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Carbohydrate Polymers 70 (2007) 181–191
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Quantitative prediction of molecular miscibility in dextran systems as model carbohydrate polymers

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Received 20 February 2007; accepted 23 March 2007
Available online 30 March 2007

Abstract

This paper demonstrates the application of an advanced thermodynamic model to quantitatively predict molecular miscibility in model carbohydrate mixtures. It adds onto our previous paper on application of original Flory–Huggins theory that did not enable successful prediction of miscibility in dextran systems. In the current paper, Painter–Coleman association model was examined with its capability to account for strong hydrogen-bonding interactions on miscibility. Thermodynamics of mixing (free energy of mixing and its 2nd derivative, enthalpy and entropy of mixing, free energy of hydrogen-bonding contribution) were calculated using Miscibility Guide and Phase Calculator Software. It was quantitatively demonstrated that hydrogen-bonding significantly contributed to predictive miscibility in carbohydrate blends. When hydrogen bond formation of pentanol (an analogue compound for which hydrogen-bonding was previously characterized by Painter–Coleman group) was approximated to the hydrogen bond formation in dextrans, miscibility was successfully predicted. The generated knowledge is a step forward for understanding the thermodynamic basis for miscibility/immiscibility in carbohydrate polymer blends.

Keywords: Predictive miscibility; Carbohydrate polymer; Painter–Coleman association model

1. Introduction

Most food materials are composed of multiple polymeric molecules with different chemistry and properties. As the consumer is demanding more functional and healthier foods, new ingredients are emerging to deliver the new functionalities that are needed. In addition, the demand for foods with reduced fat or carbohydrate content requires formulations that include or excludes various ingredients. The alternate ingredients in these products should successfully replace commonly used ingredients with new and improved functionalities to satisfy the consumer needs. The process conditions, final texture, sensory quality and shelf-life stability of the final food products are greatly influenced by the interactions and miscibility/immiscibility between the polymeric components in the food formulations. Often the immiscibility and/or incompatibility of the added polymeric ingredients with the rest of the formulation limit their ability to deliver highly successful products. If the conditions that result in miscibility/immiscibility between the food biopolymers could be well-understood and *predicted*, their utilization in food products will be enhanced. Moreover, developing quantitative predictive rules for miscibility of food biopolymers would enable prior determination of how a set of ingredients selected would result in the quality attributes and stability needed in final food products.

Phase separation of food polymers can lead to texture defects during processing and storage. Morphology of the hetero-phase food systems, adhesion between phases, phase volume ratio and their mechanical and other physical properties play an important role in the final quality of the products. Molecular incompatibility in carbohydrate–protein systems manifests itself in phase separation. This is

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doi:10.1016/j.carbpol.2007.03.012

mainly due to the molecular size and hydrophilicity/hydrophobicity differences resulting from very different macromolecular chemistry, molecular conformation and affinity for water (Grinberg & Tolstoguzov, 1997; Michon, Buvelier, Launay, Parker, & Takerkart, 1995; Moraru, Lee, Karwe, & Kokini, 2002; Tolstoguzov, 1991, 1998, 2000, 2003). Immiscibility also occurs in carbohydrate–carbohydrate mixtures despite their apparently compatible chemical structures (Ahmad & Williams, 2001; Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Garnier, Schorsch, & Doublier, 1995; German, Blumenfeld, Guenin, Yuryev, & Tolstoguzov, 1992; Kalichevsky & Ring, 1987; Kalichevsky, Orford, & Ring, 1986; Zimeri & Kokini, 2003a, 2003b, 2003c). The molecular and thermodynamic bases of these phenomena are still the focus of scientific debate. A set of quantitative predictive rules are needed to be developed, which would enable ingredient replacement strategies by allowing a priori selection of carbohydrate ingredients with desired miscibility/immiscibility and would facilitate the process of food product development and quality improvement of foods.

Our previous studies with miscible dextran (glucose polymer) mixtures showed changes in hydrogen-bonding distribution of pure components in the mixture, indicating the presence of inter-molecular hydrogen-bonding as a possible mechanism of molecular miscibility (Icoz & Kokini, 2007a). We have also shown that the quantitative thermodynamic ideas based on the role of the number of configurational arrangements and quantitative measures primarily based on dispersive interactions (Flory–Huggins theory) were not sufficient to quantitatively predict the miscibility of even simple carbohydrate polymers (Icoz & Kokini, 2007b). The reason for this failure is due to the limitation of these ideas by underestimating the effect of specific bonding interactions, such as hydrogen bonds, in these systems. Most carbohydrate polymers have structural groups that can form hydrogen bonds. Therefore, prediction of molecular mixing needs thermodynamic models which can include the role of hydrogen bonds in affecting miscibility. One such quantitative framework is the Painter–Coleman association model, which builds on the conformational and configurational theories by Flory–Huggins by adding a thermodynamic component that accounts for hydrogen bonding interactions (Coleman & Painter, 1995, 2006; Coleman, Graf, & Painter, 1991). This framework has been shown to be successful in predicting miscibility in synthetic polymers, where miscibility is strongly affected by hydrogen bonding interactions (Coleman & Painter, 1995, 2006; Coleman et al., 1991; He, Zhu, & Inoue, 2004; Kuo & Chang, 2001, 2002; Painter & Coleman, 1999; Viswanathan & Dadmun, 2002).

This paper presents the application of Painter–Coleman association model to quantitatively predict miscibility/immiscibility in carbohydrate biopolymers using dextrans as model systems. Approximations were made to be able to utilize the model and thereof bring its capabilities to carbohydrate polymer science. The effects of critical parameters necessary for the theoretical model were demonstrated. Applicability and limitations of the model for carbohydrate polymers and accuracy of the predictions were also discussed.

2. Theoretical background

2.1. Thermodynamics of mixing in polymer systems

There are two thermodynamic conditions necessary to form a single phase in a binary mixture: the change in free energy of mixing (ΔG_{mix}) must be negative (Eq. (1)), while the 2nd derivative of the free energy must be positive (Coleman & Painter, 1995, 2006; Coleman et al., 1991; Icoz & Kokini, 2007b; Sperling, 2001).

