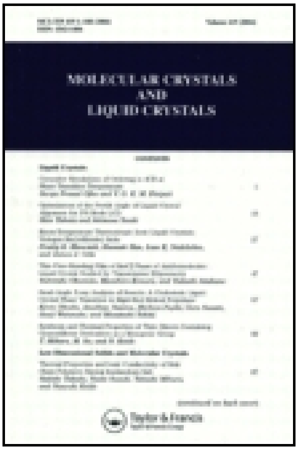

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: H. Bernhardt, W. Weissflog & H. Kresse (1999): Hydrogen-Bonded Ionic Liquid Crystals Showing Different Mesophases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 207-211

To link to this article: http://dx.doi.org/10.1080/10587259908025593

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 207-211
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Hydrogen-Bonded Ionic Liquid Crystals Showing Different Mesophases

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Binary systems of 1-heptyl-4-(4-pyridyl)pyridinium bromide with different proton acceptors were investigated. The existence of hydrogen bonded liquid-crystalline associates was proven.

Keywords: ionic hydrogen-bonded associates; self-assembly; liquid crystalline phases

INTRODUCTION

It is well known that amphotropic liquid crystals can be build up from ionic molecules [1]. Examples for it are alkylammonium [1], pyridinium [2,3], vinamidinium [4] and phosphonium [5] salts. Recently it was shown by phase diagrams that such samples can be „build up“ from suitable proton donors and acceptors via hydrogen bonds [6-8]. As acceptor in all cases 1-heptyl-4-(4-pyridyl)pyridinium bromide was used. The main features of the former investigations are:

1. Thermodynamically stable 1:1 associates indicated by two eutectic points are detected in the solid state [7].
2. The formation of smectic A phases is preferred.
3. The maximum of the stability of S_A-phase can considerably deviate from the mole fraction 0.5 (1:1 associate).

A typical example for such a binary system is given in Figure 1. It has to be pointed out that a stable associate with a clearing temperature of 162.5 °C is

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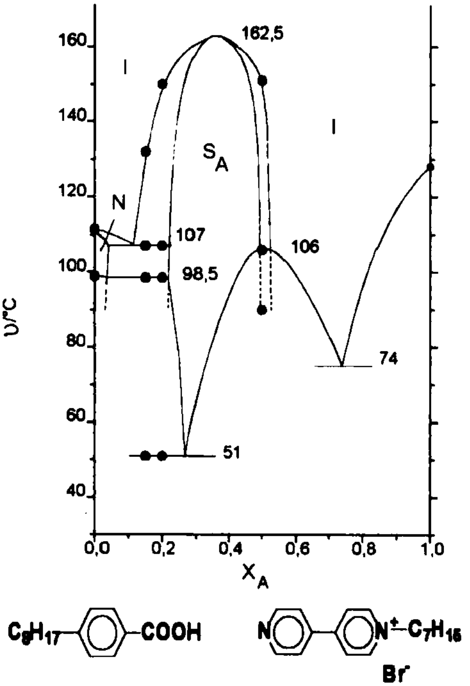

FIGURE 1: Typical phase diagram of a derivative of benzoic acid with 1-heptyl-4-(4-pyridyl)pyridinium bromide (A) according to [7]. The numbers are related to results from the contact preparation, the points to single concentrations.

induced. It was also demonstrated that ionic and non-ionic associates are not miscible with each other [6]. The aim of this paper is to investigate associates in which the acids are two- or threefold branched in order to study the relationship between steric and electrostatic interactions in hydrogen bonded liquid crystals.

EXPERIMENTS AND DISCUSSION

The phase diagrams were investigated by hot stage microscopy using polarized light. In some cases single concentrations were prepared. Figure 2 shows the binary system of 1-heptyl-4-(4-pyridyl)pyridinium bromide as proton acceptor with 3,4-di-n-heptyloxybenzoic acid as donor. In contradiction to

Figure 1 the maxima of both, the solid and the smectic A phases are observed at the mole fraction 0.5. The respective non-ionic associate with 4-(4-n-hexyloxyphenyl)pyridine exhibit a clearing temperature which is about 65 °C lower then that of the ionic acceptor. This indicates firstly the formation of very stable associates and secondly that there is a very sensitive equilibrium between the additional ionic forces and the repulsive forces connected with lateral branch. It is known from X-ray investigations of ionic molecules that the ionic part is separated from the other part of the molecule . The anions are situated between the pyridinium ions [9]. Assuming the same packing for our system the lateral distance between the 1-heptyl-4-(4-pyridyl)pyridinium bromide molecules should be elongated. This should be the reason why in the associate with the rod-like 4-alkylbenzoic acids additionally donor molecules are incorporated. In this way the free volume is reduced and the mesophase is stabilized. Therefore, the maximum in the diagram 1 is seen at x_A=0.3. In mixtures with wedge-like molecules of 3,4-di-n-heptyloxybenzoic acid the

