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Examination of the validity of the Flory–Huggins solution theory in terms of miscibility in dextran systems

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Abstract

The validity of the original Flory–Huggins theory was examined in terms of predicting molecular miscibility in carbohydrate polymers using dextrans as model system. The solubility parameter of the monomeric unit of dextran was calculated from two different group contribution methods using the molecular structure. A predictive methodology to calculate the solubility parameters of dextrans with different molecular weights as a function of their glass transition temperatures was presented, with an inverse relationship between molecular weight and solubility parameter. The calculated solubility parameters were then used to predict the free energy of mixing two dextrans with molecular weights of 1000 and 2,000,000. The Flory–Huggins theory was demonstrated to be unsatisfactory for predicting miscibility in carbohydrate systems since it underestimates the presence of strong specific intermolecular interactions, such as hydrogen bonds, which may enhance the actual miscibility in such systems and which should be handled by more advanced thermodynamic models.

Keywords: Flory–Huggins theory; Solubility parameter; Miscibility; Dextran; Carbohydrate polymer

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1. Introduction

Understanding of molecular and thermodynamic basis for miscibility/immiscibility in food polymer systems is critical for the process conditions, final texture, palatability and stability of products with multiple ingredients. Fundamental knowledge on the compatibility between food polymers would enable *a priori* rules for molecular miscibility between components, which would result in selection of appropriate set of ingredients for a food product with the desired quality attributes and stability. The ability to apply quantitative thermodynamic models that can predict miscibility/immiscibility in synthetic polymers to the more complex carbohydrate polymers would enhance the state-of-art in food polymer science, which would lead to development of carbohydrate replacement strategies, the development of new carbohydrate food systems and for quality improvement of the existing food products.

According to the thermodynamics of mixing, the first condition for miscibility of one component in another is obtaining negative change in free energy of mixing (Coleman, Graf, & Painter, 1991; Coleman & Painter, 2006; Painter & Coleman, 1997; Sperling, 2001), where the change in free energy of mixing is related to enthalpic and entropic contributions as;

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T \cdot \Delta S_{\mathrm{mix}}. \quad (1)$$

ΔG_{mix} is the Gibbs' free energy of mixing; ΔH_{mix} is the enthalpy of mixing; ΔS_{mix} is the entropy of mixing; and T is the absolute temperature. A negative value of ΔG_{mix} shows that the mixing process is spontaneous. ΔS_{mix} arises from the number of possible configurations of a solute in solution (also called combinatorial entropy) (Painter & Coleman, 1997). ΔS_{mix} is always positive since entropy increases upon mixing, due to the increase in randomness. Therefore, the sign of ΔG_{mix} depends on the magnitude and

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sign of ΔH_{mix} (Sperling, 2001), which arises from interactions between monomeric units (Painter & Coleman, 1997).

The second condition required for miscibility is to have positive second derivative of ΔG_{mix} (Coleman et al., 1991; Coleman & Painter, 2006). If the negative valued ΔG_{mix} as a function of composition plots are concave upwards for all compositions, then the components of the mixture are miscible in all proportions. These types of plots give positive second derivative of ΔG_{mix} over the entire composition range. On the other hand, if the negative valued ΔG_{mix} vs. composition plots show portions that are concave downwards, then the blend components are not miscible in that specific composition range although the ΔG_{mix} is negative (Coleman et al., 1991). Therefore, it is important to consider both the ΔG_{mix} and the second derivative of ΔG_{mix} to decide if the blend components are miscible or not.

When two types of small molecules are present in a mixture, the molecules can rearrange themselves in the available volume in many ways. Therefore, the randomness in the system and entropy of mixing is very high. When one of the small molecules is replaced with a polymer molecule, then the randomness in the system and entropy of mixing decreases significantly, as compared to the system of two small molecules. Furthermore, if there are two types of polymers present in the system, then the order in the system increases, the randomness and entropy of mixing decreases even more (Sperling, 2001). In statistical thermodynamics of mixing, entropy of mixing can be determined by obtaining a quantitative measure of the number of possible arrangements of the molecules in the system. A simple method for counting the possible configurations is the use of a lattice model (Fig. 1) (Sperling, 2001). A simplification in the lattice model is to assume that the energy of interactions between any molecules is an average energy over all possible configurations, called mean-field approximation (Painter & Coleman, 1997).

1.1. Flory–Huggins solution theory

The basic thermodynamic equation for mixing polymer systems is given by the Flory–Huggins solution theory (Flory, 1952). Flory–Huggins theory is a lattice model originally derived for small molecules and it assumes that each molecule occupies one site on the lattice (Fig. 1). The theory assumes random distribution of the segments (Flory, 1952; Painter & Coleman, 1997; Viswanathan & Dadmun, 2002). This assumption may not hold when there are strong polar forces or specific interactions, such as hydrogen bonding, between the components of the blends due to the fact that strong intermolecular interactions limit the mobility of the chains and force the chains into non-random configurations (Coleman et al., 1991; Viswanathan & Dadmun, 2002). The theory also assumes no free volume in the system (all lattice sites are occupied) and the volume change upon mixing is negligible (Flory, 1952; Painter & Coleman, 1997).

