Characterizing Water Behavior in $\alpha$-Gel ($\alpha$-Type Hydrated Crystal) Formed from Monohexadecyl Phosphate and L-Arginine

Keisuke Tanaka$^{1,2}$, Yuki Hirai$^2$, Toshiyuki Suzuki$^{1,2}$, Masaaki Akamatsu$^2$, Kenichi Sakai$^{2,3,*}$, and Hideki Sakai$^{2,3,*}$

$^1$NIKKOL GROUP Cosmos Technical Center Co., Ltd., 3-24-3 Hasune, Itabashi, Tokyo 174-0046, JAPAN
$^2$Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, JAPAN
$^3$Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, JAPAN

Abstract: Monohexadecyl phosphate, neutralized by L-arginine (C16MP-Arg), forms an $\alpha$-gel ($\alpha$-type hydrated crystal) with water. In this study, we characterized the behavior of water in the C16MP-Arg $\alpha$-gel system by means of small/medium angle X-ray scattering (SWAXS), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), and $^1$H nuclear magnetic resonance (NMR) spectroscopy. An increased water concentration resulted in an increase in the $d$-spacing of the lamellar bilayers as well as an increased wavenumber for the O-H stretching vibration peak. In addition, the melting enthalpy increased with increasing water concentration, while freezing was not observed below a water concentration of 20 wt%. These results suggest that the overall properties of water changed as a function of its concentration in the sample. $^1$H-NMR spin-spin relaxation time ($T_2$) measurements further suggest that the protons of water and C16MP-Arg can be classified into three components (low-, middle-, and high-$T_2$ components) as a function of the temperature and concentration. The low-$T_2$ component mainly arose from the protons of C16MP-Arg alkyl chains, and its mobility increased with increasing temperature. The high-$T_2$ component arose from the protons of water. The water behaved as “bound water” for the C16MP-Arg headgroups at $-30^\circ$C and a water concentration of 20 wt%, and the mobility increased with increasing temperature and water concentration. These changes suggest that an increased water concentration results in an increased amount of water being incorporated between the C16MP-Arg lamellar bilayers as well as in spaces surrounded by $\alpha$-gel domains.

Key words: $\alpha$-gel, $\alpha$-type hydrated crystal, monohexadecyl phosphate, water, L-arginine, spin-spin relaxation time ($T_2$)

1 Introduction

Surfactants form a variety of aggregates in water$^1$. These aggregates, for instance, micelles, lamellar liquid crystals (LC), and hexagonal LCs, are thermodynamically stable. $\alpha$-Gels, also called $\alpha$-type hydrated crystals, or $\alpha$-form hydrated crystalline phases, are one type of molecular assembly formed from surfactants and water. The structural features of $\alpha$-gels are summarized as follows$^{2-5}$: First, the surfactant and fatty alcohol (long-chain alcohol) molecules forming the $\alpha$-gel form a repeated structure of lamellar bilayers. A large quantity of water can be incorporated between the bilayers, and hence $\alpha$-gel has been widely used in cosmetic, toiletry, and pharmaceutical products. Second, the alkyl chains of the surfactant and fatty alcohol molecules are hexagonally packed in a solid state. This is a substantial difference from lamellar LCs, where alkyl chains are molten$^6$. In addition, $\alpha$-gels are generally thermodynamically unstable, which is a significant difference from lamellar LCs. Most earlier studies focusing on the formation and characterization of $\alpha$-gels have employed ternary mixtures of ionic surfactants, fatty alcohols, and water$^7-12$.

Recently, we reported that highly purified monohexadecyl phosphate neutralized by L-arginine (C16MP-Arg) could form an $\alpha$-gel with water, over wide ranges of water concentrations and temperatures$^{13}$. Generally, $\alpha$-gel...
systems can be prepared by mixing the materials at a temperature above their melting points and subsequently cooling the mixture to below their melting points\textsuperscript{10}. C16MP-Arg contains a large amount of water just after its preparation. However, the structure transforms to thermodynamically stable precipitates (e.g. β- or γ-crystal) by releasing its inner water over time. In other words, the presence of the internal water is important in the stabilization of the α-gel structure for long periods of time\textsuperscript{16,19}. Watanabe et al. reported that two types of water with different mobilities coexisted in a sodium methyl stearoyl taurate/behenyl alcohol/water ternary α-gel system. They distinguished these two types of water using a Fourier transform infrared spectroscopy (FT-IR) technique to monitor the self-diffusion coefficients of \( \delta C \)\textsuperscript{1}\textsuperscript{2}\textsuperscript{1}\textsuperscript{3}\textsuperscript{-}crystal by re-

\textsuperscript{13}H nuclear magnetic resonance (NMR) spectroscopy. The purpose of this study is to determine the presence of water with different mobilities and interactions in the C16MP-Arg/water α-gel system.

