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# Does transparent nematic phase exist in 5CB/DDAB/water microemulsions? From the viewpoint of temperature dependent dielectric spectroscopy

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Liquid crystal colloids have received tremendous attention because of its great potential both in the understanding of the liquid crystalline phase and in searching for new application of liquid crystals. Inverse microemulsion composed of 4-cyano-4-*n*-pentylbiphenyl (5CB), didodecyl dimethyl ammonium bromide, and water was investigated by means of broadband dielectric spectroscopy in this study. Based on the understanding of previous investigations on the same system, the isotropic phase was taken into account to quantitatively characterize the bulklike relaxations after the isotropic-to-nematic phase transition. Analogous results concerning the phase transition and phase composition to other investigations were obtained. In addition to bulklike relaxations, a new relaxation was observed at the frequency range about two orders lower than bulklike relaxations. This new relaxation shows abnormal temperature dependence, suggesting that superstructures composed of water droplets and confined 5CB molecules exist. This superstructure possibly possesses a confined nanoscaled liquid crystal ordering and may correspond to the notion of the transparent nematic phase. © 2011 American Institute of Physics. [doi:10.1063/1.3530782]

## I. INTRODUCTION

Liquid crystal (LC) colloids, which consist of colloidal particles or liquid droplets dispersed in a LC host, have attracted considerable scientific and technological interest in the last two decades.<sup>1–20</sup> What make them highly intriguing are the novel properties arising from the elastic distortion of LCs induced by the dispersed particles or droplets and fascinating colloidal structures attributed to the interparticle interaction mediated by the elastic distortions of the LC host. These new properties and structures are generally absent in conventional LCs and colloidal systems but important in technological application and fundamental science.

This study is concerned with a liquid crystal microemulsion (LCM), which is composed of surfactant-coated, nanoscaled water droplets dispersed in a typical LC [4-cyano-4-*n*-pentylbiphenyl (5CB)]. The phase behavior and phase composition of this LCM have been intensively studied in recent years by many methods,<sup>5,10,16,19,20</sup> but controversy still remains. First reported by Yamamoto and Tanaka,<sup>5</sup> this system exhibits on cooling two-phase transformations: a transition from isotropic to a new phase called “transparent nematic” (TN) phase occurs first; with further cooling, a phase separation occurs and leads to a coexistence of bulklike nematic phase and TN phase. The TN phase is macroscopically transparent but locally ordered on scales of several nanometers, which became the focus of the controversy. Later studies<sup>10,16</sup> on the same system suggested that instead of the appearance of the TN phase the system undergoes a phase demixing due to the expulsion of micelles by orientational ordering. This suggestion was supported by the result of high-resolution calorimetric experiments<sup>17</sup> on a similar system by substituting 5CB with 8CB. Nevertheless,

as pointed out in the recent study,<sup>20</sup> the phase transition and phase composition of this system depend on the sample preparation, and the “absence” of the TN phase in the later studies is possibly just because its nematic order parameter is too small to be resolvable with current methods. Accordingly, new experimental methods, for instance those capable of determining nematic order parameter values on quite small scales, are highly desirable to be employed.

Dielectric spectroscopy (DS) is believed to be one of the highly desirable methods, because it can easily cover more than 10 orders in frequency and it is very sensitive to molecular or collective dynamics on different length scales ranging from macroscopic to microscopic.<sup>21</sup> As showcased in many LC-based complex systems,<sup>21–28</sup> this method is effective to distinguish the dynamics of LC molecules at different phase states. In addition, it is noninvasive and fast letting *in situ* investigation possible and convenient. More importantly, dielectric parameters derived from different length scales are intercomplementary, which thus essentially guarantees the interpretation self-consistent. In this study, we use DS to investigate the phase transition and dynamic aspect of the same LCM as used in other studies, by which we hope to provide some information on whether the TN phase exists.

## II. EXPERIMENT AND METHODS

### A. Materials

The liquid crystal 5CB was purchased from Sigma-Aldrich and used as received. With the decreasing temperature, bulk 5CB displays an isotropic-to-nematic (IN) transition at about 35.3°C and a nematic-to-crystal (NC) transition at about 22.5°C; however, in many cases this liquid crystal can be easily supercooled to about –3°C.<sup>29</sup> The surfactant

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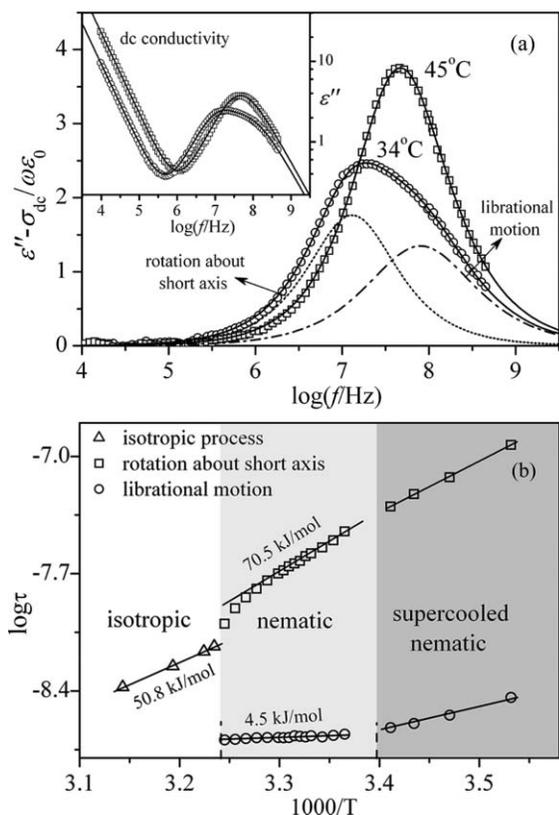


FIG. 1. (a) Frequency dependence of dielectric loss of bulk 5CB at 34 and 45°C; (b) temperature dependence of relaxation time for bulk 5CB.

didodecyl-dimethyl-ammonium-bromide (DDAB) was purchased from Tokyo Chemical Industry (Japan) and used without further purification. Water was distilled and deionized.

## B. Preparation of 5CB/DDAB/water microemulsions

The LCM under study is an inverse microemulsion composed of 5CB, water, and DDAB. We used the same preparation method as described in Refs. 5 and 20 to prepare the microemulsions. Briefly, the samples were prepared by adding 5CB to well-homogenized mixture of DDAB and water at room temperature. The DDAB/water mixture is jellylike after being fully homogenized, and the weight fraction of water in the DDAB/water mixture is fixed to 15%. The weight fractions ( $\phi_m$ ) of the DDAB/water mixture (water droplet) in LCM are 0.03, 0.05, and 0.15 (denoted as 0.03LCM, 0.05LCM, and 0.15LCM hereinafter). Prior to the dielectric measurement, the samples were subjected to ultrasonication at 60 °C for 40 min to ensure homogeneity.

## C. Dielectric measurement

The complex dielectric permittivity ( $\epsilon^* = \epsilon' - i\epsilon''$ , where  $\epsilon'$  and  $\epsilon''$  are dielectric constant and dielectric loss, respectively) of pure 5CB and LCMs were measured by an impedance analyzer (Agilent 4294A) in the frequency range from 40 to 110 MHz and a low-frequency network analyzer (HP 4195A) in the frequency range from 1 to 500 MHz. The

values of the complex permittivity were obtained from reflection measurements with a coaxial sample cell located at the end of a coaxial line. The sample cell, schematically illustrated in Fig. 5.4 in Ref. 30, is composed of an outer conductor with an inner diameter of 3.5 mm and a center conductor with an outer diameter of 2 mm. The lengths of the inner and outer conductor are 2 mm and 25 mm, respectively. Only the bottom part of the sample that locates in the gap between the inner and outer conductors (effective measurement area) can be effectively measured.

