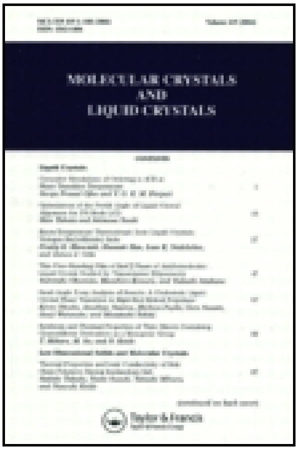

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Enthalpies of Lyotropic Liquid Crystalline Phases. : 2. The Partial Molar Enthalpies of the Lamellar and Hexagonal Phases in the System N-Pentanol-Sodium N-Octanoate-Water

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Enthalpies of Lyotropic Liquid Crystalline Phases.

2. The Partial Molar Enthalpies of the Lamellar and Hexagonal Phases in the System *N*-Pentanol-Sodium *N*-Octanoate-Water

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The relative partial molar enthalpies of the components in the system *N*-pentanol-sodium *N*-octanoate-water ($C_5OH—NaC_8—H_2O$) have been determined in the lamellar (*D*-) and hexagonal (*E*-) liquid crystalline phases formed in this system at 25°C. The enthalpies are correlated with Bragg spacings and earlier nmr studies. They indicate that (a) the minimum amount of water needed to hydrate the polar groups limits the region of existence of both *D*- and *E*-phase towards low water contents, (b) the interaction between —OH and $—COO^-$ is especially important in stabilizing the *D*-phase containing large amounts of water, (c) the Bragg spacings and the enthalpies both change their concentration dependence markedly when the maximum amount of water that can be bound by primary hydration of the polar groups and the counter ions in the *D*-phase is exceeded, (d) enthalpies of transition from one phase to another are small compared to enthalpy changes with composition within the phases; the same holds for Bragg spacings. Hence, the composition of the sample (above all, the mole fraction of NaC_8) is more important than the phase structure in determining these properties. It is obvious that further studies of enthalpies in similar systems can give important information on the factors governing phase stabilities and structural changes within the phases.

INTRODUCTION

The structure of the aggregates formed in systems consisting of a surfactant, a weakly amphiphilic or non-polar compound and water over wide ranges of compositions has received much attention recently due to the similarity with structures formed in lipid systems[1–4] and the many technical applications of surfactant association.[5–7] In conformity with many lipid systems, several

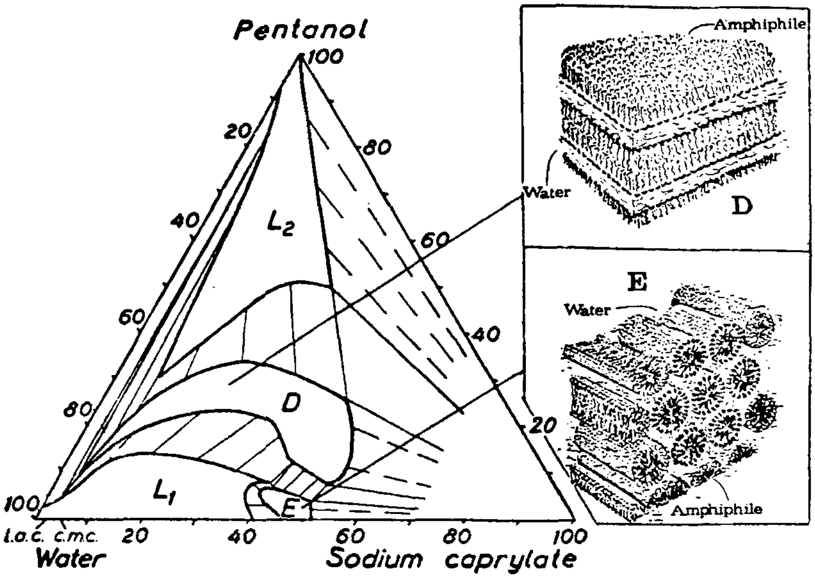

FIGURE 1 Phase diagram for the system sodium *N*-octanoate (sodium caprylate)-*N*-pentanol-water at 20°C (8). The structure of the mesophases is shown schematically, L_1 = isotropic aqueous solution. L_2 = isotropic solution of water and sodium octanoate in pentanol.

different liquid crystalline phases are formed.[8–10] Of these, the biologically most important structures are the lamellar phase *D*, the hexagonal phase *E* and the isotropic aqueous micellar solution L_1 (see Figure 1). When large quantities of non-ionic amphiphile are added an inverted hexagonal structure (*F*) and a solution containing reversed micelles (*L*2) may be formed.

In several investigations it has been shown that these phases are formed in systems where the surfactant is the alkali metal salt of a long-chain fatty acid (soap) and the amphiphile is a long-chain aliphatic alcohol. The properties studied include phase equilibria,[14] phase structures from X-ray diffraction,[12,16] volumetric changes,[15] rheology,[17] and the activity of water.[13] Detailed studies of the ionic interactions and the state of the water at the aggregate surface by different nmr methods have been published by Lindman *et al.*[18–29] As a summary of all these studies, it has been suggested that the regions of existence of the phases are restricted by

a) The volume fraction of amphiphilic material in the system,

b) The hydrogen bonding between water and the carboxyl and hydroxyl groups (i.e. the molar ratio of alcohol to carboxylate)

c) The minimum amount of water needed to hydrate the alkali metal ion and the carboxyl group (this determines the smallest amount of water needed to obtain a homogenous phase).[32]

d) The maximum amount of water that can be bound by the polar groups, the surface charge density of the polar surfaces of the mesophase aggregates and their ability to liberate counter ions (this determines the maximum amount of water in homogeneous mesophase regions).

e) The structure of the aggregates.

In this work we report studies of the calorimetrically determined enthalpies of the *D* and *E* phases in the system *N*-pentanol-sodium *N*-octanoate-water ($C_5OH—NaC_8—H_2O$) at 25°C. The results given in our first report[11] have been supplemented to some extent and, hence, are also summarized here. The lyotropic mesophases often are sensitive to temperature.[3,10,30] For this reason, we expected that the partial molar enthalpies of the components might yield information on the importance for the stabilization of the various mesophase structures of water binding and ionic interactions. We also have tried to correlate the enthalpies with changes in the Bragg spacings in the *D* and *E* phases.

EXPERIMENTAL METHODS

In the calorimetric experiments, the molar enthalpy for the following process was determined at 25°C and 1 atm (101.3 kPa):

$$H_2O(l) + NaC_8(aq) + C_5OH(l) \longrightarrow (D\text{- or } E\text{-phase}) \qquad (1)$$

Thus the standard states were pure water, pure pentanol and infinitely dilute sodium octanoate in water. The relative molar enthalpy of a phase is defined by[11]

$$L_m = x(H_2O)l(H_2O) + x(NaC_8)l(NaC_8) + x(C_5OH)l(C_5OH) \qquad (2)$$

where $x(A)$ is the mole fraction of component A and $l(A)$ is the corresponding relative partial molar enthalpy which is defined by

$$l(A) = h(A) - h^{\ominus}(A) \qquad (3)$$

$h(A)$ is the partial molar enthalpy of A and $^{\ominus}$ denotes the standard state. Details of the calculation of the relative partial molar enthalpies are to be published elsewhere;[31] in the calculations reported here all differentiations were made graphically. The experimental reproducibility of the L_m-values is $\approx 2\,\%$. The errors in the partial molar enthalpies, hence, are considerably larger, probably of the order $\pm 10\,\%$.

