Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Liquid crystalline hydrogen-bonded ionic associates

Y. M. Sahin; S. Diele; H. Kresse

To cite this Article Sahin, Y. M. , Diele, S. and Kresse, H.(1998) 'Liquid crystalline hydrogen-bonded ionic associates', Liquid Crystals, 25: 2, 175 — 178
To link to this Article: DOI: 10.1080/026782998206317
URL: http://dx.doi.org/10.1080/026782998206317

LIQUID CRYSTALS, 1998, VOL. 25, NO. 2, 175–178

Liquid crystalline hydrogen-bonded ionic associates

by Y. M. SAHIN†, S. DIELE and H. KRESSE*

Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie,
Mühlpforte 1, 06108 Halle, Germany

(*Received 12 January 1998; accepted 16 February 1998*)

Phase diagrams of different substituted acids with 1-heptyl-4-(4-pyridyl)pyridinium bromide were investigated. The formation of ionic hydrogen-bonded 1:1 and 1:2 associates can be detected in the solid state. In some cases thermodynamically stable smectic A phases are observed. The maximum phase stability in the liquid crystalline state can differ considerably from the expected value for the 1:1 associates. The layer thickness of the smectic layers measured by X-ray methods is smaller than the value calculated from molecular models. This indicates a complicated packing behaviour of the molecular building units in the SmA layers.

1. Introduction

Self-organization and dynamics are fundamental principles of life science. Both of them can be realized in hydrogen-bonded associates. Because every association is connected with a loss of entropy, the enthalpy of association must be negative and must overcome the term $T^*\Delta S$. For this reason a strong hydrogen-bonding is necessary. Furthermore, model systems can be designed in a way such that they show liquid crystalline phases. Therefore, it is possible to study molecular and collective processes of self-assembly [1].

First experiments in this direction were carried out on different substituted aromatic acids [2]. Later, Kato and Frechet introduced systems consisting of derivatives of pyridine and acids showing very stable liquid crystalline associates [3]. This idea was further successfully developed by different authors and now many associates showing a range of mesophases are known [4–8].

An interesting variation of this concept is possible if building units with a charge are introduced. In this way thermotropic liquid crystalline hydrogen-bonded ions—a new class of substances—can be 'constructed'. Till now only few examples of covalently bonded ionic thermotropic liquid crystals have been synthesized [9], filling the gap between thermotropic and the well known lyotropic mesophases [10]. Preliminary investigations of two ionic associates show the existence of a stable liquid crystalline phase only in one system containing a fluorinated acid [11]. The main result was that an ionic and a non-ionic associate with comparable structures are not miscible.

2. Experiments

In order to detect such associates, binary systems between 1-heptyl-4-(4-pyridyl)pyridinium bromide (Cr 127 I) as proton acceptor and different acids as donor were investigated. The phase transition temperatures are given in °C. Figure 1 shows the system with 4-*n*-octylbenzoic acid (Cr 99 N 111·5 I). The given temperatures were detected by heating and cooling of a contact preparation. Single concentrations were measured to determine the phase transition temperatures as a function of concentration. The SmA phase was identified by its fan-shaped texture together with homeotropic parts. The two eutectic points confirm the existence of a solid associate of the 1:1 type. It must be pointed out that the maximum temperature for the induced SmA phase is observed at a mole fraction of the pyridine component of 0·33. Furthermore, the 1:1 associate did not show a thermodynamically stable mesophase. This means that the liquid crystalline phase is formed from both the associate and the dimer donor molecules in a molar ratio of about 4:1. The SmA phase is separated from the other phases by an extended two-phase range.

For the second diagram we have chosen *trans*-4-*n*-octylcyclohexane-1-carboxylic acid (Cr 37 SmB 90 N 98 I) as donor. The phase diagram in figure 2 is similar to that given in figure 1. The difference lies only in the smectic B phase of the acid which is also separated by an extended two phase range from the SmA phase. There is no stabilization of the SmB phase. It is pointed out that the maximum stability of the SmA state occurs at a molar fraction of the pyridine component of about 0·37, which is considerably smaller than that for the 1:1 associate. In order to confirm the classification of the liquid crystalline phase, X-ray measurements were

---

* Author for correspondence.

† Permanent address: Istanbul Technical University, Turkey.

