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Compared Organization of the Molecules of NaDEHP and AOT: Determination of the Microscopic Organization of the Sodium Bis(2-ethylhexyl)phosphate Molecule in the Solid State in the Reversed Hexagonal Liquid Crystal State

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A method to determine the average shape of some molecules is described and applied to sodium bis(2-ethylhexyl)phosphate (NaDEHP) and sodium bis(2-ethylhexyl)sulfosuccinate (AOT). The volumes and lengths of the polar and apolar parts of these molecules are obtained from specific gravity measurements and from the lattice parameters of the hexagonal and lamellar liquid crystal structures. The shape of both molecules is described as a prism. The cross section of the elementary rod in the hexagonal structure intercepts respectively 2.5 and 6 molecules. The noninteger value obtained for NaDEHP is explained by a disorder inside the rod, and the mean value of 6 obtained for AOT is related neither to the symmetry of the lattice nor to the hexagonal average shape of the rod. The parameter limiting the height of the prism is the size of the phosphate coordinance tetrahedron, in the case of NaDEHP, and the length of the succinate chain, in the case of AOT.

Introduction

Different kinds of lyotropic liquid crystals have been pointed out in aqueous or organic solutions at room temperature, for instance, with sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (*1*), or with sodium bis(2-ethylhexyl)phosphate (NaDEHP) (*2*, *3*). The arrangement of the molecules may be direct or reversed (for instance, in hexagonal or cubic liquid crystals), or even "symmetrical" (for instance, lamellar liquid crystals, vesicles, bicontinuous microemulsions). In particular, the stable configuration depends on both the polar and apolar volumes of the hydrated (in an organic medium) or hydrocarbonated (in an

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aqueous medium) molecule of the surfactant.

In order to estimate the microscopic characteristics of various surfactant molecules, and to better understand inter- and intramolecular arrangements, a method based on measurements of specific gravity and of lattice parameters of the hexagonal and lamellar liquid crystal structures has been developed. This method allows one to obtain the main microscopic parameters of the molecule, principally the total volume and the volume and the length of its polar and apolar parts. Moreover, a geometric schematization of the molecule can be deduced from this modeling.

The method is presented with and applied to NaDEHP, and then applied to AOT.

Experimental

NaDEHP was prepared according to a method similar to the one described by Eicke and Arnold (*4*). The purity of Na DEHP, which was greater than 99%, was obtained by alcoholic titration with NaOH in a solvent (80% ethanol, 20% water in weight), after transformation into HDEHP on a cationic resin. Specific gravity of the NaDEHP synthesized by the previously described method (solid at room temperature) was measured by the hydrostatic method. The NaDEHP sample was previously compacted into pastille form. We chose three immersion liquids in which NaDEHP is insoluble:

—dodecane (at 23.5°C),

—silicone oil or hexadecane (at 22.0°C).

In the three cases, the pastille was suspended by a wire from a precision balance (10^{-4} g) then immersed into the liquid. The results have been corrected for the Archimedean force on the wire and the influence of temperature. We obtain in the final result an error of 3×10^{-3} g cm^{-3} in silicone oil and of 1×10^{-3} g cm^{-3} in dodecane and hexadecane.

Molar Volume of NaDEHP

The specific gravity, ρ, of pure NaDEHP was 1.039 ± 0.001 g cm^{-3} at 23.5°. Taking into account that molar weight of NaDEHP is $M = 344.43$ g mole^{-1}, we can infer the molar volume ($V = M/\rho$) to be 331.5 ± 0.3 cm^3 mole^{-1} and the volume of a molecule ($v = V/N$), 550.4 ± 0.5 Å^3 molecule^{-1}, where N is Avogadro's number.

The molar volume that we found for the solid is comparable to those determined by Faure *et al.* (*5*) by densitometry of Na DEHP–water–benzene mixtures (320 and 310 cm^3 mole^{-1}, according to whether the surfactant concentration is lower or higher than the critical micellar concentration). The deviation, small as it is between these three values, is certainly due to the different configurations taken by the NaDEHP molecules in the pure state (reversed hexagonal liquid crystal), as a molecular solution, or as a micellar solution.

Volume of the Polar and Apolar Part of NaDEHP Molecule

Although the sodium phosphate group belongs unquestionably to the polar part of the molecule, there is much debate whether the first CH_2 group (bound to the phosphate) belongs to the polar or apolar part. Tanford (*6*) and Zemb (*7*) consider the first CH_2 group, in water-rich micelles, to belong to the polar head because of the strong attraction due to water.

