Chapter 6 Thermodynamics of Carbohydrate Monomers and Polymers in Aqueous Solution

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Symbols

\begin{align*}
J: & \text{ any thermodynamic property} \\
\Delta J: & \text{ any change in a thermodynamic property} \\
J^\varepsilon: & \text{ any “excess” thermodynamic property} \\
J^0: & \text{ any thermodynamic property in a standard state} \\
\bar{J}: & \text{ any partial molal property} \\
J^\infty: & \text{ any property at infinite dilution} \\
C_p^\varepsilon: & \text{ partial molal heat capacity} \\
\Delta H^\varepsilon: & \text{ heat of formation} \\
g_r(r): & \text{ radial distribution function} \\
B^*: & \text{ second virial coefficient} \\
j_{ij}: & \text{ virial-like coefficients of the property } J \\
K_0^\varepsilon: & \text{ partial molar isoentropic compressibility} \\
\bar{\alpha}^\varepsilon: & \text{ partial molal isobaric expansibility} \\
m: & \text{ molality} \\
\phi: & \text{ osmotic coefficient} \\
R: & \text{ concentration ratio} \\
\alpha: & \text{ degree of dissociation} \\
\beta: & \text{ degree of binding (complexation, protonation)} \\
\xi: & \text{ charge density parameter} \\
k: & \text{ Debye screening parameter}
\end{align*}

1 Introduction

Carbohydrate monomers and polymers are the most ubiquitous natural products, and are the subject of expanding interest because of their physical, biochemical, and industrially useful properties. Among the known polymers, starch and cellulose are frequently cited as the two canonical examples of homopolysaccharides that display different properties due to different linkage geometry. Starch has been subjected to intensive investigation for many years, probably to a greater extent than any other biopolymer, but much of the early work is confusing and unsatisfactory to the point that in 1975 Suggett [1] wrote: “Although many volumes have been written over the years on the chemistry of starches, it is often difficult to separate scientific observations from folklore”. In the same year, a note in the J Chem Education [2] revealed that out of 22 popular organic textbooks “only four correctly stated that amylopectin is the water-soluble, and amylose the water-insoluble starch component”. The two cited examples perhaps give an idea of the difficulties in selecting good thermodynamic data in the field of carbohydrates. By and large these are due either to the inadequate sensitivity of the tech-
niques, which were developed for other polymers and then extended to carbohydrates, or to the poor chemical characterization of the materials sometimes employed with even advanced physicochemical methods.

The subtle equilibria (i.e., the mixture of several isomers) that exist in solutions of monomeric and oligomeric carbohydrates, and the unavoidable inhomogeneity of polymeric preparations have also contributed to the state of confusion. The first problem is now being solved, through the extensive theoretical and experimental studies that have established the relative stabilities, and hence the equilibrium populations, of alternative conformations and isomers [3, 4]. To overcome the second problem, one should either use standard protocols for purification, which in no way guarantees homogeneous samples [5], or establish a sample bank 1.

From the more specific thermodynamic point of view, it should also be noted that, despite their solubility in water, solutions of even simple sugars have been little studied in the past. This may be a consequence of the widely held belief that sugars form ideal solutions in water and are therefore of little interest. Whatever the reason, up until 1975, the very few thermal studies in solution were limited to the heat of solution of glucose [6, 7], isomerization equilibria [7–9] and some hydrolysis reactions of sugars [10]. The seemingly ideal behavior of aqueous sugar solution has been ascribed to the preference given to isopiestic measurements [11, 12], which provide little or no information about the properties of such solutes in dilute solution [12]. It will be shown that, in fact, many processes involving carbohydrate exhibit a wide range of ΔH values, while ΔG is nearly constant, indicating a large variety of ΔS values.

Isomeric sugar compounds are often cited as typical examples of contrasting behavior. Franks has noted that although galactaric and glucaric acids differ only in the hydroxyl configuration at carbon [3], the former is almost insoluble, while the latter is very soluble in water [13]. Although, in this example, the different stabilities of the crystal structures are more relevant than specific solvation effects (the melting temperatures are 255 ° and 125 °C, respectively), it nonetheless warns against the general tendency to relegate carbohydrate solutes to a single thermodynamic class. It is also becoming apparent that, among a great variety of hydrophilic substances, sugars may exhibit quite peculiar thermal properties. For example, the empirical scheme suggested by Wadso [14] for the estimation of $C_p^0$ values for nonionic compounds was shown to work quite well for many substances including simple hydroxyl compounds, but not for sugars. Hence the importance of direct calorimetric data for understanding solute properties and of their relation to solute structure cannot be stressed too strongly.

The scope of this review is not simply to provide tables of the (few) thermodynamic data that are available for carbohydrate systems, but also to organize them into a framework of facts from which consistent models can be derived. It has been too often repeated that thermodynamics cannot provide models, but it is incontestable that it provides data against which different models can be tested. This review, therefore, will also touch upon some of the debates in the carbohy-

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1 This need was favorably considered at the European Science Foundation (ESF) Meeting on Polysaccharides held in Uppsala, 1983.