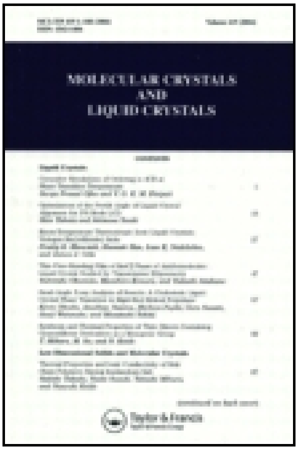

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Fourier Transform Infrared Study on the Phase Transitions of a Water-Dioctadecyldimethylammonium Chloride System

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Fourier Transform Infrared Study on the Phase Transitions of a Water-Dioctadecyldimethylammonium Chloride System

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Fourier transform infrared spectroscopy have been applied to study thermotropic phase transitions of the 21 g% water-dioctadecyldimethylammonium chloride (DODAC) system, in which three successive phases of coagel, gel, and liquid crystal appear with increasing temperature. In the coagel phase, the methylene chains take the *trans*-zigzag conformation packed in parallel with each other. The hydrophilic part of DODAC in this phase is in a fixed state, and the presence of the bound water is evident. In the gel phase, the rotational motion of the methylene chain around the chain axis occurs in the hexagonal lattice. There exists more bound water in this phase than in the coagel phase, and the hydrophilic part in a rather fixed state. These findings are in conflict with the generally accepted concept of the gel state by x-ray studies. It is found molecular-spectroscopically that there exists an intermediate state between the coagel and gel phases, which is associated with the cooperative rearrangement of the hydrophilic part of DODAC and water. In the liquid crystalline phase, both hydrophobic and hydrophilic parts of DODAC are in fused states and the water spectrum becomes similar to that of liquid water. These structural aspects in each phase were compared with the previous results for the water-octadecyltrimethylammonium chloride system.

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INTRODUCTION

Cationic surfactants with two long alkyl chains in the aqueous environment often behave in a similar manner with biological lipids. The aqueous dispersion of dioctadecyldimethylammonium chloride [DODAC, $(CH_3(CH_2)_{17})_2N^+(CH_3)_2Cl^-$] is known to form the bilayer structure analogous to biological membranes.[1,2] Kodama *et al.* have examined the phase behavior of the water—DODAC system by differential scanning calorimetry (DSC) and established the phase diagram.[3-5] According to that, the systems with water content greater than ~11 g% exhibit coagel/gel/liquid crystalline phase transitions with increasing temperature. It is generally believed that in the gel phase the hydrocarbon chains are crystallized whereas the polar groups are brought into the ionized fused state by the interaction with solvent water.[6,7] In fact, such was the case of the previous water-octadecyltrimethylammonium chloride (ODAC) system as revealed by our Fourier transform infrared (FT-IR) spectroscopic study.[8]

In this work, we examined the structural features of the phase transitions in the system of water and DODAC having double hydrocarbon chains by using FT-IR spectroscopy. The results were compared with those for the system of water and ODAC having single hydrocarbon chain.[8]

MATERIALS AND METHODS

DODAC (Arosurf 100™ produced by Shelex Chemical Co., Inc., Dublin, OH) was kindly supplied by Kao Soap Co., Ltd., Tokyo and was recrystallized five times from acetone solution. The purity of the sample thus obtained was 96 g% as determined by a Hitachi M-80 GC-Mass analyser. It contained 2 g% each of $C_{16}H_{33}C_{18}H_{37}N^+(CH_3)_2Cl^-$ and $C_{20}H_{41}C_{18}H_{37}N^+(CH_3)_2Cl^-$ as minor components.

A mixture of DODAC and doubly distilled water in a vial was allowed to stand for 6 h at 50°C to achieve the homogeneous mixing. For infrared measurements, a Harrick DLC-M25 demountable liquid cell was employed with wedged calcium fluroide (for 4000-1000 cm^{-1} region) or barium fluoride (for 1000-700 cm^{-1} region) windows. No spacer was used and hence the sample thickness is estimated to be a few μm. Since the cell was assembled in an oven kept at 55°C (the liquid crystalline phase), evaporation of water during the assembly was inevitable. Thus, the water content of the sample was determined as 21 ± 2 g% by referring the infrared spectroscopic data to the phase diagram,[3] as described previously.[8] The sample cell was placed in a mount with water jacket thermostated by a Neslab RTE-8 refrigerated bath circulator with a 1 : 1 mixture of ethylene glycol and water. The temperature was monitored by a copper-constantan thermocouple inserted between a window edge and an O-ring. The overall accuracy of temperature control and reading was within ±0.1°C.

The sample was annealed at 20°C for 12 h to achieve the complete transformation from the supercooled gel to the stable coagel phases.[3-5] Then the coagel sample was subjected to FT-IR measurements during heating process in the temperature range from -10 to $+56$°C. The rate of heating of the bath circulator was ~0.5°C/min. After the temperature of the bath circulator reached each set point, 15 minutes were spent to establish the thermal equilibrium of the sample. Spectra were recorded on a Nicolet 6000 FT-IR spectrophotometer with an MCT detector. Five hundred to one thousand interferograms collected in 7~15 min in the maximum optical retardation of 0.25 cm were coadded, apodized with a Happ–Genzel function, and Fourier transformed with one-level of zero filling to yield spectra of high S/N ratio with a resolution better than 4 cm^{-1}.

