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# Identification and Characterization of Aggregates Formed by a Partly Neutralized Isophthalic Acid Derivative in Aqueous Solution

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Fiber-shaped aggregates were obtained from aqueous solutions of 5-octadecyloxyisophthalic acid neutralized with 1.5 equiv of KOH. The structure of the aggregates in the resulting suspensions was investigated by X-ray and electron diffraction (ED) studies; the morphological observations reported here stem from atomic force microscopy (AFM) studies and from polarized optical microscopy (OM). The aggregate formation was examined as a function of the concentration and temperature of the isophthalate solutions or suspensions. The structure elucidation shows that the aggregates consist of crystals as the smallest subunits. Their structure was determined, and the cell parameters of the unit cell could be established. Furthermore, it is demonstrated that the material obtained from the aqueous suspensions, by pulling fiber-shaped species mechanically, is a continuous sequence of crystals.

## 1. Introduction

Supramolecular chemistry attracts increasing attention in science,<sup>1–3</sup> particularly for supramolecular structures that are self-assembled by directional hydrogen bonds.<sup>9–16</sup> The increasing interest is understood, as the ability to

build well-defined supramolecular structures from small molecules is essential in, for example, biochemistry. Furthermore, spontaneously formed supramolecular structures offer interesting perspectives for the development of tailor-made materials with strict specifications on the structural organization as in the case of organic crystals exhibiting ferromagnetic<sup>22</sup> or second-order nonlinear optical properties,<sup>23</sup> for example.

Within the broad field of supramolecular structures, some molecules can spontaneously assemble into long macroscopic aggregates, sometimes referred to as "fibres",<sup>4,5,17</sup> which could be functionalized with unidirectionally aligned chromophores.<sup>24</sup> Several mechanisms for the formation of fiber-shaped self-assembled macrostructures have been proposed, for example helix formation of elongated micellar structures or packing of micellar disks.<sup>17</sup> For the use of self-assembly to form predictable macroscopic structures, it is vital to gain a profound knowledge of the underlying mechanisms of aggregation and a detailed understanding of the structures formed, on a macroscopic as well as on a microscopic level.

A manifold of spontaneously formed supramolecular structures are formed by amphiphilic molecules. They can be formed in solution<sup>4,5,18</sup> or from the melt of the pure compound.<sup>6</sup> In both cases, the aggregates formed are stable and can be examined by various techniques.

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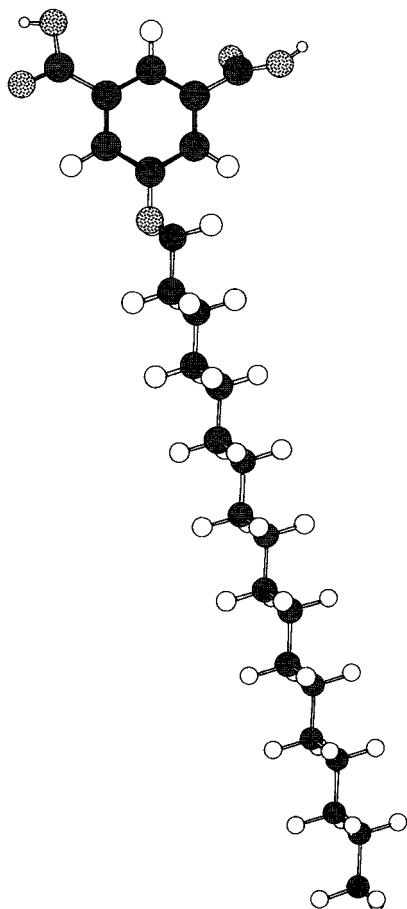
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**Figure 1.** 5-Octadecyloxyisophthalic acid,  $C_{18}ISA$ .

Derivatives of isophthalic acid have been shown to be useful compounds for formation of macroscopic supramolecular aggregates in various phases.<sup>4–8,9,12–16</sup> Recently, Pfaadt et al. investigated the supramolecular organization of 5-octadecyloxyisophthalic acid ( $C_{18}ISA$ ), pure and in the presence of added organic bases.<sup>6</sup> They found that  $C_{18}ISA$  exhibits thermotropic mesomorphic behavior. The pure acid forms a monotropic smectic phase in the cooling cycle, whereas an equimolar ionic mixture of the acid with the bifunctional base piperazine leads to the formation of an enantiotropic, that is, thermodynamically stable, smectic mesophase with lamellar organization.

In this contribution, the structures of the aggregates formed from  $C_{18}ISA$  in aqueous solution in the presence of the added *inorganic* base potassium hydroxide are reported. From the results obtained by different techniques, for example, optical microscopy, differential scanning calorimetry (DSC), transmission electron microscopy, and X-ray scattering, it is possible to assign phase transitions as a function of temperature for  $C_{18}ISA \cdot 1.5KOH$  as well as to determine the unit cell of the macroscopic crystalline aggregates formed.

