Rheological properties of lyotropic liquid crystals encapsulating curcumin

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ABSTRACT
This study constructed new curcumin-loaded lyotropic liquid crystals containing pharmaceutically accepted oil, and ethyl oleate (EtOL). Three liquid crystalline phases including lamellar, hexagonal, and cubic phases were identified by means of the polarized optical microscopy and rheology method. By analyzing the shear viscosity ($\eta_0.1$), the viscosity of curcumin-liquid crystals is smaller than those without curcumin. Dynamic rheological results show that: Dissolved curcumin in EtOL can make the elastic modulus of hexagonal and cubic phase increase compared with that without curcumin, while the elastic modulus of lamellar phase decreases. Dissolved curcumin in Brij 97 can lead to the decreasing of the elastic modulus for cubic and lamellar phases, whereas it has little influence on hexagonal phase. When the curcumin is solubilized in both EtOL and Brij 97, the elastic modus of hexagonal phase increase, the elastic modus of lamellar and cubic phases decrease compared with that without curcumin. Furthermore, three temperature turning points were identified by the change in the slope of $\tan \delta (G'/G)$ for curcumin-hexagonal liquid crystal. These studies might be a help to study the storage of drug carrier and in vitro release properties of lyotropic liquid crystals containing curcumin.

GRAPHICAL ABSTRACT

1. Introduction
Surfactant molecules can self-assemble into a large variety of morphologies, including liquid crystalline phases such as lamellar, cubic, and hexagonal phases. Hydrophilic and lipophilic substances may be solubilized into the liquid crystals forming monophasic ternary or more complex systems. These thermodynamically stable molecular aggregates have a great potential in a broad multidisciplinary field, including pharmaceutical industry, food technology, and dispersion techniques.

Curcumin, a yellow pigment, is the active ingredient extracted from the rhizome of turmeric which is commonly used in traditional medicines. In the past decades, curcumin has already become a research focus due to its numerous beneficial, biological, and pharmacological activities such as antioxidant, anticancer, anti-inflammatory, and other desirable medicinal benefits. However, poorly solubility of curcumin in water and unstable at acidic or neutral pH make curcumin hard to absorb from the gastrointestinal tract after oral administration, hence these defect of curcumin can reduce the bioavailability of curcumin.

Various encapsulation approaches have been designed to improve the bioavailability of curcumin, such as liposome, phospholipid complex, cyclodextrin inclusion, and...
microemulsion. Recently, lyotropic liquid crystals have received increasing attention due to their better stability, storage-stable and controlled-release advantage as drug delivery. However, to our best knowledge, the rheological property of lyotropic liquid crystals encapsulating curcumin is still not well understood. In our recent investigations, it is found the curcumin molecules may be solubilized both into the apolar core of cylinders together with IPM and in the polar domain coexisting with PEG 400 between the cylinders. In our study, the effect of curcumin dissolved in oil and surfactant on rheological property for three kinds of liquid crystals was studied.

In this work, NaDC and Brij 97 are chosen as the mixed surfactants, in which synergism in mixed micelle formation was found. In structure, Brij 97, with a long unsaturated chain, can exhibit abundant phase behaviors. NaDC consists of a rigid steroid backbone, two hydroxyl groups and a carboxylate group, which can adjust and control the capacity of self-assembly. It is also found the protection effect of curcumin under the light was enhanced with the addition of NaDC in a Brij 97-based liquid crystal. Ethyl Oleate (EtOL), possess good safety profile for food, is widely used in food additives and drug delivery systems and has a relatively higher solubility of curcumin compared with some other food grade oil phase, such as isopropyl myristate, peppermint oil, and oleic acid.

Taking into consideration the above-mentioned facts, in this study, phase behavior of Brij 97/NaDC/EtOL/H\textsubscript{2}O system was constructed. The structure of the lyotropic liquid crystals in this system are identified by polarization microscopy method and rheology. The effect of curcumin dissolved in different component and the change of surfactant/oil ratio (fixed the water content) on the rheological properties were investigated for liquid crystals. Furthermore, the temperature effect on the rheological properties of curcumin-hexagonal liquid crystal was also studied. Some interesting results were obtained.