\section*{2 Experimental Section}
\subsection*{2.1 Materials and sample preparation}

The information about the materials used in this study, C16MP-Arg and water, and the method of preparation for the α-gel samples were presented in a previous report\textsuperscript{13}. The chemical structure of C16MP-Arg is depicted in Fig. 1. In our current study, we prepared 1 g samples for SWAXS, DSC and FT-IR measurements, and 4 g samples for \( ^{13} \text{H-NMR} \) measurements.

\subsection*{2.2 Measurements}

The experimental details for SWAXS and DSC measurements were presented in a previous report\textsuperscript{13}. In our current study, the measurement temperature was set at 25°C for SWAXS, and ranged from −50 to 25°C for DSC.

FT-IR measurements were carried out using a JEOL FT/IR-6100 spectrometer using the attenuated total reflection (ATR) method. FT-IR ATR spectra were recorded using a single reflection horizontal ATR accessory with a spherical ZnSe crystal fixed at an incident angle of 45°. Spin-spin relaxation time (\( T_2 \)) measurements were performed on a JEOL JNM-MU25 NMR spectrometer using the solid echo method. The frequency of a proton (\( ^{1} \text{H} \)) was 25 MHz and the measurement temperatures were set at −30°C, 25°C, and 65°C. The \( T_2 \) values were calculated with the solid echo pulse sequence; pulse length = 2 \( \mu \text{s} \), recycle delay time = 8 s, and four repetitions. The free induction decay (FID) curves were fitted using Equation 1:\textsuperscript{18–20};

\begin{equation}
M(t) = \sum M_i(0) \exp \left(-\frac{t}{T_2^{i}}\right)^{w_i}
\end{equation}

where, \( M(t) \) is the decay of the magnetization at time \( t \), \( M_i(0) \) is the magnetization of component \( i \) at time 0, and \( w_i \) is power value of component \( i \). The \( w_i \) value indicates the shape of the FID curves. For example, \( w_i = 1.0 \) was applied when the logarithmic FID data decreased linearly with time. This indicates the presence of the “soft” component with high proton mobility. However, \( w_i = 1.5 \) or 2.0 was applied when the logarithmic FID data did not decrease linearly. This indicates the presence of the “hard” component with low proton mobility. In this study, the \( T_2 \) of each component was determined from one FID.

\subsection*{2.3 Results and Discussion}

Figure 2 shows the long-range \( d \)-spacings of the α-gel system at various water concentrations\textsuperscript{10}, determined from the first peak position in the SWAXS patterns. The SWAXS patterns were reported in our recent study\textsuperscript{19}, where we confirmed α-gel formation on the basis of the following results: (i) the lamellar structure was confirmed by the presence of repeated peaks in the small-angle region (\( q \) value ratio = 1:2:3); and (ii) the hexagonal packing arrangement of the hydrophobic alkyl chains was confirmed by the presence of a sharp peak detected at \( q = 15 \text{ nm}^{-1} \). In Fig. 2, we have included the estimated \( d \)-spacings (solid curve), determined using Equation 2, under the assumption that all of the water added to the system was incorporated into the lamellar bilayers:\textsuperscript{24}

\begin{equation}
d = 2l \frac{(1-C)\rho_w + C\rho_s}{C\rho_s}
\end{equation}

where \( C \) is the C16MP-Arg weight fraction, \( l \) is the molecular length of C16MP, \( \rho_w \) is the water density, and \( \rho_s \) is the C16MP density. We assumed the following values for this study: \( l = 2.000 \text{ nm} \), \( \rho_w = 1.000 \text{ g} \cdot \text{cm}^{-3} \), and \( \rho_s = 1.013 \text{ g} \cdot \text{cm}^{-3} \).
cm$^{-3}$. The long-range $d$-spacing increased with increasing water concentration. This behavior is typical for α-gel systems\cite{15,14}. When the water concentration was above 80 wt\%, a large difference between the measured and calculated values of $d$-spacing was observed, indicating that the C16MP-Arg α-gel system could not incorporate all of the water within its lamellar bilayers. Previously we reported that water separation was not visually observed even above a water concentration of 80 wt\%\cite{10}. Hence the excess water that could not be incorporated into the α-gel bilayers might have been trapped in the interspaces of the dispersed α-gel domains. In contrast, below a concentration of 80 wt\%, it seems likely that the water was incorporated into the α-gel lamellar bilayers.

