THERMAL STUDY ON THE INTERACTION OF CRYSTALLINE SURFACTANT WITH WATER: THE DIOCTADECYLDIMETHYLAMMONIUM CHLORIDE—WATER SYSTEM

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ABSTRACT

Dioctadecyldimethylammonium chloride (DOAC) was completely dehydrated under high vacuum and at a temperature above its transition temperature ($93.7°C$) which was first discovered by us. Thermoanalytical studies on DOAC—water systems indicate that two successive phase changes of coagel $\rightarrow$ gel and gel $\rightarrow$ liquid crystal appear due to the increasing structural disorders of polar head groups and hydrocarbon chains, respectively. Furthermore, it is revealed that three types of water exist, i.e., bound, intermediate and free. On the basis of a bilayer—lamellar structure model, a predominant role of the intermediate water in these transitions is pointed out.

INTRODUCTION

In recent years, amphiphilic compounds have been attracting the attention of many investigators in connection with biological membranes. A great number of papers and review articles concerning lipids, both anhydrous and water-containing, have appeared [1—7] and, in particular, studies on the phase transition phenomenon in view of lyotropic liquid crystals are still underway. In contrast to this trend, it may be pointed out that the studies of surfactants in this field, except the extensive investigations on fatty acid alkali soaps [1,4,8—11], have fallen behind in their progress, and a large part has been concerned with micelle formation in dilute solutions.

DOAC, which possesses a cationic polar head group and two long hydrocarbon chains and is known to have analogous properties to lipids [12—14], was chosen as the surfactant in the present work. It has been proposed that in biopolymers [15] and macromolecular gels [16,17], in addition to the so-so-called bound water and free water, there exists a new type of water called "secondary bound water". In this study, the thermal analyses of about 40 specimens in the DOAC—water system, ranging from a completely dehydrated compound to about 85 g% water content, were carried out in terms of both "chain-melting" and "ice-melting". The results obtained are discussed from the viewpoint of roles and properties of water in the present system.

EXPERIMENTAL

Sample

DOAC was kindly supplied by Kao Soap Co. Ltd., and was purified by recrystallization from acetone solution three times. As this compound is extremely hygroscopic, the condition for complete dehydration was examined by plotting the weight-loss vs. time curve with the use of a Cahn electrobalance Model 2000 under high vacuum and at various temperatures. As shown in Fig. 1, the weight of the sample decreased continuously with time under high vacuum (10^{-4} Pa) and reached a constant value after 15 h at room temperature, and kept at constant value during further evacuation for about 20 h. However, at a temperature above the transition temperature, which was first discovered in the present work as described below, more weight-loss was detected. Based on these findings, it was revealed that the complete dehydration could be achieved only when the compound was dehydrated under high vacuum and at a temperature above its transition temperature.

DSC measurements

The following procedure was used to pack the completely dehydrated sample into the DSC crucible. The purified compound (40—50 mg) was first put in an aluminium container. After complete dehydration, its weight
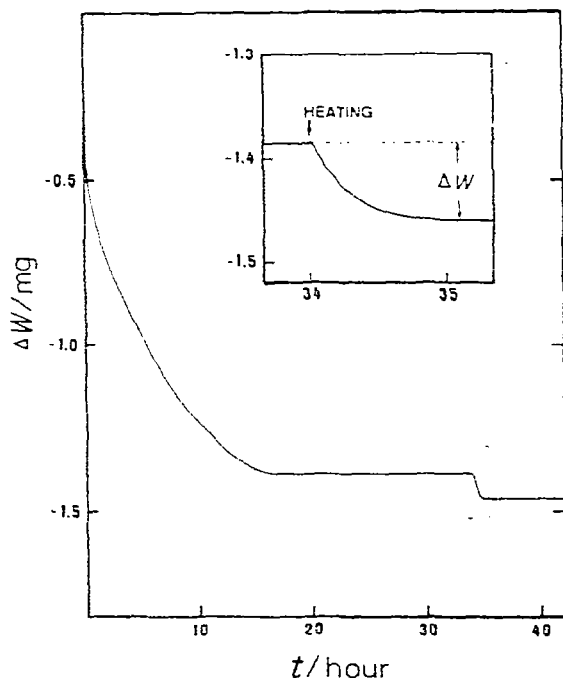

Fig. 1. Dehydration curve of DOAC. The scale for the part surrounded by the broken line is enlarged.