## 2. Experimental Section

$C_{18}ISA$  (Figure 1) was synthesized as described previously.<sup>19</sup> Potassium hydroxide (KOH) was provided in ampules from Merck, from which basic solutions were made prior to usage. All solutions were prepared by gently heating under nitrogen atmosphere and stored in sealed tubes. All solutions were 2:3 with respect to  $C_{18}ISA/KOH$  (75% of the  $C_{18}ISA$  acid groups neutralized). The results of elemental analysis and  $^1H$  NMR, however, suggest that the added KOH did not quantitatively neutralize the carboxylic acid; in the dried suspensions the degree of neutralization is assessed to about 65% instead of 75% in the

organic potassium carboxylate salt. Likewise Menger and Lee have reported that the shorter analogue  $C_{16}ISA$  is not quantitatively neutralized by added KOH.<sup>4</sup>

The samples were studied by several techniques: polarized optical microscopy (OM) was performed on a Nikon Optiphot type 104 optical microscope, equipped with a Mettler FP80 central processor and a Mettler FP82 hot stage. For calorimetric observations (DSC) a Perkin-Elmer DSC 2 was used, equipped with a thermal analysis data station. Large volume sample pans, containing about 25 mg of solution, were used; the scanning rate was 5 K/min.

For X-ray diffraction experiments a Siemens  $\theta-\theta$  diffractometer D 500 was used, equipped with a scintillation counter, using  $Cu K\alpha$  radiation and a graphite monochromator with  $\lambda = 1.541 \text{ \AA}$ . The divergence of the slit-collimated beam amounted to  $0.3^\circ$ . The diffractometer was equipped with a heating sample holder, and the temperatures were corrected. Two-dimensional X-ray diffraction experiments were performed on a Rigaku rotating anode RU 300 (max. operating power 18 kW) using also graphite-filtered  $Cu K\alpha$  radiation and pinhole collimation. The setup was equipped with a Siemens proportional area detector and a hot stage. Temperatures were not calibrated to the same precision as that for the diffractometer setup.

Electron microscopy and diffraction were performed in a LEO 912 transmission electron microscope (TEM) with an integrated EEL spectrometer as an imaging filter. The instrument was equipped with rotation and cooling sample holders, and the experiment was run at a high voltage of 120 kV. This type of electron microscope possesses a Koehler illumination system, which allows us to substitute selected area diffraction diaphragms with condenser apertures of various sizes. This has the advantage of limiting illumination damage to the area used to record a diffraction pattern. Subsequent translation of the single crystal allows us to get additional diffraction patterns (in particular after tilting the crystal) of adjacent and hitherto not irradiated areas. For a series of zone diffraction patterns in general an area with a diameter of  $2.7 \mu m$  was irradiated. Micrographs and electron diffraction patterns were recorded onto Ilford PAN F 35 mm film. The camera length was calibrated with a  $TiCl_3$  standard. Diffraction data were evaluated after determining reflection distances for 10-fold magnified projections of the original diffraction patterns in a darkroom magnifier.

For AFM studies, samples were prepared on glass substrates by evaporation of the solvent. Subsequent AFM imaging was carried out with a commercial setup (Topometrix Discoverer TMX 2000 STM/AFM system) in the contact mode in air, using  $Si_3N_4$  cantilevers with a force constant of 0.032 N/m. Simultaneous with the topography measurements, a hardness/elasticity image was also acquired, by applying a small modulation signal (0.3 nm) to the z-piezo and recording the cantilever response at the specific modulation frequency.

For OM measurements solutions with several  $C_{18}ISA$  concentrations were employed, that is, 40, 50, 70, 80, 100, 150, and 200 mM  $C_{18}ISA$ . For electron diffraction (ED) samples from 69 and 71 mM solutions were used, and X-ray scattering was performed with 5, 35, 36, 69, and 71 mM  $C_{18}ISA$  samples. Elemental analysis was performed on dried 50 mM  $C_{18}ISA \cdot 1.5KOH$  samples.

## 3. Results and Discussion

Only the investigation on salts produced by added KOH is reported here, while Menger et al. reported on macroscopic supramolecular structures formed in aqueous solutions in the presence of various bases<sup>4,5</sup> from the shorter homologue  $C_{16}ISA$ . In contrast,  $C_{18}ISA$  neutralized to 100% by KOH exhibits predominantly small crystals when an isotropic solution is cooled to room temperature. The 50% neutralized  $C_{18}ISA$  did not dissolve completely, and only at 75% neutralization were the macroscopic aggregates easily obtained upon cooling an isotropic from temperatures in the range between 70 and 90 °C to room temperature.