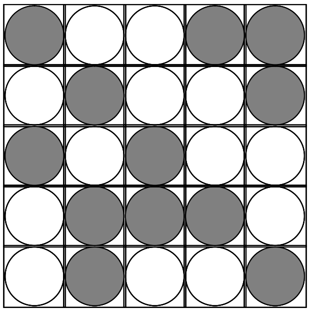


Fig. 1. Schematic representation of mixing two small molecules of equal size on a lattice.

The original Flory–Huggins theory is expanded for polymer systems, assuming that the polymer is a flexible chain composed of a series of connected monomers (repeating units) and each monomer occupies one lattice site, which is also equal in size (volume) to a solvent molecule (Madkour, 2001; Painter & Coleman, 1997; Patnaik & Pachter, 2002). Accordingly, the polymer is placed on the lattice as shown in Fig. 2, occupying lattice sites next to each other.

The general expression of Flory–Huggins theory for free energy of mixing (applicable both for polymer–solvent and polymer–polymer systems) is given as;

$$\left[\frac{\Delta G_{\text{mix}}}{R\cdot T}\right]^{*}\cdot\left[\frac{V_{\text{r}}}{V}\right]=\frac{\Phi_{\text{A}}}{M_{\text{A}}}\cdot\ln\Phi_{\text{A}}+\frac{\Phi_{\text{B}}}{M_{\text{B}}}\cdot\ln\Phi_{\text{B}}+\chi_{\text{AB}}\cdot\Phi_{\text{A}}\cdot\Phi_{\text{B}}, \tag{2}$$

where Φ is the volume fraction of each component; M is the number of segments; χ is the Flory–Huggins interaction parameter; V_{r} is the reference volume; V is the total molar volume of the system; and subscripts A and B refer to the two components in the mixture (Kuo & Chang, 2002; Madkour, 2001; Painter & Coleman, 1997; Patnaik & Pachter, 2002; Viswanathan & Dadmun, 2002). Eq. (2) can also be written in terms of free energy of mixing per mole of lattice sites, paying attention to the reference volume, as;

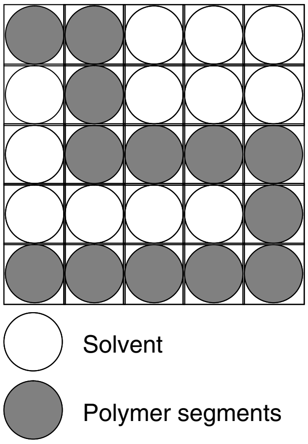


Fig. 2. Schematic representation of a polymer on a lattice.

$$\left[\frac{\Delta G_{\mathrm{mix}}}{R\cdot T}\right]=\frac{\Phi_{\mathrm{A}}}{M_{\mathrm{A}}}\cdot\ln\Phi_{\mathrm{A}}+\frac{\Phi_{\mathrm{B}}}{M_{\mathrm{B}}}\cdot\ln\Phi_{\mathrm{B}}+\chi_{\mathrm{AB}}\cdot\Phi_{\mathrm{A}}\cdot\Phi_{\mathrm{B}}. \tag{3}$$

The first two terms on the right-hand side in Eq. (3) corresponds to the combinatorial entropy contribution, which is always negative, since natural logarithm of volume fraction (a number smaller than 1) is always negative. The third term on the right-hand side of Eq. (3) corresponds to the enthalpy of mixing representing interactions between components (Kuo & Chang, 2002; Madkour, 2001; Patnaik & Pachter, 2002; Sperling, 2001; Viswanathan & Dadmun, 2002).

The selection of the reference volume, V_r, on a lattice, which in general corresponds to the volume of each lattice site, is critical as it is a determinant factor for the selection of M in Eq. (3). If components A and B are small molecules of equal size, then $V_r = V_A = V_B$ and $M_A = M_B = 1$. If component A is a solvent and component B is a polymer, then $V_r = V_A$, where V_A is the volume of the solvent that is equal to the volume of each polymer segment. In this case, $M_A = 1$ and $M_B \gg 1$. If both components A and B are polymers, then V_r is chosen as the volume of the monomeric unit of one of the components and M_A and M_B will be large (Painter & Coleman, 1997).

Volume fractions (Φ) in Eq. (3) are defined as;

$$\Phi_{\mathrm{A}}=\frac{n_{\mathrm{A}}\cdot M_{\mathrm{A}}}{n_{\mathrm{A}}\cdot M_{\mathrm{A}}+n_{\mathrm{B}}\cdot M_{\mathrm{B}}},\quad \Phi_{\mathrm{B}}=\frac{n_{\mathrm{B}}\cdot M_{\mathrm{B}}}{n_{\mathrm{A}}\cdot M_{\mathrm{A}}+n_{\mathrm{B}}\cdot M_{\mathrm{B}}}, \tag{4}$$

where n_A and n_B are the moles of polymers in the mixture; M_A and M_B are the number of segments in each polymer chain (Painter & Coleman, 1997). Since Φ is the volume fraction of components, $\Phi_A + \Phi_B = 1$.

