RELAZIONE DI FINE PROGRAMMA DI RICERCA STM - PIETRO CALANDRA (CNR-ISMN)

Title of the program

Dynamical studies on surfactant based liquid mixtures to highlight their emerging properties

Choice of the partner: The Short Term Mobility Program has been carried out at The Department of Physics, Section Experimental Physics III, of the TU Dortmund University (Fakultät Physik, Experimentelle Physik III – Technische Universität Dortmund, in Dortmund (Germany).
This choice has been dictated by the fact that this Physics Department is well equipped with state-of-the-art facilities to carry out structural and dynamic studies on soft matter, which is the kind of matter studied in Dr. Calandra's activities. In particular, with Prof. Dr. R. Böhmer, who is specialized in the investigation of soft-matter systems by methods such as broadband dielectric spectroscopy and high-resolution rheology, a study of high-resolution viscosity has been carried out. The program has been carried out in the period 23/06/2016 – 13/07/2016

Choice of the systems

Surfactants are widely used in many fields like detergency, emulsification, lubrication, nanoparticle synthesis etc. and have become promising molecules for uses in nanotechnology since they mimic bio-molecules in complex biological systems.

However, up to date, surfactants have been generally dissolved as solute in a suitable solvent; instead, an innovative approach I have recently developed at CNR-ISMN, involves the use of PURE liquid surfactants (with no solvent) in place of their solutions. The absence of any solvent maximizes the surfactant concentration therefore the merits of the system, deriving from the presence of the surfactant, are obviously driven to their extreme. The main objective of the proposed STM research activity is to shed light on the molecular dynamics by gaining high-resolution viscosity information in mixtures of opportunely chosen surfactants.

Objectives

The main goal of the project is to shed light on the molecular dynamics in surfactant liquid mixtures. In details the objectives of the proposed research are:

a) to gain dynamical information by viscosity measurements

b) to rationalize the results in order to explain the bulk properties in terms of dynamical processes at the molecular base.

Activity: Opportunely chosen alkylamines / alkylphosphates (specifically *n*-propyl amine (PA) / dibutyl phosphate (DBP) and isopropyl amine (IS) / dibutyl phosphate(DBP)) liquid mixtures have been prepared at seven different compositions. For each mixture the emerging properties have been evaluated by the activity reported below:

a) measure of the viscosity by rotating plate as a function of the sheer rate and composition. For each sample a study at different sheer rates has been carried out to extrapolate the zero-sheer viscosity;

b) The study of item a) has been carried out at different temperatures around the Room Temperature (RT), Specifically the temperature explored have been: 10, 15, 20, 25 °C to derive the apparent activation energy at RT;

c) Try to explore the mechanical properties by high-resolution frequency-dependent viscosimetry: the complex viscosity (both real and imaginary parts) have been measured as a function of temperature;

d) derivation of the emerging properties: the deviation of the experimental data from the ideal behavior has been shown to point out the properties emerging when the two amphililes are mixed, allowing interesting theoretical clues to be highlighted.

Results

a) The viscosity at zero sheer rate at room temperature is shown in Fig. 1 as a function of X (X= n-propilamine or iso-propilamine molar ratio). As it can be seen a maximum at the 1:1 composition (X=0.5) takes place. This can be taken as a first clue for DBP-PA or DBP-IS direct interaction with formation of local structures whose DBP-PA or DBP-IS adducts are the building blocks.

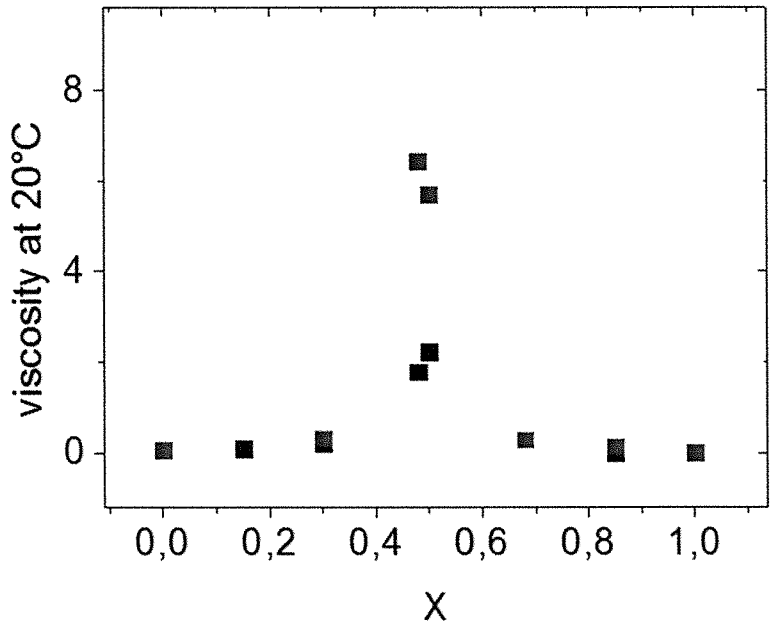

Fig. 1: viscosity at zero sheer rate at room temperature for DBP-PA mixtures (black points) and DBP-IS ones (red points)

b) The apparent activation energy around room temperature is shown in Fig. 2 as a function of X. The Graph also shows the pre-exponential factor (lower panel). As it can be seen a maximum at X=0.5 takes place in the activation energy, whereas a minimum in the pre-exponential factor is observed. This is in accordance with the trend of the viscosity as a function of composition and confirms a change of the local structure of the system.