In order to understand the interactions of each water phase, the O-H stretching frequency of water was examined by FT-IR spectroscopy. The FT-IR spectra measured at various water concentrations are shown in Fig. 3. The O-H stretching peak shifts to higher wavenumbers with increasing water concentration. It should be recalled that all of the water was incorporated into the α-gel lamellar bilayers below a water concentration of 80 wt\%, according to the SWAXS results. Morita et al. reported that the shift in O-H vibration depended on the interactions of the O-H groups with a bio-compatible polymer and water\cite{25}. They found that the O-H vibrations for water were dependent on the mobility of water under different conditions; increased interactions resulted in a shift of the O-H vibration toward lower wavenumbers. In agreement with these observations, an O-H stretching vibration appeared in the low-wavenumber region in our study. This suggests that water molecules interact not only with each other, but also with the hydrophilic part of C16MP-Arg. However, at high water concentrations, the interactions between water molecules become predominant. Hence, the O-H stretching vibration shifted to that of water.

Thermal behavior of water in the α-gel system was evaluated by DSC as a function of the water concentration. All samples were frozen at $-50^\circ$C for two hours and then the water in each sample was determined by measuring the melting enthalpy $\Delta H$ (J·g$^{-1}$) at approximately 0°C. DSC data obtained at various water concentrations are depicted in Fig. 4. $\Delta H$ was calculated from the endothermic peak areas detected at approximately 0°C for each water concentration. The calculation results are illustrated in Fig. 5. $\Delta H$ increased with increasing water concentration. Interestingly, $\Delta H$ could not be determined below a water concentration of 20 wt\%, suggesting that the water incorporated into the α-gel bilayers did not freeze even below 0°C. In other words, all of the water at this concentration existed adjacent to hydrophilic groups of C16MP-Arg as bound water (i.e., non-freezing water\cite{24,20}). The linear increase in $\Delta H$ values vs. the water concentration (>20 wt\%) suggests that the quantity of water molecules bound to the C16MP-Arg headgroups is constant for water concentrations above 20 wt\%.

In order to characterize the behavior of water in the α-gel system in more detail, the spin-spin relaxation time (T$_2$) was measured by $^1$H NMR spectroscopy. The resultant FID data are shown in the Supporting Information, Fig. S1, with fitting curves based on Equation 1. This equation yielded the T$_2$ for each relaxation component as well as its relative abundance. When the logarithmic FID data decrease linearly with time, the result can be fitted with one “soft” component. In our current case, however, it was not possible to fit the FID data with one component. This indicates that multiple components with different proton mobilities coexist in each sample. We note that the calculated T$_2$ values for each component were significantly different from each other. This further strengthens our hypothesis that multiple components coexist in each sample.

The $^1$H NMR results for a sample with a water concentration of 20 wt\%, as a function of temperature are included in Fig. 6. We found that three kinds of protons coexisted at these temperatures. First, we discuss the component having the lowest T$_2$ at each temperature. In principle, it is not possible to distinguish the proton signals originating from water and from C16MP-Arg in these measurements. Hence, the abundances of each component calculated here represent the total amount of protons from these materials. It has been reported that the T$_2$ of protons originating from frozen water at $-11^\circ$C is approximately 14 μs\cite{20}, and that originating from polyethylene below its glass transition temperature (T$_g$) is approx. 9 μs\cite{37}. Taking these values into consideration, both the protons originating from frozen water and from the alkyl chains of C16MP-Arg could contribute to the T$_2$ of 11.0 μs measured at $-30^\circ$C. It seems likely, however, that the lowest T$_2$ measured at $-30^\circ$C mainly arises from the protons of the C16MP-Arg alkyl chains for the following reasons. First, the absence of endothermic peak at 0°C suggests the absence of frozen
water at this water concentration (20 wt%). Second, the abundance of protons originating from the C16MP-Arg alkyl chains was calculated as 52 mol% at this water concentration, which is consistent with the abundance of the highest T<sub>2</sub> component at −30°C.

