Aggregation behavior of mannosylerythritol lipid in aqueous ethanol solutions: structural transitions and ethanol localization by SANS

T. Yoshimura, H. Takami

Nara Women's Univ.

Mannosylerythritol lipid (MEL) is a glycolipid-type biosurfactant produced by yeast, featuring a ceramide-like amphiphilic structure. It exhibits excellent surface activity, biodegradability, and skin affinity, making it suitable for cosmetic formulations. In such formulations, ethanol is frequently used as a co-solvent, which can significantly alter the aggregation behavior of amphiphiles. Despite the increasing use of MEL in ethanol-containing systems, little is known about how ethanol affects its self-assembly and the spatial distribution of ethanol within the aggregates. In this study, we examined the structural transitions of MEL aggregates in aqueous ethanol mixtures using small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), and surface activity measurements. In particular, we employed small-angle neutron scattering (SANS) with contrast matching to clarify whether ethanol is incorporated into the interior of MEL aggregates, providing new insights into the design of ethanol-based formulations.

MEL aggregation behavior was examined in H_2O/EtOH and D_2O/EtOD mixtures with varying volume ratios (H_2O:EtOH = 10:0 to 0:10) at 25 and 60 °C. The structure and size of aggregates were evaluated by SAXS and DLS. Surface activity was characterized by static surface tension and interfacial pressure measurements.

SANS measurements were conducted at SANS-U (JRR-3, Tokai, Japan) using a sample-to-detector distance of 4 m and neutron wavelength λ = 0.6 nm, covering a q-range of 0.05–2.0 nm^{-1}. To probe ethanol localization within the aggregates, contrast matching techniques were employed by varying the D_2O/H_2O ratio in the solvent and by substituting hydrogenated ethanol with perdeuterated ethanol (EtOD).

SAXS and DLS data showed that MEL forms vesicles in water-rich mixtures (10:0 to 8:2 H_2O:EtOH), spherical micelles in intermediate mixtures (7:3 to 6:4), and is molecularly dispersed in ethanol-rich conditions (5:5 to 0:10). Higher temperature (60 °C) led to reduced scattering intensity and hydrodynamic radius, indicating partial disaggregation.

In the SANS measurements, distinct changes were observed in the scattering intensity and shape across varying solvent contrasts. As D_2O replaced H_2O, scattering intensity from the aqueous phase increased due to enhanced contrast with MEL. When using deuterated ethanol (EtOD), further changes in mid-q scattering were observed, suggesting ethanol distribution inside the aggregates.

By plotting the scattering intensity at fixed q against the D_2O volume fraction, the contrast match point (CMP) was estimated. CMP shifts in the presence of EtOD indicated that ethanol is not only present in the corona or solvation layer but partially incorporated into the core region of the aggregates. The scattering curves were best fitted using a core–shell sphere model with an inner hydrophobic region partially solvated by ethanol, particularly at 6:4 and 7:3 mixtures where micelles were predominant.

These SANS findings are consistent with NOESY NMR results, where cross peaks between MEL hydrophobic chains and ethanol protons confirmed molecular-level interaction and ethanol penetration.

MEL undergoes clear structural transitions (vesicle → micelle → monomer) as ethanol content increases. SANS contrast variation and model fitting revealed that ethanol molecules are distributed not only in the shell but also inside the hydrophobic core of the aggregates. This highlights the structural plasticity of MEL in ethanol-rich environments and provides insight into designing ethanol-containing formulations with bio-derived amphiphiles.