Generation current of charged micelles in nonaqueous liquids: Measurements and simulations

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Abstract

Electrically charged species in nonaqueous media still hold many questions. Recent studies and applications show the need for a better understanding of the origin and nature of these charged species. Transient current measurements have been used to study the conductivity of nonaqueous liquid containing charged inverse micelles. At small time scales (1–100 ms) drift and diffusion of charged species are the main contributions to the measured current. At larger timescales (above 1 s) a nonzero quasi steady-state current at high voltages (above 0.5 V) remains. This indicates that besides drift and diffusion an additional process occurs. The dependence of the quasi steady-state current on the applied voltage, micelle concentration, and device thickness has been investigated. Experimental results have been compared to simulations and analytical calculations. It is concluded that the quasi steady-state current results from a bulk disproportionation reaction between neutral micelles that generates charged micelles. And therefore this technique allows for direct quantification of the reaction kinetics from which the charged species originate.
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1. Introduction

In an aqueous environment simple ions such as Na^+ or Cl^- can exist, and ionic processes are quite well understood. In nonaqueous liquids there are many questions about the origin and nature of electrically charged species [1]. Electrostatic forces in nonpolar solvents ($\varepsilon \cong 2$) are about 40 times larger than in polar solvents ($\varepsilon \cong 80$), making it much more difficult for free charges to exist. In some cases however, for instance where surfactant is added to a nonpolar solvent, charged species are abundantly present. It is generally accepted that this is possible because electrical charges are dissolved in the aquatic interior of inverse micelles holding opposite charges sufficiently far apart. For electrical charges to remain free, a minimal separating distance is needed so that the thermal energy is bigger than the attracting electrostatic force. The most studied surfactants are aerosol-OT (AOT, or di-2-ethylhexylsulfosuccinate) [2,3],

and succinimides such as polyisobutylene succinimide (PIBSI) [4,5]. When dissolved in a nonpolar liquid, these surfactant molecules aggregate and form inverse micelles above the critical micelle concentration (CMC) [6]. Below the CMC surfactant molecules are present as monomers unable to separate opposite electrical charges, resulting in a sudden drop of the conductivity. Electrical charges in nonpolar media are studied increasingly in recent years. For instance the nucleation and growth of electrostatically stabilized colloidal crystals are being investigated as a model system for atomic systems [7]. In many applications surfactants are added to dielectric liquids. For instance for the stabilization of soot particles in engine oil [8]. Also electrophoretic displays [9,10] are based on the movement of charged pigments in a transparent or dyed insulating fluid. The surfactant, then called the charging agent, is used to charge the pigment particles. However, a large part of the charging agent is not absorbed on the pigment particles and remains in the solution partially as charged inverse micelles. These charged micelles influence the electric field and need to be taken into account for understanding the electrophoretic transport characteristics of the pigment. New measurement tech-

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niques have been developed in recent years to study the nature of charged species in nonpolar media (laser Doppler velocity, phase-analysis light scattering, electroacoustics, electrical conductivity, and transient measurements). Transient current measurements of solutions with charging agent can be used to determine the concentration, mobility, and charge of the charged species [11]. The main contribution to the transient current results from the motion of the initially present charged micelles. This motion of charged species under influence of an electric field is well understood, and can be accurately modeled with drift and diffusion. However, transient current measurements show a small quasi steady-state current, which cannot be explained by drift and diffusion. Here we present an explanation for this quasi steady-state current based on generation of charged micelles in the bulk of the solution.