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T \cdot \Delta S_{\mathrm{mix}} \tag{1}$$

The most widely used model for the free energy of mixing of polymers is the Flory–Huggins equation (Flory, 1952), which in its original form assumes weak interactions and random mixing of segments. The theory also neglects free volume in the system and assumes there is no volume change upon mixing. The general expression of Flory–Huggins theory for the free energy of mixing two polymers is given as;

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

where 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, 2007b; Madkour, 2001; Painter & Coleman, 1997). The first two terms on the right-hand side in Eq. (2) correspond to combinatorial entropy (representing the term "$-T \cdot \Delta S_{\mathrm{mix}}$"). This is always favorable to mixing with negative values, but in polymer mixtures where M gets large values, it is usually very small. The third term on the right-hand side of Eq. (2) corresponds to the enthalpy of mixing (representing the term "ΔH_{mix}") that is related to the physical forces between the components. The Flory–Huggins interaction parameter (χ) is a function of Hildebrand's widely used solubility parameters (δ) (Hildebrand & Scott, 1950) as;

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

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 proportional to the square of the difference between the solubility parameters of the blend components, 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 (Coleman et al., 1991; Icoz & Kokini, 2007b;

Painter & Coleman, 1997; Sperling, 2001; Van Krevelen & Hoftyzer, 1976).

2.2. Painter–Coleman association model

The major assumption of the original Flory–Huggins theory is that the two polymers mix randomly. However, this assumption does not hold when there are strong polar forces or specific interactions, such as hydrogen bonds, between the components of the blends. The presence of hydrogen bonds between components (inter-molecular interactions) would enhance their miscibility by creating sufficient thermodynamics of interactions (Coleman & Painter, 1995, 2006; Coleman et al., 1991; Painter & Coleman, 1997; Viswanathan & Dadmun, 2002). It should also be mentioned that although the formation of hydrogen bonds could result in a favorable change in enthalpy, they also impose constraints on orientational and translational degrees of freedom which affect the entropy change on mixing (Coleman & Painter, 1995, 2006; Coleman et al., 1991; Viswanathan & Dadmun, 2002).

The extent of inter-molecular hydrogen bonding between two polymers depends on many parameters. If one or both of the polymers have intra-molecular hydrogen bonding in pure state, also called “self-association”, then the number of possible inter-molecular hydrogen bonding will be limited (Coleman et al., 1991; Viswanathan & Dadmun, 2002). Another important factor is that a flexible chain can bend back upon itself to avoid inter-molecular interactions, called “intra-molecular screening” (Coleman, Guigley, & Painter, 1999; Painter, Berg, Veytsman, & Coleman, 1997a; Painter et al., 1997b; Viswanathan & Dadmun, 2002). The accessibility of the functional groups that can form inter-molecular interactions is another determinant factor for the extent of the inter-molecular hydrogen bonding. For instance, increasing spacing between functional groups on a chain increases the amount of inter-molecular hydrogen bonding, where the optimum spacing is system dependent (Coleman, Pehlert, & Painter, 1996; Viswanathan & Dadmun, 2002). Steric crowding of hydrogen-bonded groups, due to limited spacing between the functional groups, also affects the extent of inter-molecular interactions between the polymer chains (Pehlert, Painter, & Coleman, 1998; Viswanathan & Dadmun, 2002).

Painter–Coleman group (Coleman & Painter, 1995, 2006; Coleman et al., 1991) have developed an association model approach for thermodynamics of mixing two polymers that have strong molecular interactions and suggested adding a free energy of hydrogen bond formation term into the Flory–Huggins expression in Eq. (2) as;

$$\frac{\Delta G_{\mathrm{mix}}}{R\cdot T}=\frac{\Phi_{\mathrm{A}}}{M_{\mathrm{A}}}\cdot\ln\Phi_{\mathrm{A}}+\frac{\Phi_{\mathrm{B}}}{M_{\mathrm{B}}}\cdot\ln\Phi_{\mathrm{B}}+\chi_{\mathrm{AB}}\cdot\Phi_{\mathrm{A}}\cdot\Phi_{\mathrm{B}}+\frac{\Delta G_{\mathrm{H}}}{R\cdot T}\tag{4}$$

where ΔG_{H} is a free energy term that imposes the constraints due to hydrogen bonding and represents chemical forces that have favorable, negative valued contribution to the free energy of mixing. The most extensively studied mixtures in Painter–Coleman association model are the mixtures where the first component self-associates (i.e., has functional groups, such as –OH, that can hydrogen bond to one another in the pure state), while the second component does not self-associate, but has a functional group that can form hydrogen bonds with the first component. When a self-associating polymer is mixed with a non-self-associating polymer, free energy can be gained from the balance between breaking hydrogen bonds between “like” molecules and forming hydrogen bonds between “unlike” ones (Coleman et al., 1991). Hydrogen bonds are in a dynamic equilibrium state and exist as distribution of non-hydrogen-bonded (‘free’) and hydrogen-bonded species at any instant at a given temperature and concentration (Coleman & Painter, 1995). Accordingly, the free energy of hydrogen bond formation in the mixture can be described as;

$$\frac{\Delta G_{\mathrm{H}}^{*}}{R\cdot T}=n_{\mathrm{A}}\ln\frac{\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}+n_{\mathrm{B}}\ln\frac{\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}+n_{\mathrm{BB}}^{\mathrm{h}}+n_{\mathrm{AB}}^{\mathrm{h}}\tag{5}$$

where n_{A}, n_{B} are the number of A and B type segments; $\Phi_{\mathrm{A}_1}/\Phi_{\mathrm{A}}$, $\Phi_{\mathrm{A}_1}/\Phi_{\mathrm{B}}$ are the fractions of ‘free’ (non-hydrogen-bonded) A and B segments; and $n^{\mathrm{h}}_{\mathrm{BB}}$, $n^{\mathrm{h}}_{\mathrm{AB}}$ are the number of B–B and A–B hydrogen bonds, respectively. Similar equations for the free energy of hydrogen bonding in the pure components ($\Delta G^{0}_{\mathrm{H}}RT$) is subtracted from Eq. (5) to get the final contribution of hydrogen bonding to the free energy of mixing ($\Delta G_{\mathrm{H}}/RT$). The fraction of ‘free’ and hydrogen-bonded groups is determined as a function of self- and inter-association equilibrium constants that are determined through systematically designed infrared spectroscopy measurements (Coleman & Painter, 1995, 2006; Coleman et al., 1991).

One significant factor that affects the magnitude of ΔG_{H} is the relative magnitudes of self-association vs. inter-association. In general, if inter-association between two different components is more favorable than self-association within the pure components, then this trend is favorable for miscibility. The magnitude of ΔG_{H} also depends on the number of specific interaction sites per unit volume of the blend. For example, if the number of specific interaction sites per unit volume is decreased in a system, this would result in lower ΔG_{H} in the system compared to the original state (Coleman & Painter, 1995; Coleman et al., 1991).

