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Temperature dependence of Water Self-Diffusion in the Gel Phase of a Potassium Palmitate System

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Abstract. — The temperature dependence of water self-diffusion in the gel and liquid crystalline phases of the potassium palmitate/water system was examined using pulsed field gradient spin-echo (PGSE) low resolution NMR experiments. The temperature dependence of the water self-diffusion in lamellar and hexagonal phases was characterised by trends parallel to pure water. The average "two-site" self-diffusion model was used to analyse the composition dependence of the self-diffusion coefficients. Temperature dependence of water self-diffusion in the gel phase presented different and interesting behaviour. The slopes of the Arrhenius self-diffusion were strongly composition dependent. The results were interpreted as a dependence on $T$ of the bound water fraction, while the self-diffusion obstruction factor was considered constant.

Introduction

Amphiphilic molecules, which range in complexity from simple soaps to multichain biological molecules, form a variety of phases as a function of temperature and water concentration. In each phase the hydrophilic polar head associates to define a surface which serves to separate the hydrocarbon chain from the water region [1,2]. Soap molecules form several liquid crystalline or solution phases for different water content. Of these, the most important structures are the lamellar phase ($L_\alpha$), the hexagonal phase ($H_\alpha$) and the isotropic aqueous micellar solution ($L_1$). In the lamellar phase the amphiphilic molecules form bilayers which are stacked upon each other, separated by a water layer. The hexagonal phase consists of hexagonal arrays of polar cylinders with the hydrocarbon tails oriented towards the cylinder axis. Micellar solutions are constituted by small spherical or cylindrical aggregates [3].

When the temperature is lowered in some lyotropic systems the ordinary mesophases are transformed to a transparent “gel” phase, $L_\beta$. In this phase, which is also lamellar, the hydrocarbon chains are stiff and lie parallel to one another. The gel phase has been examined most closely in potassium soaps of saturated fatty acids [4]. X-ray diffraction data suggested that the soap molecules are hexagonally packed and interdigitated from either side of the bilayer. A coagel phase has been observed at even lower temperatures and represents a heterogeneous mixture of regions of crystalline soap and dilute soap-water solutions [4]. A typical phase diagram of an aqueous potassium soap ($KC_n$)/water system is illustrated in Figure 1.

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An analysis of water self-diffusion in the lyotropic mesophases of several liquid crystals has been reported by Chidichimo et al. [5,6] in terms of the water content and an obstruction factor. The water self-diffusion coefficient in the mesophase, as measured by Pulsed field Gradient Spin Echo (PGSE) NMR experiments, can be expressed according to an apparent coefficient [6]:

$$D_{app} = f[(1 - P)D_f + PD_b]$$

(1)

which assumes that water molecules exist as "free" and "bound" water in rapid exchange compared with the NMR times involved in the experiments. In equation (1) $D_f$ and $D_b$ are the diffusion coefficients of free and hydrated water, respectively, while $P$ is the fraction of water molecules that are hydrated. $f$ is the obstruction factor and takes into account the constraints on water mobility due to lyotropic aggregates. Its value ranges between zero (no diffusion) and 1 (free state). In the past, values of $f$ have been used to probe the microstructure of several mesophases.

In the present communication, we deal with the temperature dependence of water self-diffusion occurring in the gel phase formed by the mixing of potassium palmitate (KC16) with water. This study was carried out by changing both the temperature and the sample composition.

The gel phase of the KC16/water system is particularly interesting due to its wide composition range. In addition, at higher temperatures where the soap molecular organisation may vary between lamellar and hexagonal arrays, the system is bordered by many mesophases. The water self-diffusion study revealed interesting features regarding the structure and the aggregate changes close to the phase transition and also verified the reliability of equation (1) to analyse the temperature dependence of diffusion coefficients.

