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Electric charging of inverse micelles in a nonpolar liquid with surfactant

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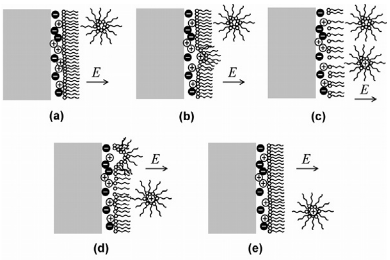
HIGHLIGHTS

- Current measurements in response to a voltage step provide information about the origin, nature and properties of charges in nonpolar liquids.
- A model for the generation of charged inverse micelles needs to include both bulk and surface interactions.
- Inverse micelles exchange charge with an adsorbed layer of surfactant molecules at the electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The origin of charges in nonpolar liquids with surfactant is not completely understood. This study does not only look at bulk mechanisms as the origin of charged inverse micelles, but includes processes at the liquid/electrode interfaces. We apply a voltage over a layer of nonpolar liquid with surfactant and measure the current. Information about the generation of new charges is obtained from the remaining current after the initially present charges have reached equilibrium. We find that, for low voltages, the residual current is proportional with the electric field near the electrodes. This can not be explained by bulk generation alone. We interpret these results by assuming that inverse micelles exchange charge with an adsorbed layer of surfactant molecules at the electrodes. The findings of this study are relevant for technologies such as microfluidics and electrophoretic ink, where injection of charge from the electrodes contributes to power consumption and hydrodynamic instabilities.

1. Introduction

Surfactants in nonpolar liquids are added as lubricants, dispersants and charging agents in applications such as motor oil [1], inks [2], toners [3], developers [4] and ceramic processing [5,6]. Their ability to stabilize charges on the surface of colloidal particles [3,7–15] or in the core of inverse micelles [3,12–21] is becoming increasingly important, mainly because of the relevance for electrophoretic ink [22–28], the most successful candidate for the implementation of electronic paper, but also for other applications, in which charges in nonpolar liquids are an undesired side-effect [29–31]. The possibility to control the conductivity of a nonpolar liquid by varying the concentration of surfactant [3,12–20] is also interesting for fundamental research. Mixtures of nonpolar liquid and surfactant are used in studies of colloidal crystals [32,33] and as a model system for general electrolytes [34,35]. Despite

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Table 1
Properties of the measured devices with a polyimide layer.

Spacer diameter (μm)	Surfactant concentration (wt%)	Device thickness d (μm)	Concentration of charged inverse micelles $\bar{n}_\pm$ (μm^{-3})	Micelle mobility μ (μm^{2}V^{-1}s^{-1})
7	0.2	6.9	10.2	1005
7	1	5.7	58.7	674
7	5	5.4	218	1001
12	0.1	12.6	4.9	1048
12	0.2	13.9	9	997
12	0.5	8.9	20.8	897
12	1	14.1	56.1	632
12	2	13.9	95.4	705
12	5	12.2	220	827
23	0.2	29.3	12.4	735
23	1	30.4	51.2	827
23	5	23.1	234.7	696

their importance, the physical mechanisms underlying the origin of charges in nonpolar liquids are not completely understood [3,8–10,12–14,36,37].

In a nonpolar liquid with surfactant, free charges can only exist in the form of inverse micelles which provide the necessary separation with the countercharges [12–16,19–21]. Electric current measurements during the application of a voltage step over a layer of nonpolar liquid with surfactant between plan-parallel electrodes are used to obtain detailed information about the properties, the behavior and the generation of charged inverse micelles in nonpolar liquids [16,34,35,38–45]. In most cases the interpretation of these currents is different from that in polar media, due to the smaller charge concentration and the fact that the liquid can become completely depleted of charge when a high enough voltage is applied [34,35,38,39,42,43,46].