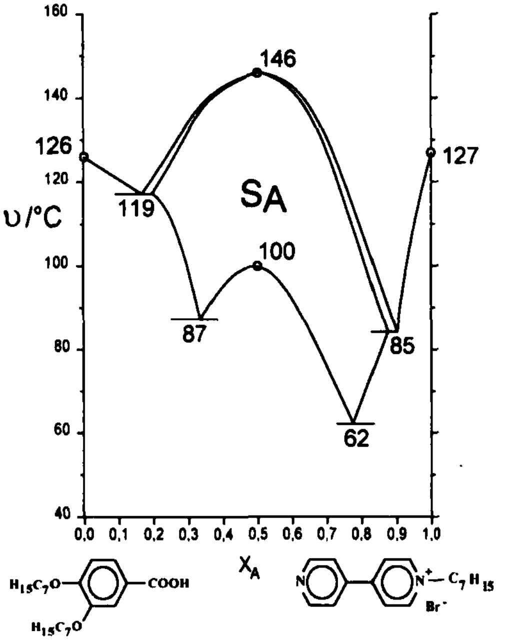

FIGURE 2: Diagram of ionic pyridine with 3,4-di-n-heptyloxybenzoic acid.

expected position of the maximum at the 1:1 associate is observed (Fig. 2). The laterally enlarged 4-(3,4,5-tri-n-dodecyloxybenzoyloxy)benzoic acid as proton donor should continue this tendency. Figure 3 shows, that in contradiction to all former investigated diagrams with 1-heptyl-4-(4-pyridyl)pyridinium bromide, two different liquid crystalline phases were found. The expected stabilization of S_A- phase at higher acceptor concentrations is observed. The existence of the smectic A phase was confirmed by X-ray

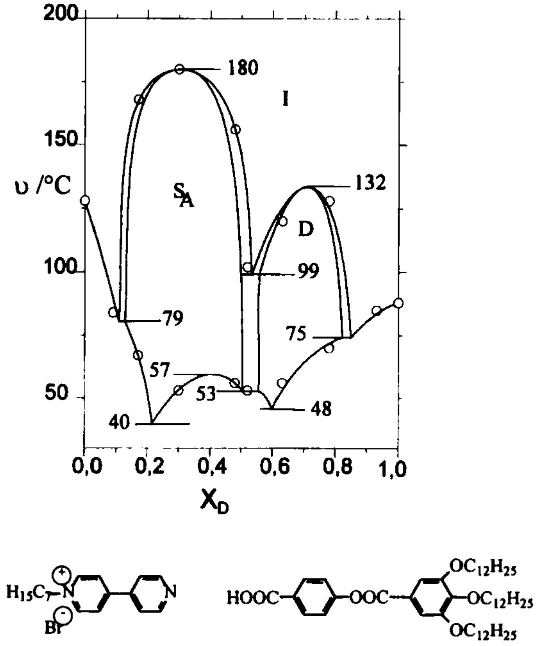

FIGURE 3: Phase diagram of 1-heptyl-4-(4-pyridyl)pyridinium bromide with 4-(3,4,5-tri-n-dodecyloxybenzoyloxy)benzoic acid.

investigations at x_A=0.7. A sharp inner and a diffuse outer reflex were found by the Guinier-method. A layer distance of d=(4.8±0.1) nm was calculated from the inner reflex. This value agrees well with the calculated length of the associate of 4.9 nm and confirms a structure formed by layers of the associate in which additionally acceptor molecules are incorporated.

The phase seen at x_D=0.7 could only be classified by microscopic observations to be probably a columnar one. However only one sharp X-ray reflection corresponding to a layer thickness d=4.07 nm was found. Other X-ray pattern were not detected.

Summarizing the results we can say:

- the interplay between steric and Coulomb forces results in a systematic change of the maximum of phase stability of the S_A state from x_A=0.35, 0.5 to 0.7 using acceptors having one, two and three terminal alkyloxy chains. Probably this interaction can be also studied in phase diagrams of ionic amphiphils without hydrogen bonds.
- in agreement with ionic liquid crystals without hydrogen bond [4] a columnar phase could be expected for the respective hydrogen bonded associate too (Fig. 3].

Acknowledgments

The authors are indebted to Dr. Diele for X-ray investigations and to the DFG for financial support.

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