The temperature was controlled by using a Compact Ultra Low Temperature Chamber (MC-811, ESPEC Corp., Japan). The samples held by the sample cell were initially kept at 60 °C for 10 min, and then the dielectric measurements were performed at the following temperature points with an accuracy of  $\pm 0.1^\circ\text{C}$ : 45, 40, 37, 36, 35, 34, 33, 32, 31, 30, 29.5, 29, 28.5, 28, 27.5, 27, 26, 25, 24, 20, 18, 15, and 10°C. It should be pointed out that because it took over 2 h to complete each dielectric measurement run, during which the diffusion of water droplet and coexisted isotropic phase out of the effective measurement area occurs, the dielectric spectra of the LCMs might not be “real.” Fortunately, the diffusion rate of water droplet and isotropic 5CB is so low<sup>16,20</sup> that significant discrepancy from the “real” case will not exist.

## III. RESULTS AND DISCUSSION

### A. Bulk 5CB

Bulk 5CB is one of the most frequently used LC materials for DS investigation, whose dielectric behavior in different phase is well documented.<sup>24,29,31,32</sup> In the isotropic phase, it exhibits only one relaxation process assigned to the random reorientation of 5CB molecules. In the nematic phase, two relaxation processes can be observed: the slower one is related to the hindered rotation of 5CB molecules about their short axis, and the faster one is ascribed to the librational motion. If 5CB molecules are perfectly aligned ( $\mathbf{E} \parallel \mathbf{n}$ , homeotropic;  $\mathbf{E} \perp \mathbf{n}$ , planar), only either of the relaxations can be detected in the nematic phase. However, in most cases, the molecules cannot be perfectly aligned and both relaxations can be observed.

Figure 1(a) shows the frequency dependence of the dielectric loss of 5CB (after subtraction of dc conductivity) at two chosen temperatures, 45 and 34°C, corresponding to the isotropic phase and nematic phase, respectively; the total dielectric loss spectra is shown in the inset. As can be seen, only one relaxation is observed in the isotropic phase and two relaxations are observed in the nematic phase. Although we did not apply an external magnetic field or decorate the surface of the dielectric cell to orient the 5CB molecules, the molecules are mostly homeotropically aligned in the nematic phase because the dielectric cell is made of copper that favors the homeotropic alignment of LC.<sup>33</sup> Therefore, both relaxations due to short axis rotation and librational motion can be clearly observed at 34°C. The dc conductivity is observed in the low-frequency side of the total dielectric loss spectra [inset in Fig. 1(a)], which is because 5CB is not absolutely free from impurities.

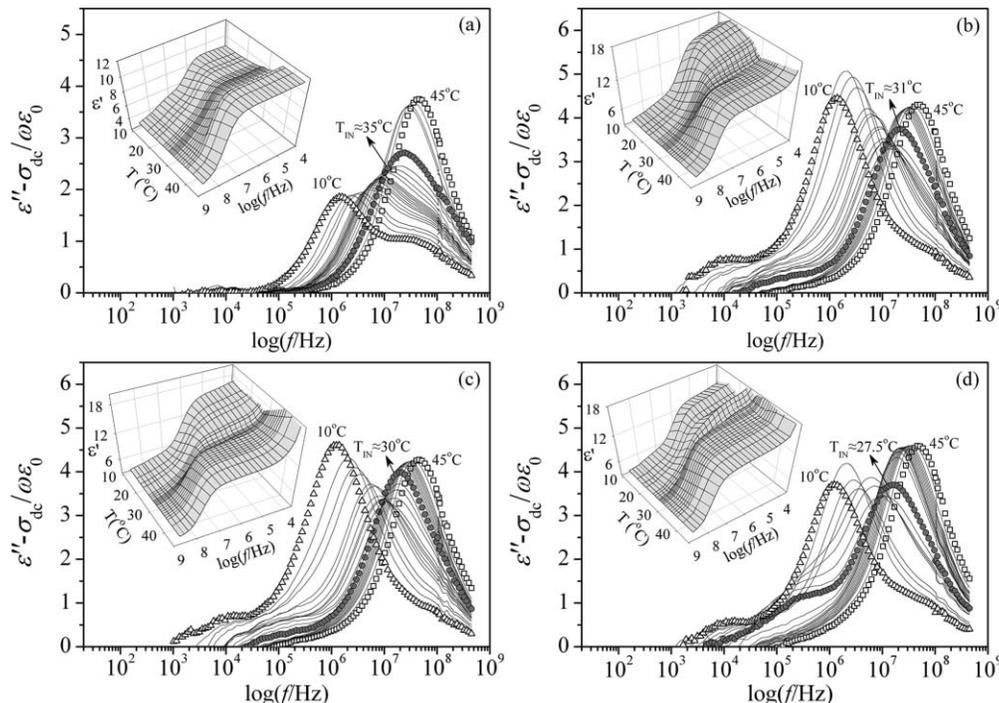


FIG. 2. (a) Dielectric loss ascribing to dielectric relaxation as a function of frequency for bulk 5CB, (b) 0.03 LCM, (c) 0.05 LCM, and (d) 0.15 LCM. The insert shows the corresponding 3D plot of dielectric constant as functions of frequency and temperature.

To quantitatively analyze the complex dielectric permittivity, we employed the following fitting function:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_j F_j^*(\omega) + \frac{\sigma_{dc}}{i\omega\varepsilon_0}, \quad (1)$$

where  $\varepsilon_\infty$  is the high-frequency limit of dielectric constant,  $\varepsilon_0$  is the permittivity of vacuum, the term  $F_j^*(\omega)$  accounts for the contribution of each dielectric relaxation, and the term  $\sigma_{dc}/i\omega\varepsilon_0$  accounts for the contribution of dc conductivity  $\sigma_{dc}$ . For  $F_j^*(\omega)$ , we use either the Havriliak–Negami function<sup>34</sup> or the Cole–Cole function,<sup>35</sup> resting with the nature of each relaxation. The Havriliak–Negami function is given by

$$F_j^*(\omega) = \frac{\Delta\varepsilon_j}{[1 + (i\omega\tau)^\beta]^\alpha}, \quad (2)$$

where  $\Delta\varepsilon_j$  is the dielectric strength,  $\tau (= 1/2\pi f_0)$  is the relaxation time,  $f_0$  is the characteristic frequency, and  $\beta$  ( $0 < \beta \leq 1$ ) and  $\alpha$  ( $0 < \alpha \leq 1$ ) are the parameters describing the shape of the curve. When  $\alpha = 1$  and  $0 < \beta \leq 1$ , Eq. (2) goes to the Cole–Cole function. In the isotropic phase, we use the Havriliak–Negami function for  $F_j^*(\omega)$  because the relaxation is broadened and asymmetric. In the nematic phase, because 5CB molecules are not perfectly aligned, the relaxations are broadened due to the distribution of relaxation time but still remain symmetric, we use Cole–Cole functions for  $F_j^*(\omega)$ . Representative curve fitting is presented in Fig. 1(a).

