

Supporting Information

1 Material and Methods

Dodecanyl succinic anhydride, which was used to synthesize ASA, and polyethylene glycol(PEG) were obtained from Sigma-Aldrich. Polyoxyethylene alkyl ether surfactants ($C_{12}EO_7$ and $C_{12}EO_9$) were from Galaxy Surfactants. The synthesis of ASA is described elsewhere [1]. The chemical structure of ASA is shown if fig.1 Small-angle x-ray scattering studies were performed using a Hecus S3-Micro system equipped with a one-dimensional position sensitive detector. Samples were taken in sealed glass capillaries and diffraction patterns were collected at temperatures between 40°C to 90°C . The microstructure of the coacervate phase was also visualized using freeze fracture scanning electron microscopy. The procedure involved exposing a freshly prepared sample into liquid nitrogen at -196°C . The frozen sample was transferred to an evacuated, low temperature preparation chamber where it was fractured, and observed on the cold stage of a scanning electron microscope (Hitachi S 4700).

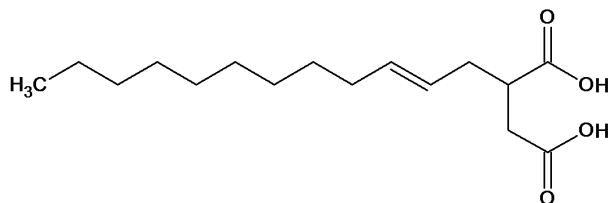


Figure 1: Chemical structure of C_{12} -alkenylsuccinic acid.

2 Estimation of the strength of the bridging interaction

The strength of the bridging interaction was estimated by equating it to the sum of all other interbilayer interactions at the observed bilayer separation, namely, van der Waal's, hydration and electrostatic. The total interbilayer interaction potential per unit area (excluding bridging) at separation z , is given by,

$$U_t(z) = U_v(z) + U_h(z) + U_e(z) \quad (1)$$

The van der Waals interaction energy, U_v can be written as,

$$U_v(z) = -\frac{H}{12\pi} \left[\frac{1}{z^2} - \frac{2}{(d_B + z)^2} + \frac{1}{(2d_B + z)^2} \right], \quad (2)$$

where H is the Hamaker constant and d_B the membrane thickness.

The hydration energy, $U_h(z)$, has the empirical form,

$$U_h(z) = A_h \exp\left(-\frac{z}{\lambda_h}\right), \quad (3)$$

where λ_h is a decay length and A_h the amplitude.

The electrostatic energy, U_e , is given by [2, 3],

$$U_e(z) = 2 \left(\frac{\sigma_o^2 \lambda_e}{\epsilon_o \epsilon_r} \right) \exp\left(-\frac{z}{\lambda_e}\right), \quad (4)$$

where σ_o is the surface charge density, λ_e the Debye length, ϵ_o the permittivity of vacuum and ϵ_r the relative permittivity of the solvent.

The pH of 20 wt% ASA solution is found to be 1.7, which corresponds to a H^+ concentration of 0.020 M or 0.022 H^+ ions per ASA molecule. The values of the surface charge density and the Debye length can then be estimated to be $\sigma_o = -1.05 \times 10^{-20} C/nm^2$ and $\lambda_e = 2.15 nm$.

Values of the other parameters used in calculation are [2]: $A_h = 0.2 J/m^2$, $\lambda_h = 0.175 nm$, $d_B = 2.88 nm$ and $H = 6 \times 10^{-21} J$.

3 Data analysis

The diffraction data were analyzed using the procedure described by Pabst et al. [4]. The scattered intensity is given by

$$I(q) = S(q)|F(q)|^2/q^2 + N_u|F(q)|^2/q^2 \quad (5)$$

where $S(q)$ is the structure factor and $F(q)$ is the form factor of the bilayers.

$F(q)$ is given by the Fourier transform of the bilayer electron density profile $\rho(z)$, which is described by two Gaussians, representing the headgroups, of width σ_H centered at $z = \pm z_H$, and a third Gaussian of width σ_C at the bilayer center ($z = 0$) representing the terminal methyl groups,

$$\rho(z) = \rho_{CH_2} + \overline{\rho_H} \left[\exp\left(-\frac{(z - z_H)^2}{2\sigma_H^2}\right) + \exp\left(-\frac{(z + z_H)^2}{2\sigma_H^2}\right) \right] + \overline{\rho_C} \exp\left(-\frac{z^2}{2\sigma_C^2}\right) \quad (6)$$

where the electron densities of the headgroup $\overline{\rho_H}$ and hydrocarbon tails $\overline{\rho_C}$ are defined relative to the methylene electron density ρ_{CH_2} .