In the case of anhydrous NaDEHP, it is likely that the absence of water and the ethyl branching onto the atom of carbon in position 2 increase the apolar character of the alkane chain. Thus, we will consider that the apolar part of the NaDEHP mole-

TABLE I

SOME VALUES OF MOLAR WEIGHTS M, DENSITY d, AND CALCULATED MOLECULAR VOLUMES v

Compound	M (g mole^{-1})	d	v (Å^3 molecule^{-1})	Reference
3-Ethylhexane	114.23	0.7136	265.8	(*10*)
4-Ethylheptane	128.26	0.7270	292.9	(*10*)
2-Ethylhexanol	130.23	0.8328	259.6	(*10*)
Succinic acid	118.09	1.572	124.7	(*10*)
Na_2SO_3 (solid state)	126.04	2.633	79.5	(*10*)
NaDEHP	344.43	1.039	550.4	(*3*)
AOT	444.6	1.15	644	(*1*)

cule contains the whole 2-ethylhexyl chains.

The unit volumes of the CH_3 and CH_2 groups are known: 54.3 Å^3 and 27.4 Å^3 according to Tanford (*6*) and 53.2 ± 3.3 Å^3 and 26.6 ± 1.7 Å^3 at 24°C according to Reiss-Husson and Luzzati and Cabane (*8*, *9*). We can estimate the volume of the 2-ethylhexyl radical from the volume of the closely related molecule of 3-ethylhexane (265.8 Å^3, see Table I), in which a CH_3 terminal group is replaced by a CH_2 group (*9*, *10*), which leads to the value:

$$(v)_{\text{2-ethylhexyl}} = 265.8 - 53.2 + 26.6 = 239.2 \pm 6 \text{ Å}^3.$$

A slightly different value (239.7 ± 4 Å^3) is obtained by taking the volume of the 4-ethylheptane molecule (292.9 Å^3, see Table I) and removing from it the volume of a CH_3 group.

The apolar volume of the NaDEHP molecule is thus estimated at $239.5 \times 2 = v_a = 479.0 \pm 10$ Å^3, the complementary v_p, as in $v = v_p + v_a = 550.4$ Å^3, represents the volume of the polar part, i.e., $v_p = 71.4 \pm 10$ Å^3.

Length of the Polar and Apolar Parts of the NaDEHP Molecule

The total length l of the molecule and the lengths l_p and l_a of the polar and apolar parts can be evaluated from the liquid crystal structures that we previously determined (*2*). We have shown that pure NaDEHP has a reversed hexagonal structure. This structure is formed by molecules arranged radially (polar heads toward the center, hydrocarbon tails outside) and stacked as rods. These rods are placed side by side, in parallel, forming a bidimensional hexagonal lattice, its parameter being $a = 17.54$ Å. In the hexagonal cross section of the rod, the molecule occupies a length with a value taken to be equal to the radius of a circle having the same area as the cross section of the rod, $l = 9.2 \pm 0.3$ Å.

On the other hand, the length l_a of the apolar part of the NaDEHP molecule can be evaluated from another liquid crystal structure (lamellar) that we observed in the NaDEHP–water system (*2*). This structure is formed by an alternate stacking of polar layers (containing oppositely placed phosphate groups and water) and of apolar layers, where the hydrocarbon chains are found. The thickness of this apolar layer is independent of the concentration of water (*2*), and equal to ca. 11.5–12.0 Å (average 11.8 ± 0.2 Å), which allows the attribution of an apolar length, $l_a = 11.8/2$, of 5.9 ± 0.1 Å to the apolar part of the molecule (2-ethylhexyl chains). The length of the polar part is then $l_p = l - l_a \approx 3.3 \pm 0.4$ Å.

By attributing to the volume of the polar head (71.4 Å^3) a simple shape (respectively, cube, sphere, or tetrahedron), it becomes apparent that its largest measurement (respectively, side = 4.15 Å, radius = 5.15 Å or side = 8.46 Å) is clearly higher than the previously determined length l_p of the polar head. This will be explained when the geometric shape of the average volume attributed to each molecule is discussed further (Fig. 1b) and the α angle determined.