The dielectric spectra of bulk 5CB at all measured temperatures are displayed in Fig. 2(a). The sudden change at  $T=35^\circ\text{C}$  indicates the IN transition. When the temperature is lower than the NC transition temperature, obvious dielectric relaxations are still observed, which suggests that the system is in the supercooled nematic (SN) phase. Fig. 1(b) shows

the temperature dependence of the relaxation time, namely, Arrhenius plot. The temperature dependence of the relaxation time in the isotropic and nematic phase follows Arrhenius law that is given by

$$\tau = \tau_0 \exp\left(\frac{E_A}{k_B T}\right), \quad (3)$$

where  $E_A$  is the activation energy,  $\tau_0$  is the pre-exponential factor,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. The activation energy is determined by fitting the Arrhenius plot in line with the Arrhenius law, which is displayed in Fig. 1(b). The values of  $E_A$  in the isotropic and nematic phase are consistent with those reported in other literatures.<sup>24,26,29</sup> In the SN phase, the temperature dependence of relaxation time of both relaxations is also Arrhenius-like.  $E_A$  of the short axis rotation and the librational motion were determined to be 58.2 and 27.8 kJ/mol, respectively. The former is slightly lower than that in the nematic phase, but the latter is enormously higher. If this is the case, this result suggests that positional ordering is obviously increased in the SN phase. It should be pointed out that, however, because of the lack of experimental data in the supercooled temperature range, to assign the temperature dependence of relaxation time to Arrhenius type is somewhat arbitrary.

## B. 5CB/DDAB/water microemulsion: Dielectric spectra and dc conductivity

The phase transition of 5CB/DDAB/water microemulsion has been intensively investigated. Although controversy remains, some common features share:<sup>5,10,16,20</sup> (1) the IN phase transition is a weakly first-order transition, and the transition temperature ( $T_{IN}$ ) decreases as the concentration of

water droplet ( $\phi_m$ ) increases; (2) after the IN phase transition, there is a coexistence of the droplet-rich isotropic phase (TN phase in Yamamoto and Tanaka's case) and the droplet-poor nematic phase, and the coexistence spans a wide temperature range; (3) in the coexistence region, the droplet-rich isotropic phase diminishes with decreasing temperature.

Although the dielectric properties of LCMs have not been investigated, as far as we know, the dielectric behavior of similar LC colloids, aerosil dispersed liquid crystals (ADLC), has been well characterized by DS.<sup>25,26,28,29</sup> Two new features as compared with bulk LC were observed in ADLC: an additional slow process that occurs at a frequency range about two orders lower than the bulklike relaxations, and an acceleration of the rotation of LC molecules about their short axis. Aerosil is different from DDAB-coated water droplet in many aspects, e.g., it can strongly interact with 5CB molecules through hydrogen bond and can self-aggregate to form a network at sufficient concentration; however, the anchoring of 5CB on the surface of water droplet is believed to be weak<sup>19</sup> and the droplets are essentially self-repulsive. However, the droplet-rich isotropic phase exists even when the temperature is far below  $T_{IN}$ ; furthermore, in the vicinity of  $T_{IN}$  this isotropic phase occupies a dominant proportion of the whole system.<sup>16,20</sup> We stress that this coexisted isotropic phase must have considerable contribution to the bulklike relaxations.

Figure 2 shows the dielectric loss (after subtraction of dc conductivity) as a function of frequency for 5CB (a), 0.03 LCM, (b), 0.05 LCM (c), and 0.15 LCM (d) at different temperatures; the inset shows the corresponding 3D plots of dielectric constant spectra. As compared with bulk 5CB, an additional dielectric relaxation located at the low-frequency flank of the bulklike relaxations can be observed for LCMs over the whole investigated temperature range. Similar to bulk 5CB, the LCMs also exhibit two macroscopic phase transitions upon cooling. Before the IN transition, except for a very weak low-frequency relaxation, only one bulklike relaxation can be observed. When  $T < T_{IN}$ , the bulklike relaxation is separated into at least two relaxations; meanwhile, the dielectric strength of the low-frequency relaxation is obviously increased. After the NS transition, the low-frequency relaxation suddenly shifts to even lower frequency range. The dielectric loss behavior of each phase is represented by the symbol curves in Fig. 2, where the filled circle curve represents the case approaching IN transition.

The IN transition can be also well identified by the temperature dependence of dc conductivity ( $\sigma_{dc}$ ), as shown in Fig. 3, where we can see  $T_{IN}$  for all samples are the same as observed in their dielectric behaviors. A rough phase diagram is made on the basis of these experimental results, which is presented in the inset of Fig. 3. In the isotropic region (I), water droplets are supposed to be homogeneously dispersed in isotropic 5CB; in the coexistence region (I+N), the droplet-rich isotropic phase coexists with the droplet-poor nematic phase; in the supercooled region (I+SN), most of the 5CB molecules are in a supercooled nematic state, and small amount of isotropic 5CB may still coexist. For simplification, the droplet-rich isotropic phase and the droplet-poor nematic phase in the coexistence region will be called an isotropic phase and nematic phase hereinafter, respectively. The green

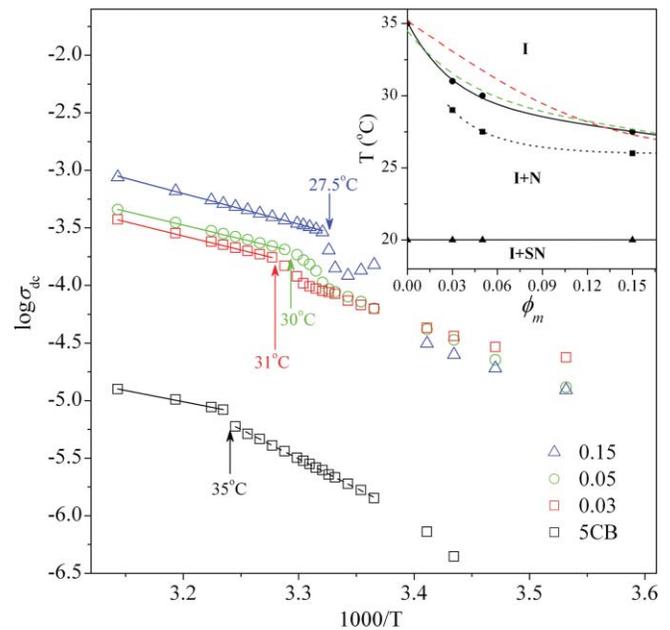


FIG. 3. Arrhenius plots of the dc conductivity of bulk 5CB and LCMs. The lines are best fits in line with the Arrhenius law, and the arrows indicate the IN phase transition temperature. The inset shows the phase diagram based on the dielectric experiment result. The solid lines are phase boundaries. I: isotropic phase; I+N: coexistence phase; SN: supercooled nematic phase. The dashed lines are the phase boundaries taken from Ref. 5 (green) and Ref. 16 (red). The dotted line indicates the microphase transition boundary in the coexistence phase (see text).

and red dashed lines in this inset represent the IN transition boundary obtained by Yamamoto and Tanaka<sup>5</sup> and Caggioni *et al.*,<sup>16</sup> respectively. As can be seen, our result is nearly consistent with that of the former group. The relatively larger discrepancy between our result and that of the latter group may be mainly because of the difference in the water content in the water/DDAB mixture.

For bulk 5CB, the temperature dependence of  $\sigma_{dc}$  in the isotropic and nematic phase follows well with the Arrhenius law but has obviously different slopes. The Arrhenius law for  $\sigma_{dc}$  is given by<sup>36</sup>

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_{dc}}{k_B T}\right), \quad (4)$$

where  $\sigma_0$  is the high temperature limit of conductivity and  $E_{dc}$  is the activation energy. In the SN phase, although  $\sigma_{dc}$  was not observed at 15 and 10°C, the temperature dependence of  $\sigma_{dc}$  is different from that in the nematic phase.  $E_{dc}$  of bulk 5CB are determined to be 37.4 and 97.6 kJ/mol for the isotropic and nematic phase, respectively. The latter is much higher than the former, indicating that the conductance in the nematic phase is more difficult than in the isotropic phase.