The last term in the model eq. 1 is due to diffuse scattering from uncorrelated bilayers. Structure factor is taken according to modified Caille theory and is given by [4, 5, 6],

$$S(q) = N + 2 \sum_{k=1}^{N-1} (N - k) \cos(kqd) \times e^{-(d/2\pi)^2 q^2 \eta \gamma} (\pi k)^{-(d/2\pi)^2 q^2 \eta} \quad (7)$$

where N is the mean number of coherent scattering bilayers in the stack, γ is the Eulers' constant, and d the lamellar periodicity. The Caille parameter $\eta = q^2 k_B T / (8\pi\sqrt{KB})$, where K and B are the bending and bulk moduli of the lamellar stack, respectively. The model parameters were adjusted to get the best fit between the observed and calculated intensity. Two such fits are shown in Figure 1 in the text, for the swollen L_α^1 and the isotropic L_X phases. The values of the model parameters obtained from the best fit for the two data sets are given in the table below.

Model parameter	[C ₁₂ EO ₇]/[ASA]=0.22 $T = 80.0^\circ C$	[C ₁₂ EO ₇]/[ASA]=0.02 $T = 60.0^\circ C$
z_H (nm)	1.34 ± 0.03	1.167 ± 0.006
σ_H (nm)	0.25 ± 0.04	0.25 ± 0.01
σ_C (nm)	0.23 ± 0.08	0.37 ± 0.05
$\overline{\rho_C}/\overline{\rho_H}$	-1.4 ± 0.3	-1.46 ± 0.06
d (nm)	3.522 ± 0.007	11.67 ± 0.01
η_1	0.36 ± 0.01	0.39 ± 0.01
N	2.3 ± 0.2	9 ± 1
N_{diff}	0.43 ± 0.08	0.92 ± 0.03

Table 1: Values of the model parameters obtained from the best fit to scattering data from the isotropic L_X and the swollen L_α^1 phases, respectively.

4 Additional cryo-SEM image

Figure 2 shows a cryo-SEM image of the coacervate in the ASA-peg1500 system, which shows bilayer-like features produced presumably due to shearing of the sample during preparation. Very similar images have been reported from coacervates of other bilayer-forming amphiphile systems [7].

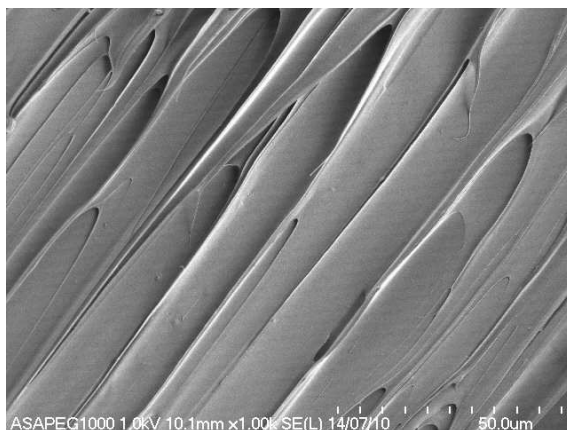


Figure 2: Cryo-SEM image of the coacervate in the ASA-peg1500 system.

References

- [1] S. G. Dastidar, P. Bharath, A. Pal and V. A. Raghunathan, *Ind. Eng. Chem. Res.* **2009** 48, 8856-8864.
- [2] J. N. Israelachvili, *Intermolecular and surface forces* (Academic press, London, 1992).
- [3] R. Lipowsky, *Z. Phys. B* **1995** 97, 193.
- [4] G. Pabst, M. Rappolt, H. Amenitsch and P. Laggner, *Phys. Rev. E* **2000** 62, 4000-4009.
- [5] R. Zhang, R. M. Suter and J. F. Nagle, *Phys. Rev. E* **1994** 50, 5047
- [6] F. Nallet, R. Laversanne and D. Roux, *J. Phys. II* **1993**, 3, 487.
- [7] F. M. Menger, A. V. Peresyphkin, K. L. Caran and R. P. Apkarian, *Langmuir* **2000**, 16, 9113-9116.