Colloids and Surfaces A: Physicochem. Eng. Aspects 429 (2013) 31–37

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Spontaneous interfacial tension changes at the interface of a $ZnCl_2$ nitrobenzene solution and aqueous stearyltrimethylammonium chloride solution

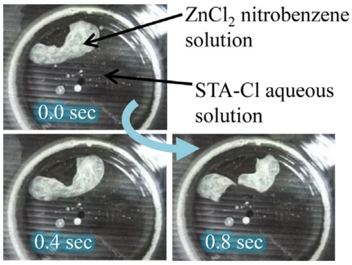
Yuta Tsuruki[a], Shou Yoneda[b], Yohey Shibuya[b], Toshihiro Isobe[a], Akira Nakajima[a], Sachiko Matsushita[a,b,*]

[a] Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 S7-8, Ookayama, Meguro, Tokyo 152-8550, Japan
[b] College of Humanities and Sciences, Nihon University, 3-25-40 Sakura-josui, Setagaya-ku, Tokyo 156-8550, Japan

HIGHLIGHTS

- Spontaneous motions at the interface of STA-Cl aq./$ZnCl_2$ nitrobenzene solution was observed.
- High ion-transfer potentials of Zn^{2+} is important.
- Concentration distribution of Cl^- at/near the interface is also important.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form 1 March 2013
Accepted 22 March 2013
Available online 3 April 2013

Keywords:
Nonlinear phenomena
Spontaneous oscillation
Nonequilibrium phenomena
Self-organization
Solubilization
Concentration gradient

ABSTRACT

This study examines the roles of chemical compounds that can generate spontaneous interfacial motion, especially in the Nakache and Dupeyrat system, which normally used a stearyltrimethylammonium chloride (STA-Cl) aqueous solution and a $KI + I_2$ nitrobenzene solution. Spontaneous behavior at the interface of a system comprising the STA-Cl aqueous solution and a nitrobenzene solution of $ZnCl_2$ or $FeCl_3$ was observed. To explore the mechanism, measurements of the interfacial tension, critical micelle concentration (CMC), and solubilization rate were performed for the $ZnCl_2$ system. The aggregates produced at the oil/water interface were subjected to infrared spectroscopic analysis, and the time dependence of aggregate coverage at the interface was measured. The analyses suggested that the spontaneous changes were generated because Fe^{3+} and Zn^{2+}, which have high ion-transfer potentials, could not easily move to the aqueous phase from the oil phase, and the counterion, Cl^-, also remained near the interface, resulting in a reduction of the CMC and promotion of solubilization. This information affords an understanding of the kinds of materials that can be used to produce a high level of spontaneous interfacial motion and aids in the development of a spontaneous interfacial motion system not utilizing toxic substances.

1. Introduction

Since the discovery of spontaneous interfacial motion at the interface between two immiscible phases under isothermal conditions (e.g., an aqueous phase containing an organic acid or complex ion and an organic phase with a long-chain surfactant molecule) by Nakache and Dupeyrat [1], the incidence of spontaneous oscillation has been actively studied for developing an understanding of non-equilibrium systems [2–4] and constructing new

---

* Corresponding author at: Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 S7-8, Ookayama, Meguro, Tokyo 152-8550, Japan. Tel.: +81 3 5734 2525; fax: +81 3 5734 3355.
E-mail address: matsushita.s.ab@m.titech.ac.jp (S. Matsushita).

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.03.052

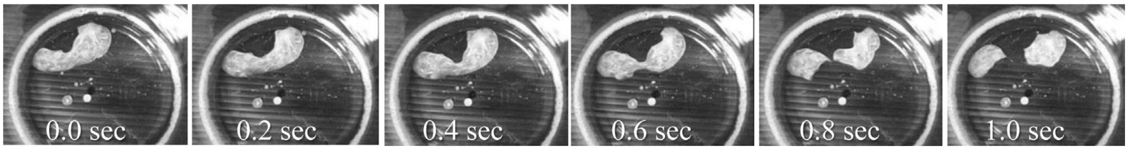


Fig. 1. Video captures of the spontaneous motion of a $ZnCl_2$ nitrobenzene droplet in an aqueous solution of stearyltrimethylammonium chloride.

chemomechanical transduction systems [5]. It is generally accepted that oscillations are related to some interfacial mass transfer [6,7], often involving a chemical reaction or ion pairing, the products of which are periodically adsorbed/desorbed from the interface, giving rise to abrupt changes in interfacial tension.

Reported applications of such spontaneous interfacial motion include the extraction of dynamics energy [5,8], generation of biological models [9], and development of a new model of nonequilibrium physics described in the context of electric capillary force [10]. For applying this phenomenon in engineering, information regarding the kind of material that can be used is very important. To date, surfactants, including cationic [11–13], anionic [3,14], and nonionic forms [15–17], have been examined. Moreover, some spontaneous interfacial motion has also been observed in systems not incorporating a surfactant [18]. Furthermore, with respect to the oil phase, systems using chlorobenzene [19], tetradecane [13,20], and pentane [15,16] have been studied.

