



# Spontaneous emulsification at surfactantless liquid/liquid interfaces



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## ABSTRACT

Liquid/liquid interfaces can undergo spontaneous emulsification when a common-ion is distributed between both phases. By careful selection of electrolyte and solvent, stable nano-sized water-in-oil emulsions containing electrolyte can be produced. The emulsification process can be monitored indirectly via transient open circuit potential measurements using an electrochemical measuring cell, initially poised at equilibrium, within the organic phase. Theoretical analysis of experimental data indicates that the interfacial emulsification process is probably controlled by diffusion.

## 1. Introduction

Spontaneous emulsification can occur when two immiscible liquids, out of equilibrium, are placed in physical contact [1,2]. Spontaneous emulsification can proceed without the aid of external energy inputs and without surfactant. This is because chemical potential energy gradients, in liquid-liquid systems which are out of equilibrium, are large enough to drive interfacial emulsification [2]. Spontaneous emulsification is currently an active area of research, although as noted by Aoki [3], a large proportion of previous work dealing with surfactantless spontaneous emulsification at immiscible liquid-liquid interfaces does not emphasise an electrochemical aspect to any great extent.

Conventional ITIES (interface between two immiscible electrolyte solutions) may also be able to undergo spontaneous emulsification without external polarization [3]. Much of the previous work in this regard has however, dealt almost exclusively, with spontaneous oscillations in interfacial tension and general interfacial instability in the presence of added surfactant [4–9]. Under externally polarised conditions though, interfacial emulsification and interfacial instabilities in the presence of an ionic surfactant, arise from the formation of an ‘instability window’ [8]. This ‘window’ is caused by potential-dependent adsorption and partitioning of surfactant at the ITIES [10].

Within a conventional ITIES-type experimental arrangement, both phases contain electrolyte. Electrolytes used within the aqueous phase are hydrophilic salts such as lithium chloride. The organic phase (usually nitrobenzene or 1, 2-dichloroethane) contains hydrophobic electrolyte, such as tetrabutylammonium tetraphenylborate for example (TBATPB). A recent small angle neutron scattering (SANS) study by Sadakane et al. [11] demonstrated that in the presence of tetraphenylborate the water/3-methylpyridine interface can produce

periodic mesoscopic structures [12]. Water soluble tetraphenylborate salts (such as NaTPB) are sometimes termed as “antagonistic” [13,14]. In other words, the salt is comprised of both strongly hydrophilic ( $\text{Na}^+$ ) and strongly hydrophobic ( $\text{TPB}^-$ ) ions. In the presence of a composition heterogeneity, such as that found at an ITIES, antagonistic salts can lead to the formation of mesophase structures with charge density waves and decreases in interfacial tension [14]. Similar structures have also been recently reported at the water/2,6-dimethylpyridine interface with the addition of a tetra alkyl-ammonium bromide [15].

In this present article we demonstrate that ITIES, possessing a common-ion distributed between both phases, are able to undergo spontaneous emulsification and form stable water-in-oil nanoemulsions. This effect is exemplified using two model systems. Methodology detailed herein allows one to monitor the emulsification process indirectly using an electrochemical monitoring cell located within the organic phase. A theoretical framework is provided to analyse results of one of the experimental systems.

## 2. Materials and methods

Tetrabutylammonium tetraphenylborate (TBATPB, > 99%), tetramethylammonium chloride (TMAcL, > 98%), tetraphenylarsonium chloride (TPhAsCl, polarography grade), sodium tetraphenylborate (NaTPB, 99.5%) and agar-agar were all supplied by Fluka Analytical, Czech Republic. Tetrabutylammonium chloride (TBACl, > 97%) was supplied by Sigma Aldrich, Czech Republic. Tetramethylammonium tetraphenylborate (TMATPB) was prepared by metathesis.