RESULTS AND DISCUSSION

CH stretching bands of the methylene chains

Infrared spectra of the DODAC sample in the CH stretching region are shown in Figure 1. The two strong bands at ~2920 and ~2850 cm^{-1} are assigned to the antisymmetric and symmetric CH_2 stretching modes of the methylene chain, respectively.[8] Changes in spectral feature with temperature are apparent in this figure. The temperature dependence of the wavenumber and halfbandwidth of the antisymmetric CH_2 stretching band is given in Figure 2. There appeared two drastic changes centered at 35.5 and 45.5°C which correspond to the coagel-gel and gel-liquid crystalline phase transitions, respectively.[5-7] Except for the transition temperatures, the features in Figure 2 are similar to those of the previous water-ODAC system.[8] The increases in wavenumber and bandwidth on the phase transitions of the coagel-gel and the gel-liquid crystal indicate the augmentation in the number of *gauche* conformer and in the rotational motion of the methylene

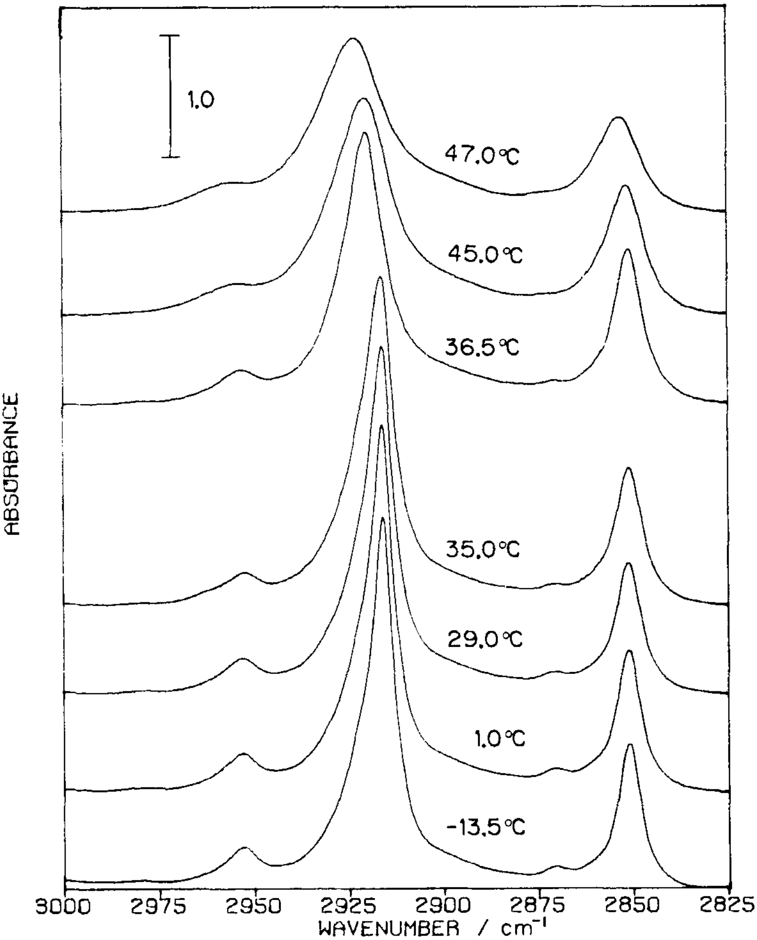

FIGURE 1 Infrared spectra of a 21 g% water-DODAC system in the 3000-2825 cm^{-1} region at various temperatures.

chains, respectively.[8] The peak positions of these bands in various phases are given in Table I, together with those of other major infrared bands.

The CH_2 scissoring and rocking bands

The CH_2 scissoring and rocking bands are known to be very sensitive to the intermolecular forces, and they serve as key bands for examining the state of packing of the methylene chain in various phases.[8-10] Figures 3 and 4, respectively, depict the temperature dependence of