For LCMs, their  $\sigma_{dc}$  in the isotropic region is enormously larger than that of bulk 5CB, and the bigger  $\phi_m$  the larger  $\sigma_{dc}$ . The activation energies were determined to be 46.2, 45.9, and 50.0 kJ/mol, respectively, for 0.03, 0.05, and 0.15 LCM. They are larger than that of bulk 5CB and increase with increasing  $\phi_m$ . Because 5CB molecules are disordered as a normal oil phase, the LCMs are normal water-in-oil microemulsions in the isotropic region.

Considering the relatively low concentration and the nanoscaled size of water droplet, we believe the conductivity of the LCMs is mainly attributed to the migration of charged water droplets in the electric field, namely, the charge fluctuation model.<sup>37,38</sup> For bulk 5CB, however, the charge carrier should be small ionic impurities. Therefore, the higher  $E_{dc}$  and larger  $\sigma_{dc}$  in LCMs as compared with those of bulk 5CB should be due to the larger size and higher concentration of the charge carrier, respectively. The increase of  $E_{dc}$  with increasing  $\phi_m$  may be a result of increasing interaction between the droplets and/or increasing viscosity of the system.

When  $T < T_{IN}$ ,  $\sigma_{dc}$  decreases gradually for several degrees and then basically follows the Arrhenius law, which should be a result of the coexistence of the isotropic phase and nematic phase. According to the previous studies,<sup>16,20</sup> the isotropic phase is the dominant phase in the vicinity of  $T_{IN}$ ; with temperature decreasing, the isotropic phase keeps diminishing while the nematic phase keeps growing. As a result, the nematic phase finally becomes the dominant phase and the temperature dependence of  $\sigma_{dc}$  finally follows the Arrhenius law. We noticed that far from  $T_{IN}$  the slope of  $\sigma_{dc}$  vs  $1/T$  for 0.03 and 0.05 LCMs is obviously smaller than that of bulk 5CB, meaning that  $E_{dc}$  of LCMs is much lower than that of bulk 5CB. This result suggests that considerable amount of the isotropic phase still exists even in the low temperature range. Particularly for 0.15 LCM,  $\sigma_{dc}$  in the temperature range from 26 to 24°C shows an anti-Arrhenius behavior. A local percolation may occur as a result of the aggregation of water droplets, considering that the concentration of water droplet in the isotropic phase will increase as isotropic 5CB diminishes. However, long-range percolation is not likely formed, because  $\sigma_{dc}$  decreases again in lower temperature and follows a similar way to other LCMs.

### C. 5CB/DDAB/water microemulsion: Bulklike relaxations

As discussed above, the dielectric behavior of LCMs may be much different from that of ADLC because of the different properties of colloidal particles and the coexistence of the isotropic phase after the IN transition. To better understand the bulklike relaxation of LCMs, we compare their dielectric behavior at certain temperatures with that of bulk 5CB in Fig. 4. In the isotropic region, the max loss peak of all samples almost consists with each other, as shown in Fig. 4(a). This result suggests that the water droplets cannot remarkably influence the dynamics of the 5CB molecules. When  $T=29.5^\circ\text{C}$ , bulk 5CB, 0.03 LCM, and 0.05 LCM go to the coexistence region, but 0.15 LCM is still in the isotropic region. We can see that the max loss peak of LCMs obviously deviates from the loss peak attributed to the short axis rotation of bulk 5CB. It is rational to assume that the dynamics of 5CB molecules in the same state keep consistent. Therefore, the cases of 0.15 LCM and bulk 5CB represent the dynamics of isotropic 5CB and nematic 5CB, respectively, at this temperature. Because the fraction of the isotropic phase increases with increasing  $\phi_m$ , there are more isotropic 5CB molecules in 0.05 LCM than in 0.03 LCM. We can find from Fig. 4(b)

that the max loss peak of 0.03 LCM is closer to that of bulk 5CB than the case of 0.05 LCM, which means the more isotropic phase in LCM the larger deviation from the case of bulk 5CB. A similar phenomenon can be also observed in Fig. 4(c). At this temperature, all samples are in the coexistence region, and the deviation of the max loss peak from bulk 5CB is increasing as  $\phi_m$  increases. When  $T=10^\circ\text{C}$ , all the samples are in the supercooled region in which the isotropic phase is mostly excluded from the supercooled nematic phase if not totally. The contribution of isotropic 5CB to the bulklike dielectric behavior in LCMs should be negligibly small. Interestingly, we can find from Fig. 4(d) that the loss peaks of all samples are nearly consistent with each other again.

According to these facts, the contribution of isotropic 5CB should be taken into account in the quantitative characterization of the dielectric spectra of LCMs in the coexistence region and supercooled region. Figure 5 exemplifies the curve fitting results for LCMs in the isotropic region (a) and the coexistence/supercooled region (b). In the isotropic region, we use one Cole–Cole function for the low-frequency relaxation and one Havriliak–Negami function for the bulklike

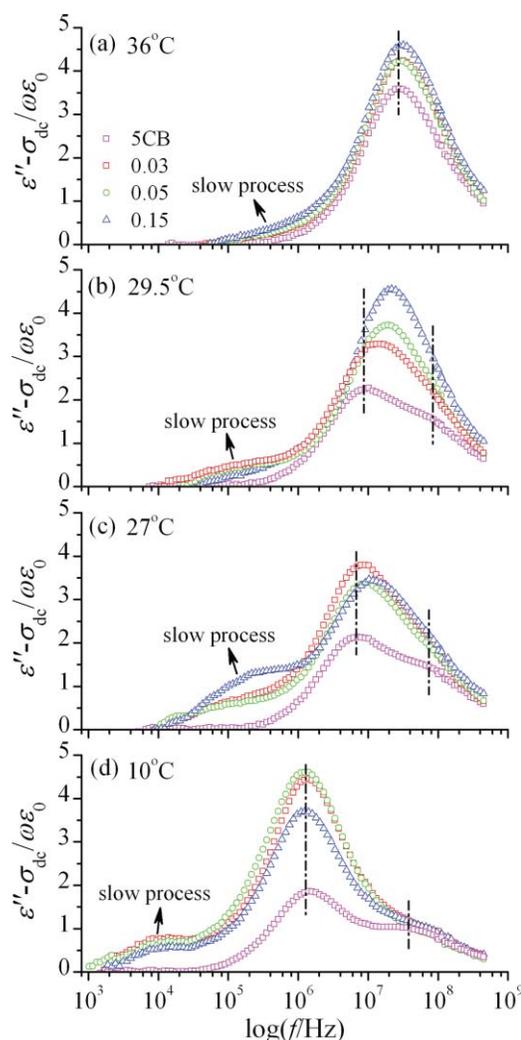


FIG. 4. Dielectric loss spectra of bulk 5CB and LCMs with different concentration of water droplet. The dash-dot-dash lines show the dielectric loss peak of bulk 5CB.

