ORIGINAL ARTICLE

Interfacial rheology as a tool to study the potential of cyclodextrin polymers to stabilize oil–water interfaces

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Abstract The aim of this work is to characterize rheologically the interfacial properties of oil/water interfaces stabilized with β-cyclodextrin (CD)-based inclusion complexes. Interfacial experiments were conducted using two different hydrophobic oils: Parsol MCX and Squalene. Dilatational interfacial rheology was performed with a dynamic drop tensiometer, allowing the determination of the interfacial tension from the drop profile, and the calculation of rheological values (phase angle, elastic and viscous moduli) from the correlation between the drop area and the interfacial tension sinusoidal variations. Practically, an oil drop was formed in the aqueous phase containing the CD-derivative. With Parsol MCX, no correlation was observed, indicating that surfactants were not adsorbed at the interface. With Squalene, two β-CD-derivatives were used: monomers and polymers. With monomers, a solid membrane was created, impeding any rheological measurements. This is consistent with the crystallization of the system and the impossibility to formulate an emulsion with monomers. With polymers, an effective correlation of the drop area with the interfacial tension variation demonstrated the adsorption of the CD-complex at the interface. Rheological values clearly indicated the formation of an elastic interface, preventing droplets coalescence: an emulsion formulated with β-CD polymers results in a better stabilization.

Keywords Cyclodextrin · Squalene · Parsol MCX · Emulsion · Dilatational interfacial rheology · Drop tensiometer

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Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides able to form inclusion complexes with numerous organic molecules. The physicochemical properties of the guest molecules can be dramatically modified due to complex formation, resulting in several possible advantages, such as: (i) the increase of the apparent solubility of the invited molecule in water; (ii) the increase of the stability of the complexed molecule against light or oxygen; (iii) the reduction of vapor pressure; (iv) the reduction of bad taste or smell; (v) in the case of drugs, an increased bioavailability.

In particular, many oily compounds are advantageously used in combination with CDs to facilitate their solubilisation, avoid their degradation, reduce their evaporation or obtain a long lasting action [1]. When using CD monomers, the stability against light and oxygen of tea tree oil increases [2], and the unpleasant odours of chamomile extracts or oil are reduced [3].

More generally, CDs form inclusion complexes with a variety of vegetable, mineral or synthetic oils [2, 4–8]. In most cases, complexes have a crystalline structure and precipitate [4–6, 8]. For example, soybean oil [4], oleic acid and several essential oils [6] form crystalline inclusion complexes with both α- and β-CD. CD molecules are threaded onto a long oil or polymeric "axle" forming "necklace-type" inclusion structures of crystalline nature [9–11]. "Molecular tubes" can also be prepared when CD rings in the molecular neckless are interconnected by epichlorohydrin in an alkaline solution [12].

In a simple three component system of paraffin oil, water and β-CD, stable emulsions are formed [7]. Besides, CDs stabilize multiple emulsions by complex formation with oils [13], and this property is further used to prepare

beads of around 1.6 mm, by a straightforward technique starting from a mixture of α-CD aqueous solution and soybean oil, without the use of any organic solvent or surface-active agent [4].

Contrarily to CDs, CDs polymers efficiently stabilize oil-in-water emulsions without forming crystalline inclusion complexes with the oils [14]. Our aim here is to compare the ability of β-CD monomers and polymers to stabilize the oil/water interface. For this, we have used two hydrophobic oils, Parsol MCX and Squalene. Parsol MCX is one of the most tested and most widely used UV-B filters, whereas Squalene is one of the main components of sebum (10–15%) [15]. Without this compound, the skin becomes rough, dry and vulnerable. Both oils (Parsol MCX and Squalene) are insoluble in water, which hinders their applications, mainly in the cosmetic field.

Emulsion formation and stability were assessed by using interfacial rheology, i.e. by probing the interfacial and mechanical deformation and flow of the oil/water interface.

Experimental section

Materials

Squalene and Parsol MCX were purchased from Sigma-Aldrich (BP701, Saint-Quentin-Fallavier, France) and Cooper (Melun, France) respectively. Squalene density is 0.855 g/cm^3, and Parsol MCX density is 0.985 g/cm^3. The poly-β-CD polymer (poly-β-CD) was prepared by polycondensation of β-CD with epichlorhydrin under alkaline conditions [16]. Epichlorhydrin as a crosslinker leads to the formation of water-soluble high molar mass polymers, contrary to other crosslinkers. These observations have been reported previously [16]. The poly-β-CD average molecular weight M_w was 10^5 g/mol and the polydispersity was 1.5, according to size exclusion chromatography. Such a small value of the polydispersity allows to consider the polymer as a model and homogeneous system. The CD weight content in the poly-β-CD polymer was 70% according to the ^{1}H NMR spectra as previously described [16]. The aqueous phase contained β-CD at 150 mg/mL for experiments with Parsol MCX, and β-CD at 100 mg/mL for experiments with Squalene. Pure water obtained from a Millipore Super-Q unit was used in this study.

