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Theoretical analysis of predictive miscibility of carbohydrate polymers – Software calculations for inulin–amylopectin systems

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Abstract

In this paper, the quantitative understanding of predictive miscibility gained with dextrans (which was demonstrated in our earlier paper, [Icoz, D. Z., & Kokini, J. L. (2007c). Quantitative prediction of miscibility in dextran systems as model carbohydrate polymers using Painter–Coleman association model. *Carbohydrate Polymers*, doi:10.1016/j.carbpol.2007.03.012] was tested on predictive miscibility/immiscibility in inulin–amylopectin blends at limited moisture conditions. Painter–Coleman association model was used with its capability to account for hydrogen bonding interactions on predictive miscibility. Thermodynamics of mixing, including free energy of mixing and its 2nd derivative, enthalpy and entropy of mixing, and free energy of hydrogen bonding contribution were calculated. The approximate prediction rules set with dextran systems using Painter–Coleman association model (i.e., use of hydrogen bond formation of analogue compounds to approximate hydrogen bonding in carbohydrates; using the intra-molecular screening parameter of $\gamma = 0.30$; and selecting low M_w polymer as the self-associating component) was shown to successfully predict miscibility/immiscibility in inulin–amylopectin systems as an example for real carbohydrate blends.

Keywords: Predictive miscibility; Inulin; Amylopectin; Painter–Coleman association model

1. Introduction

Food materials are composed of multiple polymer molecules with different chemistry and properties, such as carbohydrates, proteins and lipids. Increasing demand for new food formulations, with reduced carbohydrate or fat content and added nutraceutical compounds to deliver healthier foods, require formulating food products to include or exclude various ingredients. The alternate ingredients in these products should successfully replace commonly used ingredients with new and improved functionalities to satisfy the consumer needs. Ingredient compatibility (or incompatibility) is critical to control the processability, texture, palatability and stability of the final food products. Often the compatibility/miscibility of a new ingredient with the formulation limits its ability to deliver highly successful products. If the conditions that favor miscibility of food biopolymers with each other could be well-understood and *predicted*, they can be successfully used in food applications and their utilization in novel food products will be enhanced. Fundamentally understanding the molecular origins of the miscibility of one polymer molecule with another and developing *a priori* thermodynamic rules for molecular miscibility will enable determination of how a set of ingredients selected will result in the quality attributes and stability needed in the final food products. Carbohydrate replacement strategies can be developed by allowing a priori selection of ingredients with desired miscibility/immiscibility, which will facilitate the process of food product development and quality improvement of foods.

Our previous studies demonstrated the application of thermodynamic models to quantitatively predict molecular miscibility in dextran mixtures at limited moisture contents as model carbohydrate mixtures. Flory–Huggins theory

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(Flory, 1952), which is based on the number of configurational arrangements and quantitative measure of weak dispersive interactions, has been shown to be unsatisfactory for predicting miscibility in dextran (glucose polymer) systems (Icoz & Kokini, 2007a). This was due to its limitation to account for specific interactions in the blends, which is important in carbohydrate systems where the repeating units consist of multiple hydroxyl groups with strong hydrogen bonding capacity. Our previous experimental studies with miscible dextran mixtures also showed changes in hydrogen-bonding distribution of pure components in the mixture, indicating the presence of hydrogen-bonding as a possible mechanism of molecular miscibility (Icoz & Kokini, 2007b). By utilizing a more advanced thermodynamic model, Painter–Coleman association model, (Coleman, Graf, & Painter, 1991; Coleman & Painter, 1995, 2006) with its capability to account for strong hydrogen bonding interactions, we have demonstrated that hydrogen bonding significantly contributed to quantitatively miscibility in carbohydrate blends (Icoz & Kokini, 2007c). By approximating hydrogen bond formation of model analogue compounds to the hydrogen bonding in dextrans, Painter–Coleman association model has been shown to improve the miscibility predictions of original Flory–Huggins theory (Icoz & Kokini, 2007c).

This paper presents an example of testing the overall understanding and learning about predictive miscibility with dextrans on real carbohydrate systems of inulin and amylopectin at limited moisture conditions. The approximate prediction rules set with dextran systems using Painter–Coleman association model was used to predict miscibility/immiscibility in inulin–amylopectin systems, which were compared to experimental miscibility results reported by Zimeri and Kokini (2003).