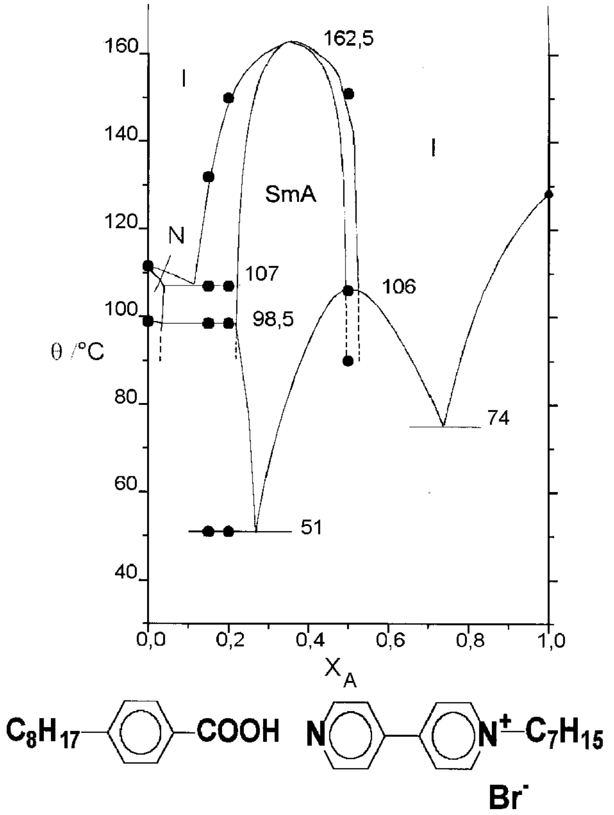

Figure 1. Phase diagram of 4-octylbenzoic acid with 1-heptyl-4-(4-pyridyl)pyridinium bromide. The numbers in the figure are temperatures in °C detected from the contact preparation. The points were measured at single concentrations.

carried out at $X_{(\text{pyridine})} = 0{\cdot}4$ using a Guinier camera. The typical X-ray patterns of the SmA phase with a sharp inner reflection and a diffuse outer scattering were obtained. At lower temperatures the second order of the inner reflection was also observed. From the inner reflection, layer distances *d* between 3·14 (105°C) and 3·00 nm (145°C) could be calculated. The great difference between the *d*-value and the estimated length of the ionic associate (3·6 nm) and the dimeric acid (also 3·6 nm) points to a highly flexible molecular shape of the associate.

The next test was related to double ionic associates. Therefore, as donor 1,12-dodecanedicarboxylic acid (Cr 127 I) was chosen. Figure 3 shows the formation of a solid 1 : 2 associate and no liquid crystalline phase. Addition of water to the associate results in partial solubilization, but in no microscopically observable lyotropic phase. By addition of perfluoro-1,10-decanedicarboxylic acid (Cr 151–160 I) to the same acceptor, a similar type of phase diagram was observed. In this case decomposition of the solid associate occurred at about 170°C.

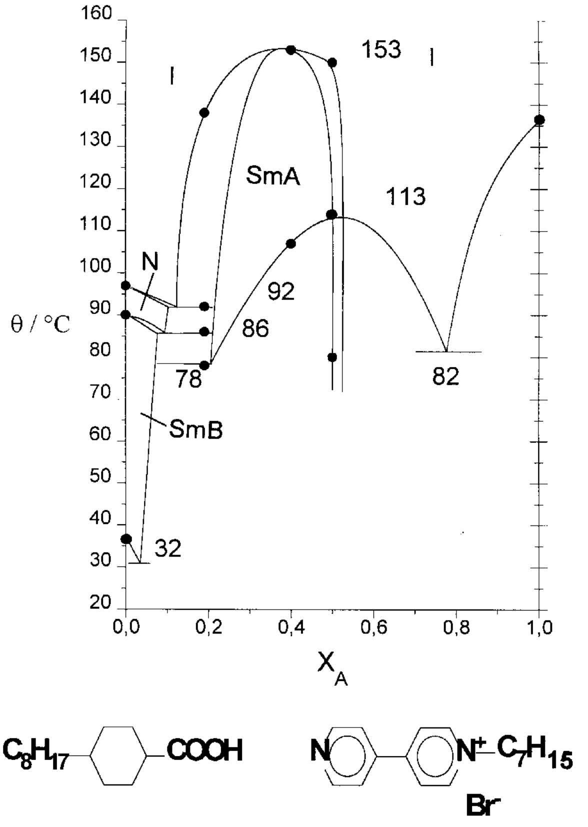

Figure 2. Phase transition temperatures of mixtures of *trans*-4-*n*-octylcyclohexane-1-carboxylic acid and 1-heptyl-4-(4-pyridyl)pyridinium bromide.