An LKB 10700 Batch Microcalorimeter as well as the titration and ampoule units of the LKB 8700 precision calorimetry system were used in the calorimetric experiments. Details of the experimental procedure are given in Ref.[11]

In the X-ray diffraction measurements, a Rigaku Denki small angle X-ray scattering camera connected with a Philips X-ray diffraction generator and an AEG-Telefunken F50/31 X-ray tube was used. The Cu-K$_\alpha$ line scattering was monitored with a Wallac Decem Series AS-11 Analyser and a SC-32 Scaler unit. The samples studied were some of those previously used in ^{23}Na nmr studies and details of their preparation can be found in Ref. 26. Since the symmetry of the phases is known,[8,10] in order to save time, only the reflexion of highest intensity in the low-angle region was studied since this is sufficient to determine the Bragg spacing of the phases.[12]

The sodium octanoate was prepared by neutralisation of octanoic acid with NaOH and was >99.5% pure.[11,26] The pentanol was of Merck Ag *pro analysi* grade. The water was doubly distilled.

EXPERIMENTAL RESULTS

In Figure 2, the compositions are given of the samples for which L_m and the Bragg spacings were measured (denoted by filled dots and triangles, respectively). Points for which the Bragg spacings are known from previous

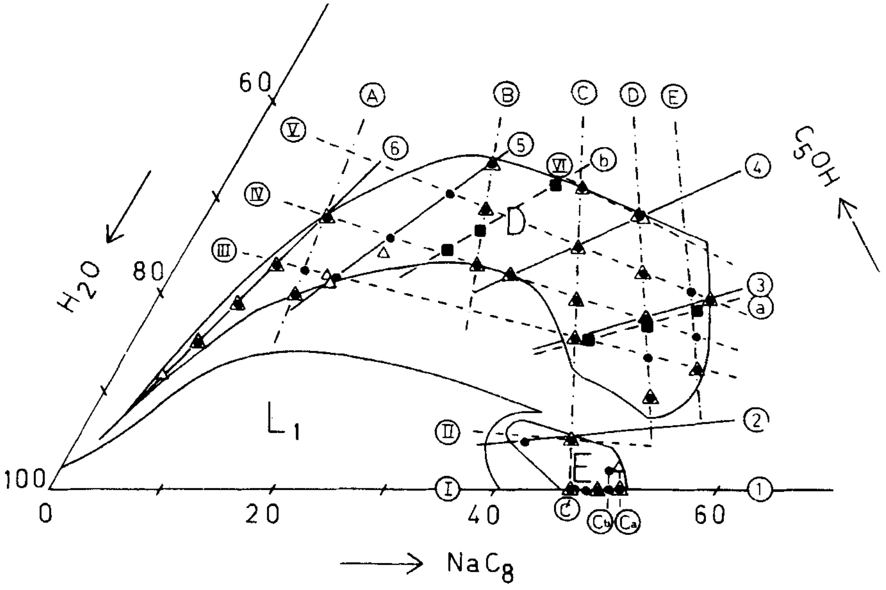

FIGURE 2 The composition of the samples for which the molar enthalpies of formation (L_m, denoted with dots) and the Bragg spacings (d, denoted with triangles) have been determined plotted in part of the phase diagram in Figure 1. The letters and numbers refer to samples for which the amount of one component is varied as the molar ratio of the two others is kept constant (see text). The filled squares refer to the samples for which d-values were determined photometrically, and were taken from Ref. 12.

photometric measurements[12] are also given (denoted by filled squares). The compositions have been systematically chosen to fall on lines corresponding to constant molar ratios $n(C_5OH)/n(NaC_8)$ (lines 1-6, *a* and *b*), $n(H_2O)/n(NaC_8)$ (lines A-E) and $n(H_2O)/n(C_5OH)$ (lines I-VI), respectively. This method simplifies the calculation of partial molar enthalpies[31] as well as the interpretation of the effect of each component on the phase properties.

1 Lines with constant $n(C_5OH)/n(NaC_8)$

In Figure 3 are given the L_m when the water content is increased for lines with constant $n(C_5OH)/n(NaC_8)$. The L_m decreases with the water content in

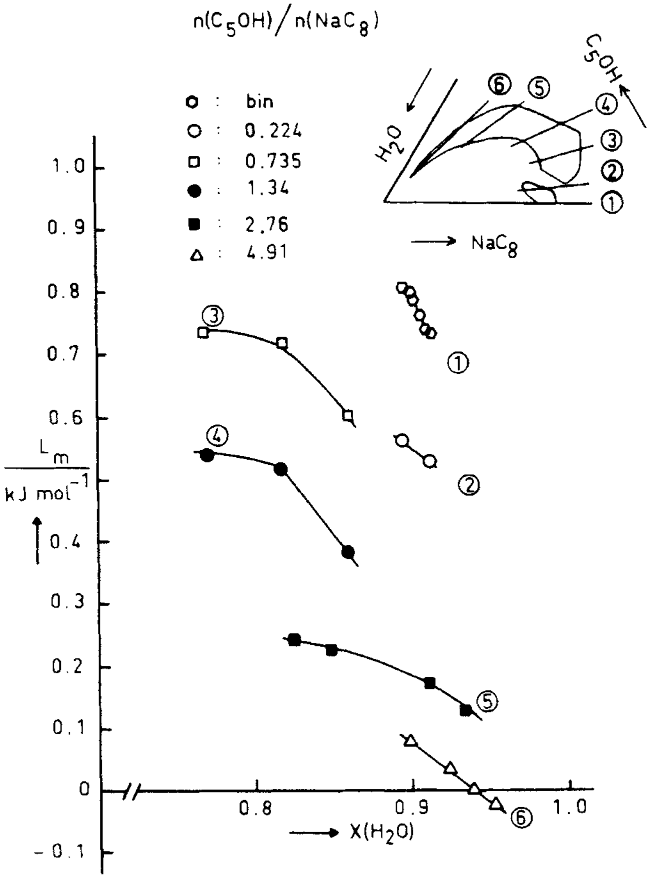

FIGURE 3 The relative molar enthalpies of the *D*- and *E*-phases given as function of $x(H_2O)$ for different constant molar ratios of C_5OH to NaC_8 at 25°C. The numbers refer to the lines given in Figure 2.

