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STRUCTURE OF CUBIC (I_1) MESOPHASES BELONGING TO SPACE GROUP Pm3n

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ABSTRACT: It is shown that the structure of the cubic (I_1) mesophase of the $C_{12}TACl$/water system can be described as 48 spherical micelles per unit cell, with micellar centres at the coordinates of equivalent positions for the general case of space group Pm3n. This reconciles the X-ray and NMR data for this system. This model can also be applied to the I_1 mesophase of the sodium caprylate/p-xylene/water system.

Nuclear magnetic resonance (NMR) and X-ray diffraction data indicate contradictory structures for some lyotropic liquid crystals in the cubic (I_1) phase [1], which lies between micellar solution (L_1) and the hexagonal (H_1) liquid crystalline phase for certain surfactant/water systems. The I_1 systems involved are those where I_1 has been shown by X-ray diffraction studies to belong to space group Pm3n [2], which has been postulated [3] to consist of rod-like cages which enclose two spherical micelles per unit cell. The NMR self-diffusion measurements[4,5] for one of these systems, dodecyltrimethylammonium chloride/water ($C_{12}TACl$)[6], are not compatible with a continuous rod-like structure, but exhibit the more restricted self-diffusion expected for discrete globular micelles. The purpose of this letter is to show that the NMR and X-ray data can be reconciled, if the X-ray results are assigned to the general case for space group Pm3n, rather than to a combination of two of the specific cases.

The X-ray data for the I_1 phase of the $C_{12}TACl/H_2O$ system have been reported by Balmbra et al.[6]. For a sample with 43% $C_{12}TACl$, the data correspond to a lattice parameter a_o = 8.6 nm for a primitive cubic lattice. Balmbra et al[6] suggest that the general case of either space group $P\bar{4}3n$ or Pm3n will fit the data. For both of these space groups reflections from the planes (hkl) = (100) are forbidden, with the first observed reflection being the $a_0/\sqrt{2}$ reflection from the (110) planes[2]. Thus the length of the unit cell for either space group is 122Å. This unit cell contains either 48 globular micelles for space group Pm3n, or 24 globular micelles per unit cell for space group $P\bar{4}3n$, with each micelle centred at one of the coordinates of equivalent positions for the general case. From measured specific volumes determined by Luzzati's group[7], the radius

TABLE 1 Micellar radii and surface areas per molecule calculated assuming different space groups.

Space Group	Number of spheres in unit cell	ϕ_a	a_0 Å	r_a Å	S Å^2	Sample	Ref
Pm3n	48	.4507[7]	122	16.0	89.5	(43%/57% ($C_{12}TACl$/	6
$P\bar{4}3n$	24	.4507[7]	122	20.1	71.7	(H_2O	6
Pm3n	48	.4845	75	10.0	87.4	(41%/5%/54%	3
$P\bar{4}3n$	24	.4845	75	12.7	69.4	($NaCOO(CH_2)_6CH_3$/ (p-xylene/H_2O	3

of each micelle and surface area per monomer at the surfactant/water interface can be determined. These data are shown in the table.

For the 43% $C_{12}TACl$/57% H_2O sample studied by Balmbra et al[6] the spherical radius calculated for space group Pm3n is reasonable, while that calculated for space group $P\bar{4}3n$ is large, based on a length of 18.2Å for $CH_3(CH_2)_{11}N(CH_3)_3^+$ with an all-trans hydrocarbon chain[8]. The surface areas in both cases are large enough to satisfy the criterion[3] that they exceed those for the hexagonal phase. Theoretical considerations[9] indicate that the surface area per molecule at the hydrocarbon/headgroup interface, S_h, should be > 70Å² for a C_{12} chain. This criterion is satisfied for Pm3n, (S_h = 72.6Å²), but not for $P\bar{4}3n$, (S_h = 57.6Å²). Thus Pm3n is the more likely space group for this system.

The table also shows calculated radii and surface areas per head group for the system 41% sodium caprylate, 5% p-xylene, 54% water studied by Tardieu and Luzzati[3]. The calculations assume that all of the p-xylene is associated with the sodium caprylate micelles, and that none of it is dissolved in the water. The calculated radii of 12.7Å for space group $P\bar{4}3n$ and 10.0Å for space group Pm3n compare with 10.9Å for $CH_3(CH_2)_6COO^-$ with an all trans hydrocarbon chain[8]. Again the surface area per head group is ample for either space group, but the more reasonable radius makes Pm3n seem more likely.