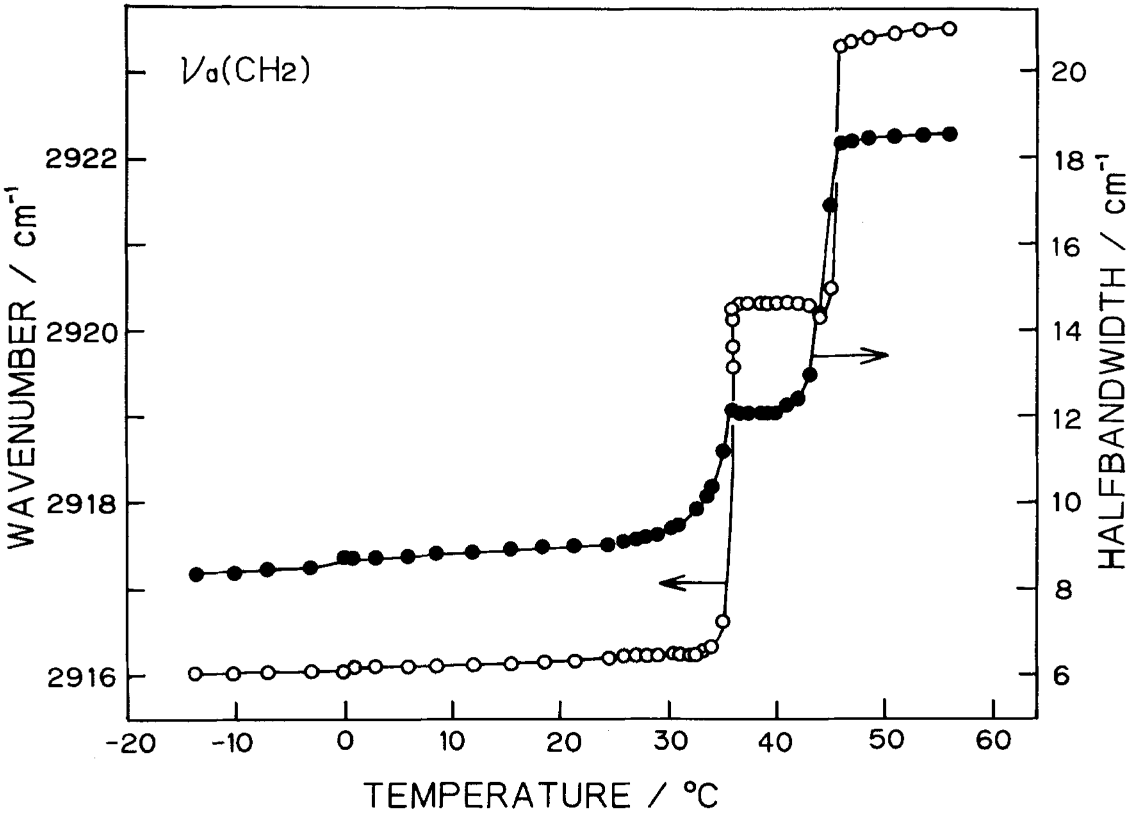

FIGURE 2 Temperature dependence of the wavenumber (○) and halfbandwidth (●) of the antisymmetric CH_2 stretching band of a 21 g% water-DODAC system.

TABLE I

Major infrared absorption bands of the 21 g% water-DODAC sample in various thermotropic phases.[a]

Coagel (1°C)	Intermediate state (35°C)	Gel (36.5°C)	Liquid crystal (47°C)	Assignment[b]
—	—	3489		
3442	3418	3404	3410	ν(OH)
3370	3320	3354		
3246	3246	3246	—	2δ(HOH)[c]
3058	3054	3057	—	
3047	3046	3042	—	
3042	3038	3042	3042	$\nu_a(CH_3(N^+))$
3031	3027	3029	3026	
2979.5	2980.7	2979.5	—	$\nu_s(CH_3(N^+))$
2953.6	2952.7	2953.0	2954.5	$\nu_a(CH_3(N^+))$
2916.1	2916.6	2920.3	2923.3	$\nu_a(CH_2)$
2870.5	2870.4	2870.2	—	$\nu_s(CH_3)$
2851.1	2850.9	2850.9	2853.5	$\nu_s(CH_2)$
1647.3	1647.4	1635.3	1641.5	δ(HOH)
1488.7	1487.3	1488.8	1487.8	$\delta_a(CH_3(N^+))$
1471.7	1471.3	1469.7	1467.2	$\delta(CH_2)$
1419.1	1419.7	1423.2	1422.4	$\delta_s(CH_3(N^+))$
909.9	910.0	914.1	919	ν(CN)
717.8	718.7	723.2	722	$\gamma(CH_2)$

[a] peak positions in cm^{-1}.

[b] ν; stretching, δ; bending, γ, rocking.

[c] A band due to ice appears at 3250 cm^{-1} below 0°C.

the CH_2 scissoring and rocking bands. Changes in spectral feature with temperature are evident. The peak wavenumbers of these bands are plotted against temperature in Figure 5. In the coagel phase below 32°C, the wavenumber of the CH_2 scissoring band is in the range from 1471.9 (−10°C) to 1471.2 cm^{-1} (32°C). This suggests that the methylene *trans*-zigzag planes are packed in parallel with each other (subcell structure being orthorhombic parallel or triclinic), as in the case of coagel phase of the water-ODAC system.[8] The CH_2 rocking band in the coagel phase appear as a singlet in the range 717.7 (−10°C)–718.3 cm^{-1} (32°C), confirming the parallel chain packing.[10]

In the gel phase, the wavenumber of the CH_2 scissoring band gradually decreases from 1470.3 (36.3°C) to 1469.2 cm^{-1} (41.6°C) with increasing temperature. The spectrum at 36.5°C in Figure 3 demonstrates the doubling of the CH_2 scissoring band, just like the one found in hexagonal phase of *n*-alkanes.[11] The wavenumber of the CH_2 rocking band is 723.2-722.8 cm^{-1} in the temperature range from

