# $^{31}$P NMR Investigation of a Ringing Gel Phase and Adjacent Phases

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## Abstract

The temperature-surfactant concentration phase diagram was examined for the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system. The phase diagram contained a highly elastic gel phase which is known as a "ringing gel phase". The ringing gel phase and adjacent phases in the ternary system were investigated by polarized optical microscopy, freeze-fracture transmission electron microscopy, and $^{31}$P NMR. Globular textures were observed in an optically isotropic gel phase. Since the globules were larger than those found in an isotropic solution, the texture consists of domains of aggregated units in the cubic ($I_1$) phase. Structure units of domains are equivalent to microemulsions which are constructed by surfactant molecules and swollen by alcohol in the isotropic ($L_1$) phase. Characteristic polarized microscopic textures were visualized in two phases with higher surfactant concentrations. These phases were identified as being hexagonal ($H_1$) and lamellar ($L_\alpha$) liquid crystals which was confirmed by transmission electron microscopy. The $^{31}$P NMR signal of the ringing gel showed a sharp singlet the same as that of the $L_1$ phase, indicating the fully averaged anisotropic interaction of the aggregates. The characteristic NMR signals of the anisotropic hexagonal and lamellar liquid crystal phases displayed chemical shielding with an asymmetric lineshape.

*Keywords:* Cubic phase; Dodecyltrimethylammonium dimethylphosphate; Hexagonal liquid crystal; Lamellar liquid crystal; $^{31}$P NMR; Ringing gel

## 1. Introduction

In binary phase diagrams of surfactant and water, there is an isotropic phase, found at dilute

surfactant concentrations, where micelles are formed. In contrast, hexagonal and lamellar liquid crystal phases are formed at higher concentrations [1,2]. For multicomponent systems including oils and cosurfactants, there are many different kinds of phases and molecular arrangements and physicochemical properties have been investigated for such phases.

One of the interesting phases displays gel or gel-like character. Typical gel-like binary phases are

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transparent viscous solutions of rodlike micelles [3]. Especially remarkable viscoelastic properties were reported for micellar solutions of alkyltrimethylammonium with aromatic counterions such as salicylate [4,5]. Alkyldimethylamine oxide micelles also exhibited similar properties [6]. Some of the binary systems were translucent gel-like solutions, where fibrous assemblies or hexagonal and lamellar arrangements were constructed [3,7]. Characteristic rheology, with elastic properties, resulted from network or liquid crystal structures.

Gels were also found in ternary systems with surfactant, water, and hydrocarbon (oil). The liquid crystalline cubic ($I_1$) phase is rheologically elastic, and is a transparent gel. The cubic phase is optically an isotropic mesophase, which is thermodynamically stable [8,9]. Some of these gels exhibit a "ringing" phenomenon. They produce metallic sounds when solutions are tapped with a soft object [10]. "Ringing gels", named after this unique property, were reported for tetradecyldimethylamine oxide ($C_{14}DAO$)/water/hydrocarbon ternary systems [11–13]. They were investigated by light scattering, small-angle neutron scattering, rheology, and NMR self-diffusion. The detailed structure of ringing gels was examined and discussed. The most rational model for ringing gels is one where individual particles construct the liquid crystalline cubic ($I_1$) phase [12].

In this work, a new type of ringing gel composed of dodecyltrimethylammonium dimethylphosphate is investigated by $^{31}P$ NMR and microscopy in order to elucidate its structure and physicochemical properties. Signal width measurement of $^{31}P$ NMR absorption is possible for a surfactant system including phosphate, such as $(CH_3O)_2PO_2{}^-$.

## 2. Experimental

Dodecyldimethylamine ($C_{12}H_{25}N(CH_3)_2$; 1 mole) was mixed with 3-methyl-3-methoxybutanol (0.43 moles) in water. Trimethylphosphate (($CH_3O)_3PO$; 1 mole) was added to the mixture with stirring at high temperature. After heating for 3 h, the solution concentration was adjusted by adding a suitable amount of water. The solution was cooled to room temperature, resulting in the

formation of dodecyltrimethylammonium dimethylphosphate ($C_{12}H_{25}N^+(CH_3)_3 \cdot (CH_3O)_2PO_2{}^-$) gel. Then, the weight ratio of surfactant to 3-methyl-3-methoxybutanol in solution was kept constant.

