

Electrical impedance spectroscopy for determining critical micelle concentration of ionic emulsifiers



Samira Ghasemi^a, Mariam T. Darestani^a, Zohreh Abdollahi^a,
Brian S. Hawkett^b, Vincent G. Gomes^{a,*}

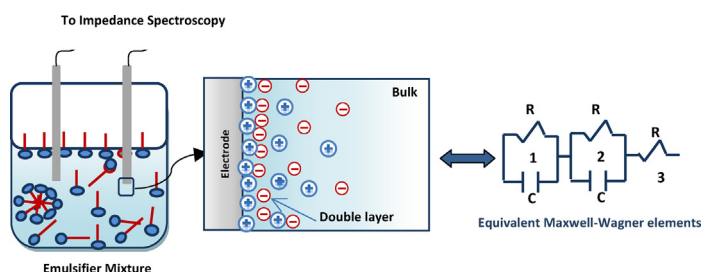
^a School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

^b Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, NSW 2006, Australia

HIGHLIGHTS

- Electrical impedance spectroscopy (EIS) was used to determine CMC of ionic emulsifiers.
- Maxwell–Wagner elements were optimized through least-squares model error minimization.
- EIS was suitable for measuring CMC of high and low conductivity mixtures.
- Both conductance and capacitance parameters from EIS were valid.
- Conventional conductometry was suitable only for low conductivity mixture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 July 2013

Received in revised form 3 September 2013

Accepted 4 September 2013

Available online 16 September 2013

Keywords:

Surfactant

Electrical impedance spectroscopy

Critical micelle concentration ionic

emulsifier

Conductometry

ABSTRACT

Electrical impedance spectroscopy (EIS) was conducted to investigate the micelle formation process for ionic emulsifiers, sodium dodecyl sulfate (SDS) and Aerosol MA80. Electrical impedance values were measured with variable emulsifier concentrations at frequencies ranging from 1 Hz to 100 kHz. The data were analyzed with the help of equivalent circuits to resolve the conductance, capacitance and phase angle parameters as a function of frequency and sample concentration. The EIS parameters were found to exhibit sharp changes due to structured transformations in emulsion and established that critical micelle concentration (CMC) could be determined accurately at specific frequency ranges. We compared the capability and accuracy of measuring the CMC using the EIS impedimetry approach with that of DC conductivity measured using a conductometer for the ionic emulsifiers. We found that conductometry is not able to identify the CMC of Aerosol MA80, while the EIS is able to determine the CMC accurately for both types of emulsifiers.

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1. Introduction

Characterizing the physicochemical properties of surfactants has been a topic of vital interest to scientists and engineers for

years. Surfactants or emulsifiers are surface-active agents that are widely used in a range of industries, spanning from textile, leather, oil recovery, detergents, sub-surface remediation to biomedical applications. Emulsifiers are essential ingredients in a number of manufacturing industries, such as production of polymers via emulsion, suspension and dispersion polymerization processes. In these applications, the surfactant concentration and the colloidal state are crucial in determining the process mechanism and efficiency. On increasing the quantity of an emulsifier to a state of

* Corresponding author. Tel.: +61 293514868; fax: +61 293512854.

E-mail addresses: v.gomes@usyd.edu.au, vincent.gomes@sydney.edu.au (V.G. Gomes).

critical concentration, the emulsifier molecules start associating into aggregates called micelles. This process is known as micellization, and the corresponding concentration, the critical micelle concentration (CMC), is a unique characteristic of an emulsifier [1].

Evaluating the CMC is critical in emulsion polymerization and other similar processes where it plays crucial roles in colloidal stability, binding affinity, nucleation process and reaction kinetics among others. In certain heterophase polymerization processes (e.g., emulsion), micellar nucleation dominates when the emulsifier concentration is kept above the CMC, while below the CMC, homogenous, coagulative and/or droplet nucleation dominate [2,3]. Therefore, controlling the emulsifier concentration is important in such processes for obtaining the desired products. For example, in terms of the final polymer properties, operating above the CMC in emulsion polymerization results in a significant proportion of mono-dispersed particles [3]. Whereas, in applications as encapsulation of fine inorganic powder, operating above the CMC results in a non-uniform encapsulation process [4].

At CMC, several physicochemical properties such as surface tension, turbidity and electrical conductivity of a system undergo substantial change [5–8]. Thus, several techniques have been developed to determine the CMC in colloidal systems, including tensiometry, conductometry (electrical conductivity), osmotic pressure, refractive index, light scattering, spectrofluorometry, ultrasonic absorption, dye solubilization, viscosity and rheological measurement [9–12]. Among these, surface tension using a tensiometer and electrical conductivity with a DC conductometer are the most widely used techniques. A tensiometer is relatively easy to operate and is suitable for various types of surfactants. However, the method is expensive and time consuming. The electrical conductivity method provides simplicity and a rapid and relatively inexpensive measurement; however, DC conductivity is limited by low accuracy and sensitivity, especially with media having relatively high conductivities [13].