According to the association model, non-specific interactions should be handled by solubility parameters calculated from group contributions that are specifically designed to exclude the effect of specific interactions (Coleman, Serman, Bahgwagner, & Painter, 1990). Because the effect of specific interactions (i.e., hydrogen bonding) is included in ΔG_{H} term in Eq. (4) (Coleman & Painter, 1995, 2006; Coleman et al., 1991). Therefore, the third term on the right-hand side of Eq. (4) is calculated from solubility parameters excluding the effect of specific interactions between components and will still have unfavorable, positive valued contribution to the free energy of mixing, because it is calculated from the square of the difference between the solubility parameters of the components (Eq. (3)).

2.2.1. Intra-molecular screening parameter

Painter–Coleman group have shown that intra-molecular screening is a significant effect in miscibility predictions (Coleman & Painter, 2006; Coleman et al., 1999; Painter et al., 1997a, 1997b). It is a consequence of chain connectivity in polymers: the covalent linkages between the polymer segments result in an increase in the number of same-chain contacts over that calculated on the basis of a simpler random mixing of segments. Because the chain can bend back upon itself both locally and through long-range effects, which may disable hydrogen bonding functional groups and consequently decrease the number of possible inter-molecular interactions (Coleman & Painter, 2006). The association model is modified by Painter–Coleman group to include this effect as;

$$\frac{\Delta G_{\mathrm{mix}}}{R \cdot T} = \frac{\Phi_{\mathrm{A}}}{M_{\mathrm{A}}} . \ln \Phi_{\mathrm{A}} + \frac{\Phi_{\mathrm{B}}}{M_{\mathrm{B}}} \cdot \ln \Phi_{\mathrm{B}} + \chi_{\mathrm{AB}} \cdot \Phi_{\mathrm{A}} \cdot \Phi_{\mathrm{B}} \cdot (1 - \gamma) + \frac{\Delta G_{\mathrm{H}}}{R \cdot T} \tag{6}$$

where γ 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. It should be emphasized that incorporating the intra-molecular screening parameter (γ) not only modifies the enthalpic term (3rd term on right-hand side) in Eq. (4), but also modifies the free energy of hydrogen bonding term ($\Delta G_{\mathrm{H}}/RT$) implicitly through the modification of self- and inter-association equilibrium constants (Coleman & Painter, 2006). In other words, $\Delta G_{\mathrm{H}}/RT$ in Eq. (6) is different than that in Eq. (4). It has also been shown that value of γ between 0.25 and 0.35 gives the best comparison with the experimental results of various synthetic polymers and an average value of $\gamma = 0.30$ is being accepted for most polymer systems (Coleman & Painter, 2006; Painter et al., 1997b).

3. Methodology

Understanding how these theories apply to food carbohydrate polymers and their use/modification to develop tools to predict miscibility/immiscibility would advance the state-of-art in food polymer science. However, the applicability of the Painter–Coleman hydrogen bonding association model for carbohydrate systems is still limited. Because the model is designed where the repeating unit of the 1st polymer has one functional group that can self-associate (such as —OH), and the repeating unit of the 2nd polymer has one functional group that can form bonding with the first polymer. If 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 dextran, amylopectin etc. (Fig. 1)), 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 directly be applied to predict miscibility in such systems.

We have used "Miscibility Guide and Phase Calculator" (MG & PC) Software, which was originally introduced by Coleman et al. (1991) and then modified by inclusions of intra-molecular screening parameter (Coleman et al., 1999). This modified version of the software was kindly provided by Dr. Paul Painter of Material Science and Engineering Department at Pennsylvania State University. In order to bring the capabilities of this model to food polymer science and to demonstrate the importance of hydrogen bonding contributions to predictive miscibility, we have used some approximations for carbohydrate polymers, which are explained in the next section.

3.1. Approximations made to utilize the Painter–Coleman association model for carbohydrate polymers

Model analogue compounds can be used to approximate the hydrogen bonding of the 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. The focus in the current paper was quantitative prediction of miscibility in two component dextran–dextran systems; dextran with $M_{\mathrm{w}} = 1000$ mixed with dextran with $M_{\mathrm{w}} = 2{,}000{,}000$. Three analogue compounds (Fig. 2) were identified whose hydrogen bonding through OH groups (parameters describing self- and inter-association) were previously reported by Painter–Coleman group (Coleman & Painter, 2006); and that have the closest available structure to the repeating unit of dextrans (Fig. 1); 'pentanol'; 'phenol'; and 'dimethylphenol'.

In order to be able to use the MG & PC software and make quantitative predictions of miscibility, dextran with $M_{\mathrm{w}} = 1000$ was defined as the self-associating component, whereas dextran with $M_{\mathrm{w}} = 2{,}000{,}000$ was defined not to self-associate, but could form inter-molecular hydrogen bonds with dextran of $M_{\mathrm{w}} = 1000$. Moreover, it was assumed that the multiple OH groups in repeating unit of dextran did not significantly affect the overall hydrogen-bond distribution in the system.

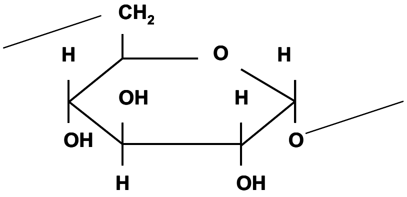

Fig. 1. Repeating unit of dextran.

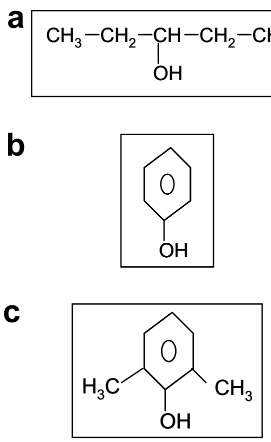

Fig. 2. Analogue compounds whose hydrogen bonding is approximated to the hydrogen bonding of dextrans (model carbohydrate polymers) (a) pentanol; (b) phenol; (c) dimethylphenol.

3.2. Association equilibrium constants for the selected analogue compounds

Self-association and inter-association equilibrium constants are the two required parameters necessary in the MG & PC Software to calculate the ΔG_H in Eq. (6). For molecules that self-associate, the equilibrium constants describing "di-mer" formation (two 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). Table 1 shows the 'standard' self-association equilibrium constants for hydrogen bond formation of the analogue compounds in Fig. 2 (Coleman & Painter, 2006).