Polarized microscopy observation was carried out on an Olympus BH optical microscope under crossed nicols. For transmission electron microscopy (TEM) observation, a Hitachi H-800 electron microscope was used. Freeze-fracture replica films were prepared by using a Balzers BAF 400 freeze-fracture device. Both microscopic observations were performed at room temperature (~25°C).

$^{31}P$ NMR spectra were recorded on a Bruker MSL-300 spectrometer at a frequency of 121.50 MHz, applying a $\pi/2 - \tau - \pi/2$ (90° shifted) echo pulse sequence with a pulse interval of 10 μs and a $\pi/2$ pulse width of 4.7 μs. The pulse sequence time was set at 6.0 s and 32 signals were accumulated. The sample temperature was 24°C.

## 3. Results

A temperature–surfactant concentration ($T–c$) phase diagram for the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system is shown in Fig. 1. While region I comprised transparent and fluid solutions, gels were formed above 35 wt.(w/w)% surfactant concentration. Although transparent gels in region II were stiff, those in region III were rather soft. Softer gels were obtained in regions of higher concentration than region III. The gels in region IV of Fig. 1 were translucent. Metallic ringing
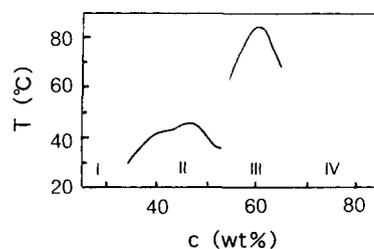


Fig. 1. Temperature-surfactant concentration phase diagram of the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system.

sounds, characteristic of ringing gels, were confirmed in region II at 35–50 wt.%.

Optical microscopic observation under crossed nicols was carried out for a 25 wt.% solution and 45, 60 and 75 wt.% gels, which belong to regions I, II, III, and IV respectively. Fig. 2 shows polarized micrographs. No textures were found for either the 25 wt.% solution or for the 45 wt.% gel, indicating isotropic character. In contrast, polarized micrographs for 60 and 75 wt.% gels displayed textures characteristic of the hexagonal (middle, $H_1$) and lamellar (neat, $L_z$) liquid crystals respectively [1,2].

Fig. 3 shows TEM images of a 25 wt.% solution and of 45, 60, and 75 wt.% gels. Texture for globular particles of diameter < 10 nm was observed for the 25 wt.% solution. Particles, which were dispersed randomly, are assigned as microemulsions in the $L_1$ phase. The micrographic texture of globular particles in the 45 wt.% gel was larger than that in the 25 wt.% solution. Particles are identified with domains of aggregated units in the cubic ($I_1$) phase. Similar micrographs have been reported as representing cubic phases in a polyoxyethylene oleylether/water binary system and in a Brij 96/paraffin/water ternary system [14,15]. In the TEM image for the 60 wt.% gel, fractured planes with ribbed, parallel lines were observed. The upper

right part of Fig. 3 is a cross-sectional view of these lines. Long lines represent a hexagonal array of rods consisting of surfactant [14]. Layer texture, characteristic of the lamellar phase, was observed in a replica film from the 75 wt.% gel. The texture was very similar to that previously reported [14,15].

The $^{31}P$ NMR spectrum for a 25 wt.% solution, shown in Fig. 4, displayed a sharp peak, which is characteristic of isotropically averaged motion [16–18]. The same sharp peak was also observed for the 45 wt.% gel in the cubic $I_1$ phase. The NMR signal for the 60 wt.% gel became slightly asymmetric and wider in the high magnetic field compared with that of the 45 wt.% gel in the cubic $I_1$ phase. In contrast, the NMR signal for the 75 wt.% gel expanded greatly in the low magnetic field. These profiles are characteristic of hexagonal and lamellar phases respectively [18].

