

---

01 Jan 1984

## Order Parameters Of Hydrocarbons Solubilized In A Lamellar Liquid Crystal

Anthony J.I. Ward

Stig Friberg

Missouri University of Science and Technology, stic30kan@gmail.com

David W. Larsen

Shankar B. Rananavare

Follow this and additional works at: [https://scholarsmine.mst.edu/chem\\_facwork](https://scholarsmine.mst.edu/chem_facwork)

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

A. J. Ward et al., "Order Parameters Of Hydrocarbons Solubilized In A Lamellar Liquid Crystal," *Journal of Physical Chemistry*, vol. 88, no. 4, pp. 826 - 827, American Chemical Society, Jan 1984.

The definitive version is available at <https://doi.org/10.1021/j150648a042>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemistry Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

## Order Parameters of Hydrocarbons Solubilized in a Lamellar Liquid Crystal

Anthony J. I. Ward, Stig E. Friberg,\*

Chemistry Department, University of Missouri at Rolla, Rolla, Missouri 65401

David W. Larsen, and Shankar B. Ranavare

Chemistry Department, University of Missouri at St. Louis, St. Louis, Missouri 63121

(Received: May 23, 1983; In Final Form: July 26, 1983)

A preliminary study of the  $^2\text{H}$  NMR spectrum of *n*-hexadecane- $d_{34}$  solubilized in the lamellar phase of tetraethylene glycol *n*-dodecyl ether has been made as a function of solubilize content. Complex spectra comprising eight overlapping powder spectra were observed, which showed a complex oil concentration dependence. These spectra were unusually rich in detail and indicate a considerably higher degree of complexity than has earlier been reported for solubilized hydrocarbons. The derived order profile was found to be different from that normally found for amphiphiles in lamellar environments. A tentative model involving some penetration of solubilize molecules between the host amphiphiles at low concentration while nonpenetrating oil molecules exist between the host layers at high oil contents is proposed.

Aqueous lamellar dispersions of nonionic surfactants of the type polyethylene glycol *n*-dodecyl ether ( $\text{C}_{12}\text{E}_4$ ) have been shown<sup>1</sup> to solubilize large quantities of hydrocarbons. An example of this ability has been demonstrated by the lamellar phase of tetraethylene glycol *n*-dodecyl ether, which can incorporate up to 55% (w/w) of *n*-hexadecane. This number implies a volume ratio of hydrocarbon to nonhydrocarbon constituents of 1.6. A formal calculation of the thickness of the hydrocarbon layer<sup>2</sup> would give a value of 60 Å. It is difficult to conceive a reason for stability of such a layer, especially in light of the fact that the X-ray data gave little indication of a substantial penetration of the hydrocarbon chains into the amphiphilic layer. In fact, the magnitude of the observed increase in interlayer spacing,  $d$ , is too large to be accounted for even by allowing the surfactant molecules to adopt a fully extended conformation at the addition of the hydrocarbon. The preliminary interpretation of the X-ray results<sup>1</sup> favored the increase of spacing to be due to the formation of an oil layer in the hydrocarbon part of the lamellar structure.

In order to clarify the reason for the stability of these surprisingly thick oil layers, we are currently working to characterize the structure and dynamics within the bilayer interior in this system by use of deuterium NMR quadrupole splittings. The  $^2\text{H}$  NMR spectra of the lamellar phases formed by  $\text{C}_{12}\text{E}_4$ , water, and various deuterated *n*-alkanes were observed for various phase compositions. These spectra were unusually rich in detail, and they indicate a considerably higher degree of complexity than has earlier been reported for solubilized hydrocarbons. According to Reeves and collaborators,<sup>3,4</sup> solubilized hydrocarbons with a medium chain length displayed splittings that are nearly constant along the chain in contrast to the typical variation of order parameters for an incorporated amphiphile.<sup>5</sup>

An illustrative example of our results is shown in Figure 1: the phase is composed of  $\text{C}_{12}\text{E}_4$ , water, and *n*-hexadecane- $d_{34}$ , and the alkane content varies between 1.6% (top spectrum) and 48% (bottom spectrum). Each line shape is a sum of eight overlapping "powder-pattern" quadrupole doublets.<sup>6</sup> These arise because of random orientation of lamellar directors and anisotropic motion of the chains. The overall spectral width decreases with increasing oil content as anticipated, but the detailed splitting profile along

