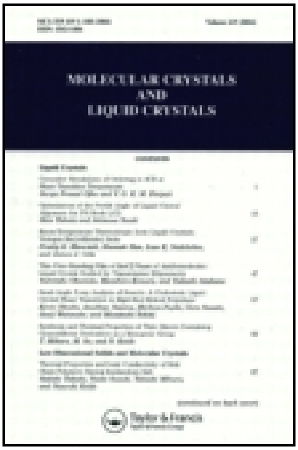

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Alkyl Derivatives of Iminodiacetic Acid: A Novel Class of Compounds Forming Thermotropic Liquid Crystals and Aqueous Micelles

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ALKYL DERIVATIVES OF IMINODIACETIC ACID: A NOVEL CLASS OF COMPOUNDS FORMING THERMOTROPIC LIQUID CRYSTALS AND AQUEOUS MICELLES

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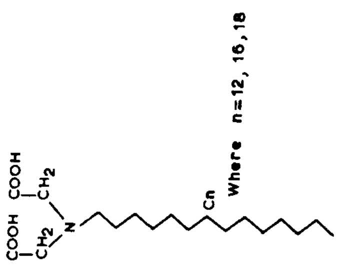
Abstract In the present study the liquid crystalline character of some long chain-alkyl iminodiacetic acid derivatives have been established by optical microscopy and DSC studies. Mesomorphic textures were attributed to the formation of alternating polar and lipophilic lamellar structures. In addition the micellar properties of dipotassium salts of the iminodiacetic acids were investigated by electroconductometry and fluorescence spectroscopy and it was found that the CMC ranges between 0.022 and 0.0012, M aggregation numbers 60-94, and that the micelles have a loose structure that allows considerable water penetration in their palisade region.

INTRODUCTION

In the course of our studies on functionalized[1-4] monomeric and polymeric micelles, some iminodiacetic acid derivatives were prepared (Scheme I). It was the peculiar melting behavior of these compounds which triggered our interest in investigating their thermotropic behavior. However, taking into account the structure of these molecules, their observed melting point behavior is not unexpected after all. Indeed, the main structural feature of these compounds is the existence of distinct lipophilic and hydrophilic segments in the same molecule, a fact which is known to induce mesomorphism[5-18]. The difference in polarity between the hydrophilic and hydrophobic parts of the molecule determines the exhibition of liquid crystallinity by this type of compound . Finally, recall that recent investigations [2,5,17] have shown that these molecules, commonly known as surfactants, in addition to their ability to form aggregates in solution (micelles, vesicles,etc), in the solid state they crystallize in lamellar structures consisting of lipophilic and hydrophilic sublayers. Furthermore, this layer structure is preserved in the melt resulting to the formation of smectic phases, as proved by optical microscopy, DSC studies and X-ray diffractometry



Scheme I

In the present study we primarily examine the ability of the polar group $-N(CH_2COOH)_2$, when it is attached to a long aliphatic chain, to produce micelle-forming surfactants and thermotropic liquid crystals. Additionally, the liquid crystalline character and micellar properties of alkali metal salts of the iminodiacetic acids in aqueous media are also investigated.

EXPERIMENTAL

Synthesis:

The iminodiacetic acids were prepared by the method described by Stein et al[18] while their dipotassium salts were obtained by the neutralization of the corresponding acids with potassium hydroxide. Thus, in aqueous dispersions of the acids, calculated amounts of potassium hydroxide solution were added. The resulting mixtures were filtered (0.45μm millipore filters), lyophilized and the obtained salts were finally dried over phosphorous pentoxide.

Characterization

Optical microscopy studies were performed with a Reichert Thermopan microscope under crossed polarizers. DSC diagrams were obtained using a DSC-4 Calorimeter equipped with a System-4 Programmer. Infrared spectra were recorded on a Perkin-Elmer 283. CMC values were determined spectrophotometrically using Sudan Red 7B (Aldrich) as the micelle soluble dye, which exhibits a strong absorption band around 538 nm. Micellar aggregation numbers were estimated by means of static fluorescence quenching[18] using pyrene as the fluorophor and cetylpyridinium chloride as the quencher.

