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Light-Modulated Rheological Properties in Green Innovative Formulations

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Abstract. The addition of azorubine to a viscoelastic aqueous dispersion of sodium oleate (NaOL, 0.43 M, 13% w/w) and KCl (up to 4% w/w) leads to a green gel-like system whose rheological behavior can be efficiently and reversibly triggered from remote by using UV light. Rheology, Differential Scanning Calorimetry (DSC) measurements and phase behavior studies indicate that the original texture of the NaOL dispersion is significantly hardened upon UV irradiation for 8 hours in the presence of azorubine, showing a seven hundred-fold increase in viscosity. The UV treatment brings about the *trans* to *cis* isomerization of azorubine, which modifies the structure of the NaOL wormlike micellar system, leading to a more entangled, close-textured network. The cooperative effect of KCl on the fluid viscosity is found to be concentration-dependent. The system slowly reverts to its original rheological behaviour after standing for about 1 day. These results are relevant for the development of stimuli-responsive innovative systems based on biocompatible, non expensive and commercially available materials that can be used in a wide range of applications, such as in drug delivery or enhanced oil recovery, where a quick change in the physico-chemical features of the system is required but difficult to be performed.

Keywords: green chemistry, sodium oleate, azorubine, viscosity, stimulus-responsive.

INTRODUCTION

Responsive or “smart” materials are functional materials whose properties can undergo controlled and reversible changes in response to an external stimulus [1–4]. The applied stimulus or external field include thermal, electrical, magnetic, pH, UV-visible light, ionic or metallic interactions or combinations thereof [5,6]. The formulation of gel-based stimuli-responsive systems with specific performances is crucial for a great number of applications, and particularly when it is impossible or very difficult to switch on/off their properties, and a remotely controlled trigger is necessary [5,7].

Among these systems, viscoelastic surfactant (VES) solutions have attracted great attention due to their unique features and versatility that can be harnessed in a variety of high-tech and everyday applications [8–15].

The amphiphilic nature of VES molecules leads to the self-assembly in solution into small aggregates, which show a complex phase behavior: the

simplest structure are spherical micelles, but also hexagonal, lamellar, vesicular, cubic, reverse phases can be observed, depending on the surfactant packing parameter and global packing constraints [2,16–19].

Under certain conditions (*i.e.* surfactant concentration, salinity, temperature, presence of different counterions, change in the composition of the solvent, etc.) spherical micelles may undergo uniaxial growth and form elongated and flexible structures, usually referred to as “wormlike” micelles (WLM) [19–21].

Above a critical concentration these systems show viscoelastic properties, like polymer solutions or bicontinuous three-component ionic microemulsions, as a result of the formation of a densely entangled network [19,22–26].

In our previous series of works we extensively investigated the main physicochemical properties and the phase behavior of wormlike micellar systems based on sodium oleate (NaOL), a safe, eco-friendly and cost-effective surfactant [19,26]. In the first part we reported on the structure, thermal properties and rheological behavior of NaOL aqueous dispersions in the presence of a single salt (KCl) via cryo-TEM, rheology and DSC experiments [19]. In part 2 we illustrated the specific ion effect induced by the addition of different salts on viscoelastic dispersions of sodium and potassium oleate, and we systematically discussed it in terms of the Hofmeister series [26]. In a previous work we imparted a voltage-dependent responsiveness to an NaOL aqueous dispersion through the addition of carbon black particles [27].

Prompted by these studies on green formulations with suitable responsiveness to different physical stimuli, in the present contribution we developed a NaOL-based viscoelastic dispersions that, in the presence of minimal amounts of azorubine, a biocompatible dye, and a salt (KCl) undergo a remarkable change in their rheological properties upon irradiation at a specific wavelength.

NaOL finds application in a wide number of industrial products and commercial formulations, like healthcare products, cleansers, thickening agents, emulsifiers, lubricants and fluids for enhanced oil recovery [28–32]. Thanks to its negative charge, NaOL is more biodegradable and less harmful for the environment compared to cationic surfactants [33].