2. Theoretical background

2.1. Thermodynamics of mixing in polymer blends

The two thermodynamic requirements to form a single phase in a binary mixture are that; the change in free energy of mixing (ΔG_{mix}) must be negative (Eq. (1)), and the second derivative of the free energy must be positive (Coleman et al., 1991; Coleman & Painter, 1995, 2006; Sperling, 2001).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T.\Delta S_{\text{mix}} \tag{1}$$

Flory–Huggins equation (Eq. (2)) (Flory, 1952) is the most widely used model for the free energy of mixing of polymers. In its original form, this model assumes weak interactions and random mixing of segments, neglects free volume in the system, and assumes that there is no volume change upon mixing.

$$\left[\frac{\Delta G_{\text{mix}}}{R.T}\right] = \frac{\phi_{\text{A}}}{M_{\text{A}}}\ln\phi_{\text{A}} + \frac{\phi_{\text{B}}}{M_{\text{B}}}\ln\phi_{\text{B}} + \chi_{\text{AB}}.\phi_{\text{A}}.\phi_{\text{B}} \tag{2}$$

Φ is the volume fraction of each component; M is the number of polymerized segments; χ is the Flory–Huggins interaction parameter; and subscripts A and B refer to the two components in the mixture (Icoz & Kokini, 2007c; Madkour, 2001; Painter & Coleman, 1997). The first two terms on the right-hand side in Eq. (2) correspond to combinatorial entropy ("$-T.\Delta\ S_{\text{mix}}$" term in Eq. (1)), and is always favorable to mixing, but in polymer mixtures where M get large values, it is usually very small. The third term on the right-hand side of Eq. (2) corresponds to the enthalpy of mixing ("ΔH_{mix}" term in Eq. (1)) that is related to the physical forces between the components. The Flory–Huggins interaction parameter (χ) is a function of Hildebrand solubility parameters (δ) (Hildebrand & Scott, 1950) as;

$$\chi_{\text{AB}} = \frac{V_{\text{r}}}{R.T}(\delta_{\text{A}} - \delta_{\text{B}})^2 \tag{3}$$

where V_{r} is the reference volume; δ is the solubility parameter of the components; R is the universal gas constant; and T is the absolute temperature. Since χ is calculated from the square difference between the solubility parameters of the blend components A and B, the enthalpy term in Eq. (2) is always positive, opposing mixing. Solubility parameters are related to the cohesive energy density, and for polymers are usually calculated using group contribution methods based on the chemical structure of the repeating unit of the polymer (Van Krevelen & Hoftyzer, 1976; Coleman et al., 1991; Icoz & Kokini, 2007c; Painter & Coleman, 1997; Sperling, 2001).

Flory–Huggins thermodynamic model has limitations in systems with strong polar forces or specific interactions, such as H-bonds, between the components of the blends. It has been shown that the H-bonds between the components in a system may enhance the miscibility in the system through sufficient thermodynamics of interactions (Coleman et al., 1991; Coleman & Painter, 1995, 2006; Painter & Coleman, 1997; Viswanathan & Dadmun, 2002). Therefore, prediction of molecular mixing in systems with H-bond forming groups (such as carbohydrate blends) needs theoretical models that are able to include the role of H-bonds in affecting miscibility. One such quantitative framework is the Painter–Coleman association model, which builds on the conformational and configurational theories advanced by Flory–Huggins by adding a thermodynamic component that accounts for H-bonding interactions. This framework has been shown to be successful in predicting miscibility of synthetic polymers where miscibility is strongly affected by H-bonding interactions (Coleman et al., 1991; Coleman & Painter, 2006; He, Zhu, & Inoue, 2004; Kuo & Chang, 2001, 2002). According to Painter–Coleman association model, the thermodynamics of mixing two polymers with strong H-bonding interactions is calculated from (Coleman, Guigley, & Painter, 1999; Coleman & Painter, 1995, 2006);

$$\frac{\Delta G_{\text{mix}}}{R.T} = \frac{\Phi_{\text{A}}}{M_{\text{A}}}.\ln\Phi_{\text{A}} + \frac{\Phi_{\text{B}}}{M_{\text{B}}}.\ln\Phi_{\text{B}} + \chi_{\text{AB}}.\Phi_{\text{A}}.\Phi_{\text{B}}.(1-\gamma) + \frac{\Delta G_{\text{H}}}{R.T} \tag{4}$$

The first two terms on the right-hand side in Eq. (4) correspond to combinatorial entropy ("$-T.\Delta S_{\text{mix}}$" term in Eq. (1)), and the third term on the right-hand side of Eq. (4) corresponds to the enthalpy of mixing ("ΔH_{mix}" term in Eq. (1)). γ in Eq. (4) is intra-molecular screening parameter and defined as the fraction of same chain contacts that originate from polymer chain bending back upon itself through local and long-range connectivity effects. This intra-molecular screening effect is important to be included in the theoretical framework, because when a polymer chain bends back upon itself, molecular interactions would be disabled. It has been shown that value of γ between 0.25 and 0.35 gives the best comparison with the experimental results with various synthetic polymers (Coleman & Painter, 2006; Painter et al., 1997) and an average value of $\gamma = 0.30$ is being accepted for most polymer systems.