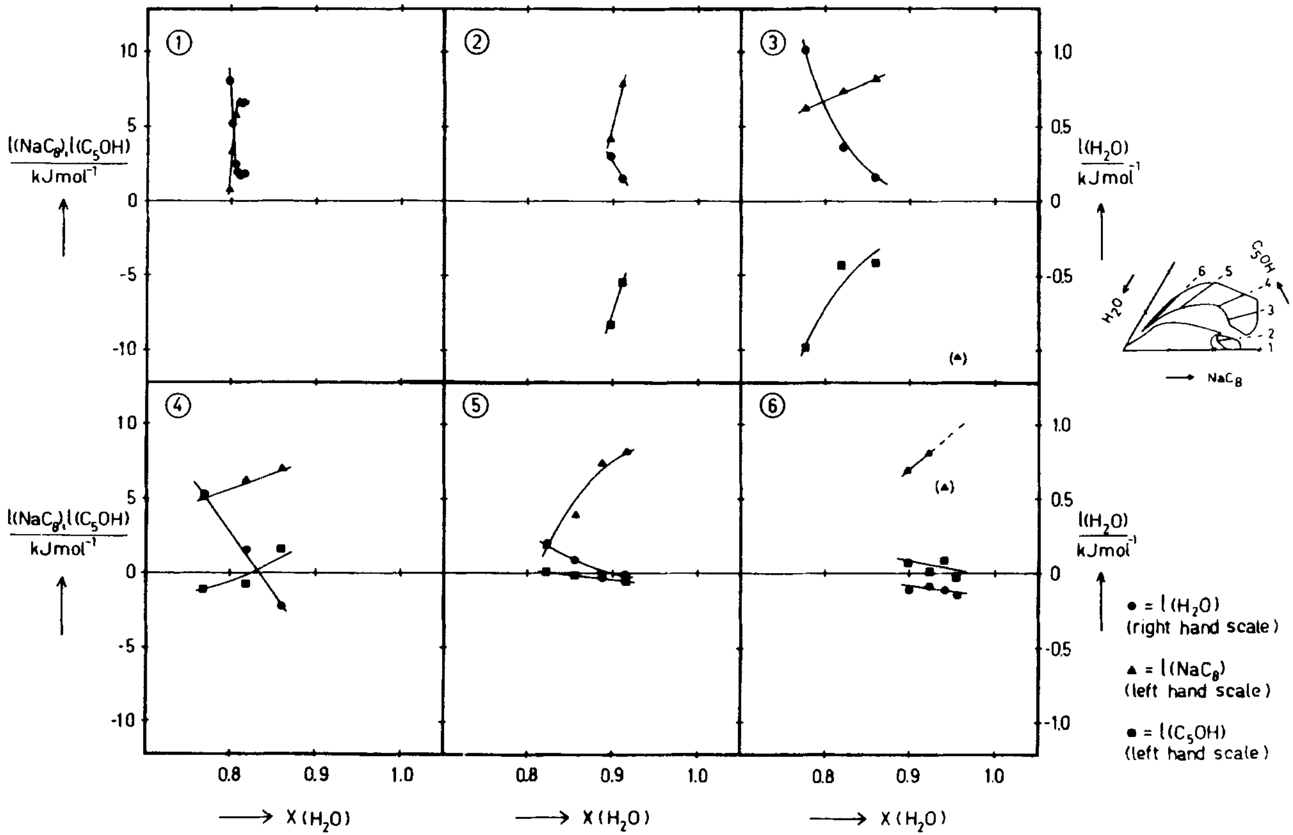

FIGURE 4 The relative partial molar enthalpies of the components in the system $H_2O—NaC_8—C_5OH$ of the *D*- and *E*-phases given as a function of $x(H_2O)$ for the different constant molar ratios of C_5OH to NaC_8 of the corresponding lines in Figure 3. The numbers refer to the lines in Figures 2 and 3.

all cases, the dependence being the largest for small molar ratios (lines 1–4) and quite small for low octanoate contents (lines 5, 6). The absolute value of L_m decreases as $n(C_5OH)/n(NaC_8)$ increases. There is no dramatic difference between the enthalpies of the *E*- and *D*-phases.

In Figure 4 are shown the changes in the relative partial molar enthalpies of each component along each of lines 1–6. At low water contents in the *E*-phase (lines 1 and 2) the enthalpy of the water is high and that of the NaC_8

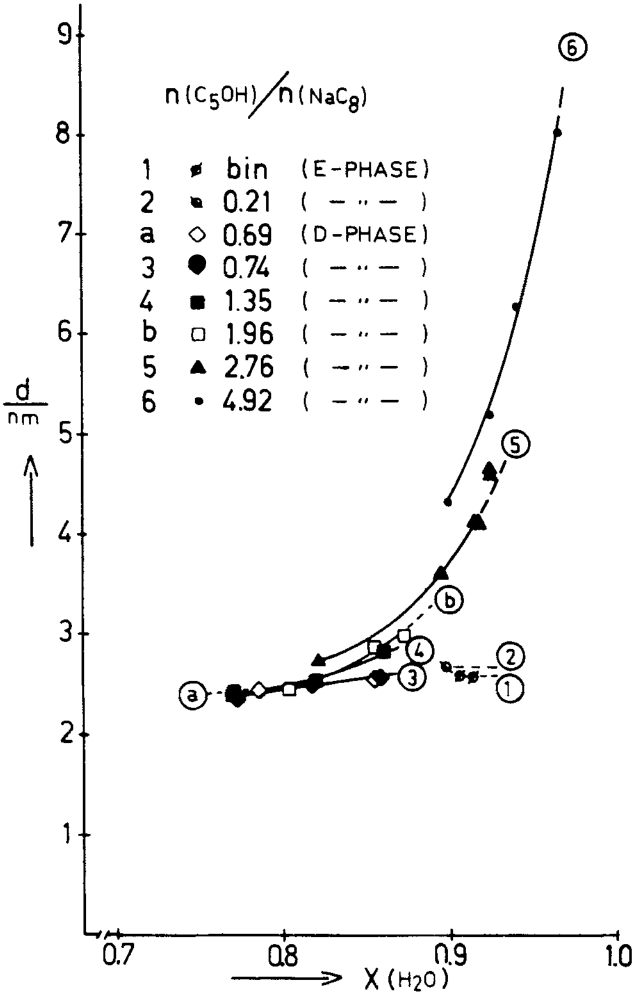

FIGURE 5 The Bragg spacing, *d*, of the *D*- and *E*-phases given as a function of $x(H_2O)$ for different constant molar ratios of C_5OH to NaC_8 at 25°C. The numbers and small letters refer to the lines given in Figure 2.