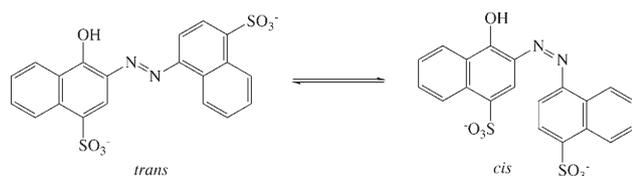


Figure 1. Trans-cis isomerization of azorubine.

NaOL shows a very interesting phase behavior [34] and forms different nano- and micro-structures in solution upon the addition of electrolytes or as a result of pH variation [19]. For an extensive discussion about the structural features and the rheological behavior of NaOL dispersions please see references [19,26,35–41] and references therein.

In this work we report on a moderately concentrated (0.43 M, 13% w/w) dispersion of NaOL in water that gives rise to a wormlike micellar network with peculiar structural properties and rheology. The choice of this surfactant concentration is related to the NaOL/water systems’ phase diagram: at this concentration and 25° C the dispersion converts from a simple fluid micellar L_1 to a viscous L_1^* phase that shows shear-dependent birefringence [19].

Azorubine is a synthetic azo dye approved for food decorations and coatings and as drink additive [42]. Its chemical structure is shown in Figure 1. The presence of the azo moiety enables a *trans-cis* isomerization upon irradiation with light at an appropriate wavelength, usually in the UV region [43–46].

The process may revert spontaneously upon heating since the *trans* isomer is thermodynamically more stable, or can be induced through irradiation with a visible light [47].

Previous studies reported on the introduction of different chromophores in VES systems in order to obtain light-responsive fluids with tunable rheological properties. These photo-active molecules include synthetically modified azobenzenes, [48–54] *p*-coumaric acid [55,56] and cinnamic acid derivatives [57–59]. We selected azorubine because of its unique advantages in terms of availability, simple manipulation, low cost and, above all, safety.

This work is a proof-of-concept that shows the efficacy of combining completely biocompatible and non-toxic materials to obtain a versatile formulation with a viscosity and rheological behaviour that can be remarkably modified through the irradiation with UV light.

Moreover, all these features make these systems very attractive for a wide range of applications, including agriculture, food industry, cosmetics, “smart” materials, enhanced oil recovery, shale gas extraction, drug delivery and controlled release.

MATERIALS AND METHODS

Materials

Sodium oleate (ACS reagent grade, Riedel-De Haën, Seelze, Germany) and potassium chloride (> 99 %, Sigma-Aldrich, Milan, Italy) were used as received without any further purification. Azorubine (Carmoisine, Food

red 3 or E 122, disodium 4-hydroxy-3-((4-sulphonatophenyl)azo)naphthalenesulfonate, food grade quality) was supplied by F.lli Rebecchi S.r.l. (Piacenza, Italy) and used without any further purification. All solutions and dispersions were prepared with Milli-Q water (resistivity > 18 M Ω cm at 25°C).

Sample Preparation

Sodium oleate viscoelastic formulations were prepared by the addition of a weighted amount of surfactant to KCl aqueous solutions at different concentrations (0, 0.1, 0.5, 1, 2, 3, 3.5, 4 % w/w) under constant stirring at room temperature. The final concentration of NaOL was 0.43 M (13 % w/w) in all the samples. The dye-loaded samples were prepared following a similar procedure: to a 0.18 % w/w (3.6 10^{-3} M) azorubine aqueous solution the proper amount of potassium chloride and then of the surfactant were added. The final concentrations of KCl were 0.1, 0.5, 1, 2, 3, 3.5, 4% w/w. For all the samples we used Milli-Q water, which was boiled for 4 h, filtrated and stocked under argon. As reported in our previous works the samples were freshly prepared and tested within 1 hour for the rheological and DSC experiments [19,26]. All these precautions are necessary in order to avoid the uptake of atmospheric CO₂ by the samples [60].

UV Irradiation

About 10 mL of sample were placed in a quartz container and irradiated using a Camag UV lamp (wavelength 254 nm, 8 W, Muttenz, Switzerland) for 8 hours. All the experiments were conducted at 25 °C, and the distance between the sample and light source was fixed at 5 cm.