Methods

Dynamic interfacial and mechanical properties were investigated using a dynamic drop tensiometer (IT Concept/Teclis, France).

The interfacial tension and membrane structure is investigated from a drop profile. In our study, a millimetric rising oil droplet (Parsol MCX or Squalene) of approximately 20 μL is delivered from a needle (gauge 14, i.e. inner diameter: 1.60 mm) into an optical glass cuvette filled with 10 cm^3 of the aqueous phase with the poly-β-CD polymer or monomer (the drop is rising since the oil density is lower than the density of the aqueous phase). Temperature is controlled at 20 °C.

Before any measurements, a drop is expelled from the needle, and the measurement is performed on a new drop (formed within a few seconds). More details about these techniques are given by Benjamins et al. [17].

The interfacial tension was determined from the drop profile and analyzed using a CCD camera connected to a computer. The drop profile results from a competition between gravity and capillary forces: the gravity forces tend to elongate the drop profile, whereas the capillary forces (which depend on the interfacial tension γ) tend to round the drop profile. If the drop profile fits the theoretical Laplace equation (which is related to capillarity), then drop is said to be Laplacian, and the interfacial tension can be processed from a numerical procedure.

The mechanical (viscoelastic) properties are measured from the sinusoidal variation of the interfacial tension following a sinusoidal drop area variation. The absolute complex modulus $|E|$ is calculated from the interfacial tension variation $\Delta\gamma$, which results from the drop area variation ΔA; the equation relating both values is: $\Delta\gamma = |E| \Delta A/A$. The elastic modulus E' and the viscous modulus E'' are given from the absolute complex modulus $|E|$ and from the phase angle (or loss angle) φ between the interfacial variation and the area variation: $E' = |E| \cos\varphi$, and $E'' = |E| \sin\varphi$. These equations are analogous to the viscoelastic equations leading to the elastic modulus G' and the viscous modulus G'' in bulk rheology. However, it should be noted that in interfacial rheology, Pa.m (or N m^{-1}) is the unit for the moduli (while in bulk rheology, Pa is the unit for the moduli). The sinusoidal frequency of the area variation was 0.1 Hz. The amplitude of the volume variation, in the linear regime of excitation, was 10%.

Results and discussion

The formation and the stability of an interface rely on the presence of surfactants on this very interface. Indeed, surfactants lower the interfacial tension, facilitating the formation of droplets. Moreover, surfactants generate an elastic oil/water interface, which prevents coalescence, and consequently are likely to improve the stability of the emulsion, as explained below. The small value of the polydispersity of the poly-β-CD has to be noted, since it leads to an adsorption which can be qualified as model and homogeneous. With a much higher value of polydispersity,

i.e. with polymers of very different sizes one with each other, the effect on the stability could have been very different, with the formation of a different membrane structure.

In interfacial rheology, two different characterizations can be performed on the interface: shear and dilatational. In shear interfacial rheology, the interface is sheared while its area of the interface does not vary. In dilatational interfacial rheology, the interface is dilated and/or compressed (though its shape is retained), leading to a change of the interfacial stress (cf. Krägel 2008, for a recent review) [18]. We discuss here only the dilatational interfacial rheology technique, as this is the one used in our study.

In dilatational interfacial rheology, two mechanisms can explain the elasticity, and consequently the stability, of the interface, depending on the size of the molecular mass of the surfactants. For low molecular mass surfactants, the Gibbs-Marangoni prevails: a local dilatation of the interface causes a local increase of the interface area, hence a local diminution of the surfactant concentration. It ensues an interfacial tension gradient and a migration of the surfactants in the dilated area in order to lower this gradient, hence a draft force opposing the deformation and generating elasticity [19, 20]. For macromolecular surfactants, a viscoelastic network is formed at the interface, where macromolecules are mainly not soluble [21]. This network opposes the interface dilatation, hence an interface stabilization. Dilatational interfacial rheology has been recently successfully used to investigate the viscoelastic response of proteins [17, 22] and hybrid polyelectrolytes [23] at the interface.