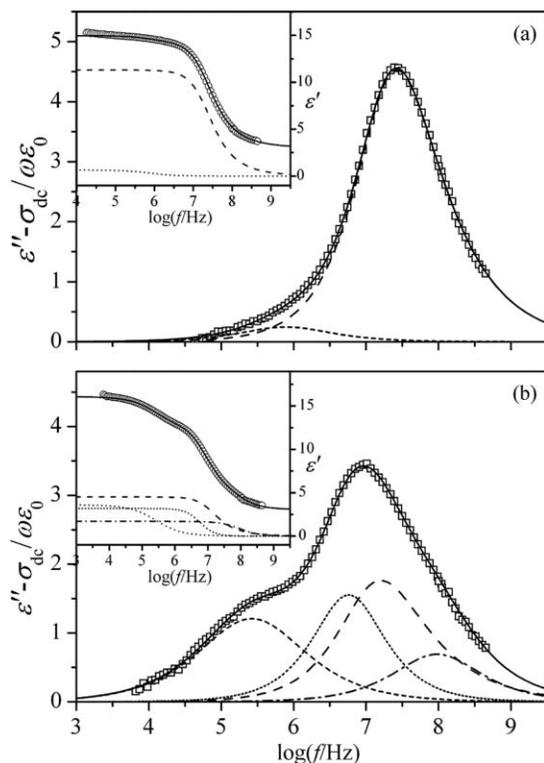


FIG. 5. (a) Representative curve fitting for 0.15 LCM in the isotropic region and (b) the coexistence or supercooled region. Short dashed line: slow process; dotted line: short axis rotation of nematic 5CB; dashed line: random reorientation of isotropic 5CB; dash-dot line: librational motion of nematic 5CB; solid line: superposition of all relaxations.

relaxation of isotropic 5CB. In the coexistence/supercooled region, we use three Cole–Cole functions for the low-frequency relaxation, the rotation of 5CB molecules about their short axis, and the librational motion, respectively, and use one Havriliak–Negami function to account for the contribution of isotropic 5CB. To ensure the fitting result is more justified, the fitting procedure for LCMs in the coexistence/supercooled region was performed on the basis of the fitting result of bulk 5CB that represents the dynamics of the 5CB molecules in the (supercooled) nematic phase.

Figure 6 shows the temperature dependence of the relaxation time of bulklike relaxations for LCMs, where the case of bulk 5CB is also presented as lines for comparison. We did not observe obvious acceleration of the relaxation due to

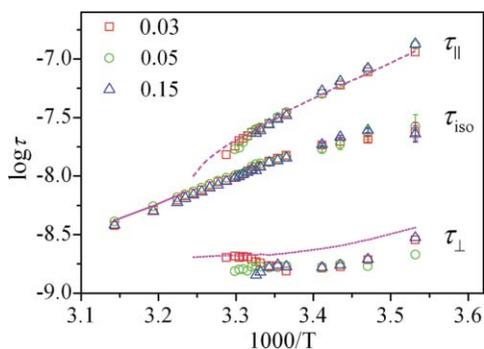


FIG. 6. Temperature dependence of the relaxation time of bulklike relaxations in LCMs. The lines stand for the case of bulk 5CB.

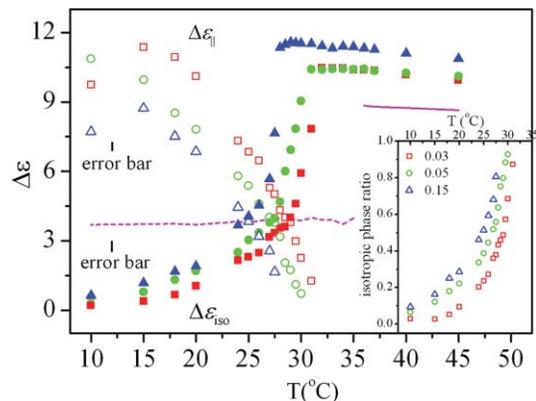


FIG. 7. Temperature dependence of the dielectric strength of the relaxation due to short axis rotation of 5CB (open symbols, dashed line) and isotropic 5CB (filled symbols, solid line). The inset shows the temperature dependence of isotropic phase ratio. squares: 0.03 LCM; circles: 0.05 LCM; triangles: 0.15 LCM; lines: bulk 5CB.

the short axis rotation of nematic 5CB molecules, but in the supercooled region this process shifts slightly to the lower frequency range as compared with that of bulk 5CB. The fraction of the isotropic phase in the supercooled region is so small that the relaxation attributed to the isotropic 5CB is much less decomposable, which results in large fitting errors for  $\tau_{\text{iso}}$ . Nevertheless, it can be seen from Fig. 6 that  $\tau_{\text{iso}}$  in the rough follows the Arrhenius law over the whole temperature range.  $\tau_{\perp}$  of LCMs is smaller than that of bulk 5CB, which is possibly because this relaxation is influenced by a faster relaxation process ascribed to the rotation of the bound water molecules in the water droplets.

Figure 7 shows the temperature dependence of the dielectric strength of the short axis rotation of nematic 5CB ( $\Delta \epsilon_{\parallel}$ ) and the relaxation of isotropic 5CB ( $\Delta \epsilon_{\text{iso}}$ ). The typical fitting error is represented as a single error bar for each relaxation, and the lines represent the case of bulk 5CB. In the isotropic region,  $\Delta \epsilon_{\text{iso}}$  of LCMs is apparently larger than that of bulk 5CB and basically increases with increasing  $\phi_m$ . The dielectric strength of dipolar fluctuation is related with the concentration and the mean square dipole moment  $\mu_0$  of the dipoles by the Kirkwood–Fröhlich equation,<sup>39,40</sup>

$$\Delta \epsilon = \frac{\epsilon_s(\epsilon_{\infty} + 2)^2}{3(2\epsilon_s + \epsilon_{\infty})} \frac{g \mu_0^2 N}{9\epsilon_0 k_B T V}, \quad (5)$$

where  $\epsilon_s$  is the static dielectric constant,  $N$  is the number of dipoles in a volume of  $V$  in the system, and  $g$  is the Kirkwood correlation factor ( $g = \mu_{\text{eff}}^2 / \mu_0^2$ ,  $\mu_{\text{eff}}$  the effective dipole moment). According to Eq. (5), the increase of  $\Delta \epsilon_{\text{iso}}$  with increasing  $\phi_m$  is strange because with increasing  $\phi_m$  the concentration of the 5CB molecule ( $N/V$ ) should decrease. The reason for such increase thus goes to the increase of the Kirkwood correlation factor.<sup>39</sup> This factor quantifies the interaction of neighboring dipoles by  $0 < g < 1$  for antiparallel correlation,  $g = 1$  for no correlation, and  $g > 1$  for parallel correlation. It is known that the 5CB molecules tend to form antiparallel pairs.<sup>41,42</sup> The addition of water droplets may break some of the antiparallel pairs and thus increase the  $g$  factor. With more water droplets added, more antiparallel pairs will be broken; therefore,  $g$  factor increases with increasing

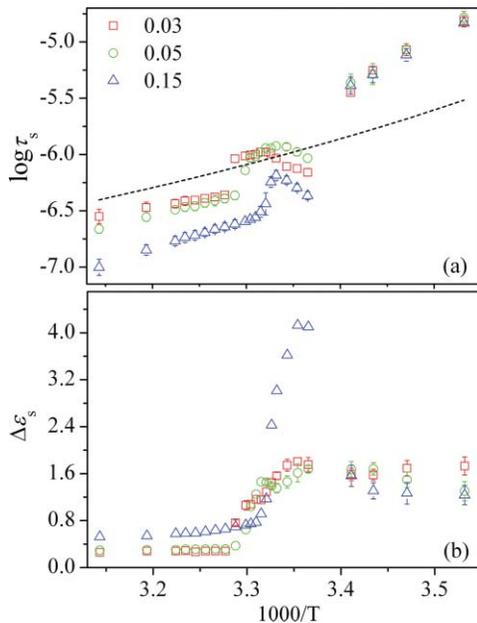


FIG. 8. Temperature dependence of relaxation time (a) and dielectric strength (b) of the slow process of LCMs. The dashed line represents the theoretical relaxation time of the rotational diffusion of water droplet.

