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Lyotropic liquid crystal phase behaviour of the zwitterionic surfactants 4-*n*-tridecyl- and 4-*n*-heptadecyl-pyridinium *N*-oxide in water

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The phase behaviour, liquid crystal structures and head group hydration of two 4-*n*-alkylpyridine-*N*-oxide surfactants have been studied using optical microscopy, DSC and ^{2}H NMR spectroscopy. Only a limited swelling of the surfactant phase occurs in water, so that no micellar solution phase (L_1) occurs. The lamellar phase is the only mesophase observed. Water (^{2}H) quadrupole splittings indicate that the head group binds *c.* 6 water molecules.

1. Introduction

Zwitterionic surfactants are an important class of amphiphiles, yet except for phospholipid derivatives, they have received much less attention from researchers than ionic or non-ionic materials. Unlike most other surfactants, their micellar solutions frequently show lower and/or upper consolute curves. Thus micellar solutions of alkyldimethylphosphine oxides have a closed partial miscibility loop or show a lower consolute curve in the temperature range 0–200°C [1, 2]. Alkyldimethylamine oxides do not show this partial miscibility [3–5], but the behaviour is easily induced by addition of electrolytes [5, 6]. Alkyldimethylamoniopropane sulphonates and related compounds often show an upper consulate temperature [7, 8]. The origins of the intermicellar attractive forces which cause this behaviour are not understood, It is known [9] that with two interacting ionic surfaces, net attractive forces can arise when divalent counter-ions (as opposed to monovalent ions) are present. A similar force could arise where the counter-ions are chemically bound, i.e. with zwitterionic surfactants.

From the types of liquid crystal phases formed, zwitterionic surfactants in general act as if the area per molecule at the micelle surface (*a*) is large. Thus alkyldimethylamine oxides form the hexagonal (H_1) phase, implying $a \geqslant c.\ 47\,Å^2$, while the alkyl dimethylaminopropane sulphonates form cubic phases prior to hexagonal phases

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[3–5, 7, 8]. This implies that the cubic phase is a close-packed small micelle structure (I_1) rather than being of the bicontinuous variety (V_1) [10, 11]. (Frequently, two distinct regions within I_1 can be distinguished by optical microscopy [12], although the published reports have not drawn attention to this. It indicates that several types of small micelle close-packing are possible.) Thus for these compounds, the head group area within the micelle is even larger than for alkylamine oxides (i.e. $a \geqslant 65$ Å^2). We are interested to compare the behaviour of these compounds with that of a novel zwitterionic surfactant type, the 4-*n*-alkylpyridine 1-oxides. The cross-sectional area of the aromatic pyridine ring (*c.* 50 Å^2) is not unlike that of the dimethylamine oxide group, but clearly the aromatic group is more polarizable and the charge is delocalized. Hence its hydrated volume (area) could be anticipated to be larger than that of the amine oxide. Moreover, we might anticipate that this charge delocalization could enhance electrostatic attractions, hence giving rise to extensive partial miscibility with water.

In this study we report the phase behaviour of two pyridine *N*-oxide surfactants, the 4-C_{13} and 4-C_{17} derivatives (**I** and **II** respectively). For both compounds we have examined the liquid crystal behaviour using the optical microscope penetration technique [10, 11]. Differential scanning calorimetry (DSC) measurements on the pure surfactants have also been carried out to investigate possible gel phase formation [11]. Following this, the full composition range of **I** and water was investigated by optical microscopy and nuclear magnetic resonance (^2H_2O) to elucidate the composition limits of the mesophases and the nature of water/head group binding.

2. Experimental

Surfactant synthesis: the surfactants were synthesized according to the procedures described previously [12]. They were recrystallized prior to use and characterized by proton and carbon-13 NMR. Normal water was deionized and distilled. Heavy water was obtained from Aldrich (> 99·7 per cent). Optical microscopy was carried out using an Olympus BH2 polarizing microscope with a Linkam hot stage. For DSC measurements a Mettler TA 3000 system with a TC10TA processor was employed. The NMR data were obtained using a Bruker CXP 300 spectrometer operating at 46·07 MHz.