(w_1) was determined using a Cahn electrobalance. Once exposed to the atmosphere, the compound was then poured into the high-pressure crucible of a Mettler DSC TA2000 directly from the aluminium container, and was completely dehydrated again following the procedures described above. After this treatment, the high-pressure crucible was sealed in a dry box filled with dry N_2 gas. The weight (w_2) of the minute amount of specimen attached to the wall of the aluminium container was determined using a Cahn electrobalance after the complete dehydration treatment. The weight of the sample contained in the high-pressure crucible was finally determined as $w_1 - w_2$.

Samples of the DOAC—water mixture were prepared by adding a controlled amount of water to the completely dehydrated compound using a microsyringe. These mixtures were preheated to 100°C before thermal analysis in order to assure complete mixing, and were then cooled to —20°C (allowing about 1 h).

Thirty samples, which covered the water content from zero to about 85 g%, were prepared. For all samples, the measurements were carried out in the temperature range —20 to 150°C, and the heating rate adopted was $1°C \, min^{-1}$, unless otherwise specified.

RESULTS

Figure 2 shows a series of DSC curves in the heating process for various samples: anhydrous DOAC and DOAC—water mixtures. Completely dehydrated DOAC exhibits only a pronounced, primary endothermic peak at
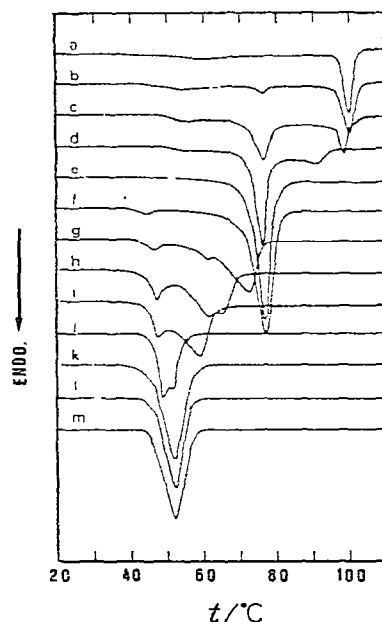

Fig. 2. Typical DSC curves for 13 samples with increasing amounts of water (g%). a, 0; b, 0.08; c, 0.78; d, 1.36; e, 2.32; f, 4.10; g, 6.49; h, 8.76; i, 11.2; j, 17.4; k, 21.3; l, 39.8; m, 85.7.

96.7°C (see curve a). Values of enthalpy and entropy changes in this transition are 37.3 kJ mole^{-1} and 103.0 J K^{-1} mole^{-1}, respectively. The minute amount of water (as low as 0.08 g%), which corresponds to Δw in Fig. 1, causes a new, second endothermic peak at about 70°C (see curve b). With further increase in water content in the mixture, the second peak becomes larger, while the primary peak becomes broader and smaller and, at the same time, the transition temperature decreases (see curves c and d). When the water content reaches about 2.5 g%, the second peak becomes the largest and any other transition is no longer observed (see curve e). For the samples with a water content between 4 and 17 g%, the second peak becomes broader and, at the same time, is followed by the appearance of new third and fourth endothermic peaks at about 60°C and 46°C, respectively (see curves f—j). The third peak becomes broader after further growth and the fourth peak becomes progressively greater. When the water content reaches about 20 g%, only the fourth peak persists in the temperature region above 20°C (see curve k). The area and the temperature of this transition remain nearly constant up to 85.7 g% (see curve m). Table 1 summarizes the enthalpy and entropy changes in the transition at 46°C for five specimens in the region 20—85 g%, showing their nearly constant values. Figure 3 shows the phase diagram of the DOAC—water system obtained from all the DSC heating curves. With the increase of water content, the transition temperature reaches the limiting value of 46°C, which is represented by a straight line parallel to the abscissa. This temperature may be assumed to correspond to the so-called Krafft point of DOAC.

