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Probing The Dynamics Of Carbohydrate-Lipid Interactions In Systems

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A B S T R A C T

This paper reviews the rate at which attempts have been presented in the quantitative analyses of carbohydrate-lipid interactions. The methods which have been employed to determine these features are dependent upon expansive magnitude on the reliability, specificity and precision whereby remarkable molecular events emphasize significant complexities and integrity of molecular interactions, as they provide the latitude for aqueous miscibility and interaction sites.

Key words: *carbohydrates, lipids, interactions, systems, miscibility, aqueous*

Introduction

Carbohydrates and lipids constitute the energetic molecules, and are major ingredients of the metabolic system. Carbohydrates are the major energetic molecules which are utilised by active tissue, such as muscles, and undergo conversion to lipid molecules for storage in the adipose tissue during starvation. Carbohydrate-lipid interactions are essential attributes in the control mechanism or regulation of energy metabolic system. For instance, dietary fat class could influence glucose metabolism in salmon muscle that portends an important niche of dietary n-3/n-6 ratio in carbohydrate-lipid interactions which may be of potential significance to nutritionists in the development and improvement of energy yields in salmon feeding as a source for carbohydrates (Menoyo et al., 2005).

Thermodynamic parameters with dipalmitoylphosphatidylcholine (DPPC)

Thermodynamic analyses of carbohydrate-lipid interactions by investigating the impacts of a carbohydrate series, such as monosaccharides, disaccharides and trisaccharides on the phase-transition characteristics of aqueous dispersions of 1,2-dipalmitoyl phosphatidylcholine (DPPC) (Chen et al., 1981). The temperature of the lipid major phase transition from gel to liquid-crystalline phase is mainly unaltered in carbohydrate presence. The free energy change, delta G of the transition was observed to be zero on addition of carbohydrate to aqueous solutions in the enthalpy delta H and the entropy of the melting DPPC. The results elucidated the thermodynamic properties of carbohydrate-lipid interactions as regards specific attributes of carbohydrates in aqueous solutions and erstwhile proposed hydrophobic interaction associations with hydrocarbon tails of lipids in aqueous dispersions (Chen et al., 1981).

Investigation of the interactions of six carbohydrates, viz: trehalose, glucose, sucrose, glycerol, inositol and raffinose with dry dipalmitoylphosphatidylcholine (DPPC) was performed using differential scanning calorimetry (DSC) and infrared spectroscopy (ir) to explicate and determine the mechanism via which certain of these carbohydrates maintain the dry membranes morphological and functional integrities (Crowe et al., 1985). Findings with DPPC depicted that trehalose reduced the major transition temperature (Tmid) of dry DPPC less than that for completely hydrated DPPC, and elevated the enthalpy of that transition greater than when water was added. Findings from ir spectroscopy ostensibly depicted a potential interaction mechanism. In the presence of a majority of these carbohydrates, the ir spectrum for DPPC depicted alterations identical to those observed with the addition of water to dry DPPC, and the asymmetric P-0 stretching band became decreased in intensity. The extent to which the examined carbohydrates influenced the integrated intensity of this band and the Tmid showed direct correlation with the potential of those carbohydrates in the maintenance of dry membranes. Furthermore, in the presence of DPPC, bands ascribed to -OH deformations in trehalose and other carbohydrates were depressed. The findings suggest that the interaction mechanism between the carbohydrate and lipid is associated with hydrogen bonding between -OH groups on the carbohydrate and the phospholipid phosphate head group, excepting glycerol that depresses dry DPPC Tmid, as well as myo-inositol that presents no impact on Tmid or the DPPC ir spectrum; also, none of the carbohydrates is capable of preserving dry

membranes. Based on the ir spectroscopy and other detections on monolayer preparations, it is suggested that glycerol-phospholipid interaction is via a mechanism that differs from that presented by other carbohydrates (Crowe et al., 1985).