1.2. Flory–Huggins interaction parameter

Another term that needs attention in Eq. (3) is Flory–Huggins interaction parameter (χ) (Flory, 1952). χ is used to characterize interactions in mixtures of small molecules, in polymer solutions (polymer–solvent systems) and polymer blends (polymer–polymer systems). It is a dimensionless number and is related to the solubility parameters (δ) as;

$$\chi_{\mathrm{AB}}=\frac{V_{\mathrm{r}}}{R\cdot T}(\delta_{\mathrm{A}}-\delta_{\mathrm{B}})^2, \tag{5}$$

where V_r is the reference volume; δ_A and δ_B are the solubility parameters of each component; R is the universal gas constant; and T is the absolute temperature. For polymer–solvent systems, an added fudge factor of 0.34 to right-hand side of Eq. (5) gives better match (Painter & Coleman, 1997; Sperling, 2001). Since χ is proportional to the square of the difference between the solubility parameters of the blend components $[(\delta_A - \delta_B)^2]$, enthalpy term in Eq. (3) is always positive, opposing mixing, resulting in phase separation in many cases (Coleman et al., 1991; Kuo & Chang, 2002; Madkour, 2001; Viswanathan & Dadmun, 2002).

1.3. Hildebrand solubility parameter

Solubility parameter of a material with physical interactions (Hildebrand & Scott, 1950) is defined as;

$$\delta=\left(\frac{E_{\mathrm{coh}}}{V_{\mathrm{m}}}\right)^{1/2}, \tag{6}$$

where E_{coh} is the energy of vaporization at zero pressure, known as the cohesive energy; and V_m is the molar volume. Cohesive energy corresponds to the total attractive forces in a condensed state material. Molecules that are highly attracted to one another have high cohesion and solubility parameters; and materials that have high solubility parameters require more energy for dispersion than materials with low solubility parameters (Olabisi, Robeson, & Shaw, 1979).

Cohesive energy per molar volume (E_{coh}/V_m) is called the cohesive energy density (CED) and it is related to the energy required to break all intermolecular physical links in the unit volume (Greenhalgh, Williams, Timmins, & York, 1999). When two components have similar CED values, they are likely to be soluble in each other as the interactions in one component would be similar to those in the other component. The overall energy needed to facilitate mixing of the components would be small, because the energy required to break the interactions within the components would be equally compensated by the energy released due to formation of interactions between unlike molecules (Greenhalgh et al., 1999). Moreover, two materials with very similar CED values approximately makes the enthalpy term in Eq. (3) zero, minimizing the opposing effect to mixing.

Solubility parameters (δ) of polymers cannot be directly determined from their energy of vaporization, because polymers cannot be evaporated by heating as they decompose below their theoretical vaporization temperature. One way of determining solubility parameter of a polymer is through predictions using group contribution methods based on the chemical structure of the monomeric unit of the polymer (Coleman et al., 1991; Painter & Coleman, 1997; Sperling, 2001; Van Krevelen & Hoftyzer, 1976). The cohesive energies and molar volumes of chemical groups that conform the molecule are additive and δ can be calculated as;

$$\delta=\left(\frac{\sum E_{\mathrm{coh}}}{\sum V_{\mathrm{m}}}\right)^{1/2}, \tag{7}$$

following Eq. (6), where $\sum E_{\mathrm{coh}}$ is the sum of the cohesive energies; and $\sum V_m$ is the sum of the molar volumes of all chemical groups in the structure of the monomeric unit. It should be noted that calculation of δ using Eq. (7) gives the overall cohesive energy in the materials and do not give specific information on the relative strengths of the forces in a system, such as hydrogen bonding (Greenhalgh et al., 1999).

A modified approach to determine solubility parameters for polymers where cohesive energy is dependent not only on the dispersion forces but also on interactions between polar groups and on hydrogen bonding is to divide δ into its dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) contributions, and calculated as (Van Krevelen & Hoftyzer, 1976);

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \tag{8}$$

where

$$\delta_d = \frac{\sum F_{di}}{V_m}, \quad \delta_p = \frac{\left(\sum F_{pi}^2\right)^{1/2}}{V_m}, \quad \delta_h = \left(\frac{\sum E_{hi}}{V_m}\right)^{1/2}. \tag{9}$$

However, the available data for F_{di}, F_{pi} and E_{hi} (Eq. (9)) for calculation of Eq. (8) is very limited for different atomic groups compared to the E_{coh} in Eq. (7) (Van Krevelen & Hoftyzer, 1976). A limitation of determining solubility parameter of a polymer using either Eqs. (7) or (8) is that the calculation of δ based on the chemical groups on the monomeric unit of the polymer does not take into account the effect of molecular weight (M_w) and chain conformation, including branching and linkages between monomer units (Olabisi et al., 1979; Patnaik & Pachter, 2002), which are important factors for solubility of one polymer in a solvent or for miscibility with another polymer. For example, according to δ calculation using Eqs. (7) or (8), two polymers with different M_w (i.e. a glucose polymer with small or large M_w) or two polymers that are composed of only one type of monomers (i.e. amylose and amylopectin) would be predicted to have the exact same solubility parameters. More accurate predictions of solubility parameters for polymers should take these factors into account which would provide better miscibility predictions in polymer blends.

The aim of this paper was to investigate the validity of the original Flory–Huggins theory in terms of predictive capability for miscibility in dextran blends as model carbohydrate systems. Determination of the solubility parameters of dextrans with different molecular weights was presented with a quantitative methodology using their glass transition temperatures. Free energy of mixing together with its second derivative was calculated in order to predict miscibility in the dextran blend with high and low molecular weights.