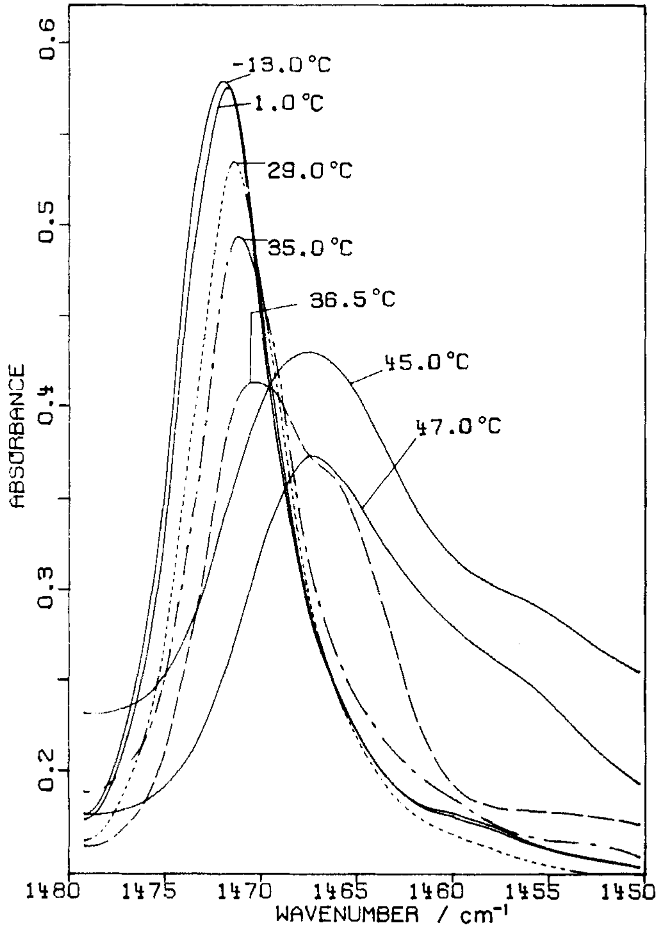

FIGURE 3 Infrared spectra of a 21 g% water-DODAC system in the 1480-1450 cm^{-1} region at various temperatures.

36.3 to 41.6°C. These facts reveal that the methylene chains are packed in the hexagonal lattice.[8,10,11]

In the liquid crystalline phase above 46°C, the CH_2 scissoring and rocking bands locate at 1467.3 and ~722 cm^{-1}, which are typical of methylene chains in the fused state.[12]

From these results, it can be concluded that as far as the methylene chains are concerned the structural features in each thermotropic phase are just the same as those in the water-ODAC system.[8]

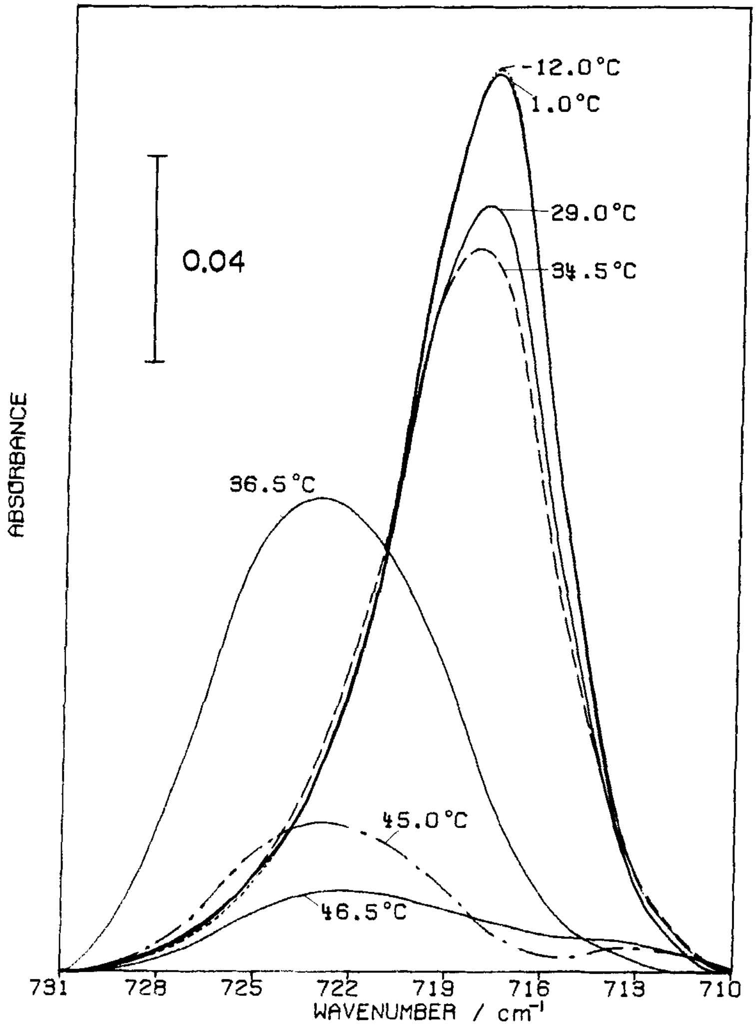

FIGURE 4 Infrared spectra of a 21 g% water-DODAC system in the 731-710 cm^{-1} region at various temperatures, after base-line correction.