3. Results

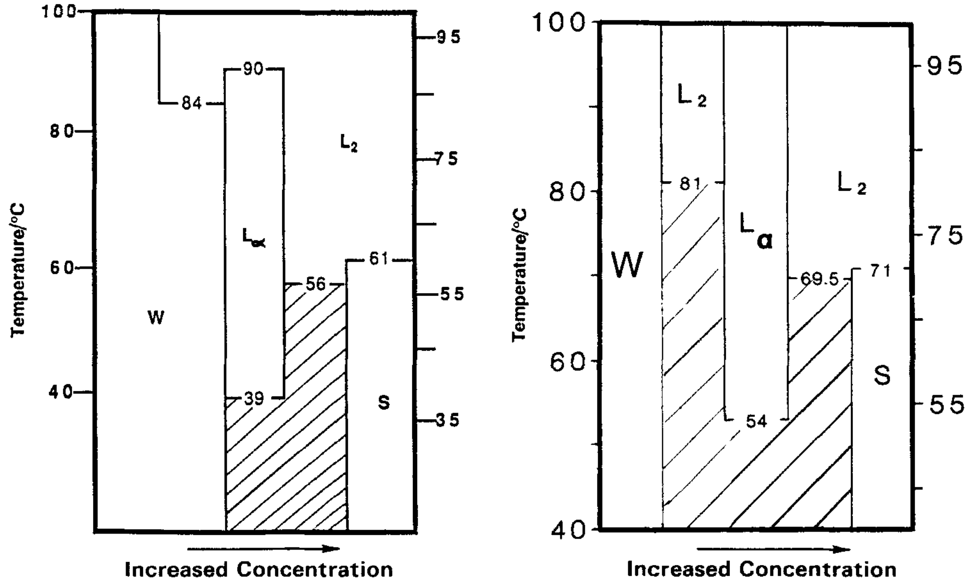
3.1. *DSC and microscopy*

Both **I** and **II** gave single DSC endotherms on heating and single exotherms on cooling (see the table). The temperatures correspond to the crystal melting transitions observed by optical microscopy. From the magnitudes of the heats, and the absence of 'gel' formation by microscopy, we conclude that neither surfactant forms a gel phase. For both compounds, the liquid surfactant phase exhibited 20–30°C of super-cooling before crystallization occurred.

The 'penetration scan' optical microscopy results are illustrated in figure 1. They show that only the lamellar mesophase (L_α) is formed by both surfactants, at least up to 100°C. This phase forms *c.* 20°C below the melting point of the anhydrous surfactants. The liquid surfactant phase (L_2) is observed a few degrees below the melting point, and for **I**, also occurs at the water-rich edge of L_2 *c.* 5°C below the maximum L_α melting temperature. Note that the label L_2 simply indicates a concentrated surfactant liquid phase (rather than reversed micelles as is commonly assumed). The liquid structure is likely to comprise small aggregates with some segregation of polar and non-polar

DSC data for **I** and **II**.

Compound	Transition temperature/°C	Transition enthalpy/kJ mol^{-1}
I	60	60·7
II	71	63·2



(*a*) (*b*)

Figure 1. Schematic phase diagrams obtained by the optical microscope penetration scan for (*a*) the 4-*n*-tridecylpyridine *N*-oxide/water system; (*b*) the 4-*n*-heptadecylpyridine *N*-oxide/water system (W, dilute aqueous solution; L_α, lamellar phase; S, crystalline surfactant; L_2, surfactant-rich isotropic liquid phase; shaded region, multi-phase coexistence).

moieties. Most significantly, a sharp boundary between the dilute aqueous solution (W) and the surfactant phase is always observed, even following various heating/cooling cycles where formation of solid surfactant (s) is avoided. Thus the normal micellar and L_3 phases are absent for these surfactants. The L_3 phase is a narrow liquid band often seen with polyoxyethylene surfactants as the lamellar phase melts to L_2. It is thought to contain a network micellar structure, where the micelles have a net negative curvature; see [11] and [references 53, 54] therein for further details. Also, no gel phase was observed on cooling the L_2 phase below its Krafft boundary. This type of behaviour is typical of weakly hydrated surfactants such as monoglycerides [13]. It indicates that the pyridine *N*-oxide head group is much less strongly hydrated than even the amine or phosphine oxide groups.