As shown in Fig. 4, when the DSC measurement is made at a heating rate as slow as 0.2 °C min^{-1} instead of 1°C min^{-1} mentioned above, a broad exothermic peak appears around 20°C, followed by endothermic peaks with complex structures at about 36°C (about 10°C lower than the limiting temperature of 46°C) for the samples with a water content of more than 11 g%. In order to examine the nature of this exothermic effect, the samples were annealed at a temperature close to 20°C for about 12 h. Figure 5 shows the DSC heating curves for these annealed samples in comparison with the untreated ones. Evidently the annealed samples exhibit a well-developed endothermic peak at about 36°C, successively followed by the endothermic peak at the limiting temperature of 46°C, and experienced no exothermic peak even at the slow heating rate of 0.2°C min^{-1}. In addition, the annealed

TABLE 1

Enthalpy and entropy changes at the gel—liquid crystal phase transition (Krafft point)

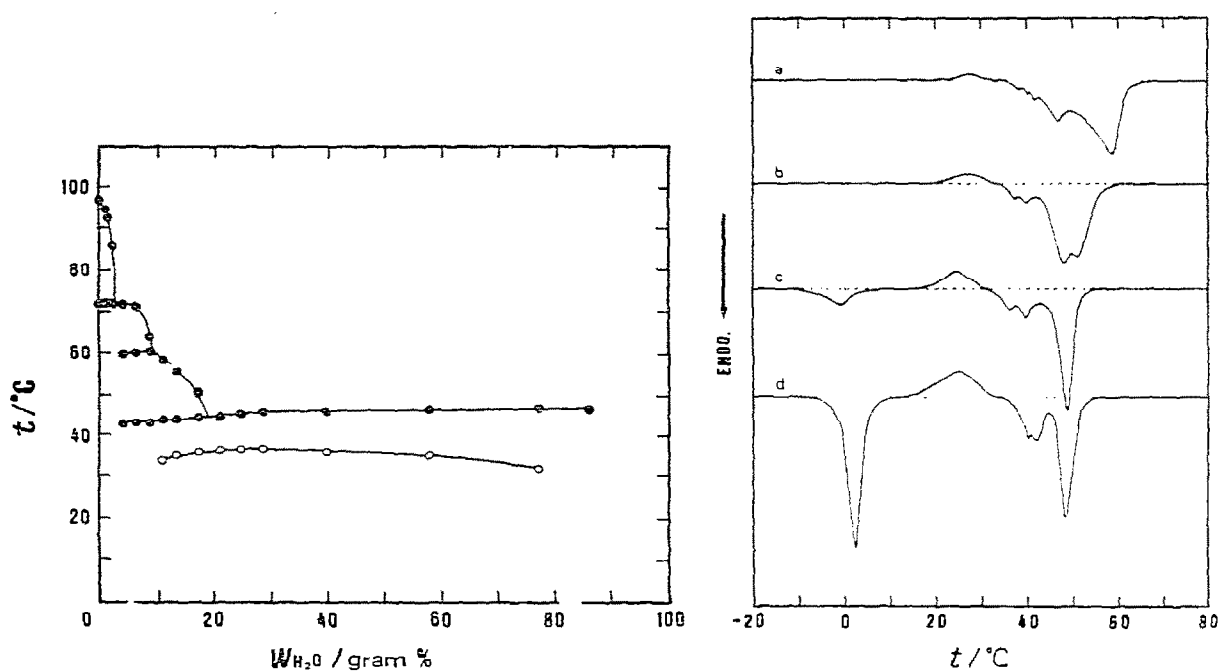| w_{H_2O}(g%)	ΔH(kJ mole^{-1})	ΔS(J mole^{-1} K^{-1})
21.16	25.5	79.9
28.54	24.6	77.1
39.80	24.4	76.4
57.92	24.1	75.4
85.70	23.7	74.1

Fig. 3. Phase diagram of the DOAC—water system, ○, Temperatures for coagel—gel phase transitions.

Fig. 4. DSC curves obtained at the scanning rate of $0.2°C\ min^{-1}$ for four specimens with different amounts of water (g%). a, 11.18; b, 17.40; c, 21.26; d, 39.80.
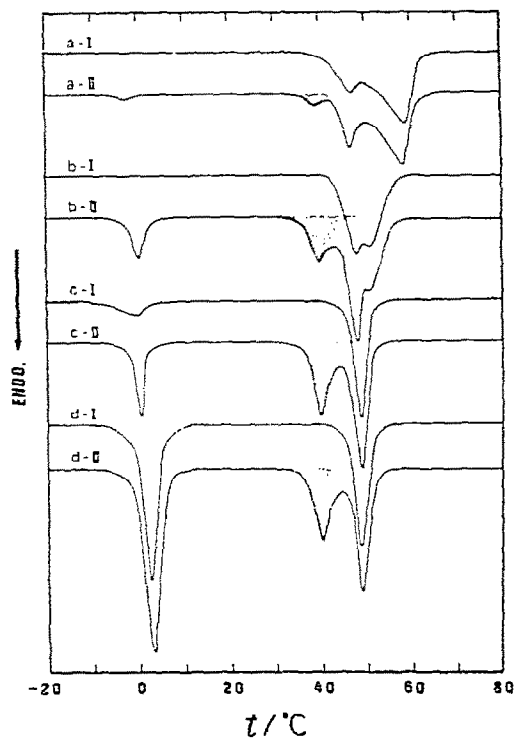