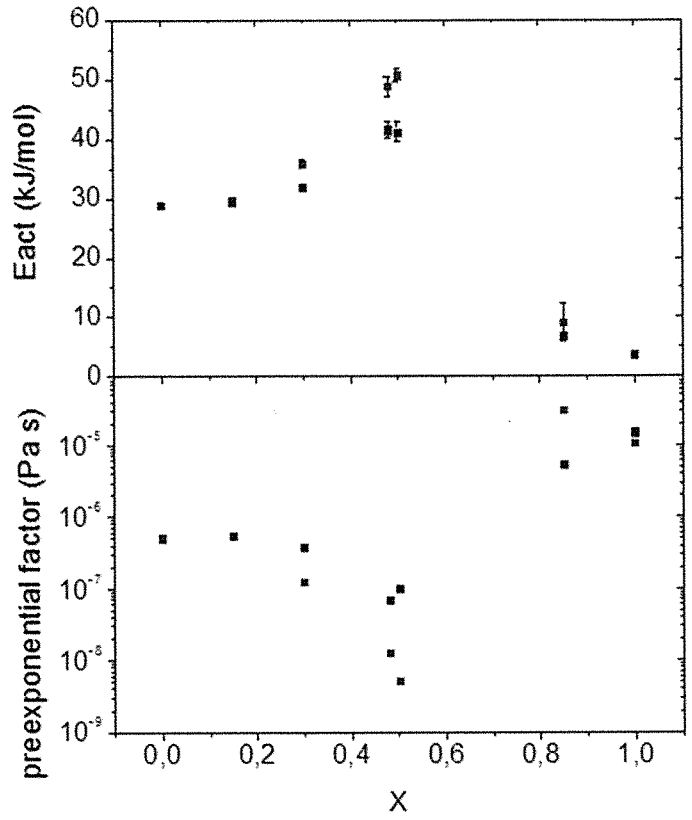

Fig. 2: Results of the Arrhenius analysis for DBP-PA mixtures (black points) and DBP-IS ones (red points)

c) the complex viscosity (both real and imaginary parts) measured by high-resolution frequency-dependent viscosimetry has been explored for the pure components and for the representative mixtures DBP-PA at X=0.5, the composition which showed the most enhanced viscosity as a function of temperature, down to their glass-rubber transition temperature (Tg). Pure amines crystallize so it was not possible to explore their behavior close to Tg. The results, compared to the room-temperature viscosities are reported in Fig. 3

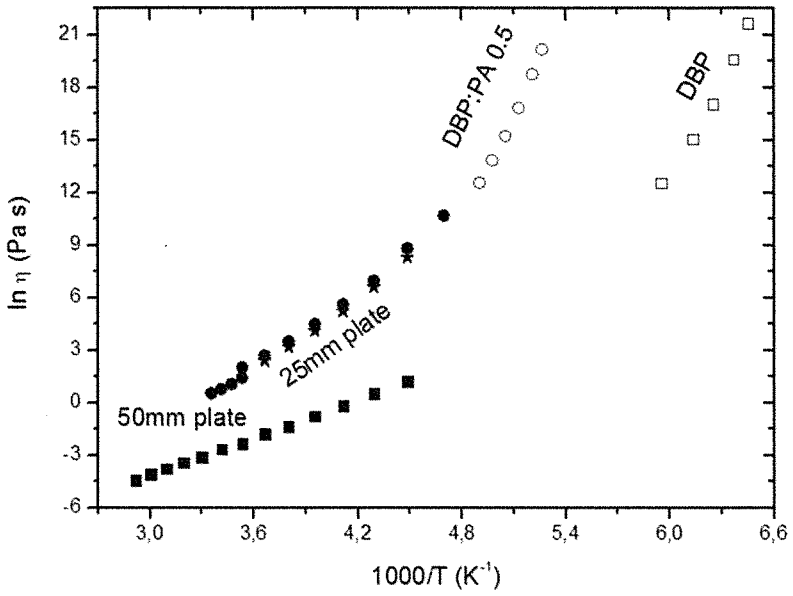

Fig. 3: Results of the investigation of the viscosity at lower temperatures, down to Tg, for the DBP and DBP-PA at X=0.5 mixture, chosen as representative, as compared to the corresponding results at higher temperatures.

d) The systems showed emerging properties especially at X=0.5 due to the H-bond formation which triggers the formation of DBP-PA or DBP-IS adducts. Due to the moderate heating observed in the mixing of DBP and PA (or IS) during the system preparation, it can be argued that an acid-base reaction can take place. This finding suggests that such systems are good candidates for proton-conductive anhydrous material to be used for specialized applications as liquid membranes for fuel cells.

Additional value of the short term mobility

The STM and the collaboration with Prof. Böhmer and Dr. Catalin Gainaru, allowed the acquisition of relevant know-how on the necessary methodologies for the derivation of dynamical information from high-resolution viscosity measurements. Thanks to the availability of many instrumental accessories, the effect of temperature down to the Tg has also been estimated.

Monterotondo 21/07/2016

Firma del Fruitore