'Standard' self-association constants indicate values determined for standard molar volume (V_m^{std}) of 100 cm^3/mol and at temperature of 25 °C. If equilibrium constants for a molecule with different molar volume are needed, then the actual values are calculated using a conversion as;

$$K^{std} \cdot V_m^{std} = K^{actual} \cdot V_m^{actual} \tag{7}$$

Molar volume of repeating unit of dextrans using group contributions (Coleman et al., 1991), was calculated as 51.5 cm^3/mol. Moreover, since the system of interest in this paper was the mixtures of two dextran molecules that have the same repeating unit, inter-association equilibrium constant was taken to be equal to the self-association equilibrium constant describing multi-mer formation. Accordingly, the equilibrium constants for self-association and inter-association in dextrans approximated using H-bond formation of different analogue compounds are given in Table 2.

Table 1
Standard self-association equilibrium constants for hydrogen bond formation of OH group in pentanol, phenol and dimethylphenol

	K_2^{std}	K_B^{std}
Pentanol OH	26.6	44.1
Phenol OH	21.0	66.8
Dimethylphenol OH	6.7	24.5

K_2^{std}, self-association equilibrium constant for di-mer formation.
K_B^{std}, self-association equilibrium constant for multi-mer formation.

3.3. Calculation of non-hydrogen-bonded solubility parameters of dextrans (solubility parameters that exclude the effect of hydrogen bonding)

Non-hydrogen-bonded solubility parameter of the repeating unit of dextran was calculated as described in Coleman et al. (1991) from group contributions. A value of 14.00 (cal/cm^3)$^{0.5}$ was calculated by dividing total molar attraction constants that exclude hydrogen bonding effects to total molar volume of the repeating unit of the molecule (Coleman et al., 1990). Then, non-hydrogen-bonded solubility parameters of dextrans with different molecular weights were determined as described in Icoz and Kokini (2007b). Calculated values are given in Table 3, showing decrease in solubility parameters as M_w increased (Icoz & Kokini, 2007b; Patnaik & Pachter, 1999, 2002).

4. Results and Discussion

4.1. Effect of analogue compound selected to approximate hydrogen bonding in carbohydrates on thermodynamic calculations of miscibility

Figs. 3–5 show the calculated free energy (Eq. (6)) and 2nd derivative of free energy of mixing two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ as a function of volume fraction of $M_w = 1000$ (Φ_B). Negative free energy of mixing

Table 2
Actual self- and inter-association equilibrium constants for hydrogen bond formation of dextran when approximated through hydrogen bond formation of pentanol, phenol and dimethylphenol OH

	K_2	K_B	K_A
Pentanol OH	51.6	85.6	85.6
Phenol OH	40.7	129.6	129.6
Dimethylphenol OH	13.0	47.6	47.6

K_2, self-association equilibrium constant for di-mer formation in dextran.
K_B, self-association equilibrium constant for multi-mer formation in dextran.
K_A, inter-association equilibrium constant between dextrans.

Table 3
Non-hydrogen bonded solubility parameters of dextrans with different molecular weights

Dextrans with different M_w	Non-hydrogen-bonded solubility parameters (δ) (cal/cm^3)$^{0.5}$
1000	13.10
5000	10.96
10,000	10.27
2,000,000	9.40

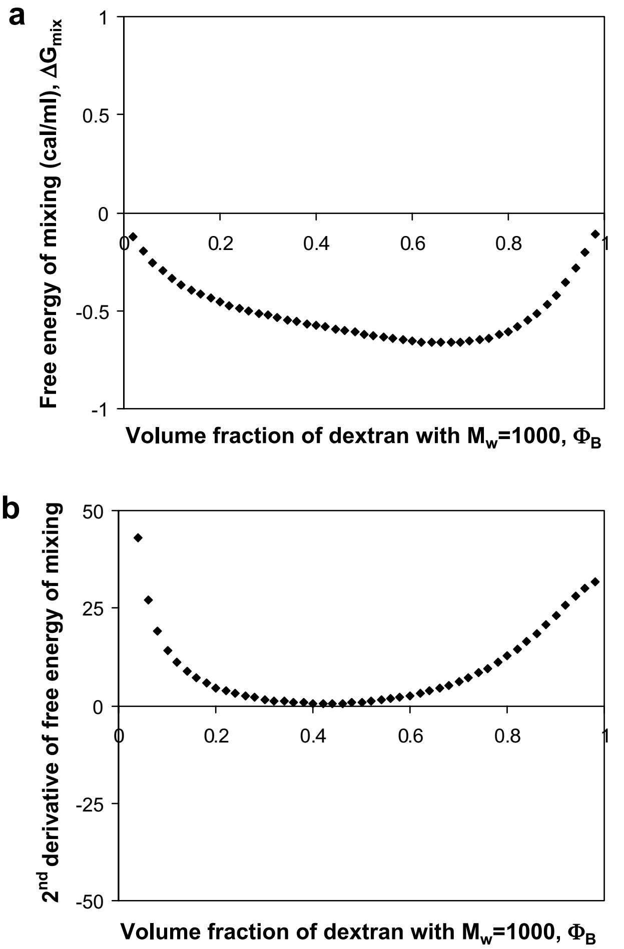

Fig. 3. Predicted miscibility of two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C when H-bond formation of *pentanol OH* was approximated for H-bonding of dextrans; (a) free energy of mixing; (b) 2nd derivative of free energy of mixing.

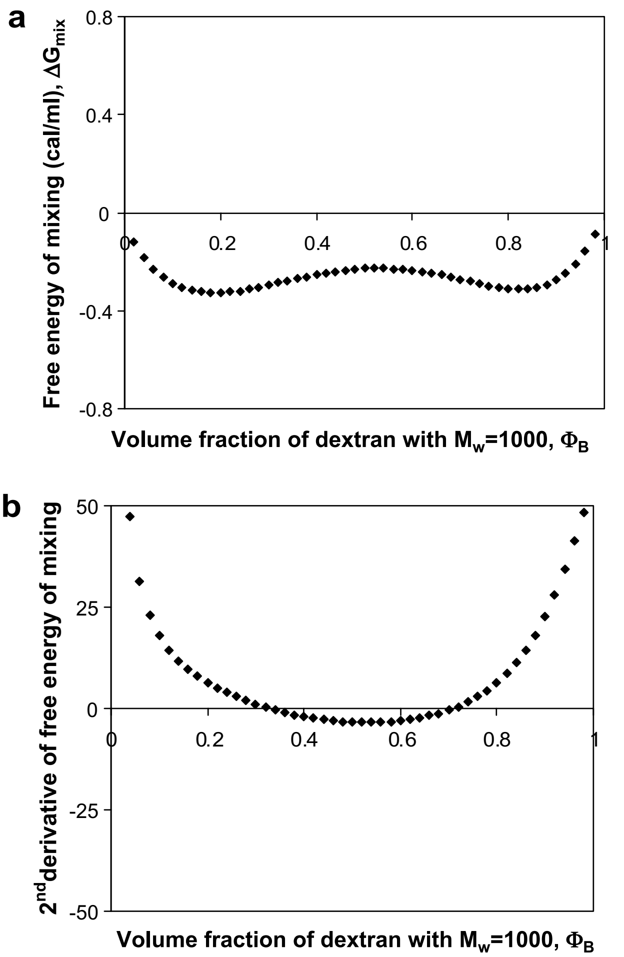

Fig. 4. Predicted miscibility of two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C when H-bond formation of *phenol OH* was approximated for H-bonding of dextrans; (a) free energy of mixing; (b) 2nd derivative of free energy of mixing.