Schematization of the NaDEHP Molecular Shape

One may consider three types of schematization for the NaDEHP molecule (Fig. 1):

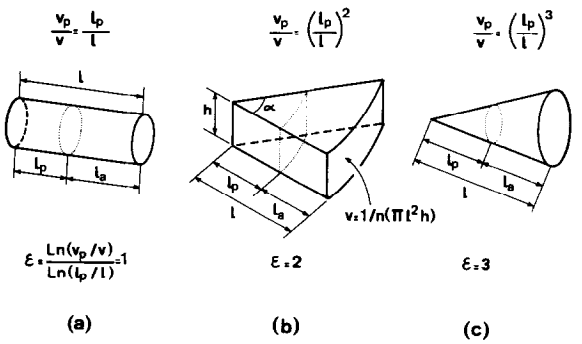

FIG. 1. Cylindrical (a), prismatic (b), and conic (c) schematization of NaDEHP molecule. In the three instances, volumes, and lengths of polar and apolar parts are such that $v = v_a + v_p$ and $l = l_a + l_p$.

cylindric, prismatic, or conic. For each type the parameter

$$\varepsilon = \frac{\ln(V_p/V)}{\ln(l_p/l)}$$

takes the theoretical values of 1, 2, or 3. The value of the parameter ε deduced from our experimental results of v_p, v, l_p, and l is: 1.99 ± 0.4. This value of ε suggests a prismatic schematization. In this hypothesis, the average shape of the molecule is a prism resting on a circular sector, the radius of which is the length l determined above ($l \approx 9.2$ Å), and the height of which is h (Fig. 1b), determined below.

Disposition of the Molecules in the Hexagonal Liquid Crystal Structure of Pure NaDEHP

Taking into account the dimensions of the molecule, it is possible to determine the mean number n of molecules in a cross section of the rod. In order to do this, we calculate the number n of elements of prismatic volume (Fig. 1b) which can be juxtaposed in a fraction of the rod limited by two cross sections h apart. The volume of this element can be expressed as:

$$v = (\pi l^2 h)/n. \qquad (1)$$

The maximum size of the polar head (phosphate group) can be determined from the crystallographic data obtained, for example, for lead phosphate $Pb_3(PO_4)_2$ in the solid state (*11*) where the average distance between the centers of the various oxygen atoms is ca. 2.5 Å. A value of twice the oxygen radius (i.e., ca. 2×1.5 Å) must be added to this distance in order to obtain the maximum size of the PO_4 coordination tetrahedron (ca. 5.5Å). This maximum size arises in two instances of the configuration (Fig. 2a):

(i) when the oxygen atoms bound to the aliphatic chains R are on the edge V_1 of the tetrahedron which is parallel to the axis of the rod,

(ii) when the two oxygen atoms not

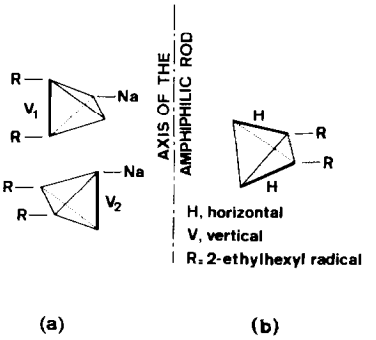

FIG. 2. Possible dispositions of the PO_4 tetrahedron in relation to the axis of the amphiphilic rod in the NaDEHP hexagonal liquid crystal: (a) one side of the tetrahedron (noted V) parallel to the axis; (b) two opposite sides (noted H) perpendicular to the axis.

bound to the aliphatic chains R are on the edge V_2 which is parallel to the axis of the rod.

Conversely, the minimum value (Fig. 2b) is obtained when two of the edges of the PO_4 tetrahedron are perpendicular to the axis of the rod. The vertical size is then ca. 4.8 Å considering the radii of the oxygen atoms. Therefore, the height h of the prism which can contain the molecule and which is consistent with the size of the polar head can be found in the interval 4.8–5.5 Å. Taking into account $v = 550.4$ Å^3, it follows from equation (1) that:

$$n \in [2.3\text{–}2.7].$$

We emphasize that the closest integer values of n, i.e., $n = 2$ and $n = 3$, would lead to $h = 4.13$ Å and $h = 6.20$ Å, values which are inconsistent with the real size of the polar head. A noninteger value of n must therefore be admitted; i.e., $n \approx 2.5$. The meaning of a noninteger value, which is rather surprising, is discussed later.

It is to be noticed that the shape of the polar part of the prism (Fig. 1b), with $\alpha = 360°/n \approx 144°$, is not consistent with the real shape of the polar head of the molecule: particularly the length $l_p = 3.3$ Å determined above is much lower than the real size [4.8–5.5 Å] of this head. But this polar part of the prism has the signification of a mean volume attributed to the polar head.

Schematization of the AOT Molecule in the Pure State

Let us determine the schematization of the AOT molecule (Fig. 1) by considering the volumes and the lengths of the polar and apolar parts of the molecule as we have done for NaDEHP. By taking as the partial volume of AOT the value obtained by Ekwall *et al.* (*1*) in a micellar solution of AOT, water, and xylene (ca. 388 cm^3 mole^{-1}), the density of AOT is estimated to be ca. 1.15. The molecular volume is therefore ca. $v_{AOT} = 644$ Å^3 molecule^{-1} (see Table I).