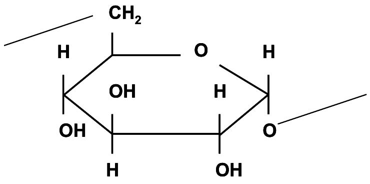
2. Methodology

2.1. Determination of solubility parameter of monomeric unit of dextran

Solubility parameter (δ) for the monomeric unit of dextran using Eq. (7) and atomic groups that conform the molecule was calculated as 19.8 $(\text{cal/cm}^3)^{1/2}$ (Fig. 3). Using the modified predictive equation for the solubility parameter (Eqs. (8) and (9)), δ for the monomer unit of dextran was recalculated as 22.6 $(\text{cal/cm}^3)^{1/2}$ (Fig. 4), which was relatively different from the one calculated in Fig. 3. Further in this paper, a predictive methodology to calculate the solubility parameters of dextrans with different molecular weights would be presented, making use of the δ of monomer calculated in Figs. 3 and 4; and also would be looked into which δ approximation gives better results for prediction of miscibility in dextran systems.

2.2. Placing dextrans on the hypothetical lattice

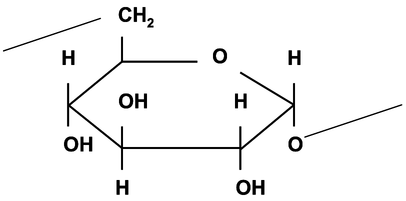
The molar volume (V_m) of the monomeric unit of dextran was calculated to be 57.7 cm^3/mol using group contri-



GROUP	Number of group	E_{coh} (J/mol)	ΣE_{coh} (J/mol)	V_m (cm^3/mol)	ΣV_m (cm^3/mol)
$-CH_2$	1	4,950	4,950	16.1	16.1
$>CH-$	5	3,430	17,150	-1.0	-5.0
$-OH$	3	21,850	65,550	13.0	39.0
$-O-$	2	3,350	6,700	3.8	7.6

$$\delta_{\substack{monomerof\\dextran}} = \left(\frac{\sum E_{coh}}{\sum V_m}\right)^{1/2} = \left(\frac{94{,}350}{57.7}\right)^{1/2}\left(\frac{J}{cm^3}\right)^{1/2} = 40.4\left(\frac{J}{cm^3}\right)^{1/2} = 19.8\left(\frac{cal}{cm^3}\right)^{1/2}$$

Fig. 3. Calculation of the solubility parameter for monomer of dextran (E_{coh} and V_m values for different atomic groups were obtained from Van Krevelen and Hoftyzer (1976)).



GROUP	Number of group	F_{di} $(J.cm^3/mol)^{1/2}$	F_{pi} $(J.cm^3/mol)^{1/2}$	F_{pi}^2 $(J.cm^3/mol)$	E_{hi} (J/mol)
— CH_2	1	(270)*1	0	(0)*1	(0)*1
>CH—	5	(80)*5	0	(0)*5	(0)*5
— OH	3	(210)*3	500	(250,000)*3	(20,000)*3
— O —	2	(100)*2	400	(160,000)*2	(3,000)*2

$$\delta_{\substack{monomer of\\ dextran}} = \left(26^2 + 17.9^2 + 33.8^2\right)^{1/2} = 46.3\left(\frac{J}{cm^3}\right)^{1/2} = 22.6\left(\frac{cal}{cm^3}\right)^{1/2}$$

Fig. 4. A second method for calculation of the solubility parameter for monomer of dextran (F_{di}, F_{pi} and E_{hi} values for different atomic groups were obtained from Van Krevelen and Hoftyzer (1976)).

bution methods (Fig. 3), being the reference volume, V_r, for a system involving two dextran polymers (to be used in Eq. (5)).

2.3. Determination of volume fractions in dextran mixtures

For theoretical calculations, two dextrans with weight-average molecular weights (M_w) of approximately 1000 and 2,000,000 were used. The molecular weight of the monomeric unit of dextran is 162 g/mol (Fig. 3). Eq. (4) was used to calculate the volume fractions in the selected system. The calculated volume fractions of dextran with $M_w = 1000$ (Φ_A) as a function of % weight/weight ratio (m_A) is shown in Fig. 5. For the polymer system under investigation, for example, 40/60% ratio of $M_w = 1000$/$M_w = 2{,}000{,}000$ had volume fractions as $\Phi_A = 0.4$ ($M_w = 1000$) and $\Phi_B = 0.6$ ($M_w = 2{,}000{,}000$), respectively. For any other system, the volume fractions for a similar percentage ratio may be different depending on the reference volume selected and how the polymer segments would be placed on the lattice.

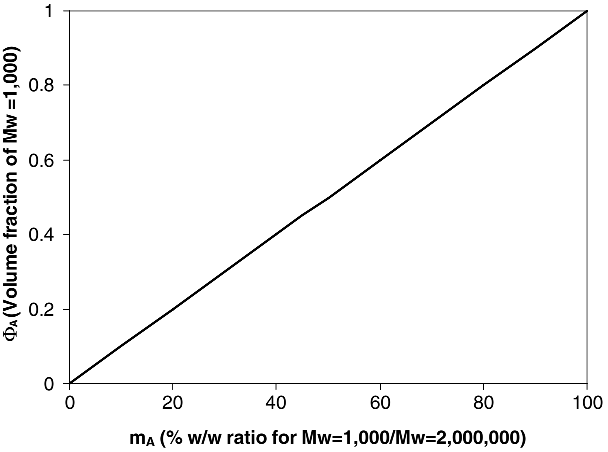


Fig. 5. Calculated volume fractions in the system of two dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ as a function of % w/w ratio (m_A).

