



Simulation of the effect of hydrogen bonds on water activity of glucose and dextran using the Veytsman model



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ABSTRACT

Carbohydrates exhibit either van der Waals and ionic interactions or strong hydrogen bonding interactions. The prominence and large number of hydrogen bonds results in major contributions to phase behavior. A thermodynamic framework that accounts for hydrogen bonding interactions is therefore necessary. We have developed an extension of the thermodynamic model based on the Veytsman association theory to predict the contribution of hydrogen bonds to the behavior of glucose–water and dextran–water systems and we have calculated the free energy of mixing and its derivative leading to chemical potential and water activity. We compared our calculations with experimental data of water activity for glucose and dextran and found excellent agreement far superior to the Flory–Huggins theory. The validation of our calculations using experimental data demonstrated the validity of the Veytsman model in properly accounting for the hydrogen bonding interactions and successfully predicting water activity of glucose and dextran. Our calculations of the concentration of hydrogen bonds using the Veytsman model were instrumental in our ability to explain the difference between glucose and dextran and the role that hydrogen bonds play in contributing to these differences. The miscibility predictions showed that the Veytsman model is also able to correctly describe the phase behavior of glucose and dextran.

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1. Introduction

Carbohydrates are structurally complex food biopolymers. They exhibit van der Waals and ionic interactions as well as strong, specific interactions such as hydrogen bonds. Hydrogen bonds dominate phase behavior in many instances. An understanding of the phase behavior of mixtures of carbohydrates and the solubility of monosaccharides, oligosaccharides and polysaccharides in water is important in food science, and food product development. Phase changes include gelation, melting, crystallization and glass

transitions which affect the texture, stability, processability and shelf life of many foods.

Phase separation has been observed in several carbohydrates including dextran, starch, amylose, amylopectin, locust bean gum (LGB) and guar gum in aqueous solutions individually or in their mixtures (Kalicevsky, Orford, & Ring, 1986; Kalichevsky & Ring, 1987; Garnier, Schorsch, & Doublier, 1995; Ahmad & Williams, 2001; Zimeri & Kokini, 2003a; Zimeri & Kokini, 2003b; Zimeri & Kokini, 2003c). However, the thermodynamic basis of these phenomena are not well understood and are the object of continuous scientific debate (Icoz & Kokini, 2007a).

Hydrogen bonding plays a crucial role in determining the phase behavior of carbohydrate polymers and their miscibility/immiscibility (Icoz & Kokini, 2007a). When polymer/polymer hydrogen bonding is stronger than water/polymer hydrogen bonding, the polymer molecules aggregate and are immiscible. When the opposite happens, the polymer usually disperses in water.

Various models have been developed in order to describe bonding interactions in biopolymer mixtures (Catte, Dussap, & Gros,

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1995; Mengarelli, Brignole, & Bottini, 1999; Starzak, Peacock, & Mathlouthi, 2000; Ben Gaida, Dussap, & Gros, 2006), and also in mixtures ranging from low molecular weight molecules such as alcohols and hydrocarbons (Asprion, Hasse, & Maurer, 2001; Asprion, Hasse, & Maurer, 2003a; Asprion, Hasse, & Maurer, 2003b), to polymer blends (Coleman, Graf, & Painter, 1991; Coleman & Painter, 1995; Painter & Coleman, 2000). These approaches can be roughly subdivided into two general classes, as “chemical” and “physical”.

Physical models such as the Wilson, NRTL and UNIQUAC models treat hydrogen bonds as strong, physical interactions. They often postulate different types of hydrogen bonding locations on a molecule. The resulting set of predictive equations is usually quite complex and involves a number of adjustable parameters that need to be measured or estimated from thermodynamic data.

A chemical theory proposed by Dolezalek (1908) and later models developed by Heidemann and Prausnitz (1976) and Acree (1984) on the other hand, treat the mixture by considering the equilibrium distribution of hydrogen-bonded species. The distribution of the associated species is usually described in terms of equilibrium constants related, to the enthalpy and entropy of hydrogen-bond formation. These species are allowed to mix randomly and the physical interactions between them (e.g., dispersion forces) are described by separate parameter(s). An advantage of this approach is the separation of hydrogen bonds from van der Waals or weak polar interactions, thus accounting for their very different chemical forces and temperature dependencies: for example, dispersion forces often vary as $1/T$, while hydrogen bonds follow the van't Hoff relationship. Nevertheless, even in this approach there are still a number of unknown parameters usually obtained by a fit to thermodynamic data. Often these parameters only provide a good description of the data set from which they were obtained and have limited applicability for other even similar mixtures.