To show that the general case of space group Pm3n is a reasonable model for the I_1 phase of $C_{12}TACl/H_2O$, it remains to be shown that 48 spherical micelles of radius 16Å can be inserted into a unit cell of 122Å length, with their centres at the coordinates of equivalent positions given in ref 2. Following the notation of ref 2, the centre of the unit cell will be taken as the origin of the coordinate system, and three sets of orthogonal axes of length $a_0/2$ in both the positive and negative directions will define the unit cell. The dimensions are reduced by setting $a_0 = 1$, and the micellar radius similarly reduced to 16Å/122Å = 0.13.

Although the coordinates are completely general, it is possible to make statements about the system which place limits upon their values. For convenience, x, y, and z will be assumed to be positive, with $x < y < z$. Since those micelles closest to the origin (the first 24 in the table, all of which have one coordinate of $|x|$, one of $|y|$ and one of $|z|$) cannot contain the origin,

$$[x^2 + y^2 + z^2]^{\frac{1}{2}} > 0.13 \qquad (1)$$

where 0.13 is the reduced micellar radius. Also, the closest distance between micellar centres must be greater than twice the radius of the micelle. Within the first octant of the unit cell the distance between i.e. (x, y, z) and (z, x, y) is

$$[(x-z)^2 + (y-x)^2 + (z-y)^2]^{\frac{1}{2}} > 0.26 \qquad (2)$$

Equation 2 also describes the shortest distance between micellar centres for coordinates such as $(\frac{1}{2}+x, \frac{1}{2}+z, \frac{1}{2}+y)$ and $(\frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}+z)$. Within the first quadrant, the shortest separation between micelles in the 'inner' and 'outer' parts is that between $(\frac{1}{2}-x, \frac{1}{2}-z, \frac{1}{2}-y)$ and (z, x, y), which gives equation 3.

$$[(\tfrac{1}{2}-x-z)^2 + (\tfrac{1}{2}-z-x)^2 + (\tfrac{1}{2}-2y)^2]^{\frac{1}{2}} > 0.26 \qquad (3)$$

Another short separation is that between micelles in adjacent quadrants, i.e. between (x, y, z) and ($\overline{x}$, $\overline{y}$, z). This gives

$$[(2x)^2 + (2y)^2]^{\frac{1}{2}} > 0.26 \qquad (4)$$

All other separations between coordinates of equivalent positions can be shown to be greater than these.

The limiting equations (1) to (4) will now be used to define the range of x, y, and z. From (2), and the expectation from symmetry considerations that $|x-y| \backsim |y-z| \backsim \frac{1}{2}|z-x|$, by setting $|x-y| = |y-z| = \frac{1}{2}|z-x|$ one obtains

$$|x-y| > .107 \qquad (2a)$$

Equation (4) states that the minimum x and y values compatible with (2a), x = 0.01, y = 0.12, are too small, but will allow slightly greater x and y values (i.e. x = 0.01, y = 0.13 or x = 0.02, y = 0.13). Equation 3 sets a maximum value for x, y, and z. The maximum value of $|x-y|$ compatible with (3) is 0.16, with x = 0.01, y = 0.17, z = 0.33. For $|x-y|$ = 0.11, values of (x, y, z) ranging from (.01, .13, .24) to (0.06, 0.17, 0.28) will satisfy equations 1 to 4. An example in the middle of the range would be $|x-y|$ = 0.14, x = 0.03, y = 0.17, z = 0.31. Reasonable uncertainties for these values would be ± 0.02, though obviously z could be allowed to decrease to 0.24 if the x and y values were appropriate. Transforming these coordinates out of reduced space gives x = 3.7 ± 2.5Å, y = 20.7 + 2.5Å, z = 37.8 ± 2.5Å. Thus, using this fairly narrow range of x, y, and z values for the coordinates of

equivalent positions, the $C_{12}TACl/H_2O$ system at 43% by weight surfactant can be described as containing 48 spherical micelles of 16Å radius in a unit cell of a_0 = 122Å, where the micelles are centred at the coordinates of equivalent positions for the general case of space group Pm3n.

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