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Preliminary communication
Hydrogen-bonded ionic liquid crystals

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Ionic and non-ionic building units were connected via hydrogen bonds. Stable liquid crystalline phases were obtained by a suitable choice of the units. The ionic associates are not miscible with the respective non-ionic associates.

Coulomb forces cause the strongest intermolecular attraction. For this reason they are very important for all structure forming processes in condensed matter. Furthermore, it is known that hydrogen bonds are able to perform complicated processes of self-organization. The mutual influence of these interactions on the formation of mesophases is the spherical subject of these considerations.

The 'construction' of non-ionic thermotropic liquid crystals by the combination of smaller building units via hydrogen bonds is a scientific area of active interest [1–3]. On the other hand ionic compounds, for example alkylammonium and alkylpyridinium salts, forming thermotropic and/or lyotropic mesophases are also known [4–6]. There have been only few attempts to equip a non-ionic calamitic mesogen with an ionic group. This can be done by means of a spacer in a terminal position [7], or the ionic group can be introduced as a part of the aromatic core, as realized in *N*-ethyl-4-(5-*n*-decyl-1,3-dioxan-2-yl)pyridinium bromide [8]. Liquid crystals of the last mentioned type are of interest for the considerations that follow, and to obtain information on the different influences of hydrogen bonds and of ionic interaction on the formation of mesophases we have investigated hydrogen-bonded calamitic associates bearing an ionic group.

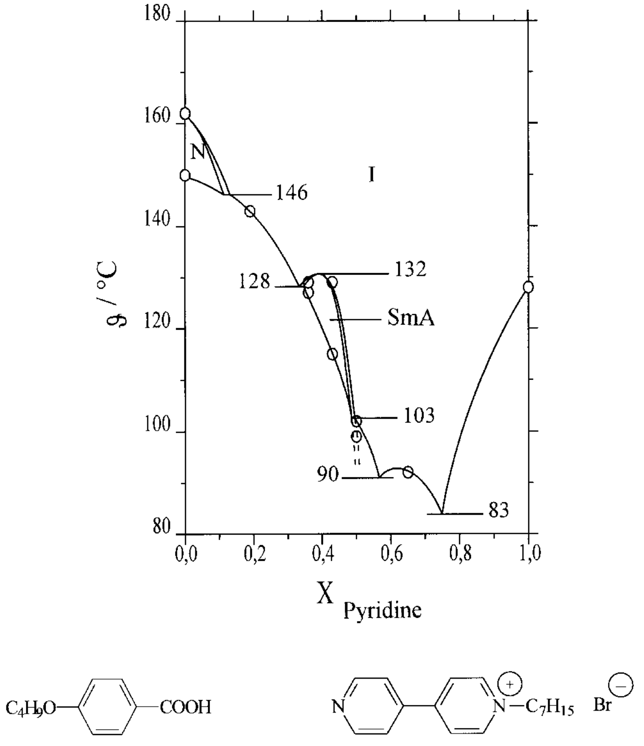

Figure 1. Phase diagram for 4-*n*-butyloxybenzoic acid and 1-*n*-heptyl-4-(4-pyridyl)pyridinium bromide.

Our concept is demonstrated using the binary system of 4-*n*-butyloxybenzoic acid as proton donor and 1-*n*-heptyl-4-(4-pyridyl)pyridinium bromide as ionic proton acceptor A (figure 1). There are two eutectic points indicating the formation of a solid associate. Furthermore a smectic A phase with a maximum stability at X(A) = 0·4 is induced. In order to separate the influence of the ionic group from that of the hydrogen bond, figure 1 can be compared with the binary system of the same donor and the non-ionic 4-(4-*n*-hexyloxyphenyl)pyridine [9]. In this case a hydrogen-bonded 1 : 1 associate with the polymorphism Cr 87 SmA 133 N 138 I is observed. It has to be pointed out that the maximum clearing temperature in figure 1 is not at the equimolar ratio of donor and acceptor molecules. Furthermore one can see that the nematic phase of the 4-*n*-butyloxybenzoic acid disappears with addition of small concentrations of the ionic pyridine derivative. This indicates a strong incompatibility between ionic and non-ionic liquid

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crystalline phases. In order to support this finding, the 1 : 1 associates of both systems under discussion were mixed. Figure 2 shows the phase diagram of this pseudobinary system. There is no complete miscibility. It is noted specially that the SmA phase of the non-ionic associate cannot be dissolved in that of the ionic one. In the phase diagram both SmA ranges are separated by a broad two phase range.

An interesting structural variation can be obtained by use of partially fluorinated alkyl chains situated in the donor [9]. A phase diagram of 4-*n*-1*H*,1*H*-perfluorobutyloxybenzoic acid and 1-*n*-heptyl-4-(4-pyridyl)pyridinium bromide is given in figure 3. Also in this case, the smectic A modification is stabilized. In contradition to figure 1 the maximum of the induced SmA phase is observed at ϑ the equimolar relation. Probably the exchange of the hydrogenated by the more stiffer and more voluminous perfluorinated alkyl chain results in a change of the packing of the molecules. The phase behaviour given in figure 3 can be compared with that of the associates formed by the same acid and the non-ionic 4-(4-*n*-hexyloxyphenyl)pyridine. For this 1 : 1 associate the polymorphism Cr 68 SmA 166 I was detected [9]. Comparing the results from figures 1 and 3, one can see a clear increase in the stability of the mesophase due to the perfluorinated group.