3. Results and discussion

3.1. A predictive methodology to determine the solubility parameters of dextrans with different M_w as a function of glass transition temperature (T_g)

Hayes (1961) has suggested that molar cohesive energy of a polymer can be written directly proportional to the molar rotational energy of the polymer and suggested a relationship between rotational energy and the glass transition temperature using a number of different synthetic polymers with known structures and T_g values. During cooling, the rotation of various atoms and groups in a polymer becomes less and at T_g, this rotation is finally inhibited due to lack of enough rotational energy to overcome the forces holding the molecules together (Hayes, 1961). At T_g;

$$E_{coh} = E_R + C \cdot n, \qquad (10)$$

where E_{coh} is the molar cohesive energy; E_R is the molar rotational energy; n is the degrees of freedom that is related to the ability of atoms to rotate; and C is a constant. E_R can be written as a function of T_g as (Hayes, 1961);

$$E_R = (0.5) \cdot n \cdot R \cdot T_g, \qquad (11)$$

where R is the gas constant.

The rules to determine "n", in Eqs. (10) and (11), as suggested by Hayes (1961) are; "1" is assigned for each atom or group that can rotate without causing any chain motion; "6" is assigned for each atom or group that causes chain motion when it rotates; an additional "2" is assigned when any branch group cannot rotate without bumping into the polymer chain due to its size; when a double bond or phenyl group prevents the rotation of a particular atom or group of atoms, the group that is restricted is counted as one atom (Hayes, 1961). Based on these rules, "n" for the monomer unit of dextran was calculated as follows: 7 H atoms connected to C atoms that can rotate without causing any chain motion ($7 \times 1 = 7$); 3 H atoms on OH groups that can rotate without causing any chain motion ($3 \times 1 = 3$); 3 O atoms on OH groups that can cause chain motion when they rotate ($3 \times 6 = 18$); 2 individual O atoms that can cause chain motion when they rotate ($2 \times 6 = 12$); 6 C atoms that can cause chain motion when they rotate ($6 \times 6 = 36$). Therefore, the total number of "n" for the monomeric unit of dextran was calculated to be $n = 76$.

Inserting Eq. (11) into Eq. (10) and dividing both sides of the resulting equation by molar volume of the monomer (V_m), Eq. (12) would be obtained following Eq. (6):

$$\frac{E_{coh}}{V_m} = \mathrm{CED} = \delta^2 = \frac{(0.5) \cdot n \cdot R \cdot T_g + C \cdot n}{V_m}, \tag{12}$$

where CED is the cohesive energy density. As mentioned earlier, CED is related to the energy changes needed to separate molecules from each other during mixing or solution process. According to Eq. (12), CED would increase with T_g. For a polymer of different molecular weights, it has been shown that T_g increases as M_w increases (Aklonis & MacKnight, 1983; Cowie, 1975; Gropper, Moraru, & Kokini, 2002; Icoz, Moraru, & Kokini, 2005; Ruan et al., 1999; Slade & Levine, 1991a, 1991b; Sperling, 2001). So, according to Eq. (12), CED would increase with M_w. However, there should be an inverse relationship between CED and M_w, because as the molecule gets larger, lower energy would be sufficient to separate the molecules from each other (easier separation). For example, for simple liquids, CED is inversely related to M_w and given as (Barton, 1975);

$$\mathrm{CED} = \frac{\Delta H_v - R \cdot T}{M_w/\rho}, \tag{13}$$

where ΔH_v is the heat of vaporization; R is the gas constant; T is the temperature; and ρ is the density. Moreover, Patnaik and Pachter (1999, 2002) have shown the inverse relationship between CED and M_w of poly(methyl methacrylate) (PMMA) using molecular dynamics simulations. An initial steep drop in CED with the number of methacrylate units for PMMA (which is directly related to the M_w) has been shown which then levels off as M_w increases further (Patnaik & Pachter, 1999, 2002). The reason why there is a direct relationship between cohesive energy and T_g according to Hayes (1961) (Eq. (11)) is because the researcher did not focus on the polymers with different M_w, but polymers with different T_g values. A polymer with a high T_g value would not necessarily mean that it would have a higher M_w for different polymers in Hayes (1961) study. Since solubility parameters as a function of M_w for one type of polymer (dextran, in our study) was needed, we have done a modification on the suggested relation by Hayes (1961), following the molecular dynamic simulations by Patnaik and Pachter (1999, 2002), described as follows: Using the data points reported in Patnaik and Pachter (2002), a logarithmic relationship between CED and number of monomers was fitted with an exceptional regression coefficient (Fig. 6 and Eq. (14)).

$$\mathrm{CED} = (-44.69) \cdot \ln(\#\text{ of monomers}) + 356.93$$
$$R^2 = 0.85, \tag{14}$$

where $\#\text{ of monomers} = \frac{\mathrm{M}_{\mathrm{w}_{\mathrm{polymer}}}}{\mathrm{M}_{\mathrm{w}_{\mathrm{monomer}}}}$. As a more generalized form, Eq. (14) can be written as;

$$CED = (-A) \cdot \ln(\mathrm{M}_{\mathrm{w}_{\mathrm{polymer}}}) + B, \tag{15}$$

where A and B are constants, showing the inverse relationship between CED and M_w of the polymer. In order to obtain a similar relationship between solubility parameters and M_w of the dextrans, the T_g–M_w relationships reported by Icoz et al. (2005) were used. The regression lines for T_g–M_w relations for dextrans at $a_w = 0.00$ was given as;