**Experimental Design**

**Materials.** — The lyotropic mixtures investigated are reported in Table I. Sample compositions were selected on the basis of the KC16/water phase diagram, using appropriate ratios of pure/heavy water [1]. Lyotropic phases and temperature transitions were determined using DSC thermograms and water $^2$H-NMR spectra.
Table I. — Mixture compositions (by wt %) and phase transitions with increasing temperature. The stars indicate the samples where deuterated potassium palmitate was used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>KP</th>
<th>H₂O</th>
<th>D₂O</th>
<th>Phase Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>72.8</td>
<td>24.2</td>
<td>3.0</td>
<td>Lβ → Lα</td>
</tr>
<tr>
<td>b</td>
<td>59.6</td>
<td>37.0</td>
<td>3.4</td>
<td>Lβ → Lα</td>
</tr>
<tr>
<td>c*</td>
<td>57.5</td>
<td>42.5</td>
<td>-</td>
<td>Lβ → Hα</td>
</tr>
<tr>
<td>d</td>
<td>51.7</td>
<td>42.9</td>
<td>5.3</td>
<td>Lβ → Hα</td>
</tr>
<tr>
<td>e*</td>
<td>42.4</td>
<td>57.6</td>
<td>-</td>
<td>Lβ → Hα</td>
</tr>
<tr>
<td>f</td>
<td>39.8</td>
<td>53.7</td>
<td>0.5</td>
<td>Lβ → Hα</td>
</tr>
</tbody>
</table>

Potassium palmitate was prepared by treating commercially available palmitic acid with alcoholic KOH. A satisfactory purity of the component was achieved by several recrystallizations of ethanoic solutions.

Deuterated potassium palmitate (KC₁₆₋α−CD₂) was used for measuring α−CD₂ quadrupolar splittings. KC₁₆₋α−CD₂ molecules were synthetized by G. Chidichimo’s group (Chemistry Dept. Univ. of Calabria-Italy) and used as received.

The samples were prepared by mixing the components in 5 mm NMR tubes, sealed under nitrogen and homogenised by alternate centrifuging and heating of the sample.

PGSE NMR. — Water self diffusion coefficients were determined using the pulsed field gradient spin-echo (PGSE) NMR technique. In PGSE experiments, a spin echo sequence and two equal gradient pulses are used; the echo attenuation of the spin echo signal, R, was measured with increasing magnitude or duration of the magnetic field gradient.

The PGSE attenuation in a lyotropic mesophase can be written in terms of an apparent self-diffusion coefficient according to [7,8]:

\[ R = \frac{I(g)}{I(0)} = \exp[-KD_{app}] \] (2)

where \( K = (\gamma \delta g)^2 (\Delta t - \delta/3) \) and \( I(g) \) and \( I(0) \) are the spin-echo intensities in the presence of and without gradient pulses. \( \gamma \) is the gyromagnetic ratio of the proton, \( g \) and \( \delta \) are the magnitude and the width of the magnetic gradients respectively. \( \Delta t \) is the delay between the first and second gradient pulses. It has been demonstrated [8] that equation (2) holds within the experimental limit \( KD_t \leq 1 \).

Water self-diffusion measurements were performed on a home-built NMR spectrometer operating at a proton resonance frequency of 16 MHz. The time of the pulsed field gradient was varied between 1-10 ms with a constant diffusion time, \( \Delta t \), of ca. 40 ms. The \( T_2 \) relaxation times of the surfactant protons in the gel phase was found to be ca. 15 ms in samples prepared with only heavy water, changing little when the composition and the temperature were varied. Thus the undesired signals of the aggregate proton did not interfere with the solvent water signal in which we were interested.

Details of the pulsed current supply and related thermostatic unit have been reported elsewhere [5].

Deuterium NMR and Quadrupole Splittings. — In systems, where no molecular motion averages the quadrupole coupling, a \(^2\text{H}-\text{NMR}\) spectrum consists of a superposition of doublets. For a powder sample constituted by uniaxial domains randomly oriented with respect to magnetic field, the spectrum is a broad absorption curve where the quadrupole splitting is defined...
as the separation between the two marked peaks of the resonance curve. The water quadrupole splittings of lyotropic systems may give interesting informations about the degree of the orientation and the hydration of the water molecules. Within the limit of very fast water exchange. Halle and Wennestrom have demonstrated that the quadrupole splitting is given by [9]:

$$\Delta (^2\text{H}_2\text{O}) = \frac{3}{4}P|\chi S|$$

(3)

where \( S \) is the molecular order parameter, \( \chi \) the quadrupolar coupling constant, and \( P \) the fraction of water which is bound to lyotropic aggregates.

