



Conductivity in nonpolar media: Experimental and numerical studies on sodium AOT–hexadecane, lecithin–hexadecane and aluminum(III)-3,5-diisopropyl salicylate–hexadecane systems

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ARTICLE INFO

Article history:

Received 19 April 2012

Accepted 18 July 2012

Available online 1 August 2012

Keywords:

Direct numerical simulation
Finite element analysis
Poisson–Nernst–Planck model
Electrochemical impedance spectroscopy
Degree of dissociation
Reverse micelles

ABSTRACT

The conductivity behavior of doped hydrocarbon systems is studied by applying impedance spectroscopy. In the case of 3,5-diisopropyl salicylate aluminum (III) the charge carriers are formed by dissociation of the compound and their concentration is proportional to the square root of the solute concentration. In hydrocarbon systems that consist of micelle forming compounds (sodium AOT/ lecithin) a linear dependence of charge carrier concentration on solute concentration is observed in the concentration regime where micelles are present.

The conduction mechanisms are studied by numerical solution of a Poisson–Nernst–Planck system that describes the charge transport. We follow two different approaches to extract the degree of micelle dissociation from the impedance data. Firstly, by computing the response of a linear approximation of the Poisson–Nernst–Planck model, and secondly by computing the fully nonlinear response from direct numerical simulations using finite elements. For high and moderate frequencies both approaches agree very well with the experimental data. For small frequencies the response becomes nonlinear and the concept of impedance fails. Furthermore, the numerically computed values for the degree of dissociation are of the same order of magnitude as the values obtained with classical formulas, but still differ by a factor of about 1/3. The direct numerical simulation allows new insight into the conduction mechanisms for different frequency regimes.

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1. Introduction

Several practical applications have been recognized for years where tailoring electrical conductivity of hydrocarbon systems is essential. A detailed understanding of ionic and charge generation in nonaqueous systems is needed to develop successful strategies for stabilizing nonpolar dispersions by tailoring particle particle interactions [1–5]. Frequently, compounds that may enhance hydrocarbon conductivity will influence particle charging. These so-called charge control agents are used as an additive for the dispersion formulation of ink-jet printing and liquid toner systems [6,7]. They are used to stabilize soot particles in engine oils [8,9] or for application in electrophoretic displays [10]. Moreover, such

compounds are indispensable additives in fuels to prevent electrostatic charging during handling.

Although the underlying mechanisms of ionic conduction in aqueous environment are well-known there still is considerable controversy about charge transport and charge generation in nonpolar environment. In pure nonpolar media charge transport due to a hopping mechanism of photo-generated electrons has been reported [11,12]. In the case of doped hydrocarbons charged reverse micelles have been identified to act as charge carriers in nonpolar environment [1,13,4,14]. In this case the generation of charge carriers and charge carrier size will be strongly influenced by the amount of residual water present in the system [15]. For long-chained alkanes experimental conductivity data exist that differ by orders of magnitude. The reasons for these differences in conductivity are obvious: even traces of polar impurities that are dissolved in the hydrocarbon may enhance the conductivity considerably.

Within the experimental section of this article the impedance behavior of a nonpolar solvent doped with charge control agents,

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i.e. the micellar system lecithin (α -phosphatidylcholine)-hexadecane and hexadecane solutions of an aluminum salicylic acid complex compound (3,5-diisopropyl salicylato aluminum (III)) is addressed and compared to data obtained for the well characterized micellar hydrocarbon-sodium AOT system [16,17]. The concentration dependent conductivity behavior of the aforementioned systems is described by simple chemical equilibrium considerations.

Further insights into our experimental results including the spatial distribution of ions are achieved by the formulation and solution of an appropriate model describing the system. For small concentrations we set up a time-dependent version of the Poisson–Nernst–Planck (PNP) model coupled to the Stokes equation. For an introduction to the PNP model we refer to [18–22] and references therein.

Simulations are done for the lecithin–hexadecane system. Within the simulations the impedance calculated is fitted to the measured data of the system to determine the degree of dissociation. The simulations were performed for a linearized time-periodic version of the PNP-system and for the full nonlinear model. A short derivation of the numerical method, including a justification of the algorithms used, is given in the numerical section of this article.

Finally, we show that the values of the degree of dissociation of charged micelles are of the same order of magnitude as the values estimated from simple equilibrium considerations. Differences in impedance behavior of micellar systems (AOT, lecithin) and the aluminum salicylate system are also discussed and the cmc regions of AOT and lecithin in hexadecane system are determined.