In a first approach, the apolar volume of AOT molecule can be calculated from the hypothetical diesterification of succinic acid by ethylhexanol, according to:

$$2R\text{–OH} + \text{HOOC–CH}_2\text{–CH}_2\text{–COOH} \rightleftharpoons R\text{OOC–CH}_2\text{–CH}_2\text{–COO}R + 2\text{H}_2\text{O},$$

where R– means the 2-ethylhexyl radical $-CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$. According to the values in Table I, we determine $(v_a)_{AOT}$ to be approximately 583 Å^3. This value is slightly overestimated, because the volume of the hydrogen atom, which is substituted by the $-SO_3Na$ group in the AOT apolar part, has been neglected. Consequently:

$$\begin{aligned}(v_p)_{AOT} &= (v)_{AOT} - (v_a)_{AOT} \\ &= 644 - 583 \\ &= 61 \text{ Å}^3 \text{ (underestimated).}\end{aligned}$$

This value is compatible with the molecular volume 79.5 Å^3 of Na_2SO_3 in the solid state (see Table I).

The length l of the AOT molecule in the hexagonal liquid crystal is obtained from the cell parameter ($a = 23.9$ Å (*1*), a value obtained by low-angle X-ray diffraction). By a similar argument to that applied to Na DEHP (and assuming a prismatic model of the molecule) we can attribute the length $l_{AOT} \approx 13$ Å to the side of the prism as well as to the molecule. The length of the apolar part of AOT is much greater than that of NaDEHP, as the space taken up by the succinate chain parallel to the axis of the rod must be taken into account. Indeed the length of the apolar part is calculated as (Fig. 3):

$$(l_a)_{AOT} = l_1 + l_2,$$

where $l_1 = (l_a)_{NaDEHP} = 5.9$ Å, and l_2 is the width of the succinate chain. In a first ap-

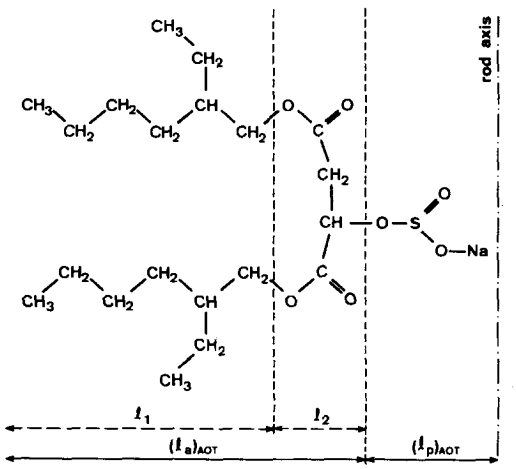

FIG. 3. Formula and schematic disposition of a molecule of pure AOT in the solid state. According to Ekwall *et al.* (*1*), the succinate chain stands parallel to the axis of the rod. As a consequence the apolar length of the AOT molecule can be expressed by $(l_a)_{AOT} = l_1 + l_2$, where l_1 is the *length* of the 2-ethylhexyl chain, and l_2 the *width* of the space taken up by the succinate chain.

proach, this width is taken as two C–O bonds, that is,

$$l_2 \approx 1.4 \times 2 = 2.8 \text{ Å}.$$

Hence:

$$(l_a)_{AOT} \approx 5.9 + 2.8 = 8.7 \text{ Å}$$

and

$$(l_p)_{AOT} = (l)_{AOT} - (l_a)_{AOT}$$
$$\approx 13 - 8.7 = 4.3 \text{ Å}.$$

The parameter ε (Fig. 1) assumes the value,

$$\varepsilon = \frac{\ln\{(v_p)_{AOT}/(v)_{AOT}\}}{\ln\{(l_p)_{AOT}/(l)_{AOT}\}} = 2.13,$$

which suggests a prismatic shape, as in the case of NaDEHP.

Adopting Ekwall *et al.*'s hypothesis (*1*) of $n = 6$ molecules disposed radially (six prismatic volumes of side l and of height h, see Fig. 1), it follows from Eq. (1) that h equals 7.2 Å. The value of $n = 6$ is thus confirmed by the fact that the height $h = 7.2$ Å is consistent with the maximum extention of ≈7.5 Å of the succinate chain parallel to the axis of the rod. This estimated extension takes into account three C–C and two C=O bonds with the true angles (6.0 Å) and a contribution of the covalent oxygen atoms.