## 4. Discussion

A ringing gel (cubic liquid crystal) phase was observed for the $C_{14}DAO$/water/hydrocarbon ternary system with 50–65 wt.% water and for a $C_{14}DAO$: decane ratio of 4:1 (w/w) [11–13]. The
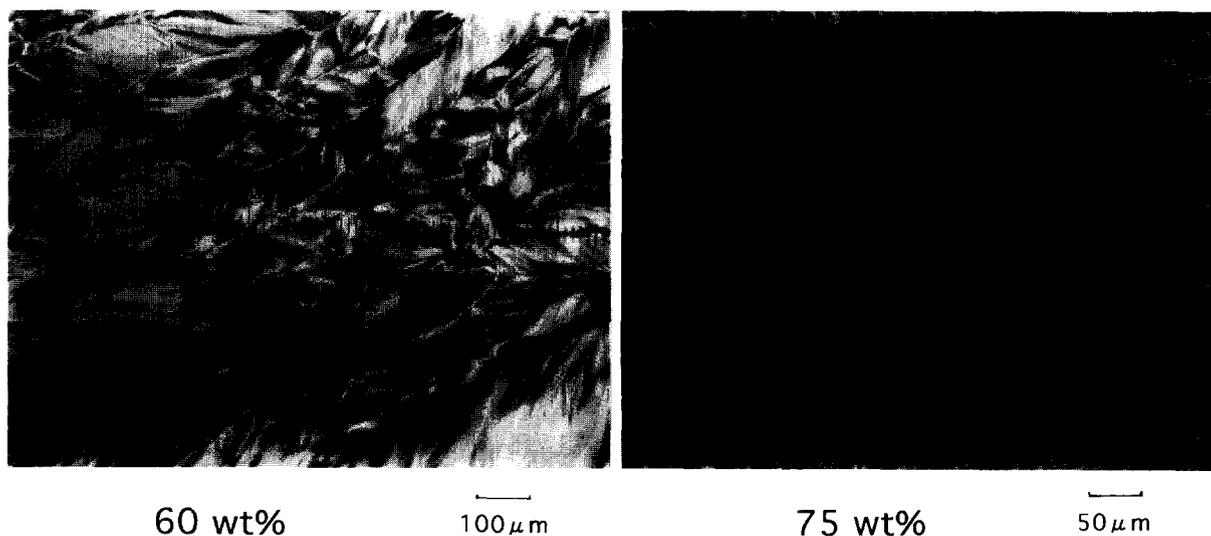