Fig. 5. DSC curves for four specimens with different water contents at the scanning rate of $1°C\ min^{-1}$, each corresponding to the samples given in Fig. 4. Unannealed (I) and annealed (II) samples with the same water content are compared in pairs. The dotted peaks indicate the coagel—gel phase transitions.

samples containing more than 11 g% water content exhibit a new endo-
thermic peak at about 0°C due to the melting of ice, the area of the peak
becoming larger with an increase in water content. On the other hand, for
unannealed samples, the peak at 0°C is not observed until the water con-
tent reaches more than 18 g%. The estimation of the enthalpy change due to
the melting of ice at 0°C enables the determination of the amount of the
so-called "free water" which is present in the specimen. The variations of the
enthalpy change at 0°C with water content for the annealed and unannealed
samples are shown in Fig. 6, where the enthalpy change, ΔH, is plotted vs.
the amount of water added to 1 g of DOAC. In Fig. 6 the dashed line
indicates the value of ΔH calculated on the assumption that all the water in
the samples is present as free water. ΔH for both the annealed and the
unannealed samples increases linearly and parallel to the dashed line starting
from the points of water contents of 11 and 18 g%, respectively. The results
of thermal analysis on the states of water in the present system given in Fig.
6 elucidate the following.

(a) When the water content for the annealed and the unannealed samples
reaches 11 and 18 g%, respectively, the state of free water appears for the
first time.

(b) The difference in ΔH between the dashed line and that of the unan-
nealed sample corresponds to the amount of water which does not crystallize
on cooling to $-20°C$. The amount of non-freezable water for the unan-
nealed sample reached maximum value at a water content of 18 g%, so the
addition of further water furnishes the freezable free water.

(c) Similarly to case (b), the maximum amount of non-freezable water for
the annealed sample is achieved at a water content of 11 g%, beyond which
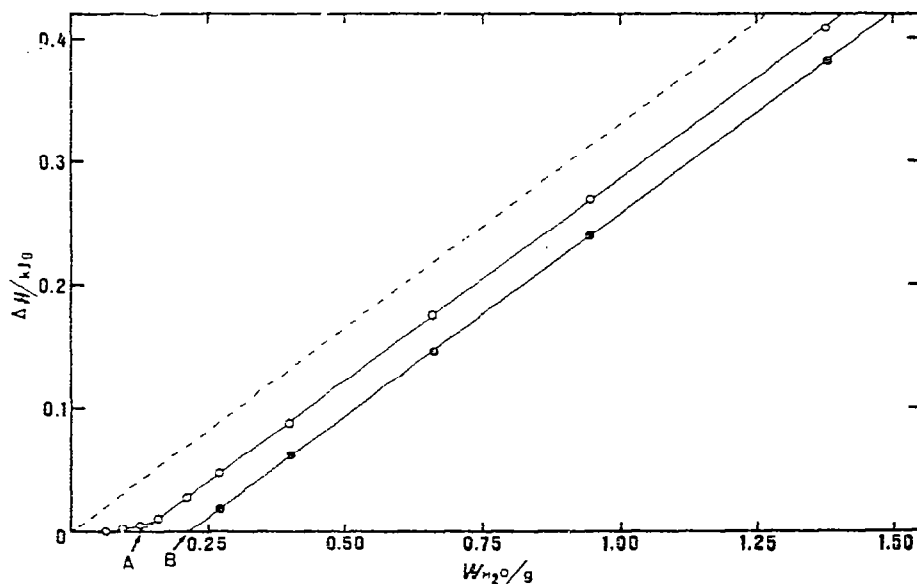the freezable water is furnished.