**3.1. Microscopy Studies.** *3.1.1. Optical Microscopy (OM).* For most of the optical microscopic studies, a 150

**Table 1. Transition Temperatures Detected by Differential Scanning Calorimetry for the First Heating**

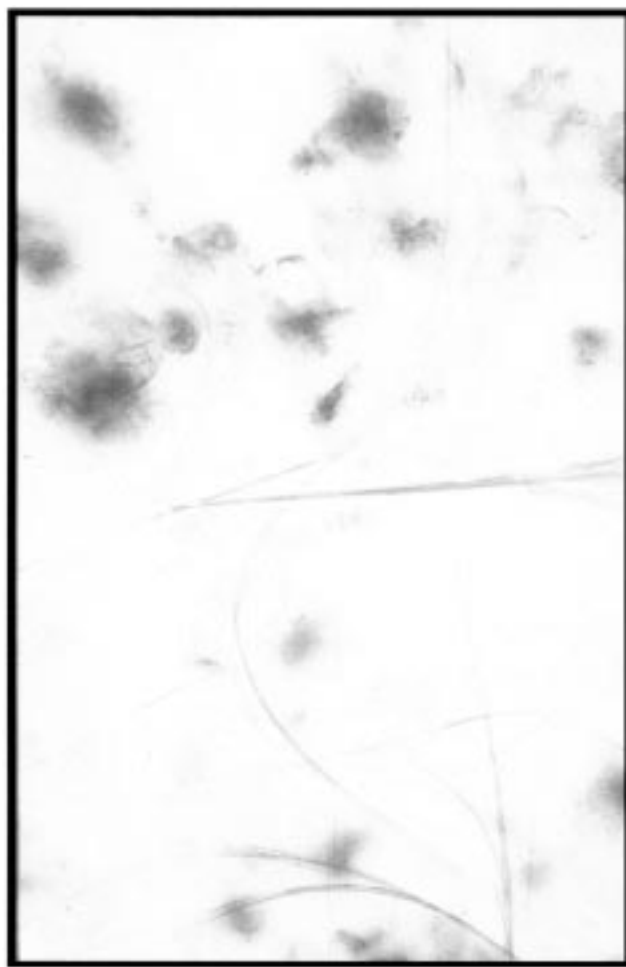
temp (°C)	48	52	67
transition	endotherm	endotherm	endotherm

mM C<sub>18</sub>ISA·1.5KOH solution was used. This concentration was chosen because it showed a manifold of transitions as a function of temperature, for example, transitions from isotropy to anisotropic structures where the growth of aggregates is not uniform (Table 1). Isolated lath-shaped species occur together with solid material concentrated in small volumes (blobs). Changes of C<sub>18</sub>ISA·1.5KOH aggregates were observed by OM as a function of temperature.

At 75% neutralization, the C<sub>18</sub>ISA solutions were transparent at 70–90 °C for all concentrations studied. The formation of supramolecular structures can be influenced by repeated heating and cooling of the solutions. Gentle heating during sample preparation and subsequent cooling of the solution the first time to room temperature will be denoted as the zeroth heating–cooling cycle. During cooling, the solutions become turbid and very viscous. In the viscous solution, various structures are formed as a function of time and temperature, and macroscopic equilibrium is approached very slowly. To ensure equilibrium conditions, the samples were sealed and stored for at least 1 month at room temperature prior to OM measurements.

Investigation of the precipitate by OM after the zeroth cycle (C<sub>18</sub>ISA concentration 50 mM) displays a slurry structure, consisting of the so-called “blobs” (Figure 2). Heating and cooling the aqueous suspensions one time more results in the formation of larger, elongated aggregates and bundles of aggregates after 1 week of storage. From more concentrated solutions (70 mM and higher), those bundles were formed immediately after the zeroth cooling cycle.

Solutions of various concentrations display, besides the small “blob” structures (TEM studies show the blobs to consist of agglomerates of small lath-shaped crystals), larger precipitated aggregates that are most likely single crystals. As expected, the higher the concentration of C<sub>18</sub>ISA, the more rapid is the crystallization as a function of supersaturation. Also the detailed texture is influenced by the crystallization conditions and—as already stated—crystals may aggregate to bundles having a common seed (Figure 3). When crystallized from the melt, one would denote this morphological superstructure as poorly developed spherulites.<sup>26</sup> Similar morphologies are also seen in binary solutions of lamella-forming amphiphilic compounds.<sup>27</sup> With increasing concentration in the range 100–200 mM C<sub>18</sub>ISA, the number ratio of large crystals to blob structures decreases because the latter become more and more abundant. Samples of 150 mM C<sub>18</sub>ISA formed hardly any aggregates of macroscopic dimensions when equilibrated after the zeroth cycle at room temperature for 1 month. The predominant structure found by OM is the blob structure. Consistent with TEM studies, OM shows under crossed polarizers that this structure consists of crystals which are, neglecting their size, not significantly different from the larger species growing out from the blobs as elongated crystals when heating the sample to



