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H. Kresse

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Ionic liquid crystalline hydrogen-bonded associates based on phenols

by H. KRESSE

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

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Different 4-substituted phenols were mixed with 1-*n*-heptyl-4-(4-pyridyl)pyridinium chloride. In the phase diagrams thermodynamically stable solid 1 : 1 hydrogen-bonded ionic associates were detected. Smectic A phases are stabilized in mixtures between the proton donor and the associate.

1. Introduction

The 'construction' of large aggregates by the self-assembling of small building units via hydrogen bonds is of active interest for scientists working in various fields [1]. In this paper we will restrict our considerations to singular associates consisting of proton donors and acceptors in the molar ratio 1 : 1. A hydrogen bond can be formed between a pyridine derivative as acceptor and a hydroxyl compound as donor. Such systems can show liquid crystalline phases as demonstrated for the first time by Kato and Frechet [2]. By systematic investigations, many different thermotropic liquid crystalline phases were observed [3–13].

Ionic associates can be expected if 1-*n*-heptyl-4-(4-pyridyl)pyridinium chloride (Cr 127 I) is used as acceptor. A simple phase diagram with benzoic acid as donor is shown in figure 1. The transition temperatures

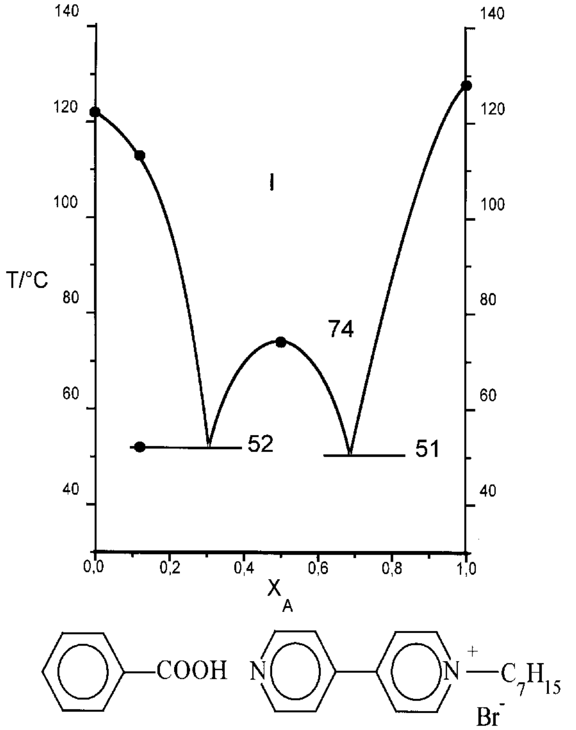

Figure 1. Phase diagram of benzoic acid and 1-*n*-heptyl-4-(4-pyridyl)pyridinium chloride (A = acceptor).

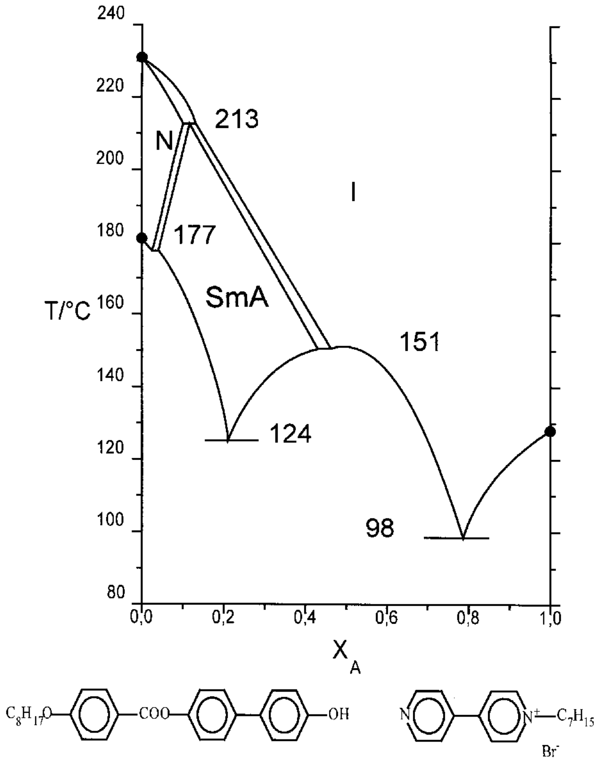

Figure 2. Binary systems of 4′-hydroxybiphenyl-4-yl 4-*n*-octyloxybenzoate and 4′-(4-hydroxyphenyliminomethyl)-phenyl 4-*n*-nonyloxybenzoate with 1-*n*-heptyl-4-(4-pyridyl)-pyridinium chloride (A = acceptor).