2. Materials and methods

2.1. Materials

Polyoxyethylene-10-oleyl ether (Brij 97) and sodium deoxycholate (NaDC) were purchased from Sigma-Aldrich China, Shanghai, China. Ethyl Oleate (EtOL) and curcumin were purchased from Sinopharm Chemicals Reagent Company (Shanghai, China). All chemicals were used without further purification. Deionized water was used after double distilled.

2.2. Phase diagram

Brij 97 and NaDC were previously mixed at the weight ratio of 9:1 using a vortex mixer. Twenty preweighed mixtures of Brij 97/NaDC and EtOL, with weight ratios varying from 0:10 to 10:0 were well stirred at a temperature of about 60–70°C be homogenized. Then the water was added sequentially and the samples were mixed using a vortex mixer and repeated centrifugation. When the mixtures were homogeneous, the samples were kept in a water bath at 25°C to achieve phase equilibrium. Phase equilibrium were determined by visual observation of the samples in normal light and also observed with polarization microscopy for anisotropy or isotropy.

2.3. Preparation of curcumin-liquid crystals

Curcumin saturated oil phase and Brij 97 The solubility of curcumin in EtOL and Brij 97 were required to prepare the samples. An excess amount of curcumin was added to a glass bottle with a lid containing a certain amount of EtOL and Brij 97. After sealing, the mixture was mixed using a vortex mixer (X-HT, Shanghai Jintan medical instrument factory, China) for 10 minutes in order to facilitate proper mixing of curcumin with the vehicles. Mixtures were then stirred using the magnetic stirrer (79–1, Jintan medical apparatus factory, China) in the dark condition at room temperature for 24 hours in order to achieve equilibrium. Afterwards, the suspension of curcumin was centrifuged triply at 10,000 rpm for 10 minutes using a high speed centrifuge (Sigma 1–14, Sigma Laborzentrifugen GmbH, Harz, Germany). The supernatants were collected into brown laboratory bottle and stored at room temperature until required for analysis. Curcumin saturated oil phase and Brij97 diluted with ethanol were detected by UV spectroscopy (UV-1700 Spectrum, Shimadzu Suzhou Instruments Wfg. Co., Ltd., Suzhou, Jiangsu, China) at a wavelength of 425 nm. The solubility of curcumin in EtOL is 0.93 mg/g and is 82.65 mg/g in Brij 97 in our study. The samples incorporating curcumin were prepared by using the saturated oil phase or surfactant of curcumin.

Curcumin-liquid crystals The samples were prepared by mixing all the components at the given weight percentage, and then they were homogenized by using a vortex mixer. The liquid crystals were heated at 60–70°C until homogenization, and after it they were left in a 25°C bath to achieve phase equilibrium. A series of sample preparation were conducted as follows. Samples A\textsubscript{1}, A\textsubscript{2}, A\textsubscript{3}, B\textsubscript{1}, B\textsubscript{2}, B\textsubscript{3} and C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3} were prepared without curcumin. The samples A\textsubscript{1}O, A\textsubscript{2}O, A\textsubscript{3}O, B\textsubscript{1}O, B\textsubscript{2}O, B\textsubscript{3}O, B\textsubscript{4}O, C\textsubscript{1}O, C\textsubscript{2}O, C\textsubscript{3}O were prepared by using the curcumin saturated EtOL. Samples A\textsubscript{2}S, B\textsubscript{3}S, C\textsubscript{2}S were prepared by using curcumin Brij97. Curcumin is dissolved in both EtOL and Brij 97 for samples A\textsubscript{2}SO, B\textsubscript{3}SO and C\textsubscript{2}SO.

2.4. Polarization microscopy

A BK-POL (Chongqing Aote optician Co) polarization microscope with a maximum magnification of 1000 was applied in the microscopic observation. The relevant pictures were digitalized using an OPTEC TP DV500 camera and the proper computer hardware.