The influence of 0-0.1M sucrose on the phase-transition features of 1,2-dipalmitoyl-3-sn-phosphatidylcholine (1,2-DPPC) was investigated using high-sensitivity differential scanning calorimetry at 0.1km/min scan rate (Chowdhry et al., 1984). Augmenting the sucrose content resulted in a minimal but experimentally significant elevation in the temperature (Tm) of optimum excess ostensible specific heat (Cmax) and in delta T1/2 being the transition breadth at1/2 Cmax, and a slight reduction of circa 8-10% at 1.0M sucrose in contrast to 0M sucrose in the calorimetric enthalpy (delta Hcal) of the crystalline transition from gel to liquid. The calorimetric features of the 1,2-DPPC pretransition were not palpably influenced by sucrose in the examined concentration range; rather a 1.0 degree centigrade temperature Tp elevation of maximal excess ostensible specific heat in 1.0M sucrose presence was observed (Chen et al., 1981; Chowdhry et al., 1984).

The thermophilic attributes of mixtures of DPPC and natural glycosphospholipids, such as galactoglyceramide, lactosylceramide, asialo GM1, sulphatide, GM3, GM1, GD1a, GD1b in dilute aqueous dispersions were investigated using high sensitivity differential calorimetry encompassing the whole composition range. The DPPC pretransition was dissipated and the principal transition cooperativity reduced significantly at glycosphingolipid at mole fractions less than 0.2. The entire systems depicted non-ideal temperature composition phase diagrams. The mono- and di-hexosylceramides were easily miscible with DPPC when the system glycosphingolipid proportion was elevated. A minimal proportion of 1-6 molecules of DPPC per glycophospholipid molecule (GSL) was inculcated in a homogeneously mixed liquid phase. DPPC domains which were immiscible with other mixed GSL-DPPC phase that depicted negative cooperative phase were determined as DPPC was observed in excess of a determine amount in the system. A sulphatide negative charge or four asialo-GM1 neutral carbohydrate residues in the glycosphingolipid oligosaccharide chain culminated in phase diagrams depicting cooperativity of gel and liquid phases within an expansive temperature composite range. Systems having gangliosides exhibited complex phase diagrams in excess of one phase transition, with absence in phase-distinguished domains of pure gangliosides species. The thermotropic properties of systems having DPPC and glycosphingolipids correlated with their interactions in monolayers at the interface of air/water (Maggio et al., 1985).

Cyclodextrins (CDs) and DPPC liposome interactions were investigated by means of differential scanning calorimetry (DSC) (Nishijo & Mizuno, 1998). The changes in the enthalpy and phase transition temperature resulting from the gel-to-liquid of the liposome crystalline phase transition were determined respectively, in the presence of alpha-CD, beta-CD, gamma-CD, heptakis (2,3,6-tri-0-methyl_-beta-CD (TOM-beta-CD and 2-hydroxylpropyl beta-CD. The influence of the enthalpy change of the transition temperature were in the magnitude of DOM-beta-CD > alpha-CD>TOM-beta-CD. The residual CDs produced transient changes in the transition temperature and enthalpy changes. The sorts of interactions produced between CDs and DPPC were investigated to elucidate the DSC curves in the presence of the aforementioned CDs. The results showed that DOM-beta-CD produced a soluble complex whereas alpha-CD produced an insoluble complex with DPPC liposomes, with just a minute proportion of TOM-beta-CD penetrating the liposome matrix (Nishijo & Mizuno, 1998).

Investigations using 3-0-methyl-mannose polysaccharides (MMPS) and fatty acids (FAs)