In a further experiment 4-*n*-hexylphenylacetic acid (Cr 74 I) was added. The aim of this test was to study the influence of changes in the rod-like shape of the associate. As in non-ionic associates, no mesomorphic phases were found [12].

To test steric influences on the mesophase stability, the mixture of the same acceptor with the swallow-tailed 4-[2,2,-bis(tetradecyloxycarbonyl)ethenyl]benzoic acid (Cr 86 I) was investigated. As demonstrated in figure 4, an extended SmA range could be detected. The maximum in the stability is in this case shifted to higher concentrations of the acceptor.

In comparison with swallow-tailed compounds consisting of three ring systems [13] the stability of this hydrogen-bonded ionic mesophase is astonishingly high. There is no indication for a high melting solid associate. X-ray measurements have been performed at the molar fraction 0·5. Again the SmA phase was confirmed. A layer distance of 4·2 nm was estimated from the inner reflection. The calculated length of the associated molecule in the *trans*-conformation at 4·6 nm is again smaller than the measured *d*-value.

In additional experiments, 4-*n*-pentyl-4′-cyanobiphenyl and 4-ethoxyphenyl 4-*n*-butyloxybenzoate were

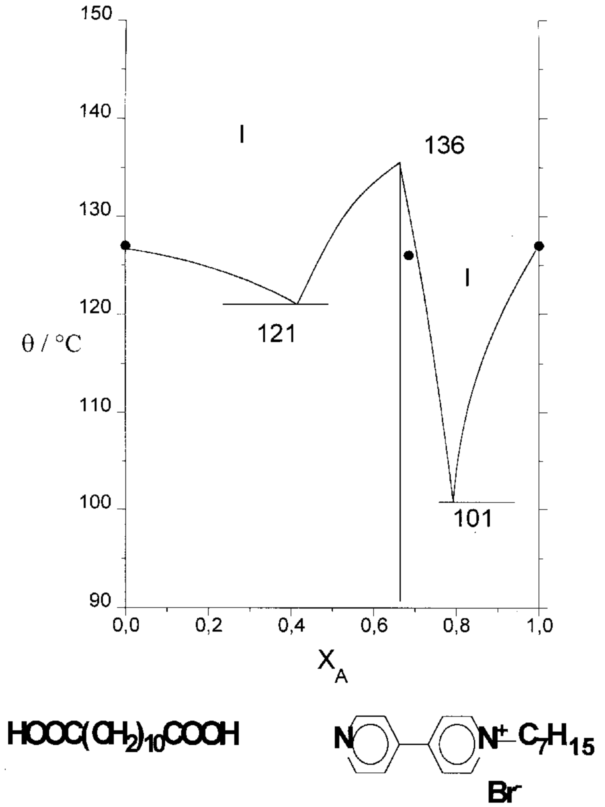

Figure 3. Binary system of 1,12-dodecanedicarboxylic acid and 1-heptyl-4-(4-pyridyl)pyridinium bromide.