ΔG_{H} in Eq. (4) is a free energy term that imposes the constraints due to H-bonding and is a function of chemical forces that have favorable contribution to the free energy of mixing. According to Painter–Coleman association model, Flory–Huggins interaction parameter (χ) in Eq. (4) is a function of solubility parameters as in Eq. (3), but these solubility parameters are calculated from group contributions that are specifically designed to exclude the effect of specific interactions (Coleman, Serman, Bahgwagner, & Painter, 1990) because the specific interactions (H-bonding) are handled by the ΔG_{H} term (Coleman & Painter, 1995, 2006; Coleman et al., 1991). ΔG_{H} term is calculated through the determination of fraction of free and H-bonded groups in the system, and number of A–B and B–B type H-bonds in a system of components A and B, where component B has the property to self-associate (can form H-bonds in pure state), whereas component A has the property of not to form H-bonds in pure state, but can form H-bonds with component B. These quantities are determined as a function of self- and inter-association equilibrium constants determined through systematically designed infrared spectroscopy measurements (Coleman & Painter, 1995, 2006; Coleman et al., 1991).

3. Methodology

Application of the theoretical thermodynamic models (i.e., Painter–Coleman association model) for carbohydrate polymer blends would enable prediction of miscibility/immiscibility in these systems. However, there are limitations of directly applying the association model to carbohydrate systems, because the model is designed where the repeating unit of the 1st polymer (i.e. component B) has one functional group that can self-associate, and the repeating unit of the 2nd polymer (i.e., component A) has one functional group that can form H-bond with the first polymer. When there are multiple or different types of functional groups on the repeating units of the blend components (as in the case of most carbohydrate polymers; for example, biopolymers with glucose repeating unit, such as amylopectin, amylose etc.), or if both components self-associate in the pure state (which also describes the behavior in many carbohydrate polymers), then the calculation of hydrogen bonding contribution to the free energy becomes complicated (Coleman & Painter, 1995), and the association model can not be directly applied to predict miscibility. However, some approximations can be made to be able to utilize the association model to predict miscibility in carbohydrate blends. In order to demonstrate the capabilities of the model for predicting miscibility/immiscibility in food polymers, prediction approximations set with dextran systems in our previous paper (Icoz & Kokini, 2007c) has been applied to calculate thermodynamics of mixing in inulin–amylopectin systems at limited moisture environments.

3.1. Application of prediction approximations set with dextran systems to inulin–amylopectin systems

Thermodynamic calculations for predicting miscibility/immiscibility using Painter–Coleman association model (Coleman et al., 1999) in inulin–amylopectin systems was performed through "Miscibility Guide and Phase Calculator" (MG&PC) Software. The MG&PC software was kindly provided by Dr. Paul Painter of Material Science and Engineering Department at Pennsylvania State University. The software has the capabilities to calculate free energy of mixing (ΔG_{mix}) and its second derivative, entropy of mixing, enthalpy of mixing, and free energy of hydrogen bonding (ΔG_{H}) as a function of volume fraction (Φ_{B}) in Eq. (4).

One of the parameters that is required in the association model includes non-hydrogen bonded solubility parameters (δ) of both inulin and amylopectin (to be used in Eq. (3) which was then to be inserted in Eq. (4)). Amylopectin is a glucose polymer (Fig. 1), similar to dextran, with α-D-(1-4) linkages together with some α-D-(1-6) linked branches (Jacobs & Delcour, 1998; Parker & Ring, 2001). Non-hydrogen-bonded solubility parameter of the repeating unit of amylopectin (glucose) was calculated as described in Coleman et al. (1991) from group contributions. A value of 14.00 $(\text{cal/cm}^3)^{0.5}$ was calculated by dividing total molar attraction constants that exclude hydrogen bonding effects

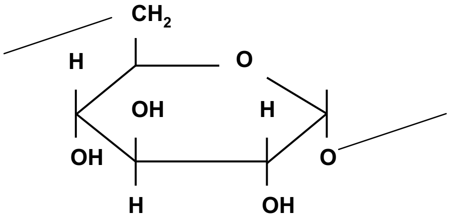

Fig. 1. Repeating unit of amylopectin.

(Coleman et al., 1990) to total molar volume of the repeating unit of the molecule ($V_m = 51.5\text{cm}^3/\text{mol}$), with the same procedure to calculate non-hydrogen-bonded solubility parameter of repeating unit of dextran (which, is also glucose) (Icoz & Kokini, 2007c). Non-hydrogen-bonded solubility parameters of amylopectin with a molecular weight (M_w) around 400,000,000 (Gluck-Hirsch, 1998) was determined as 8.99 $(\text{cal/cm}^3)^{0.5}$, following the procedure described in Icoz and Kokini (2007a, 2007c).

Inulin is a oligo-fructose with a molecular weight (M_w) around 6000. Non-hydrogen-bonded solubility parameter of its repeating unit (Fig. 2) was also determined as described in Coleman et al. (1991) from group contributions. A value of 14.4 $(\text{cal/cm}^3)^{0.5}$ was calculated by dividing total molar attraction constants that exclude hydrogen bonding effects (Coleman et al., 1990) to the corresponding total molar volume of the repeating unit ($V_m = 49.4\text{cm}^3/\text{mol}$). Using a similar procedure as that for amylopectin, non-hydrogen-bonded solubility parameter of inulin with $M_w = 6000$ was calculated as 14.26 $(\text{cal/cm}^3)^{0.5}$.