It should be noted here that in the methylene chain packing there is some resemblance between the coagel phase of the water-DODAC system and the stable phase at the temperature below the subtransition of the water-L-dipalmitoylphosphatidylcholine (L-DPPC) system.[13,14] The methylene chains in both phases are packed more or less

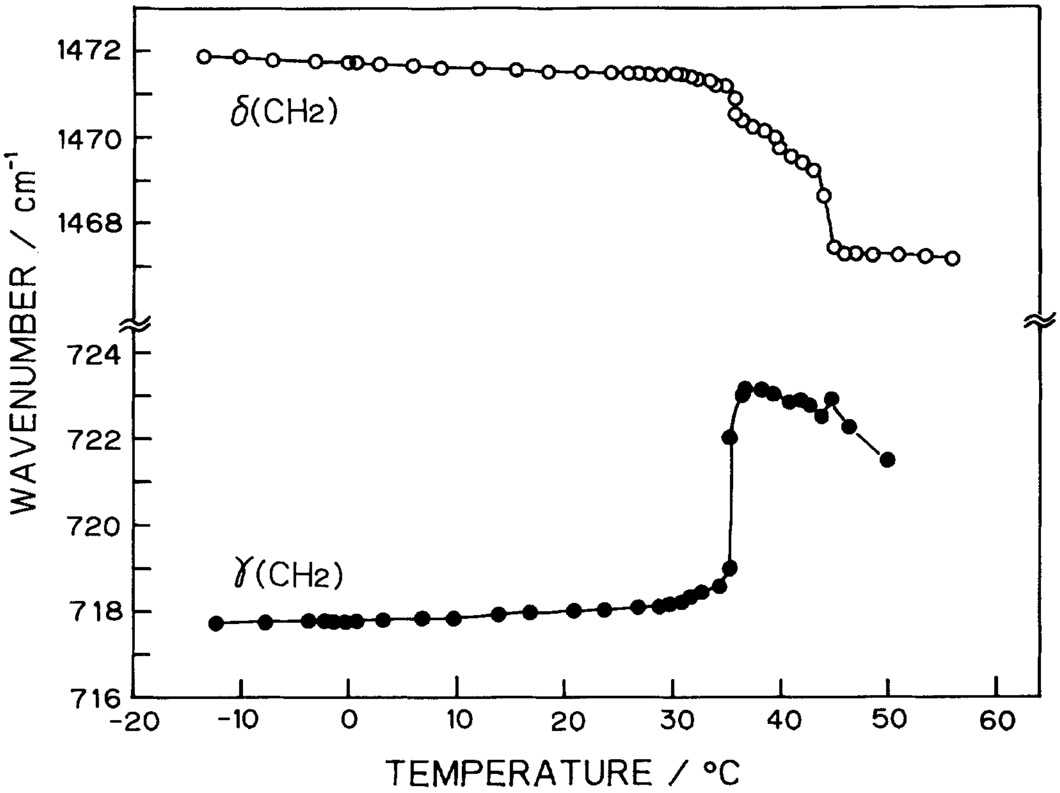

FIGURE 5 Temperature dependence of the wavenumbers of the CH_2 scissoring (○) and CH_2 rocking (●) bands of a 21 g% water-DODAC system.

in parallel to each other,[14] and these two phases appear only after suitable annealing processes.

The asymmetric $CH_3(N^+)$ stretching band

The asymmetric stretching band of the methyl group attached to the N^+ atom appears in the range 3020-3050 cm^{-1},[8,15,16] and can be a key band for monitoring the structural behaviour of the hydrophilic part of the amphiphilic substance. Figure 6 depicts the spectra of this vibrational region at various temperatures. Coagel spectra at −13.5, 1.0, and 29.0°C, gel spectrum at 36.5°C, and liquid crystalline spectrum at 47.0°C have their own characteristic features. Besides, the

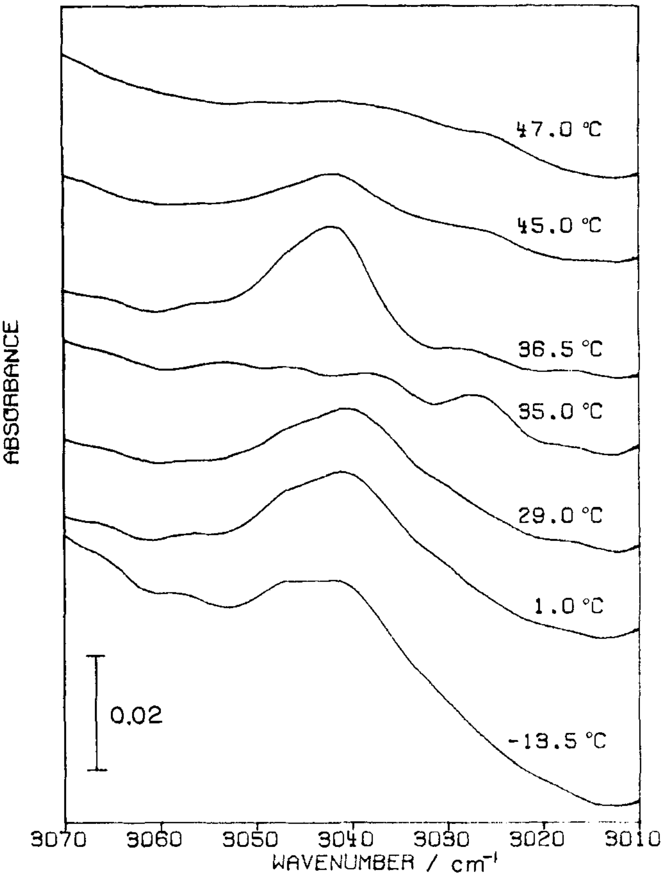

FIGURE 6 Infrared spectra of a 21 g% water-DODAC system in the 3070–3010 cm^{-1} region at various temperatures.