$\phi_m$ . Similar phenomena were also observed in ADLC and 5CB/benzene mixtures.<sup>42</sup>

When  $T < T_{IN}$ ,  $\Delta\epsilon_{\parallel}$  increases while  $\Delta\epsilon_{iso}$  decreases obviously as temperature decreases. An increase of  $g$  factor cannot give rise to such a big change; this result thereby indicates a diminishing of the isotropic phase and meanwhile a growing of the nematic phase. At given temperatures, we can observe that  $\Delta\epsilon_{\parallel}$  decreases but  $\Delta\epsilon_{iso}$  increases with increasing  $\phi_m$ , which means the higher  $\phi_m$  the more isotropic phase coexists with the nematic phase. It is noteworthy that at the temperature far from  $T_{IN}$ , especially in the supercooled region,  $\Delta\epsilon_{\parallel}$  is remarkably larger than that of bulk 5CB, which can also be observed in Fig. 4(d). Also, the increase of  $g$  factor cannot give rise to such a large increase in  $\Delta\epsilon_{\parallel}$ . We believe this increase is attributed to the increase of nematic ordering parameter  $S$ ; namely, the 5CB molecules are more ordered in LCMs than in bulk 5CB. Conversely, we observed that  $\Delta\epsilon_{\perp}$  of LCMs is obviously smaller than that of bulk 5CB, which is another evidence of the increase in  $S$ . Although we do not know why the water droplet can increase the ordering parameter, it is totally possible because the samples in the dielectric cell are not intentionally oriented, as mentioned above.

The  $g$  factor at a given temperature is believed to be equivalent for the 5CB molecules both in the isotropic and nematic state; therefore, we can use  $\Delta\epsilon_{\parallel}$  and  $\Delta\epsilon_{iso}$  to represent the volume (concentration) of the nematic and isotropic phase, respectively, according to Eq. (5). The isotropic phase ratio in the coexistence and supercooled region thus can be roughly estimated by  $\Delta\epsilon_{iso}/(\Delta\epsilon_{iso} + \Delta\epsilon_{\parallel})$ . The inset in Fig. 7 shows the estimated isotropic phase ratio at different temperatures, which is similar to those determined by other experiments.<sup>16,20</sup>

#### D. 5CB/DDAB/water microemulsion: Slow process

The slow process observed in ADLC is attributed to the retarded relaxation of the LC molecules at the particle surface. The main features of this process include its presence in both isotropic and nematic phase, a dielectric strength that scales with particle concentration, and a temperature dependence of relaxation time that is almost independent of the phase transition.<sup>25,26,28,29</sup> Figure 8 shows the temperature dependence of the relaxation time  $\tau_s$  (a) and the dielectric strength  $\Delta\epsilon_s$  (b) of the slow process for the LCMs. We can notice that both  $\tau_s$  and  $\Delta\epsilon_s$  are strongly dependent on the phase transition, especially for 0.15 LCM whose  $\Delta\epsilon_s$  in the coexistence region has a magnitude comparable to that of bulk relaxations. We consider that the mechanism of retarded surface LC molecular relaxation proposed in ADLC alone cannot account for the slow process in all these phase regions; namely, the slow process in different phase regions may be attributed to different mechanisms.

In addition to the retarded rotation of surface LC molecules, other mechanisms are possibly responsible for the slow process. One of the possibilities is the Maxwell–Wagner effect due to the heterogeneity of the LCMs. The relaxation time of this effect for a spherical particle is given by

$$\tau_{MW} = \frac{2\epsilon_m + \epsilon_p + \phi_v(\epsilon_m - \epsilon_p)}{2\sigma_m + \sigma_p + \phi_v(\sigma_m - \sigma_p)}\epsilon_0, \quad (6)$$

where the subscripts  $m$  and  $p$  denote the dispersing medium and dispersed particle, respectively, and  $\phi_v$  is the volume fraction of the particle ( $\phi_v \sim 1.15 \cdot \phi_m$ , calculated from the density profiles of the components).<sup>16</sup> According to the weight fraction of water in the droplet (0.15), the molar ratio of water to DDAB is about 4, which means all water molecules are tightly bound with the counterion ( $\text{Br}^+$ ) and/or the head of DDAB.<sup>44</sup> Therefore, the dielectric constant of bound water ( $\approx 5$ ) should be given to  $\epsilon_p$ . The value of  $\sigma_m$  determined from Fig. 3 is of the order of  $10^{-5}$  S/m. The value of  $\sigma_p$ , however, should be very large because the concentration of  $\text{Br}^+$  in the water pool is estimated to be about 14 mol/L. An exact value for  $\sigma_p$  is not possibly provided since all water molecules are bound. We take a value of 1 S/m for a typical microemulsion for  $\sigma_p$ .  $\tau_{MW}$  thus is estimated to be 0.2–0.3 ns, which is far smaller than  $\tau_s$  in any phase regions. This mechanism thereby cannot be the origin of the slow process in any phase regions.

The dynamics correlated with the water droplet is another possible mechanism. Because of the low molar ratio of water to DDAB, the water droplet is believed to be “rigid.” The rearrangement process and the thermal shape fluctuation of droplet are therefore forbidden. However, the rotational diffusion of the whole water droplet may contribute to the slow process. The corresponding relaxation time is given by<sup>38,45</sup>

$$\tau_{rot} = \frac{4\pi\eta a^3}{k_B T}, \quad (7)$$

where  $\eta$  is the viscosity of the dispersing medium (5CB), and  $a$  is the radius of the particle, which in the present case nearly equals to 2 nm.<sup>5,16,19,20</sup> By taking the value of  $\eta$  of bulk 5CB from Ref. 43, we can estimate  $\tau_{rot}$  in the investigated temperature range, which is plotted in Fig. 8(a). We can see that the

theoretical  $\tau_{rot}$  remains on a scale comparable to  $\tau_s$ . Therefore, this mechanism may be responsible for the slow process in some phase regions.

In the isotropic region, the LCMs are normal water-in-oil microemulsions free from paranematic fluctuation. The slow process is very weak and has a temperature dependence of  $\tau_s$  that nearly follows the Arrhenius law. The activation energies determined by the Arrhenius law are 26.8, 38.9, and 45.7 kJ/mol, respectively, for 0.03, 0.05, and 0.15 LCM. These values remain on a scale comparable to that derived from the temperature dependence of the viscosity of 5CB (Ref. 43), implying that the slow process correlates to the viscosity of 5CB. Comparing  $\tau_s$  in this case with that in ADLC, we can find  $\tau_s$  in both cases remain on the same time scale and have a similar dependence on  $\phi_m$ . On the other hand, from Fig. 8(a) we can see that  $\tau_{rot}$  systematically exceeds  $\tau_s$  in the isotropic region. Furthermore, because  $a$  and  $\eta$  are supposed to be equivalent for all LCMs,  $\tau_s$  should be independent of  $\phi_m$  if the rotational diffusion of water droplet accounts for the slow process. This is not the case as can be seen in Fig. 8(a). According to these facts, the slow process in the isotropic region should be attributed to the retarded rotation of the 5CB molecules on the surface of water droplets.

In the coexistence region approaching  $T_{IN}$ , both  $\tau_s$  and  $\Delta\epsilon_s$  are suddenly increased by a factor of about two. It is noteworthy that,  $\tau_s$  in this phase region has a nonmonotonic dependence on the temperature, with an inflexion temperature nearly corresponds to the temperature that  $\Delta\epsilon_{||}$  starts to get bigger than  $\Delta\epsilon_{iso}$ . The inflexion temperature is plotted in the inset in Fig. 3. On the other hand,  $\Delta\epsilon_s$  monotonically increases with decreasing temperature and finally achieves a magnitude more than five times of that in the isotropic region. It is impossible to expect the rotation of the surface 5CB molecules to give rise to such behaviors, because  $\phi_m$  will not increase during the phase transition, i.e., the concentration of surface 5CB molecules cannot keep increasing. We believe this behavior reflects the change of phase composition with temperature.

