Relevance of hydrogen bonds in glycolipids to liquid crystals self-assembly

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Glycolipids are amphiphiles, charactreized by the presence of hydrophilic sugar head groups and hydrophobic alkyl chains. Some are amphitropic capable to form liquid crystals in dry state and when solvated. [1,2] Usually glycolipids are associated with membranes, due to the lyotropic and surfactant properties. The glycolipid self-assembly is governed by the presence of hydrophilic region due to an extensive hydrogen bonding network and is distinctly separated from that of the hydrophobic domain, largely dominated by repulsive, geometric driven interaction of the alkyl chains, often assumed to be randomly arranged giving its fluidity nature. The simplistic concept of the glycolipid self-assembly requires a systematic examination on how the complex sugar streochemical structure relates to its properties to uncover some of the driving force responsible for its formation. Detailed investigations were carried out using Density Functional Theory calculations on some glucosides in solvent phase using Polarizable Continuum Model (PCM) to investigate their electro-molecular properties. [3-5] The topological parameters of intramolecular X-H···Y hydrogen bonds (both conventional and unconventional) were analyzed and the nature of these interactions were considered using the atoms in molecules (AIM) approach. Moreover, natural bond orbital analysis (NBO) was performed to define bond orders, charge and lone pair electrons on each atom and effective non-bonding interactions. MOs analysis allowed HOMO/LUMO description of investigated isomers and led to further understanding of their behaviors. Here we discuss these computational results, especially the intramolecular hydrogen bonding and molecular electronic potential analysis, and compare to some experimental observations which are directly relevant to liquid crystal self-assembly. [6]

References

[1] Rauzah Hashim, Seyed M. Mirzadeh, Thorsten Heidelberg, Hiroyuki Minamikawa, Tanaka Yoshiaki, and Akhiko Sugimura, “A Reevaluation of the epimeric and anomeric relationship of glucosides and galactosides in thermotropic liquid crystal self-assemblies,” *Carbohydrate Research,* **346**(18), 2948–2956 (2011).

[2] Rauzah Hashim, Akihiko Sugimura, Hiroyuki Minamikawa, and Thorsten Heidelberg, “Nature-like synthetic alkyl branched chain glycolipids: a review on chemical structure and self-assembly properties,” *Liquid Crystals,* **39**(1), 1–17 (2012).

[3] Zahrabatoul Mosapour Kotena, Reza Behjatmanesh-Ardakani, and Rauzah Hashim, “AIM and NBO analyses on hydrogen bonds formation in sugar-based surfactants (α/β-D-mannose and n-octyl-α/β-D-mannopyranoside): a density functional theory study,” *Liquid Crystals,* **41**(6), 784–792 (2014).

[4] Zahrabatoul Mosapour Kotena, Reza Behjatmanesh-Ardakani, and Rauzah Hashim, Vijayan Manickam Achari, “Hydrogen bonds in galactopyranoside and glucopyranoside: a density functional theory study,” *Journal of Molecular Modeling,* **19**(2), 589–599, (2013).

[5] I. Bayach, V. Manickam Achari, W.F.N.W. Iskandar, A. Sugimura, and R. Hashim, “Computational insights into octyl-D-xyloside isomers toward understanding the liquid crystalline structure: physico-chemical features,” *Liquid Crystals,* Doi:10.1080/02678292.2016.1185173. (2016)

[6] Chia Yen Liew, Malinda Salim, N. Idayu Zahid, and Rauzah Hashim, “Biomass derived xylose Guerbet surfactants: thermotropic and lyotropic properties from small-angle X-ray scattering,” *RSC Advances,* **5**(120), 99125–99132 (2015).

Speaker Biography

Rauzah Hashim (FRSC, FASc) received B.S. degree in Chemistry with Mathematics from Southampton University in 1980, and continued to obtain a Ph.D. degree from the same University in *Computer Simulation of Liquid Crystals* under the tutelage of Prof. G. R. Luckhurst. Since 1985, she joined the Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia, where she is currently a Professor. She led two major top-down projects, the *Glycolipids Science and Technology* (2002-2006) under the Ministry of Science and Technology and Innovation and the *Fundamental Science of Self-Assembly* (2011-2016) under the Ministry of Education. She holds many important positions nationally and internationally, and recently she is the chairperson of the ACCIS 2017 and ACCMS 2017. She is an editorial board member the journal Liquid Crystals since 2013. She was awarded as the Top Research Scientist in Malaysia in 2014 from the Academy of Science Malaysia and the University of Malaya Excellence Award for Woman Scientist (2014). She is the Fellow of the Royal Society of Chemistry (UK) and the Fellow of the Academy of Science Malaysia.