In consideration of these innovative studies, we have attempted to understand the roles of chemical compounds capable of generating spontaneous interfacial motion from the standpoint of their chemical behavior, in the Nakache and Dupeyrat system, which used an STA-Cl aqueous solution and a KI + I_2 nitrobenzene solution [1]. We had previously suggested that nitrobenzene facilitated the electrophilic reaction $STA^+ + I_3^- \rightarrow STA\text{-}I + I_2$ [19]. Shioi, et al. also confirmed the importance of the formation of chemical compounds at the interface in a system employing an oil phase containing DEHPA and a water phase with a dissolved salt [14].

In this study, to check whether compound generation at the interface is required for spontaneous interfacial motion, we mixed various chloride salts in nitrobenzene and observed the changes at the interface of this solution and an STA-Cl aqueous solution. In this case, it is assumed that generation of the compound by a chemical reaction, which was mentioned above, at the oil/water interface does not occur. As a result, we observed spontaneous interfacial motion in $FeCl_3$ and $ZnCl_2$ systems (Fig. 1, Supporting Information 1) and observed white aggregations at the interface. This discovery is contradictory to previous reports that suggest the importance of the chemical reaction, $STA^+ + I_3^- \rightarrow STA\text{-}I + I_2$. To understand the mechanism of this newly observed phenomenon, we focused on the $ZnCl_2$ system and measured and analyzed various parameters, such as the interfacial tension, critical micelle concentration (CMC), solubilization rate, and the time dependence of aggregate coverage at the interface.

2. Materials and methods

2.1. Materials

The aqueous phases were 0, 0.1, 0.5, and 1 mM stearyltrimethylammonium chloride (STA-Cl) solutions. The oil phases were solutions of nitrobenzene containing saturated $AlCl_3{\cdot}6H_2O$, saturated $FeCl_3{\cdot}6H_2O$, saturated $CaCl_2{\cdot}2H_2O$, saturated KCl, and 1.6, 3.2, 4.8, and 6.4 mM and saturated $ZnCl_2$. These mixtures were stirred for one day. All reagents were purchased from Wako, Japan, and the experiments were performed at room temperature (~21 °C). Detailed procedures for each experiment are described in the following section.

2.2. Interfacial tension measurement

The aqueous phase solutions were poured into UV cells (10 mm × 10 mm × 45 mm) (Fig. 2). Oil phase solutions of nitrobenzene containing the various concentrations of reagents were injected via a microsyringe into an aqueous solution to suspend them as droplets (Fig. 2a). The volume of each droplet was 30 μL, and the injection rate was 300.1 μL/min. The droplet shape was continuously recorded using a charge-coupled device (CCD) camera and analyzed via the pendant drop method using a dynamic interfacial tension measurement device (DSA20, KRUSS). The experiments were performed at room temperature (~21 °C).

Interfacial tension measurements were performed for 20 s at intervals of 1 s. The time at which the oil droplet was injected was set as 0 s.

2.3. Critical micelle concentration measurement

The aqueous solution of STA-Cl (3 mM) was added in portions (0.5 mL increments) to 250 mL of an aqueous solution of $ZnCl_2$ (0, 0.1, 0.5, and 1 mM) or KCl (0.2, 1, and 2 mM), and the electrical conductivity as well as the CMC was measured following each addition.

2.4. FT-IR measurement of the aggregates

The white aggregates produced at the oil/water interface as a result of spontaneous interfacial motion were very unstable and were difficult to isolate by suction filtration. The aggregates were therefore extracted from the interface using a syringe, and the liquid containing the aggregates was dropped on a watch glass, but the aggregates disappeared during the process in which the liquid component evaporated. The extracted aggregate could be stably saved only in water.

The white aggregates were subjected to IR spectroscopy (FT/IR-6100 type A, Shimadzu) using the attenuated total reflectance (ATR) method. Triglycine sulfate (TGS) was used as an infrared detector.

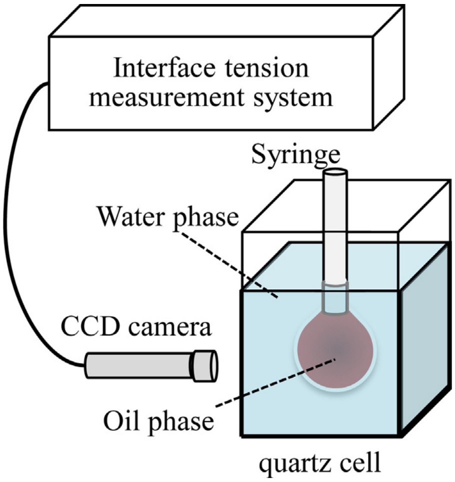


Fig. 2. Schematic of the interface tension measurement system.