2.5. Rheological measurement

The rheological experiment have been performed in an American Discovery HR-2 rheometer (TA Instruments, USA) using a cone-plate sensor (20 mm diameter, 2° angle).
The sample thickness in the middle of the sensor was 0.105 mm. The sample was gently added to the Peltier board and then the cone-plate was slowly reduced to its measuring position with constant velocity. The sample squeezed out from the sensor system was then gently removed. The temperature was controlled by a Peltier system applied on the outer thermostatic water bath and the maximum permitted deviation in temperature was ±0.1°C during the measurements. Measurements were carried out after a period of 10 minutes to allow for the stress relaxation. Temperature scans of elastic and viscous moduli were carried out at heating rate of 1°C/min in the range of 20–80°C. Dynamic frequency sweep measurements were performed at a constant stress in linear viscoelastic regime, as determined by the oscillation stress sweep measurement. Steady shear measurements were performed on all the samples using a range of shear rate from 0.01 to 1000 s⁻¹.

3. Results and discussion

3.1. Phase behavior

A rough phase diagram to describe the single phases of the Brij 97–NaDC (9:1)/EtOL/water system at 25°C is presented in Figure 1. Similar with our previous Brij 97/IPM/H₂O system,[21] rich liquid crystal phases (Lα, H₁, I) were also found in this study. The lamellar phase is formed between 15.4 wt% and 35.5 wt% water, solubilizing 23.4 wt% of EtOL. A clear and birefringent hexagonal phase is obtained between 37.8 wt% and 56.1 wt% water, solubilizing 12.0 wt% of EtOL. On increase of the EtOL concentration at relative high water content of 46.2–69.4 wt%, a stiff and transparent isotropic cubic phase is found between the O/W microemulsion and hexagonal phase, which solubilizes 16.1 wt% EtOL. The location of the cubic phase in the diagram suggests that it is composed of micelles that have crystallized in a cubic lattice.[21] The type of the liquid crystal has been defined by their characteristic polar textures of optical micrographs. Some samples are chosen to take the polarization photos. Typical polar textures of two kinds of liquid crystals formed in the phase diagram are presented in Figure S1 (Supplemental Material). The sample A₂ shows some cross flower texture, which is typical of lamellar phase.[21] The micrograph of the sample B₃ shows the marbled textures, the textures coincide with the texture of the hexagonal phase,[15] the cubic phase is isotropic, so the sample C₂ does not have any polar texture. The isotropic solution phase, O/W microemulsion (L₁), is present at higher water content.

3.2. Rheological properties

The rheology has been utilized to understand the property and structure of self-assemblies.[22–25] Dynamic and steady rheological measurements were performed on all the investigated liquid crystal samples.

3.2.1. The effect of curcumin

3.2.1.1. Hexagonal phase. The changes of the flow curves for hexagonal phase with curcumin dissolved in different component are demonstrated in Figure 2. The viscosity of the investigated samples decreases with increasing the shear rate, showing a shear-thinning behavior. The viscosity curve of sample B₃O is almost coincided with B₃ at low shear rate and B₃S is a little lower than B₃. While the viscosity curve of B₃SO is obviously lower than the other samples when the shear rate is in the range from the 0.01 s⁻¹ to 6 s⁻¹. When the shear rate surpasses the 6 s⁻¹, the viscosity of the hexagonal phase without curcumin is lower than those samples containing curcumin, indicating that the hexagonal phase without curcumin is easier to be destroyed at high shear rate. These flow curves can be described by a power law equation,[22] \( \eta = K \gamma^{-a} \). Usually the flow curve does not fit the power law in the entire shear rate region,[23] so the range (0.03–1 s⁻¹) is chosen to analyze by use of this power law relationship in our study. The fitting curves are shown in the embedded map in Figure 2. The values of the flow coefficient (K) and rate index (−a) are listed in Table 1. The exponents of the investigated liquid crystal samples are close to −1 which corresponds to plastic.