The current in response to a voltage step typically consists of two phases [16,34]. In the first phase, the current is the result of the movement of initially present charges, and decreases quickly when the distribution of charges reaches a new equilibrium [34,42,43]. This phase is understood well and can be described by electrophoretic drift and diffusion of charged inverse micelles, together with the screening effect on the electric field when the charges are separated [34,42,43,47–49]. The second phase of the current, which is not as well understood, continues for a much longer time and is the result of the generation of new charges after the initially present charges have reached a new equilibrium [16]. This current can be partially interpreted by the comproportionation and disproportionation of inverse micelles [13–17,19], but in many situations these processes alone fail to explain the measured currents [16].

In this work, we present a detailed study of the influence of different parameters on the measured current when a voltage step is applied over a layer of nonpolar liquid with surfactant. We focus specifically on the ‘quasi steady state’ current, which is defined as the current after the initially present charges have reached equilibrium, but before the generation of new charges has a significant influence on the electric field and on the amount and distribution of charged inverse micelles. We find that processes near the electrodes [37,50,51] have an important effect on the quasi steady state current. Based on the dependencies of the quasi steady state current on the device and measurement parameters, we propose a model for the injection and adsorption of inverse micelles at surfaces near an electrode, which explains the current under a wide variety of conditions, and which provides a better understanding of the origin of charge in nonpolar liquids.

2. Experimental methods

The devices used for the measurements in this work consist of two glass plates , coated with a transparent ITO-electrode (indium tin oxide) with surface area $S_{\mathrm{el}} = 1\,\mathrm{cm}^2$. The glass plates are attached to each other using ultraviolet curing glue. Spacer beads in the glue keep the two plates separated at a distance d. There is no connection between the electrodes through the glue or through the spacers, to avoid leakage currents. The space between the plates is filled with a mixture of high purity (99.9%) n-dodecane (Aldrich) and different weight percentages of OLOA-1200 (Chevron), which contains 50 wt% mineral oil and 50 wt% of the surfactant polyisobutylene succinimide [8,14,16,19,52,53].

In a first series of devices (Table 1), the plates are spincoated with a polyimide layer with thickness $d_{\mathrm{IL}} \approx 50\mathrm{nm}$ covering the ITO-electrode. In another series (Table 2), the plates are left uncoated. For each series, devices are made with combinations of the spacer diameters 7 μm, 12 μm and 23 μm and the OLOA-1200 concentrations 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt%. The actual thickness d of each device is determined from a capacitance measurement before filling.

Before every current measurement the electrodes of the device are short-circuited for at least 10,000 s. Then, at time $t = 0$, a step to a voltage V_{A} between 0.01 V and 5 V is applied between the electrodes and the resulting electric current I is measured with a Keithley 6517A electrometer. The long short-circuiting time ensures that the charges in the device are in equilibrium when the step is applied, not only for drift and diffusion but also for the longer term mechanisms investigated in this work. For the same reason, measurements at higher voltages are always performed after measurements at lower voltages.

A rough estimation of the average concentration $\bar{n}_\pm$ and mobility μ of initially present charged inverse micelles in each device is obtained from the integral and the initial value of the transient current for the highest voltage (5 V) [34,38,42]. These values are then used as a starting point for a more accurate estimation by fitting simulations of the transient current for all voltages to the measured data.

In many cases, especially for high voltages, the distinction between the transient part and the quasi steady state part of the measured current is clear [16,34,43] and a value for the quasi steady state current can be estimated from the measurement in a reproducible way. In other cases, mostly for low voltages, the distinction is not so clear [16,34,43]. Therefore, an objective procedure is used to obtain values for the quasi steady state current I_{qss} immediately after the transient period. First, for every measurement, the best fitting simulation of the transient current is found, using the Poisson–Nernst–Planck equations [34,47,54] which model drift, diffusion and screening (but without any charge generating mechanism in the bulk or near the surfaces). This simulated current goes to zero when equilibrium is reached, while in the measurements there is still a current. At the moment when the simulated current is a factor 100 smaller than the measured current, the transient