An alternative method is the electrical impedance spectroscopy (EIS), which measures the impedance of a medium as a function of variable frequency. EIS is a direct and non-destructive technique to study colloidal systems [14–17]. However, its capabilities remain largely unexplored and its performance in comparison with the electrical conductivity technique for testing colloids is yet to be established. For colloids, researchers have thus far applied the EIS [12,18–22] to investigate the dielectric relaxation properties of ionic surfactants, changes in conductance with concentration and dielectric characteristics of surfactant molecules caused by self-assembly [12,21]. Recently, de Oliveira et al. [7,17,23] investigated changes in electrical resistance as a function of concentration to study aggregate formation with dyes and surfactants.

In this work, we investigated the application of a high resolution EIS to evaluate the CMC of two ionic emulsifiers, Aerosol MA80 and sodium dodecyl sulfate (SDS). These two emulsifiers were chosen because of their vastly different aggregate formation characteristics (mono- versus poly-dispersed) and distinctly different CMC values in water. We tested the EIS to detect the formation of aggregates in the aqueous phase and compared the accuracy and sensitivity of this technique with that of the conductometry method to determine the CMC.

2. Materials and methods

The emulsifiers sodium dodecyl sulfate (SDS) supplied by Sigma–Aldrich and Aerosol MA80 by Cytec were used as received. Mixtures of each emulsifier in deionized water at various levels of concentration were prepared by adding water to pre-weighed amounts of each emulsifier followed by stirring at 300 rpm. The

mixtures were then used for EIS and conductometry measurements.

A high resolution electrical impedance spectrometer (EIS, INP-HAZE, Australia) was used to apply a voltage of 500 mV amplitude between the two electrodes, while the frequency was swept in the range of 1 Hz to 100 kHz. Two BASi gold disk voltammetry electrodes coated with Teflon were used to monitor the emulsifier/water mixtures. The electrodes were dipped 1 cm apart in a closed container having 40 g of the mixture. Gold electrodes were used to eliminate any possible interaction between the emulsifier and the electrode.

Electrical impedance spectroscopy (EIS) involves the measurement of the electrical potential v_0 and the phase shift φ of a system in response to an alternating current of small amplitude i_0 and a known angular frequency ω [24]. The voltage across the sample is v and has the same frequency as the current (i). However, the current and voltage are out of phase by φ .

The impedance (Z) is defined in terms of its magnitude ($|Z| = |v_0/i_0|$) and phase angle (φ), which denotes the phase shift between the AC voltage and the current. The impedance which is usually frequency-dependent can be expressed in terms of the conductance (G) and capacitance (C) as follows:

$$G(\omega) = \frac{1}{(\omega|Z|)} \sin(\varphi) \quad (1)$$

$$C(\omega) = \frac{1}{(\omega|Z|)} \sin(\varphi) \quad (2)$$

Additional information on impedance spectroscopy is given elsewhere [25,26].

The surface of the electrode exposed to the aqueous mixture was fixed (1.6 mm ID) due to the Teflon coating. This coating was helpful in limiting the interaction of emulsifier molecules with electrode material. As part of our investigations, we also tested a set-up with four-terminal EIS arrangement, using two Ag/AgCl electrode for current distribution and two gold electrodes for voltage sensing. However, no significant improvement in detecting micelle formation with accuracy in CMC estimation was observed in comparison with our two terminal arrangements. Therefore, the latter system was used due to its simplicity.

The DC conductivity of each sample was measured using a high precision conductivity meter (Orion Star, Thermo Scientific, USA) in order to compare with the electrical conductivity data from the EIS. All measurements were performed under ambient conditions ($25 \pm 1^\circ\text{C}$). Three measurements were performed for each sample and an arithmetic average of the results was used in our evaluations.

3. Results and discussions

3.1. Electrical impedance spectroscopy

Fig. 1 shows the conductance, capacitance and phase shift for emulsifier/water mixtures as a function of the imposed signal frequency. The concentration of emulsifier in each sample was normalized with respect to the critical micelle concentrations reported for that emulsifier [27–29]. We note that the electrical properties are strong functions of frequency. This is because of signal attenuation by the materials tested in response to the alternating signals.

When an alternating current (AC) is applied to a material, the electromagnetic field inherent to the internal structure of the material generates polarized positive and negative ions. These ions move in accordance with the direction of the electric field. When the direction of the electric field changes, a time delay occurs because of the time it takes to recover the status of the ions. This time delay or relaxation time depends on the frequency and the properties of the material [30]. Accordingly, electrical impedance spectroscopy

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