were measured by hot stage microscopy using polarized light. Contact preparations, as well as a single concentrations were investigated. The existence of two eutectic points at 51 and 52°C, together with the maximum in the melting temperature of 74°C at the molar fraction 0·5, is clear thermodynamic evidence for the solid 1 : 1 associate. Furthermore, there is no reason from the thermodynamic point of view that the associate will be destroyed completely during the melting process (see also FTIR investigations [5]). Therefore, one should observe such rod-like associates in the liquid too; and with a suitable molecular shape of the associate, liquid crystalline phases should also appear. This was recently demonstrated by us [14, 15]. In our extension of these investigations we next tried to obtain mesophases with *p*-substituted phenols as donor.

2. Experiments and discussion

Binary systems of 1-*n*-heptyl-4-(4-pyridyl)pyridinium chloride with 4′-hydroxybiphenyl-4-yl 4-*n*-octyloxybenzoate (Cr 181 N 231 I) and 4′-(4-hydroxyphenyliminomethyl)phenyl 4-*n*-nonyloxybenzoate (Cr 183 N 197 I) were investigated by the contact method and the results are presented in figures 2 and 3. Again the existence of the respective solid associates is confirmed by the two eutectic points in each diagram. In both cases the nematic (N) phase disappears and a smectic A phase is induced. Furthermore, it could be observed in the contact preparations that the solid associate shown in figure 2 transforms by heating into the isotropic state and that of figure 3 into a two phase region. From this it can be concluded that neither associates exhibited a thermodynamically stable liquid crystalline phase. On cooling, in both cases the two-phase range I/SmA transition could be seen. Further cooling results in crystallization of the associates. To observe a maximum in the stability of the mesophase in a phase diagram, the length of the donor molecule was reduced. Figure 4 presents the phase diagram with 4-*n*-nonyloxyphenol (Cr 59 I). This donor did not exhibit a mesophase, unlike the former samples. In this case the solid 1 : 1 associate and an induced smectic A phase could be detected. It should be emphasized that the maximum SmA stability was found at a molar fraction of the donor

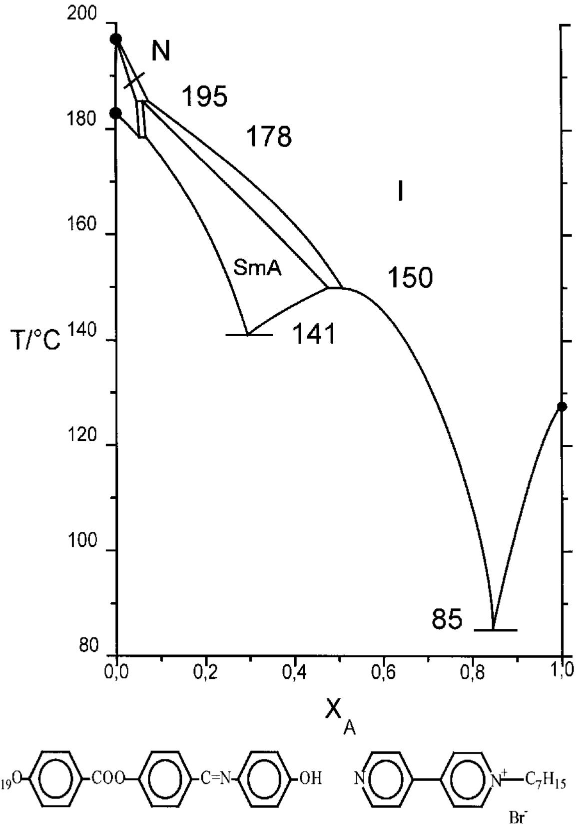

Figure 3. Binary systems of 4′-hydroxybiphenyl-4-yl 4-*n*-octyloxybenzoate and 4′-(4-hydroxyphenyliminomethyl)-phenyl 4-*n*-nonyloxybenzoate with 1-*n*-heptyl-4-(4-pyridyl)-pyridinium chloride (A = acceptor).

