



Electrochemical characterization of viscoelastic solutions of supramolecular polymers in phosphonium-based ionic liquids



K. Aoudia^a, N. Brinis^a, L. Chaal^a, B. Saidani^a, L. Benyahia^b, C. Chassenieux^b, C. Deslouis^{c,d,*}

^a Laboratoire d'Electrochimie, Corrosion et de Valorisation Energétique (LECVE), Faculté de Technologie, Université A. MIRA, Bejaia 06000, Algeria

^b LUNAM, Université du Maine, IMMM UMR CNRS 6283, département PCI, 1 Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

^c Sorbonne Universités, UPMC Univ Paris 06, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), 4 place Jussieu, 75252 Paris Cedex 05, France

^d CNRS, UMR 8235, LISE, Case 133, 4 place Jussieu, 75252 Paris Cedex 05, France

ARTICLE INFO

Article history:

Received 10 July 2014

Received in revised form 12 February 2015

Accepted 13 February 2015

Available online 21 February 2015

Keywords:

Bis-urea

Toluene

Ionic liquid

EIS

Rate constant

Rheology

ABSTRACT

We have combined electrochemical, rheological and light scattering measurements to investigate the viscoelastic character of solutions of (2,4-bis (2-ethylhexylureido) toluene) (EHUT) in toluene in the presence of two ionic liquids: (triethyl(tetradecyl) phosphonium hexafluorophosphate “Cyphos 110”) and (tris(pentafluoroethyl) trifluorophosphate “aph4-cph12”) used to substantially increase the solution conductivity required for the electrochemical study.

The heterogeneous rate constant k_o of the Fc/Fc^+ redox couple, the diffusivity (D_{Fc}), and the equivalent capacitance values of the double layer were measured in the presence and in the absence of EHUT. For Cyphos 110, the viscosity of solutions increases in the presence of EHUT, but the diffusion current exhibited no fluctuations. By opposition, for aph4-cph12, strong fluctuations of the diffusion current allowed to assign a viscoelastic character to the solutions when EHUT is added.

Rheological and light scattering measurements revealed that the two ionic liquids act as chain stoppers for EHUT supramolecular chains. However, aph4-cph12 maintains the viscoelastic character of the EHUT solution whereas Cyphos 110 destroys the supramolecular structure.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Supramolecular polymers are aggregates of small molecules which self-associate in solvent through non-covalent bonds. It was recently emphasized that they can be used in a variety of applications [1,2] and that for a given chemical structure of their monomer, their self assembled structures depend strongly on various parameters such as temperature, solvent and concentration [3]. In particular, it has been mentioned that such self assembled structures may feature a viscoelastic character at low concentration in apolar organic solvent [4–6]. Like wormlike micelles do in aqueous media [7,8], bis-urea based low molar mass compound namely EHUT (2,4-bis (2-ethylhexylureido) toluene) has been reported to self-assemble in nonpolar solvents into two distinct supramolecular structures, i.e. either a long hydrogen-bonded filament, or thicker and more rigid tubes depending on the experimental parameters (temperature and concentration) [6]. Moreover,

hydrodynamic drag reduction (DR) in a Couette cell was observed for EHUT in octane and in toluene, allowing thereby highlighting this system as the first self-assembled drag reducer for hydrocarbon solvents [2]. As well as surfactants, which may achieve high drag reduction amounts in water [9,10], one can expect that supramolecular polymers are liable to repair themselves after mechanical degradation due to the reversible character of their self-association process. This is a decisive advantage over linear polymers which are irreversibly broken after their drag reducing action.

The occurrence of drag reduction in both polymer and surfactant solutions has often been associated to viscoelastic properties such as the existence of a first normal stresses difference. These drag reducing solutions in turbulent flow display correlatively anomalous effects in laminar flows (e.g. Weissenberg effect, anomalous pressure drop/flow rate behavior, entrance flows) as shown for polymer solutions [11–14] and their drag reducing ability can therefore be studied in well-defined laminar flows.

It has been reported that by using electrochemical methods in polymer or surfactant aqueous solutions, the mass transfer measured towards a rotating disk electrode in laminar flow exhibits a first order transition [15,16] for a critical value of the angular

* Corresponding author at: Sorbonne Universités, UPMC Univ Paris 06, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), 4 place Jussieu, 75252 Paris Cedex 05, France. Tel.: +33 1 44 27 41 49; fax: +33 1 44 27 40 74.

E-mail address: claudio.deslouis@upmc.fr (C. Deslouis).

velocity of the disk. This transition is marked by a significant drop of the mass transfer rate which turns unsteady and is characterized by an hysteresis cycle. This behavior was caused by the elongational strain existing at the outer limit of the hydrodynamic boundary layer and was considered as a signature of the viscoelastic character of the fluid [16–18]. The transition was also accompanied by flow birefringence in the hydrodynamic boundary layer attesting the presence of elongated objects (stretched polymer chains [19] or disentangled threadlike micelles).

The main motivation for the present work was to carry out an electrochemical mass transport study with a rotating disk electrode in laminar flow for a supramolecular polymer in toluene to see if it displays the same features as those depicted previously for polymers and surfactants in aqueous solution. A particular interest of proving then the viscoelastic properties as a major indication of the drag reducing ability of such solutions is to limit direct tests in turbulent flows which imply large volumes and high flow velocities.

However, due to the weak or non polar character of such a solvent, electrochemical measurements are difficult to carry out due to low conductivity.

