Mixed Crystals of Linear Oleogelator Molecules: Existence Criteria

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Oleogels comprise an oil as a solvent, preferably trapped by solid structures which are generally crystalline. Little is known about the defects (dislocations, disclinations, etc.) in the crystals. On question is whether the gelators used need to be in the form of essentially pure crystals or whether there is any advantage in utilising solid structures involving two or more gelators: can we create mixed crystals of pairs or triplets of gelators and is this advantageous to trapping oils and exhibiting the desired mechanical properties? To answer this, we need to specify the criteria for such mixed crystals to exist. Here we consider oleogelators which comprise unbranched long hydrocarbon chains such as Triacontane (TC), Stearic acid (SA), and Behenyl Lignocerate (BL). There are three different interactions for the three molecules studied here that will lead to a monolayer formation: (1) TC, an n-alkane hydrocarbon chain, interacts only via attractive 1/r6 dispersion energies [Parsegian, 200], (2) SA which forms hydrogen-bonded dimers at the carboxylic acid end [Garti et al., 1981; Goto & Asada, 1978]. (3) BL molecules possess an ester group in its center, which exhibits non-zero partial charges which cause a pair of adjacent molecules to be repelled. The Gibbs free energy changes, ∆ = Δ - Δ1, is defined to be, ∆ = Δ - Δ1 = 30° the number of gauche excitations on a TC chain in a crystal comprising close-packed TC molecules is effectively zero. If we assume that hindered rotations of these rigid chains can be ignored, then there is only one chain state and the entropy change is ∆ = 0, so that free energy is determined by dispersion energies. In this work, we show “locked-in” configurations in accord with the calculation of Peyronel et al. (2023 to be submitted). These lock in configurations exhibit the lowest dispersion energies as shown in Fig.1. a, c, where red lines and arrows show surfaces and orientations, and the chains are shown terminated only for convenience. Cases b and c are close-packed but further apart. The tilt angles, , shown are 0° (a), and, approximately, 15° (b), 33° (c), and 43° (d). It was found that our models for TC and SA crystals predicted that the tilt angles for TC and SA dimers are ≈ 33°, with SAXS peaks at ≈ 0.195 Å-1, and at ≈ 0.159 Å-1 respectively, in acceptable agreement with the observations of ≈ 0.181 Å-1 and = 0.150 Å-1

Fig.1. Locked-in configurations (a, c) Fig.2. A: Two locked-in TC. B: TC and SA dimer. C: Locked-in TC and hypothetical chain

However, we found no SAXS evidence for the existence of crystals which comprised any two of TC, SA and BL. This was or with all three molecules (mixed crystals), and we asked ourselves why. Our answer is shown in Fig.2. There we see a pair of locked-in TC chains (A) with the surfaces shown as red lines and a tilt angle of ≈ 33°. If we try to create an analogous crystal from TC and SA molecules, however, and require that the left hand surface yields ≈ 33°, then the right hand surface will not yield a similar result (B), and it appears that a smooth surface is statistically-unlikely to form. We can, however, form a mixed crystal from chains of different lengths as shown in (C), where the long red chain is locked into the first and third TC chains, but not into the central chain. It is clear that the positions of two long chains across a repeat distance boundary need not be spatially correlated as would have to be SA dimers in analogous positions.

Experimental measurements using ultra small angle X-ray scattering showed that the crystals arising in mixed systems are smaller than those in systems with only one kind of molecule and we ascribe this to the lower concentration of molecules of each kind. This is in accord with our observation that mixed crystals are not formed.


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