

Interactions between Saccharides and Phosphate-based Salts: A Mini Review on their Physicochemical Properties

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Saccharides being integral parts of some coenzymes and nucleic acids (DNA and RNA), constitute one of the most diverse and important classes of biomolecules in nature. Saccharides are important due to their hydroxyl (–OH) rich periphery, coordination ability and stereospecificity. Oligosaccharides found on the surface of cells as part of glycoproteins and glycolipids play key roles in the control of various normal and pathological processes in living organisms such as protein folding, cell-cell communication, bacterial adhesion, viral infection, masking of immunological epitopes, fertilization, neural development and cell proliferation and organization into specific tissues. A number of important polymers which occur in living cells are composed of glucose, hyaluronic acid and other saccharides [1-4].

In the pharmaceutical and biotechnological industries, sucrose and trehalose can be used as cryoprotectants against the destabilization and degradation of enzymes and drugs during lyophilization procedures. It has been shown that salts can be used to modulate the cryoprotectant action of saccharides on biological macromolecules. This has been attributed to thermodynamic effects such as changes in saccharide hydration and changes in viscosity, diffusion and crystallization kinetics. Thus, experimental characterization of thermodynamic and transport properties of saccharide-salt aqueous mixtures is important not only for basic research, but also for applications in the biochemical and biotechnological fields [5-9].

The hydration characteristics of saccharides and their interactions with electrolytes/non-electrolytes in aqueous media are of significant biological and thermodynamic importance. The interaction between saccharides and electrolytes in aqueous solutions has been closely looked at since Angyal's [10] pioneering studies. In spite that the conformational and configurational factors, which can affect the structures of saccharides in different solvents, are very complicated, these studies are useful for examining the characteristics of carbohydrates in body fluids. The study on the interactions of various saccharides/derivatives with ions in water is useful in rationalizing their hydration

characteristics, and identifying the possible relationship between the thermodynamic parameters and the stereochemistry of solute molecules. The industrial and biological importance of phosphate systems has resulted in extensive investigations of physicochemical properties of aqueous solutions of phosphoric acid and phosphate salts.

The volumetric, viscometric and other thermodynamic data provide valuable information regarding solute-solvent/co-solute interactions. Calorimetry is a sensitive technique that gives useful thermodynamic data revealing various inter- and intra-molecular interactions. Compressibility, being a second derivative of free energy, is known to be sensitive to the nature of hydration and thus a very useful thermodynamic parameter for elucidating the behavior of a solute in solution [11-13].

The volumetric studies indicate that the hydrophilic-ionic type interactions between polar sites (–OH, –C=O, –O–) of the saccharide molecules and ions of the phosphate-based salts predominate over the hydrophobic-ionic interactions. The phosphate anions (H_2PO_4^- , PO_4^{3-}) have a great affinity for hydrogen bonding with the hydrophilic sites of the saccharide molecules. The ΔtV_2° values are higher in tribasic (K_3PO_4) salt than monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$, KH_2PO_4 and NaH_2PO_4) salts, indicating stronger interactions between the solutes and PO_4^{3-} than with H_2PO_4^- . This suggests a higher kosmotropicity of K_3PO_4 than KH_2PO_4 , NaH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ phosphate salts. This effect is attributable not only to the salts anion charge but also to the changes in pH and ionic strength. The comparison of ΔtV_2° values for saccharides in various phosphate-based salts generally

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follows the order: $K_3PO_4 > NH_4H_2PO_4 > KH_2PO_4 > NaH_2PO_4$ [14,15]. Based on the criterion used by Hepler [16]; $(\partial C^{\circ}_p, 2/\partial P)_T = -T(\partial^2 V_2^{\circ}/\partial T^2)_p$, positive $(\partial^2 V_2^{\circ}/\partial T^2)_p$ values for the saccharides indicate their kosmotropicity.

The comparison of volumetric results for saccharides in phosphate-based salts with other electrolytes generally follows the order: $C_6H_{11}O_7 < CH_3COO^- < H_2PO_4^- < Cl^- < PO_4^{3-} < SO_4^{2-} < B_4O_7^{2-}$. This trend shows the strong influence of (1:2/1:3) salts in comparison to (1:1) salts, which is in accordance with the Hofmeister series.

The viscosity B-coefficients give information about the kosmotropic or chaotropic ability of solutes. The B-coefficients of the saccharides are positive and increase in the presence of salts indicating a kosmotropic nature of the saccharides in the phosphate salts. The B-coefficients also increase with the complexity of solutes from mono- to di- to tri-saccharides, suggesting a structural enhancement in the same order. The temperature dependence of the B-coefficients gives better information about the kosmo-/chaotropic effects of salts. The negative dB/dT coefficients for the saccharides in all the phosphate salts, suggest that saccharides and their derivatives act as 'kosmotropes' in phosphate salts [17].

Calorimetric studies of saccharides in aqueous phosphate-based salts reveal that the process of titration is exothermic and the exothermicity decreases with increase in concentration of the saccharide as well as with increase of temperature except for few cases. The limiting enthalpies of dilution ($\Delta_{dil}H^{\circ}$) of the saccharides are negative. The interactions between the hydrophilic ($-OH$, $-C=O$, $-O-$) sites of the saccharide and ions ($M^+/H_2PO_4^-$, PO_4^{3-}) of the cosolute contribute exothermicity to $\Delta_{dil}H^{\circ}$ while the interactions between the hydrophobic ($R=CH$, CH_2 , CH_3) alkyl groups of the saccharide and ions of cosolute make $\Delta_{dil}H^{\circ}$ more positive (endothermicity). The observed negative $\Delta_{dil}H^{\circ}$ values suggest that hydrophilic-ionic interactions between saccharide/derivative and co-solutes predominate over hydrophobic-ionic interactions and are responsible for the overall exothermicity. The exothermicity is greater in K_3PO_4 than monobasic salts solutions due to stronger interactions of PO_4^{3-} ions with saccharides. The calorimetric results also suggest that saccharides act as kosmotropes in aqueous phosphate-based inorganic salts. The hydration numbers determined from compressibility studies are positive which indicates that phosphate salts exhibit dehydration effects. K_3PO_4 has a stronger dehydration effect than the monobasic salts [18,19].

CONCLUSION

The study of the physicochemical properties, i.e., volumetric, viscometric, calorimetric and isentropic compressibility generally suggests that saccharides and their derivatives act as kosmotropes in aqueous phosphate-based salt solutions. Also, there is strong effect of highly basic and

charged PO_4^{3-} anion in potassium phosphate tribasic salt than that of $H_2PO_4^-$ anion in monobasic salts and these follow the order: $K_3PO_4 > NH_4H_2PO_4 > KH_2PO_4 > NaH_2PO_4$.

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