\(^2\text{H}_2\text{O} \) NMR spectra and quadrupole splittings were recorded on an NMR Bruker WM300 spectrometer equipped with a broadband probe working for deuterium at 46 MHz. In order to avoid loss of signal due to receiver dead time, the quadrupolar echo method was used.

**Result and Discussion**

Gel phase boundaries and phase transitions of KP/water system were determined by \(^2\text{H}-\text{NMR} \) spectral profiles for mixtures prepared with heavy water or deuterated potassium palmitate. The temperature range monitored was between 25 and 60 °C. Figure 2 illustrates a series of \(^2\text{H}_2\text{O}-\text{NMR} \) spectra where the gel phase is characterised by uniaxial powders over the whole range of temperatures and compositions.

A direct analysis of powder spectral profiles suggests that the gel is a stable phase and is characterised by an uniaxial lamellar microstructure with high crystalline order. The spectra also show the temperature interval where the gel phase is in equilibrium with the lamellar or hexagonal mesophases. The \( L_\beta \rightarrow L_\alpha \) and \( L_\beta \rightarrow H_\alpha \) transitions are pointed out by a decreasing of the quadrupolar splitting which may be correlated to a reduction of molecular ordering with increasing temperature.

The temperature dependence of the self-diffusion coefficients in lyotropic crystals is an intriguing argument that has received little attention. The most simple approach is to consider that the water diffusion coefficient in a liquid crystalline system follows an Arrhenius-like behaviour. In this assumption equation (1) may be expressed as a function of the temperature by:

$$D_f \approx \exp \left(-\frac{E_a^f}{KT}\right)$$

and

$$D_b \approx \exp \left(-\frac{E_a^b}{KT}\right)$$

(4)

Here \( T \) is the absolute temperature while \( E_a^f \) and \( E_a^b \) are the activation energies for the free and bound water, respectively. \( K \) is Boltzmann's constant. In a temperature range where the structure of a mesophase does not change, it is reasonable to assume that the obstruction factor and the bound water, described in equation (1), change little. Under these conditions, plots of \( D_{app} \) versus the inverse of the temperature, should exhibit a biexponential behaviour which depends both on the magnitude of the two energetic parameters and on the bound water fraction.

The temperature dependence of the water self-diffusion into the gel and liquid crystalline mesophases of the \( \text{KC}_{16}/\text{water} \) system was studied by PGSE NMR experiments. Figure 3 shows some apparent water self-diffusion coefficients as a function of the inverse temperature and water composition. The trend emphasises the structural modifications which may be correlated with the phase behaviour obtained by \(^2\text{H}-\text{NMR} \). Water self-diffusion coefficients
Fig. 2. — $^2$H-NMR spectral profiles as a function temperature (°C). Left side: mixture a; right side: mixture f.

exhibit a well defined minimum at the $L_\beta - H_\alpha$ transition due to the appearance of cylindrically shaped aggregates which, having a greater mean area per polar head [6], could generate localised restriction in the interplanar gaps.

For temperatures within the lamellar or hexagonal region, the water self-diffusion coefficient sketches a behaviour parallel to that of pure water. To illustrate this more clearly, we reported in Table II the ratio between the experimental slope of the apparent coefficient (deduced according to $Q = -k \left[ \frac{\partial \ln D_{\text{app}}}{\partial (1/T)} \right]$) and the activation energy for pure water $E_a^f$.

In the temperature range of lyotropic mesophases this ratio is very close to unity. $D_{\text{app}}$ depends on the temperature as does the self-diffusion of pure water, and then the experimental
Fig. 3. — Arrhenius plot of the water self-diffusion coefficients. Solid and dashed lines represent the best fit to experimental data for the gel and liquid crystalline phases, respectively. Upper dashed lines indicate the pure water trends. a, d and f are sample compositions as in Table I. Lβ = gel phase and LC = liquid crystalline region.

Data of Figure 3 can be interpreted by the following relation:

\[ D_{\text{app}} \approx f(1 - P) \exp \left( -\frac{E_i}{kT} \right) \]  

obtained by combining equations (1) and (3), and assuming that bound water contribution to average diffusion is negligible.