**Figure 2.** Micrograph of a 50 mM C<sub>18</sub>ISA solution, 75% neutralized with KOH. After the first heating–cooling cycle, solitary, long aggregates are found together with the blob structures. The diameter of the largest blob structures is approximately 60 μm; the dimensions of the long aggregates are given in Figures 4 and 5.

temperatures above 50 °C. The formation of aggregates consumes gradually the smaller blob structures as a kind of Oswald ripening. Increasing the temperature further, the large lath-shaped crystals disappear at about 65 °C. Cooling the sample to room temperature immediately after heating shows re-formation of the blob structures at approximately 45 °C.

When the sample is reheated subsequently after the first heating–cooling cycle, the large aggregates are not re-formed, a fact which should be ascribed to crystallization kinetics.

**3.1.2. Polarized Optical Microscopy on Threads of C<sub>18</sub>ISA·1.5KOH.** Examination of the precipitate of a 36 mM suspension in a polarizing microscope shows—in accordance with SNOM and AFM studies—very anisotropic lath-shaped aggregates: The length reaches the order of magnitude of millimeters, the width does not exceed a few micrometers. The ratio of width to thickness is approximately 4:1. This size is confirmed by AFM results (Figure 4).

In a polarizing microscope the threads appear bright as long as they are not aligned parallel to the polarizer or analyzer of the microscope. In this orientation the linear polarized light is extinguished in analogy to the behavior of single crystals. The single-crystal character of the threads is further confirmed by the results of electron diffraction, discussed below. The thicknesses of the thinnest structures

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**Figure 3.** Micrograph of a 80 mM  $C_{18}ISA$  solution, 75% neutralized with KOH. The sample was treated with four cycles of heating-cooling. "Super-sheaves" are formed without storage in sealed tubes. The dimensions of the aggregates are given in Figures 4 and 5.

as estimated from the colors between crossed polarizers, do not exceed about 30 nm.

When a bundle of lath-shaped crystals is slowly drawn out of the suspension with a pair of tweezers, the formation of much longer threadlike structures can be observed. These structures can easily reach the length of a few centimeters. When the same process is monitored by optical microscopy, however, a continuous strand of overlapping lath-shaped crystals is observed, in particular toward the thinner ends of the threads, (Figure 5). The ends of the crystals can be observed by the occurrence of sudden changes of the intensity of the transmitted light and by the variations of the interference color between crossed polarizers. Most likely, the uniformly aligned crystals are held together by cohesion and electrostatic interactions. Although some of the crystals are significantly bent, a fragment of the terminal single crystal of the thread reveals that even the hydrated crystals are quite brittle (Figure 5).

**3.2. Structure of the Macroscopic Aggregates.** To determine the structure of the macroscopic aggregates, they were further investigated by X-ray diffraction.

