

grams have been calculated for model systems with various values of the amphiphile length-to-width ratio r and the interaction energies ϵ_{AA} , ϵ_{AB} , etc. in an effort to elucidate more fully the molecular factors which govern the formation and stability of lipid bilayers. This basic model has been modified by allowing the amphiphilic 'r-mers' to form bilayer vesicles which can be packed on the lattice together with water molecules and individual amphiphile molecules. It is hoped that this modified model will be useful for studying the phase transition between the bilayer smectic phase and a solution of bilayer vesicles.

Unusual Mesogenic Compounds; Molecular Geometry and Stability of Ordered Fluid Mixtures

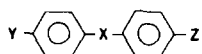
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The most known mesogenic molecules have the following structure



(calamitic molecules) conducting to nematic and smectic mesophases.

With this general scheme and particular terminal groups pure compounds exhibiting stable nematic or smectic mesophases and particular physical properties can be obtained. For example with stable free radicals we obtain mesomorphic spin labels for the structural studies by ESR technique. With a side group incorporating an appropriate heavy metal atom we obtain derivatives suitable for Mössbauer measurements.

Other mesophases can be obtained with non extended molecules: plastic crystals with globular molecules and discotic mesophases with disk-like molecules.

A simple way to study the respective stabilities of the mesomorphic and isotropic binary mixtures versus temperature and concentration is the setting of isobaric phase diagrams.

Generally two mesogenic molecules having a similar geometrical form are totally miscible in the mesomorphic states. Contrarily, two mesogenic molecules exhibiting dissimilar forms (calamitic and

globular, calamitic and disk-like, globular and discotic) are totally miscible in the liquid phase, but the common miscibilities in the partially ordered states are very small.

Relaxation Effects and Molecular Interactions

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The molecular rotational motion is one of the most important mechanisms determining relaxation of macroscopic physical properties and spectral profiles in liquid crystals. Under these circumstances, the relaxation effects are interpreted in terms of a conditional probability $P(\Omega_0; \Omega, t)$ for the change of orientation from Ω_0 to Ω . When this is assumed to occur through small angular steps, $P(\Omega_0; \Omega, t)$ is the solution of a generalized diffusion equation in which the anisotropic pseudo-potential $V(\Omega)$ responsible for the liquid crystalline ordering is introduced [1]:

$$\begin{aligned} (\partial/\partial t) P(\Omega_0; \Omega, t) = \\ -L \cdot D \cdot [L + (LV)/kT] P(\Omega_0; \Omega, t) \end{aligned}$$

where L is the operator generating infinitesimal rotations and D the diffusion tensor.

In this way, information on the long-range interactions which give rise to the orientational ordering can be obtained from relaxation experiments. As an example, it is examined the effect of a 'diffuse cone' or 'tilted' rotation [2, 3] in smectic-A mesophases on a variety of spectroscopical techniques, including NMR relaxation, ESR lineshapes, dielectric dispersion and neutron scattering. To describe the tilted rotation, the orientational potential is written as a sum of second and fourth-rank legendre polynomials:

$$V(\beta) = \alpha [P_2(\cos \beta) + \lambda P_4(\cos \beta)]$$

the parameters α and λ being adjusted to give selected order parameters \bar{P}_2 and tilt angle. With this choice $V(\beta) = V(\pi - \beta)$, as it is the case for uniaxial, non-polar mesophases. The orientational distribution function generated from this potential can give negative values for \bar{P}_4 .

The validity of the diffusional model is theoretically supported by a general memory-function approach, which also provides additional information on the short-range frictional forces. The method