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Determination of charge carrier concentration in doped nonpolar liquids by impedance spectroscopy in the presence of charge adsorption

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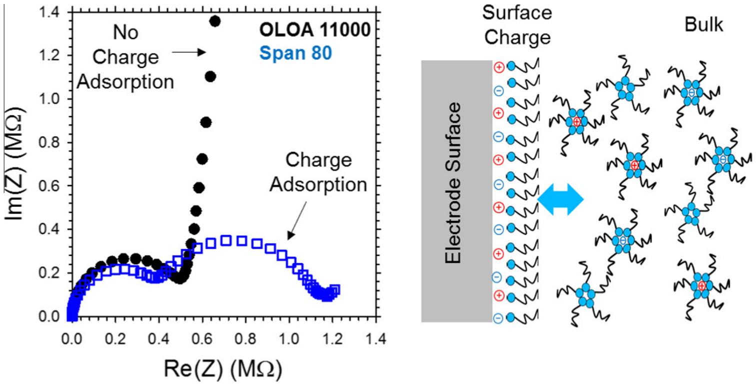
GRAPHICAL ABSTRACT



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ABSTRACT

The impedance of dodecane doped with sorbitan trioleate (Span 85), sorbitan monooleate (Span 80) and sorbitan monolaurate (Span 20) was measured as a function of frequency using a 10 mV amplitude sinusoidal voltage applied across a parallel plate cell with a 10 μm spacing. The tested solutions varied in concentration from 1 mM to 100 mM and the frequency range was 10^{-2}–10^{4} Hz. Nyquist plots of all three surfactants showed the high frequency semicircle characteristic of parallel resistance and capacitance but often exhibited a second semicircle at low frequencies which was attributed to charge adsorption and desorption. The electrical conductivity of each surfactant was proportional to surfactant concentration for concentrations above 10 mM. Fitting the data to models for charge migration, differential capacitance, and adsorption allowed extraction of both charge concentration and two kinetic parameters that characterize the rate of adsorption and desorption. Above 10 mM the ratio of charge carriers per surfactant molecule was 22 ppm for Span 20, 3 ppm for Span 80, and 0.2 ppm for Span 85. A higher number of charge carriers per molecule of surfactant was associated with larger micelles. The adsorption rate constants were independent of surfactant concentration while the desorption rate constants were proportional to the surfactant concentration. This dependence indicated that uncharged surfactant, whether in micelles or not, participated in the desorption of charge. Predictions of the adsorption/desorption model for large constant electric fields agreed qualitatively with data from the literature (Karvar et al., 2014).

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1. Introduction

Nonpolar liquids such as alkanes have virtually no conductivity, but the addition of surfactants can produce measurable conductivity [1]. For example, practitioners add surfactants to highly refined hydrocarbons to mitigate charge accumulation during transfer of the liquid from one vessel to another, which reduces the risk of ignition by arcing. More recently the addition of surfactants as charge inducing dopants has been used to stabilize particle dispersions electrostatically. For example, adding the commercial surfactant OLOA 11000 (poly-isobutylene succinimide) to engine oils suspends soot particles and prevents the buildup of sludge [2]. Other applications include electrophoretic ink displays [3] and printing inks [4,5]. Aerosol-OT (dioctyl sodium sulfosuccinate), another widely studied dopant, includes an ionic head group [6–10], but ionic groups are not necessary. Even nonionic surfactants including Span® 85 (sorbitan trioleate), Span® 80 (sorbitan monooleate), and Span® 20 (sorbitan monolaurate) raise conductivity in nonpolar media [11–15].

Various mechanisms have been proposed to explain the stabilization of charge by surfactants in nonpolar media. Amphiphilic surfactants form reverse micelles that display their nonpolar tails to the host liquid while providing a polar core to host the charge. Collisions of two neutral micelles may result in the transfer of a proton (or other small ion). The interaction creates an ion pair, whose subsequent degree of dissociation is determined by the resulting electrostatic attraction relative to the thermal energy kT. Ionic surfactants might dissociate to some extent to produce separately charged entities. Nonionic surfactants might solubilize and dissociate ionic contaminants present in the solvent, dopant, and surfaces. Finally, because the concentration of charge carriers is extremely small, even alcohols – which would be considered nonionic among aqueous electrolytes – can donate or accept protons to a very limited extent and thus impart conductivity to solutions with nonpolar solvents [16]. Perhaps the “nonionic” Span surfactants work similarly.