The phase diagram for **I** constructed by microscopy and NMR studies on a range of compositions (in ^2H_2O) is shown in figure 2. It confirms the penetration scan observations. There was some difficulty in accurately establishing the maximum swelling limit of the L_α phase, as indicated by the dashed line. However, certainly there is not a large variation of this boundary with temperature, since excess of water was clearly observed in samples containing *c*. 40% surfactant.

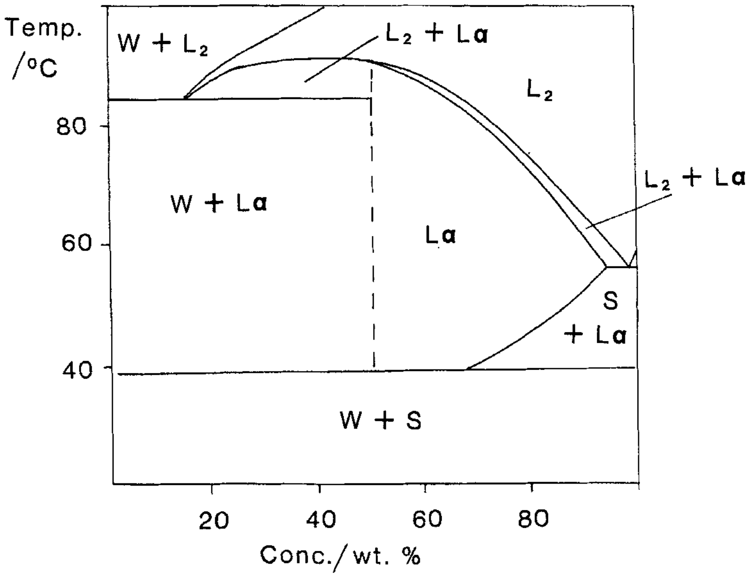


Figure 2. Phase diagram of 4-*n*-tridecylpyridine *N*-oxide/water (^2H_2O) system determined from microscopy and NMR measurements. Dotted lines indicate approximate boundaries.

3.2. *NMR studies*

To investigate the head group/water interactions in more detail we have studied the ^2H NMR quadrupole splittings in samples containing ^2H_2O. Since the background theory underpinning the technique has been described extensively elsewhere [14, 15], only a brief summary is given here.

Nuclei with spin quantum numbers $I > \frac{1}{2}$ possess an electric quadrupole moment which interacts with electric field gradients. In anisotropic media, the resonance line splits into $2I$ peaks. For nuclei, such as ^2H, with a spin quantum number $I = 1$, where the electric field gradient is axially symmetric (as in the L_α phase), the magnitude of the quadrupole splitting Δ, is given by

$$\Delta = \tfrac{3}{4} E_q S, \tag{1}$$

where E_q is the quadrupole coupling, which is dependent on both nuclear properties and the magnitude of the electric field gradient. S is an order parameter which describes the degree of order of the species studied and is given by

$$S = \tfrac{1}{2}(3\cos^2\theta_{DM} - 1) \tag{2}$$

where θ_{DM} is the time-averaged angle between the electric field gradient (the O^2H bond) and the mesophase axis. For ^2H_2O molecules in lyotropic liquid crystals, the quadrupole splittings are determined by the fraction of water molecules at the surfactant/water interface. These water molecules (termed 'bound' water) are in rapid exchange with the rest of the water ('free' water). It is generally assumed that $\Delta^w = 0$ for free water [11]. Thus

$$P_b \Delta_b = P_b E_{qb} S_b, \tag{3}$$

where P_b is the fraction of bound water and the subscript b denotes properties of bound water. We represent the binding of water to the head groups by an equilibrium of the type

$$nH_2O + S = S[H_2O]_n \tag{4}$$

(where S is surfactant and n is the number of bound water molecules) [16]. At low surfactant concentrations (C_s) P_b is given by

$$P_b = nC_s/C_w,$$

i.e. Δ increases linearly with C_s. However, in concentrated systems, where nearly all water molecules are 'bound', this no longer applies. For the simple model above (equation (4)), it has been shown [16] that a maximum in the dependence of Δ versus $C_s/C_w = 1/n - 1$. Astonishingly (at least to GJTT) this model describes the behaviour of a range of surfactants [16–20].