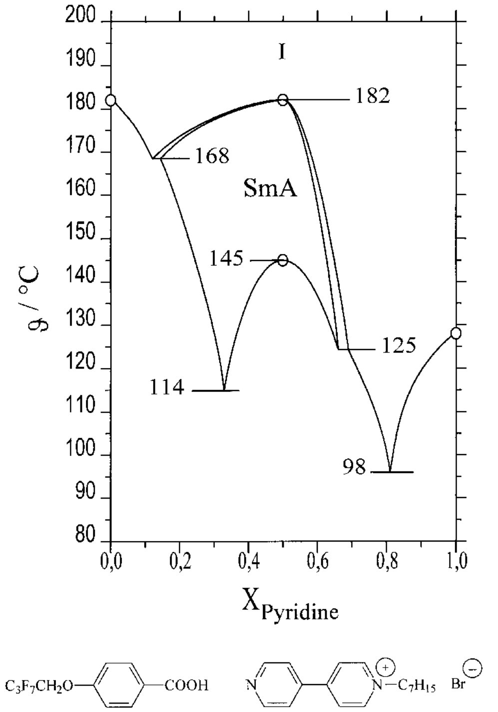

Figure 3. Phase diagram for 4-*n*-1*H*,1*H*-perfluorobutyloxybenzoic acid and 1-*n*-heptyl-4-(4-pyridyl)pyridinium bromide.

Hydrogen-bonded associates with ionic building units can thus exhibit stable liquid crystalline phases. The additional Coulomb interactions can cause an increase or decrease of the mesophase stability in comparison with the comparable non-ionic systems. To define general trends between the liquid crystalline behaviour and the chemical structure of hydrogen-bonded ionic associates, further investigations have to be made. The transfer of

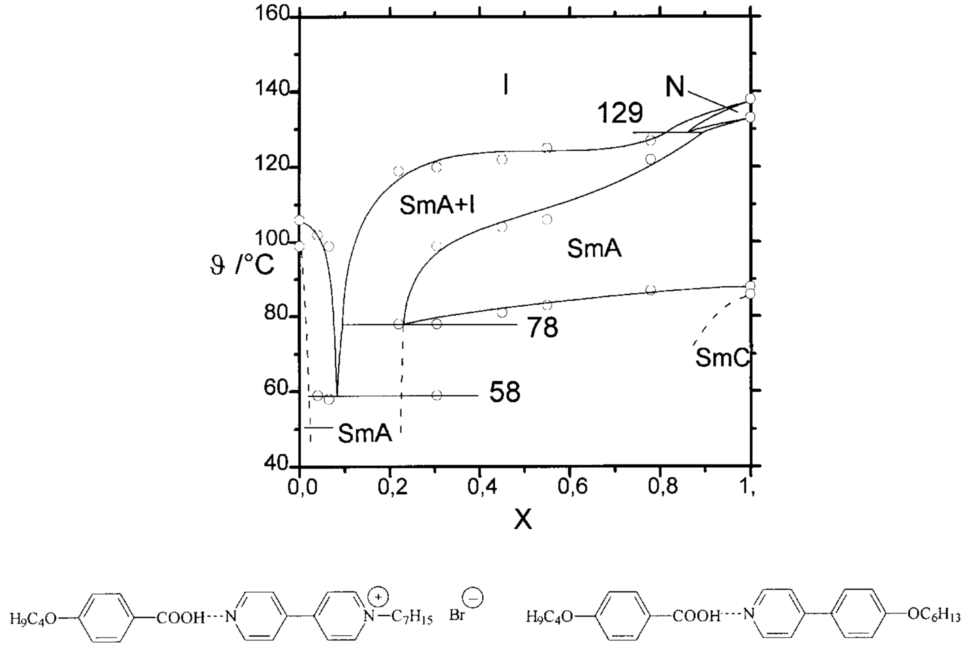

Figure 2. Binary system between the ionic and the non-ionic hydrogen-bonded 1 : 1 associates.

results obtained to relevant lyotropic biological systems could be an interesting aspect of such further studies.

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References

[1] Paleos, M., and Tsiourvas, D., 1995, *Angew. Chem.*, **107,** 1839 (1994, *Angew. Chem. int. Ed. Engl.*, **34,** 1696).

[2] Kato, T., Kihara, H., Kumar, U., Uryu, T., and Frechet, J. M. J., 1994, *Angew. Chem.*, **106,** 1728 (1994, *Angew. Chem. int. Ed. Engl.*, **33,** 1644).

[3] Bernhardt, B., Weissflog, W., and Kresse, H., 1996, *Angew. Chem.*, **108,** 966 (1996, *Angew. Chem. int. Ed. Engl.*, **35,** 874).

[4] Tschierske, C., 1996, *Prog. polym. Sci.*, **21,** 775.

[5] Alami, A., Levy, H., Zana, R., Weber, P., and Skoulios, A., 1993, *Liq. Cryst.*, **13,** 201.

[6] Nusselder, J. J. H., Engberts, J. B. F. N., and van Doren, H. A., 1993, *Liq. Cryst.*, **13,** 213.

[7] Kunitake, T., and Okahata, Y., 1980, *J. Am. chem. Soc.*, **102,** 549.

[8] Haramoto, Y., Ujiie, S., and Nanasawa, M., 1996, *Liq. Cryst.*, **21,** 923.

[9] Bernhardt, H., Weissflog, W., and Kresse, H., 1997, *Chem. Lett.*, (Jpn.), 151.