Tetraphenylarsonium bis-1,2-dicarbollylcobaltate (TPhAsDCC) was prepared at the Institute of Inorganic Chemistry ASCR, v.v.i. Chemicals and was used as received. Highly purified, deionised water (DI,

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conductance:  $< 0.1 \mu\text{S cm}^{-1}$ , GORO system, Czech Republic) was used to prepare all aqueous solutions. 1, 2-dichloroethane (1,2-DCE, 99%) and nitrobenzene (NB, 99.5%) were supplied by Fluka Analytical (Czech Republic) and were used to prepare organic solutions.

### 2.1. Glass plate experiments

Equal aliquots (as much as 75  $\mu\text{l}$ ) of an aqueous phase and an organic phase (of varied compositions) were placed in close proximity to one another at the centre of a clean glass plate. The glass plate was of rectangular geometry and was approximately 1.5 mm thick. Glass cover slips of approximately 100  $\mu\text{m}$  thickness were placed in each corner. A second glass plate (of the same thickness and geometry) was placed on top of the first which allows the two phases to contact. This 'sandwich' arrangement formed a thin-layer cell and allowed oil/water interfaces to be readily viewed using optical microscopy. Evaporation of the two phases was negligible in this arrangement over the course of a typical experiment.

### 2.2. Open circuit potential (OCP) monitoring experiments

A cartoon depiction of the glass apparatus used in OCP monitoring experiments is illustrated in Fig. 1. The glass apparatus comprises two electrochemical cells.

The first cell is formed by an aqueous phase and an organic phase. These two phase form a large area interface. This water/oil interface is the droplet forming interface (DFI). The cell is initially filled with organic phase (5 ml), upon which, deionized water (4 ml) is slowly layered. At the beginning of the OCP measurement, a concentrated aliquot of aqueous electrolyte is carefully injected into the distilled water yielding the required concentration of electrolyte in the aqueous phase. The injection initiates the spontaneous emulsification process. Water-in-oil droplets are homogenised within the organic phase by slow stirring, 2–3 revolutions per second, with a magnetic stir bar.

The second electrochemical cell (MC), consisting of two Luggin capillaries (inner diameter 1.5 mm) placed in the organic phase, is used to monitor the emulsification process. The upper Luggin capillary with the reference interface inside the capillary serves as a reference electrode. The lower Luggin capillary serves as an indicator electrode.

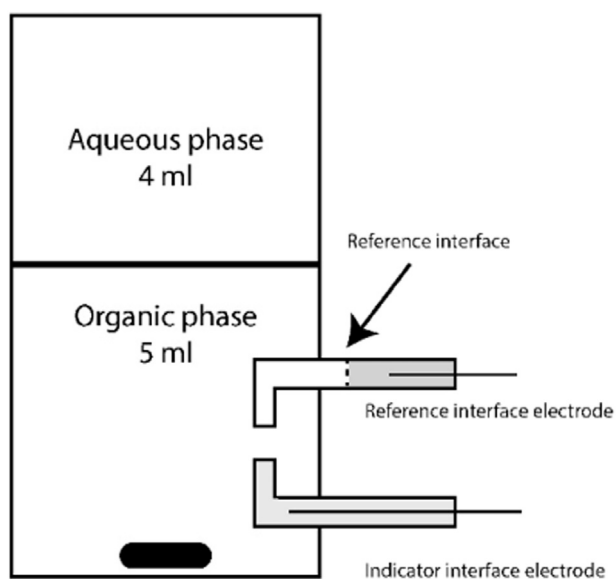


Fig. 1. Cartoon depiction of the glass apparatus used for OCP monitoring experiments. The dashed line within the upper Luggin capillary (indicated by an arrow) shows the position of the liquid/liquid reference interface. Shading in both capillaries indicates an aqueous phase. The dark ellipsoidal shape at the bottom of the organic phase represents the small Teflon stir bar.

Electrolyte in the indicator electrode was gelled to the tip with 2% (w/v) agar for mechanical stability. Water-in-oil droplets impact the indicator electrode at the very tip of the capillary. The reference interface, in contrast, is situated well inside the Luggin capillary, to protect it from the droplet impact. (Fig. 1).