Additionally, values of $n < 6$ (e.g., $n = 5$ or $n = 4$ which would lead to $h = 6.0$ or $h = 4.8$ Å) would imply either the nonparallel position of succinate chains in relation to the axis of the rod, or an inconsistency with the volume of the SO_3 tetrahedron, of about the same size as PO_4 group, i.e., ca. 5.5 Å at its greatest measurement. The value of $n = 6$ seems therefore the most probable for AOT.

Discussion: Structural Comparison between NaDEHP and AOT

Geometric considerations, compared with experimental values obtained from the hexagonal lattices of two important surfactants (NaDEHP and AOT) lead to values of average numbers of molecules in a cross section which can be either noninteger or different from 6. We intend to discuss these apparent contradictions below.

In the case of NaDEHP, the X-ray diffraction diagram can be completely indexed with the indices of a hexagonal bidimensional lattice of parameter $a = 17.54$ Å (Miller index $l = 0$) and it does not reveal any periodicity below 147 Å (which corresponds to the lower limit of observation of 0.3° on the goniometer) (*2*). The periodic arrangement corresponds to the compact assembly of parallel rods. X-ray diffraction points out exclusively a plane lattice, without any other level of order in the rods. The noninteger value of 2.5 reveals moreover a disorder inside the rod, i.e., a disorder in the mutual disposition of the molecules.

The real disposition of the molecules within each rod can be described as follows, according to Ekwall *et al.* (*1*):

(i) the disordered packing of the polar heads around the axis of the rod (forming the core),

(ii) the equally disordered semiliquid and rather radial distribution of the hydrocarbon chains around the core, which is evidenced by the X-ray diffusion ring centered on the 10.3° angle (corresponding to ca. 4.3 Å).

No particular evidence of an integer value may be deduced from the model; the mean value of 2.5 likely suggests a statistical distribution of cross sections with 2 Na DEHP molecules, and others with 3 molecules.

In the case of AOT, the real disposition of the molecules can be described in the same way as for NaDEHP, but it must be emphasized that the average value of 6 molecules per cross section is only determined by the volume considerations developed above, and not by the sixfold symmetry of the crystal or the average hexagonal shape of the rod. As in the case of NaDEHP, no periodicity parallel to the axis (no Miller indices with $l \neq 0$) has been reported (*1*). The authors only mention the presence of a diffuse reflection around 4.5 Å (corresponding to an angle of ca. 10°), similar to that observed for NaDEHP, and which Ekwall *et al.* (*1*) attribute to the more or less liquid state of the aliphatic chains. The most likely arrangement of the 6 molecules per cross section discussed by Ekwall *et al.* implies that the succinate chains are parallel to the axis of the rod, and that the sulfonate groups which form the polar core located in the center of the rod are alternately disposed above and below. This arrangement of the polar heads in two subgroups does not generate any periodicity parallel to the axis of the rod, and must be considered as the average of a disordered configuration.

Work is in progress to correlate the characteristics of hydrated surfactant molecules to the type of liquid crystal which may be obtained, and similarly to the size of the micelles obtained in various media.

Conclusions

The volume of the molecule and the volumes of the polar and apolar parts have been calculated from the specific gravity of pure NaDEHP and from the estimated volume of 2-ethylhexyl radicals. The length of the molecule and the lengths of the polar and apolar parts have been calculated with the help of the structural parameters of lamellar and hexagonal liquid crystals which have been previously published (*2*). The same method has been applied to bibliographic results concerning AOT (*1*).

Taking these geometric characteristics and the size of the polar head (sodium phosphate or sulphite) into account, it becomes apparent that the cross section of the rods which make up the reversed hexagonal liquid crystal structure of anhydrous Na DEHP (respectively, AOT) intercepts on average 2.5 molecules (respectively, 6 molecules).

The number of surfactant molecules per cross section of the rod may thus take any value, integer or noninteger, which is only determined by geometric and volumic considerations attached to the individual molecule, and which does not imply any periodicity along the rod axis. It must be emphasized that the value of 6 AOT molecules per cross section is a priori related neither to the sixfold symmetry of the bidimensional hexagonal lattice of the liquid crystal nor to the average hexagonal section of the rod.

The NaDEHP and AOT molecules are schematized by prisms. The width of the prism can be estimated from the cell parameter of the hexagonal liquid crystal and its height is correlated to the size of the phosphate group coordinance tetrahedron in the case of NaDEHP, and to the length of the succinate chain probably arranged in parallel to the axis of the rod in the case of AOT.

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