2. Experimental

2.1. Instrumental and chemicals used

Impedance analyses of solutions of AOT sodium salt (NaAOT) in hexadecane, 3,5-diisopropyl salicylato aluminum (III) (Al (dips)₃) in hexadecane and lecithin in hexadecane, respectively, have been carried out using the dielectric spectrometer Alpha-Analyzer (Novocontrol) equipped with a ZGS head. Solutions were prepared by dissolving appropriate amounts of AOT sodium salt, Al (dips)₃ or lecithin (Fluka, 99%), respectively, in hexadecane (95%, Alfa Aesar) at room temperature. The water content of the hydrocarbon has been determined to be (67.5 ± 2.8) mg/kg using the coulometric Karl-Fischer titration device 720 KFS Titrino (Metrohm). Unless otherwise stated the chemicals have been used without any further purification. Prior to use the AOT sodium salt (Acros, 96%) has been purified by re-crystallization from methanol (Roth, $\geq 99.5\%$ Ph. Eur.). The solutions were allowed to equilibrate for at least 24 h at room temperature prior to impedance measurements. The solutions have been introduced into a cylindrical sample cell (BDS1307, Novocontrol) connected to the impedance analyzer. Measurements have been performed at temperatures between 20 °C and 70 °C in the frequency range 10^{-4} Hz to 20 MHz (at 1 V (root mean square)) in nitrogen atmosphere. Before performing the measurements the sample cell has been thoroughly flushed with the sample solution and has been equilibrated at the destined temperature for 30 min which was sufficient to attain thermal equilibrium. The temperature has been maintained constant during impedance characterization with an accuracy of 0.1 K by purging with dry nitrogen gas flow of desired temperature using the Quatro Cryosystem (Novocontrol). Impedance data have been evaluated using WinFit software (Novocontrol).

The size of micelles has been determined by dynamic light scattering (DLS) using a Zetasizer Nano-ZS (Malvern Instruments).

2.2. Preparation of aluminum chelate complex

The synthesis of Al (dips)₃ is outlined in detail elsewhere [23]. Briefly, 3,5-diisopropyl salicylic acid (96%, Acros Organics) is

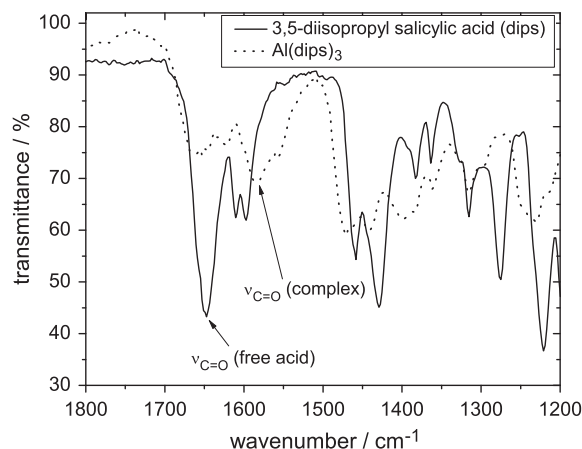


Fig. 1. IR spectra of 3,5-diisopropyl salicylic acid (dips) and the aluminum chelate complex Al (dips)₃.

dissolved in dried methanol ($\geq 99.5\%$ Ph. Eur., Roth) and given to a MeOH solution of an equimolar amount of AlCl₃ (99.99% metal basis, Sigma Aldrich) that contains the threefold molar concentration of sodium methoxide with respect to aluminum. This mixture is allowed to react for 30 min. Then the solvent is withdrawn by a rotary evaporator and the solid residue is dissolved in benzene. The benzene solution is stored in a refrigerator at about 8 °C in order to allow crystallization of formed NaCl. The supernatant is separated by decantation and the solvent again is withdrawn by rotary evaporation at reduced pressure. After recrystallization from diethyl ether, evaporation of this solvent and drying in fine vacuum the aluminum complex is obtained as a powder. The reaction product is readily soluble in hexadecane up to millimolar concentrations.

Formation of the metal chelate compound has been proven by means of IR spectroscopy. IR spectra have been sampled using a Digilab FTS3100 FTIR spectrometer in ATR setup. A shift of $\nu_{C=O}$ of 3,5-diisopropyl salicylic acid from 1655 cm^{-1} (free acid) to 1580 cm^{-1} (chelate) is observed (Fig. 1). This shift to lower wave numbers due to chelate formation between metal ions and salicylic acid derivatives is due to a weakening of the C=O bond [24]. Moreover, the free acid is characterized by spectral bands at 1226 cm^{-1} and 1280 cm^{-1} [25]. These bands are not observed in the case of 3,5-diisopropyl salicylic acid acting as a complex ligand.

3. Results and discussion

3.1. DC conductivity in dependence on solute concentration

3.1.1. DC conductivity of AOT hexadecane solutions

Fig. 2 summarizes the dependence of low frequency conductivity of sodium AOT solutions on concentration determined by impedance analysis at 10^{-2} Hz. The magnitude of low frequency (complex) conductivity shown is mainly governed by the real part of conductivity and thus is a good approximation for DC conductivity.

As can be seen, conductivity σ (Fig. 2) in dependence on solute concentration c cannot be fully explained with well-known theories applicable to aqueous electrolytes. In the case of (complete) dissociation of a binary 1:1-electrolyte in water – which holds for small solute concentrations and small activities – the linear dependence of conductivity on the square root of solute concentration is well-known (Kohlrausch's law). A closer inspection of Fig. 2 reveals, however, that the graph may be divided into three sections: At low solute concentrations up to approximately 10^{-6} mol/kg the dependence of conductivity on concentration may be sufficiently explained by a dependence on the square root of the solute concentration ($\sigma \propto c^{1/2}$). A neutral solute NaAOT

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