Two experimental systems are used for experiments, namely:

The  $\text{TPB}^-/\text{NB}$  system

DFI:

$x \text{ mM NaTPB(w)}/10 \text{ mM TBATPB(NB)}$ .

MC:

$\text{Ag/AgCl}/10 \text{ mM TBACl (in 2\% agar(w)}/10 \text{ mM TBATPB(NB)}/10 \text{ mM TBACl(w)}/\text{AgCl/AgCl}$ .

The  $\text{TPhAs}^+/\text{1,2-DCE}$  system

DFI:

$x \text{ mM TPhAsCl(w)}/10 \text{ mM TPhAsDCC (1,2-DCE)} + 5 \text{ mM TMATPB (1,2-DCE)}$ .

MC:

$\text{Ag/AgCl}/5 \text{ mM TMACl (in 2\% agar(w)}/10 \text{ mM TPhAsDCC(1,2-DCE)} + 5 \text{ mM TMATPB(1,2-DCE)}/5 \text{ mM TMACl(w)}/\text{AgCl/Ag}$ .

Two Ag/AgCl wires were used as electrodes. The OCP of the MC is continuously monitored/recorded. A concentrated aliquot (normally 100 mM) of aqueous phase electrolyte was injected at 60s (in all cases) after the initiation of OCP monitoring. The OCP was monitored using a CHI 660c potentiostat (CHI Instruments).

## 3. Results

### 3.1. Glass plate experiments

A vigorous and spontaneous interfacial emulsification process is observed at the ITIES shortly after placing the two phases in physical contact (both  $\text{TPB}^-/\text{NB}$  and  $\text{TPhAs}^+/\text{1,2-DCE}$  systems). The sub-micron sized water-in-oil droplets (see DLS results, Supplementary section) formed exclusively on the oil side of the ITIES, makes proper resolution impossible using optical microscopy. Although one can, with the aid of microscopy, observe masses of sub-micron, spherical and translucent entities originating from the interface and pervade the bulk of the organic phase. Some larger micron-sized droplets are observed in bulk after a period of a few minutes. Fig. 2 illustrates the extent of the spontaneous emulsification process within the  $\text{TPB}^-/\text{NB}$  system. No obvious signs of precipitate are observable.

Droplets remain intact for long periods and for relatively long distances away from the liquid/liquid interface. This indicates droplet stability. Droplet stability allowed extensive droplet accumulation within the volume of the organic phase (Fig. 2 and Supplementary section).

Within the  $\text{TPB}^-/\text{NB}$  system, droplet accumulation results in organic phase turbidity (with slow stirring of the organic phase) over a period of a few hours (Fig. 2). Although a similarly vigorous and spontaneous interfacial emulsification process was observed for the  $\text{TPhAs}^+/\text{1,2-DCE}$  system, organic phase turbidity was not as extensive as that of the  $\text{TPB}^-/\text{NB}$  system over the same period of time.

Standard transfer potentials are similar for the transfer of  $\text{TPB}^-$  from water to nitrobenzene and for its transfer from water to 1,2-dichloroethane [16]. Hence, by using the same electrolytes in each phase, but changing only the solvent (from NB to 1,2-DCE), similar Galvani potentials across the ITIES are expected. Both a  $\text{TPB}^-/\text{NB}$  system and a  $\text{TPB}^-/\text{1,2-DCE}$  system (using the same electrolytes), produce vigorous spontaneous emulsification at the interface.

Although, within the  $\text{TPB}^-/\text{1,2-DCE}$  system, water droplets formed within the oil phase are observed to clearly 'pop' and coalesce on the surface of the glass after a few minutes and at a short distance away from the interface (Figs. 1S and 2S).

Furthermore, no accumulation in bulk, and thus no observable turbidity is evident after 12 h of stirring (as in Fig. 2). Rather, glass walls of the vial in the case of  $\text{TPB}^-/\text{1,2-DCE}$  system, took on a 'frosted'

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