2. Transient current measurements

For the transient measurements, planar glass substrates are used with plan-parallel ITO-electrodes with a 50 nm insulating polyimide coating (AL1051, JSR). The electrodes are separated by quartz spacer balls with diameter between 4 and 33 µm. Capacitance measurements were used to verify the cell thickness d. The overlapping electrode-area S is 0.5 cm^2, justifying a one-dimensional mathematical modeling. At room temperature, cells are filled with a mixture of high purity n-dodecane (Aldrich) and a charging agent, a widely used oil-containing surfactant polyisobutylene succinimide (OLOA 1200, Chevron). This product is not distributed outside of Europe anymore, but OLOA 11,000 is for sale everywhere and behaves in the same way. The weight percentage of OLOA in the mixture is designated as w_{OLOA} (wt%). Cells filled with only n-dodecane are highly insulating. The addition of OLOA leads to the formation of charged species. It has been shown [11] that no charged species are present below a certain concentration, indicating that the conductivity is related to the surfactant aggregates. The current is measured with a custom-built current amplifier, combining high speed (milliseconds) with high sensitivity (picoamperes). In the transient current measurements a zero voltage is applied for a sufficiently long time—to assure uniform charge distributions—followed by a step voltage V at $t = 0$. Typical current measurements are shown in Fig. 1. The initial current is due to drift of positive and negative charged species and is proportional to the applied voltage. The higher the voltage, the sooner the ions reach the electrodes, the sooner the current drops significantly. At voltages above 1 V a quasi steady-state current is observed after 1 s that is practically independent of the applied voltage. It is called quasi steady-state because at even larger timescales the current decreases slowly. At times between 0.1 and 10 s additional mechanisms are causing a time dependency with a stretched exponential like behavior. Therefore the steady-state current is measured at the time where these effects have died out. The saturated quasi steady-state current for $V = 5$ V at $t = 40$ s was measured in cells with various thicknesses $d = 4, 7, 11, 16,$ and 33 µm, and weight percentages $w_{OLOA} = 0.1, 0.3, 0.6, 1, 1.74, 3,$ and 9.3 wt%. These currents follow a quadratic dependency on the concentra-
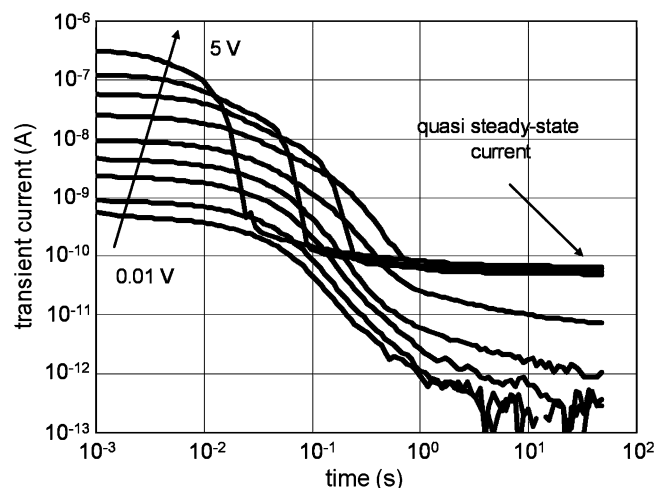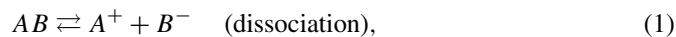

Fig. 1. Transient currents measured in 1 wt% OLOA in dodecane with $d = 7$ µm, $V = 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2,$ and 5 V.

tion of OLOA (Fig. 2a), while there is a linear relation with the cell thickness (Fig. 2b). This is summarized in Fig. 2c, where all data collapse in one curve. Notice that an increasing current for increasing cell thickness is the opposite from what is expected from a classical conductive medium, like for instance a simple resistor. Here we are dealing with a special conductive medium with mobile charged species in a nonconductive liquid. In Fig. 2d the data is plotted in function of $w_{OLOA}d$, which will be useful to distinguish the underlying mechanism.

3. The generation mechanism

The measurements indicate that the quasi steady-state current is related to the surfactant OLOA. Two mechanisms leading to generation of charges can be proposed:

$$AB \rightleftarrows A^+ + B^- \quad \text{(dissociation)}, \tag{1}$$

$$2A \rightleftarrows A^+ + A^- \quad \text{(disproportionation)}. \tag{2}$$

For both these reaction mechanisms the neutral species (left)—which are included in the OLOA—are converted to charged species (right). The quasi steady-state current is proportional to the reaction rate. So, in case of dissociation the current is expected to be linearly dependent on the OLOA concentration, and in case of disproportionation quadratically. The measurements of Fig. 2 favor a disproportionation reaction, as can be verified by comparing Figs. 2c and 2d, where the linear trendline shows what is expected for disproportionation and dissociation, respectively.

Above the critical OLOA concentration inverse micelles are formed spontaneously (Fig. 3a) [1,6]. These are aggregates of a number of polyisobutylene succinimide molecules in a nonpolar environment. The polar succinimide groups gather in the center, while the apolar polyisobutylene chains stick outwards. Evidence for these micelles is the observation of a CMC of about 0.005 wt%. The fact that the average mobility measured for the charged species yields a Stokes radius (about 10 nm) that is larger than the length of a single surfactant molecule (about 7 nm) proves that the charged species are aggregates of