60 wt%    100 μm          75 wt%    50 μm

Fig. 2. Polarized, optical micrographs of 60 and 75 wt.% concentrated gels of the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system.
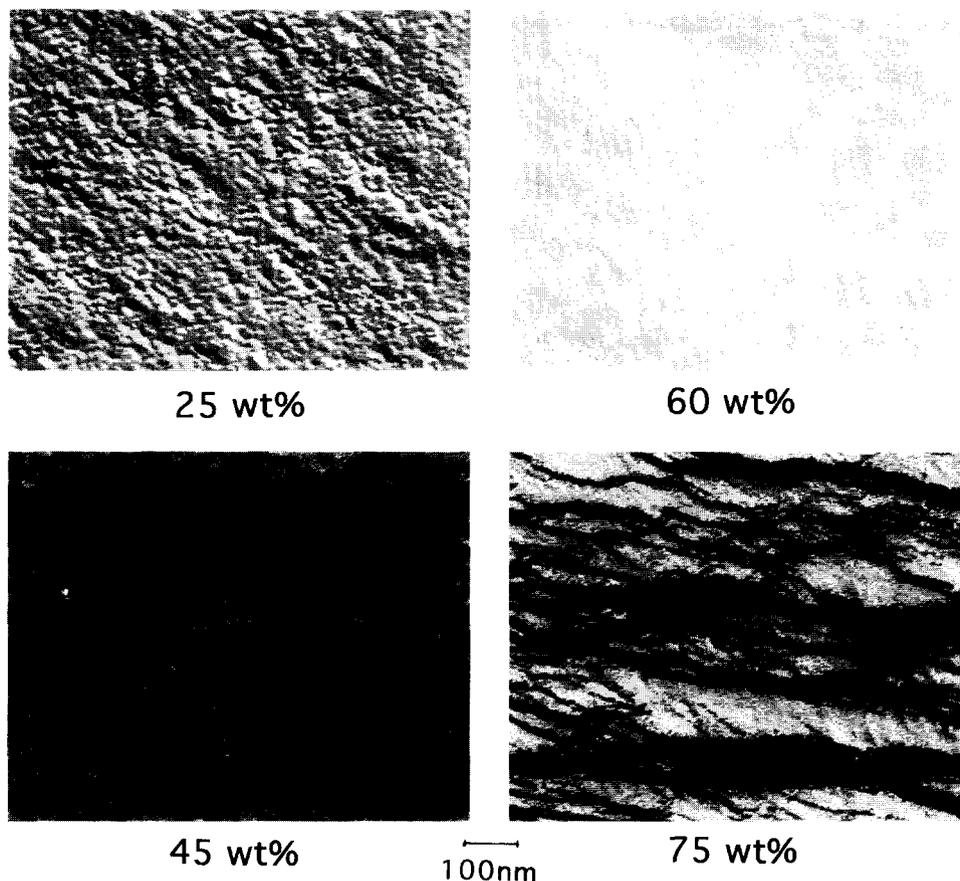
Fig. 3. Freeze-fracture electron micrographs of a 25 wt.% solution and of 45, 60, and 75 wt.% gels of the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system.

gel phase was located between the isotropic and hexagonal phases. The ringing gel consisted of spherical microemulsion droplets with solubilized hydrocarbon as well as droplets in the adjacent $L_1$ phase. Its scattering curves were explained by the hard sphere model.

Molecular aggregates in the $L_1$ phase of the dodecyltrimethylammonium dimethylphosphate/ 3-methyl-3-methoxybutanol/water ternary system examined here were globular as estimated from freeze-fracture TEM. Aggregates are micro-emulsion droplets swollen by alcohol. The globular texture in the ringing gel (cubic) phase was larger than that in the $L_1$ phase. Globules in the cubic ($I_1$) phase are not unit particles but domains of aggregated units, i.e. aggregated microemulsions. It is not yet known whether the globules are

spheres or short rods. The gel phase was observed for mixtures with 30–60 wt.% water and a surfactant: alcohol ratio of 6–9:1. This component fraction is consistent with that for the $C_{14}DAO$/water/ hydrocarbon ternary system. Another consistency is the formation of a gel phase between the isotropic and hexagonal phases.

The structure of the molecular aggregates in the cubic $I_1$ phase has been investigated by some workers [11,15,19–27]. The sphere model was proposed as the structure of unit particles [11,15,19] which are close-packed [15,19,22] or in contact [11] in the gel. In the second model, the structure consisted of a network of tubes and spheres [20]. In the third model, the unit structure of a hemisphere-capped rod with a small axial ratio of < 2 was deduced from NMR measurements
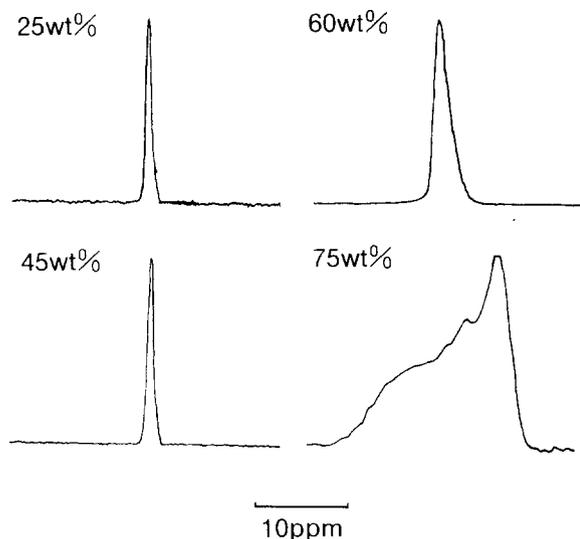
25wt%          60wt%

45wt%          75wt%

10ppm

Fig. 4. $^{31}$P NMR spectra of a 25 wt.% solution and of 45, 60, and 75 wt.% gels of the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system.