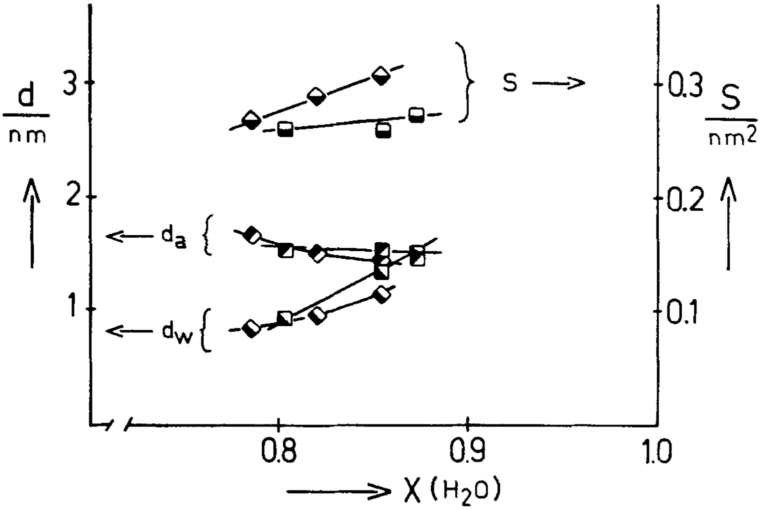

FIGURE 6 The thickness of the amphiphilic layers, d_a, the thickness of the water layer, d_w, and the mean area per polar group, S (calculated on the assumption that all the groups lie in the amphiphile/water interface), of the D-phase given as a function on $x(H_2O)$ for different constant molar ratios of C_5OH to NaC_8 at 25°C. The symbols refer to the corresponding open symbols in Figures 2 and 5 ($n(C_5OH)/n(H_2O)$ = 0.69 (⬘, ⬗, ⬖) and = 1.96 (⬓, ◩, ◪). The data were taken from Ref. 12.

is low. The former decreases and the latter increases strongly with increasing water content. The partial molar enthalpy of pentanol is in the E-phase strongly negative and also increases rapidly with increased $x(H_2O)$ (line 2).

In the D-phase the enthalpies of the H_2O and the C_5OH depend strongly on the water concentration in the phase regions with high content of NaC_8 (lines 3 and 4); the dependence decreases as $n(C_5OH)/n(NaC_8)$ increases (lines 5 and 6). In this latter region, $l(H_2O)$ and $l(C_5OH)$ are close to zero. $l(NaC_8)$, on the other hand, changes little along lines 3 and 4 but is strongly dependent on $x(H_2O)$ along lines 5 and 6.

As expected, addition of more water to the D-phase than can reasonably be bound by primary hydration of the polar groups and counter ions[8,10,16] causes a rapid increase in the Bragg spacing (d) (Figure 5).† At low concentrations of water and for low $n(C_5OH)/n(NaC_8)$ d becomes less and less dependent on the concentration. In the E phase the d values are comparatively constant.

---

† The Bragg spacing for the D-phase is the distance between the polar head group layer in one lamella and the corresponding layer in an adjacent lamella. The Bragg spacing for the E-phase is that between the planes defined by the centers of the rods in two hexagonally close-packed layer of rods.

The measured Bragg distances are in good agreement with previously determined values[12] (open symbols in Figure 5). Estimates of the thickness of the amphiphilic (d_a) and aqueous (d_w) layers and the surface area per polar group (S) from Ref. 12 are given in Figure 6.

2 Lines with constant $n(H_2O)/n(C_5OH)$

Figure 7 shows L_m as a function of the mole fraction of NaC_8 for lines with constant ratio $n(H_2O)/n(C_5OH)$. These curves clearly indicate that, above all,

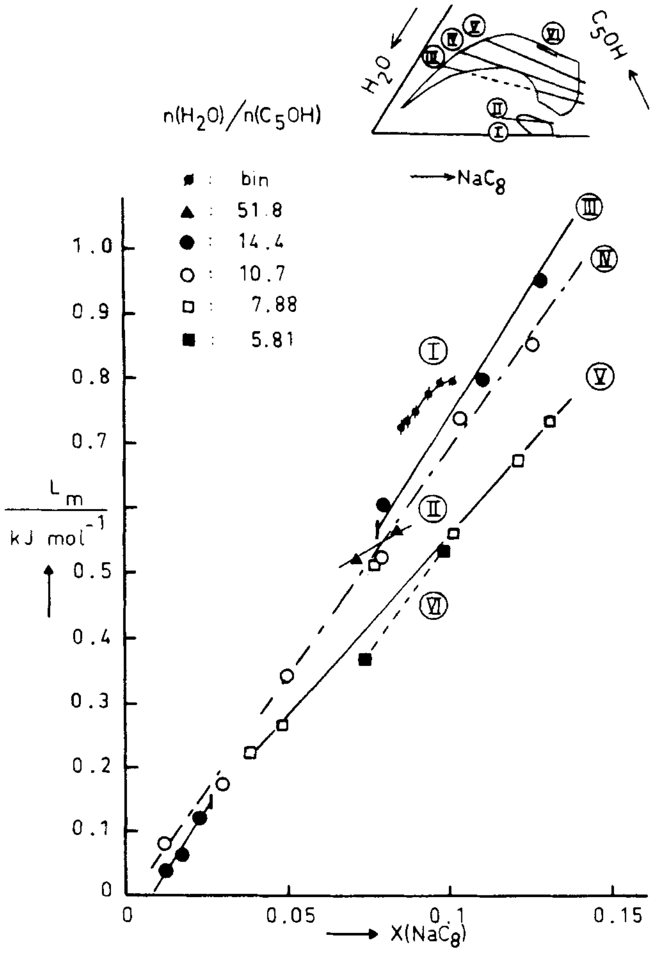

FIGURE 7 The relative molar enthalpies of the D and E-phases given as a function of $x(NaC_8)$ for different constant molar ratios of H_2O to C_5OH at 25°C. The Roman numbers refer to the lines in Figure 2.