One approximation that should be made to be able to utilize the association model for carbohydrate polymers is to use model analogue compounds to approximate the H-bonding of OH groups on the repeating units of carbohydrates. Analogue compounds are small molecular weight molecules with similar chemical structure to the repeating unit of the polymer in interest. In our previous paper (Icoz & Kokini, 2007c), we have identified three analogue compounds, pentanol, phenol and dimethylphenol, whose H-bonding through their OH groups (parameters describing self- and inter-association) were previously reported by Painter–Coleman group (Coleman & Painter, 2006); and those have the closest available structure to the repeating unit of carbohydrates. It has been shown that the use of pentanol to approximate H-bonding in carbohydrates provided the best approximate miscibility predictions in dextran blends (Icoz & Kokini, 2007c), therefore, in this current paper, we have focused on the use of pentanol as the model analogue compound.

Moreover, the utilization of the association model requires that only one of the components in the system would be selected as the self-associating components in pure state, whereas the other one can form inter-molecular bonding with the first component. In our previous paper (Icoz & Kokini, 2007c), we have shown that selecting the small molecular weight component as the self-associating component provided better miscibility predictions in dextran system. Therefore, in this current paper, inulin, the smaller M_w component in inulin–amylopectin system, has been selected as the self-associating component.

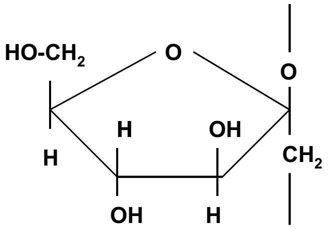

Fig. 2. Repeating unit of inulin.

Accordingly, self-association and inter-association equilibrium constants are the other required parameters in the association model to calculate the ΔG_H in Eq. (4). For molecules that self-associate, the equilibrium constants describing “di-mer” formation (2 repeating units (mers) making hydrogen bonds and forming “di-mers”) is different from that describing subsequent “multi-mer” formation (multiple repeating units (mers) making hydrogen bonds and forming hydrogen-bonded chain) (Coleman et al., 1991). Therefore, in a particular system, three equilibrium constants are needed: two for self-association (K_2 and K_B for di-mer and multi-mer formation, respectively) and one for inter-association (K_A). The self-association constants (K_2 and K_B) of the model analogue compounds selected were reported in Coleman and Painter (2006). However, recalculations were needed to be made due to the difference between the molar volume of the analogue compound and the molar volume of the repeating unit of carbohydrates. Moreover, since the system of interest was the mixtures of two carbohydrates with similar repeating units, inter-association equilibrium constant (K_A) was taken to be equal to the self-association equilibrium constant describing multi-mer formation (K_B). The details of the reported values and recalculations according to molar volumes are given in detail in Icoz and Kokini (2007c).

In our previous paper (Icoz & Kokini, 2007c), approximate prediction rules have been set to roughly but successfully predict miscibility in dextran blends (model carbohydrate systems) using the association model. In this current paper those approximations (i.e., use of hydrogen bond formation of analogue compounds to approximate hydrogen bonding in carbohydrates; having the intramolecular screening parameter as $\gamma = 0.30$; and selecting low M_w polymer as the self-associating component) have been tested on miscibility predictions of inulin–amylopectin systems as an example of ‘real’ carbohydrate polymer systems. The quantitative predictions in inulin and amylopectin systems were compared to the experimental miscibility/immiscibility reported by Zimeri and Kokini (2003).

According to Zimeri and Kokini (2003), mixed systems of waxy maize starch (WMS), which is composed of 98% amylopectin, and inulin were prepared as follows: (a) 10.5% inulin, 24.5% WMS and 65% water (w/w, w.b.), corresponding to an inulin to WMS ratio of 30:70 (% d.b.), and (b) 20% inulin, 15% WMS and 65% water (w/w, w.b.), corresponding to an inulin to WMS ratio of 60:40 (% d.b.) were mixed, dried and milled into a fine powder. Details of the sample preparation procedures can be found in Zimeri and Kokini (2003). The 30:70 and 60:40 (%, d.b.) ratios of inulin–amylopectin corresponds to volume fractions of inulin at $\Phi_B = 0.3$ and $\Phi_B = 0.6$, respectively. [The molecular weight and molar volume of the repeating unit of inulin and amylopectin are similar (Figs. 1 and 2). Volume fractions in the two-component inulin–amylopectin system were calculated similar to that in dextran–dextran system, so their volume fraction vs. %w/w component ratio was calculated to be same as given in Icoz and Kokini (2007a)]. The samples used to experimentally determine miscibility in Zimeri and Kokini (2003), which were compared to the predictive miscibility in this current paper, were obtained by equilibrating the mixed inulin–amylopectin blends at $a_w = 0.33$ and miscibility was experimentally measured by DSC through glass transition temperature determination. At this water activity (limited moisture environments with approximately 10% moisture content), it is approximated that there were only two components in the system (inulin and amylopectin, only). This rough approximation was needed because the inclusion of water into predictive miscibility framework is not possible at this point due to its complicated H-bonding capacity.

