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# Role of non-covalent interactions in the molecular organization of N-*n*-hexadecanoyl amino acid amphiphiles with hydrophobic $C_\alpha$-side chains in Tris buffer (pH 9.3)

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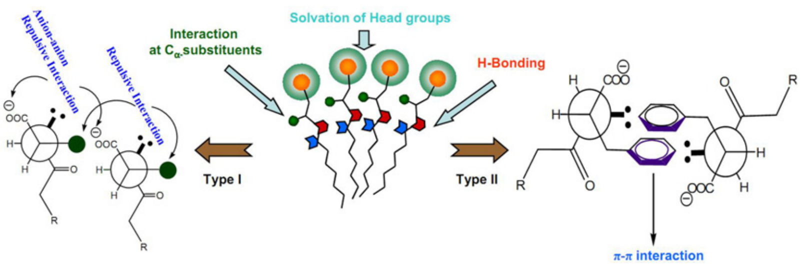
## HIGHLIGHTS

- Hydrophobicity of $C_\alpha$-substituents effectively lowers free energy of micellization.
- Strength of self assembly reduces due to repulsive interaction among $C_\alpha$-substituents.
- Amongst all, better molecular packing was observed for alanine based system.
- A fluorimetric protocol has been adopted to assess the strength of the self assemblies.
- A π–π dimer type aggregation was proposed for phenylalanine based amphiphiles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Role of non-covalent interactions on the molecular packing of N-*n*-hexadecanoyl amino acid amphiphiles (NHAA) has been studied using a set of corresponding L-amino acid (glycine, alanine, valine, proline and phenylalanine) derivatives in 50 mM Tris buffer at pH 9.3. Self-assembly properties in aqueous dispersion were characterized by various physical techniques like tensiometry, fluorimetry, UV–vis spectroscopy, circular dichroism (CD) and differential scanning calorimetry (DSC). The results reveal that the hydrophobic interaction plays the driving role for such self assembly phenomena which is synergistically influenced by additional non-covalent interactions among the surfactants arising from the amino acid units present on the molecular backbone. Despite major similarities in structural elements (except their $C_\alpha$-side chain residues) among all the NHAA amphiphiles described here, three issues were found to be important towards their self assembly properties viz, (a) optimal intermolecular distance that arises from van der Waals repulsions of the side chain residues and the electrostatic repulsions among anionic head groups; (b) intermolecular H-bonding and π–π type attractive interaction that reduces the intermolecular distance and (c) the effective solvation of the head groups required for the self assembly. Since, primary amide group is ubiquitous for all the amphiphiles except NHPro, the strength of H-bonding interaction among the amphiphiles was also investigated and found to be affected by the nature of the $C_\alpha$-side chain residues. NHPhe was found to be unique compared to others due to the π–π type attractive interaction operative at the aromatic $C_\alpha$-side chain while for others, the repulsive interactions among the $C_\alpha$-side chain residues make them behave differently. Optimized non-covalent interactions with requisite solvation of the head group, molecular packing was found to be better for NHAla, while such packing was affected by van der Waals repulsion among the bulky $C_\alpha$ substituents (e.g. isopropyl group for NHVal)

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