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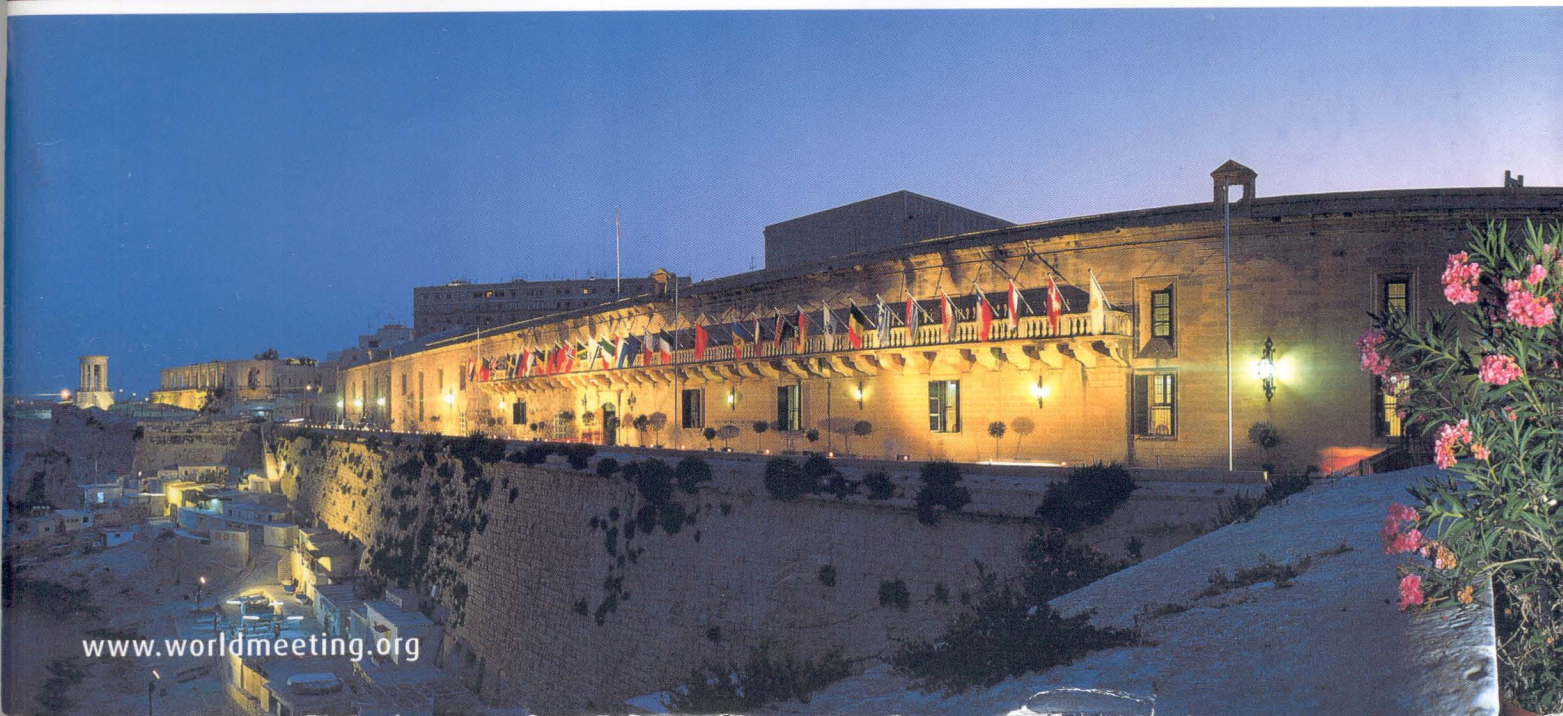
Valletta



8th to 11th March 2010

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HIGH RESOLUTION ULTRASONIC SPECTROSCOPY IN THE ANALYSIS OF POLOXAMERS BEHAVIOUR

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INTRODUCTION

Poloxamers are triblock copolymers of poly (ethylene oxide) (PEO) and poly (propylene oxide) (PPO) available in different molecular weights and PPO/PEO ratios. The presence of PEO and PPO blocks in a single polymer chain gives rise to essentially amphiphilic molecules whose self-assembling properties display a wide range of phase behaviour. This ability to form micelles is strongly temperature and concentration dependent [1]. The aggregation and the structural characteristics of micelles have been investigated with the aid of different techniques, such as static and dynamic light scattering (DLS), small angle neutron scattering (SANS) [2], TEM, laser doppler anemometry [3] and (NMR) [4]. However, due to the complexity of these methodologies, a more general characterization of poloxamer systems, (as the CMC and the CMT determination), is performed using more common and widespread techniques such as UV spectroscopy, light scattering [5, 6] and differential scanning calorimetry (DSC) [2, 7].