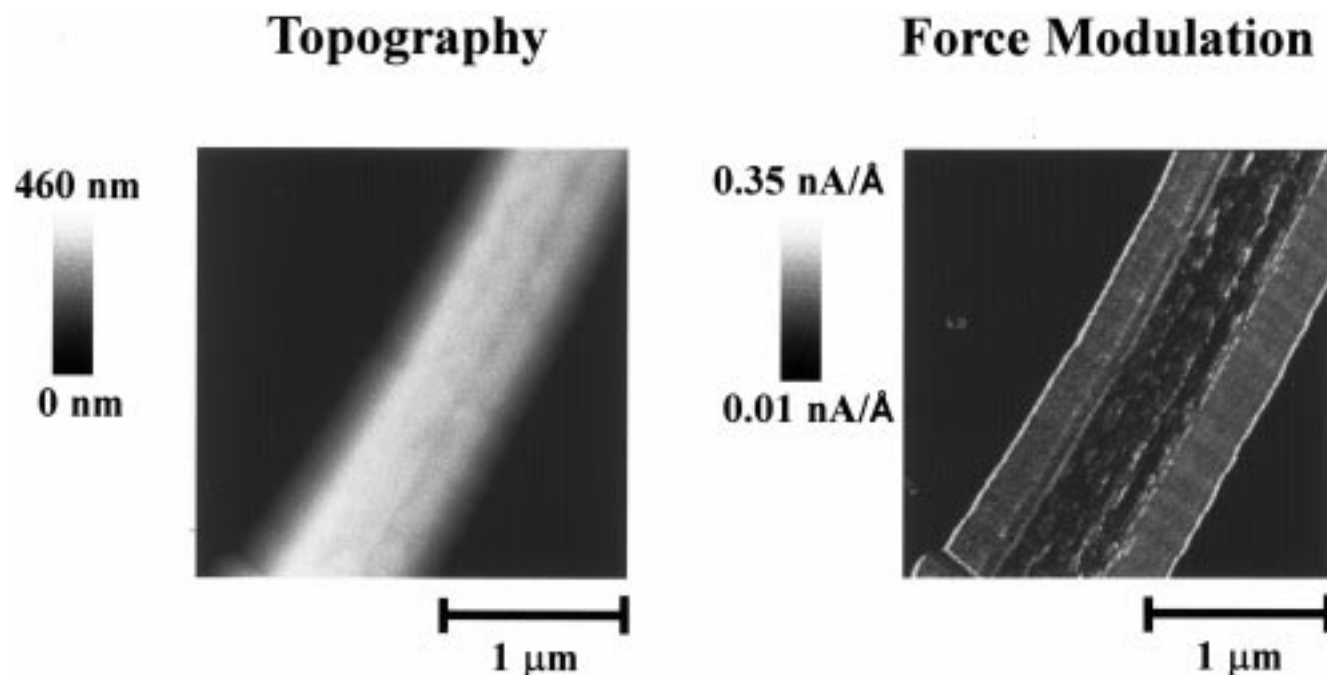
X-ray powder diffraction was performed on both dried and wet-wiped aggregates. Also the original aqueous suspensions of  $C_{18}OISAEnDash\cdot 1.5KOH$  were investigated in the concentration range 5–71 mM. Very long fiber-like aggregates obtained by pulling a bundle of aggregates out of a 5 mM suspension were oriented along

a thin glass rod and examined by X-ray diffraction. Furthermore the blob-shaped structures were studied by TEM.

**3.2.1. X-ray Diffraction Studies.** For all examined aggregate preparations, the diffraction patterns exhibit features typical for crystals: in the small-angle regime, an intense reflection is observed that correlates with a periodicity of about 35–36 Å. This spacing is in agreement with the assumption that the molecules interdigitate mutually, forming lamellae in which the polar headgroups are spatially separated from the regions of the lipophilic alkyl chains.<sup>11</sup> Considering the results from the electron diffraction studies, the most intense reflection can be interpreted as a second-order reflection to a basic reflection (not observed) with a  $d$  value of about 72 Å. The indexing of the reflections was based on a 72 Å basic reflection, assuming that adjacent layers are in register for dried and hydrated samples. However, since no electron microscopy studies can be performed with hydrated wet samples due to the high vacuum under measurement conditions, it is not possible to determine whether neighboring layers in hydrated crystals are in register with one another or not, as the uptake of water in the polar regions of the headgroups of the amphiphiles could bring about the loss of this register. From X-ray scattering, this difference cannot be detected, since even in the dried lath-shaped crystals which are fully isostructural with the species studied by electron diffraction, the basic reflection is extinguished due to symmetry restrictions. In the wide-angle regime, the presence of three "fingerprint" reflections (cf. Table 2), which can be indexed as 040, 200, and 240 reflections, corroborates that a triclinic alkyl chain packing is observed in all preparations of the lath-shaped crystals (these crystals also being referred to as macroscopic or large aggregates in the text). These three characteristic reflections have already been observed in the crystal structures of triclinic octadecane, of eicosane,<sup>20</sup> and of triclinic poly(ethylene).<sup>21</sup>

Irrespective of the manner of preparation of the potassium isophthalate and the initial concentration of the solutions, the observed reflections fit into the same system of crystal lattices, meaning that only one crystalline species could be detected in suspensions containing large and microcrystalline aggregates. Only minor variations of the  $d$  values are observed (about 4% maximum deviation of the  $d$  values, uncertainty of  $\Delta(2\theta)$  about 0.1°, corresponding to fluctuations of about 1.5 and 0.5 Å for the 002 and 004 reflections, respectively). This slight reduction of the layer spacing in hydrated samples compared to that in dried crystals was confirmed by small-angle X-ray diffraction. The layer spacing fluctuation did not exceed 4%. Only the number of the observed reflections varies in the diffractograms, a fact that can be attributed to the nature of the sample: In manually obtained wet fibrous aggregates and in the suspensions, the absence of higher reflections ( $l > 4$ ) is ascribed to the superimposition of the reflections with the scattering of water and the smaller scattering volume. The observed  $d$  values and their  $hkl$  triples are listed in Table 2.