Previous work by Painter and colleagues on synthetic polymers has focused on hydrogen bonding based association models for the prediction of primarily hydrogen bonded synthetic polymer solutions and blends (Coleman et al., 1991; Coleman & Painter, 1995; Painter & Coleman, 2000). It has been shown that the contribution of hydrogen bonds to the free energy of mixing depends only on the number of hydrogen bonds of each type. One consequence of this result is that when the solvent is non-polar the equilibrium constants can be measured using FT-IR, thus reducing the number of adjustable parameters needed to describe phase behavior. It was found that group contributions to solubility parameters describing dispersion and weak polar forces, could be used in conjunction with these equilibrium constants to predict phase behavior (Coleman et al., 1991).

Initial applications of the association theory to predict phase behavior in polysaccharide blends have also been conducted. on blends formed by two dextrans of different molecular weight and inulin–amylopectin systems (Icoz & Kokini, 2007b; Icoz & Kokini, 2008). The use of the model necessitated approximations that led to semi-accurate thermodynamic predictions.

The division of approaches into “chemical” and “physical” is clearly artificial, and they simply are alternative ways of describing the same thing. This was demonstrated by Veytsman in 1990, who developed a lattice model that describes how hydrogen bonds are distributed between donor and acceptor groups. It was subsequently shown that the results obtained using association models (which can be related to Flory's lattice model) are identical to those obtained using Veytsman statistics (Coleman & Painter, 1995; Painter & Coleman, 2000). However, the latter approach is more easily and transparently applied to mixtures where the components have multiple donor and acceptor sites (Park, Veytsman, Coleman, & Painter, 2005).

In this paper, we present an extension of the Veytsman contact theory to predict the contribution of hydrogen bonds on the water activity and we developed a phase diagram for glucose–water system and the carbohydrate dextran in water. The glucose–water system was used as a simpler model to obtain the data for the modeling of the more complex dextran–water system. This enables molecular level understanding of the contribution of hydrogen bonding to the phase behavior of carbohydrate mixtures. Free energy of mixing together with its second derivative was calculated in order to predict the phase behavior of glucose water and dextran water solutions.

2. Miscibility theory

2.1. The free energy of mixing for a system involving hydrogen bonds

The free energy of mixing ΔF_{mix} for a mixture of solvent/molecules involving hydrogen bonds can be expressed as the sum of the free energy of mixing due to non-specific interactions ΔF_{NHB} , and the free energy of mixing due to hydrogen bonds ΔF_{HB} (Veytsman, 1990):

$$\Delta F_{\text{mix}} = \Delta F_{\text{NHB}} + \Delta F_{\text{HB}} \quad (1)$$

2.2. The hydrogen bonds contribution: Veytsman lattice model

In the Veytsman lattice model (1990) a single molecule of each species occupies a number of cells and has a number of H-donor and H-acceptor sites. Veytsman's combinatorial approach allows counting the number of hydrogen bonds distributed between the donor and acceptor groups in the mixture. The model assumes that a donor site of an i th kind can form an H-bond with an acceptor site of a j th kind only if the active sites occupy adjacent cells on the lattice. Such a bond is referred to as an (i and j) bond. The first index refers to the donor group and the second one to the acceptor group.

The following expression for the free energy of hydrogen bonding from the contribution of the components in a mixture is obtained (Veytsman, 1990):

$$\begin{aligned} \frac{F_{\text{HB}}}{VRT} = & \sum_{i=1}^k \sum_{j=1}^k m_{ij} + \sum_{i=1}^k n_i a_i \ln \left(\frac{n_i d_i - \sum_{j=1}^k m_{ij}}{n_i d_i} \right) \\ & + \sum_{j=1}^n n_j a_j \ln \left(\frac{n_j a_j - \sum_{i=1}^k m_{ij}}{n_j a_j} \right) \end{aligned} \quad (2)$$

The stoichiometric equations are written as:

$$m_{ij} = K_{ij} \left(n_i d_i - \sum_k m_{ik} \right) \left(n_j a_j - \sum_k m_{kj} \right) \quad (3)$$

where m_{ij} is the number of moles of (i and j) hydrogen bonds per unit volume where i is the donor group coupled with the acceptor species j ; n_i is the number of moles of reference units (molecules or monomer) of i kind per unit volume, d_i is the number of donor groups of i th kind per unit (molecule or segment), a_j is the number of acceptor groups of j th kind per unit (molecule or segment), V is the total volume of the mixture, R is the universal gas constant and T is the absolute temperature. The quantities K_{ij} are the equilibrium constants for the formation of hydrogen bonds of each type. The values n_i can be expressed through the molecular masses

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