The apparent self-diffusion coefficients in Figure 3 are in agreement with equation (5) if the product \( f(1 - P) \) is considered independent of the temperature. This hypothesis is reasonable for stable liquid crystalline mesophases, where both the obstruction factor and the fraction of the bound water change little with the temperature. Some year ago, in fact, we calculated the obstruction factor in several lyotropic mixtures [10]. Self-diffusion experiments
Table II. — *Ratios between the experimental* \((Q)\) *and pure water activation energies* \((E_r^i = 0.18\ \text{eV})\). \(Q\) *is obtained from the self-diffusion trends as* \(-K\frac{\partial \ln D_{app}}{\partial(1/T)}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Q(L_a)/E_r^i)</th>
<th>(Q(H_a)/E_r^i)</th>
<th>(Q(L_b)/E_r^i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.86</td>
<td>–</td>
<td>0.091</td>
</tr>
<tr>
<td>b</td>
<td>1.16</td>
<td>–</td>
<td>0.28</td>
</tr>
<tr>
<td>c</td>
<td>–</td>
<td>1.05</td>
<td>0.79</td>
</tr>
<tr>
<td>d</td>
<td>–</td>
<td>1.07</td>
<td>0.88</td>
</tr>
<tr>
<td>e</td>
<td>–</td>
<td>1.09</td>
<td>1.50</td>
</tr>
<tr>
<td>f</td>
<td>–</td>
<td>1.20</td>
<td>2.90</td>
</tr>
</tbody>
</table>

gave, in a wide temperature range, constant obstruction factors which were 0.66 and 0.74 for lamellar and hexagonal phases, respectively. A similar study has recently been conducted by Holmes *et al.* [11] in order to confirm the defected nature of lamellar lyomesophase in the pentadecafluorooctanoate/water system.

Finally the temperature dependence of the self-diffusion coefficient in the gel range was analysed. The data shown in Figure 3 illustrate that the temperature dependence of the water self-diffusion coefficient is different from that of the liquid crystalline phases. The gel state is characterised by a diffusion behaviour not parallel to pure water but which changes with the water composition. The ratios between the experimental and pure water activation energies are shown in Table II and vary between 0.091 to 2.90 with increasing dilution of the mixtures. If these results are interpreted in accordance with equation (5) it is evident now that the product \(f(1 - P)\) must change with the temperature. However the gel microstructure of potassium soaps of saturated fatty acids was examined some years ago by Vincent *et al.* [4] who stressed the presence of a layered structure with continuous hydrocarbon sheets. This consideration suggests that the obstruction factor of the gel state can be considered constant and equal to 2/3 as for lamellar phases [5,6].

Consequently, the anomaly of the temperature dependence observed on the water self-diffusion coefficient must be attributed to the particular behaviour of the term \((1 - P)\) which appears sensitive to changes of temperature and composition.

A study of the hydration behaviour of the KC16/water system has been conducted using the water quadrupole splittings which were collected for all the mixtures as a function of the temperature. In Figure 4 we report the temperature dependence of the quadrupole splitting for two mixtures and we compare the splitting behaviour with the self-diffusion data of Figure 3, taking care to distinguish between liquid crystalline and gel regimes.

In the liquid crystalline mesophases the water splitting remains constant with increasing temperature. By considering that the water order parameter in a lyomesophase changes little with temperature, except near an order-disorder phase transition, the bound water fraction may be considered constant.

A different temperature dependence of the quadrupole splitting is observed in the gel state. The behaviour, just as for the self-diffusion coefficients, is dependent also on the composition. We begin by examining the mixture-d which, in the gel state, showed an activation energy equal to that of pure water. In this case the quadrupole splittings are constant over a wide range of temperatures and suddenly increase when the system starts to become bi-phasic. Here the increase in splittings corresponds to a decrease in the self-diffusion coefficients, as seen in Figure 3. Except in this two-phase region, the mixture-d is likely to be characterised by a bound water fraction which is constant with changing temperature.
Fig. 4. — Deuteron quadrupole splittings as a function of the temperature. The arrows indicate the starting temperature of the liquid crystalline phases while a and d are the mixture composition as in Table I.