X-ray diffraction patterns of bundles wiped-off from a 5 mM suspension exhibit solely two reflections in the small-angle regime ( $d$  values 35.5 and 17.65 Å, respectively), which can be indexed as 002 and 004 reflections. The observed reflections in the wide-angle regime are summarized in Table 2. As stated above, the absence of further reflections is due to the superimposition of the scattering intensities of water and the sample. The three pronounced reflections at wide angles hint at a crystalline packing of the alkyl chains. Similarly, X-ray diffraction was per-



**Figure 4.** Images from atomic force microscopy on  $C_{18}ISA \cdot 1.5KOH$  aggregates.

**Table 2.**  $d_{hkl}$ -values of 5 and 69 mM Preparations of  $C_{18}ISA \cdot 1.5KOH$  at 25 °C from X-ray Powder Diffraction Data<sup>a</sup>

5 mM Suspension													
$d_{hkl}$ (Å)	36.04	18.02								4.57			
Wiped-Off Bundles from 5 mM Suspension													
$d_{hkl}$ (Å)	35.5	17.65								4.53	3.82	3.67	
69 mM Suspension													
$d_{hkl}$ (Å)	35.18	17.48								4.55			
Wiped-Off Bundles from 69 mM Suspension													
$d_{hkl}$ (Å)	34.74	17.47	12.19	9.02	7.02	6.08	4.57						3.66
Dried Aggregates Prepared from 69 mM Suspension													
$d_{hkl}$ (Å)	35.87	17.94	11.51	9.02	7.93	6.83	6.11	6.08	4.59	3.86	3.64	3.36	3.1
hkl	002	004	006	008	*	*	030	*	040	200	2-40	*	*

<sup>a</sup>  $d$  values marked with an asterisk (\*) cannot be assigned to a specific  $hkl$  triple due to the overlap of various reflections.

formed on 5 mM suspensions, and the  $d$  values, derived from the Bragg reflections of the diffractogram, are listed in Table 2.

Moreover, the 69 mM suspensions and aggregates wiped-off from the 69 mM suspensions have been examined. As can be seen in Table 2, the wiped-off bundles exhibit slightly reduced  $d_{002}$  and  $d_{004}$  values as compared to those of the suspension. The deviation, however, is within the limits of the assessed experimental error,  $\Delta(2\theta) = 0.1^\circ$ . The data obtained from the wiped-off bundles once more prove the crystalline nature of the aggregates and are in accordance with the data set derived from the results of electron microscopy discussed below.

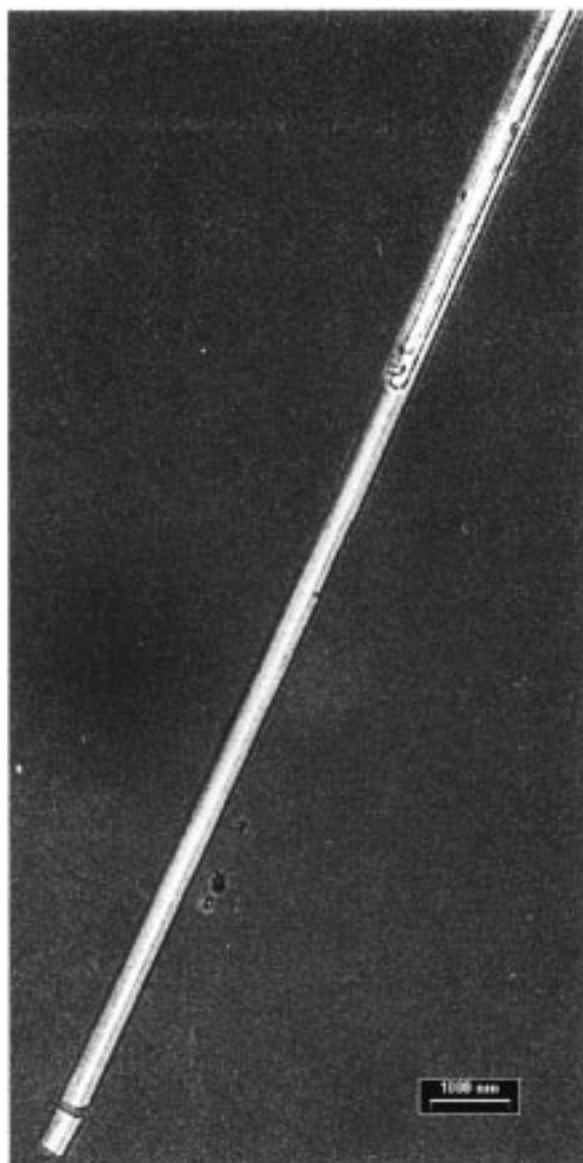
Finally, dried crystalline aggregates were checked by X-ray diffraction. Numerous reflections are observed that meet the data of the electron diffraction studies.<sup>25</sup> Slight deviations of the interplanar distances between X-ray diffraction and electron diffraction data can be explained by a superposition of a dense sequence of reflections which cannot be resolved in the X-ray diffractograms. X-ray diffraction patterns also exhibit three pronounced reflections at wide angles stemming from the crystalline triclinic alkyl chain organization.