Increasing the temperature from −30°C to 25°C resulted in a larger T<sub>2</sub> for the lowest T<sub>2</sub> component. Previous studies reported a T<sub>2</sub> of 30 ± 3 μs for the gel (L<sub>α</sub>) phase of trioxethylene hexadecyl ether (C<sub>16</sub>EO<sub>3</sub>) with D<sub>2</sub>O<sup>28</sup>, and a T<sub>2</sub> of 30.5 ± 1 μs for the L<sub>e</sub> phase in an aqueous hexadecyltrimethylammonium chloride system<sup>29</sup>. Furthermore, the T<sub>2</sub> of a polyethylene segment above its T<sub>α</sub> was reported as 15–30 μs<sup>27</sup>. The T<sub>2</sub> value (23.7 μs) measured at 25°C in this study was consistent with these values, suggesting that the protons originating from the alkyl chains of C16MP-Arg contributed significantly to the lowest T<sub>2</sub> component at this temperature. A further increase in temperature to 65°C resulted in a larger T<sub>2</sub> (120 μs). The change in T<sub>2</sub> observed here may reflect the phase transition from the α-gel to the lamellar LC phase, as reported in our previous study<sup>13</sup>. The decreased abundance of the lowest T<sub>2</sub> component with increasing temperature is the result of a significant increase in the mobility of protons near the C16MP-Arg headgroups. We assume that the contribution of these protons gradually shifts to the middle T<sub>2</sub> component with increasing temperature (see later discussion).

Secondly, we focus on the highest T<sub>2</sub> component observed at the three measurement temperatures. At −30°C, the T<sub>2</sub> of this component, and its abundance, were estimated as 351 μs and 28 mol%, respectively. We calculated the abundance of protons originating from water as 22 mol% at this water concentration, which is in broad agreement with the abundance of the highest T<sub>2</sub> component at −30°C.

This suggests that the highest T<sub>2</sub> component is mainly comprised of protons originating from water at this temperature. We hypothesized that the water molecules contributing to the highest T<sub>2</sub> component act as "bound water" to the headgroups of C16MP-Arg. This is supported by the absence of the endothermic peak at 0°C in the experimental DSC results shown in Figs. 4 and 5, which indicates that there is no frozen water at this water concentration (20 wt%).

An increased temperature resulted in increases in the abundance of the highest T<sub>2</sub> component and its T<sub>2</sub> value. It should be noted that the reliability of the result is not sufficiently high to discuss the T<sub>2</sub> value in detail when the estimated value exceeds 1000 μs. Hence, we describe the T<sub>2</sub> value simply as “>1000 μs” in Fig. 6. We can suggest,
however, that the $T_2$ values estimated here (approx. 2900 μs at 25°C and 3700 μs at 65°C) are significantly lower than that of “free” pure water (2479 ms and 2471 ms). This indicates that the mobility of the water molecules is highly restricted at a water concentration of 20 wt%, even at high temperatures. The increased abundance of the highest $T_2$ component reflects the increased contribution of protons originating from the C16MP-Arg headgroups with increasing temperature.

Thirdly, we focus on the middle $T_2$ component observed at the three measurement temperatures. An increase in temperature resulted in an increased $T_2$. This indicates the increased mobility of this component with temperature. The middle $T_2$ component is comprised of a contribution from the C16MP-Arg alkyl chain protons, which increases with increasing temperature, and one from the C16MP-Arg headgroup protons, which decreases with increasing temperature. This complicates meaningful discussion of the middle $T_2$ component, however we can suggest that it arises from protons near the C16MP-Arg headgroups. In particular, Arg protons contribute significantly to the middle component at −30°C.