RESULTS AND DISCUSSION

In the present study two different modes of molecular organization are examined, i.e. organization in the melt and in solution. The former case refers to thermotropic liquid crystals, and the later to ionic aqueous micelles. Indeed, molecules bearing groups such as the iminodiacetic moiety, have not been studied as yet from the point of view of their ability to organize in the melt and form mesomorphic phases, and/or aggregate in solution to form micelles.

a. Organization in the melt.

Melts of all three iminodiacetic acid derivatives with C=12, 16 and 18 (Scheme I) when examined under the polarizing microscope exhibited liquid crystalline behavior. A typical texture for the C_{16} derivative is shown in Figure 1. Note that these textures do not normally transform to their corresponding isotropic phases, at the clearing point, instead they undergo gradual decarboxylation as indicated by the continuous bubbling (evidently CO_2) observed during optical studies.

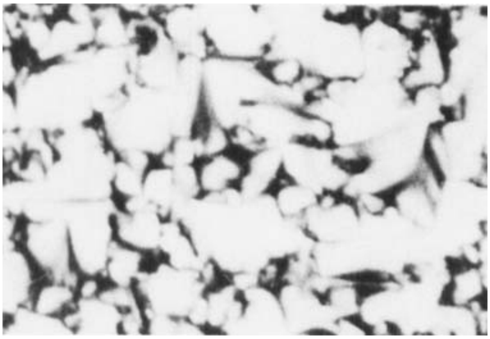


FIGURE 1. Mesomorphic texture of C_{16} iminodiacetic acid derivative

The mesomorphic bahavior of these molecules was further confirmed by differential scanning calorimetry, as shown in the DSC diagrams of the three derivatives (Fig.2-4) which exhibit significant similarities. Thus, the first strong endothermic peak corresponds to solid-mesomorphic transition, while the second mesomorphic-isotropic transition occurs over a range of temperatures and is not clearly observed because of the previously mentioned decarboxylation of these molecules.

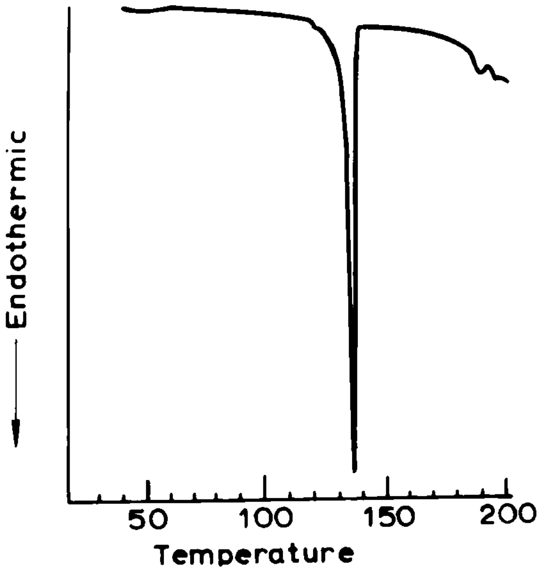


FIGURE 2. DSC diagram of C_{12} iminodiacetic acid derivative.

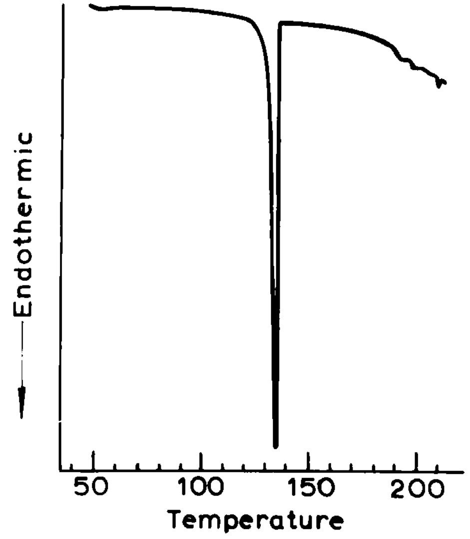


FIGURE 3. DSC diagram of C_{16} iminodiacetic acid derivative.