4. Results and discussion

Fig. 3 shows the predicted entropic, enthalpic and hydrogen bonding contributions to the total free energy of mixing (Eq. (4)) and its second derivative in inulin and amylopectin systems. Entropy of mixing (negative valued, favorable to mixing), calculated from the first two terms on the right-hand-side of Eq. (4), took very small values (Fig. 3a) (almost equal to zero) over the entire volume fraction range due to the very high molecular weight of components, particularly amylopectin. Enthalpy of mixing, calculated from the third term on the right-hand-side of Eq. (4), took large positive values (Fig. 3a), which was unfavorable to mixing. It was calculated from the square of the difference between the non-hydrogen bonded solubility parameters (δ) (Eq. (2)). The difference between δ of inulin and amylopectin

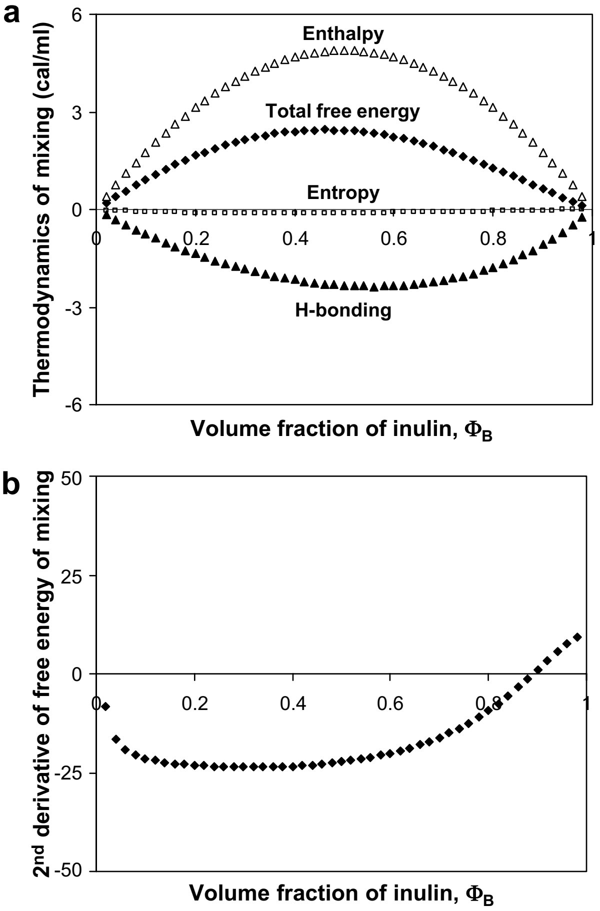

Fig. 3. Predicted miscibility of inulin and amylopectin at 25 °C when H-bonding of pentanol OH was approximated for H-bonding in carbohydrates; (a) entropic, enthalpic, and H-bonding contributions to the total free energy of mixing; (b) 2nd derivative of free energy of mixing ($\gamma = 0.30$).

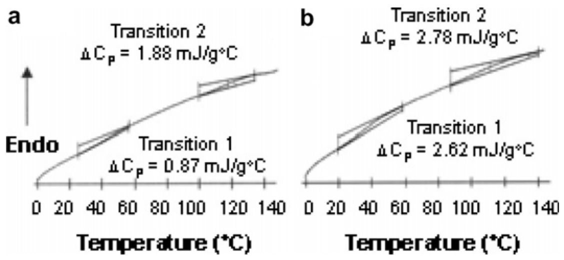

Fig. 4. DSC rescans of mixed inulin-amylopectin systems stored at $a_w = 0.33$ for inulin to amylopectin ratio of; (a) 30:70; and (b) 60:40 (%, d.b.) (Reprinted from Zimeri, J. E., & Kokini, J. L. (2003). Copyright (2003), with permission from Elsevier).

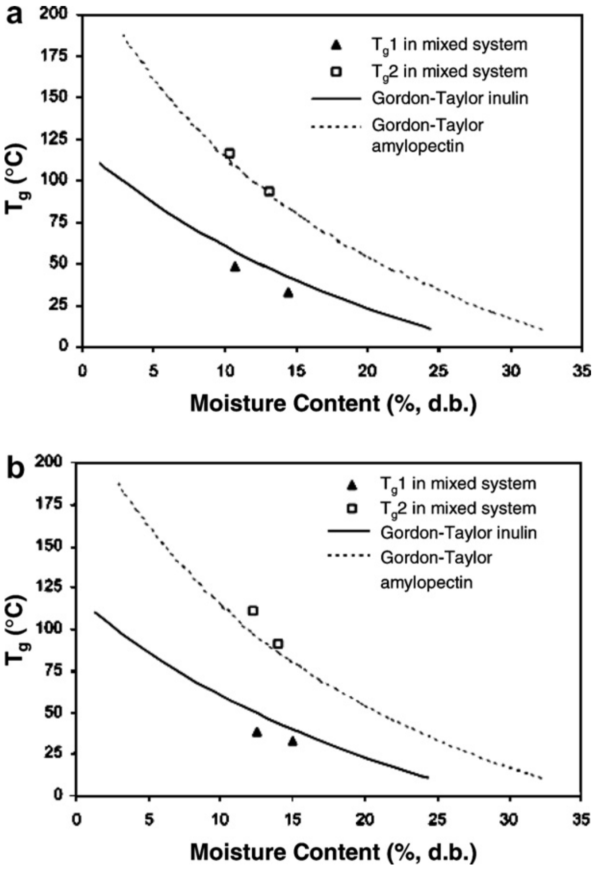

Fig. 5. Two glass transition temperatures in mixed samples containing inulin to amylopectin ratio of (a) 30:70 and (b) 60:40 (%, d.b.) (Reprinted from Zimeri, J. E., & Kokini, J. L. (2003). Copyright (2003), with permission from Elsevier).