Figure 1. Phase diagram for Brij 97–NaDC (9:1)/EtOL/H₂O system at 25°C. L₁, isotropic O/W microemulsion; Lα, lamellar liquid crystal phase; H₁, hexagonal liquid crystal phase; I, micellar cubic liquid crystal.

Figure 2. Steady viscosity as a function of shear rate for curcumin-hexagonal liquid crystals at 25°C.
The shear viscosity \( \eta_{0.1}(\gamma = 0.1 \text{ s}^{-1}) \) was studied in our work listed in Table 1. As can be seen that the \( \eta_{0.1} \) values of hexagonal liquid crystal decrease in the sequence of \( B_3 \rightarrow B_3O \rightarrow B_3S \rightarrow B_3SO \). These reflect that the addition of curcumin can decrease the viscosity of hexagonal liquid crystal, especially for \( B_3SO \).

More information on the network structure of the liquid crystal phase can be obtained from oscillatory frequency sweep measurement.\(^{[22]}\) The effect of curcumin on frequency-dependent moduli for hexagonal phase is shown in Figure 3. It is shown that the viscous response dominates at low frequency while the hexagonal phase shows elastic behavior at higher frequency. The curves intersect at a characteristic frequency (\( \omega_0 \)). The rheological results mean that the hexagonal samples exhibit viscoelastic behavior, which is consistent with the typical rheological behavior of \( H_1 \) phases.\(^{[24]}\) From the frequency spectrum, the investigated curcumin-hexagonal liquid crystals still keep the hexagonal structure. In order to know the effect of curcumin dissolved in different component on the elastic modulus of hexagonal liquid crystal, the elastic modulus is investigated at one fixed frequency (1 Hz). The elastic modulus of samples \( B_3S \) is similar to the sample \( B_3 \) at the frequency (1 Hz), which means the addition of curcumin in Brij 97 has not obviously influence on the elastic structure of the hexagonal liquid crystal. Moreover, the elastic modulus of sample \( B_3O \) and \( B_3SO \) is higher than that of sample \( B_3 \) at the frequency (1 Hz), indicating the better elastic network is formed in the hexagonal liquid crystal with curcumin dissolved in EtOL. The inverse of the \( \omega_0 \) is defined as a characteristic relaxation time \( \tau_0 \), which is a measure of how easily the liquid crystal network can be formed.\(^{[24]}\) The characteristic relaxation time of the hexagonal phase samples increases in the sequence of \( B_3SO \rightarrow B_3S \rightarrow B_3O \). It is shown that the relaxation procedure of \( B_3O \) is the longest which reflects that the formation of network structure become the most complex when the curcumin is solubilized in EtOL.\(^{[15]}\) The frequency dependency sweep measurement of the liquid crystals in the linear viscoelastic regime can be further interpreted by a multiple Maxwell model.\(^{[25,26]}\) The frequency dependence of \( G' \) and \( G'' \) of Maxwell-type fluids are given as:\(^{[25]}\)

\[
G' (\omega) = \sum_{i=1}^{n} G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \tag{1}
\]

\[
G'' (\omega) = \sum_{i=1}^{n} G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \tag{2}
\]

where \( G_i \) is the elastic modulus corresponding to a particular \( \tau_i \), \( \omega \) is the frequency of oscillation, \( n \) stands for the number of Maxwell elements and \( \tau_i \) is the relaxation time. Experimental \( G' \) and \( G'' \) values are successfully overlaid by the fitting curves using the multiple Maxwell model in our study. The discrete relaxation spectra of hexagonal liquid crystals are shown in the inset of Figure 3. The relaxation modulus of the investigated samples distribute monotonic with a negative slope. Moreover, it can be observed that the addition of curcumin leads to the increasing of the relaxation modulus. This demonstrates that the higher elasticity is formed in the curcumin-hexagonal liquid crystal.\(^{[24]}\) The shortest relaxation time of the sample \( B_3O \) and \( B_3SO \) increases compared with other samples, reflecting curcumin in EtOL can prolong the time of the water molecule back to orderliness.\(^{[26]}\)