Because the isotropic phase keeps diminishing while the nematic phase keeps growing, a microscopic phase evolution from a nematic-in-isotropic phase via a bicontinuous phase to an isotropic-in-nematic phase is expected in the coexistence region. At the early stage, droplets of the nematic phase appear and are dispersed in the isotropic phase. This is evidenced by the polarizing microscope observation.<sup>5</sup> The nematic phase keeps growing as temperature decreases, and the bicontinuous phase will be formed when the amount of the nematic phase and the isotropic phase are comparable. With further growing, the nematic phase finally becomes the continuous phase and the isotropic phase is dispersed as droplets. In the nematic-in-isotropic phase, although the volume fraction of the nematic phase is small, the paranematic fluctuation becomes important, which along with van der Waals force will yield an attractive force among the water droplets.<sup>19</sup> The diminishing of the isotropic phase, on the other hand, actually increases the local concentration of water droplets. Therefore, the water droplets in the isotropic phase have a strong tendency to aggregate. This aggregation, however, should remain in short range because no percolation phenomenon is

observed during the phase transition for all LCMs. With the growing of the nematic phase, more and more small aggregates will be formed, but most of them are free in the isotropic phase. When in the isotropic-in-nematic phase, since the isotropic phase itself is dispersed as droplets, we believe that the water droplet aggregates are confined in the isotropic droplets.

This evolution of the phase composition is manifested itself by the dielectric behavior of the slow process. In the nematic-in-isotropic phase, the sudden increase of  $\tau_s$  and  $\Delta\epsilon_s$  cannot be a result of the rotation of water droplet aggregates, because even a two-droplet pair will increase  $a$  by a factor of more than 2 (regarding each aggregate as a dipole), which will lead to an increase of  $\tau_s$  by a factor of more than 8. We suggest that the aggregates are superstructure composed of not only water droplets but also the 5CB molecules confined among the droplets. Because of the surface anchoring, these 5CB molecules may possess a local ordering with a scale of several nanometers. We judge this based on the following consideration:  $\Delta\epsilon_s$  keeps increasing with decreasing temperature, which means the concentration of the relaxing unit (dipole) that accounts for the slow process has a continuous increase. The concentration of the nematic phase and the aggregates increases with decreasing temperature; however, both of them cannot give rise to the slow process. Consequently, the slow process in this phase is most likely attributed to the retarded rotation of the confined 5CB molecules within the aggregates. Further evidence of this scenario is given by the dielectric behavior of the slow process in the isotropic-in-nematic phase. In this phase the aggregate itself is confined in the isotropic droplets. Different from the nematic-in-isotropic or the bicontinuous phase where there are enough bulk isotropic 5CB that can transform to nematic 5CB, in the isotropic-in-nematic phase the bulk isotropic 5CB is insufficient and therefore some of 5CB molecules originally confined in the aggregates will be released. As a result, the number of 5CB molecules confined in the aggregates will be decreased, and the rotation of the remaining molecules will be accelerated because of the increasing free volume for each molecule to perform the rotation. This acceleration of confined molecules has been reported in many confined systems and concluded in a recent review.<sup>46</sup> This also explains the abnormal temperature dependence of  $\tau_s$  shown in Fig. 8(a).

In the supercooled region,  $\tau_s$  is remarkably increased again (about one order) while  $\Delta\epsilon_s$  is slightly decreased (except for the case of 0.15 LCM), and the magnitude of both  $\tau_s$  and  $\Delta\epsilon_s$  for all LCMs are nearly equivalent. The  $\phi_m$ -independent  $\tau_s$  and  $\Delta\epsilon_s$  suggest that the phase composition of all the LCMs is quite similar. The slow process in this region is not possibly attributed to the relaxation of the confined 5CB molecules within the aggregates, because this relaxation has an obvious dependence on  $\phi_m$ , as shown in the coexistence region. The rotation of the surface 5CB molecules cannot give rise to this slow process either, considering that  $\Delta\epsilon_s$  is much larger than that in the isotropic region. The most possible mechanism is the rotational diffusion of water droplet because the radius of the droplet is equivalent for all LCMs, which can result in a  $\phi_m$ -independent  $\tau_s$ . The nearly  $\phi_m$ -independent  $\Delta\epsilon_s$  suggests that the concentration of water droplet in this region

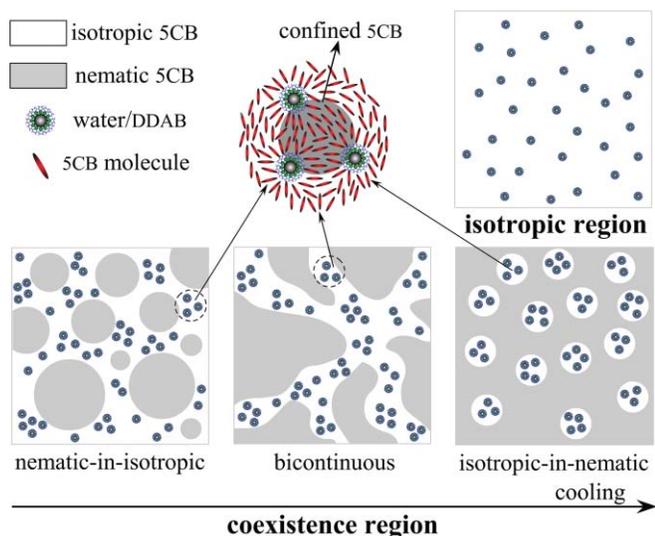


FIG. 9. Schematically illustration of possible morphologies and phase composition of LCMs in the isotropic and coexistence region.

is comparable for all LCMs. This may be because the concentration of water droplets in the effective measurement area is equivalent for all LCMs. From Fig. 8(a) we can find that  $\tau_s$  in this region is obviously lower than the theoretical  $\tau_{rot}$ . This seems to suggest that the water droplets in this region might be accompanied by topological defect such as hedgehog and Saturn-ring,<sup>1,2</sup> which is able to increase the effective radius of the water droplets.

#### IV. CONCLUDING REMARKS

The dielectric property of 5CB/DDAB/water microemulsion as a function of temperature is characterized by means of dielectric spectroscopy. In addition to the bulklike dielectric relaxations, a slow process located at the low-frequency side of the bulklike relaxation is also observed. The variation of the relaxation behavior with temperature clearly indicates the phase transition.

For the bulklike relaxations, the result suggests that the contribution of the coexisted isotropic 5CB should be taken into account in the quantitative analysis on the dielectric spectra in the coexistence and supercooled region. The macroscopic phase transition and phase composition are confirmed in this way, which are consistent with those determined by other methods.

The dielectric behavior of the slow process shows strong dependence on the phase transition. We found this slow process in different phase region has a different origin: in the isotropic region, it is attributed to the retarded rotation of the 5CB molecules on the surface of the water droplet; in the coexistence region, it is attributed to the rotation of the confined 5CB molecules within water droplet aggregates; and in the supercooled region, it is a result of the rotational diffusion of water droplets. The dielectric behavior of the slow process thus suggests a possible microscopic phase evolution as summarized in Fig. 9. In the isotropic region, the water droplets are homogeneously dispersed and the whole system acts like a normal water-in-oil microemulsion. In the coexistence region,

the system evolves from a nematic-in-isotropic phase via a bicontinuous phase to an isotropic-in-nematic phase with the decreasing temperature. Water droplets starts to aggregate at the IN transition. The aggregates may have a superstructure composed of several water droplets and some 5CB molecules. These 5CB molecules could be confined and may have a local ordering on a scale of several nanometers. This superstructure possibly corresponds to the notion of the transparent nematic phase.

Finally, we would like to point out that, due to the diffusion of water droplets and isotropic 5CB out of the effective measurement area, the dielectric behavior of LCMs at certain temperature, especially in lower temperature range, might not reflect exactly the “real” phase composition, as mentioned in Sec. II. In order to more accurately understand the phase behavior of such system, we stress that the factor of time should be also taken into account. The investigation on the dielectric behavior of the same system as a function of time is on the way.