(ΔG_{mix}) together with positive 2nd derivative is the quantitative indication of miscible systems. According to this, when H-bonding of dextrans was approximated using H-bond formation of *pentanol OH*, ΔG_{mix} was calculated to be negative (Fig. 3a) and 2nd derivative of ΔG_{mix} took positive values for all Φ_B (Fig. 3b), satisfying the two thermodynamic conditions for miscibility and predicting miscible systems at all component ratios in this system. When H-bonding of dextrans was approximated with H-bond formation of *phenol OH*, ΔG_{mix} was determined to be negative at all Φ_B (Fig. 4a), but 2nd derivative of ΔG_{mix} took negative values at $\Phi_B = 0.33$–0.71 (Fig. 4b), predicting immiscible systems between this range. On the other hand, when H-bonding of dextrans was approximated to H-bond formation of *dimethylphenol OH*, ΔG_{mix} took positive values at volume fraction = 0.36–0.91 (Fig. 5a), and 2nd derivative was negative at volume fraction = 0.32–0.82 (Fig. 5b), predicting immiscibility between $\Phi_B = 0.32$–0.91 in the system. Icoz, Moraru, and Kokini (2005) have previously shown that these two dextrans were experimentally miscible at all proportions with single T_g behavior. Although these two dextrans have different molecular weights, they basically have the same chemical structure as the repeating unit and form miscible systems due to their compatible nature. Figs. 3–5 demonstrates that using "pentanol" as the analogue model compound for H-bond formation of dextrans enabled miscible system predictions over the entire composition range, demonstrating that pentanol was the best model for H-bonding in the carbohydrate systems.

In order to clearly demonstrate what causes the difference between miscibility predictions of dextrans using the three analogue compounds (Figs. 3–5), individual contributions of entropy, enthalpy and H-bonding on total free energy of mixing (Eq. (6)) were plotted in Fig. 6. Both enthalpic and entropic contributions had the same values in Fig. 6a–c. Entropic contributions were calculated from first two terms on the right-hand side of Eq. (6) using volume fractions and degree of polymerization of dextrans themselves, and were favorable to mixing with negative values (Fig. 6). Enthalpic contributions were calculated from 3rd term on the right-hand side of Eq. (6) using non-hydrogen-bonded solubility parameters of dextrans (Table 3), and were unfavorable to mixing with positive values (Fig. 6). H-bonding contributions (last term on the right-

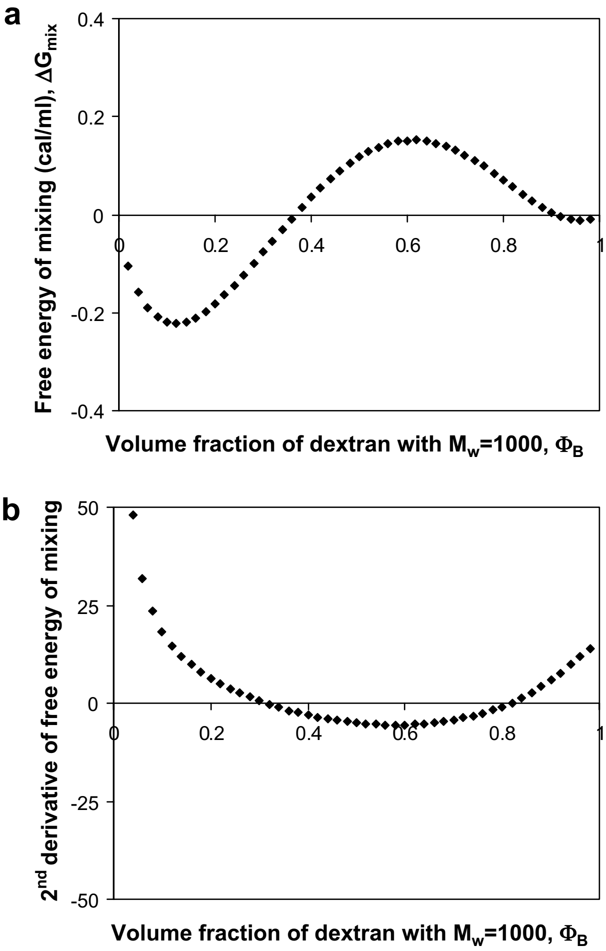

Fig. 5. Predicted miscibility of two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C when H-bond formation of *dimethylphenol OH* was approximated for H-bonding of dextrans; (a) free energy of mixing; (b) 2nd derivative of free energy of mixing.

hand side of Eq. (6)) were calculated to be negative (Fig. 6), showing strong favorable contribution to mixing. These contributions were calculated as a function of self- and inter-association equilibrium constants of dextrans (Table 2) that were approximated from H-bonding in pentanol, phenol and dimethylphenol. H-bonding contribution decreased in the order of the use of pentanol, phenol and dimethylphenol as the analogue compound.

Since entropic and enthalpic contributions to total free energy of mixing were the same (Fig. 6a–c), the difference in total free energy of mixing was only due to the differences in H-bonding approximations. The structure of pentanol is the closest to the repeating unit of dextran with its linearly bonded carbon atoms making it the most possible for its OH group to be involved in H-bonding (Fig. 6a). Phenol, on the other hand, has a double bonded ring structure which creates steric hindrance in the structure making it less possible for its OH group to be involved in H-bonding (Fig. 6b). Dimethylphenol has two additional methyl groups on phenol that causes even more steric hindrance and, therefore, less H-bonding capability demonstrated by the smallest H-bonding contribution (Fig. 6c).

