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## Single Compound Forming a Lyotropic Liquid Crystal at Room Temperature

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The compound triethanolammonium oleate forms a lamellar liquid crystal at room temperature. The basis for the lyotropic mesomorphism is the fact that part of the triethanolammonium oleate has changed to triethanolamine and oleic acid. These two compounds serve as solvents in the liquid crystalline structure.

## Introduction

Lyotropic liquid crystals formed from surfactants, water, and more hydrophilic compounds give rise to a large variety of structures depending on the composition.<sup>1-4</sup>

Recently, lyotropic liquid crystals have been obtained from lecithin and polar organic liquids with no water present.<sup>5-9</sup> Lecithin in combination with a low-melting organic salt, ethylammonium bromide, has also been shown to form a lamellar liquid crystal at room temperature.<sup>10</sup> This latter compound may be viewed against the pioneering research on amphiphilic micellization in organic electrolytes by Evans and collaborators.<sup>11,12</sup>

Ionic surfactants may form mesomorphic phases at room temperature if the hydrocarbon chain is sufficiently branched to prevent crystallization as pointed out by Winsor<sup>13</sup> about 10 years ago. These kinds of compounds were appropriately named fused salts by Winsor and should be considered as thermotropic liquid crystals.

With this communication, we would like to introduce a case in which a single compound forms a *lyotropic* liquid crystalline phase at room temperature. The compound was triethanolammonium oleate prepared directly from its constituents, triethanolamine (Fisher certified 99.2%,  $\leq 0.1\%$  water) and oleic acid (Fisher certified) in equimolar ratio. The lamellar liquid crystal was identified from its optical pattern (Figure 1). The interlayer spacing was calculated to be 38 Å from the low-angle X-ray diffraction pattern.

The explanation for the surprising mesomorphism of a single amphiphilic compound was provided by its infrared spectra (Figure 2). These showed the presence of both ionized carboxylate groups ( $\nu = 1550 \text{ cm}^{-1}$ ) and protonated carboxylic groups ( $\nu = 1715 \text{ cm}^{-1}$ ). In addition, the infrared spectra showed only insignificant absorbance at  $935 \text{ cm}^{-1}$ , the out-of-plane bonding vibration of the

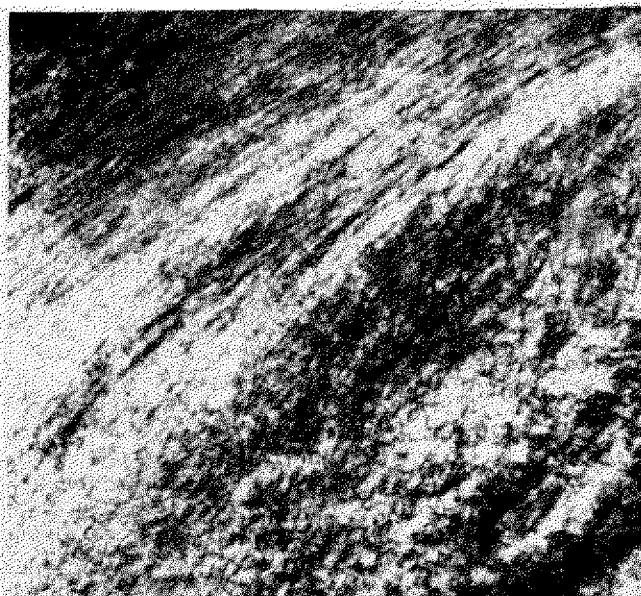


Figure 1. The optical pattern was typical of a lamellar liquid crystalline phase.

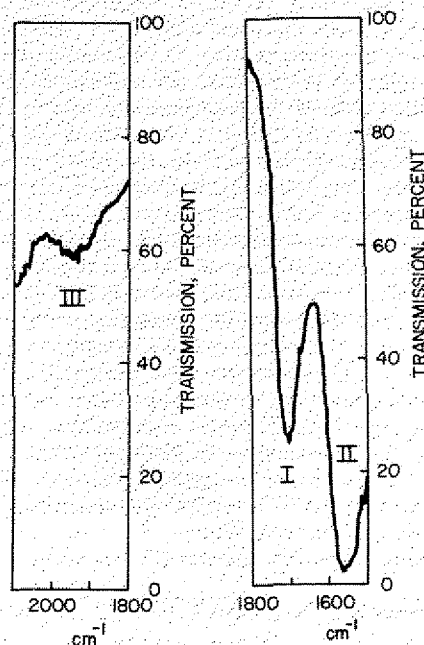


Figure 2. The infrared spectra of triethanolammonium oleate showed absorptions typical of the antisymmetric stretching of vibration of a carboxylic acid (I) and of an ionized carboxylic group (II) and the absorbance from a strong hydrogen bond between the two (III). Cell dimensions (mm): 0.015 (I and II) and 0.05 (III).

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acid OH group in an acid dimer,<sup>14</sup> but a substantial absorbance at 1900 cm<sup>-1</sup>. The latter absorption is characteristic of a carboxylic group strongly hydrogen bonded to the ionized carboxylate group.<sup>15</sup>

These results readily lend themselves to an interpretation explaining the formation of a liquid crystal from the triethanol-

ammonium oleate. The infrared spectra revealed the acid not to be completely deprotonated by the amine. This means that some triethanolamine did not accept the acid proton but remained as a molecular specimen in the structure. The liquid crystalline structure contained three components: triethanolammonium oleate, oleic acid, and triethanolamine. The two latter in all probability serve as solvents to form a lyotropic liquid crystalline phase.