Fig. 6. Relationship between ΔH due to the melting of ice and the amount of water
added to 1 g of DOAC. A and B indicate 11 and 18 g% water, respectively. ○, Annealed
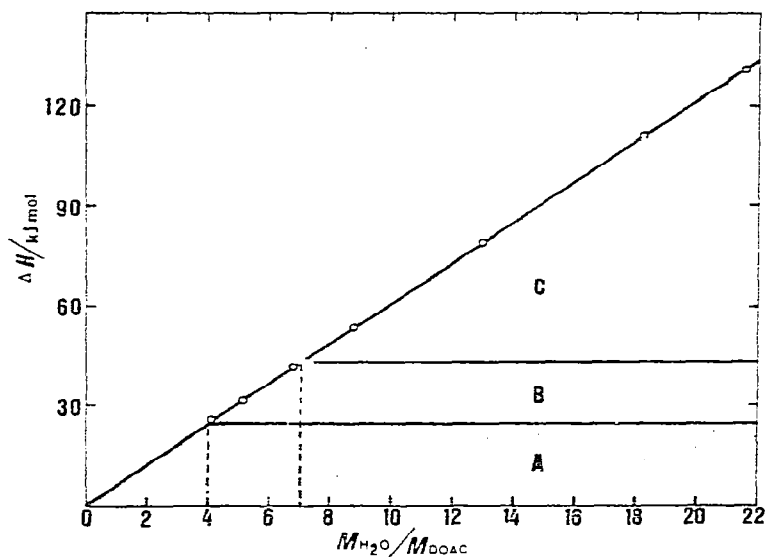sample; ◑, unannealed sample; — — —, theoretical curve.

Fig. 7. Relation between ΔH and mole numbers of water per mole of DOAC. A, B, and C represent the bound, intermediate, and free water, respectively.

(d) The difference in ΔH between the annealed and unannealed samples corresponds to an increased amount of the free water brought about by the annealing treatment, indicating that some part of the non-freezable water before annealing is converted to free water after treatment.

Based on these facts, it may be said that three types of water exist in the DOAC—water system, as shown in Fig. 7 where ΔH is plotted against the molar ratio of water to DOAC. In Fig. 7, A corresponds to the so-called bound water which does not crystallize on cooling to $-20°C$ and is strongly hydrated with DOAC molecules in a fixed molar ratio of 4 : 1; B corresponds to the so-called intermediate water, i.e., the weak-bound water, which can be converted to the free water on annealing treatment. This water is also associated with the DOAC molecule in a fixed molar ratio of 3 : 1; C corresponds to the free water, i.e., the ordinary water. In conclusion, it may be noted that in the system below 11 g% water content, only the bound water is allowed to exist; in the region of 11—18 g% the bound water and the intermediate water can coexist and above 18 g% all three kinds of water can coexist.

DISCUSSION

In amphiphillic compounds, such as lipids and surfactants having long hydrocarbon chains and polar head groups, their hydrocarbon chains are known to undergo order—disorder transitions, depending on both temperature and water content, before reaching the final transition to the liquid state. The entropy change in the transition of the completely dehydrated DOAC crystal at 96.7°C is about half that of n-alkane with the same chain

length at its melting point, which is in good agreement with the results obtained for some lipids reported by Chapman et al. [6,7]. This small value may be attributed to the reduction in the variation of molecular motion due to two hydrocarbon chains anchored to the polar head groups with the ordered configuration, as pointed out by Phillips et al. [7]. Accordingly, the hydrocarbon chains of DOAC above the transition temperature may be said to exist in a partly fused state. As represented by the phase diagram of the DOAC—water system shown in Fig. 3, the transition temperature decreases stepwise to the limiting value of the Krafft point with an increase in water content. Thus, the limiting temperature can be attained not by a direct shift of the primary endothermic peak itself to that temperature, but by the new appearance of the fourth endothermic peak located around the Krafft temperature. This is quite different from the results concerning the lipids—water system studied by Chapman et al. [6].

It has recently been proposed by some workers that in the present system the phase change from the gel to the liquid crystalline phases, due to the chain melting, occurs at the Krafft point [12—14]. Above the Krafft point DOAC—water mixtures form a lamellar liquid crystalline phase which consists of bimolecular layers of DOAC molecules separated by the water layers, while for the surfactant with one long hydrocarbon chain and the same kind of polar head group, a transition to the micellar solution (not to the liquid crystal) takes place at the corresponding temperature [13,18]. When DOAC—water mixtures are cooled to a temperature below the Krafft point, the so-called lamellar gel phase comes into existence where the hydrocarbon chains adopt the ordered structure and the water will be retained between these surfactant bilayers [1,5,11]. The liquid crystalline and gel phases arising from the co-operational interaction between DOAC and water molecules in the present system may be compared with the similar situation in the lipid system.