The isostructural nature of the constituents of the suspensions (crystals) with the fiber-shaped specimens obtained by pulling a bundle of crystals out of a 5 mM suspension was shown by X-ray diffraction: small-angle

reflections corresponding to  $d$  values of 34.4 ( $d_{002}$ ) and 17.2 Å ( $d_{004}$ ) plus three sharp reflections at wide angles ( $d_{040} = 4.6$  Å,  $d_{200} = 3.86$  Å,  $d_{240} = 3.64$  Å) are displayed in the diffractograms.

In accordance with the observations from optical (polarizing) microscopy, it is concluded that the long, manually obtained, fiber-shaped aggregates consist of the lath-shaped crystals.

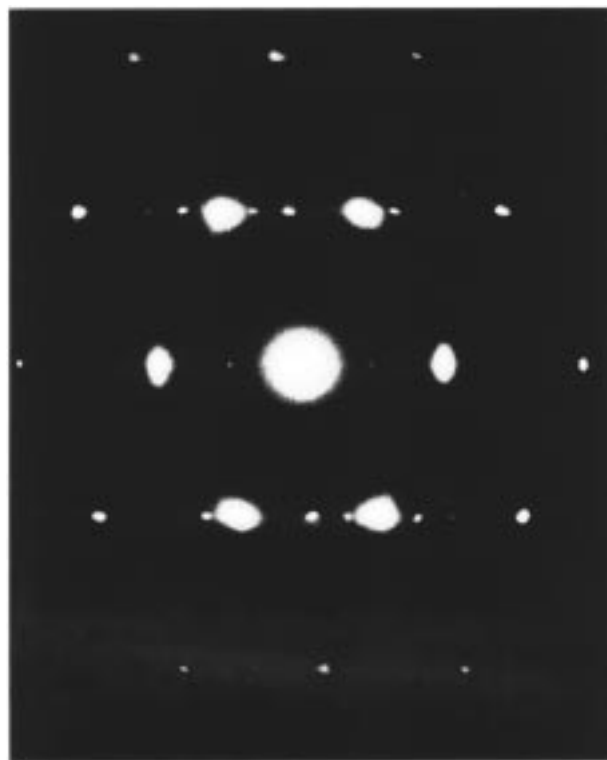
Further reflections, which would point to the presence of other highly ordered species besides the mentioned crystals, were not observed in any of the examined suspensions. Temperature-dependent X-ray scattering experiments with  $C_{18}ISA \cdot 1.5KOH$  suspensions showed—in accordance with OM—the collapse of the crystalline structures at about 70 °C; no changes in the diffraction patterns are observed from room temperature up to the collapse of the crystalline lath-shaped structures. Hence, it can be concluded that, if lyotropic liquid crystalline phases or vesicular specimens are present in the suspensions, they do not possess an ordered layer structure, or alternatively, their scattering intensities are too small to be detected or their reflections coincide with reflections of the crystalline species. On cooling a 69 mM potassium isophthalate solution from 80 °C, the initial diffractograms stemming from the crystalline aggregates were observed at room temperature after 30 min of equilibration of the samples.



**Figure 5.** Fiber-like structure obtained manually from a 36 mM potassium isophthalate suspension with crossed polarizers and a  $\lambda$ -plate. A fragment of a single crystal shows that even the hydrated fibers must be quite brittle. Inserted bar is 1  $\mu\text{m}$ .

**3.2.2. Electron Diffraction.** For investigations by electron diffraction, suspensions of the  $\text{C}_{18}\text{ISA}\cdot 1.5\text{KOH}$  salt (starting concentrations 69 and 71 mM) were deposited onto carbon coated copper grids. The only morphological features of the samples are anisotropic lath-shaped crystals with thicknesses orders of magnitude smaller than the longitudinal extension and, consequently, transparent for electrons. As pointed out, only dehydrated samples can be studied inside an electron microscope, since the preparations are exposed to a vacuum ( $<10^{-4}$  Pa) during the measurements. Table 2, where the reflections for suspensions and wiped-off bundles on the one hand and for dried preparations on the other hand are compiled, shows that the difference of  $d$  values is not significant for various preparations. Therefore the lath-shaped crystals could be investigated by electron diffraction at ambient temperature. Fiber diffraction patterns in particular were not found by electron diffraction. This indicates that the aggregates in the suspensions are exclusively crystals and not fibers.

