surrounding environment away from water. In the BME systems, clear electrochemical responses of the redox species in a micro-oil phase are observed even if there is no electrolyte in the toluene phase. This indicates that the ionic conductivity is maintained via a continuous micro-

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