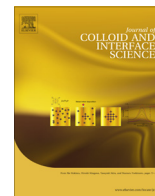




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Use of electrochemical impedance spectroscopy to determine double-layer capacitance in doped nonpolar liquids

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ABSTRACT

Electrochemical impedance spectroscopy in a thin cell (10 μm) was used to infer conductivity, permittivity and the differential double-layer capacitance of solutions of dodecane doped with OLOA 11000 [poly(isobutylene) succinimide] for concentrations of dopant between 0.1% and 10% by weight. All spectra (frequencies between 1 Hz and 100 kHz) were well fit by an equivalent circuit having four elements including a constant-phase element representing the double-layer capacitance. Using Gouy–Chapman theory for small zeta potentials and assuming univalent charge carriers, the double-layer capacitances were converted into charge carrier concentration which was found to be directly proportional to the weight percent of dopant with a 1 wt% solution having 87 carriers/ μm^3 (the concentration of either positive or negative charges). This is only 17 ppm of the total monomer concentration calculated from the average molecule weight of the dopant. Dividing the measured conductivities by the charge carrier concentration, we inferred the mobility and hydrodynamic diameters for the charged micelles. The hydrodynamic diameters of carriers were significantly larger than the average diameter of all micelles measured independently by dynamic light scattering. This suggests that only large micelles become charged.

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1. Introduction

Nonpolar liquids like alkanes are good insulators. Nonetheless the presence of as little as one part-per-billion of certain chemicals can cause electrical effects [1]. For example, in 1954 the pumping of highly refined hydrocarbons led to explosions in refineries, whose cause was found to be sparks produced by very large streaming potentials needed to neutralize small streaming currents arising from trace charges on metal pipe walls [1]. To prevent these explosions, Klinkenberg and van der Minne [1] recommend the addition of a dopant to raise the conductivity to at least 50 pS/m which lowers any streaming potential by orders of magnitude. This extremely low conductivity (distilled de-ionized water has a conductivity 10^5 times higher) can be achieved with the addition of as little as 20 $\mu\text{mol}/\text{m}^3$ of the particular dopant recommended by them.

Dopants are frequently added to oils either to raise the conductivity or to generate charges at interfaces. For example, the OLOA 11000 used in this study is routinely added to motor oil to control soot formation in internal combustion engines [2]. Dopants are also added to dispersions of pigments in oils for use in electrophoretic

display technology [3]. In this second example, the opposite charge on black and white pigment particles plays an essential role by linking the black or white status of any pixel to the polarity of an applied electric field. Many other applications of charges in nonpolar liquids are described in two excellent reviews by Novotny [4] and Morrison [2].

Dopants are usually surfactants, molecules containing a polar headgroup connected to one or more nonpolar tails. For example, the main ingredient in OLOA 11000 is poly(isobutylene) succinimide while Aerosol-OT (AOT) is dioctyl sodium sulfosuccinate. The succinimide headgroup is basic and can accept a proton to become positively charged, while headgroup of NaAOT can dissociate into a sodium ion and the remainder. These reactions are likely involved in the formation of charge carriers or surface charge. However ionic headgroups are not required. For example, Span 85 (sorbitan oleate) is a nonionic surfactant. Yet Behrens et al. [5,6] found that both solution conductivity and solid–liquid charge density increase when Span 85 is added to a nonpolar liquid. With OLOA, the charge carriers are identified as water-swollen micelles of the surfactant which exchange a proton during random collisions [2]. With Span 85, conductivity increases with concentration both above and below the critical micelle concentration. How any monomer or micelle of the surfactant becomes charged has not been established with certainty; charge might simply arise from

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ionic contaminants present in the dopant. Dukhin and Goetz [7] discuss earlier studies of nonionic surfactants which cause significant conductivity in nonpolar media. They explain that nonionic surfactants might sterically stabilize small ions by solvating them. Two important recent reviews on charge formation in nonpolar media include Dukhin and Parlia [8] and Smith and Eastoe [9].

Knowledge about the concentration of charge carriers as a function of the total concentration of surfactant is used to screen potential mechanisms for charge formation. The most commonly measured property is conductivity which depends both of the number of charge carriers as well as their mobility (size). Many past studies of charge formation have relied on dynamic light scattering [10,11] to measure the carrier mobility. Having a value for carrier mobility, measurements of conductivity can be used to infer the concentration of carriers. Unfortunately most of the commercial surfactants are highly polydisperse mixtures which produce a wide range of micelle sizes. Light scattering detects all micelles whereas our earlier results suggest that only the largest micelles are charge carriers [12]. Using the average micelle size (from light scattering) to infer charge carrier concentration from conductivity can lead to significant errors.

In this manuscript, we explore what electrochemical impedance spectroscopy (EIS) reveals about doped nonpolar liquids. In EIS, low-amplitude sinusoidal oscillations in applied voltage difference are applied between electrodes and the resulting sinusoidal oscillations in current are measured for a wide range of frequencies. This procedure avoids large, hard-to-measure “spikes” in current which result when a step-change in voltage is made at the start of potentiostatic experiments used in most past studies [13–15].