Figure 7 shows the $T_2$ relaxation times and the relative abundances of the high, middle and low $T_2$ components as a function of the water concentration at a fixed temperature of 25°C. The abundance of the highest $T_2$ component increases significantly with increasing water concentration. This is reasonable as the highest $T_2$ component mainly reflects the behavior of water molecules, as mentioned earlier. This component was dominant at a water concen-
Conclusions
We have characterized the behavior of water in the C16MP-Arg α-gel system by means of SWAXS, FT-IR, DSC, and 1H-NMR measurements. An increased water concentration resulted in an increased d-spacing of lamellar bilayers, the appearance of an inter-lamellar water phase, and an increased O-H stretching frequency. In addition, the melting enthalpy ∆H (in J·g⁻¹) increased with increasing water concentration, while freezing was not observed below a water concentration of 20 wt%. These results suggest that the overall properties of water change as a function of its concentration in the sample. 1H-NMR T₂ measurements further suggest that the protons of water and C16MP-Arg can be classified into three components (low-, middle- and high-T₂ components) as a function of the temperature and concentration, although it was not possible to distinguish the proton signals originating from water and C16MP-Arg in these measurements. The low-T₂ component mainly arose from the protons of C16MP-Arg alkyl chains, and its mobility increased with increasing temperature. The high-T₂ component mainly arose from the protons of water. The water behaved as "bound water" for the C16MP-Arg headgroups at −30°C at a water concentration of 20 wt% and the mobility increased with increasing temperature and water concentration. These changes suggest that an increased water concentration results in an increased amount of water being incorporated between the C16MP-Arg lamellar bilayers as well as in spaces surrounded by α-gel domains.

Acknowledgements
We thank Mitsui Chemical Analysis & Consulting Service, Inc. for useful discussion about 1H-NMR measurements.

Supporting Information
This material is available free of charge via the Internet at http://dx.doi.org/10.5650/jos.ess.18211

