Orientation and lateral mobility of insoluble Tempo amphiphiles at the air/water interface

Deng Guo Wu [a], Andrew D. Malec [a], Jaroslaw Majewski [b], Marcin Majda [a],*

[a] *Department of Chemistry, University of California, Berkeley, CA 9470-1460, USA*
[b] *Los Alamos Neutron Science Center, H-805, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

Dedicated to Professor Dr. Hab. Zbigniew Galus on the occasion of his 70th birthday and in
recognition of his many contributions to the electrochemical sciences.

Abstract

The lateral diffusion constants of two water insoluble redox surfactants, 4-alkaneamide derivatives of 2,2,6,6-tetramethyl-1-piperidynyloxy radical (C_nTempo where $n = 14$ or 18) were measured using 2D voltammetry with 500 μm long line electrodes positioned in the plane of the air/water interface. In order to extend these measurements into a region of low surface concentrations, we first examined the line micro-band electrodes as well as the stability of the Tempo surfactants on the water surface. Only C_{18}Tempo proved to be sufficiently insoluble in water to form stable monolayer films over sufficiently long periods of time to assure reproducible measurements in the range of mean molecular areas (MMA) of 50–750 Å^2/molecule. In this range, its diffusion constant increases linearly with MMA. At MMA of ca. 450 Å^2/molecule, this dependence becomes significantly weaker suggesting proximity of a plateau region with a D of ca. 1.5×10^{-5} cm^2/s. The orientation of C_{18}Tempo on the water surface in a compressed monolayer at 52 Å^2/molecule was determined by X-ray reflectivity using a synchrotron source. Only the amide group of C_{18}Tempo appears to be immersed in the aqueous subphase while the alkane chain and the piperidine ring are located above the water surface pointing upwards.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Lateral diffusion; 2D voltammetry; C_nTempo

1. Introduction

Lateral mobility of amphiphilic molecules on the water surface is primarily affected by the size and the immersion depth of their polar head groups, and their surface concentration [1,2]. The magnitude of the immersion depth of non-ionic functional groups typically does not exceed 3–4 Å. This is an estimate stemming from the assessment of the size of polar moieties such as hydroxide, amide, or carboxylic acid, as well as from molecular dynamic simulations of single amphiphiles at the water surface such as phenol [3], *p,n*-pentylphenol [4], methanol and ethanol [5] showing that their immersion depth is by and large limited to their polar group. Thus

the immersion depth of surfactants head-groups mentioned above is comparable to the width of the aqueous liquid/vapor interfacial region. Measurements of the lateral mobility of amphiphiles at the air/water interface could, therefore, lead to the determination of the viscoelastic properties of the interfacial region of water.

Aqueous interfaces, and the air/water interface in particular are of considerable importance to chemical, biological and environmental sciences [6–11]. Adsorption, partitioning and retention of molecules at the surface of water droplets serve as an example of many fundamentally important atmospheric processes affecting our life [6–8]. Much structural information concerning the aqueous interfacial region has been gained in recent years by the second harmonic and sum frequency spectroscopies [12–16], by X-ray reflectivity [17,18], and EXAFS [19]. Additional

---

* Corresponding author. Fax: +1 510 642 0269.
 E-mail address: majda@berkeley.edu (M. Majda).

structural details characterizing this interfacial region have emerged from molecular dynamics calculations [20–26]. Yet, new experimental strategies must be developed to deduce dynamic properties of the aqueous interfacial region, which thus far have not been experimentally accessible.

This paper concerns electrochemical investigations of the lateral mobility of the long alkyl chain derivatives of 4-alkaneamide derivatives of 2,2,6,6-tetramethyl-1-piperidynyloxy radical referred to as C_nTempo where $n = 14$ or 18 and indicates the number of carbon atoms in the hydrocarbon chain of the amphiphiles. Preliminary measurements of the lateral mobility of C_{14}Tempo were published earlier [27]. The structure of C_{18}Tempo is shown below:
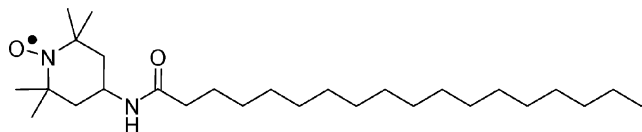
In view of our long-term goal, we intended to test the capabilities of our experimental approach and to expand the measurements of the lateral diffusion constants to as low surface concentrations of these surfactants as possible. The argument that we had in mind suggested that the lateral mobility of surfactants should be less strongly dependent on their surface concentration via dynamics of intermolecular collisions, and thus more directly related to the viscosity of the interfacial water in the region of low surface concentrations. This argument is based on the relationship between the viscosity of colloidal suspensions of particles in a fluid (η^*), the viscosity of the pure fluid (η), and the volume fraction of the particles in the fluid (α). The relationship was first formulated by Einstein [28,29]:

$$\eta^* = \eta(1 + 2.5\alpha) \tag{1}$$

It applies for $\alpha \leq 0.02$. In other words, the lateral mobility of surfactants can be meaningfully interpreted in terms of the viscosity of the interfacial water only in the limit of small surface concentrations. The experiments described in this report were aimed to explore that limit.

C_{18}Tempo and its tetradecane analogue were selected for two reasons. First, their long alkane chains promised water insolubility, a hypothesis, which in the course of these studies proved to be correct only in the case of the octadecane derivative. The surface concentration of the insoluble surfactants can be easily controlled by spreading a known quantity of a surfactant (as a chloroform solution) on the water surface in a Langmuir trough [30–32]. The second, more important reason to work with C_nTempo amphiphiles is the fact that their monolayer films are 2D supercritical fluids at room temperature [27,33]. We showed earlier that all Tempo derivatives with the number of the carbon atoms in the chain less than 22 have their critical temperatures (T_c^I) below room temperature [33]. For C_{20}Tempo, we measured T_c^I to be $28 \pm 1\,^\circ$C. For all shorter chain Tempo derivatives, the critical temperature of the liquid/gas (L/G) phase transition is below $0\,^\circ$C [33].

The discovery of the supercritical fluidity of C_{18}Tempo and other shorter chain derivatives was of great importance to our investigations of the lateral mobility of these surfactants because the micro-electrodes used at the air/water interface in these measurements behave as nucleating sites of a surfactant 2D gas phase [27,33]. This phenomenon prevented us from doing electrochemical measurements on the water surface beyond the L/G phase transition. The position of the latter is typically at less than 100 Å^2/molecule.

This report presents the lateral diffusion constant measurements extending to ca. 800 Å^2/molecule. We discuss potential instrumental limitations of these measurements. We also report a set of X-ray reflectivity data that enabled us to obtain a preliminary assessment of the orientation of C_{18}Tempo on the water surface. We conclude by discussing the significance of these measurements in view of our long-term goal of assessing interfacial water viscosity.

2. Experimental section

2.1. Materials

The purity of all chemicals and solvents is of utmost importance as it determines the magnitude and the reproducibility of the 2D voltammetric current data. 4-Tetradecaneamido-2,2,6,6-tetramethyl-1-piperidynyloxy (C_{14}Tempo) and its octadecane analog, C_{18}Tempo were synthesized according to a literature procedure as described previously [27,33]. The purification of the final products involved several silica gel column chromatographic runs with 20:1 *n*-hexane/ethyl acetate and 9:1 methylene chloride/methanol solvent mixtures. The purity of the compounds was verified by mass spectrometry and elemental analysis. The results of the latter were: C_{18}Tempo—calculated: C 74.1, H 12.2, N 6.4; found: C 74.08, H 12.21, N 6.41. C_{14}Tempo—calculated: C 72.4, H 11.9, N 7.3; found: C 72.22, H 11.89, N 7.18. Octadecyltrichlorosilane (OTS) and 3-mercaptopropyltrimethoxysilane (MPS) were from Aldrich. OTS was vacuum-distilled into glass ampules which were sealed immediately afterwards. They were opened as needed immediately prior to the individual experiments. Octadecylmercaptan (OM) (Tokyo Kadei, Tokyo, Japan) was used without further purification. Reagent-grade 70% HClO$_4$ (Fisher, ACS-certified), LiClO$_4$ (99.99%, Aldrich). House-distilled H$_2$O was passed through a four-cartridge Millipore purification train, and a 0.2 μm hollow-fiber final filter. The resistivity of the resulting water (DI water) was 18.3 MΩ cm. To further decrease the level of surface active impurities, DI water was distilled from KMnO$_4$, KOH solution.

2.2. Fabrication of the line electrodes

2D electrochemical measurements at the air/water interface required "line" micro-electrodes, which are held just