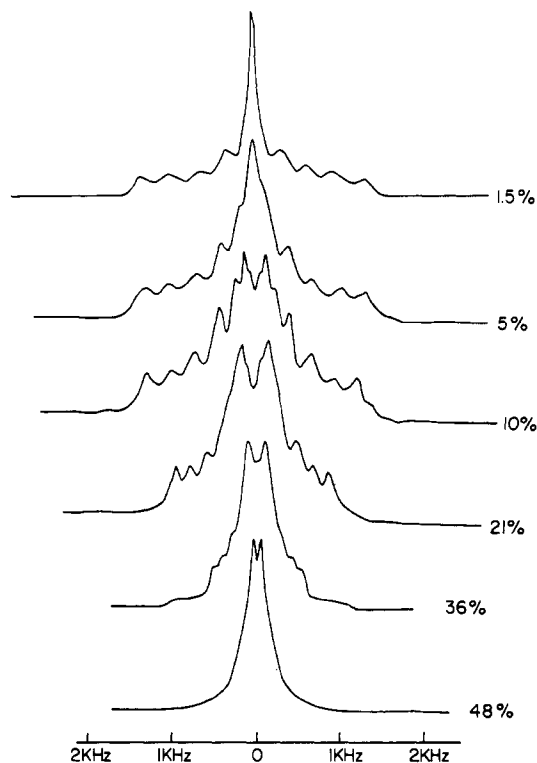


Figure 1. Deuterium NMR spectra of *n*-hexadecane- $d_{34}$  solubilized in the lamellar phase of  $\text{C}_{12}\text{E}_4/\text{H}_2\text{O}$  as a function of the weight fraction of oil ( $= w_{\text{oil}}/(w_{\text{oil}} + w_{\text{soap}})$ ) at fixed soap:water ratio (60:40 w/w).

the chain is characterized by a complex composition dependence.

Figure 2A shows in more detail the spectrum for the sample with 10.2% oil, which features (a) a range of splittings from  $\sim 150$  to  $\sim 1300$  Hz, (b) constant separation between splittings in the 400-1300-Hz splitting range, and (c) splittings for the alkane  $\sim 1/10$ th those anticipated for the amphiphile ( $\text{C}_{12}\text{E}_4$ ).

Figure 2B is a simulation that roughly corresponds to the observed spectrum. Random distribution line shapes for spin 1 nuclei undergoing rapid motions characterized by symmetry axes were used.<sup>6</sup> The splittings for each of the eight nonequivalent chain positions were used as independent parameters, and each

(1) N. Moucharafieh, S. E. Friberg, and D. W. Larsen, *Mol. Cryst. Liq. Cryst.*, **53**, 189 (1979).

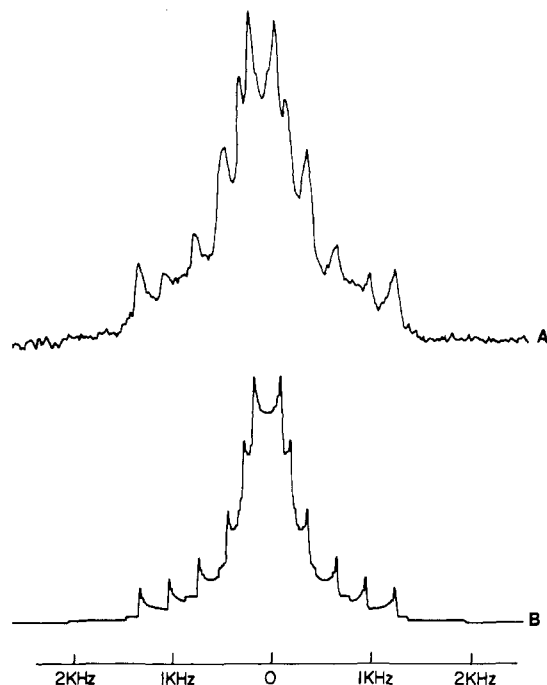
(2) K. Fontell in "Liquid Crystals and Plastic Crystals", Vol. 2, G. H. Brown, Ed., Ellis Harwood, London, 1974, p 80.