The effect of curcumin on the hexagonal liquid crystal with different surfactant/oil ratio is further investigated, as is shown in Figure S2 (Supplemental Material). It is shown that all the investigated curcumin-hexagonal liquid crystals possess high modulus, indicating the addition of curcumin can enhance the stability of hexagonal liquid crystal. The elastic modulus of \( B_2O \) and \( B_3O \) increases obviously compared with \( B_2 \) and \( B_3 \), respectively. Nevertheless, the elastic modulus of \( B_1O \) is slightly higher than the sample \( B_1 \). So the hexagonal liquid crystal with lower surfactant/oil ratio is easy to be influenced by curcumin in this system. From the relaxation spectra, it is shown that the relaxation modulus of curcumin-hexagonal liquid crystal is higher than that without curcumin. The shortest relaxation time of sample \( B_3O \) and \( B_3SO \) is longer than that of \( B_2 \) and \( B_3 \), respectively, which indicates that the time of the water molecule back to orderliness become slower.

### 3.2.1.2. Cubic phase

The flow curves of cubic phases are shown in Figure S3 (Supplemental Material). As can be observed, the investigated cubic samples also behave shear thinning. The shape of the flow curves for samples \( C_2O \) and \( C_2S \) have no obvious change compared to the sample \( C_2 \). The shear resistance property of these samples has not been studied.

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**Table 1.** Characteristic parameters of the liquid crystals.

| Samples | Phase | \( \eta_{0.1} \) (Pa.s) | \( n' \) | \( n'' \) | \( \tau_0 \) (s) |
|---------|-------|-------------------|------|--------|-------|
| A2      | La    | 240.68            | 15.27| 1.19   | –     |
| A2O     | La    | 146.02            | 8.960| 1.21   | –     |
| B3      | H1    | 7688.4            | 629.7| 1.07   | 23.38 |
| B3O     | H1    | 595.9             | 1.10 | 10.12  |
| B3S     | H1    | 486.2             | 1.09 | 6.74   |
| B3SO    | H1    | 3136.7            | 262.4| 1.10   | 4.67  |
| C2      | I     | 20642             | 2715 | 0.84   | 63.57 |
| C2O     | I     | 19088             | 1836 | 0.94   | 63.69 |
| C2S     | I     | 16086             | 699  | 0.80   | 31.25 |
| C2SO    | I     | 3190.2            | 226.9| 1.14   | 2.22  |

Figure 3. Elastic, \( G' \) (filled), and viscous, \( G'' \) (open), moduli as a function of angular frequency for curcumin-hexagonal liquid crystals at 25°C.
weakened at high shear rate. However, the flow curve of sample C2SO is much lower than the other curcumin-liquid crystals consistent with the decreasing of \( \eta_0 \) in Table 1.

Upon addition of curcumin to cubic liquid crystal in different component, the variations of frequency-dependent moduli are depicted in Figure S4 (Supplemental Material). From the frequency spectrometer, it is evident that the moduli \( G' \) and \( G'' \) of the investigated samples show traits of solid-like rheogram.[27] The elastic modulus of sample C2O is higher than that of the sample C2. The similar phenomenon can be also found in the hexagonal phase in our study. When curcumin is encapsulated into the cubic phase sample by dissolving curcumin into Brij 97, the elastic modulus of the sample C2S decreases compared with the sample C2O. This is due to the fact that the distribution of curcumin molecules may change and a part of curcumin molecules can be inserted into the palisade layer of spherical micelle coexisting with Brij 97, making the structure loose. It is noteworthy that the values of the elastic modulus for the sample C2SO are one order of magnitude lower than other samples which reflect steric configuration of cubic phase may be changed and this need to be further investigated. The characteristic relaxation time of curcumin-cubic liquid crystals increase in the order: \( \tau_c(C2SO < C2S < C2O = C2) \). The characteristic relaxation time dramatically decreases when the curcumin is dissolved into both EtOL and Brij 97, indicating a less rigid structure.[28] This change could be due to the change of the arrangement of surfactant aggregates or the disruption of the spherical micelle.[28] Besides, the relaxation spectra with several elements are shown in the insert map of Figure S4. Unlike other curcumin-cubic liquid crystals, a clear trend can be seen from the relaxation spectra which show the appearance of a minimum for the relaxation modulus of sample C2SO. These may mean that a flexible network is formed. [23] The shortest relaxation time of all samples is almost equal, indicating that an elastic network is formed.[23] The shortest relaxation time of all samples is almost equal, indicating the addition of curcumin in different component does not change the time of the water molecule back to orderliness for lamellar phase.