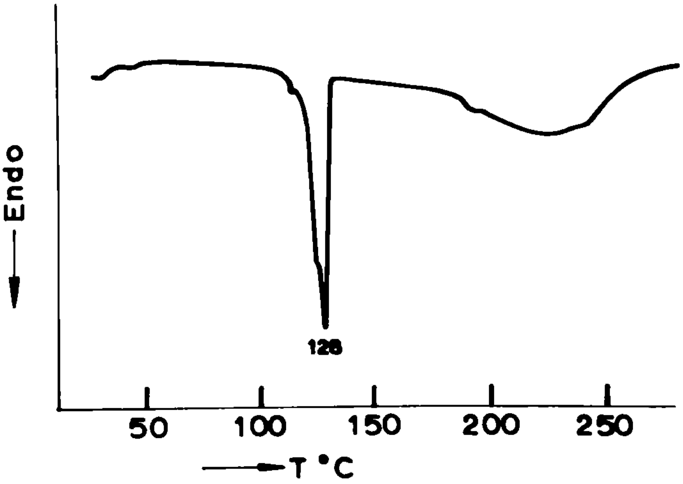
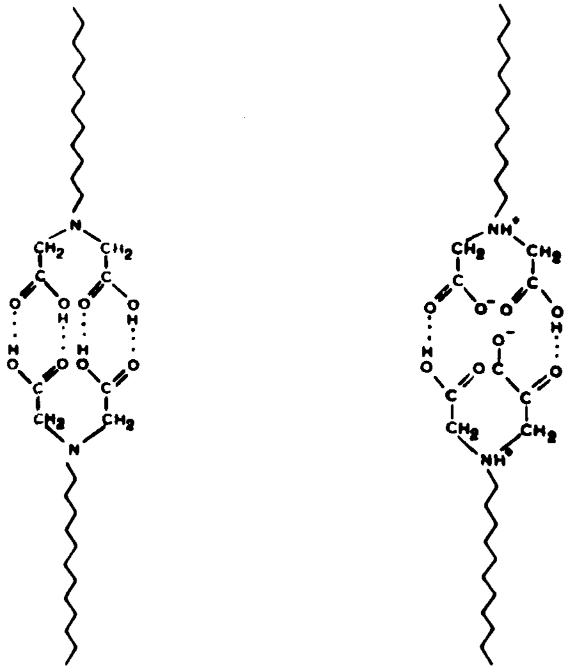


FIGURE 4. DSC diagram of C_{18} iminodiacetic acid derivative.

By analogy with ionic surfactants[2-14] and functionalized n-alkyl carbohydrates[15], the mesomorphism of the iminodiacetic acid derivatives can be attributed to the formation in the melt of distinct alternating layers of polar heads and lipophilic moieties. Thus, when $R\text{-}N(CH_2COOH)_2$ melts, the aliphatic chains are stacked in layers separated by intervening layers of head groups. These head group layers consist of four carboxylic groups with their respective hydrogen bonds, Scheme II(left). Alternatively, the zwitterionic species that are partly formed by intra- or intermolecular protonation of the iminodiacetic group, and held by ionic forces, also create a polar region segregated from the aliphatic chain layers, Scheme II (right). In either case a polar layer is always formed sandwiched by the lipophilic layers of the aliphatic chains. These structures are in line with IR assignments of the materials in the solid phase in agreement with the assignments of analogous compounds reported recently[18,20]. Thus the thermotropic liquid crystalline phases demonstrated by these molecules have been attributed to the formation of these lamellar structures.