Rheology Measurements

Rheology experiments were carried out on a Paar Physica UDS 200 rheometer using a plate-plate geometry with a diameter of 40 mm and a measurement gap of 300 μ m. The temperature was fixed at 25.0 \pm 0.1 °C using a Peltier control system for all the measurements. The samples were equilibrated for 15 min at the set temperature before being tested. Frequency sweep measurements were carried out within the linear viscoelastic range at a strain value of 1%, which was previously determined by means of an amplitude sweep test. The storage and loss moduli (G' and G'' , respectively) were

measured over the frequency range of 10^{-3} and 10^2 Hz. The flow curves were acquired in a torque range between 10^{-1} and $5 \cdot 10^3$ mN·m. The experimental viscosity (η) was fitted with the Cross model (see the Results and Discussion) to obtain the zero-shear viscosity (η_0), the infinite-shear viscosity (η_∞), the shear relaxation exponent (m) and the consistency (C). The experiments were repeated at least three times, and silicon oil was applied to the rim of the measurement geometry to prevent water evaporation from the sample.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed by means of a DSC-Q2000 by TA Instruments (Philadelphia, PA). The samples were sealed in aluminum hermetic pans and the measurements were conducted under N₂ atmosphere, with a flow rate of 50 mL/min. The samples were first cooled from 20 °C to -60 °C at 10 °C/min, then heated up to 50 °C at 5°C/min. The thermograms which show overlapping endothermic peaks were analyzed using a linear combination of exponentially modified Gaussian (EMG) functions, as reported elsewhere [19,26,61,62].

RESULTS AND DISCUSSION

Flow curve experiments

Figure 2 shows the flow curves obtained before (solid lines) and after (dashed lines) UV irradiation from the aqueous dispersions of sodium oleate (NaOL, 13% w/w) in the presence of KCl at different concentrations (0, 0.5, 2 and 3% w/w). The curves for the other KCl concentra-

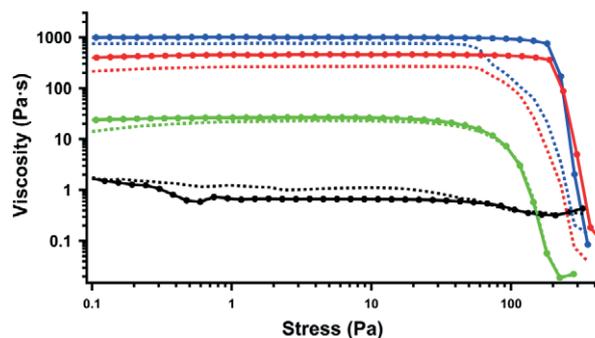


Figure 2. Flow Curves before (solid lines) and after (dashed lines) UV irradiation for 13% w/w NaOL (0.43 M, black) and in the presence of KCl at 0.5% (green), 2% (blue) and 3% w/w (red). The flow curves for non-irradiated samples are reprinted from [19] with permission from Elsevier. Copyright 2021.

tions are reported in Figure S1 in the Supporting Information. The experimental data on non-irradiated samples are reproduced from [19] with permission.

All the samples show the typical flow behavior of wormlike micellar networks, *i.e.*, a Newtonian plateau followed by a steep decrease in the viscosity at high shear stress, due to the shear-induced alignment of cylindrical aggregates. Moreover, a concentration-dependent increase in the viscosity is observed upon the addition of KCl [19,63]. The fitting of the experimental viscosity (η) data was performed using the Cross model [64]:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (C\dot{\gamma})^m} \quad (1)$$

Here η_0 is the zero-shear viscosity, m the shear relaxation exponent, η_{∞} the infinite-shear viscosity, the shear rate and C the consistency. The extracted fitting parameters are reported in Table S1 in the Supporting Information. The results nicely agree with the literature data and confirm the shear thinning behavior of the dispersions, originating from the micelles' entanglement and their progressive alignment at high shear rates [19,26,34,65,66].

The UV irradiation does not affect the flow properties of the formulations: the profiles, as well as the values of η_0 exhibit minor fluctuations within the experimental uncertainty before and after the UV treatment.