The effect of curcumin on the lamellar liquid crystal with different surfactant/oil ratio is studied in Figure S8. It is shown that the elastic modulus of A1O and A2O is higher than the lamellar liquid crystal without curcumin. The difference is that the rising degree of elastic modulus for sample A1O is larger, indicating that the elastic structure of lamellar is liable to be affect by curcumin when the ratio of surfactant/oil is higher. On the contrary, the elastic modulus of A2O is slightly lower than that of A2.

3.2.2. The effect of temperature
The effect of temperature on the rheological properties for sample B1O is further investigated. Elastic modulus \( (G') \), viscous modulus \( (G'') \), and \( \tan \delta \) as a function of temperature are plotted in Figure 4. It is worth noting that three turning points are indicated by a change in the slope of \( \tan \delta \). The first turning point (I) lies at around 34°C. The moduli of \( G' \) and \( G'' \) decrease slowly before the first turning point (I), indicating the structure of the liquid crystal still remains stable. The second turning point (II) is at around 43°C. The slope of \( \tan \delta \) increases between 34°C and 43°C. Both \( G' \) and \( G'' \) decrease gradually with the increasing of temperature while the \( G' \) declines faster.

3.2.1.3. Lamellar phase. The effect of curcumin dissolved in different component on the flow curves of the lamellar phase is shown in Figure S6 (Supplemental Material). The viscosities of the samples A2O, A2S and A2SO are lower than that of A2 at the shear rate range from 0.01 to 10 s\(^{-1}\). The values of \( \eta_0 \) \( (A2 > A2O > A2S > A2SO) \) are also shown in Table 1. This results show that curcumin dissolved in EtOL or Brij 97 can decrease the viscosity of lamellar phase, and the reduction is more obvious when curcumin is solubilized in both EtOL and Brij 97. While the viscosity of curcumin-lamellar samples almost coincide with the sample without curcumin at higher shear rate (above the 10 s\(^{-1}\)).

Frequency sweeps are described as well in Figure S7 (Supplemental Material). It can be observed that the elastic modulus of the sample A2O, A2S, A2SO is lower than that of sample A2. The result implies that the curcumin-lamellar liquid crystals have a weak strength and less stable internal structure. A little decrease of the elastic modulus is found in sample A2O, while the elastic modulus of A2S decrease apparently compared with sample A2. This reflects that curcumin dissolved in Brij 97 is easy to slack the elastic structure of lamellar liquid crystal. From the relaxation spectra (the insert of Figure S7), all the investigated curcumin-lamellar phase samples show a minimum in the relaxation modulus, indicating that an elastic network is formed.[23] The shortest relaxation time of all samples is almost equal, indicating the addition of curcumin in different component does not change the time of the water molecule back to orderliness for lamellar phase.