To overcome this difficulty and referring to a previous work [20], we have used ionic liquids for increasing the solution conductivity. Indeed, room temperature ionic liquids have recently gained increasing interest for electrochemical applications [21,22], due to their unique chemical and physical properties, including negligible vapor pressure, high chemical and thermal stability, and also a large electrochemical potential window [23–25]. Room temperature ionic liquids when their cations and anions are properly chosen should then afford a good conductivity and can be used as supporting electrolytes in organic solvents [26]. It has been shown that room temperature ionic liquids based on two bulky ions: a phosphonium cation and a fluorophosphate anion allowed an electrochemical kinetic study with a rotating disk electrode when dissolved in toluene taking ferrocene/ferrocenium (Fc/Fc^+) as redox couple [20,27,28]. Obviously such a study is quite impossible with solid ionic salts as supporting electrolytes.

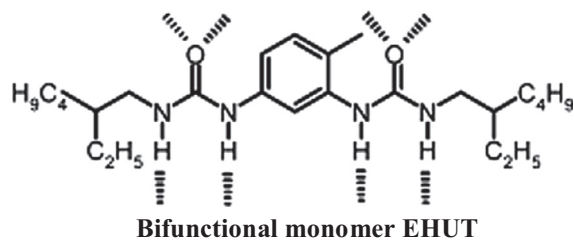
In this work, we investigated the influence of a bis urea compound (EHUT) on mass transport of ferrocene in toluene to a rotating disk electrode in the presence of two ionic liquids based on a common cation, namely trihexyl(tetradecyl)phosphonium and two different anions: hexafluorophosphate (further named “Cyphos 110”) and tris(pentafluoroethyl) trifluorophosphate (further named “aph4-cph12”). In parallel, the effect of the concentration of ionic liquids on the rheological and structural properties of the solutions was measured. It will be shown that the effect of the anion of the ionic liquids can be deleterious to the supramolecular structure since they act as so-called chain stoppers.

Both voltammetric response for the ferrocene oxidation and Electrochemical Impedance Spectroscopy (EIS) were analyzed. Therefore, a second objective of the work was to determine the heterogeneous rate constant k_0 of the ferrocene/ferrocenium (Fc/Fc^+) redox couple and the diffusivity (D_{Fc}) in a toluene/Cyphos 110 and in toluene/Cyphos 110/EHUT so as to complete the relevant values already obtained for those quantities in the presence of aph4-cph12 [20].

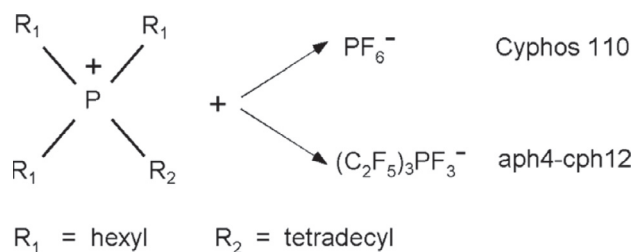
2. Experimental section

2.1. Materials

EHUT (2, 4-bis (2-ethylhexylureido) toluene) was synthesized by reacting racemic 2-ethylhexylamine with 2,4-toluene diisocyanate. Details of the synthesis and purification of EHUT have been reported else-where [3,29].



Toluene (>99%) was purchased from VWR and was used as a solvent for the sample preparation without further purification. Ferrocene (Fc) was obtained from Sigma Aldrich (98% purity) and used at 0.2, 0.5 and 1 mM. Cyphos 110 and aph4-cph12 were purchased from Strem Chemicals and Merck respectively. Due to the low conductivity of the solutions, the electrochemical measurements were impossible at concentrations below 0.075 M in Cyphos 110 and could be extended down to 0.03 M in aph4-cph12.



Cyphos 110 & aph4-cph12

Samples were prepared by dissolving EHUT in toluene at 10 g L^{-1} with 1 mM of ferrocene by stirring over night at 50°C . The same procedure also held for EHUT/Cyphos 110 and EHUT/aph4-cph12 mixtures in order to reach stationary state. Fig. 1 shows the aspect of EHUT/Cyphos 110 mixtures for two different temperatures. Above 35°C the solutions were homogenous and transparent; below 35°C they displayed phase separation and turned turbid and heterogeneous. All experiments were therefore carried out at 35°C .

2.2. Methods

2.2.1. Rheology

Measurements were performed with a stress-controlled rheometer, ARG2 from TA Instruments equipped with a cone-plate geometry (angle = 1° , diameter = 60 mm) or plate-plate (diameter = 40 mm) depending on the viscosity of the sample. The temperature was controlled with a Peltier system. The samples were protected by a solvent trap to prevent evaporation.

Steady-state shear stress was measured as function of the applied shear rate ranging from 10^{-2} to 10^3 s^{-1} .

2.2.2. Light scattering

Light scattering measurements were done using an ALV-CGS3 system operating with a vertically polarized laser (wavelength $\lambda = 632 \text{ nm}$) at various scattering angles θ between 70° and 150° , corresponding to scattering vectors $q = 4\pi n/\lambda \sin(\theta/2)$ ranging from 0.017 to 0.029 $1/\text{nm}$ with n the refractive index of the solvent. The duration of the experiments was set to 6 minutes per angle in order achieving a good signal-to-noise ratio for correlation functions.

Download English Version:

<https://daneshyari.com/en/article/218399>

Download Persian Version:

<https://daneshyari.com/article/218399>

[Daneshyari.com](https://daneshyari.com)