The interactions of 3-0-methyl-mannose polysaccharides (MMPS) which were extracted from Mycobacterium smegmatis having a mixture of MMP-10, -11, -12, and -13 or derived by chemical synthesis as MMP-5(s), -8(s), -11(s), and naphthenic acid (NA) commercial mixture in aqueous solution at 25 degrees centigrade and pH 8.5 were quantitatively analysed by ectrospray ionization mass spectrometry (ESI-MS) (Liu et al., 2012). The association constants K(a) for MMP binding to four NAs being myristic acid, palmitic acid, stearic acid and trans-parinaric acid were determined via indirect ESI-MS assay, the "proxy protein" procedure. The K(a) values ranged from 10^4-$10^5 M^{-1}$ and, with results derived from synthetic MMP and palmitic acid binding, increased with carbohydrate size. By means of a competitive binding assay or the "proxy protein/proxy ligand" ESI-MS technique, it was demonstrated that MMPS specifically bind to NAs in aqueous solution, with ostensible affinities of circa $5x10^4$ M^{-1} for the NAs mixture examined. This demonstrated that MMPs are capable of binding to hydrophobic species which present more complexity than those having linear alkyl/alkenyl chains. Furthermore, the strategy represents a procedure to elucidate carbohydrate-lipid interactions (Liu et al., 2012).

A detailed investigation of the morphology and integrity of carbohydrate-lipid interactions was conducted using complexes of MMPs derivative and fatty acids (FAs) as model systems (Liu et al., 2016). The reliance of solution affinities and gas-phase dissociation activation energies (Ea) on FA length demonstrated a paramount feature of carbohydrate-lipid interactions in the stabilization of MMP+FA complexes. Solution 1H-NMR findings demonstrated feeble MMP methyl groups and FA acyl chain interactions, with disordered complexes as depicted by MD simulations FA methyl group contributions to the Ea was identical to n-alkane transfer heats from the gas phase to polar solvents, thus indicating that MMP binds ligands via dipole-interactions. The MD findings suggest hydrophobic interactions and H-bonds in association with the FA carboxyl group, and disordered gaseous complexes compared with collision cross sections of deprotonated MMP+FA ions with MD (Liu et al., 2016).

Stabilization of carbohydrate-phospholipid complexes

Numerous pathogen-induced potential etiologic immune responses were measured via the interaction of a virulence factor inhabiting carbohydrates with host membranes. In order to decipher the basic nature of interactions between carbohydrates and lipids in molecular recognition, certain hybrid quantum mechanics/quantum mechanics (QM/QM) scheme was employed to probe the structural basis and energetic of carbohydrate-phospholipid interactions in two disparate phospholipids (POPC and DOPC) and mannose interactions by means of density functional theory (DFT), with regard to competing interactions to water. The findings unraveled the intrinsic attributes of interactions extant between the carbohydrate and phospholipid system. The relevance of the OH…O, CH…O and CH…n interactions to stabilize the intermolecular complexes are easily observable from the findings. The measured mean interaction energies for the diverse carbohydrate-water-lipid complexes demonstrate that both mannose and water have predilection in interaction with POPC than DOPC. The invariable functions of hydrogen bonding and nonpolar interactions were detected to be relevant in the recognition and enhanced stabilization of carbohydrate-phospholipid complexes. The initial hybrid QM/QM procedure on carbohydrate-lipid interactions portrays that mannose, with phospholipid interactions could culminate in changes in charge conformations and distributions; and a comparison of these QM energies with Molecular Mechanics (MM) dependent energies for the same interactions were suggested to be of assistance in refining the all-atom carbohydrate-lipid force field (Parthasarathi et al., 2010).

Discussion and Conclusion

Macromolecules are large molecules within biosystems which play vital physiological roles in energy metabolism. They include carbohydrates, lipids, proteins and nucleic acids which display several similarities and distinct disparities. Carbohydrates and lipids are the energetic molecules, and constitute the principal components of the metabolic system. Carbohydrates are normally converted to lipid molecules to be stored in the adipose tissue during starvation. Thus, carbohydrate-lipid interactions are essential properties in the control mechanism or regulation of energy metabolic system.

This paper reviewed the rate at which attempts have been made in the quantitative and qualitative analyses of carbohydrate-lipid interactions (Havel et al., 1970). Stringent methods need to be developed and improved to determine expansively the reliability, specificity and precision wherein remarkable molecular events emphasize significant complexities and integrity of molecular interactions, as they provide the latitude for the investigation of macromolecular interaction sites.

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