Classification of the Smectic Liquid Crystal Phase Exhibited by the Cholesteryl n-Alkanoates

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Summary The smectic phase given by cholesteryl n-alkanoates has been classified as smectic A by miscibility studies involving cholesteryl nonanoate or myristate and the known smectic liquid crystals exhibited by other mesogens.

THE higher homologues of the series of cholesteryl n-alkanoates,[1] *e.g.*, cholesteryl nonanoate, exhibit a single birefringent smectic liquid crystal phase in addition to a cholesteric phase. Apart from a tentative report by Arnold[2] that the smectic phase may be of type A, no classification of the phase according to Sackmann's system[3] can be traced. Wendorff and Price[4] examined the smectic phases of cholesteryl nonanoate and myristate by *X*-ray diffraction, and their results indicate a smectic A type of ordering. However, recent light scattering studies by Takase and his co-workers[5] on cholesteryl nonanoate suggest that the smectic phase may be of type C, despite the fact that the phase could be induced to give a scattering pattern typical of type A.

The classification of this smectic phase is therefore in doubt and ought to be resolved since the cholesteryl n-alkanoates are the most common and widely studied of all cholesterogens.

Sackmann's system of classification of liquid crystals is founded on the rule of selective miscibility[6] which has been used as the basis for our conclusions. The rule states that "all liquid crystalline modifications which exhibit an uninterrupted series of mixed liquid crystals in binary systems without contradiction can be marked with the same symbol".

Besides nematic (N) and cholesteric (Ch) liquid crystals which are miscible with each other, there are seven[6] types of smectic liquid crystal given the symbols A to G, none of which is miscible with N, or Ch, or with each other.

Certain binary mixtures were examined, using differential thermal analyses in conjunction with optical microscopy, and diagrams of state (miscibility curves) were obtained.

Miscibility studies of cholesteryl nonanoate (CN) and myristate (CM) showed that the smectic and cholesteric phases of the two were separately miscible, and also that the two phases of cholesteryl palmitate were miscible with those of CN. This shows that all smectogenic cholesteryl n-alkanoates exhibit the same smectic modification. The classification of this smectic modification was then accomplished by the following miscibility studies:—

(1) CN with n-butyl 4-(*p*-methoxybenzylideneamino)-cinnamate (I); the butyl ester exhibits[7] N, smectic A (S_A), and smectic B (S_B) phases.

(2) CN and CM with *p*-n-octyloxybenzoic acid; the acid exhibits[8] N and smectic C (S_C) phases.

(3) CN with n-pentyl 4-(*p*-n-nonyloxybenzylideneamino)-cinnamate; the pentyl ester exhibits[9] S_A, S_C, and S_B phases.

(4) CM with n-pentyl 4-(*p*-acetoxybenzylideneamino)-cinnamate; this pentyl ester exhibits N, S_A, and S_B phases.

The cholesteric phase exhibited by CN and CM was, as expected, miscible with all the nematic phases exhibited by these compounds. The smectic phase given by the cholesteryl n-alkanoates was also miscible with the S_A phases, but immiscible with the S_B and S_C phases. The other known smectic modifications can be ruled out because smectic D is optically isotropic,[6] smectic E is not miscible with either smectic phase of compound (I),[7] and smectic F and G phases always occur at temperatures below S_C;[6] such highly ordered smectics are therefore unlikely to originate from a cholesteric phase. Finally, although the elongated molecules in the S_B phase of compound (I) are perpendicular to the planes of the smectic layers, the phase is miscible with a tilted S_B.[7] Therefore the tilted S_B phase can also be discounted. Thus the smectic phase exhibited by the cholesteryl n-alkanoates must be classified as S_A in the present system.

The two smectic phases of the cholesterogen (—)-2-methylbutyl 4-(*p*-methoxybenzylideneamino)cinnamate[7] were separately miscible with the S_A and S_B phases of compound (I); the S_A phase of the (—)-2-methylbutyl ester was also miscible with the smectic phase (S_A) of CN.

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