The exhibition of liquid crystallinity by these saturated aliphatic carboxylic acids is worth considering, since these compounds do not belong to any of the various classes of compounds which are known to show liquid crystalline behavior. Recall for instance that aromatic carboxylic acids are well-known for their thermotropic liquid crystalline behavior[21] Note also that among these aromatics, the most



Scheme II

numerous classes are p-substituted benzoic and cinnamic acids, biphenyl-2-carboxylic acids and 6-substituted naphthalene-2-carboxylic acids which form dimers through hydrogen bonding of their carboxylic groups. On the contrary, among aliphatics, only molecules containing double bonds show liquid crystallinity[21], evidently due to the polarizability of the double bond which enhances intermolecular dipolar interactions. As a typical example we mention here the 2,4-nonadienoic acid which is a liquid crystal[21].

Among the corresponding dialkali salts, the dipotassium homologues were examined for liquid crystallinity and found to show the characteristic multiple melting behavior[2] of aliphatic surfactants. This is shown by their DSC diagrams (Fig.5-7). Liquid crystalline phases were preserved for all three salts up to at least 280 °C, although the material slowly turned to yellowish due to some decomposition of the surfactants at such high temperatures. A typical texture of C_{16} iminodiacetic acid derivative at about 160° is shown in Fig.8.

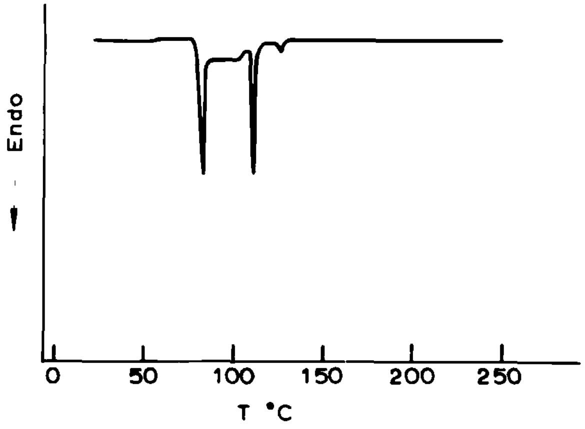


FIGURE 5. DSC diagram of C_{12} dipotassium iminodiacetate.

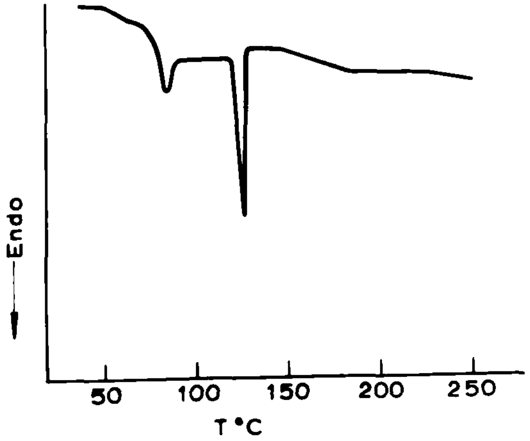


FIGURE 6. DSC diagram of C_{16} dipotassium iminodiacetate.

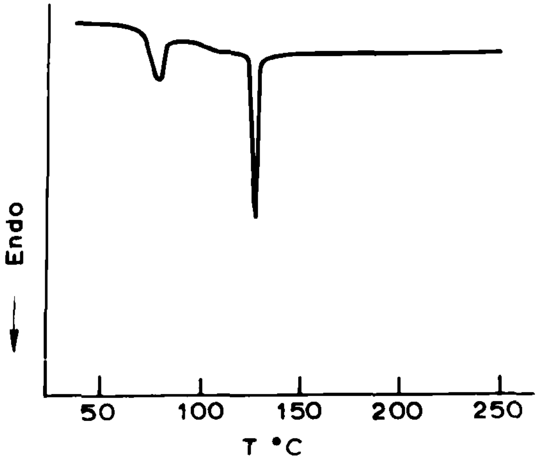


FIGURE 7. DSC diagram of C_{18} dipotassium iminodiacetate.