The flow curves for the NaOL samples at different KCl concentration (0, 0.1%, 0.5% and 4%) in the presence of 0.18% w/w ($3.6 \cdot 10^{-3}$ M) azorubine are reported in Figure 3. The flow curves at the other KCl concentrations are shown in Figure S2 (see the Supporting Information).

In the presence of azorubine all the formulations exhibit a shear-thinning behaviour that is similar to that

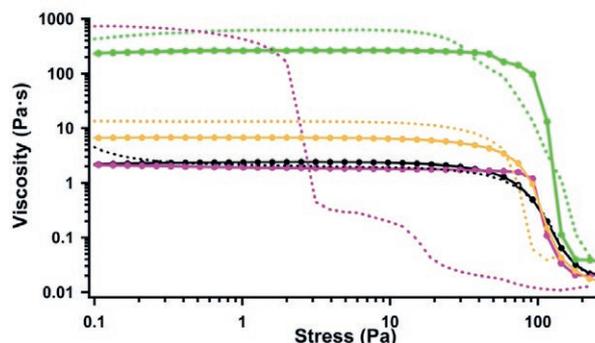


Figure 3. Flow curves before (solid lines) and after (dashed lines) UV irradiation for NaOL 0.43 M mixture in the presence of 0.18% w/w azorubine ($3.6 \cdot 10^{-3}$ M) at different KCl concentration: 0 (black), 0.1% (orange), 0.5% (green) and 4% w/w (pink).

found for the NaOL-KCl systems. The results obtained from the fitting of the experimental data with the Cross model are reported in Table S1 in the Supporting Information. After UV irradiation the viscosity of the samples with 0.1%, 0.5% and 4% KCl increases from 6.94 to 13.6, from 278.8 to 728.3 and from 1.852 to 730.1 Pa·s, respectively. For the other KCl concentrations no significant variations in the formulation viscosity are observed after the UV treatment.

These findings lead to two important conclusions: (i) azorubine has a remarkable effect as photo-active molecule in modifying the viscosity of the fluids after UV irradiation. A similar light-modulated viscosity change is reported for binary mixtures of NaOL and a light-responsive cationic azobenzene dyes [50,54]. In the work of Lu *et al.* the UV irradiation and the resulting *trans-to-cis* isomerization of the azo dye (1-[2-(4-phenylazophenoxy)-ethyl]-3-methylimidazolium bromide) induces a decrease in the viscosity of the system, with a transition from a gel-like structure to a Newtonian fluid [50]. In our case the opposite effect on the viscosity and the strengthening of the wormlike three-dimensional network is observed: a similar behavior is reported by Liu and coworkers on dilute NaOL dispersions in the presence of three different imidazolium surfactants upon UV irradiation [54]. (ii) The presence of KCl plays a key role in modulating the effect of azorubine. The experimental data reported in Table S1 show that the *trans-to-cis* isomerization of azorubine induces an increase in the formulation viscosity when KCl concentration is lower than 1% w/w. Between 1% and 3.5% no remarkable changes are observed before and after the UV irradiation, suggesting that the major contribution to the strength of the system is provided by the salt.

The behavior of the sample containing azorubine and 4% KCl is peculiar and deserves a deeper analysis. The viscosity increases by two orders of magnitude, but the rheological profile shows some differences after the UV treatment (see Figure 2, pink curves). A first Newtonian plateau appears in the low stress regime, then the viscosity rapidly decreases at a critical shear stress which is considerably lower than the viscosity breakdown point before the irradiation. After this initial decrease the flow curve shows a second, less pronounced plateau, followed by the typical shear-thinning region at high stress values. A similar behavior was reported by Griffiths *et al.* in 2004 for carbon black particles dispersed in an acrylic polymeric matrix [67]. In this case the presence of an intermediate (secondary) Newtonian plateau was ascribed to the interaction between the polymer layer and the polymer matrix, in particular to the viscous drag between the polymer chains adsorbed on the parti-

cles with the polymer in solution. In a more recent work Sochi depicts this intermediate region as a characteristic feature of viscoelastic fluids in porous media flow, that may be attributed to the time-dependent nature of the viscoelastic fluid when the relaxation time of the fluid and the characteristic time of the flow become comparable [68]. Polacco and coworkers observed two distinct shear-thinning phenomena in polymer-modified asphalts: the first shear-thinning was ascribed to a rigid rearrangement of the aggregate structure, that involves a temporary detachment of polymer chains. As a result, the polymer is able to move between different domains, inducing a transitory strengthening of the network [69].