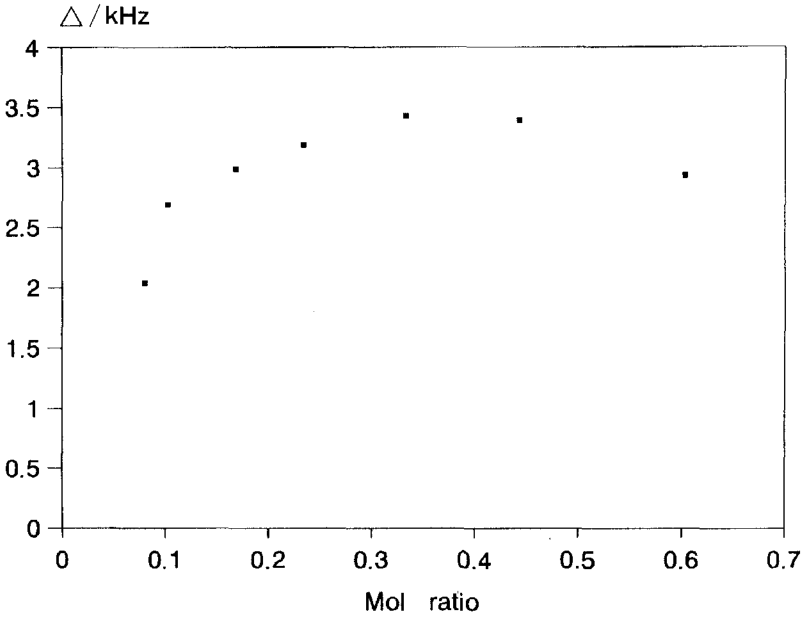
For compound **I**, the ^2H_2O quadrupole splittings have been measured for a range of composition temperatures. Frequently it was possible to cool the samples well below the Krafft boundary shown in figure 2. Because of the limited quantities of **I** available, the sample sizes were small (0·05–0·1 g). Hence particular care was taken to avoid any significant water loss due to temperature gradients within the NMR probe, by both frequent sample re-mixing and measurements during several different temperature cycles. The data were reproducible to better than ±3 per cent.

Mesophase samples which were close to the L_2/L_α phase boundary, or which were formed by cooling from L_2 in the NMR spectrometer magnetic field exhibited a single doublet spectrum rather than a Pake powder pattern. The peak separation was the same as the powder. This indicates alignment of the L_α phase with the director perpendicular to the magnetic field. At concentrations below *c*. 52 per cent surfactant, an additional prominent central peak was observed. The peak became more intense with added ^2H_2O, while the Δ value remained roughly invariant. This is attributed to the presence of an isotropic aqeous phase at the water-swelling limit of the L_α phase.

The measured Δ values shown in figures 3 and 4 are in the range *c*. 2–3·6 kHz. This falls within the range of Δ values usually observed for water in lamellar phases [16–20], although the values are towards the upper end of the range. At similar concentrations they are significantly larger than the values reported by Lawson and Flautt [21] in their pioneering NMR study of the dodecyldimethylamine oxide ($C_{12}AO$) system (*c*. 2 kHz at $C_s/C_w \sim 0{\cdot}23$–$0{\cdot}35$). A weak maximum in the concentration dependence of Δ occurs at $C_s/C_w = c.\ 0{\cdot}3$–$0{\cdot}4$, with this value possibly becoming somewhat higher at higher temperatures, Note that we do not show data above 55°C, because the narrowing of the composition range of the lamellar phase does not allow a large enough range of mol ratios to be measured for reliable conclusions to be drawn. Figure 4 illustrates that although the Δ values are almost independent of temperature, a very weak maximum appears to occur at *c*. 55°C. It is observed for several samples at higher concentrations, although only one example is shown here. The apparent maximum may arise from a decrease in Δ at high temperatures due to defect formation in the lamellar planes on approaching the L_α/L_2 boundary. This type of defect has been thoroughly studied for polyoxyethylene surfactant lamellar phases, where it certainly causes a marked decrease in the order of the lamellae on approaching the L_α/L_2 boundary [22, 23].