[14.26 and 8.99 $(\text{cal/cm}^3)^{0.5}$, respectively] was higher than the difference between δ of dextrans with $M_w = 1{,}000$ and $M_w = 2{,}000{,}000$ [13.10 and 9.40 $(\text{cal/cm}^3)^{0.5}$, respectively] (presented in Icoz and Kokini (2007c)). Therefore, a higher positive valued enthalpic contribution was calculated for inulin–amylopectin systems compared to that for dextran systems (Icoz & Kokini, 2007c).

In Fig. 3a, H-bonding in inulin–amylopectin system was approximated from H-bond formation of pentanol OH, which was shown to be the most accurate model analogue compound for H-bonding in dextrans (Icoz & Kokini, 2007c). Negative H-bonding contribution was calculated, as shown in Fig. 3a. However, positive valued, unfavorable enthalpic contribution overwhelmed the negative valued, favorable H-bonding contribution. As an overall summation of all these individual contributions, the total free energy of mixing was calculated to be positive over the entire volume fraction range for inulin–amylopectin systems (Fig. 3a). Second derivative of free energy of mixing also had negative values for volume fraction of inulin at $\Phi_B < 0.9$ (Fig. 3b); overall indicating *immiscibility predictions in inulin–amylopectin systems at all compositions in limited moisture contents.*

These predictive results can be compared to the experimental miscibility result presented in Zimeri and Kokini (2003). Fig. 4 shows the DSC thermograms of mixed inulin–amylopectin systems with 30:70 and 60:40 (%, d.b.) ratios of components. In the thermograms, there were two independent reversible endothermic transitions (Fig. 4). Fig. 5 shows glass transition temperature (T_g) vs. moisture content for inulin–amylopectin systems stored at $a_w = 0.33$ (~11% moisture) and $a_w = 0.52$ (~14% moisture) that were mixed at 30:70 and 60:40 ratios of inulin:amylopectin. In Fig. 5, the lines are the Gordon–Taylor plots for pure inulin and pure amylopectin, whereas the data points of double $T_g s$ in mixed inulin–amylopectin systems are shown with symbols. Fig. 5 shows that transition 1 (T_g1) occurred at the same temperature as T_g of pure inulin, whereas transition 2 (T_g2) occurred at the same temperature as T_g of pure amylopectin. Overall, these results experimentally indicated that there was double glass transition temperature behavior in mixed inulin–amylopectin systems at limited moisture environments, indicating immiscible systems.

30:70 ($\Phi_B = 0.3$) and 60:40 ($\Phi_B = 0.6$) ratios of inulin:amylopectin systems were the only two data points

