Dual critical micelle concentration and temperature-driven structural transitions in escin aqueous solutions

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Escin, a natural saponin with a complex amphiphilic structure, exhibits rich self-assembly behavior in aqueous solution that remains only partially understood. In this work, we present a comprehensive multi-technique study of escin across a broad concentration and temperature range, combining surface tension, isothermal titration calorimetry (ITC), proton nuclear magnetic resonance (^{1}H NMR), dynamic light scattering (DLS), differential scanning calorimetry (DSC), density, and speed of sound measurements.

ITC measurements clearly identify a first critical micelle concentration (CMC_1), while the presence of a second aggregation threshold is less evident due to the low concentration regime [1]. However, surface tension measurements reveal two distinct inflection points, located at approximately 0.3 mM and 1 mM, suggesting the existence of two critical micelle concentrations (CMC_1 and CMC_2). These findings are independently supported by ^{1}H NMR chemical shift analysis, where selected proton signals exhibit concentration-dependent shifts that define distinct aggregation regimes consistent with the CMC values obtained from surface tension.

Further insight into the nature of these aggregates is obtained from DLS, DSC, density, and acoustic measurements. These techniques reveal clear differences in the thermodynamic and structural behavior of aggregates formed above CMC_1 and CMC_2. Notably, a temperature-dependent transition is observed in the range of 25–30 °C for systems above CMC_2, indicating a possible conformational or organizational rearrangement within higher-order self-assembled structures.

Altogether, our results provide strong evidence for a hierarchical self-assembly process in escin solutions, characterized by multiple aggregation thresholds and temperature-sensitive structural transitions. This work highlights the importance of combining complementary techniques to unravel the complex phase behavior of natural surfactants.

Keywords:
Escin, Saponins, Critical concentration, Self-assembly, Thermal transitions, Hierarchical aggregation

References:

[1] V. Domínguez-Arca *et al.* , Micellization thermodynamic behavior of gemini cationic surfactants. Modeling its adsorption at air/water interface, *Journal of Molecular Liquids* , **2020** , 308, 113100

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