In our system the appearance of this secondary Newtonian plateau may reflect the formation of ordered structures with a different degree of organization. To the best of our knowledge this is the first time that such behavior is found and reported for wormlike micellar dispersions. As a matter of fact the cited literature sources deal with polymeric blends [67,69] or to a more general viscoelastic behavior in porous media flow [68]. Further work is necessary to deepen and clarify this phenomenon. The high salt concentration may be responsible for the formation of complex, more entangled structures after UV exposure. These structures are responsible for the remarkable increase in the viscosity of the formulation and exhibit a low resistance to the applied stress, as confirmed by the low critical stress value. This hypothesis is also confirmed by the fact that during the sample preparation the azorubine solution becomes turbid at this salt concentration, suggesting the formation of aggregated structures. The same salt-induced behavior is observed in pure azorubine solutions, without sodium oleate, and presumably

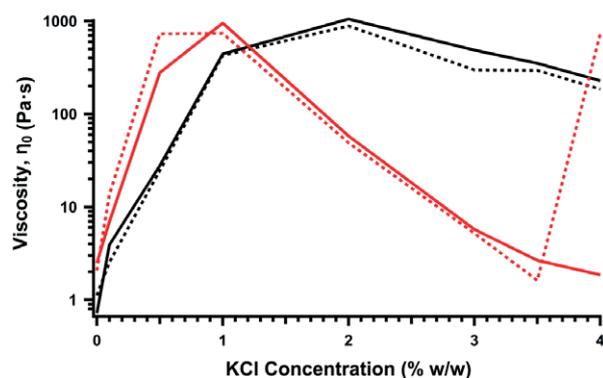


Figure 4. Zero-shear viscosity (η_0) for the formulations containing 0.18% w/w azorubine (red) and the reference samples without the dye (black) as a function of the salt concentration (a) before (solid line) and after (dashed line) UV irradiation. The trend for non-irradiated NaOL-KCl samples (black solid line) are reprinted from [19] with permission from Elsevier. Copyright 2021.

reflects the formation of piled up structures stabilized by π -stacking interactions [70,71].

For all the irradiated samples the system recovers its original rheological behavior after standing for about 1 day, indicating a complete reversibility of the process.

Figure 4 reports the values of η_0 as a function of KCl concentration before (solid lines) and after (dashed lines) the UV treatment.

For the two sets of samples the viscosity steeply increases in the dilute regime, then it reaches a maximum and progressively decreases at higher concentrations of salt. This behavior has been widely reported for a large number of wormlike micellar systems [22,39,50,63,72–80]. The initial viscosity increase is ascribed to the formation, growth and entanglement of the cylindrical aggregates. The decrease in the fluid viscosity after the maximum upon salt addition is due to the lateral branching along the rod-like micelles, that provide an extra route for mechanical stress relief [72,81,82]. A detailed discussion about the thermodynamic justification and the driving forces behind branches formation can be found in our previous works [19,26].

The experimental results show that azorubine induces two distinct effects on the salt curves (Figure 3). The first effect is the shift of the peak maximum to lower KCl concentrations. Azorubine is an amphiphilic molecule that can penetrate across the micellar interface at least partially. This results in a flattening of the micelle/water interface with a significant lowering in the surface curvature. Moreover, the electrostatic repulsion between different tubular micelles is screened and the viscosity increases even at lower concentrations of salt.

The second effect is the modification of the salt curve shape after the maximum. In the presence of azorubine the viscosity decreases more rapidly, as a consequence of the increased branching density. Rogers *et al.* reported that for several mixed surfactant/salt viscoelastic systems, the branching effect is more evident with sodium salicylate, a hydrotropic salt that can penetrate more efficiently underneath the water/micellar interface salt respect to a simple inorganic salt like KCl [83]. This effect due to branched structures is quite common and found also in nonionic or zwitterionic systems [41].