$M_w < \sim 27{,}000$,

$$T_g = (13.30) \cdot \ln(\mathrm{M}_{\mathrm{w}_{\mathrm{polymer}}}) + 39.82 \quad R^2 = 0.92, \tag{16}$$

$M_w > \sim 27{,}000$,

$$T_g = (0.98) \cdot \ln(\mathrm{M}_{\mathrm{w}_{\mathrm{polymer}}}) + 165.58 \quad R^2 = 0.97. \tag{17}$$

(Icoz et al., 2005). So when Eqs. (16) and (17) were inserted into Eq. (12) with a modification of inserting (−) sign in front of rotational energy term (keeping in mind that CED would be inversely related to M_w following Patnaik and Pachter (1999, 2002)), a relationship similar to Eq. (15) would be obtained;

$$\mathrm{CED} = (-D) \cdot \ln(\mathrm{M}_{\mathrm{w}_{\mathrm{polymer}}}) + E, \tag{18}$$

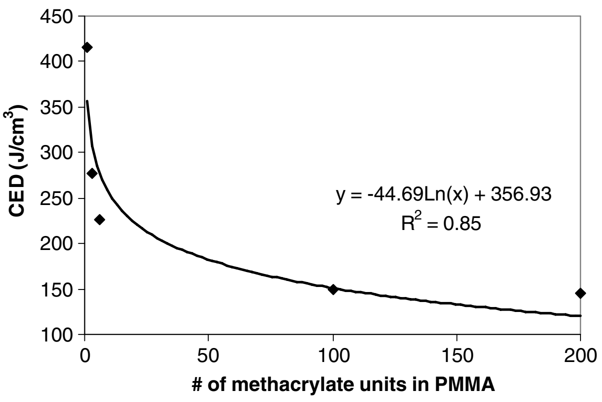


Fig. 6. Variation of cohesive energy density (CED) as a function of number of methacrylate units in poly(methyl methacrylate) – redrawn from the figure reported by Patnaik and Pachter (2002).

where D and E are constants specific to the system of interest.

Rewriting Eq. (18) in the form of Eq. (19), the solubility parameters of dextrans with different M_w could be calculated.

$$\mathrm{CED} = \delta^2 = \frac{(-0.5) \cdot n \cdot R \cdot T_g + C \cdot n}{V_m}. \quad (19)$$

First, the constant "C" was obtained calculating T_g of the monomeric unit from Eq. (16) and knowing the solubility parameter (Figs. 3 and 4), n and V_m of monomer of dextran. Then, using this calculated constant "C" (specific for dextrans) and the T_g of dextrans with different M_w (Icoz et al., 2005), solubility parameter of dextrans with different M_w were calculated using Eq. (19). In these calculations, n and V_m of monomer were used, because n and V_m for a polymer would be ($n\times$ # of monomers) and ($V_m\times$ # of monomers), where (# of monomers) would be cancelled as it would be present in both numerator and denominator of Eq. (19).

Accordingly, using $\delta_{\text{monomer of dextran}} = 19.8\ (\text{cal/cm}^3)^{1/2}$ (Fig. 3); $T_{g,1000} = 124.6$ °C and $T_{g,2,000,000} = 179.5$ °C (Icoz et al., 2005), solubility parameters for dextran with $M_w = 1000$ and $M_w = 2{,}000{,}000$ was calculated as;

$$\delta_{1000} = 19.223(\text{cal/cm}^3)^{1/2} \text{ and}$$
$$\delta_{2,000,000} = 17.221(\text{cal/cm}^3)^{1/2}. \quad (20)$$

In the similar way, using $\delta_{\text{monomer of dextran}} = 22.6\ (\text{cal/cm}^3)^{1/2}$ (Fig. 4); $T_{g,1000} = 124.6$ °C and $T_{g,2,000,000} = 179.5$ °C (Icoz et al., 2005);

$$\delta_{1000} = 22.096(\text{cal/cm}^3)^{1/2} \text{ and}$$
$$\delta_{2,000,000} = 20.378(\text{cal/cm}^3)^{1/2}. \quad (21)$$

Eqs. (20) and (21) show that as M_w of dextrans increased, the solubility parameter decreased, as expected. Solubility parameter of complex carbohydrates, such as amylopectin, can be approximated using δ of dextran with $M_w = 2{,}000{,}000$.

Molecular dynamics simulations could also be used to obtain the relationships between solubility parameters and molecular weight of polymers as in the studies by Patnaik and Pachter (1999, 2002); however, if computational tools are not available, the methodology of using CED–T_g relationship (Eq. (19)) in combination with T_g–M_w relationships (Eqs. (16) and (17)) would provide an exceptional alternative.

3.2. Prediction of miscibility in dextran blends of $M_w = 1000$ and $M_w = 2{,}000{,}000$

Figs. 7 and 8 show the free energy of mixing two dextrans with low and high molecular weights, calculated using the solubility parameters determined in Eqs. (20) and (21), respectively. The contributions from both entropic and enthalpic terms are also illustrated on each figure.

