

Binding Site Matters

The binding site of inorganic salts on lecithin affects the micellar structure, which in turn alters the rheological properties of the micellar solutions.

Lecithin, a mixture of glycerophospholipids, is well known to form reverse spherical or ellipsoidal micelles in a range of slightly polar organic solvents. Previous studies have shown that the lecithin reverse spherical micelles become transformed into reverse wormlike micelles on incorporating additive molecules, such as water, bile salts, inorganic salts and others with highly polar groups, into a lecithin solution. Such a transformation is attributed to either the expansion of the lecithin head-group area on insertion of the additives or on straightening the lecithin tails that decrease the tail area through the strong additive-lecithin attraction force, both of which alter the effective molecular geometry to a critical packing parameter (CPP) that favors the formation of cylindrical micelles. The long, flexible cylindrical (wormlike) micelles thus increase the solution viscosity and even impart viscoelastic properties or further cause gelation. For small additives, such as water and inorganic salts, it is interesting that, instead of monotonic increase, the viscosity attains a maximum and then decreases until a phase separation occurs, as the additive concentration increases (Fig. 1). Although a mechanism of growth has been rationally proposed, the decreased viscosity is intriguing; the reason has been little investigated.

The team led by Shih-Huang Tung (National Taiwan University) studied the systems of lecithin mixed with inorganic salts, such as LiCl, CaCl₂, and LaCl₃, in cyclohexane and explored the mechanisms for the viscosity change with the salt concentration. Employing small-angle neutron-scattering (SANS) facility on beamline **Bilby** at the Australian Nuclear Science and Technology Organisation (ANSTO), they demonstrated that the incorporation of various inorganic salts into lecithin sols can induce both axial and radial growth of micelles that causes the viscosity to increase.¹ The team further used the small-angle X-ray scattering (SAXS) facility of **TLS 23A1** at the NSRRC to probe the micellar

structures, aiming to answer why the viscosity decreases as the salt exceeds a critical concentration. The SAXS data are consistent with the change of viscosity (Figs. 2(a) and 2(b)).² At a small molar ratio of salt to lecithin (S_0), the

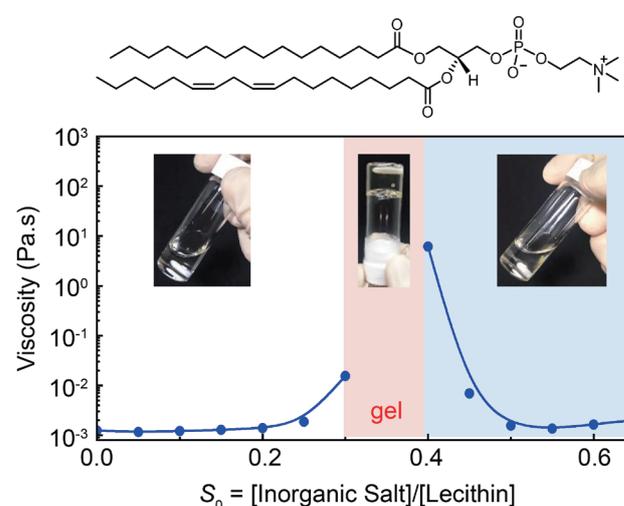


Fig. 1: Molecular structure of lecithin and viscosity of a CaCl₂/lecithin mixture in cyclohexane as a function of molar ratio. The images show the flow behaviours of the samples in various regimes. [Reproduced from Ref. 2]