![Figure 4. Temperature evolution of elastic, \( G' \) (filled), viscous, \( G'' \) (open) and \( \tan \delta \) (circle symbols) upon heating for sample B1O (the insert map is the frequency sweep at different temperature).](image-url)
than $G''$ causing the increasing of $\tan \delta$. This means the lattice structure of the liquid crystal is destroyed to some degree due to the increasing of the temperature. The third turning point (III) lies at 52°C. $G'$ and $G''$ decrease at almost the same rate between 43°C and 52°C. The $B_3O$ may become to a two-phase coexistence according to the viscoelasticity property in the temperature ranging from 43°C to 52°C.[36] At last $\tan \delta$ increases sharply at about 52°C, the magnitude of $G'$ and $G''$ sharply decreases, which implies that the structure of the hexagonal lattice is almost destroyed. Further increasing the temperature, $G'$ can not be detected, but the $G''$ still exists. Frequency behaviors of sample $B_3O$ at some representative temperature are shown in the insert map of Figure 4. It is shown that temperature has an obvious effect on the values of the moduli, $G'$ and $G''$ decrease with the temperature increasing. The shapes of their curves still follow a typical gel-like rheogram from 25°C to 37°C. This indicates a lower strength of the hexagonal phase network. The frequency tendency changed obviously at 45°C. This suggests the mixed phases in the transitive region. The rheological curves at 55°C are characterized by the fact that $G'' > G'$, as expected for a micelle solution.

The steady-state viscosity versus shear rates of sample $B_3O$ at different temperatures is shown in Figure 5. The sample shows a shear-thinning response in the whole experimental temperature region. The viscosity decreases with the temperature increasing. The value of viscosity at the shear rate 0.1 s$^{-1}$ is about $7 \times 10^3$, $6 \times 10^3$, and $3 \times 10^3$ Pa.s, at 25°C, 30°C, and 37°C, respectively. The decreasing of viscosity may be due to the increasing of temperature, accelerating the Brownian movement of molecules making the viscosity decrease.[31] The shape of the flow curves at 45°C is similar to that of at 55°C. Moreover, the values of viscosity ($6 \times 10^3$ Pa.s) decrease by one order of magnitude upon increasing temperature to 45°C and 55°C at the shear rate 0.1 s$^{-1}$. The values of viscosity decreases to about $2 \times 10^3$ Pa.s at 60°C, meaning that the liquid crystal translates to the micellar phase. The value $\eta_{0.1}$ (about 25 Pa.s) decreases sharply at 70°C. At this stage, it may be pure solution. It is worth pointing that the values of $K$ decrease with increase in temperature, which means the curcumin-hexagonal liquid crystal undergoes an order-to-disorder process. The similar variation tendency with increase in temperature can be seen in other samples $B_3O$ and $B_2O$ with lower oil content (as is shown in Figure S9 and Figure S10 of the Supplemental Material).

4. Conclusion

This work has demonstrated that Brij 97-NaDC (9:1)/EtOL/water presents very rich phases including O/W, $L_\alpha$, $H_1$, and cubic liquid crystalline phases. The rheological results show that the viscosity of curcumin-liquid crystals is smaller than those without curcumin. Curcumin dissolved in EtOL makes the elastic modulus of hexagonal and cubic phases higher than that of without curcumin, while the elastic modulus of lamellar phase is lower. These indicate a stronger elastic structure is formed in cubic and hexagonal phase but the elastic structure of lamellar phase is weakened. When curcumin is dissolved in Brij 97, the loose structure of the cubic and lamellar phase can be confirmed by the lower elastic modulus compared with that without curcumin. This means that curcumin molecules may insert into the palisade layer coexisting with Brij 97, making the structure loose. However, the elastic structure of hexagonal phase has not been obviously affected when curcumin is solubilized in Brij 97. Dissolved curcumin in both Brij 97 and EtOL can lead to more stable structure of hexagonal phase, whereas make the elastic structure of lamellar and cubic phase weaken compared with that without curcumin. Moreover, the viscosity of curcumin-hexagonal liquid crystal decreases with increase in temperature. It is worth pointing that three temperature turning points which are identified by a change in the slope of $\tan \delta (G''/G')$, reflecting the curcumin-hexagonal phase undergoes an order-to-disorder process with increase in temperature. The temperature turning point (around 52°C) is relatively higher, which is advantageous to the storage of curcumin-hexagonal liquid crystal at room temperature. So we can tune the rheological properties of the liquid crystals in this system by means of changing the sample composition, preparation method, and temperature, thereby guiding the release and antioxidant of curcumin in liquid crystals.

**Funding**

Support of this work by the National Natural Science Foundation of China (31271933, 31071603) is gratefully acknowledged.

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