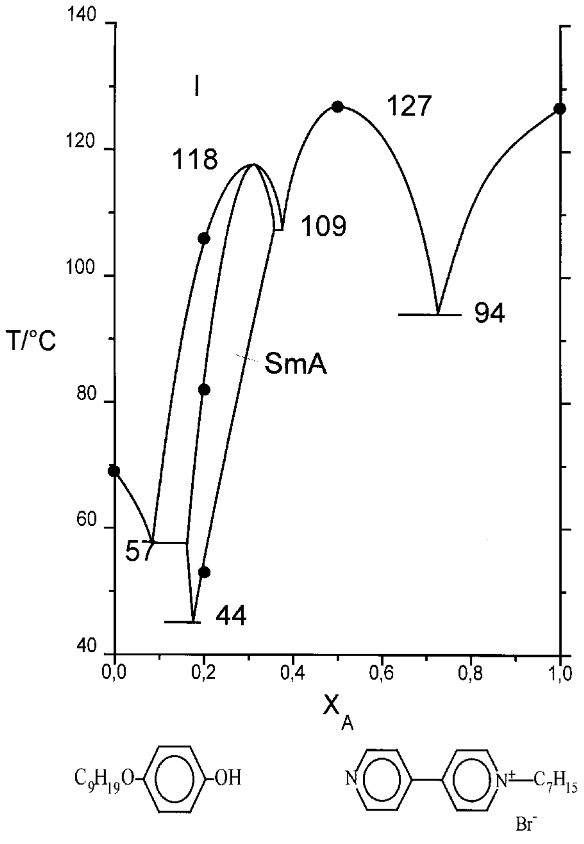

Figure 4. Binary systems of 4-*n*-nonyloxyphenol and 4-*n*-octyloxyphenyl hydroxybenzoate with 1-*n*-heptyl-4-(4-pyridyl)-pyridinium chloride (A = acceptor).

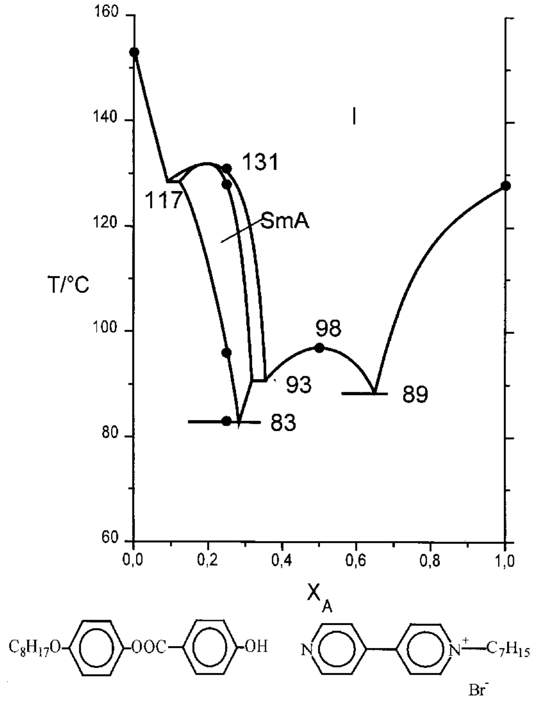

Figure 5. Binary systems of 4-*n*-nonyloxyphenol and 4-*n*-octyloxyphenyl hydroxybenzoate with 1-*n*-heptyl-4-(4-pyridyl)-pyridinium chloride (A = acceptor).

of 0·3. By supercooling of a singular mixture consisting of the 1 : 1 associate down to the crystallization temperature of about 95°C, no liquid crystalline phase was seen in the microscope.

An extension of the length of the donor molecule to 4-*n*-octyloxyphenyl 4-hydroxybenzoate (Cr 153 I) results in an increased stability of the induced SmA phase (figure 5). Again a maximal stability appears at higher donor concentrations than that for the equimolar ratio. This shift in the maximum of the mesophase stability was observed also in binary systems with substituted acids as donor [15]. The reason for this effect may lie in the strong influence of the ions on the interactions between the molecules. This effect is reduced if molecules of the neutral donor are situated between the ionic associates. Therefore, non-liquid crystalline molecules can in this case stabilize the mesophase. It has to be pointed out that addition of small rod-like molecules, e.g. 4-*n*-butoxyphenyl 4-*n*-hexylbenzoate (Cr 39 N 49 I) to the equimolar mixture of the system in figure 5 did not result in a stabilization of the SmA phase. Probably, the associate is strongly dissociated by dilution.

In a former publication it was also demonstrated that a 'fork-like' donor can considerably change the intermolecular interactions [15]. Taking di-dodecyl 4-hydroxybenzylidenemalonate (Cr 62 I) as donor, in this case, when on supercooling to room temperature, no mesophase was observed.

In conclusion, the appearance of mesophases in such ionic hydrogen-bonded systems strongly depends on the molecular shape of the phenols and the packing behaviour of the phenols with the 1 : 1 associate.

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