Previous studies of nonpolar fluids with EIS inferred the conductivity from the high-frequency portion of the spectra [10,16,17]. Here, we show that the electric permittivity of the solution can also be obtained. The main novelty of this contribution, however, is obtaining the double-layer capacitance from the moderate- to low-frequency portion of the spectra. When the electrode–fluid interface is not significantly charged (in the absence of any applied voltage), the double-layer capacitance is simply related (by the Gouy–Chapman theory) to the Debye length which, in turn is related to ionic strength of the bulk solution. To the extent that the charge carriers can be assumed to be univalent, the ionic strength is equal to the concentration of charge carriers.

At high concentrations of the dopant OLOA, we find that double-layer capacitance can be represented well in the impedance spectrum by a simple electrical capacitor. At low concentrations of the dopant and at low frequencies, however, a simple capacitor does not fit the spectra well. Instead a constant-phase element (CPE) must be used in order to obtain reasonable fit of the spectra. CPE's are commonly used in fitting electrochemical impedance spectra [18,19]. CPE-like behavior arises when the RC time constant is nonuniform over the surface of the electrode.

Debye lengths obtained by fitting the impedance spectra using a CPE are in reasonable agreement with Debye lengths obtained by measuring force-versus-distance with TIRM in a similar doped nonpolar liquid [12]. Having the charge-carrier concentration inferred from Debye lengths, we translated the measured conductivities into a hydrodynamic size for charge carriers. As in our past work [12], this size inferred from conductivity is much larger than the hydrodynamic size inferred from dynamic light scattering. This disparity can be reconciled if only the largest micelles of the dopant are charged.

While the conclusions reached in this EIS study turned out to be similar to those of our previous study [12] (using a potentiostatic method), the systemic variation of frequency allows EIS to probe phenomena having a wide range of characteristic time constants, which would be more convoluted in a potentiostatic experiment. For example, adsorption of the surfactant on the electrodes has been

predicted to change profoundly the shape of the Nyquist plot [20]. While we did not see such behavior with OLOA, when it is applied to other surfactants in the future, we expect that EIS will prove to be an important complement to potentiostatic experiments.

2. Experiment

OLOA 11000 (Chevron Oronite Co) was used as received and mixed with anhydrous dodecane (99 + %, Sigma–Aldrich). The OLOA 11000 is a commercial additive consisting of a substantial fraction of poly(isobutylene succinimide) (PIBS) dispersed in mineral oil. The PIBS had an average molecular weight of 1200 g/mol [21]. The PIBS molecule contains a nonpolar poly(isobutylene) tail connected to a polar succinimide head group [21]. The mixtures were not dried and the humidity was not controlled. All solutions of OLOA 11000 in dodecane were stored in a desiccator when not directly in use. All solutions are reported as weight percent. The hydrodynamic diameter of the reverse micelles was measured by Phase Analysis Light Scattering (PALS) using a Malvern Zetasizer Nano ZSP (Malvern Instruments, Malvern, UK).

A schematic diagram of the thin cell appears in Fig. 1. Pillars, in the form of microscopic particles, separated the electrodes of the cell used in these experiments. Silica particles 8 μm in diameter (Cospheric, Santa Barbara, CA) were added to solutions of OLOA 11000 in dodecane at a particle concentration of 1 mg/mL. The particles established a gap between the cell's electrodes and were assumed to be electrically inert by their dielectric nature and dilute presence. Using a 25 μl gas-tight syringe (Hamilton Co), fifteen microliters of the dodecane containing surfactant and spacer particles was deposited onto a glass microscope slide coated with a 100-nm-thick indium tin oxide (ITO) layer (Sigma–Aldrich). A second ITO coated slide was aligned on top of the fluid to complete the parallel plate polarization cell. Capillary forces held the cell together without the use of adhesives. The fluid filled a distinct area of the ITO surface that varied with each assembly; the area of the fluid layer was measured by image analysis using Image J software (NIH). The gap between the plates was calculated for each cell by dividing the area of the liquid film into the known added volume. Electrical leads were attached to the ITO-coated side of the glass with conductive silver epoxy (MG Chemicals). The cell was shorted until the open-circuit voltage was lower than 10 mV. After each frequency scan the cell was disassembled and the electrodes were rinsed three times with hexane (98 + % Alpha Aesar).

Electrochemical impedance spectroscopy (EIS) frequency sweeps were performed with the fluid cell connected to a potentiostat (Princeton Applied Research VersaSTAT 3). The instrument applied a 10 mV root-mean-squared (RMS) potential across the cell at frequencies decreasing from 100 kHz to 1 Hz collecting 10 points per decade while maintaining a 0 V DC bias. The impedance was calculated at each frequency after a measurement delay time of 0.1 s using a single-sine technique with a frequency analyzer and discrete Fourier transforms. The measured impedance was aver-

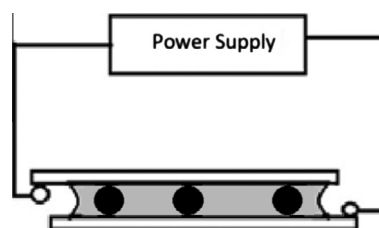


Fig. 1. Schematic of the fluid cell. Two glass microscope slides coated with ITO were separated by 8 μm diameter silica microspheres as spacer particles (black filled circles). Fluid was placed on the bottom slide before the top slide is applied and held together by capillary forces. The slides had dimensions of 2.5 cm by 7.6 cm. The thickness is exaggerated in this drawing.

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