References
1) Hassn, S.; Rowe, E.; Tiddy G.J.T. Surfactant Liquid Crystals. in Handbook of Applied Surface and Colloid Chemistry (Holmberg, K.; Shah, D.O.; Schwuger, M. eds.), John Wiley & Sons Ltd, 1, pp. 465-508 (2002).
2) Krog, N.; Kare, L. Phase behavior and rheological properties of aqueous systems of industrial distilled monoglycerides. Chem. Phys. Lipids 2, 129-143 (1968).
3) Fukushima, S.; Yamaguchi, M.A. Phasediagram of the cetostearyl alcohol-polyethoxylether-water ternary system. Yakugaku 101, 1010-1015 (1981).
4) Yamaguchi, M.; Noda, A. A formation of the complexes in the ternary system composed of 1-hexadecanol, octadecyltrimethylammonium chloride and water. J. Chem. Soc. Jpn. 1989, 1632-1638 (1989).
5) Yamaguchi, M.; Noda, A. A structures of the associates formed in the ternary system composed of 1-hexadecanol, octadecyltrimethylammonium chloride and water. J. Chem. Soc. Jpn. 1989, 26-32 (1989).
6) Suzuki, T.; Takei, H.; Yamazaki, S. Formation of fine three-phase emulsions by the liquid crystal emulsification method with arginine β-branched monoalkyl phosphate. J. Colloid Interface Sci. 129, 491-500 (1989).
7) Nagahara, Y.; Nishida, Y.; Isoda, M.; Yamagata, Y.; Nishikawa, N.; Takada, K. Structure and performance of cationic assembly dispersed in amphoteric surfactant solution as a shampoo for hair damaged by coloring. J. Oleo Sci. 56, 289-295 (2007).
8) Akatsuka, H.; Yamamoto, M.; Ohara, Y.; Otsubo, Y. Effect of polyols on the shear-induced structure and...
rheological properties of behenyl trimethyl ammonium chloride/1-octadecanol/water ternary systems. Colloids Surf. A 326, 169-174 (2008).
9) Orita, M.; Yamashita, O.; Naitou, A.; Takeuchi, K.; Katayama, Y.; Tanabe, H.; Fukuda, K.; Okada, J. Formation of pseudo-intercellular lipids membrane on the skin surface by the alpha-gel holding a large amount of water. J. Soc. Cosmet. Chem. Jpn. 46, 25-32 (2012).
10) Sakai, K.; Ohno, K.; Nomura, K.; Endo, T.; Sakamoto, K.; Sakai, H.; Abe, M. α-Gel formation by amino acid-based gemini surfactants. Langmuir 30, 7654-7659 (2014).
11) Wang, F.C.; Marangoni, A.G. Effect of intrinsic and extrinsic factors on the stability of the α-gel phase of a glyceryl monostearate – water system. RSC Adv. 5, 43121-43129 (2015).
12) Okamoto, T.; Tomonasa, S.; Nakayama, H. Preparation and thermal properties of fatty alcohol / surfactant / oil / water nanoemulsions and their cosmetic applications. J. Oleo Sci. 65, 27-36 (2016).
13) Tanaka, K.; Hirai, Y.; Suzuki, T.; Sakai, K.; Sakai, H. Phase diagram of monohexadecyl phosphate neutralized by L-arginine: α-gel formation ability. J. Oleo. Sci. 67, 851-857 (2018).
14) Watanabe, K.; Inoue, H.; Teshigawara, T.; Kimura, T. α-gel prepared in sodium methyl stearoyl taurate/behenyl alcohol/water system-characterization of structural changes with water concentration. J. Oleo. Sci. 61, 29-34 (2012).
15) Cassin, G.; Costa, C.D.; Duynhoven. J.P.M.V.; Agterof, W.G.M. Investigation of the gel to coagel phase transition in monoglyceride – water systems. Langmuir 14, 5757-5763 (1998).
16) Duynhoven, J.P.M.V.; Broekmann, I.; Sein, A.; Kempen, G.M.P.V.; Goudappel, G.J.W.; Veeman, W.S. Microstructural investigation of monoglyceride – water coagel systems by NMR and CryoSEM. J. Colloid Interface Sci. 285, 703-710 (2005).
17) Yasunaga, H.; Ando, I. Dynamic behavior of water in hydro-swollen crosslinked polymer gel as studied by PGSE 1H NMR and pulse 1H NMR. Polymer Gels and Networks 1, 83-92 (1993).
18) Powels, J.G.; Strange, J.H. Zero time resolution nuclear magnetic resonance transient in solids. Proc. Phys. Soc. 82, 6-15 (2002).
19) Carr, H.Y.; Purcell, E.M. Effects of diffusion on free precession in nuclear magnetic resonance experiments. Phys. Rev. 94, 630-638 (1954).
20) Melboom, S.; Gill, D. Modified spin-echo method for measuring nuclear relaxation times. Rev. Sci. Instrum. 29, 688-691 (1958).
21) Numata, K.; Kurokawa, H.; Kawaguchi, S.; Sekine, S.; Nakazawa, Y.; Asano, A. Evaluation of scalability for aged rubber seals by spin-spin relaxation time. Polym. Test. 49, 147-155 (2016).
22) Hayashi, J.; Norinaga, K.; Kudo, N.; Chiba, T. Estimation of size and shape of pores in moist coal utilizing sorbed water as a molecular probe. Energy Fuels 15, 903-909 (2001).
23) Morita, S.; Tanaka, M.; Ozaki, Y. Time-resolved in situ ATR-IR observations of the process of sorption of water into a poly(2-methoxyethylacrylate) film. Langmuir 23, 3750-3761 (2007).
24) Kuntz, I.D.; Brassfield, T.S.; Law, G.D.; Purcell, G.V. Hydration of macromolecules. Science 63, 1329-1331 (1969).
25) Kuntz, I.D. Hydration of macromolecules. III. Hydration of polypeptides. J. Am. Chem. Soc. 93, 514-516 (1971).
26) Okada, R.; Matsukawa, S.; Watanabe, T. Hydration structure and dynamics in pullulan aqueous solution based on 1H NMR relaxation time. J. Mol. Struct. 603, 473-483 (2002).
27) McCall, D.W.; Douglass, D.C. Molecular motion in polyethylene, IV. Polymer (Guild) 4, 433-444 (1963).
28) Adam, C.D.; Durrant, J.A.; Lowry, M.R.; Tiddy, G.J.T. Gel and liquid-crystal phase structures of the trioxyethylene glycol monohexadecyl ether/water system. J. Chem. Soc. Faraday Trans. 1 80, 789-801 (1984).
29) Blackmore, E.S.; Tiddy, G.J.T. Optical microscopy, multinuclear NMR (1H, 13N and 31Cl) and X-ray studies of dodecyl- and hexadecyltrimethylammonium chloride/water mesophases. Liq. Cryst. 8, 131-151 (1990).
30) Goldstein, A.; Marangoni, A.G.; Seetharaman, K. Monoglyceride stabilized oil in water emulsions: An investigation of structuring and shear history on phase behaviour. Food Biophys. 7, 227-235 (2012).
31) Barros, C.N.; Arèas, E.P.G.; Figueiredo, E.N.; Arèas, J.A.G. Low-resolution 1H spin-spin relaxation of n-decane/water emulsions stabilized by β-casein. Colloids Surf. B 48, 119-127 (2006).