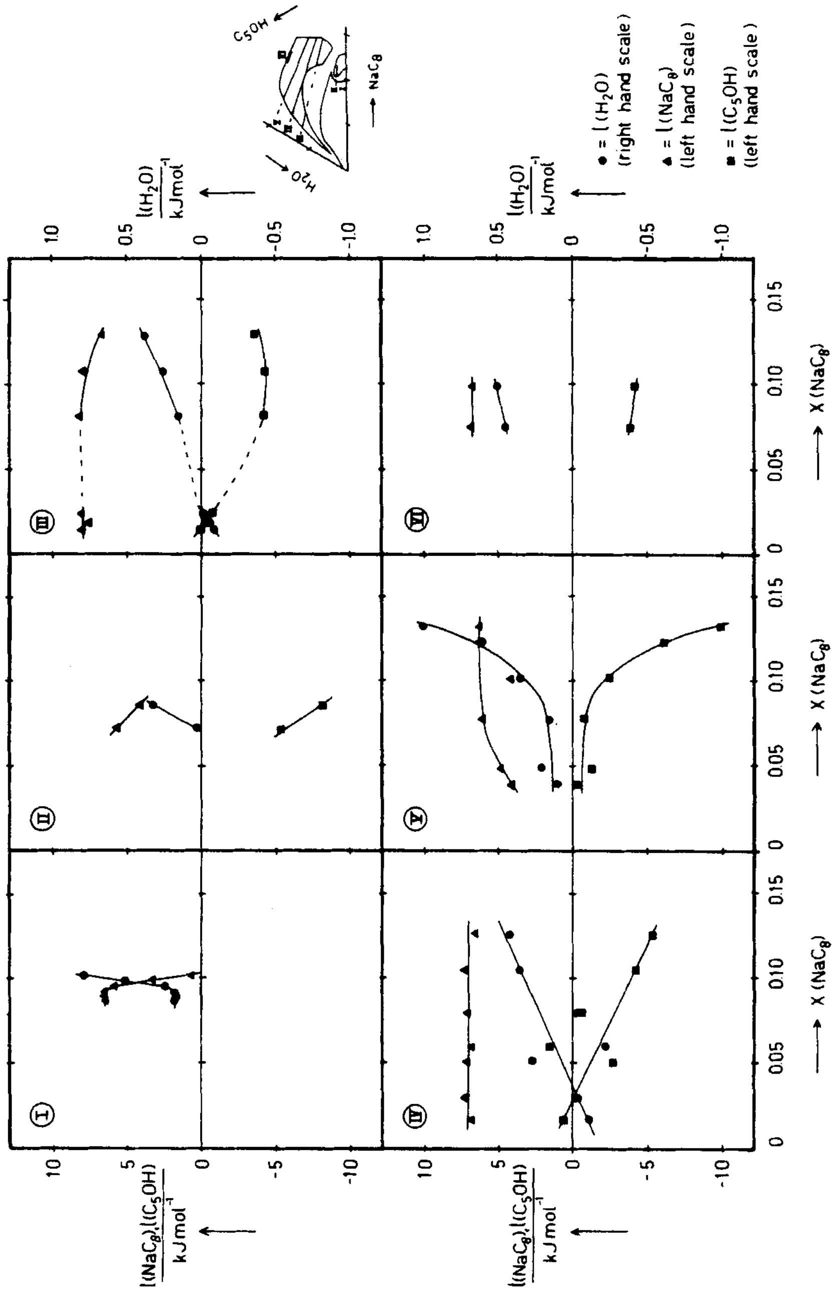

FIGURE 8 The relative partial molar enthalpies of the components in the system H_2O—NaC_8—C_5OH of the *D*- and *E*-phases given as a function of $x(NaC_8)$ for different constant molar ratios of H_2O to C_5OH. The Roman numbers refer to the lines in Figures 2 and 7.

it is the relative amount of NaC_8 that is reflected in the enthalpies of the D-phase. The dependence of L_m on $x(NaC_8)$ is linear, with a slowly decreasing slope as the relative amount of H_2O (i.e., $n(H_2O)/n(C_5OH)$), decreases. The linearity remains even through a two-phase region (line III), points for low $x(NaC_8)$ being on the same line as those for high $x(NaC_8)$. The L_m for the E-phase varies in a more complicated way.

The relative partial molar enthalpies for each component along lines I–VI are shown in Figure 8. In the E-phase the $l(H_2O)$ increases and the $l(NaC_8)$ decreases with increasing $x(NaC_8)$ (cf. the dependence on $x(H_2O)$ for lines 1 and 2 in Figure 5). The enthalpies of the D-phase (lines III–IV) are somewhat scattered but it seems that the $l(H_2O)$ is roughly linearly dependent on $x(NaC_8)$. The slopes of the lines appear to be fairly independent of the relative amount of H_2O to that of NaC_8. Line III passes through a two-phase region and in this case, the enthalpies for high $x(NaC_8)$ do not fall at the same line as those for low $x(NaC_8)$. $l(NaC_8)$ is quite independent of $x(NaC_8)$ in the D-phase, except for high C_5OH and low NaC_8 contents (line V).

As NaC_8 is added to the D-phase (lines III–VI), $l(H_2O)$ increases and $l(C_5OH)$ decreases. The values of $l(C_5OH)$ and $l(H_2O)$ are very small in the salient region of the D-phase towards the water corner in the phase diagram. The enthalpies of all three components in this region are remarkably constant, the enthalpies of water and pentanol being close to those of the pure substances.

The Bragg spacings (Figure 9) are very slightly dependent on the relative amounts of H_2O or C_5OH. Indeed, all values fall on a single curve with $x(NaC_8)$ as the parameter. The d-values for the E-phase coincide with the d-values for D-phase with the same $x(NaC_8)$.

3 Lines with constant $n(H_2O)/n(NaC_8)$

In Figure 10, we show L_m as a function of $x(C_5OH)$ for lines with constant ratios $n(H_2O)/n(NaC_8)$. These curves show the effect of solubilizing a weakly amphiphilic component in a mesophase. For low water contents the L_m depend strongly on $x(C_5OH)$, decreasing with increasing pentanol concentration. When more water is added, the dependence becomes smaller and for $n(H_2O)/n(NaC_8) = 52.5$, L_m is constant. The molar enthalpy change when passing from E-phase to D-phase at constant $n(H_2O)/n(NaC_8) = 10.6$ is very small (≈ 0.1 kJ mol^{-1}). When phases in thermodynamic equilibrium with each other are compared (ends of tie-lines in Figure 1) it is found that $L_m(D)$-$L_m(E)$ is 0.25–0.35 kJ mol^{-1}.

The corresponding relative partial molar enthalpies are given in Figure 11. $l(H_2O)$ is close to zero for line A, for which the total water content is high. As the ratio of water to NaC_8 decreases, $l(H_2O)$ becomes positive and shows

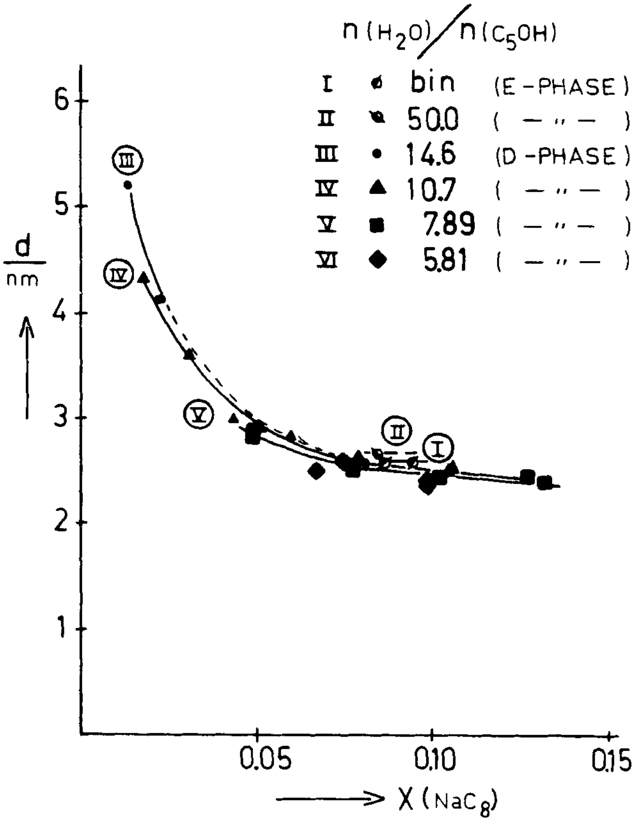

FIGURE 9 The Bragg spacing, *d*, of the *D*- and *E*-phases given as a function of $x(NaC_8)$ for different constant molar ratios of H_2O to C_5OH at 25°C. The Roman numbers refer to the lines in Figure 2.

an increasing dependence on $x(C_5OH)$. Again, $l(NaC_8)$ does not depend very much on $x(C_5OH)$, except for line B. The absolute value of $l(C_5OH)$ decreases when the amount of NaC_8 is increased. As $x(C_5OH)$ is increased, $l(C_5OH)$ increases except for line E which is close to the border line of the phase region towards the NaC_8 corner (and one point on line C).