[24–27]. Rods formed the close-packed structure. Another model, where aggregates were continuous over the macroscopic phase, was also reported [22]. It was suggested that the structure of the aggregates depended on the system. The close-packed structure of microemulsions is reasonable for the gel phase in the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system, because domains composed of few globular units were observed as larger globules in freeze-fracture TEM.

NMR investigations of the cubic liquid crystal phase and other lyotropic liquid crystal phases were reported by many workers [21–27]. Soderman and co-workers [25–27] investigated $^{2}$H, $^{13}$C, and $^{14}$N NMR spin relaxation of micellar and cubic phases. They confirmed that the unit structure of the cubic $I_1$ phase was a hemisphere-capped rod with an axial ratio of <2, and the cubic $I_1$ phase was the close-packed structure constructed of rods, as described above. Eriksson et al. [22] concluded from $^{14}$N NMR diffusion studies that the cubic liquid crystalline phase at 84 wt.% dodecyltrimethylammonium chloride ($C_{12}$DAC) in water consisted of continuous aggre-

gates in macroscopic dimensions, whereas the cubic phase at 50 wt.% $C_{12}$DAC was composed of globular aggregates in a close-packed structure.

$^{1}$H, $^{2}$H, $^{14}$N, $^{19}$F, and $^{31}$P NMR studies of the hexagonal liquid crystal phase in comparison with the cubic phase were performed by Lindblom and co-workers [21,24] and Nilsson et al. [23]. For the system of hexadecyltrimethylammonium fluoride ($C_{16}$TAF) in $D_2O$, while the $^{2}$H and $^{14}$N NMR spectra of micellar solution displayed a sharp singlet signal, spectra of the hexagonal liquid crystalline phase showed quadrupolar splitting for both of these nuclei [21]. The spectral line shape of the cubic phase of 1-palmitoyllysophosphatidylcholine (PaLPC) in water showed remarkable deviations from the isotropic lorentzian form, indicating the imperfectly averaged anisotropic chemical shift [24]. In the mixture of cubic and hexagonal phases, the spectrum of the cubic phase was superimposed on the typical spectrum of the hexagonal phase.

As shown in Fig. 4, the NMR spectrum of the cubic $I_1$ phase (45 wt.% gel) in the dodecyltrimethylammonium dimethylphosphate/3-methyl-3-methoxybutanol/water ternary system showed a sharp singlet the same as that of the 25 wt.% $L_1$ phase, suggesting the fully averaged anisotropic chemical shift of the aggregates in both phases. The spectrum of the hexagonal phase (60 wt.% gel) displayed chemical shift anisotropy with a high-field shoulder and a low-field peak. This resulted from the partial average of the chemical shift tensor. The anisotropic chemical shift was remarkable in the lamellar liquid crystalline phase (75 wt.%).

The roughly evaluated $^{31}$P linewidth of 3.5 ppm in the hexagonal phase is much smaller than that ($\approx 13$ ppm) in the lamellar phase. This result is different from the structural estimation that the NMR linewidth in the hexagonal phase should be about half of the linewidth in the lamellar phase [18]. In the case of $F^-$ or $Na^+$ ions, because the widths of the NMR spectra are proportional to the molar ratio of surfactant to bound water, the spectral width of the 60 wt.% hexagonal phase is a quarter of that of the 75 wt.% lamellar phase [28]; in contrast, when phosphorus groups are involved, the $^{31}$P spectral width does not depend

on the concentration because there is no bound water about the phosphorus atom [18]. This disagreement with the expected width, being half the lamellar width [18], means that the local chemical shielding in the hexagonal phase is differently averaged from that in the lamellar phase, suggesting that either the orientation against the local rotational axis or the motional rate of $(CH_3)_2PO_2^-$ depends on the phase.

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