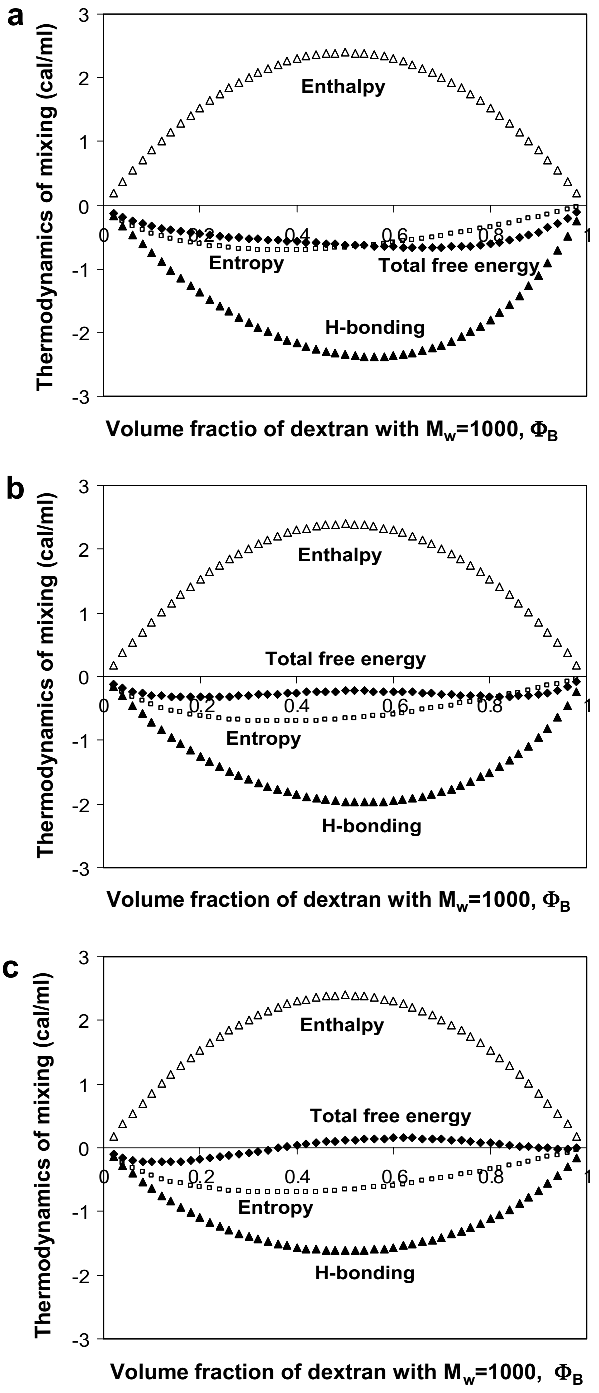

Fig. 6. Entropic, enthalpic, and H-bonding contributions to the total free energy of mixing two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C when H-bond formation of; (a) pentanol OH; (b) phenol OH; (c) dimethylphenol OH was approximated for H-bond formation in dextrans.

4.2. Effect of relative values of self-association and inter-association equilibrium constants on thermodynamic calculations of miscibility

Self-association vs. inter-association in a system is an important factor in determining the extent of hydrogen bonding contribution to free energy of mixing. If self-association is more than inter-association (i.e., higher self-association equilibrium constants than inter-association equilibrium constants), it is expected that this case will be unfavorable for mixing two components in a system. Because the self-associating component will be preferably interacting within itself rather than forming inter-molecular bonds with the other component, which may not be sufficient enough to form miscible systems. On the other hand, if inter-association is more than self-association, then this will be favorable for mixing the components and obtaining miscible systems will be enhanced. Therefore, the relative values of the equilibrium constants are the determinant factor for the extent of H-bonding and the resulting free energy of mixing.

In order to demonstrate these ideas quantitatively, Fig. 7 shows the hypothetical hydrogen bonding contribution and the resulting free energy of mixing when the relative values of self-association and inter-association equilibrium constants are changed. Only H-bonding contribution and total free energy was demonstrated in Fig. 7, because entropic and enthalpic contributions to free energy would be the same for all cases (Eq. (6) and Fig. 6). When pentanol was used as the analogue compound for H-bonding of dextrans, the self-association equilibrium constants for di-mer and multi-mer formations were $K_2 = 51.6$ and $K_B = 85.6$, whereas inter-association equilibrium constant was $K_A = 85.6$ (Table 2). When K_A was hypothetically selected smaller than K_2 or K_B (i.e., when $K_A = 40$ or $K_A = 60$), H-bonding contribution was small (Fig. 7a), and was not enough to overcome the positive valued, unfavorable enthalpic contribution, resulting in positive valued ΔG_{mix} (immiscibility) (Fig. 7b). As K_A got higher values than K_2 and K_B (i.e., when $K_A = 100$ or $K_A = 120$), higher negative values were obtained for H-bonding contribution that could overcome the unfavorable enthalpic contribution. Thereby, negative valued ΔG_{mix} (Fig. 7b), in other words, miscibility in these systems, could be obtained.

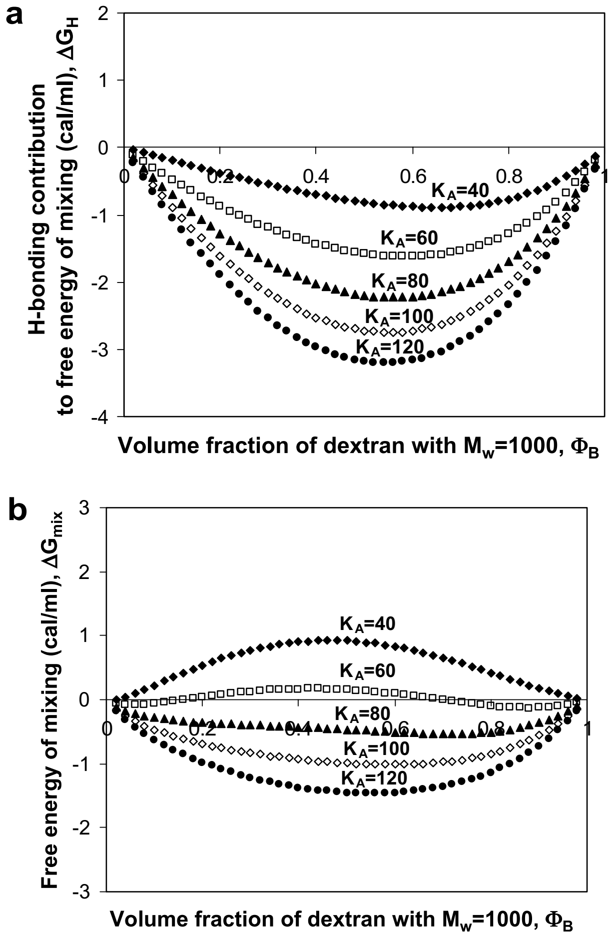

Fig. 7. Effect of the value of inter-association equilibrium constant (K_A) relative to self-association equilibrium constants (K_2 and K_B) on; (a) H-bonding contribution; (b) total free energy of mixing two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C [H-bond formation of pentanol OH was approximated for H-bond formation in dextrans].