From the value of C_s/C_w at the maximum in Δ (figure 3), we estimate that the number of bound water molecules per surfactant (n) is *c*. 3–4. However, the very steep initial rise in the Δ versus C_s/C_w plot suggests that a 'plateau' region is reached at *c*.

$C_s/C_w \simeq 0{\cdot}15$. Hence at this concentration, most of the water is 'bound' to the surfactant head group. This implies that $n \sim 5$–6, slightly larger than that implied by the maximum in Δ. In fact, it is likely that the simple assumptions involved in the original model [16] are no longer valid here. In particular, it is likely that S_b, the average order parameter of the bound water, changes with composition in the region $C_s/C_w > 0{\cdot}2$. Hence we can only obtain the approximate value of $n \sim 6$.



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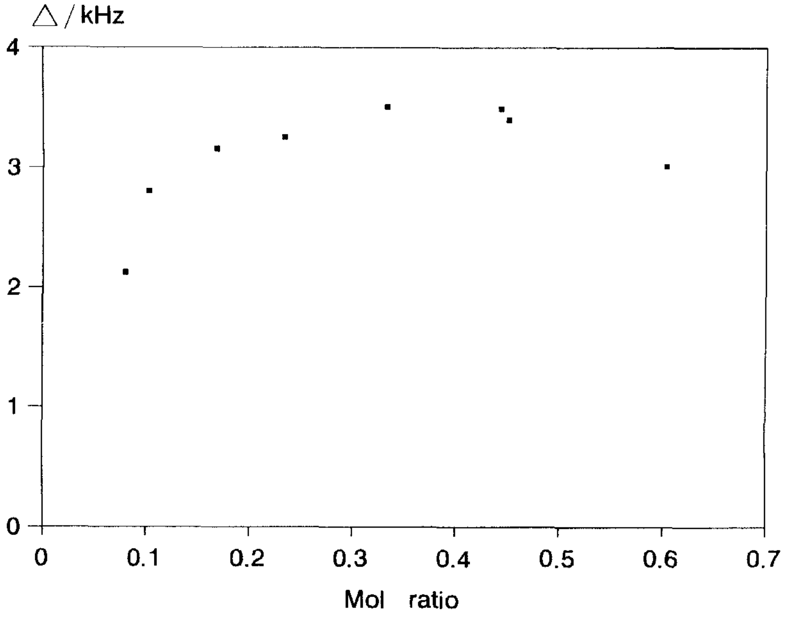

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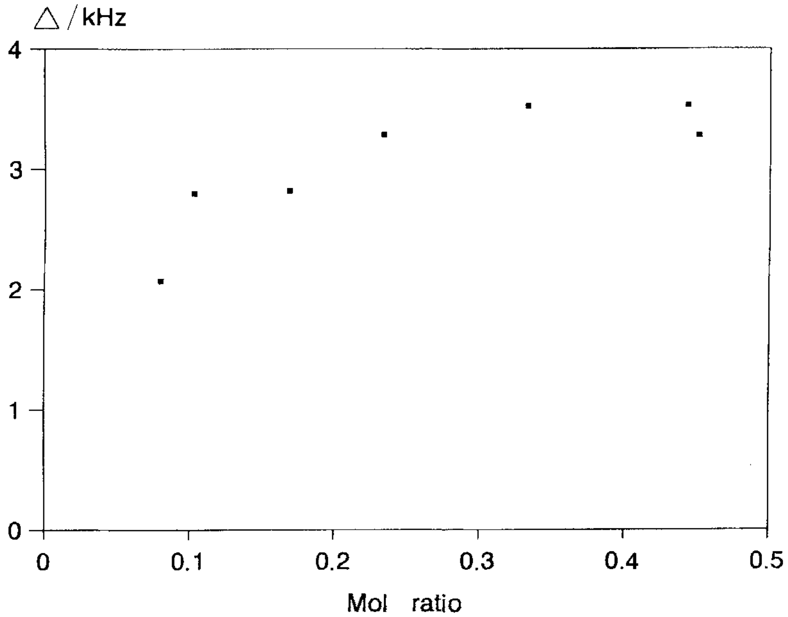