Oscillatory-shear measurements

Oscillatory shear experiments were performed to explore the viscoelastic behavior of NaOL-KCl-azorubine systems upon UV irradiation. The storage (G') and loss (G'') moduli before and after UV irradiation for the dispersions of sodium oleate in the presence of KCl at different concentrations are shown in Figure 5. The fre-

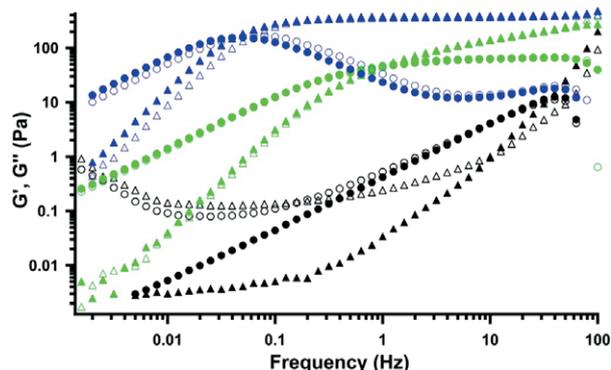


Figure 5. Storage (triangles) and loss (circles) moduli before (filled markers) and after (empty markers) UV irradiation for NaOL 0.43 M in the presence of KCl at 0 (black), 0.5% (green) and 2% (blue). The frequency sweep curves for non-irradiated samples are reprinted from [19] with permission from Elsevier. Copyright 2021.

quency sweep curves for other KCl concentrations are reported in the Supporting Information.

For all the samples two distinct regimes are observed, *i.e.* a predominant viscous behavior at low frequencies ($G'' > G'$) and mainly an elastic behavior at higher frequencies ($G'' < G'$). The *crossover point* of the storage and loss moduli (and the corresponding crossover frequency ω_c) marks the transition between the two different regions in the viscoelastic spectrum [84]. The decrease in ω_c upon salt addition reflects the formation of a more entangled WLM structure with slower relaxation mechanisms [19]. No remarkable variations in G' and G'' are observed before and after the UV irradiation with the exception of NaOL alone, that exhibits higher values of the storage and loss moduli in the low frequency region after the UV treatment.

Figure 6 reports the storage and loss moduli obtained in the frequency sweep experiments before and after UV irradiation for the samples containing azorubine in the presence of KCl at different concentrations (0, 0.5 and 2%). The frequency sweep curves for other KCl concentrations are reported in the Supporting Information. The formulations exhibit a viscoelastic behavior that looks similar to those reported in Figure 5, indicating that the two frequency-dependent regimes are present. The crossover frequency decreases when KCl concentration is increased from 0 to 0.5%, then it progressively shifts to higher values upon further increase in the salt concentration.

The UV treatment has a very minor effect on the viscoelastic properties of the formulations, with the exception of the sample containing KCl 4% (Figure S10 in the Supporting Information). In this case before the UV irradiation the storage and loss moduli show a

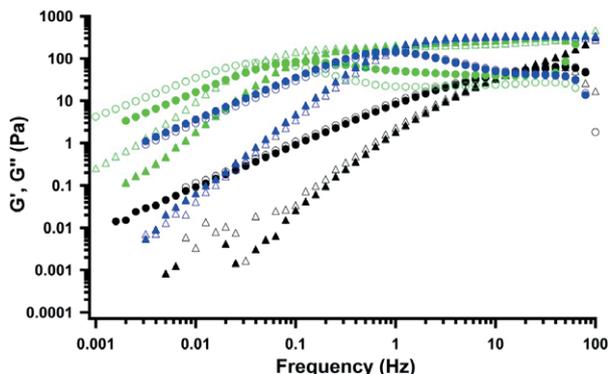


Figure 6. Storage (triangles) and loss (circles) moduli before (filled markers) and after (hollow markers) UV irradiation for NaOL 0.43 M + azorubine 0.18 % mixture in the presence of KCl at 0 (black), 0.5 % (green) and 2 % (blue).

crossover in the high-frequency region, followed by a remarkable drop at medium and low frequencies, which indicates a predominantly viscous behavior. After the UV treatment G' and G'' overlap for most part of the whole frequency range and after a slight decrease at high frequencies they level off to a relatively high constant value in the medium and low-frequency regime. This result is consistent with the remarkable viscosity increase observed after the irradiation (Figure 2) due to the presence of light-induced ordered structures.