4.3. Effect of selection of the self-associating component in the system on thermodynamic calculations of miscibility

In order to use the MG & PC Software, one of the approximations needed was to define one of the dextran molecules as the self-associating component. Section 4.1 demonstrated the results when dextran with $M_w = 1000$ was chosen as the self-associating component in $M_w = 1000 + M_w = 2{,}000{,}000$ system. Because, possibly, the molecules in the small molecular weight component would more easily place themselves next to each other and make intra-molecular hydrogen bonds in pure state than the molecules of the large molecular weight component. In this current section, thermodynamics of mixing when dextran with $M_w = 2{,}000{,}000$ was selected as the self-associating component is presented in order to investigate the selection of the self-associating component on miscibility predictions.

One point to be mentioned is that in the MG & PC Software, the self-associating component is always denoted with "B". When the thermodynamics of mixing are calculated, the values of the x-axis in the resulting plots are the volume fractions of the self-associating component (B). In the results presented in this section, the x-axis was re-calculated as the volume fraction of $M_w = 1000$ (by subtracting volume fraction of $M_w = 2{,}000{,}000$ from 1) in order to be able to compare these results with those when $M_w = 1000$ was selected as the self-associating component (Figs. 3–5).

Fig. 8 illustrates free energy and 2nd derivative of free energy when dextran with $M_w = 2{,}000{,}000$ was selected as the self-associating component rather than $M_w = 1000$. When pentanol was used as the analogue compound, negative ΔG_{mix} was calculated for all volume fractions (Fig. 8a) and 2nd derivative of ΔG_{mix} was negative at volume fraction > 0.54 (Fig. 8b) (immiscibility at volume fraction = 0.54–0.99). Selection of $M_w = 2{,}000{,}000$ as the self-associating component resulted in significantly less component ratios where the systems were predicted to be miscible when compared to the case of defining $M_w = 1000$ as the self-associating component (Fig. 3a and b). On the other hand, when dimethylphenol was used as the analogue com-

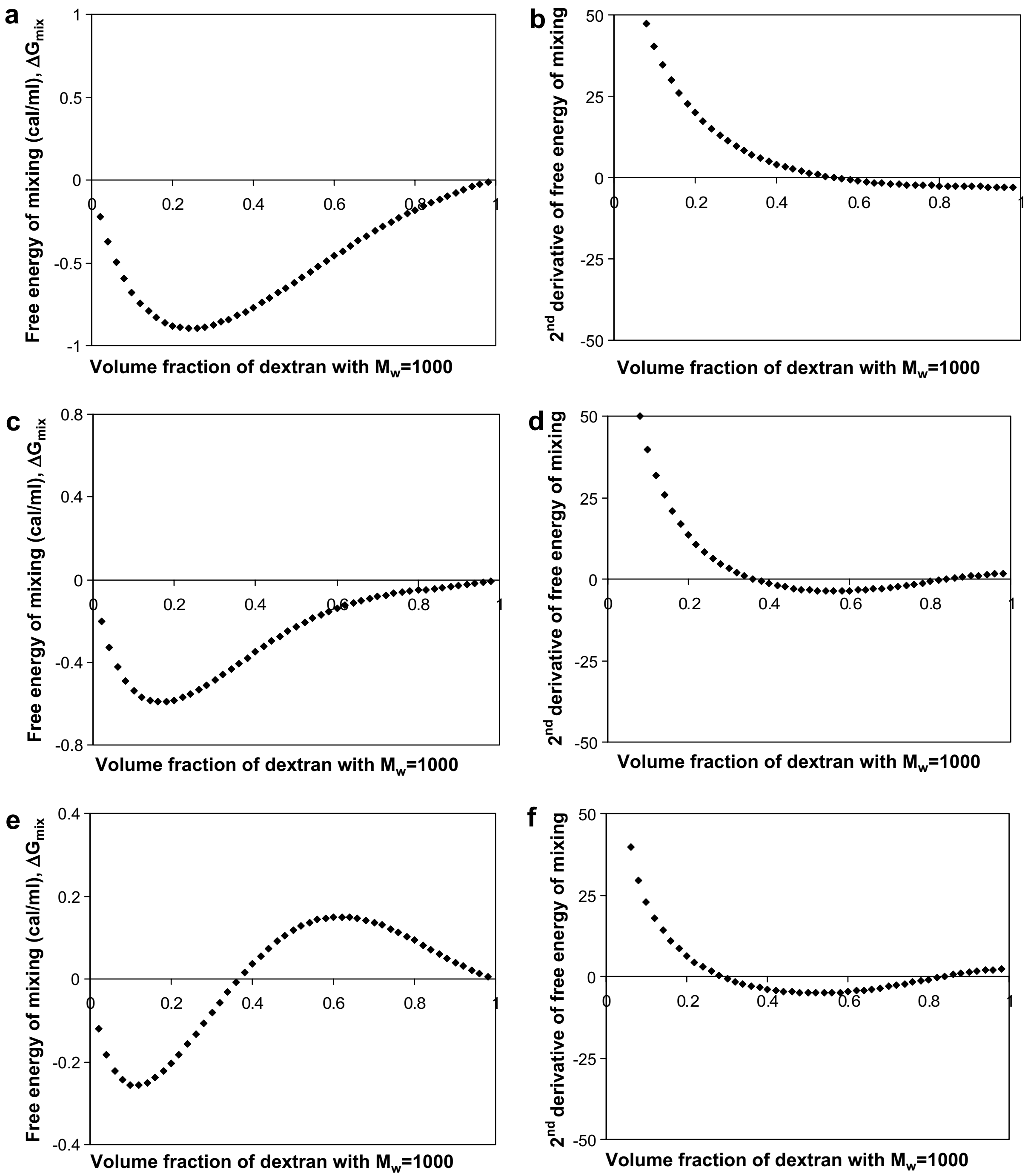

Fig. 8. Predicted miscibility (free energy and 2nd derivative of free energy of mixing) of two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C when dextran with $M_w = 2{,}000{,}000$ was selected as the self-associating component [H-bond formation of; (a)–(b) pentanol OH; (c)–(d) phenol OH; (e)–(f) dimethylphenol OH, was approximated for H-bond formation in dextrans].