The concentration of charged species, however produced and stabilized, is an important quantity for any combination of host liquid and surfactant. For example the Debye screening length in the liquid phase, a crucial length scale governing stability of dispersions by electrostatic repulsion, depends on the inverse square root of this concentration. Conductivity, the most commonly measured property of doped nonpolar liquids, is directly proportional to the charge carrier concentration but also is inversely proportional to carrier size. Thus, conductivity measurements themselves do not yield the desired charge concentration. Previous studies solved this problem by inferring the charge carrier size from dynamic light scattering [4,6], but this determination requires the assumption that the charged carriers and the scatterers have the same size, which might not be true [17]. Alternatively, one can determine the Debye length by measuring the exponential decay of double-layer repulsion [18], but that experiment is more challenging than an electrical measurement.

Electrochemical techniques have been employed to determine the concentration of charge carriers. Fitting numerical simulations to the data of a chronocoulometric experiment is one approach [19,20], or one can integrate the current with time to determine the total charge available [18,19,21,22]. Dividing this charge by the volume of fluid gives the initial concentration of carriers, but persistent “surface current” can complicate this analysis [14,23,24]. Experiments based on electrochemical impedance spectroscopy (EIS) [6,9,17] have also been used. We used EIS to measure conductivity and double layer capacitance of nonpolar liquids [17] and thereby deduce Debye lengths for various concentrations of the surfactant OLOA 11000 in dodecane. The impedance spectra exhibited classic semicircular behavior in Nyquist plots at higher frequencies and purely capacitive behavior, as modified by constant phase elements, at lower frequencies.

Continuing these studies with a series of Span surfactants, we observed more complicated impedance spectra than with the OLOA 11000 surfactant in our prior work [17]. A second semicircle appeared in the Nyquist plot at low frequencies. Here, we focus on this feature as the main topic. We model this more complicated spectrum by including charge adsorption and desorption at otherwise blocking electrodes. The modeling yielded the desired concentration of carriers (and hence the Debye length) despite the complications introduced by the adsorption. Using a Langmuir model for the kinetics of reversible adsorption of charge carriers, we also found that the *desorption* rate increased with total surfactant concentration. While one expects the *adsorption* rate to be proportional to the concentration of charge carriers, the desorption rate was not expected to increase with the bulk concentration. This finding suggests that neutral surfactant molecules or micelles were involved in the desorption of charge.

2. Theory

Three models of the impedance of surfactant solutions with charge adsorption at the electrode surface are presented. The first model is based on unsteady diffusion and electromigration of charge carriers with charge adsorption and desorption at either boundary [24]. We refer to this as the “transport model.” The second model is an equivalent circuit with adsorption resistance and capacitance at either electrode [25]. The third model, a variant of the second model, includes constant phase elements. Each of the three models can be applied to infer charge concentration, the kinetics of adsorption and desorption, and the mobilities of charge bearing species.

2.1. Transport model

Following Barbero [26] we model the unsteady distribution of charge carriers within the fluid cell including adsorption and desorption at the electrodes. Fig. 1 is a sketch of the domain and coordinate system. When the fluid cell is thin compared to its other two dimensions and the electrodes are good conductors, the unsteady transport is one-dimensional. The positive and negative charge carriers are assumed to have equal diffusion coefficients D and equal but opposite charges $\pm e$, where e is the elementary charge. The reasoning for this assumption is discussed later.

The Nernst Planck equation expresses the flux of ions due to electromigration and diffusion as

$$N_{\pm} = -D\left(\frac{\partial n_{\pm}}{\partial x} \pm \frac{n_{\pm}}{k_B T}\frac{\partial \varphi}{\partial x}\right) \quad (1)$$

where k_B is Boltzmann’s constant, T is absolute temperature, e is the charge on one proton, $n_{\pm}(x,t)$ are the ion number densities and $\varphi(x,t)$ is the electrostatic potential. The + or − subscript denotes either cation or anion, respectively. Conservation of ions requires

$$\frac{\partial n_{\pm}}{\partial t} + \frac{\partial N_{\pm}}{\partial x} = 0 \quad (2)$$

and the electrostatic potential must satisfy Poisson’s equation

$$\frac{\partial^2 \varphi}{\partial x^2} = -e\varepsilon(n_+ - n_-) \quad (3)$$

where ε is the solution permittivity. The boundary conditions on the potential at the ideally polarizable electrodes take the form of a prescribed voltage which is externally controlled as a function of time. In the absence of any faradaic reactions at the electrodes, any