(3) B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981).

(4) D. M. Chen, F. Y. Fujiwara, and L. W. Reeves, *Can. J. Chem.*, **55**, 2404 (1977).

(5) J. Charvolin, P. Manneville, and B. Deloche, *Chem. Phys. Lett.*, **23**, 345 (1973).

(6) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, Oxford, 1961, Chapter 6.

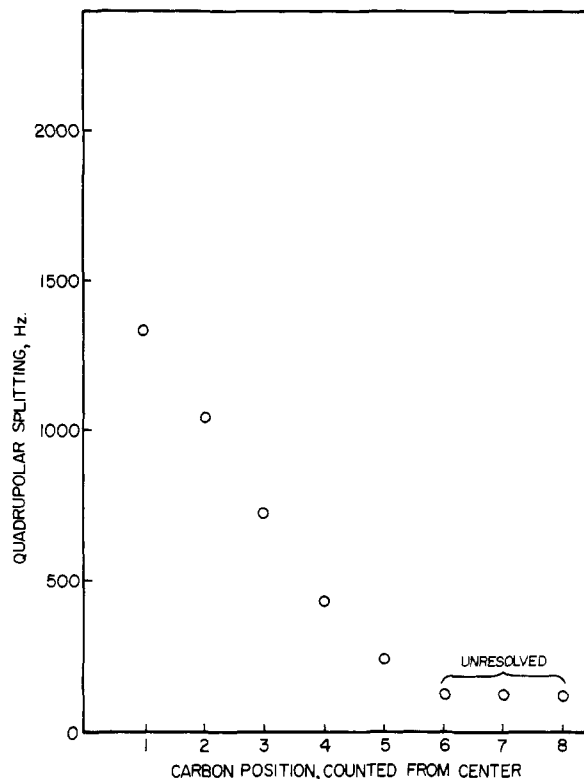


**Figure 2.** (A) The deuterium NMR spectrum of a  $C_{12}E_4/n$ -hexadecane- $d_{34}/H_2O$  lamellar phase (weight fraction of oil 10.2%). (B) Spectral simulation using eight overlapping "powder" spectra.

line shape was convoluted by a Lorentzian line shape assumed to be orientation independent. The line width of the Lorentzian broadening function was also taken to be an independent parameter for each chain position. Details about the parameters employed will be given in a more comprehensive publication.

In a preliminary interpretation of the spectra, we expect the methyl groups to show the smallest splitting. We assign the largest splitting to the chain center positions, an assumption supported by separated studies using selectively deuterated tridecane. Furthermore, assuming monotonic splitting variation along the chain, we obtained the splitting profile shown in Figure 3 from the experimental results. This profile has unique characteristics when compared with other observed profiles.<sup>3,4,7</sup> The hexadecane molecule may obviously not be characterized as a semirigid structure undergoing rapid anisotropic motion. Instead, the central part of the molecule has a considerably higher order parameter, while the terminal parts tend to approach liquidlike behavior (cf. Figure 3).

Figure 1 displays an interesting concentration dependence of the splitting pattern. This pattern can at present not be given a



**Figure 3.** Order profiles for solubilized  $n$ -hexadecane chains in terms of quadrupole splittings determined from the central chain segment (1) to the terminal methyl segments (8).

final interpretation, but earlier X-ray values<sup>1</sup> support the following tentative model. At low concentrations some penetration of the solubilized hydrocarbon occurs between the host amphiphiles. The part outside the host molecules has an extremely large degree of freedom, for which splittings are unresolved (top, Figure 1). At higher concentrations of the hydrocarbon (middle, Figure 1), there is restriction in available space between the host layers and a certain ordering takes place due to interaction between the solubilized molecules. At the highest concentrations nonpenetrating hydrocarbon molecules exist between the host layers and the order is now very limited.

We are continuing these studies by investigating other features of alkanes solubilized in nonionic surfactant liquid-crystalline phases, including relaxation times and the effect of varying the alkane chain length.

**Registry No.**  $n$ -Hexadecane- $d_{34}$ , 15716-08-2; tetraethylene glycol  $n$ -dodecyl ether, 5274-68-0.

(7) J. Seelig, *Prog. Colloid Polym. Sci.*, **65**, 172 (1978).