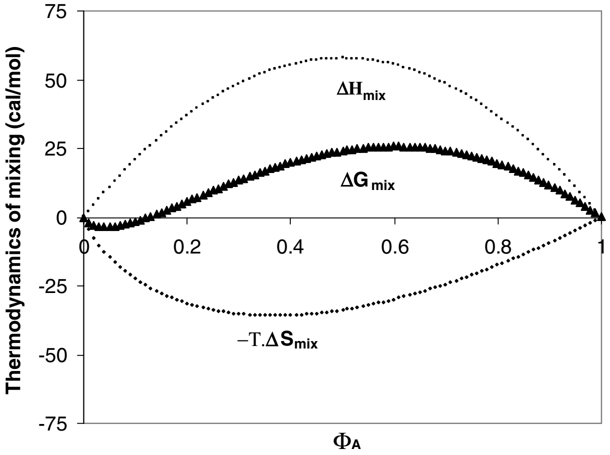


Fig. 7. Predicted free energy, enthalpy and entropy of mixing dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C as a function of volume fraction of dextran with $M_w = 1000$ (using solubility parameters in Eq. (20) following Fig. 3).

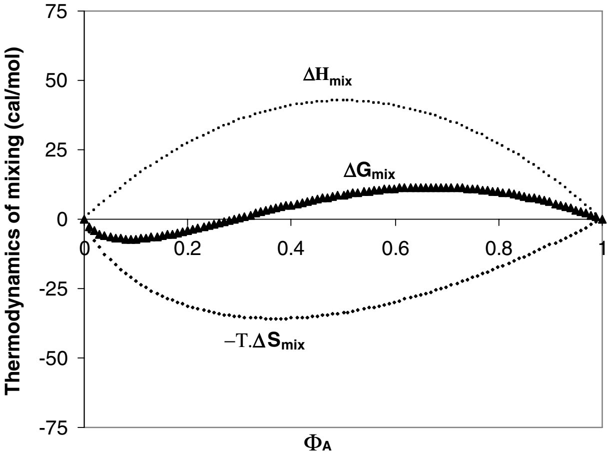


Fig. 8. Predicted free energy, enthalpy and entropy of mixing dextrans with $M_w = 1000$ and $M_w = 2{,}000{,}000$ at 25 °C as a function of volume fraction of dextran with $M_w = 1000$ (using solubility parameters in Eq. (21) following Fig. 4).

Both Figs. 7 and 8 showed (−) contribution from entropy of mixing ($-T{\cdot}\Delta S_{\text{mix}}$) over the entire volume fraction range of dextrans, since the volume fractions in Eq. (3) were smaller than 1 and logarithm of a number smaller than 1 always gives a (−) value. Since the calculation of entropic term was independent of two different versions of calculating solubility parameters determined in Figs. 3 and 4; and was only dependent on the volume fractions and the size of the polymers, both Figs. 7 and 8 had same $-T{\cdot}\Delta S_{\text{mix}}$ values. On the other hand, contribution from enthalpy of mixing (ΔH_{mix}) was calculated to be (+) over the entire composition range since enthalpic term was determined through the square of the difference between solubility parameters of components. Slightly different ΔH_{mix} values were calculated in Figs. 7 and 8 due to the difference in calculating solubility parameters given in Eqs. (20) and (21).

In order to obtain a miscible system, the first requirement is to obtain negative free energy of mixing (ΔG_{mix}). Figs. 7 and 8 both predicted partial negative and partial positive ΔG_{mix} for the range of volume fractions, depending on the contribution from enthalpic term (ΔH_{mix}). If (−) ΔG_{mix} had been obtained over the whole volume fraction range with a concave upwards plot, then dextran with $M_{\mathrm{w}} = 1000$ and $M_{\mathrm{w}} = 2{,}000{,}000$ would be predicted to be completely miscible over the entire composition range. Icoz et al. (2005) have shown miscible systems in blends of dextran with $M_{\mathrm{w}} = 970$ and $M_{\mathrm{w}} = 2{,}000{,}000$. The samples that were prepared using 30% (w/w) (w.b.) polymer concentrated solutions of dextrans; mixing them in various w/w (d.b.) ratios ranging from 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 100/0; freeze-drying these solutions; grinding into powder form; and finally equilibrating at a specific water activity, have shown a single T_g determined through thermal analysis (Icoz et al., 2005). Although component ratios of 60/40, 70/30, 80/20; 90/10 were not reported due to close T_g values to the pure low M_{w} component, these dextrans were miscible over the entire composition range due to their compatible nature. However, the free energies calculated in both Figs. 7 and 8 were unsatisfactory in predicting the actual miscibility in the system under investigation. In Fig. 7, the volume fraction where the change form negative ΔG_{mix} to positive ΔG_{mix} occurred (from miscible to immiscible system predictions) was around $\Phi_A = 0.135$ (13.5/86.5% component ratio). In Fig. 8, the same volume fraction was determined around $\Phi_A = 0.30$ (30/70% component ratio), showing a larger range of volume fractions for predicting negative ΔG_{mix} than that in Fig. 7. The reason for this was due to the difference in calculation of δ of the monomeric unit of dextran (Figs. 3 and 4) and therefore calculation of δ for dextran with different M_{w} (Eqs. (20) and (21)). Calculation of solubility parameter as in Fig. 3 has only taken into account the dispersive forces through group contribution methods. On the other hand, calculation of solubility parameter as in Fig. 4 has also partially included the effect of the polar and the hydrogen bonding forces. Since the monomeric unit of dextran is a glucose molecule with a number of hydroxyl groups, it has high capacity to participate in hydrogen bonding interactions. The difference between δs of dextran with $M_{\mathrm{w}} = 1000$ and $M_{\mathrm{w}} = 2{,}000{,}000$ given in Eq. (20) was larger than that in Eq. (21), resulting in higher enthalpic contribution through Eq. (5) and resulting in a smaller composition range of miscible systems ((−) ΔG_{mix}) (Figs. 7 vs. 8).

