2.6.12 Self-Assembled Crystalline Multilayers and Monolayers of n-Paraffins on Water Surfaces

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The n-paraffins C_nH_{2n+2} were found to spontaneous form crystalline multilayers or monolayers on water surfaces at 5° C. The alkane films were studied by pressure-area isotherms, Grazing-Incidence synchrotron X-ray Diffraction and reflectivity. The alkanes n=36, 50 form a crystalline monolayer with molecules aligned vertically in a herring-bone motif in plane group p1g1. The alkanes n=28, 29 form a similar arrangement, but two to four layers thick in orthorhombic space groups $Pbc2_1$ and Pbcm, respectively. The alkanes n=23, 24 crystallise into films about 20 layers thick, in Pbcm and (triclinic) $P\bar{1}$ space groups, respectively, as in their macroscopic crystals. With tailor made additives¹ ($C_nH_{2n+1}OH$, n = 27, 28) in the films of $C_{23}H_{48}$ and $C_{24}H_{50}$, the number of layers is reduced to two. Such multilayers may be considered as intermediates in crystallisation, where a central question concerns the structure and threshold size for molecular clusters to adopt an arrangement akin to that of the macroscopic crystal¹). The monitoring of such processes, comparable to the early stages of wax crystallisation, is of importance in the storage, transport and use of distillate petroleum fuels²).



Fig. 1. Grazing-Incidence Diffraction patterns for a) $C_{50}H_{102}$, b) $C_{24}H_{50}$, and c) $C_{24}H_{50}$ plus 10% $C_{28}H_{57}OH$.

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