35.0°C spectrum presents a completely different appearance from the gel or coagel spectra, giving four peaks at ~3054, 3046, 3038, and 3027 cm^{-1}. This shows that there exists an intermediate state between the coagel and gel phases.

In Figure 7, the wavenumber of the main peak of the asymmetric methyl stretching band is plotted against temperature. Below 32°C, the wavenumber slightly decreases with temperature. In the range 32–35°C, it shows an appreciable decrement, which may correspond to the presence of the intermediate state. Then, it is followed by a sharp and drastic increment at 35.0–35.8°C, corresponding to the principal transition to the gel phase. We fixed the temperature of the sample at 35.8°C to follow the time-course of the infrared spectrum. It took 2 h at this temperature to get the stationary spectrum of the gel phase, the wavenumber slightly decreasing during this period. This fact indicates that the coagel-gel transition is a time-consuming process. On the gel-liquid crystalline phase transition at 45–46°C, the plot shows a small wavenumber decrement. The wavenumber slightly changes in the liquid crystalline phase.

In the case of water-ODAC system,[8] the asymmetric $CH_3(N^+)$ stretching band in the gel phase was almost the same as that in the liquid crystalline phase. However, the situation is completely different in the present water-DODAC system: the gel spectrum at 36.5°C in Figure 6 gives definite peaks as compared with that at 47°C. These results are strongly related to the structural behavior of water molecules as will be mentioned below.

Water bands

According to the thermal analysis of the aggregation state of water molecules in this sytem at the water content of 21 g%,[3-5] 11 g% water exists as the bound water incorporated between the bilayers of DODAC molecules in the coagel phase, where 10 g% is the bulk free water coexisting with this coagel phase. While, in the gel phase, the interlamellar water is composed of the 11 g%-bound water and the 7 g%-intermediate water which is newly interposed between the bilayers at the elevated temperature of the coagel-gel phase transition, and the residual 3 g% water exists as the bulk free water. The spectra in the 3700–3000 cm^{-1} region at vaious temperatures are reproduced in Figure 8. The spectrum of the coagel phase at −13.5°C shows a peak at ~3250 cm^{-1} which is attributed to the OH stretching mode of the hexagonal ice derived from the bulk free water.[17] In the spectrum at 1°C, this band diminishes as results of the melting of the ice at 0°C.

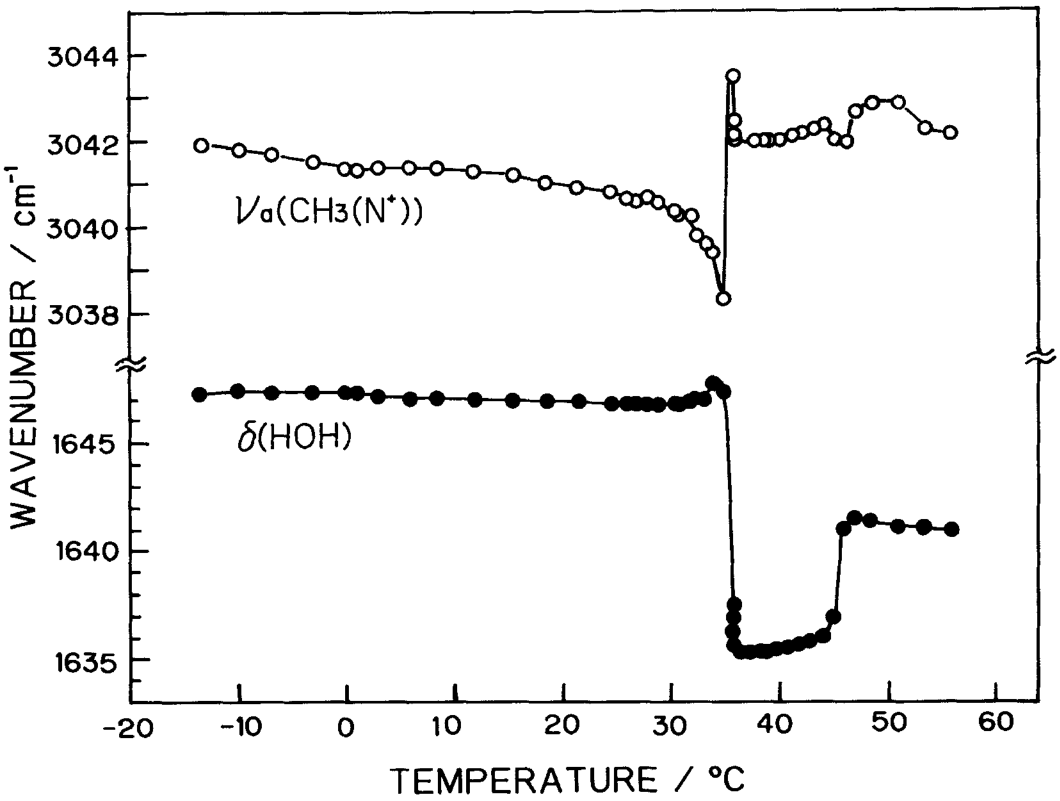

FIGURE 7 Temperature dependence of the wavenumbers of the asymmetric $CH_3(N^+)$ stretching band of DODAC (○) and the HOH bending band of water (●) in a 21 g% water-DODAC system.