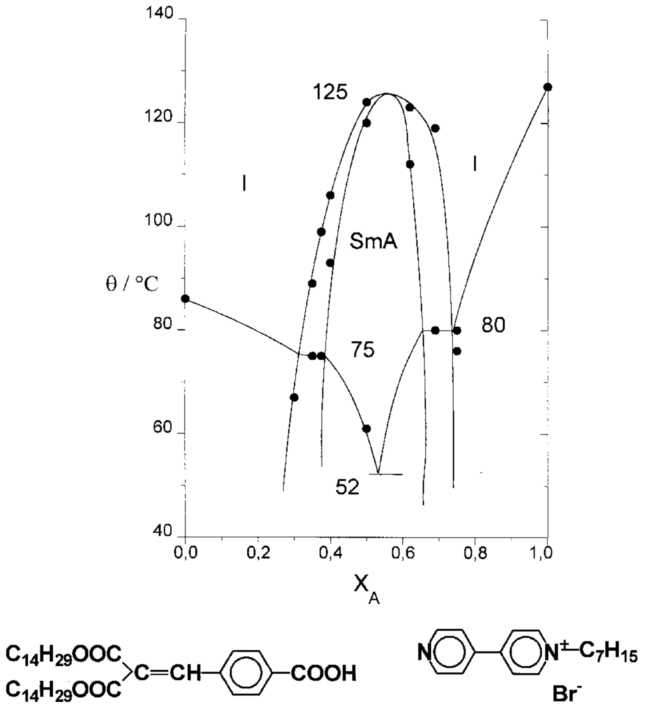

Figure 4. Binary system of 4-[2,2-bis(tetradecyloxycarbonyl)-ethenyl]benzoic acid and 1-heptyl-4-(4-pyridyl)pyridinium bromide.

added to the swallow-tailed acid in contact preparations. The aim of this investigation was to look for induced SmA phases, which could not however be detected. There exists only an equilibrium between the solid phase of the acid and the nematic phase of the added liquid crystal component. In both cases a destabilization of the nematic state on addition of the acid was found. Therefore, a ‘filled’ phase [14] formed between the dimer acid and the acceptor as the reason for the maximum in the stability of the SmA state in figure 4 can be excluded.

3. Discussion

Contrary to preliminary investigations [11], thermodynamically stable 1:1 ionic associates with non-fluorinated acids were obtained. The concentration corresponding to maximal phase stability of the SmA state is not in all cases at the equimolar ratio between donor and acceptor. In all given examples, neither nematic nor other smectic phases were observed. Therefore, we have to conclude that ionic associates are preferably packed in layers in which the building units are not very strongly ordered. Probably, the preference for the SmA phase shown by ionic associates with respect to other hydrogen-bonded associates is connected with the additional electrostatic forces. The gaps between the ‘basic’ structure of the lamellar type formed by the ionic associates are filled by acceptor or dimeric donor molecules which stabilize in this way the smectic A phase. This is the reason why the maximum in the phase stability does not always occur at the molar fraction 0·5.

The authors are grateful to the Fonds der Chemischen Industrie and to the IASTE exchange programme (Y.M.S.) for financial support.

References

[1] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem.*, **107,** 1839.

[2] Kresse, H., Sharma, N. K., and Weissflog, W., 1981, *Kristall und Technik*, **16,** 101.

[3] Kato, T., and Frechet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[4] Kato, T., Fukumasa, M., and Frechet, J. M. J., 1995, *J. chem. Mat.*, 368.

[5] Treybig, A., Bernhardt, H., Diele, S., Weissflog, W., and Kresse, H., 1997, *Mol. Cryst. liq. Cryst.*, **293,** 7.

[6] Alexander, C., Jawrila, C. P., Lee, C.-M., and Griffin, A. C., 1993, *Polm. Prep. Am. chem. Soc. Div. Polym. Chem.*, **148,** 161.

[7] Price, D., Richardson, T., and Bruce, D., 1994, *J. chem. Soc., chem. Commun.*, 1911.

[8] TIAN, Y., SU, F., ZHAO, Y., LUO, X., TANG, X., ZHAO, X., and ZHOU, E., 1995, *Liq. Cryst.*, **19,** 743.

[9] HARAMOTO, Y., UJIIE, S., and NANASAWA, M., 1996, *Liq. Cryst.*, **21,** 923.

[10] TSCHIERSKE, C., 1996, *Prog. Polym. Sci.*, **21,** 775.

[11] BERNHARDT, H., WEISSFLOG, W., and KRESSE, H., 1998, *Liq. Cryst.*, **24,** 895–897.

[12] TREYBIG, A., WEISSFLOG, W., PLASS, M., and KRESSE, H., 1997, *Mol. Cryst. liq. Cryst.*, **300,** 127.

[13] WEISSFLOG, W., WIEGELEBEN, A., DIELE, S., and DEMUS, D., 1984, *Cryst. Res. Technol.*, **19,** 583.

[14] DIELE, S., PELZL, D., WEISSFLOG, W., and DEMUS, D., 1986, *Liq. Cryst.*, **3,** 1047.