Figure 1 represents the drop area and interfacial tension variations over two periods (20 s) after 5 min (from 280 to 300 s) for two different systems: with Parsol MCX as the oil phase and β-CD polymers in the aqueous phase (150 mg/mL) (left), and with Squalene as the oil phase and β-CD polymers in the aqueous phase (100 mg/mL) (right). Experiments using Parsol MCX as the oil phase showed no clear correlation between the sinusoidal drop area variation and the interfacial tension variation during the duration of the experiment, as this is the case for an interface without surfactants. Indeed, as the interfacial tension directly depends on the concentration of the surfactants at the interface, one could expect a sinusoidal interfacial tension variation at the frequency of the sinusoidal drop area variation if surfactants are adsorbed at the interface: this was not the case here, and calculation of rheological values (phase angle, elastic and viscous moduli) was not possible. This was due to the fact that poly-β-CD polymers were not adsorbed at the interface: the hydrophilic/hydrophobic complex formed with the poly-β-CD and the Parsol MCX was not efficient enough to be adsorbed at the interface. In that case, the oil/water interface exhibits no elastic properties, and cannot provide a stable emulsion. This lack of stability was confirmed by bottle tests in which the stability of such an emulsion was studied. Indeed, even after 10 months of storage, the emulsions formed using the poly-β-CD polymer and containing 1% volume of Squalene presented the same diameter (1 μm) and were stable.

Experiments with Squalene strikingly featured a sinusoidal interfacial tension with a frequency of 0.1 Hz equal to the frequency of the sinusoidal drop area variation. This is due to the fact that an increase (resp. decrease) of the drop area causes a decrease (resp. increase) of the poly-β-CD concentration at the interface, i.e. an increase (resp. decrease) of the interfacial tension. Over the time experiment (1 h), the mean of the interfacial tension did not change and remained at 12 mN/m. A highlight of Fig. 3 is that the two curves are almost in phase: this means that the interface preferentially reacts as an elastic interface rather than a viscous interface. This can be quantitatively confirmed by the calculation of the phase angle, and of the elastic and viscous moduli of the interface.

Figure 2 represents pictures of Squalene oil drops in an aqueous phase containing β-CD monomers (left) and β-CD polymers (right). For the β-CD monomer, the left picture (taken during the decrease of the drop area) clearly showed a solid membrane at the interface, preventing the drop from being Laplacian (the drop profile does not follow the theoretical profile predicted by the Laplace equation) in the

Fig. 1 Drop area and interfacial tension as a function of time (from 280 to 300 s). *Left*: the oil phase is Parsol MCX; the aqueous phase contains poly-β-CD polymers at 150 mg/mL. *Right*: the oil phase is Squalene; the aqueous phase contains poly-β-CD polymers at 100 mg/mL
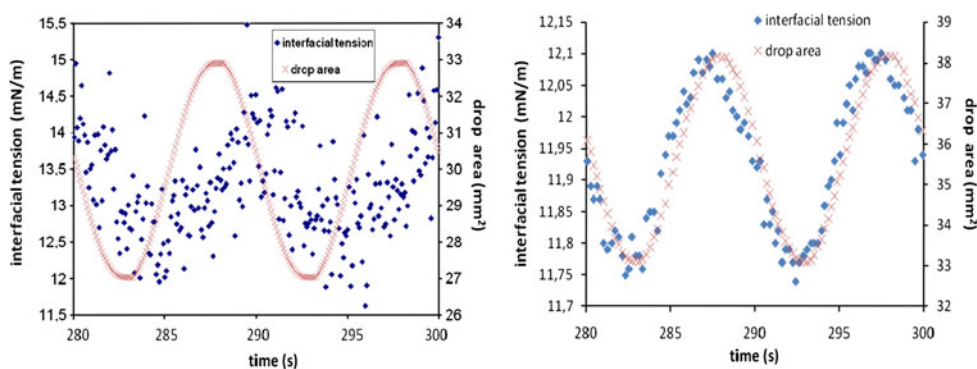
Fig. 2 Pictures of Squalene oil drops in an aqueous phase containing β-CD monomers (*left*) and poly-β-CD polymers (*right*)
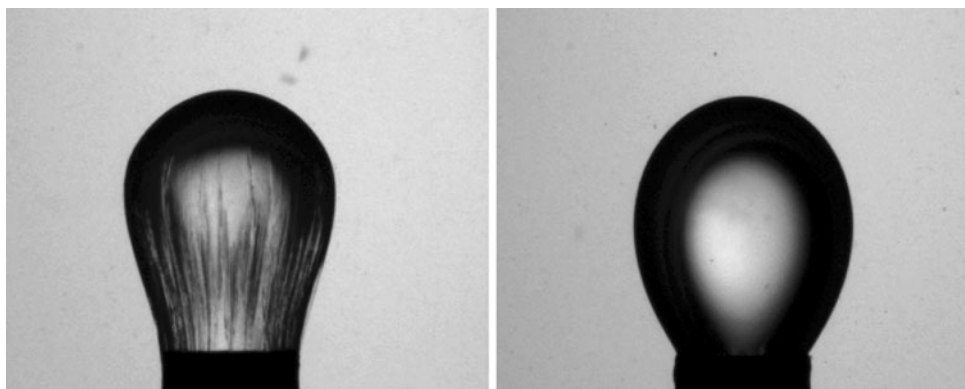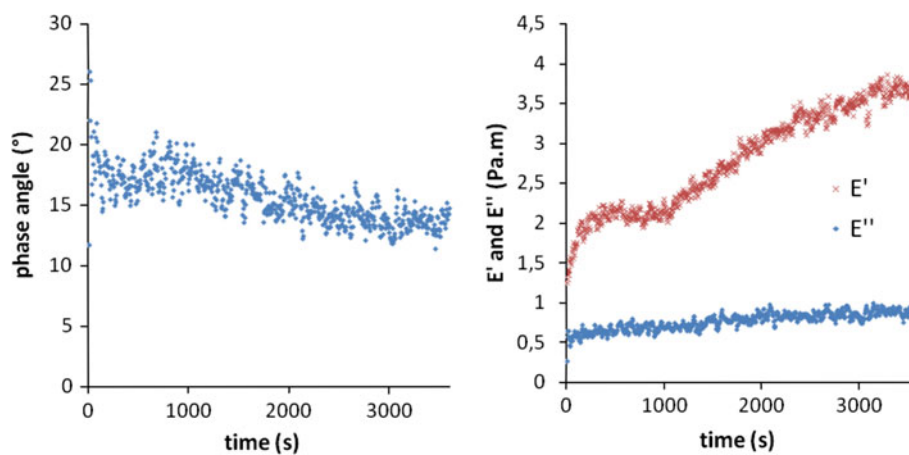