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- <sup>1</sup>P. Poulin, *Curr. Opin. Colloid Interface Sci.* **4**, 66 (1999).
- <sup>2</sup>M. Zapotocky, L. Ramos, P. Poulin, T. C. Lubensky, and D. A. Weitz, *Science* **283**, 209 (1999).
- <sup>3</sup>S. P. Meeker, W. C. K. Poon, J. Crain, and E. M. Terentjev, *Phys. Rev. E* **61**, R6083 (2000).
- <sup>4</sup>H. Stark, *Phys. Rep.* **351**, 387 (2001).
- <sup>5</sup>J. Yamamoto and H. Tanaka, *Nature (London)* **405**, 321 (2001).
- <sup>6</sup>V. J. Anderson, E. M. Terentjev, S. P. Meeker, J. Crain, and W. C. K. Poon, *Eur. Phys. J. E* **4**, 11 (2001).
- <sup>7</sup>P. G. Petrov and E. M. Terentjev, *Langmuir* **17**, 2942 (2001).
- <sup>8</sup>J. L. West, A. Glushchenko, G. Liao, Y. Reznikov, D. Andrienko, and M. P. Allen, *Phys. Rev. E* **66**, 012702 (2001).
- <sup>9</sup>V. G. Nazarenko, A. B. Nych, and B. I. Lev, *Phys. Rev. Lett.* **87**, 075504 (2001).
- <sup>10</sup>T. Bellini, M. Caggioni, N. A. Clark, F. Mantegazza, A. Maritan, and A. Pelizzola, *Phys. Rev. Lett.* **91**, 085704 (2003).
- <sup>11</sup>J. Cleaver and W. C. K. Poon, *J. Phys.: Condens. Matter* **16**, S1901 (2004).
- <sup>12</sup>D. Vollmer, G. Hinze, W. C. K. Poon, J. Cleaver, and M. E. Cates, *J. Phys.: Condens. Matter* **16**, L227 (2004).
- <sup>13</sup>J. C. Loudet, P. Barois, P. Auroy, P. Keller, H. Richard, and P. Poulin, *Langmuir* **20**, 11336 (2004).
- <sup>14</sup>I. Smalyukh, S. Chernyshuk, B. I. Lev, A. B. Nych, U. Ognysta, V. G. Nazarenko, and O. D. Lavrentovich, *Phys. Rev. Lett.* **93**, 117801 (2004).
- <sup>15</sup>I. Musevic, M. Skarabot, U. Tkalec, M. Ravnik, and S. Zumer, *Science* **313**, 954 (2004).
- <sup>16</sup>M. Caggioni, A. Giacometti, T. Bellini, N. A. Clark, F. Mantegazza, and A. Maritan, *J. Chem. Phys.* **122**, 214721 (2005).
- <sup>17</sup>Z. Kutnjak, G. Cordoyiannis, G. Nounesis, A. Lebar, B. Zalar, and S. Žumer, *J. Chem. Phys.* **122**, 224709 (2005).
- <sup>18</sup>A. B. Nych, U. M. Ognysta, V. M. Pergamenschik, B. I. Lev, V. G. Nazarenko, I. Musevic, M. Skarabot, and O. D. Lavrentovich, *Phys. Rev. Lett.* **98**, 057801 (2007).
- <sup>19</sup>G. Toquer, G. Porte, M. Nobili, J. Appell, and C. Blanc, *Langmuir* **23**, 4081 (2007).
- <sup>20</sup>A. Lebar, Z. Kutnjak, H. Tanaka, B. Zalar, and S. Žumer, *Phys. Rev. E* **78**, 031707 (2008).
- <sup>21</sup>F. Kremer and A. Schonhals, *Broadband Dielectric Spectroscopy* (Springer-Verlag, Berlin, 2002).
- <sup>22</sup>R. Stannarius and F. Kremer, “Liquid crystals in confining geometries,” in *Molecules in Interaction with Surfaces and Interfaces*, edited by

- R. Haberlandt, D. Michel, A. Pöpl, and R. Stannarius (Springer-Verlag, Berlin, 2004), pp. 301–326.
- <sup>23</sup>F. M. Aliev, Z. Nazario, and G. P. Sinha, *J. Non-Cryst. Solids* **305**, 218 (2002).
- <sup>24</sup>F. M. Aliev, M. R. Bengoechea, C. Y. Gao, H. D. Cochran, and S. Dai, *J. Non-Cryst. Solids* **351**, 2690 (2005).
- <sup>25</sup>J. Leys, G. Sinha, C. Glorieux, and J. Thoen, *Phys. Rev. E* **71**, 051709 (2005).
- <sup>26</sup>J. Leys, “Broadband dielectric spectroscopy of confined liquid crystals and hydrogen bonded liquids,” PhD dissertation (Katholieke Universiteit Leuven, 2007).
- <sup>27</sup>A. R. Brás, M. Dionísio, and A. Schönhal, *J. Phys. Chem. B* **112**, 8227 (2008).
- <sup>28</sup>J. Leys, C. Glorieux, and J. Thoen, *J. Phys.: Condens. Matter* **20**, 244111 (2008).
- <sup>29</sup>S. A. Rózański, G. P. Sinha, and J. Thoen, *Liq. Cryst.* **33**, 833 (2006).
- <sup>30</sup>T. K. Bose, R. Chahine, and R. Nozaki, in *Microwave Aquametry*, edited by A. Kraszewski (IEEE, New York, 1996), pp. 81–92.
- <sup>31</sup>J. M. Wacrenier, C. Druon, and D. Lippens, *Mol. Phys.* **43**, 97 (1981).
- <sup>32</sup>Z. Nazario, G. Sinha, and F. Aliev, *Mol. Cryst. Liq. Cryst.* **367**, 3121 (2001).
- <sup>33</sup>J. Mijovic and J. Sy, *Macromolecules* **33**, 9620 (2000).
- <sup>34</sup>S. Havriliak and S. Negami, *Polymer*, **8**, 161 (1967).
- <sup>35</sup>K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).
- <sup>36</sup>A. Catenaccio, Y. Daruich, and C. Magallanes, *Chem. Phys. Lett.* **367**, 669 (2003).
- <sup>37</sup>H. F. Eicke, M. Bercovec, and B. Das-Gupta, *J. Phys. Chem.* **93**, 314 (1989).
- <sup>38</sup>Y. Feldman, N. Kozlovich, I. Nir, and N. Garti, *Phys. Rev. E* **51**, 478 (1995).
- <sup>39</sup>J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).
- <sup>40</sup>H. Fröhlich, *Theory of Dielectrics*, 2nd ed. (Oxford University Press, Oxford, 1958).
- <sup>41</sup>C. Amovilli, I. Cacelli, S. Campanile, and G. Prampolini, *J. Chem. Phys.* **117**, 3003 (2002).
- <sup>42</sup>S. K. Kundu, S. Okudaira, M. Kosuge, N. Shinyashiki, and S. Yagihara, *J. Chem. Phys.* **129**, 164509 (2008).
- <sup>43</sup>J. Jadzyn, R. Dabrowski, T. Lech, and G. Czechowski, *J. Chem. Eng. Data* **46**, 110 (2001).
- <sup>44</sup>A. Berthod, O. Nicolas, and M. Porthault, *Anal. Chem.* **62**, 1402 (1990).
- <sup>45</sup>P. J. Debye, *Polar Molecules* (Chemical Catalog, New York, 1929).
- <sup>46</sup>Y. E. Ryabov, A. Puzenko, and Y. Feldman, *Phys. Rev. B* **69**, 014204 (2004).