(c)

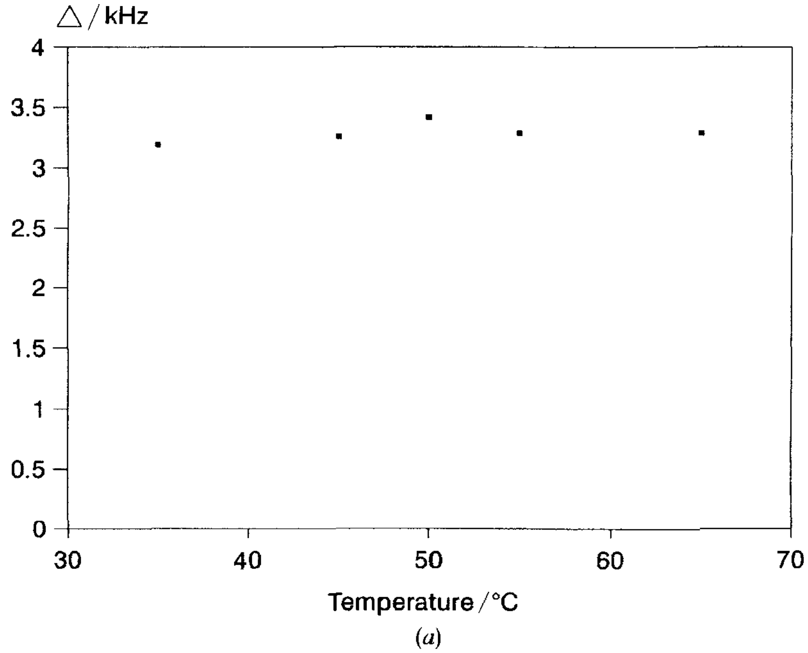
Figure 3. The dependence of water (^2H_2O) quadrupole splittings (Δ) on surfactant/water mol ratio for the 4-*n*-tridecylpyridine *N*-oxide/water system (*a*) 35°C; (*b*) 45°C; (*c*) 55°C.

We can compare our data with those for the $C_{12}AO$ lamellar phase samples reported by Lawson and Flautt [21]. Note that for $C_{12}AO$, the limited composition range of the lamellar phase prevents the examination of a wide range of mol ratios. The values are almost invariant over the range C_s/C_w 0·24–0·35. From equation (3) we expect an increase of *c*. 40 per cent if a high concentration of free water is present in the system. Clearly this does not occur. Hence the value of *n* estimated for the $C_{12}AO$ L_α phase is $n \geqslant 4$, giving the possibility of similar water binding to that for the compounds studied here.

4. General comments and summary

The most important difference between the zwitterionic surfactants studied here and others such as amine or phosphine oxides is the occurrence of the lamellar phase rather than hexagonal and cubic phases. This clearly demonstrates that the hydrated pyridinium *N*-oxide group is smaller than the other two polar groups, despite being hydrated by *c*. 6 water molecules. In fact these are insufficient to cover the surface of the polar group completely; hence we conclude that part of the heteroaromatic ring is either in contact with the alkyl chain core of the bilayer, or that there is some contact between adjacent rings.