Fig. 3 Phase angle (*left*), elastic modulus E' and viscous modulus E'' (*right*) for a Squalene/water interface, with poly-β-CD polymers at 100 mg/mL in the aqueous phase. Time experiment: 1 h

case of monomers. In that case, no measurements could be done, as it was not possible to properly impose a sinusoidal area variation. It should be noted that this observation is consistent with complementary experiments, in which the formation of a β-CD monomer precipitate was observed, making the formation of an emulsion impossible (results not shown). For β-CD polymers, the right picture showed a Laplacian drop that fitted the theoretical prediction, allowing the determination of the interfacial tension. During the whole duration of the experiment, the drop remains Laplacian, and no solid membrane is observed.

On Fig. 3, the phase angle (left), the elastic modulus E' and the viscous modulus E'' (right) were shown. During the whole experiment, the phase angle was below 45°. The phase angle began at around 20°, then decreases and reached 13°: the interface behaviour was more elastic than viscous from the beginning of the experiment, and became slightly more elastic with time. Indeed, in more details, the elastic modulus E' increased with time, while the viscous modulus E'' remained approximately at the same value (which remained lower that E' during the whole experiment, which lasts 1 h). This can be explained by the fact that poly-β-CD polymers behave like macromolecules which are being adsorbed at the interface, creating a

viscoelastic interface. This interface, more elastic than viscous according to Fig. 3 resists to the strain stress. If we consider emulsion stability, this means that if two droplets of the emulsion knock together and try to coalesce, the elastic interface resists to the strain stress created by the deformation of the droplets, thus preventing coalescence and ensuring the emulsion stability.

Conclusion

Dilatational interfacial rheology provided an elegant and efficient way to quantitatively characterize an interface, with the determination of the interfacial tension and the calculation of rheological values like the phase angle and the elastic and viscous moduli.

From interfacial experiments performed with a dynamic drop tensiometer, β-CD polymers did not seem to adsorb at the Parsol MCX/water interface. Such an interface should not prevent coalescence, if an emulsion is created with this system. Squalene/water interface with β-CD monomers in the aqueous phase appears to form a rigid membrane, unsuitable for dynamic drop tensiometer measurement. This is consistent with the crystallisation of this system

when used to elaborate an emulsion. On the contrary, β-CD polymers adsorb at the Squalene/water interface in the aqueous phase, forming an elastic interface, preventing coalescence, thus creating a stable emulsion for several hours.

Further studies will be focused on the assessment of the stability of various oil/water emulsions as a function of the nature of the oil phase and of the type of the poly-CDs.

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