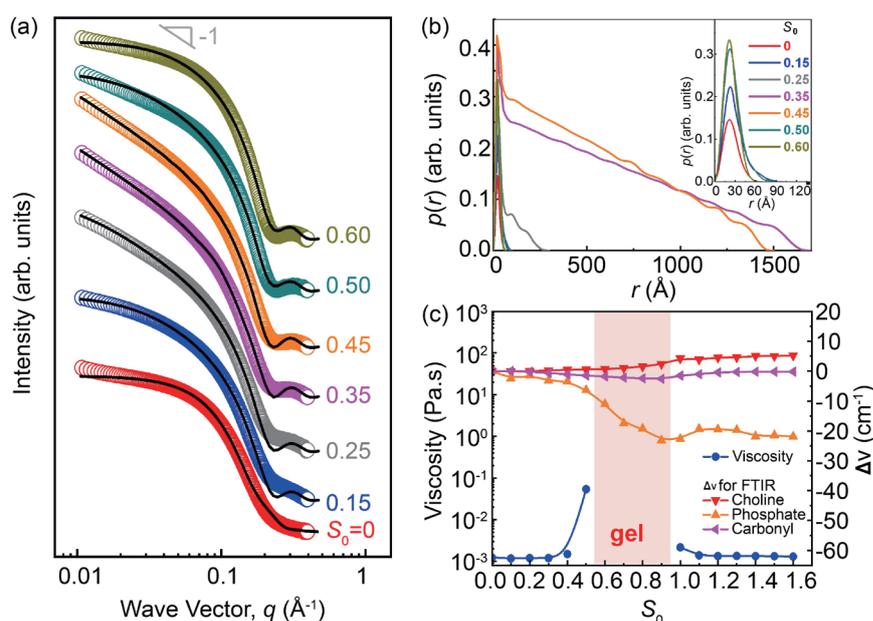


Fig. 2: (a) SAXS data of LaCl₃/lecithin in cyclohexane at lecithin concentration 20 mM with varied S_0 , (b) pair distance distribution functions $p(r)$ versus r obtained on inverse Fourier transforms (IFT) analysis of SAXS data, and (c) viscosity and FT-IR line shifts $\Delta\nu$ of choline, phosphate and carbonyl group on lecithin in cyclohexane as functions of S_0 . [Reproduced from Ref. 2]

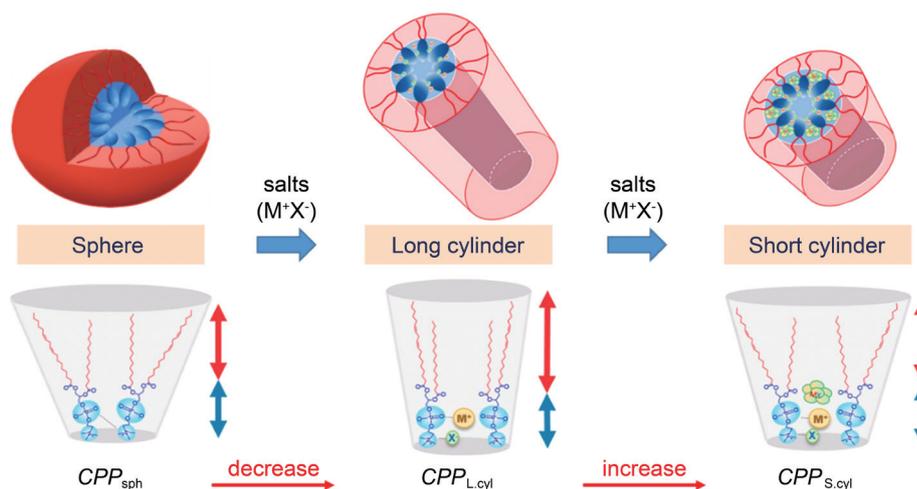


Fig. 3: Schematic of reverse micellar structures formed by lecithin with inorganic salts. The binding sites of salts on lecithin affect the effective molecular geometry and thus cause altered micellar structures. [Reproduced from Ref. 2]

shape of micelles is either elliptic or short-cylindrical, which can move freely; thus the viscosity is small. As S_0 increases, the reverse micelles grow into long, flexible cylinders that entangle one another to enhance greatly the viscosity and even lead to gelation. Above a critical S_0 , the length of micelles decreases and the viscosity decreases accordingly.

Fourier-transform infrared spectroscopy (FT-IR) techniques were utilized to investigate the interactions between inorganic salts and the functional groups on lecithin (Fig. 2(c)). The data show that the inorganic salts initially bind to the lecithin headgroup and hold lecithin more tightly through strong electrostatic interactions. The lecithin molecules are thus more straightened and more densely packed, causing a CPP change that transforms the nearly spherical micelles into cylindrical ones. Once the headgroups are saturatedly bonded with the salts, the excess salts move to the ester linkages on lecithin where they work as a spacer that separates the tails, which in turn disrupts the regular packing of the tails so that the tail area expands accordingly. The long cylindrical micelles thus break into short ones and the viscosity sharply decreases (Fig. 3). The results highlight the importance of the location of the inorganic salts on lecithin in the self-assembly of lecithin reverse micelles.

In summary, through a systematic study of the lecithin reverse worms induced by inorganic salts, the rheological properties, the self-assembled structures and the interactions between lecithin and salts were well correlated. This work manifests the crucial role of the binding site of the salts in the micellar structure and rheological behaviours of lecithin reverse micelles. Although this study focused on the reverse system, the findings in this work might be significant also for aqueous systems in which the interaction between inorganic salts and lipid bilayers is critical in physiological functions. (Reported by Shih-Huang Tung, National Taiwan University)

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TLS 23A1 Small/Wide Angle X-ray Scattering ANSTO BILBY – Small-angle Neutron Scattering

- SAXS, WAXS
- Soft Matter, Nanomaterials, Alloy

References

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2. C.-Y. Lin, S.-H. Tung, *J. Mol. Liq.* **329**, 115543 (2021).