The second derivatives of ΔG_{mix} have shown partial positive and partial negative values over the composition range (Figs. 9 and 10), predicting miscibility for limited composition ratios that support the results shown in Figs. 7 and 8, respectively.

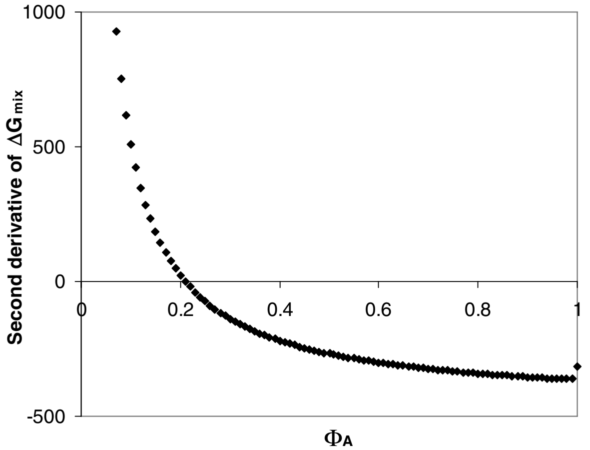


Fig. 9. Second derivative of free energy of mixing dextrans with $M_{\mathrm{w}} = 1000$ and $M_{\mathrm{w}} = 2{,}000{,}000$ at 25 °C as a function of volume fraction of dextran with $M_{\mathrm{w}} = 1000$ (following Fig. 7).

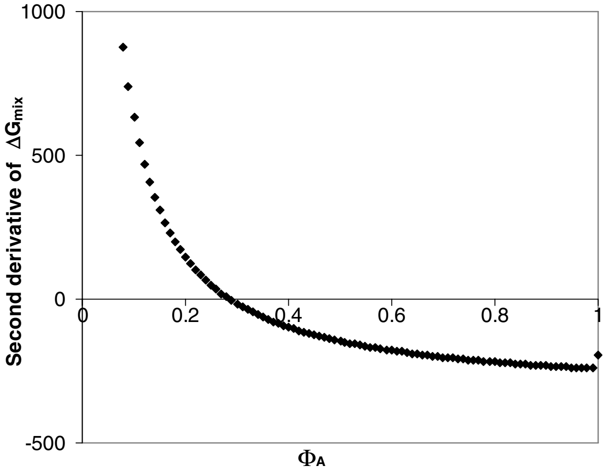


Fig. 10. Second derivative of free energy of mixing dextrans with $M_{\mathrm{W}} = 1000$ and $\mathrm{M_W} = 2{,}000{,}000$ at 25 °C as a function of vloume fraction of dextran with $M_{\mathrm{W}} = 1000$ (following Fig. 8).

The overall results have shown that the original Flory–Huggins theory was not sufficient enough to predict miscibility in dextran blends as model carbohydrate polymers. Calculating enthalpy of mixing using interaction parameters determined from the square of the difference between solubility parameters of the two components underestimated the presence of strong hydrogen bonding between the components, which would actually enhance their miscibility by creating sufficient thermodynamics of interactions. Improvement of the miscibility predictions of carbohydrate polymers requires more advanced thermodynamic models, such as Painter-Coleman Association model, which handles the specific hydrogen bonding interactions separately by inserting a free energy of hydrogen bond formation term to the right-hand side of the original Flory–Huggins equation.

Before concluding the findings in this paper, one last point to be made is that the system under consideration in the current study was dextran (1) + dextran (2) systems with two different molecular weights. If a third component (such as water) would be included into the system, then the thermodynamic analysis would be slightly complicated and the Flory–Huggins equation for the two-components (Eq. (3)) would be re-written for a three-component system. An additional entropic term would be added to the right-hand side of Eq. (3). There will also be additional enthalpic terms that describe the interactions between dextran (1) and water; and between dextran (2) and water. This would result in contributing more positive valued terms to the free energy of mixing. Moreover, since water also has strong and multiple hydrogen bonding formation capacity, the predictions using original Flory–Huggins theory would probably fail to determine the actual miscibility in such a three-component system.

4. Conclusions

The methodology of calculating solubility parameters of dextrans with different molecular weights as a function of their glass transition temperatures has been valuable and can provide a predictive tool for various other carbohydrate polymers. The calculated free energy of mixing, thereby miscibility predictions, of two dextrans with different molecular weights using Flory–Huggins theory were shown to be unsatisfactory, demonstrating the restriction of the original theory for carbohydrate systems with monomeric units consisting of multiple hydroxyl groups. Miscibility predictions may be improved with the application of Painter-Coleman association model, which is a more advanced thermodynamic model that can account for the strong hydrogen bonding interactions in a blend. The application of this advanced model on carbohydrate polymers is under investigation.

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