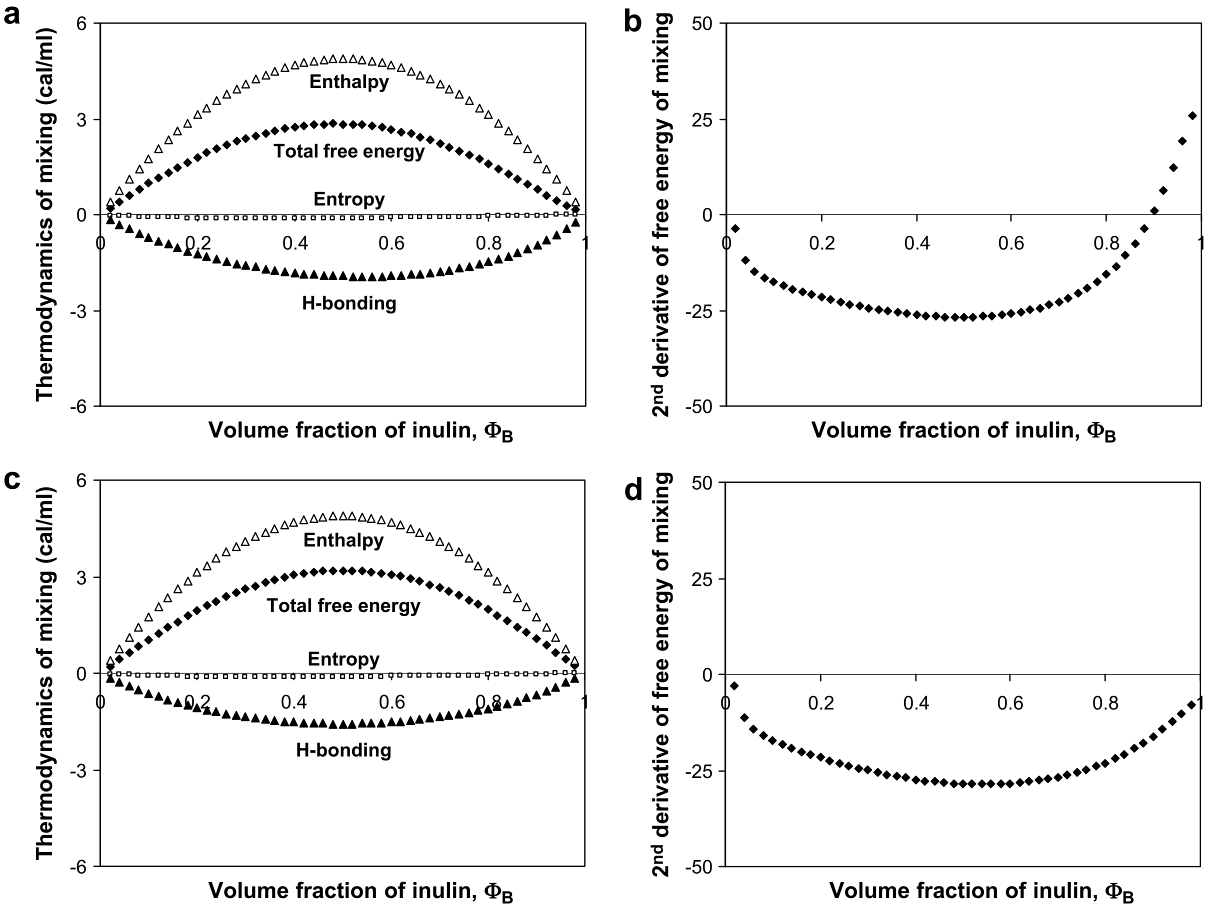

Fig. 6. Predicted miscibility of inulin and amylopectin at 25 °C when H-bonding of (a–b) phenol OH; (c–d) dimethylphenol OH was approximated for H-bonding in carbohydrates [(a–c) entropic, enthalpic, and H-bonding contributions to the total free energy of mixing; (b–d) 2nd derivative of free energy of mixing; and $\gamma = 0.30$].

reported in Zimeri and Kokini (2003) in limited moisture environments that would be suitable to compare miscibility predictions to experimental miscibility values. Together with the overall results presented in Zimeri and Kokini (2003), these specific data provided information that *inulin and amylopectin systems were experimentally immiscible at limited moisture contents.*

These results indicates that the approximate prediction rules set with dextran systems (model carbohydrates) using Painter–Coleman association model (i.e., use of pentanol as the analogue compound; accepting a value of $\gamma = 0.30$ for intra-molecular screening; and selecting low M_w polymer as the self-associating component) were also suitable to approximately predict miscibility/immiscibility in inulin–amylopectin systems as an example for real carbohydrate blends. Because theoretical predictions show immiscibility at all component ratios for inulin–amylopectin systems, and experimental miscibility results (Zimeri & Kokini, 2003) also show immiscibility for the same system.

Fig. 6 shows the similar predictions when phenol and dimethylphenol were used as the model analogue compound to approximate H-bonding in carbohydrates. These also show immiscibility over the entire volume fraction range in inulin–amylopectin systems. Because when phenol or dimethylphenol was used as analogue compounds, H-bonding contribution was less than the contribution when pentanol was used (Icoz & Kokini, 2007c). Therefore, the positive valued large contribution from the enthalpic term also overwhelmed H-bonding contributions when these analogue compounds were used, resulting in immiscibility predictions (Fig. 6).

In order to hypothetically demonstrate in what H-bonding extent inulin and amylopectin would be theoretically predicted to be miscible, Fig. 7 shows the effect of the value of inter-association equilibrium constant (K_A) relative to self-association equilibrium constants (K_2 and K_B) on H-bonding contribution and the resulting overall free energy of mixing. Only H-bonding contribution and total free energy were demonstrated in Fig. 7a and b, respectively, since entropic and enthalpic contributions to free energy would be the same as in Fig. 3a (calculated from Eq. (4)). In Fig. 7, pentanol was used as the best available model analogue compound for describing hydrogen bonding in carbohydrates with $K_2 = 51.6$, $K_B = 85.6$ and $K_A = 85.6$ (Icoz & Kokini, 2007c). When K_A was hypothetically given values of $K_A = 100$ and $K_A = 150$ (which were much higher than the actual value of $K_A = 85.6$, which also means higher inter-association between different components than self-association in pure state), H-bonding contributions got higher negative values (Fig. 7a) than the one in Fig. 3a (when $K_A = 85.6$); free energy of mixing and its 2nd derivative were calculated to be negative (Fig. 7b) and positive (Fig. 7c), respectively, still predicting completely immiscible systems. When hypothetically $K_A = 200$, H-bonding contribution increased more (Fig. 7a) and some miscibility prediction (partial positive and negative free energy of mixing and its second derivative) was started to be observed over the composition range. When hypothetically $K_A > 250$, H-bonding contribution could partially overcome the positive valued, unfavorable enthalpic contribution (Fig. 3a), resulting in mostly miscible systems (Fig. 7b and c). When hypothetically