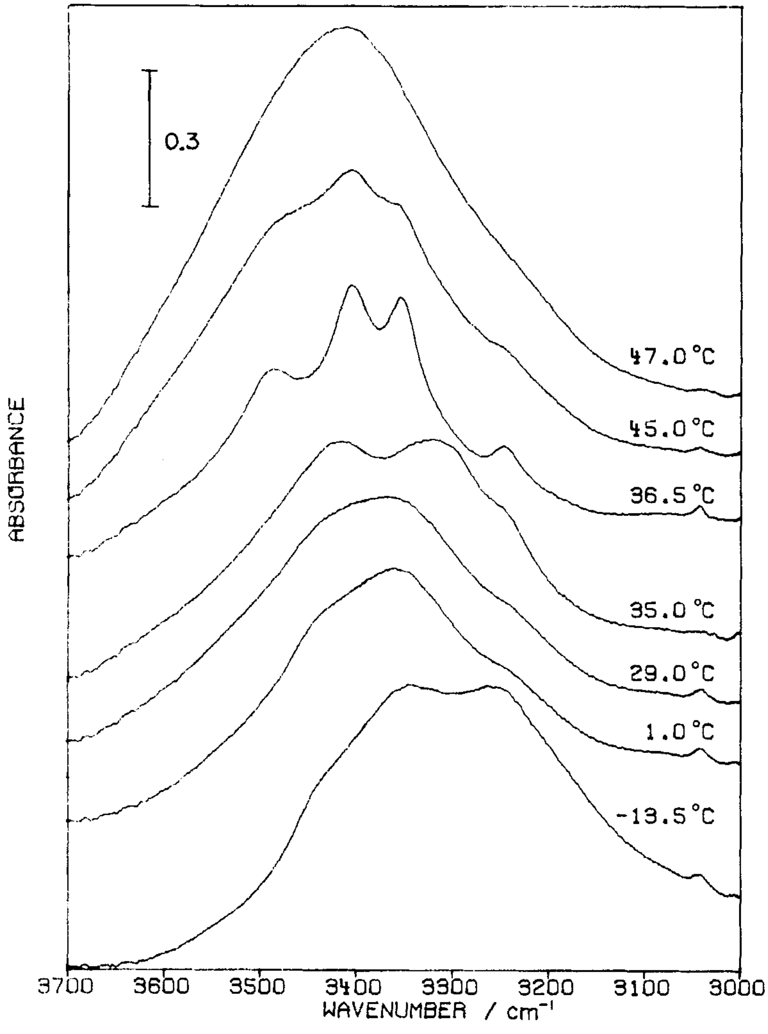

FIGURE 8 Infrared spectra of a 21 g% water-DODAC system in the 3700–3000 cm^{-1} region at various temperatures.

A smaller shoulder band remaining at this wavenumber in all the spectra in the temperature range of 1–45°C can be ascribed to an overtone of the HOH bending mode.[18] The coagel spectrum at 1°C has a main peak at ~3370 cm^{-1} and a shoulder at ~3442 cm^{-1}. This kind of band feature is indicative of the presence of the bound water,[8,18,19] being overlapped with the smooth contour of the band due to bulk free water.

Corresponding to the intermediate state between coagel and gel phases mentioned above, the spectrum at 35°C gives two peaks, each being at lower wavenumber than corresponding one of the coagel peaks at 1°C (see Table I). The lower wavenumber shifts of water peaks in the intermediate state at 35°C seem to indicate that the hydrogen bonding of water in the intermediate state is stronger than that of the coagel phase. To see the process from the coagel to intermediate state in more details, spectra in the temperature range 29-35°C are given in Figure 9. With increasing temperature, the intensity of the 3370 cm^{-1} peak decreases while those of the 3418 and 3320 cm^{-1} peaks increase. Two isosbestic points are discerned at 3411 and 3340 cm^{-1}, suggesting the presence of thermal equilibrium in the aggregation states of water between the coagel and intermediate phases.

In the gel phase at 36.5°C (Figure 8), the OH stretching band of water becomes more fine-structured than that in the coagel or intermediate states. The increase in number and sharpness of the peaks