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Registry No. Triethanolammonium oleate, 2717-15-9.

## COMMENTS

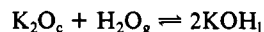
### Effect of Potassium Compounds on Strong Metal-Support Interactions in Pt/TiO<sub>2</sub> Catalysts

*Sir:* The inhibition of H<sub>2</sub> chemisorption on Pt/TiO<sub>2</sub> catalysts by potassium compounds is attributed to TiO<sub>2</sub> redistribution promoted by K<sub>2</sub>TiO<sub>3</sub> and not to electron donation from K to Pt.

Tauster et al.<sup>1</sup> found that chemisorption and catalysis over Pt/TiO<sub>2</sub> catalysts were inhibited after high-temperature reduction (HTR) and attributed the phenomenon to a strong metal-support interaction (SMSI). Other systems show the same effect and its origin is the subject of controversy.<sup>2</sup> Recently Chen and White<sup>3</sup> found that the addition of small amounts of potassium to Pt/TiO<sub>2</sub> catalysts also strongly suppressed H<sub>2</sub> chemisorption after low-temperature reduction (LTR) and this was attributed to electron charge transfer from K to Pt. If this is indeed the origin it is a surprisingly potent effect, for the suppression is by a factor of about 2 at a bulk K/Pt atomic ratio of only 0.001. MO calculations by Ray and Anderson<sup>4</sup> indicate that there is an increase in electron density in the Pt atoms adjacent to an adsorbed K atom, but it seems improbable that this effect would be sufficient to explain Chen and White's results. As their Pt dispersion was about 0.25, each adsorbed K atom, donating<sup>4</sup> about 0.4 e<sup>-</sup>, would have been required to inhibit chemisorption on a minimum of about 250 surface Pt atoms. It is likely that this understates the problem because at least some of the potassium was held in the support (see below) and also, as Ertl et al.<sup>5</sup> have found with potassium on iron in ammonia synthesis catalysts, the surface potassium was partially oxidized, thus decreasing the electron transfer per K atom. In most examples<sup>2</sup> of SMSI, both CO and H<sub>2</sub> chemisorption are suppressed by high temperature reduction. Contrary to Chen and White's results, the adsorption of CO on a potassium-covered, single-crystal Pt(111) surface was shown by Garfunkel et al.<sup>6</sup> to be enhanced, with the saturation adsorption energy of CO increased from 27 to 39 kcal/mol at half a monolayer of potassium. The changes in CO adsorption were attributed to enhanced electron back-donation from the platinum into the 2π\* antibonding orbital of CO, due to the presence of potassium. The electron transfer from the potassium to the platinum valence bands was delocalized, but over a few interatomic distances only. These results suggest that the TiO<sub>2</sub> support was essential for the phenomena found by Chen and White.

After impregnation with aqueous KNO<sub>3</sub> solutions, Chen and

White's Pt/TiO<sub>2</sub> samples were evacuated at 400 °C before reduction with hydrogen at 200 °C. Even before the generation of water at the reduction stage, KOH would have been formed under evacuation at all but ultrahigh vacuum conditions. The minimum partial pressure of water required for the conversion of K<sub>2</sub>O by the reaction



can be calculated from standard data<sup>7</sup> to be 4.3 × 10<sup>-13</sup> atm at 427 °C. Now KOH reacts<sup>8</sup> in bulk with hydrous titania at 160–170 °C to give potassium metatitanate, K<sub>2</sub>TiO<sub>3</sub>. Compounds of lower potassium content, e.g., K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>, may also be formed.<sup>9</sup> Chen and White's Pt/TiO<sub>2</sub>/K samples, after evaluation and reduction, are likely to have consisted of the TiO<sub>2</sub> support sparsely covered with a K/Ti mixed oxide as well as Pt crystallites sparsely covered with a potassium compound. As neither the stoichiometry nor the energetics of either of these potassium species is known, it is not possible to calculate relative stabilities or the distribution of potassium between the TiO<sub>2</sub> support and the Pt crystallites.

The melting point of K<sub>2</sub>TiO<sub>3</sub> is 806 °C, so its Tammann temperature is about 270 °C. A surface "patch" of K<sub>2</sub>TiO<sub>3</sub> on the TiO<sub>2</sub> would therefore be very mobile under the evacuation conditions (400 °C) and still show some mobility under reduction (200 °C). It would be expected to promote redistribution of the TiO<sub>2</sub> surface by acting as a "flux". Alkali metal compounds are well-known mineralizing agents in ceramic reactions. Thus, the presence of potassium in the Pt/TiO<sub>2</sub> samples would greatly assist any tendency to form a covering layer of Ti oxide over the Pt crystallites.

This interpretation of Chen and White's results agrees with some recent views<sup>10-13</sup> of the cause of SMSI. The suppression of chemisorption and catalysis is attributed to the geometric and local electronic effects of a reduced titanium oxide on the platinum surface rather than electronic interaction between the defective bulk support and the metal crystallite.<sup>1,2</sup> The reduced titanium oxide layer, possibly TiO, must be characterized by Pt-Ti bonds

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