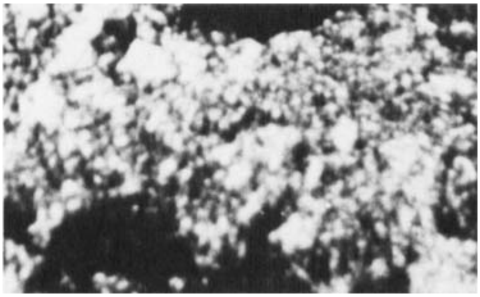


Figure 8. Mesomorphic texture of C_{16} dipotassium iminodiacetate.

b. Organization in water.

The organizational behavior of these R-$N(CH_2COOH)_2$ homologues was also examined in aqueous solutions. All three iminodiacetic acid derivatives (C=12, 14 and 16) were found to be practically insoluble in water, indicating that the group -$N(CH_2COOH)_2$ is not polar enough to induce molecular organization and formation of aqueous micelles. Similarly, of the dialkali salts,the two sodium derivatives with the hexadecyl and octadecyl aliphatic chains had Krafft points above 40° and 60°C respectively, and therefore were not further examined. The dipotasium derivatives, on the other hand, had low Krafft temperatures, as expected, and their micellization behavior was studied. All the micellar parameters obtained in the present investigation at 25°C, are summarized in Table I.

TABLE I Micellar parameters obtained at 25°C **

Surf.	[CMC]	Ns	I1/I3	[Surf]*
$C_{12}Na$	0.026	55	1.4	0.09
$C_{12}K$	0.022	60	1.35	0.10
$C_{16}K$	0.003	70	1.33	0.03
$C_{18}K$	0.0012	94	1.43	0.01

* Surfactant concentration at which the aggregation number was measured

**Symbols and units are explained within the text.

The values of the critical micelle concentration (CMC) measured here for R-N($CH_2COO)_2$ are quite higher than the corresponding values for surfactants having the same aliphatic chain length but singly charged ionic heads[22]. Thus, for example the CMC of $C_{12}COO^-K^+$ is 0.014 M while the CMC of C_{12}-N($CH_2COO^-)_2K^+{}_2$ is 0.022 M. Clearly, the doubly charged ionic head of the alkali salts of the iminodiaacetic acid derivatives make these surfactants more water soluble than their singly charged counterparts. Consequently the CMC increases.

The micellar aggregation numbers (Ns) listed in TABLE I are smaller than the Ns values calculated from the Tanford model[23] for spherical micelles with the same aliphatic chain lengths. A plausible explanation of this is that the bulky doubly charged ionic head in these surfactants, along with its hydration water molecules, creates serious packing problems in the micelle, leading to rather loose micellar structure. This is further confirmed by the I_1/I_3 ratio of the intensities of the first and third fluorescence peaks of pyrene. Recall that this ratio is a good index for water penetration at the site of solubilization of the pyrene, and that it increases with increasing water concentration (I_1/I_3 is equal to 1.6 for solvent pure water, and 0.6 for hexane)[24]. Thus, the high values of I_1/I_3 found here, ranging from 1.33 to 1.43, indicate extensive water penetration in the micellar pallisade region where pyrene is known to reside.

CONCLUDING REMARKS

The polar group -N($CH_2COOH)_2$ and the lipophilic portion of these molecules segregate separately to form lamellar structures in the melt. However, the same head group is not polar enough to render these compounds water soluble and lead to micellization. On the other hand, the low Krafft point dialkali salts of the iminodiacetic acid derivatives, are water soluble and form micelles. These micelles have different aggregational properties from the corresponding singly charged carboxylate surfactants, have a loose structure, and allow considerable water penetration in their palisade region.

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