On the basis of the bilayer—lamellar model mentioned above, the different state of aggregation of water molecules below the Krafft point will be discussed (refer to Fig. 6). For the unannealed samples, the gel phase is allowed to exist as a metastable state even at a temperature below the Krafft temperature down to −20°C. The non-freezable water given in Fig. 6 can be assumed to correspond to the water interposed between the bilayers of DOAC molecules, i.e., the water layers are composed of both bound and intermediate waters, as shown in Fig. 7. In the system with the water content below 11 g%, all the water molecules are strongly bound to the polar head group of the DOAC molecule. The limiting amount of bound water incorporated between the bilayers is accomplished by the water content of 11 g%. The addition of more water up to 18 g% water content gives the intermediate water. In this situation, the thermal motion of the intermediate water may be more or less limited, because of an ordering effect of the bound water. The water content of 18 g% suggests the limiting amount of the intermediate water incorporated between the bilayers in the gel phase. In other words, any additional water beyond this content gives rise to phase separation and two phase systems; the gel phase with the maximum amount of interlamellar water coexists with the excess free water. This gel

phase, which is hereafter referred to as the "perfect gel" phase, is shown to consist of a total of seven water molecules, four of which are of the bound water and three are of the intermediate water, incorporated between the bilayers.

It is interesting to note here that the final single endothermic peak due to the chain-melting at the Krafft point is established at the same water content at which the endothermic peak at about $0°C$, due to the ice-melting, starts to appear (see curve c-I in Fig. 5). In other words, this result indicates that the transition from the perfect gel to the liquid crystalline phase is exhibited by the single peak at the Krafft point. Therefore, it may be said that the melting phenomenon of the hydrocarbon chains anchored to the polar heads groups is closely related to the amount of water incorporated between the bilayers in the gel phase, but not to a total amount of water added to the specimen. Several workers [1,5,11,19,20] have proposed that a penetration of water into the bilayers causes loosening in the structure of the polar head groups which is due to the electrostatic repulsion resulting from their ionization. In the water content range 18—85 g%, the perfect gel phase coexists with the excess free water. This means that the constant degree of loosening in the ordered configuration of the polar head groups is retained in the region of 18—85 g% water content, so that the degree of disorder in the structure of the hydrocarbon chains above the Krafft point is also nearly the same in this region, as indicated by the entropy data in Table 1. It may be said that the chain-melting phenomenon in the present system is intimately connected with the loosening effect of the interlamellar water on the configurational change of the polar head groups in the gel phase.

Now, we should like to proceed to a discussion of the gel—coagel transition. We have already mentioned that the annealing treatment on a gel system leads to a change in the water structure from the intermediate water to the free water, indicative of a conversion from the interlamellar water as the members of the gel phase to the excess free water. On losing the intermediate water, the gel phase is expected to be transformed into a new phase. This phase may be regarded as the so-called "coagel phase" which consists of the crystalline hydrated surfactant in excess free water [5,11,19]. While the bound water is still retained, the polar head groups in the coagel phase have a more ordered configuration than those in the gel phase, because of the absence of the intermediate water between bilayers. In these respects, Fig. 6 shows the different actions of the three states of water on the gel and the coagel phases, each of which corresponds to the unannealed and annealed samples, respectively. The limiting amount of interlamellar water for the coagel phase is achieved at a water content of 11 g% and the water added beyond this limiting value is present as the excess free water, similar to the case of the gel phase mentioned above. In Fig. 5, the endothermic peaks (dotted area) at the temperature just below the Krafft point for the annealed sample correspond to the phase change from the coagel to the gel, indicative of a conversion to a less ordered configuration of the polar head groups due to the incorporation of the water between bilayers. In other words, the degree of configurational disorder of the polar head groups after that transition is determined exclusively by the amount of intermediate

TABLE 2

Enthalpy and entropy changes at the coagel—gel phase transition

w_{H_2O}	ΔH (kJ mole^{-1})	ΔS (J mole^{-1} K^{-1})
21.26	24.9	82.4
28.54	24.9	82.4
39.80	24.7	82.4
57.92	25.1	82.4
85.70	25.0	82.3

water. The excellent agreement within experimental error among the entropy changes associated with the coagel—gel transition for all five specimens in the range 20—85 g% (see Table 2) gives strong evidence for the present interpretation of the penetration mechanism of water into the lamellar structure. It may be interesting to note that the endothermic peak for the coagel—gel transition appears for the first time at the same water content at which the peak at $0°C$ for the melting of the excess water coexisting with the coagel phase starts to appear (see curve a-II in Fig. 5). This implies the necessity of the excess waters for the coagel—gel transition. This water becomes incorporated between the bilayers and is converted into the intermediate water at the transition point. Thus, the gel phase is not formed as long as the water content is less than 11 g%.