The aim of this paper was to assess the potential of low-intensity ultrasound spectroscopy (with power levels lower than $1\text{W}/\text{cm}^2$) as a valid tool for general characterization of the micellization process in a wide range of experimental conditions (temperature and polymer concentrations).

EXPERIMENTAL METHODS

Materials

Poloxamer 407 (Lutrol F127, Acef, Italy) and Deionised water (produced by Osmo Lab UPW 2Gamma 3, Italy)

Samples preparation

Poloxamer samples in the concentration range of 5%-30% w/w were prepared by simple dispersion of the materials in the required amount of water using the "cold" procedure.

Samples were then stored at 4°C for at least 24h before being analysed.

Ultrasonic measurements

Ultrasonic parameters (ultrasonic velocity and attenuation) were measured using an HR-US 102 high resolution spectrometer (Ultrasonic Scientific, Ireland) fitted with two 1 ml ultrasonic cells, one filled with water as reference and the other with the different Poloxamer 407 samples at the selected frequency of 5.2 MHz. Temperature control was achieved with a HAAKE C25P water bath. Samples were analysed from 1° to 35°C at $0.25^\circ\text{C}/\text{min}$. Measurements were performed in triplicate without stirring. Ultrasonic parameters will be reported as relative parameters, obtained by subtracting the contribution of the pure solvent from the total attenuation or sound speed ($\Delta U = U_{\text{sample}} - U_{\text{solvent}}$)

RESULT AND DISCUSSION

Ultrasonic spectroscopy is based on the measurement of sound speed (U) and ultrasonic attenuation (N). When a sound wave travels through a system, it loses part of its energy, depending on the structure of the system itself. Sound speed is directly related to the high frequency elasticity of the medium and is extremely sensitive to the intermolecular interaction and sample composition, while sound attenuation reflects the energy loss due

to scattering and absorption phenomena typical of heterogeneous samples. Relevant changes in both these parameters suggest structural modifications in the system.

The ΔU for each poloxamer concentration is reported in figure 1-A. Data can be interpreted according to Laplace equation, which state that U is inversely proportional to system adiabatic compressibility (β_s). As expected, the values rise as the polymer's concentration increases, as a consequence of the lower amount of free water in the samples (bound water can be considered incompressible if compared to free water). Furthermore, this approach is also able to explain the shape of the obtained curves, characterized by three different regions, a linear initial and a final zones, linked by a nonlinear middle part. A linear trend of the sound speed is usually due to the effect of the temperature on the whole system, while an abrupt deviation depends on a modification in the amount of water interacting with the polymer.

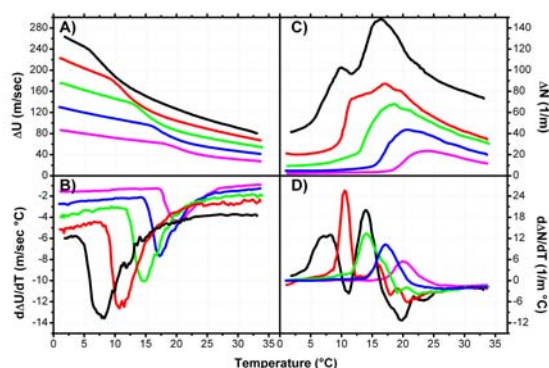


Figure 1: Effect of temperature on the A) ΔU ; B) First derivate of ΔU ; C) ΔN ; D) First derivate of ΔN , for all the analysed samples (— 30%, — 25%, — 20%, — 15%, — 10%).

Thus, the curve shape suggests the presence of a desolvation process that can be associated with a transition from unimers to micelles. The use of the first derivate (figure 1-B) permits an easier analysis of the transition, allowing the detection of its characteristic temperatures onset, peak and endset.

Sound attenuation is a more complex phenomenon, since it depends from several mechanisms.

Generally speaking, any variation of the size or thermal and viscous properties of any dispersed material modifies the total recorded attenuation. For all the analysed samples (Figure 1-C), the attenuation rose when the unimers started to aggregate, as a consequence of the increase of sample heterogeneity, due to the presence of different entities (unimers, micelles and water molecules) with different characteristics. The 30% and, in a less evident way, the 25% systems showed a second peak at higher temperatures that could be attributed to the gelation process. Also in this case the first derivate (figure 1-D) appeared to be a more powerful method for characterizing the transitions; in fact, the gel transition is also detectable for the 20% sample.

CONCLUSIONS

High resolution ultrasound spectroscopy was used to study the micellization process of a well known self assembling polymer, Poloxamer 407. Both the ultrasound parameters (sound speed and sound attenuation) resulted able to follow the micellization process. Sound speed values seem to be very effective for the analysis of the aggregation-deaggregation process, failing the detection of the gelation process. From the other side, sound attenuation data resulted able to identify both transitions, micellization and gelation. The use of first derivate appear the most powerful and sensitive way to present ultrasonic parameters.

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