Considering other surfactant types, the introduction of a benzene ring as part of an ionic head group does not alter the mesophase properties of alkyl benzenesulphonates compared to the alkyl sulphonates. Both form H_1, V_1 and L_α phases [12]. Similarly, alkylpyridinium surfactants form I_1, H_1, V_1 and L_α phases as do the alkyltrimethylammonium halides [10, 24]. However, for the non-ionic surfactants *n*-alkylpolyoxyethylene ethers, the presence of a phenyl group between the alkyl and EO groups does act to reduce the size of the head group slightly [25]. From the published



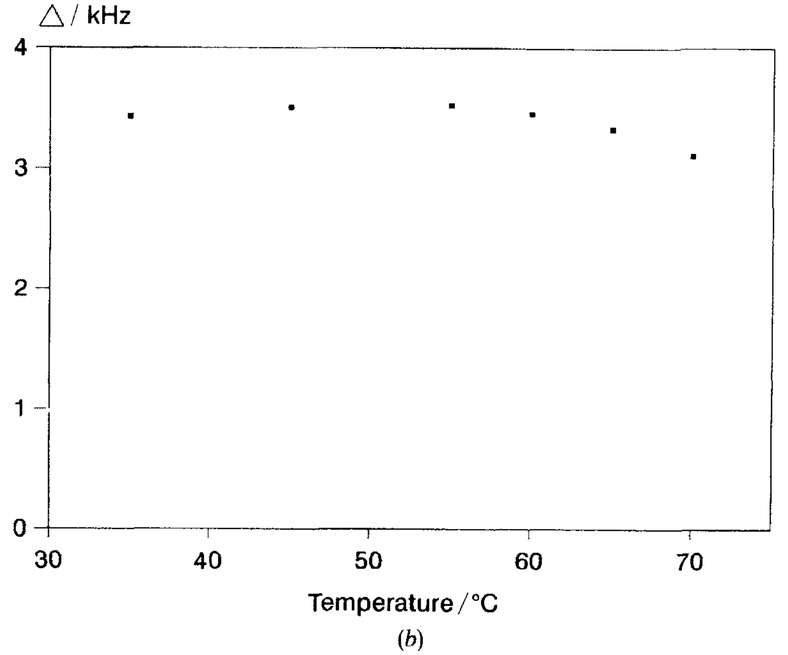


Figure 4. Temperature dependence of water Δ values at two surfactant/water mol ratios (*a*) mol ratio = 0·2337 (76·4 wt per cent); (*b*) mol ratio = 0·3334 (82·2 per cent).

X-ray data on $C_{12}AO$ [26], using standard procedures [27], we calculate the area (*a*) per head group to be *c.* 51 Å^2 at the L_1/H_1 boundary (H_1 phase), and *c.* 46 Å at the L_α/V_1 boundary (L_α). Hence only a relatively small reduction in *a* is required to prevent the formation of H_1 and V_1 phases. It is likely that *a* for the pyridine oxide surfactants is in the upper range of values typical for lamellar phases, i.e. *c.* 44 Å^2. This is supported by the occurrence of only the L_α phase for the C_{17} derivative. For surfactants with a smaller *a* value, an increase in chain length by this amount usually induces reversed cubic or H_2 phases, as for example with monoglycerides [13]. We have since carried out low angle X-ray diffraction measurements on a lamellar sample containing 79·1% I/H_2O. We obtain a d_0 spacing of 32 ± 1 Å over the temperature range 45–60°C. Calculations using standard procedures [27] give a head group area of $41 \pm 1{\cdot}5$ Å^2.)

The second surprising feature of this system is that the L_α phase does not swell beyond a C_s/C_w ratio of 1:17. Polyoxyethylene surfactants with similar *a* values ($C_{12}EO_4$, $C_{12}EO_5$) have L_α phases which swell to C_s/C_w ratios of $> 1:50$, probably due to weak undulation forces [16]. The lack of such swelling here points to the existence of medium range attractive forces between the zwitterionic surfactant layers. These are presumably the same type of interactions that are responsible for the partial miscibility of other zwitterionic surfactants with water [1, 2, 4]. The attractions could also be responsible for the absence of any L_3 phase, since this can only appear in the region of weak repulsions.

To summarize, the occurrence of only L_α phases in alkylpyridine *N*-oxide surfactants, rather than H_1, V_1 and L_α phases as with alkyl amine and phosphine oxides, is due to a relatively small reduction in hydrated head group area compared to the amine oxide. This is consistent with the influence of a benzene ring on head group areas for non-ionic surfactants, but not for ionic surfactants. Clearly, for the former, the determining factors are short range steric effects, while for the latter, long range electrostatic forces dominate.

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