pound, ΔG_{mix} as calculated to have positive values at volume fraction = 0.36–0.99 (Fig. 8e); and 2nd derivative of ΔG_{mix} had negative values at volume fraction = 0.30–0.82 (Fig. 8f). There is not significant difference when miscibility prediction in Fig. 5a and b (immiscibility between $\Phi_B = 0.32$–0.91) were compared to that in Fig. 8e and f (immiscibility at volume fraction = 0.30–0.99). H-bonding contribution was the least with this analogue compound (Fig. 6c) and thermodynamic calculations showed that selecting dextran with low or high M_w as the self-associating component did not significantly change the miscibility predictions with this analogue compound. Similarly, when phenol was used as the analogue compound, negative ΔG_{mix} was calculated for all volume fractions (Fig. 8c) and 2nd derivative of ΔG_{mix} was negative at volume fraction = 0.36–0.84 (Fig. 8d) (immiscibility prediction at volume fraction = 0.36–0.84). Figs. 6 and 8 collectively demonstrated that the possibility of the components being

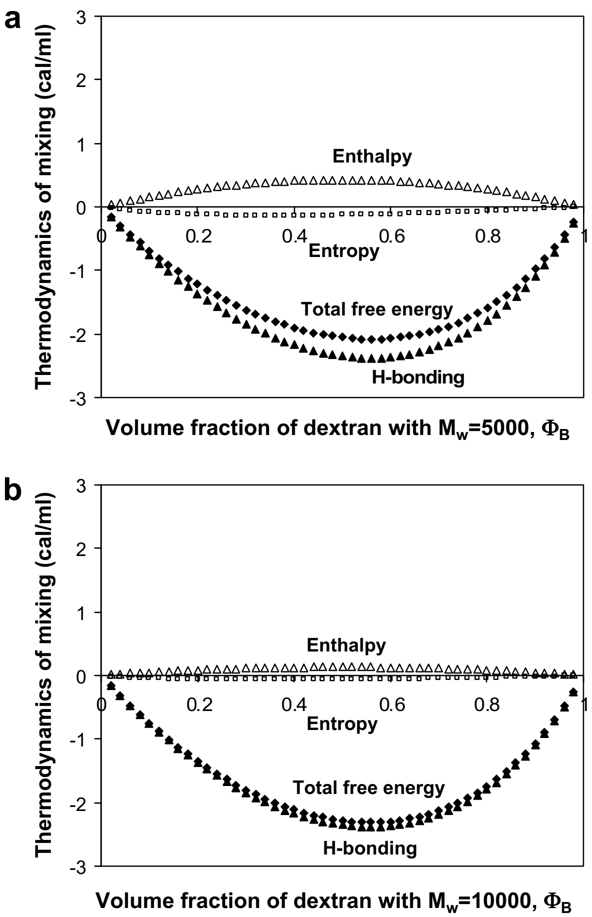

Fig. 9. Effect of component molecular weight on entropic, enthalpic, and H-bonding contributions to the total free energy of mixing two dextrans at 25 °C; systems of (a) $M_w = 5{,}000$ and $M_w = 2{,}000{,}000$; (b) $M_w = 10{,}000$ and $M_w = 2{,}000{,}000$ [H-bond formation of pentanol OH was approximated for H-bond formation in dextrans].

involved in self-associated H-bonding ($M_w = 1000$ vs. $M_w = 2{,}000{,}000$) affected the miscibility calculations as in the case of using pentanol vs. dimethylphenol as the analogue compound.

4.4. *Effect of molecular weight of components on thermodynamic calculations of miscibility*

Finally, Fig. 9a and b show the individual thermodynamic contributions when dextran with $M_w = 1000$ in the system was replaced with higher M_w dextrans ($M_w = 5000$ and $M_w = 10{,}000$, respectively). These systems have also shown to be experimentally miscible with single T_g behavior (Icoz et al., 2005). Enthalpic contributions decreased significantly as M_w of the components increased (Figs. 6a and 9a, b), which was favorable for mixing. They were calculated from the square of the difference between the non-hydrogen-bonded solubility parameters of the two components (Eqs. (3) and (6)), which got closer as the M_w of the components in the system got closer (Table 3), resulting in smaller enthalpic contribution. Entropic contributions also decreased as M_w of the components increased (Figs. 6a and 9a, b). Because the value of the first two terms in Eq. (6) decreased as 'M' got larger values with higher M_w, and this decrease was unfavorable for mixing. H-bonding contribution in all cases was calculated the same (Figs. 6a and 9a, b), which were approximated from H-bonding of pentanol as the analogue compound.

Since the entropic and, especially, enthalpic contributions decreased significantly with increased M_w of the components, total free energy of mixing resulted in higher negative values (Figs. 6a and 9a, b). This indicated more spontaneous miscibility as the components got closer to each other in structure with their M_w being closer to each other ($M_w = 1000 + M_w = 2{,}000{,}000$ vs. $M_w = 10{,}000 + M_w = 2{,}000{,}000$). The total free energy of mixing significantly depended on H-bonding contribution, which became even more important in the systems with high M_w components (Figs. 6a and 9a, b), as contributions from entropy and enthalpy vanished.

5. Conclusions

In this paper, the application of Painter–Coleman association model was investigated to approximately predict miscibility in carbohydrate polymers. Hydrogen bonding was shown to have significant contribution in the quantitative miscibility predictions for carbohydrate polymer systems. Taking into account the contributions due to hydrogen bonding using Painter–Coleman association model improved the miscibility predictions using the original Flory–Huggins theory, but as mentioned before, the association model still has limitations to be totally accurately applicable to carbohydrate polymer blends and also systems involving 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. Nevertheless, the generated knowledge in this paper is a step towards choosing which ingredients in a food formulation would form the desired miscible/immiscible systems on a predictive basis which will speed up the product development process and will increase the utilization of alternative ingredients in novel food products.

Acknowledgements

This is publication D10544-1-07 of the New Jersey Agricultural Experiment Station supported by State Funds and the Center for Advanced Food Technology (CAFT). CAFT is a New Jersey Commission on the Science and Technology (NJCST) Center. The authors would like to thank Dr. Paul Painter of Material Science and Engineering Department at Pennsylvania State University for providing the MG & PC Software program that was used for this study.

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