The Bragg spacings (Figure 12) are almost independent of $x(C_5OH)$, $n(H_2O)/n(NaC_8)$ and the structure of the phase, except when the water content of the *D*-phase is very high (line A). From Figures 5 and 9 it may be concluded that the Bragg spacing becomes more and more dependent on $x(C_5OH)$ as the content of water increases in the long salient region of the *D*-phase towards the water corner in the phase diagram. This agrees with results from the H_2O—NaC_8-decanol system.[16] There seems to be a slight increase in *d* with increasing $x(C_5OH)$ in the *E*-phase.

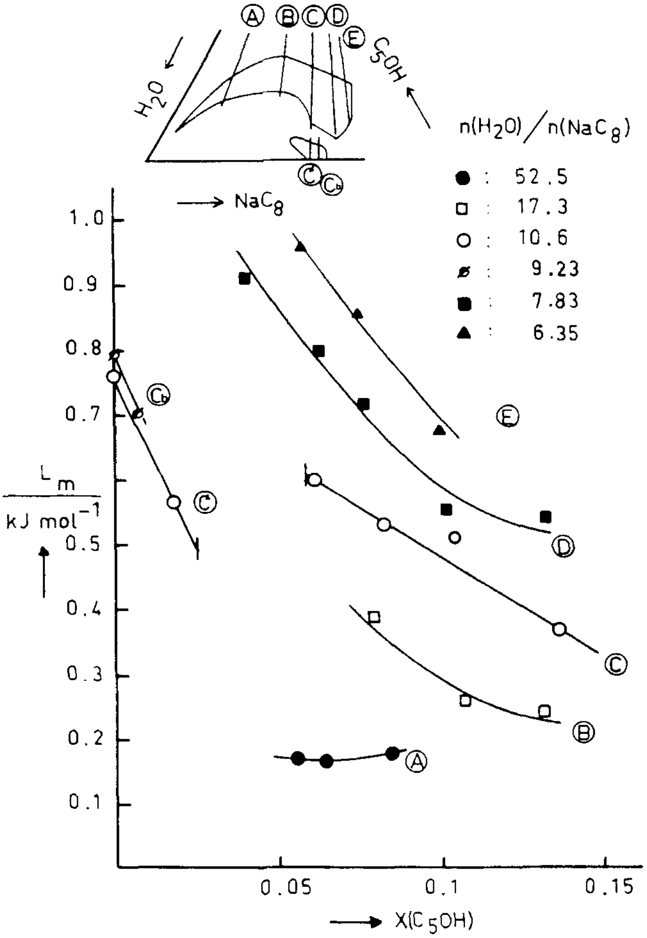

FIGURE 10 The relative molar enthalpies of the *D*- and *E*-phases given as a function of $x(C_5OH)$ for different constant molar ratios of H_2O to NaC_8 at 25°C. The letters refer to the lines in Figure 2.

DISCUSSION

1 General remarks

With the exception of two points very close to the water corner in the three-component diagram, all molar enthalpies of the phases are positive (Figure 3), despite the fact that very extensive association of the NaC_8 is required to form the mesophase aggregates. This serves to stress the importance of entropy factors as a primary driving force leading to association. The enthalpies of the phases are primarily dependent on their concentration of NaC_8.

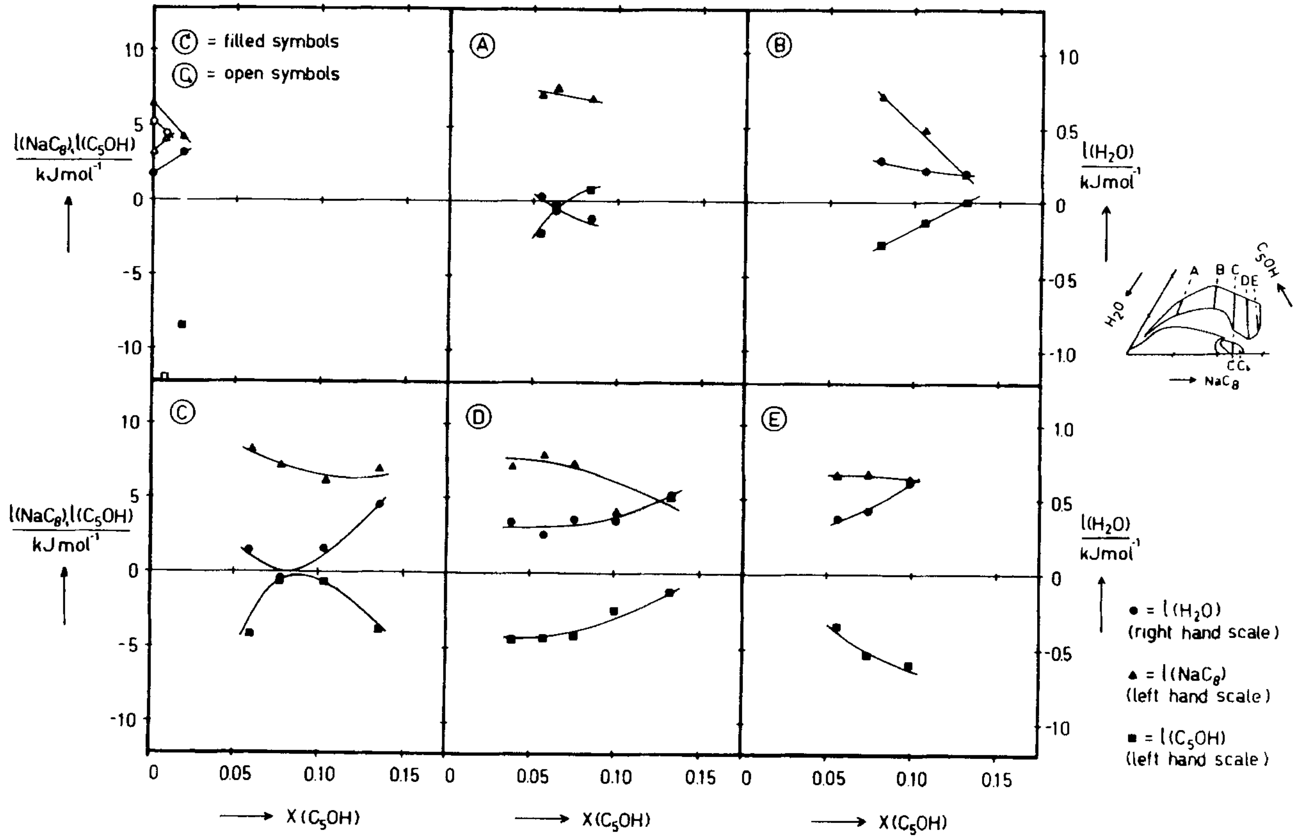

FIGURE 11 The relative partial molar enthalpies of the components in the *D*- and *E*-phases of the system H_2O—NaC_8—C_5OH given as a function of $x(C_5OH)$ for different constant molar ratios of H_2O to NaC_8. The letters refer to the lines in Figures 2 and 10.