A Cole-Cole plot analysis was performed to describe the viscoelastic behavior of the NaOL dispersions in terms of a Maxwell model with a single relaxation time (results not shown). Unfortunately, this approach does not provide an accurate prediction for the experimental values due to the presence of additional relaxation modes. For this reason, we calculated the continuous time-weighted relaxation spectrum using the values of the storage and loss moduli (Trios software, 5.2 version, TA instruments) [85,86]. The relaxation times τ_R estimated from the spectra are reported in Figure 7.

In the relaxation spectra an intense primary peak is observed for all the samples, and it was used to extrapolate the relaxation times. Additional secondary peaks are clearly detectable, demonstrating the presence of concurrent relaxation modes (reptation, breaking and recombination, Rouse motion, etc.) [19].

The comparison between the relaxation times and the viscosity values (see Figure 4) shows a similar effect on both the flow and the viscoelastic properties of the dispersions induced by azorubine: the UV irradiation, thanks to the presence of the dye, increases the structuredness of the tridimensional micellar network, resulting in similar trends of η_0 and τ_R .

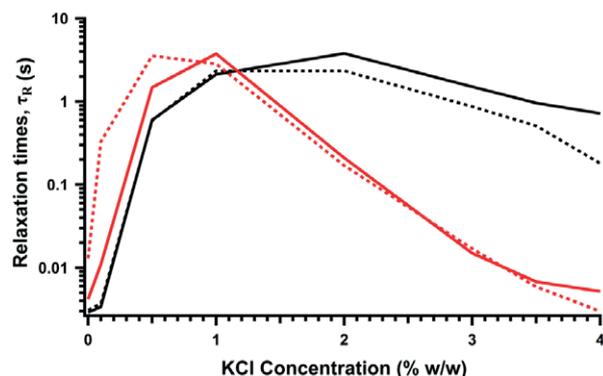


Figure 7. Relaxation time (τ_R) for the formulations containing azorubine (red) and the reference samples without the dye (black) as a function of the salt concentration before (solid line) and after (dashed line) the UV irradiation. The trend for non-irradiated NaOL-KCl samples (black solid line) are reprinted from [19] with permission from Elsevier. Copyright 2021.

The only exception is represented by NaOL + KCl 4% in the presence of azorubine: in this case the relaxation time after the UV treatment is very close to the value of the non-irradiated sample. As we mentioned in the previous section, the remarkable increase in the viscosity observed at this salt concentration is probably due to the presence of aggregated structures.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) experiments were performed to investigate the thermal properties of the NaOL-KCl-azorubine systems. The thermograms of the NaOL dispersions in the presence of KCl at different concentrations (0, 3.5 and 4%) before and after UV irradiation are reported in Figure 8. For the DSC curves of the other investigated KCl concentrations see the Supporting Information.

All the DSC thermograms show a free water melting peak at around 0°C. For KCl concentrations above 0.5 % a secondary endothermic peak occurs between -15 and -11°C, and it is related to the melting of the “interfacial” water molecules that are confined in the solvent-rich domains between the entangled cylindrical micelles [87–91]. A third endothermic peak appears when KCl concentration reaches 4%, as observed in our previous work [19]. This thermal transition is attributed to the melting of freezable bound water, *i.e.* the water molecules that closely interact with the micellar surface and show a melting temperature remarkably different from bulk water [61,92–96].