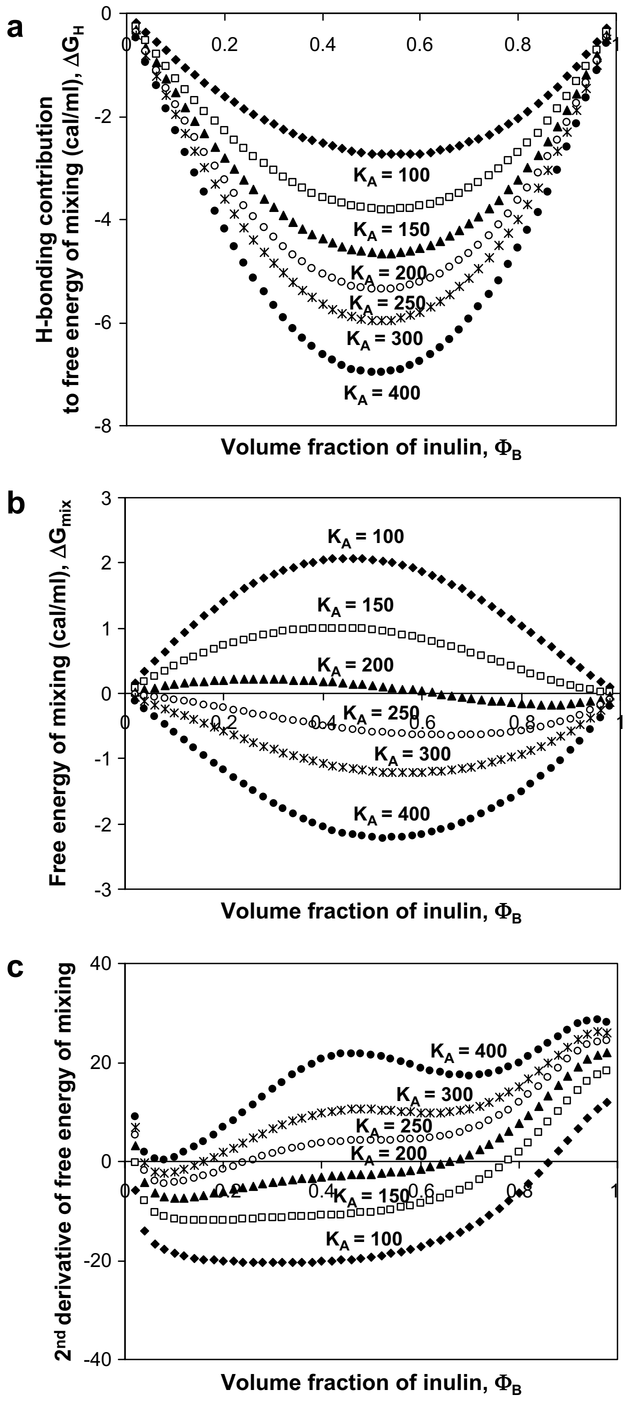

Fig. 7. Effect of the value of inter-association equilibrium constant (K_A) relative to self-association equilibrium constants (K_2 and K_B) on; (a) H-bonding contribution; (b) total free energy of mixing; (c) 2nd derivative of free energy of mixing inulin and amylopectin at 25 °C (H-bonding of pentanol OH was approximated for H-bonding in carbohydrates; and $\gamma = 0.30$).

$K_A = 400$ (when inter-association was chosen to be almost five times higher than self-association), then miscible inulin–amylopectin systems were predicted over the entire volume fraction range (Fig. 7b and c). This hypothetical analysis demonstrates that the thermodynamic effect from negative valued (favorable) H-bonding needs to be very large to overcome the large positive valued (unfavorable) enthalpy of mixing contribution.

5. Conclusions

The overall quantitative understanding of miscibility with dextrans as model carbohydrate systems was tested to predict miscibility in inulin–amylopectin as an example of ‘real’ carbohydrate systems at limited moisture conditions. The approximate prediction rules set with dextran systems using Painter–Coleman association model was shown to be suitable to roughly predict miscibility/immiscibility in real carbohydrate polymer systems. It should be kept in mind that Painter–Coleman association model has its own limitations to be totally accurately applicable to carbohydrate polymer blends and also to systems involving significant amount of water. New thermodynamic models are needed to be developed that can account for the structural complexities of carbohydrates, including the presence of multiple hydrogen bonding groups, and then, the role of significant amount of water should be included in these thermodynamic models. But it should also be emphasized that the understanding gained in these analyses is a significant step towards choosing which ingredients in a food formulation would form the desired miscible/immiscible systems on a predictive basis that will enable faster product development decisions and will increase the utilization of alternative agricultural ingredients in various food products with new functionalities.

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