Finally, we should like to explain the phase relationship given in Fig. 3 based on the nature of each phase transformation phenomenon explained above. In the region of water content less than 11 g%, the amount of water incorporated between bilayers does not reach the limiting value (4 H$_2$O) for the coagel formation, so that, to some degree, a phase may be constructed with an anhydrous crystal and a hydrated one. This phase is assumed to pass into the chain-melting state, without passing through the gel phase. In the range 11—18 g%, the coagel phase having 4 H$_2$O is able to coexist with the excess water. In the heating process, this phase is transformed into a gel phase at about $36°C$, as shown in Fig. 4. However, the gel phase obtained here is not the perfect gel, but is composed of a single phase with no excess water. When this gel phase is cooled to $-20°C$, it remains in a super-cooled state, so no endothermic peak due to the ice-melting is observed in the heating process, as shown in Fig. 5 (see curves a-I and b-I). Further, in the water content range greater than 18 g%, the coagel phase is transformed into the perfect gel phase where it coexists with the excess water phase (see curves c-I and d-I in Fig. 5).

REFERENCES

1 V. Luzzati, in D. Chapman (Ed.), Biological Membranes, Academic Press, New York, 1968, p. 81.
2 D. Chapman, in G.W. Gray and P.A. Winsor (Eds.), Liquid Crystals and Plastic Crystals, Vol. 1, Ellis Horwood, London, 1974, p. 288.
3 K. Fontell, in G.W. Gray and P.A. Winsor (Eds.), Liquid Crystals and Plastic Crystals, Vol. 2, Ellis Horwood, London, 1974, p. 80.
4 J. Charvolin and A. Tardieu, in L. Liebert (Ed.), Solid State Physics, Liquid Crystals, Suppl. 14, Academic Press, New York, 1978, p. 209.
5 H. Hauser, in F. Franks (Ed.), Water, Vol. 4, Plenum Press, New York, 1974, p. 209.
6 D. Chapman, R.M. Williams and B.D. Ladbrooke, Chem. Phys. Lipids, 1 (1967) 445.
7 M.C. Phillips, R.M. Williams and D. Chapman, Chem. Phys. Lipids, 3 (1969) 234.
8 J.W. McBain and W.W. Lee, Oil Soap, 20 (1943) 17.
9 V. Luzzati and F. Husson, J. Cell Biol., 12 (1962) 207.
10 P. Ekwall, in G.H. Brown (Ed.), Advances in Liquid Crystals, Vol. 1, Academic Press, New York, 1975, p. 1.
11 P.A. Winsor, in G.W. Gray and P.A. Winsor (Eds.), Liquid Crystals and Plastic Crystals, Vol. 1, Ellis Horwood, London, 1974, p. 71.
12 T. Kunitake and Y. Okahata, J. Am. Chem. Soc., 99 (1977) 3860.
13 T. Nagamura, S. Milhara, Y. Okahata, T. Kunitake and T. Matsuo, Ber. Bunsenges. Phys. Chem., 82 (1978) 1093.
14 H. Kunieda and K. Shinoda, J. Phys. Chem., 82 (1978) 1710.
15 R. Cook and I.D. Kuntz, Annu. Rev. Biophys. Bioeng, 3 (1974) 95.
16 M. Aizawa and S. Suzuki, Bull. Chem. Soc. Jpn., 44 (1971) 2967.
17 M. Aizawa, J. Mizuguchi, S. Suzuki, S. Hayashi, T. Suzuki, N. Mitomo and H. Toyama, Bull. Chem. Soc. Jpn., 45 (1972) 3031.
18 R.R. Balmbar, J.S. Clunie and J.F. Goodman, Nature (London), 222 (1969) 1159.
19 J.M. Vincent and A.E. Skoulios, Acta Crystallogr., 20 (1966) 432, 441, 447.
20 D. Atkinson, H. Hauser, G.G. Shipley and M. Stubbs, Biochim. Biphys. Acta, 339 (1974) 10.