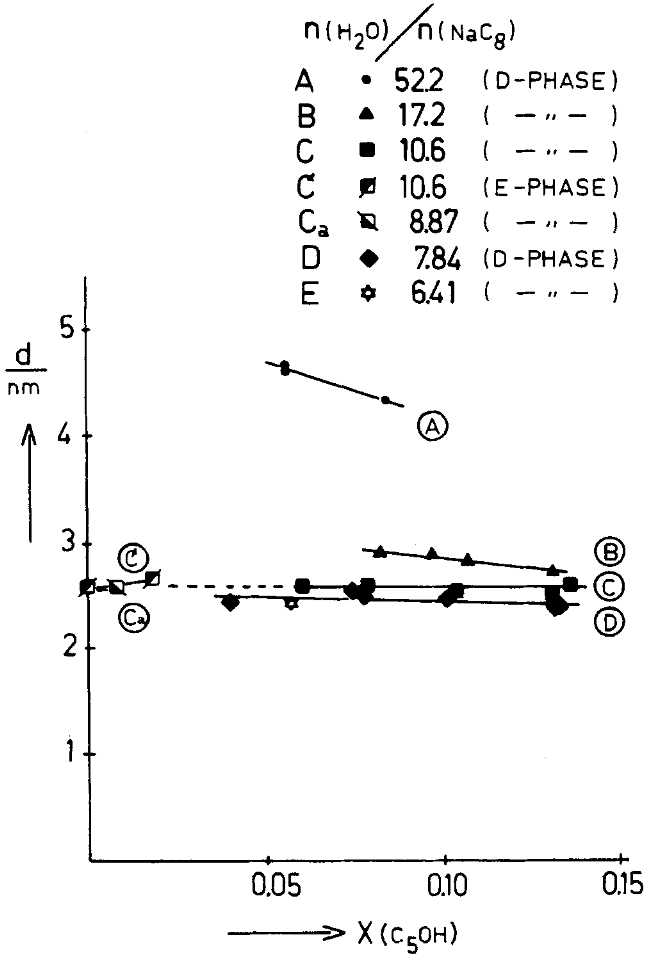

FIGURE 12 The Bragg spacing, *d*, of the *D*- and *E*-phases given as a function of $x(C_5OH)$ for different constant molar ratios of H_2O to NaC_8 at 25°C. The letters refer to the lines in Figure 2.

2 The water-rich part of the *D*-phase

The maximum amount of water that can be bound by the polar groups in a "primary" hydration layer is about $6H_2O/Na^+$, $5H_2O/C_8^-$ and $3H_2O/C_5OH$.[8,10,13] Roughly, this amount is exceeded to the left of line b in Figure 2, which corresponds to $n(C_5OH)/n(NaC_8) \approx 2$. In this region the enthalpies of H_2O and C_5OH are both close to those of the pure substances, while $l(NaC_8)$ is strongly dependent on the concentration of water (cf. lines 5, 6 in Figure 4).

It was originally suggested by Ekwall *et al.*[9–13] that counter ions are partially liberated from the polar surfaces of the mesophase aggregates in this region; the aqueous layer between the aggregates should be akin to a relatively dilute aqueous solution. One of the factors that stabilize the lamellar phase in this region, according to Ekwall, is the Donnan type equilibrium between ions bound to the surface and ions in the intercalating water layers. Whereas the exact nature of this equilibrium is not clear, there is ample evidence from nmr spectroscopy that the amount of free water and ions not bound to the polar layers does increase in the salient region of the *D*-phase towards the water corner of the phase diagram (Figure 2). The interpretations of changes in Na^+ relaxation times[23,26] as well as in the deuteron splitting of D_2O[19–21] and the proton relaxation times of water[18] in this region all support this suggestion. Our data give additional thermodynamic evidence. An increased dissociation of Na^+ should have a significant effect on $l(NaC_8)$, but if there are large amounts of water that is not strongly bound to the polar layers of the NaC_8/C_5OH lamellae one should not expect strong effects in $l(H_2O)$. The partial molal enthalpies (lines 5 and 6, Figure 4) as well as the strong increase in the Bragg distance d towards the water corner (line 6, Figure 5) are reconcilable with this model. As the water content is decreased, $l(NaC_8)$ decreases, i.e., if the changes in $l(NaC_8)$ reflect changes in the binding of Na^+ ions an increased binding of ions would be an exothermic process.

When pentanol is added to water-rich *D*-phase, the Bragg spacing decreases slightly (line A, Figure 12). $l(H_2O)$ decreases and $l(C_5OH)$ increases while $l(NaC_8)$ remains almost constant (Figure 11). When NaC_8 is added, $l(H_2O)$ increases and $l(C_5OH)$ decreases. In this case, too, $l(NaC_8)$ is roughly constant (Figure 8 III and IV). The upper border of the salient *D*-phase region in Figure 2 corresponds to 4–5 moles of C_5OH per mol of NaC_8. That this ratio is roughly constant up to line b stresses the importance of the interaction between COO^- and OH^- through intervening water molecules.[13] Changes in $x(C_5OH)$, however, have little effect on the relaxation of Na^+ ions in this region.[26] Hence, one may expect that $l(NaC_8)$ should be fairly independent of $x(C_5OH)$, as is found experimentally. That there are changes in $l(H_2O)$ and $l(C_5OH)$ indicates that the interactions between polar groups in the mesophase aggregate surface do change; the nature of these changes is not clear.

3 The region of the *D*-phase with low concentration of water

When $n(C_5OH)/n(NaC_8) < 2$, the ratio of the maximum amount of water that can be bound to the polar groups to the actual amount of water in the system seems to be crucial to the details of the *D*-phase structure.[10,13,16] S, d_a and d_w all change with $x(H_2O)$ in a way which suggests that a decrease in water content forces the amphiphilic molecules closer to each other with a resulting extension of the hydrocarbon chains (d_a increases). The total Bragg spacing, however, does not vary markedly with the composition of the phase (Figures 5, 6, 9, and 12). Further evidence for the closer packing is given by the decreased mobility of the hydrocarbon chains over the dimensions of the aggregates while the local mobility of the —CH_2-group remains constant as $x(H_2O)$ decreases (as judged from measurements of T_1 and T_2 relaxation times by p.m.r. spectroscopy[18]). Effects on the quadrupole splitting in the nmr spectrum of $^{23}Na^+$ indicate that the sodium ions are forced out from a location between the carboxyl groups into an ionic aqueous environment as $x(H_2O)$ decreases.[24–29] When the water content is decreased below the value compatible with complete hydration of the polar groups and counter ions a dehydration of the alcohol groups takes place.[13,18,21,26] The extension of the phase is determined by the minimum amount of water required to completely hydrate the carboxyl group and the Na ion ($\sim 6\,H_2O/NaC_8$).[10,32]

These structural effects all imply a decreased mobility of water, the sodium ions and the amphiphilic layer,[18,21,26] as $x(NaC_8)$ increases (lines III–IV in Figure 8). The relative partial molar enthalpy of the water, however, increases strongly with increasing $x(NaC_8)$ in the region towards the right of line b in the *D*-phase (Figure 4 (3,4), Figure 8 (III–V), Figure II (C–E)). It would seem that if the interpretation based on nmr data and the enthalpies reported here are to be reconciled, one has to assume that the increased binding of the water leads to an increase in its enthalpy.