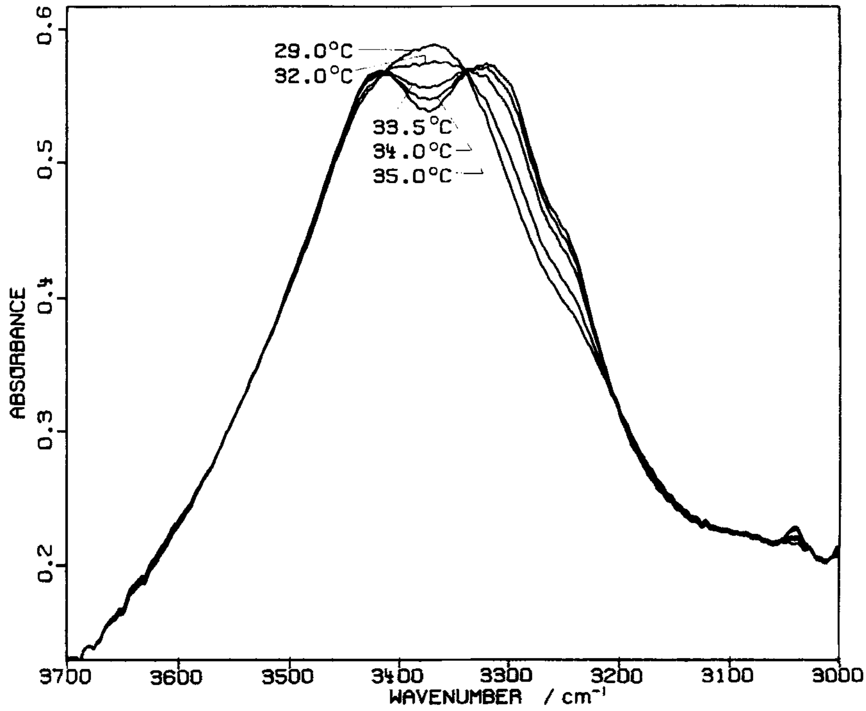

FIGURE 9 Temperature dependent behaviour of the OH stretching bands of water in the 21 g% water-DODAC sample in the temperature range 29–35°C.

indicates that more water molecules become incorporated into the bilayers as the bound water, the state of which differs from those in the coagel and intermediate phases. This result for the gel phase of the water-DODAC system makes a striking contrast to that for the water-ODAC system where any sign of the presence of bound water has not been detected as far as the infrared spectra are concerned. The spectral feature in the gel phase at 36.5°C rather resembles that of the coagel phase of the water-ODAC system.[8] Further, when we recall the appearance of the definite peak due to the asymmetric $CH_3(N^+)$ stretching band at 36.5°C in Figure 6, the generally accepted concept from the x-ray diffraction studies[6,7] that in the gel phase the polar group is in a fused state does not seem to hold any longer in this system.

The water spectrum in the liquid crystalline phase (47°C) in Figure 8 resembles that of the bulk water, suggesting the lack of strongly bound water. The spectral feature of this phase corresponds to those of the gel and liquid crystalline phases of the water-ODAC system.

In Figure 7, the peak wavenumber of the HOH bending band of water was also plotted as a function of temperature. The small increment of wavenumber in the intermediate state at 32–35°C is followed by a large wavenumber shift toward lower values in the gel phase. Then, the peak wavenumber increases again at the gel-liquid crystalline transition temperature of 45.5°C. The most striking feature in Figure 7 is that the change in the state of the $(CH_3)_2N^+$ group in the hydrophilic part of the amphiphile occurs in concert with that of water molecules in close proximity to this group.

COMPARISON WITH THE WATER-ODAC SYSTEM

The results of the present work are summarized in Table II, where that of the water-ODAC system[8] is also given for comparison. It can be found from the table that the behaviours of the methylene chain in both systems are just the same in each phase. However, the features of the hydrophilic part of the amphiphiles and of water are appreciably different: the liquid crystalline and gel phases of the water-DODAC system mimic the gel and coagel phases of the water-ODAC system, respectively. This is partly because the access of water molecules to the hydrophilic part of DODAC is more difficult than the case of ODAC in the low temperature phases, owing to the increased steric hindrance due to the increased number of long methylene chain. Another possible reason may be that in ODAC with a single hydrocarbon chain the rotation of the three methyl groups as a whole

TABLE II

Structural features of the water-DODAC system in various phases, as compared with those of the water-ODAC system.

Phase	21 g% water-DODAC system	20 g% water-ODAC system[a]
Liquid crystalline phase	1. Methylene chains in disordered state 2. Hydrophilic part in fused state 3. Only bulk water	1. Methylene chains in disordered state 2. Hydrophilic part in fused state 3. Only bulk water
Gel phase	1. Methylene chains in rotor phase 2. Hydrophilic part in fixed state 3. More bound water	1. Methylene chains in rotor phase 2. Hydrophilic part in fused state 3. Only bulk water
Coagel phase	1. Methylene chains in parallel packing 2. Hydrophilic part in fixed state 3. Less bound water	1. Methylene chains in parallel packing 2. Hydrophilic part in fixed state 3. More bound water

[a] Ref. 8.

around the $C - N^+$ axis is easy, while in DODAC with double chains this kind of rotation is practically impossible. As a result, in the gel phase, the hydrophilic part of DODAC is in a rather fixed state, while that of ODAC is in a fused state as far as the infrared studies are concerned. Thus, it is concluded that the generally accepted idea for the gel phase that the polar group is in a fused state does not hold in the present water-DODAC system.

CONCLUDING REMARKS

The present work demonstrates that the infrared spectral data provide useful structural informations concerning the changes of behaviour of hydrophobic as well as hydrophilic parts of an amphiphile and water molecules at phase transitions of water-amphiphile systems. Since we could not find any methylene chain spectra (Figures 1, 3, and 4) characteristic of the intermediate state at 35°C, it can be said that the hydrophobic methylene chains in DODAC are subjected to structural changes only on the coagel-gel and gel-liquid crystalline phase transitions. On the other hand, the hydrophilic part of DODAC and water molecules bound to it behave in a different manner from the case of ODAC-water system. In the present system, they exhibit the characteristic band features corresponding to the intermediate state between the coagel and gel phases, as seen in Figures 6–9. This means that prior to the rearrangement of the methylene chain on the coagel-gel transition, water and the hydrophilic part of DODAC experience some structural rearrangements as a kind of cooperative interaction.

More detailed analyses of the spectral features in the water-DODAC systems are in progress using the infrared polarization measurements of partially oriented samples.

Acknowledgements

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