The melting temperature, the relative enthalpy change and amount (%) of free water (ΔH_{mf} , T_{mf} and W_f),

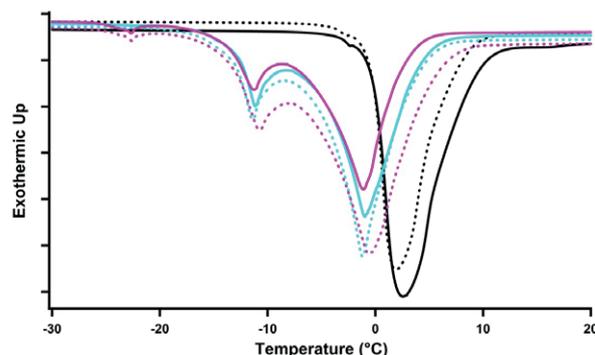


Figure 8. DSC heating curves before (solid lines) and after (dashed lines) UV irradiation for NaOL 0.43 M mixture in the presence of KCl at 0 (black), 3.5% (light blue) and 4% (pink).

interfacial water (ΔH_{mi} , T_{mi} and W_i) and freezable bound water (ΔH_{mb} , T_{mb} and W_b) for all the examined samples, before and after UV irradiation are listed in Table S2 in the Supporting Information. A detailed discussion about the theoretical background and the procedures for the calculation of the thermal parameters can be found in [19,26,61].

For the pristine non-irradiated samples W_f rapidly decreases, passing from 96% to 46% as the salt concentration increases. Similar values are obtained for the NaOL-KCl systems after the UV irradiation, demonstrating that the endothermic process (*i.e.* the melting of the free water) is not affected by the UV treatment, as expected.

When KCl concentration increases, the melting peak temperatures T_{mi} shift to lower values; conversely ΔH_{mi} shows a progressive increase. As previously reported, the addition of KCl (and the consequent Na^+/K^+ exchange at the micellar surface) leads to the formation of elongated cylindrical micelles, and above a critical concentration (see Figure 4) to the branching of the WLM network [19]. For this reason the number of connections and junctions within the micellar network increase, as well as the number of water molecules confined within the intermicellar domains, as evidenced by the values of W_i .

By comparing the values of the peak temperatures and of the enthalpy changes related to the melting of the interfacial and bound water we conclude that the UV treatment does not alter the hydration state of the NaOL/KCl systems.

For the samples containing azorubine the values of ΔH_{mf} , T_{mf} , W_f , ΔH_{mi} , T_{mi} , W_i , ΔH_{mb} , T_{mb} and W_b are reported in Table S2 in the Supporting Information.

The presence of the dye does not induce any remarkable variation in the amount of free and interfacial water, as well as in the values of peak temperatures and

the relative enthalpy changes. The main difference is represented by the freezable bound water melting peak, that appears starting from KCl 3%. As indicated by the viscosity measurements, the negatively charged sulfonate groups in the azorubine molecule have a cooperative effect with KCl in screening the electrostatic repulsion between the micellar surfaces. This synergistic action reduces the amount of salt that is required for the formation of the micellar entangled network (and eventually the branched structures) and affects the thermal transition of the water molecules that closely interacts with the micellar surface, *i.e.* the freezable bound water.

CONCLUSIONS

In this work we illustrate a simple and inexpensive procedure for the formulation of green photo-responsive viscoelastic fluids starting from non-toxic, biocompatible, commercially available materials. The addition of a food azo dye, azorubine, to a dispersion of sodium oleate in the presence of KCl enables the modification of the formulation rheological properties through an external UV light stimulus. The UV treatment brings about the *trans-cis* isomerization of azorubine, which is partially intercalated between the surfactant polar heads, resulting in a modification of the wormlike micellar structure of NaOL. This gives rise to a remarkable increase in the formulation viscosity and a variation of the rheological properties, as evidenced by viscosity and oscillatory-shear measurements. The effect of azorubine is mediated by the presence of the salt, since it occurs only in a specific range of KCl concentration. DSC measurements confirm the formation of wormlike micelles above a critical salt concentration, which is lower in the presence of azorubine. The UV treatment does not affect the thermal transitions of the NaOL dispersions, since no significant variation is detected before and after the irradiation.

All these features, combined with the complete biocompatibility and non-toxicity break new ground in a wide range of applications, from shale gas extraction to controlled release and drug delivery, where a remote control on the mechanical and physico-chemical properties of the formulation is crucial.

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