Water is relatively weakly bound to hydroxyl groups in comparison with the binding to carboxyl groups and sodium ions.[13,18,21,26] Hence, it seems reasonable that interactions between water and C_5OH should be more sensitive to changes in the composition of the polar surfaces than those between water and NaC_8.[10,13,16,32]

This is clearly reflected in the enthalpies in the water-poor region of the *D*-phase. Addition of water, which has the strongest effect on the binding of water to the pentanol also has the strongest effect on $l(C_5OH)$ and $l(H_2O)$ (Figure 4). Changes in $x(C_5OH)$ or $x(NaC_8)$ does not affect $l(NaC_8)$ very much, but $l(H_2O)$ and $l(C_5OH)$ both vary markedly, indicating that the binding of these molecules is affected. Why these changes should lead to an increase in $l(H_2O)$ and a decrease in $l(C_5OH)$ (except for line D, in Figure 11) is not clear.

A change of the composition in this region has almost no effect on the total Bragg spacing. Hence, the changes in the binding of water and the polar group interactions seem to cause slight and opposite changes in the packing of the hydrocarbon and the polar moieties.[12,16]

4 Enthalpies in the *E*-phase

The hexagonal *E*-phase is able to incorporate only relatively small amounts of solubilisates[13,22] and the variation in water content is also rather limited. When the concentration of water in pentanol-free *E*-phase is decreased from the maximal amount ($11\,H_2O/NaC_8$) to the minimum amount ($9\,H_2O/NaC_8$), $l(H_2O)$ increases by ≈ 0.57 kJ mol^{-1} (line 1 in Figure 4). This should be compared with the change in $l(H_2O)$ for the process (water in concentrated *L*1 solution) → (water in *E*-phase) which is only ≈ 0.03 kJ/mol[30]. The large increase in the relative partial molar enthalpy emphasizes that the extension of the *E*-phase towards low H_2O concentration is limited by the minimum amount of water that is needed to form a monomolecular hydration shell around each hexagonal rod, including the polar group and the counter ion.[13] Whereas the minimum of water required to stabilise the *D*-phase (and also the *L*2 solution) is that needed to hydrate the —COO Na group ($6\,H_2O/NaC_8$, Refs. 10, 32), the requirement that the water surround the amphiphilic aggregates completely increases the minimum water content of the *E*-phase to $9\,H_2O/NaC_8$. A similar sharp increase in the enthalpy of the water as the water content is decreased is found in *E*-phase containing C_5OH (line 2 in Figure 4).

The factors limiting the region of existence towards the aqueous solution are much less clear. The small change in enthalpy on passing from the *L*1 solution phase to the *E*-phase implies that the phase transition cannot involve substantial changes in either the binding of water or the state of the hydrocarbon moieties. The precipitation of *E*-phase from aqueous solution must be mainly entropy-governed; after all, most of the water must be bound to carboxyl groups or sodium ions even in saturated aqueous solution.

The capacity of the *E*-phase to solubilize aliphatic alcohols has been studied by determinations of phase equilibria[8,10] and investigations of the properties of the water.[13,22] The ability to incorporate alcohols is independent of the hydrocarbon chain length for 5–10 C atoms ($n(\text{alcohol})/n(NaC_8) \approx 0.34$).[10,13] For this reason, it has been suggested that the border of the *E*-phase towards the *D*-phase region is determined by interactions between the —OH and $—COO^-$ groups. We have made only three determinations of the molar enthalpies of *E*-phase that contains C_5OH; these indicate that L_m decreases with increasing $x(C_5OH)$ and that $l(C_5OH)$ is large and negative (C, C_b in Figure 11), i.e., to dissolve C_5OH in *E*-phase is a strongly exothermic process. The differences between enthalpies in the *E*-phase and the enthalpies in *D*-phase in equilibrium with *E*-phase, are quite large for $l(NaC_8)$ and $l(C_5OH)$ (of the order 3–7 kJ mol^{-1}) but small (and negative) for $l(H_2O)$. The experiments thus, at least, are not in conflict with the view that the interaction between C_5OH and NaC_8 determines the extension of the *E*-phase and that the transition to *D*-phase is mainly accompanied by changes in this interaction.

The Bragg spacing in the *E*-phase increases slightly when C_5OH is added, independently of $x(NaC_8)$. The increase is accompanied by a decrease in the mean area per polar group.[12,16] A simple explanation is that the small —OH groups are built into the polar surface, decreasing the repulsive forces. The strongly exothermic solubilisation of C_5OH in *E*-phase supports this mechanism. The transition to *D*-phase takes place when the repulsive forces have been decreased to a sufficient extent. Indeed, there is X-ray evidence that cross-section area of the amphiphilie rods becomes more oblate at very low water contents.[10,13,16]

The change in the Bragg spacing on transition from *E*- to *D*-phase is negligibly small. Independent Raman spectroscopy investigations[33–35] indicate changes in the amphiphile layers while the state of the water, as characterized by nmr studies, remains unchanged.[21,22]

CONCLUSIONS

We summarize the discussion as follows.

i) The relative partial molar enthalpies of the three components in the system $H_2O/NaC_8/C_5OH$ change considerably within the phases and contain important experimental information on the factors governing the formation and stabilization of the phases.

ii) Interactions between the different components are clearly reflected in their enthalpies. The concentration dependence of the enthalpies to a large extent can be understood on the basis of models of the interaction that are suggested by the X-ray investigations reported here and by previous X-ray and nmr investigations on this and other systems.

iii) The molar enthalpies of the phases are, above all, dependent on the amount of NaC_8 in them.

iv) The enthalpies clearly support the hypothesis that the factors limiting the region of existence of *D*-phase are (a) for high concentrations of water interactions between —OH and $—COO^-$ and stabilisation of the intercalating aqueous layers by way of a Donnan type equilibrium between free and bound ions, (b) for low water contents the minimum amount of water that is needed to hydrate the polar groups. For *E*-phase, an additional requirement is that the amphiphilic aggregates are completely surrounded by water.

v) The enthalpy change when any of the components is transferred between two phases in equilibrium with each other is small compared with enthalpy changes within the phases as their composition is varied. Hence, the composition of the sample, not the actual phase formed, primarily determines its enthalpy.

vi) There are clear changes in the concentration dependence of the partial molar enthalpies in the *D*-phase when the water content sinks below the amount that can reasonably be bound by primary hydration of COO^-, —OH and Na^+.

vii) The combined thermodynamic, spectroscopic and X-ray diffraction measurements on this system indicate that the equilibrium between hexagonal *E*-phase and lamellar *D*-phase is probably governed by small changes in the interactions between the polar groups of NaC_8 and C_5OH. The transition from aqueous solution to *E*-phase is mainly entropy-governed since the changes in the enthalpies are very small.

Our measurements, so far, have been limited to one single system at one single temperature, which, of course, limits the generality of our conclusions. However, the similarity of the phase diagram to diagrams for other systems containing water, a weakly amphiphilic compound and a charged surfactant[13] suggests that the same factors should be of importance in other systems. We are continuing investigations to confirm this.

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