Equally immediate is the analysis of the temperature dependence of the observed quadrupole splitting for the mixture-a which showed a diffusional activation energy less that of pure water. The quadrupole splitting in this sample increases progressively with temperature which, interpreted in the light of equation (3), suggests a clear and sensitive increase of the water bound fraction. An increase of P with temperature correspond to a decrease of the activation energy of the free water as is observed in the self-diffusion data.

Calculations of P from the self-diffusion data were obtained by equation (1) where the term due bound water self-diffusion, of the order of $10^{-7}$ cm$^2$/s [12], was neglected. P was calculated keeping $f$ equal to 0.66 while $D_0$ was measured as a function of temperature for a pure water sample.

The bound water fraction and water quadrupole splittings are related by equation (3). The $|\chi S|$ absolute values may be estimated from the quadrupole splittings of the gel phase of equimolar mixtures prepared with $\alpha$-deuterated surfactant. On this subject we measured quadrupole splittings in KC$_{16} - \alpha - $CD$_2$/water mixtures and the results were in agreement with the experiments of Chidichimo et al. [13]. In the case of a gel phase, the quadrupole splitting of $\alpha - $CD$_2$ surfactant may be given by:

$$\Delta (\alpha - $CD$_2$) = \frac{3}{4}|\chi S|^\alpha$$

(6)

where the $\alpha - $CD$_2$ order parameter may be supposed to show a behaviour with changing temperature similar to that of the bound water parameter [13]. Consequently, by combination of equations (3) and (6) we obtained the bound water fraction as a function of T by the relation:

$$P \approx \frac{\Delta (\text{H}_2\text{O})}{\Delta (\alpha - $CD$_2$)}$$

(7)
In Figure 5 we show the bound water fraction in the gel phase as obtained from water splittings and water self-diffusion data. Both NMR methods give clear evidence that the temperature dependence of $P$ is a function of sample composition. Sample a, for example, is characterized by a water hydration which increases with temperature and this effect is in agreement with the Arrhenius plot of the apparent self-diffusion characterized by a value of $(Q/E_0^i)$ much less than unity. On the contrary, the sample d shows a constant bound water fraction with changing temperature which explains why the slope of the apparent self-diffusion coefficients in an Arrhenius plot is equal to that found in the liquid crystalline phases or in pure water.

It is worth noting that the evident difference observed in the values of $P$ from two procedures could reflect the limits of the models used here, and it is likely to be due to approximations with equations (1) and (7) were derived.

The comparison between the data from these two different techniques, both sensitive to the chemical state of the bound water, show that the state gel of this system is characterised by a hydration effect whose dependence on temperature is also a function of the mixture composition. The determination of an accurate analytical dependence of $P$ in the gel phase of lyotropic systems requires further study. In particular the analysis conducted here should be extended to other surfactant mixtures where the gel state borders upon liquid crystalline mesophases with different microstructures.

Concluding Remarks

A water self-diffusion analysis in gel and liquid crystalline phases of the potassium palmitate/water system is reported in this study. The self-diffusion measurements have been per-
formed using the PGSE NMR technique which monitors the molecular displacement on a distance scale of μm.

The temperature and composition dependence of the water self-diffusion in the gel phase was defined according to a "two-site" average diffusion equation, and the results found in this study can be summarised as follows.

1) The temperature dependence of water self-diffusion in the lyotropic phases of the KC16/water system is similar to that of pure water. Arrhenius plots of the apparent diffusion have been plotted over a large range of temperatures and compositions. Equation (4), used to analyse the temperature dependence of the apparent self-diffusion data indicates that the change of both the obstruction factor and the fraction of the free water, (1 − P), with temperature is negligible.

2) The temperature dependence of water self-diffusion in the gel state was, however, very different. Ratios between the experimental and the free diffusion activation energies present a positive and negative deviation with respect to unity, that is between 0.091 to 2.90.

3) To interpret the temperature dependence of self-diffusion in the gel state, we hypothesized in equation (5) a temperature dependence factor (1 − P). The analysis of the water quadrupole splitting has pointed out that factor also depends on the composition mixture. On the contrary, the self-diffusion obstruction factor was considered constant as revealed from the study of 2H-NMR spectra profiles.

Acknowledgments

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References