Figure 6 shows an electron diffraction pattern obtained from a lath-shaped crystal at room temperature (beam



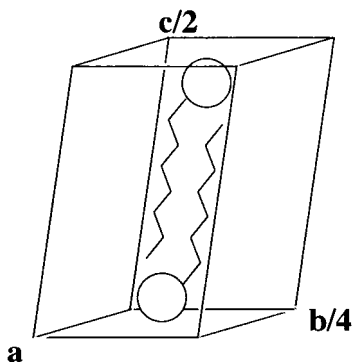
**Figure 6.** Electron diffraction pattern of a lath-shaped crystal (diameter of the irradiated area 6.0  $\mu\text{m}$ ). The innermost six intense reflections can be assigned to a triclinic alkyl chain packing with the beam path parallel to  $c$  (orientation of the alkyl chains).

incidence parallel to the alkylic chains, only  $hk0$  reflections are present). In this diffraction pattern the strongest reflections correspond to the three fingerprint reflections in the X-ray diffractograms. They can be indexed as the 010, 100 and  $\bar{1}10$  reflections of the triclinic packing of linear alkanes.<sup>20,21</sup> In the case of the  $\text{C}_{18}\text{ISA}$  salt, the indexing has to take into account the different positions of the aromatic headgroups, hence increasing the number of molecules within the unit cell. The translation period  $c$  was derived from a series of zone patterns after tilting the crystal to various angles. In addition to the data from electron diffraction,  $d$  values obtained from X-ray scattering at small angles were used in the input data set for structure determination and refinement. The four fingerprint reflections were attributed a statistical weight of 10; all other reflections had unit weight. With these data the following unit cell parameters were obtained from 52 independent reflections:

$$\begin{aligned} a &= 8.82 \text{ \AA} \pm 0.01 \text{ \AA}, b = 19.65 \text{ \AA} \pm 0.08 \text{ \AA}, \\ c &= 76.4 \pm 0.7 \text{ \AA}, \alpha = 89.3^\circ, \beta = 110.5^\circ, \\ \gamma &= 109.5^\circ, V = 11605 \text{ \AA}^3, Z = 16 \end{aligned}$$

A structural model based on those findings is displayed in Chart 1. For the sake of clarity, only one octant of the unit cell is depicted, containing two potassium carboxylate molecules. Four octants constitute a half-layer of the unit cell. The unit cell consists of two layers containing four octants, respectively, eight molecules each. The necessity of a second layer results from the sequence of reflections in diffraction patterns of tilted crystals, thus indicating that the second half-layer is not positioned precisely on top of the first half-layer but probably oriented to bring the aromatic groups and counterions into an optimal packing. The crystallographic layer spacing is about 72

**Chart 1. Structural Model for the Lath-shaped Crystals of  $C_{18}ISA \cdot 1.5KOH$  As Derived from the X-ray and Electron Diffraction Experiments**



Å. TEM and electron diffraction studies on the blob-shaped aggregates revealed that they are agglomerates of microcrystals.

#### 4. Conclusions

From solutions of  $C_{18}ISA$  neutralized to 75% with KOH, lath-shaped structures are precipitated. Optical microscopy and electron diffraction studies point out that the precipitates are single crystals in which the molecules adopt a layer structure. The lipophilic alkyl chains determine a triclinic lattice. Owing to the vacuum inside an electron microscope, obviously only dehydrated crystals can be investigated at room temperature. By comparison of the results from dried crystals and frozen hydrated crystals, however, it is inferred that differences in the molecular packing between wet and dry samples are insignificant. Electron diffraction patterns, collected at room temperature, of dried crystals, obtained by evapora-

tion of the water of a 71 mM suspension, and of wet crystals, frozen in a 69 mM sample prior to measurement, were recorded. These, as well as patterns from X-ray diffraction, do not point to different structures of dried and hydrated samples. However, the diffraction techniques used in this investigation are not sensitive enough to detect a possible loss of translation symmetry between the layers of hydrated samples. Such a loss of the register between adjacent layers would bring a reduction of the layer spacing from 72 Å to about 36 Å. The latter value meets the spatial demand of an antiparallel oriented double layer of the isophthalate molecules. The unit cell parameters of the triclinic lattice were determined, and a model of the molecular organization in the crystals (hydrated and dehydrated, as both specimens possess at least the same lateral alkyl chain packing) is suggested.

Fiber textures of the lath-shaped aggregates of  $C_{18}ISA$ , neutralized to 75% with KOH, are ruled out by electron diffraction investigations examined at room temperature and  $-130\text{ }^{\circ}\text{C}$ . The structural model discussed by Menger and Lee for  $C_{16}ISA \cdot KOH$  with a discotic organization of the molecules<sup>4</sup> can be discarded for the system  $C_{18}ISA \cdot 0.75KOH$ .

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