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Estimation of aqueous solubility of starch from various botanical sources using Flory Huggins theory approach

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ABSTRACT

The data of aqueous solubility of starch are essential for the determination of appropriate uses of starch and design of starch based food products. Unfortunately, these data are scarce and often, some are inconsistent. The aqueous solubility of starches from various botanical sources (tuber, cereal and legume) at 338.2 to 368.2 K were measured following the shake-flask method with necessary modifications. In general, the aqueous solubility of starches enhanced significantly as the system temperature increased. The newly developed solubility model as a combination of Clausius–Clapeyron relation and Flory Huggins theory was fitted to the aqueous solubility data of the starches. The model exhibits excellent aqueous solubility prediction of cereal, tuber and legume starches. Composition exhibits stronger effect on the Flory Huggins interaction parameter than the temperature. In conclusion, Flory Huggins approach can be used as a powerful tool in the estimation of aqueous solubility of starches.

KEYWORDS

Aqueous solubility; Composition; Model; Non-ideal solution; Starch; Temperature

Introduction

Starch is an inexpensive edible natural polysaccharide having excellent functional properties. Basically, starch granule consists of amylopectin (hyperbranched polymer) and amylose (linear--helical polymer), which are assembled from five hundred to several hundred thousand of anhydroglucose monomers through covalent bonds. In dilute solution, starch is utilized as a texture control agent such as thickener and stabilizer, whilst dry starch coating is applied as a gas impediment in films or controlled delivery means for drug and flavor (Whistler et al. 1984). As a complex polysaccharide, starch exhibits a peculiar state transition, called gelatinization that indicates gradual physical change of the starch granule from its semi-crystalline phase to a polymeric solution in the rubbery phase due to heating with or without presence of water. This unique phase transition plays important roles in food processings. Generally, food processings utilize gelatinization, which implicates the melting of the

crystalline structures of the starch granules and followed by the leaching of amylose (van der Sman and Goot 2009). Gelatinization is affected by the temperature and water content of the water–starch system (Farhat and Blanshard 1997). In the case of food structuring, the gelatinizing starch granules serve as a type of cooler through which the fix polymer structures can be formed somewhat rapidly during baking (Kusunose et al. 1999). Food structure is one of the principal food characteristics, which govern consumer's sensation during eating. Today's consumers demand for healthy foods with desirable textures, and that are still appetizing, tasty, comfortable and shelf stable (van der Sman and Meinders 2011). Based on the above mentioned information, the gelatinization temperature and aqueous solubility are therefore becoming the two most crucial properties that determine the appropriate uses of starch in food industries (Nwokocha et al. 2009).

Aqueous solubility can be explained as the maximum mass of starch, which can dissolve in a

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particular volume of water. According to Collado et al. (2001), starch with low aqueous solubility and stable values is preferred as raw material in the manufacturing of noodle. On the other hand, the rapidly soluble pregelatinized starches are suitable in the manufacturing of soft foods, such as instant pudding, pie fillings, soups and cake frosting (Alam and Hasnain 2009). The aqueous solubility of starch indicates the proof of physical interactions (bonding forces) between water molecules and semi-crystalline parts of the starch chains. Obviously, when starch granule is heated in water, the glycosidic bonds slack with rise in thermal influence inducing the starch granules to absorb water resulting in irreversible changes (loss of crystallinity), granule swelling, solubilization of amylose and leaching of amylose out into the water (Nwokocha et al. 2009; Gerits et al. 2015). Therefore, the aqueous solubility of starch has been believed to be influenced by amylose to amylopectin ratio in the starch granule, the original protein and lipid content, morphology, granule size, molecular structure, crystallinity, and botanical source (Zhang et al. 2017).

Commonly, the aqueous solubility of solid solute is measured by quantifying the amount of dissolved solute in the solution, generating the results expressed as mass or mole fraction. Hitherto, a number of methods have been established to determine the aqueous solubility of specific solid solutes. However, the conventional saturation shake-flask method results in the most precise aqueous solubility values and is commonly employed as the standard method to validate the newly proposed methods (Baka et al. 2008). In food science and technology, the aqueous solubility of starch is usually reported as the mass percentage of dissolved starch per gram starch (Leach et al. 1959). The food scientists quantify the aqueous solubility of starch by equilibrating starch–water slurries (2%, w/v) at elevated temperatures ranging from 50 °C to 95 °C until the achievement of equilibrium (Lin et al. 2016).

Although the starch–water systems are usually involved in food processings, their thermodynamics fundamental have not been well understood (Cuq et al. 2003; Eckelt et al. 2008). In addition, the demand and rapid growing of starch-based food products have forced the availability of

information related to the thermodynamics fundamental of the starch–water system. However, the data of aqueous solubility of starch may no longer rely on the experimental works, which are expensive, tedious and time-consuming. Therefore, a predictive model of aqueous solubility of starch, which provides an accurate estimation of aqueous solubility of starch can be a better option. Unfortunately, the available predictive model based on functional group contribution for estimation of the activity coefficient and density state approach are mostly applicable for common organic compounds and simple carbohydrates (Gabas and Laguérie 1993; Ran et al. 2002; Hojjati and Rohani 2006; Boothroyd et al. 2018), but are not suitable for starch, which is a complex carbohydrate. This study contributes an investigation of the thermodynamic description of starch–water systems involved of food processing, where starch is the main raw material. The objectives of this study are to measure the aqueous solubility of starches from different botanical sources (cereal, tuber and legume) available in the market and to develop a new aqueous solubility model based on the well-known Clausius–Clapeyron relation and Flory Huggins theory to predict the aqueous solubility of starch. To support the application of the model, some commonly measured physical properties by food scientists, such as heat of fusion, melting temperature, specific heat capacity and volume molar of the repeating unit are required. In addition, the effect of temperature and composition on the Flory Huggins interaction parameter, which was diversely reported in the literature was also investigated. It would be highly valuable if the proposed model is proficiently estimating the aqueous solubility of starch at elevated temperatures that normally applied during processing of starch-based food in which water is added and removed.

Experimental

Materials

As representatives of tuber starches, the potato and cassava starches were respectively purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan) and Jiantai Biological Technology

Co. Ltd. (Dongguan, China). Commercially isolated corn and wheat starches as the example of cereal starches were obtained from Sanwa Cornstarch Co. Ltd. (Kansai, Japan) and Sigma-Aldrich Pte. Ltd. (Singapore), respectively. The commercial mung bean starch (Ton Son Brand) was the product of Sitthinan Co. Ltd. (Thailand), while the adzuki bean starch was a kind donation from the Hashimoto Food Industry Co. Ltd. (Hokkaido, Japan). The reagent grade sulfuric acid (95.5% v/v) and phenol (80% w/w) were purchased from Sigma-Aldrich Pte. Ltd. (Singapore). To prevent any ionic effects on the solubility of starch, this study used Lab made distilled water with conductivity of lower than $3 \mu\text{S cm}^{-1}$.

Procedures for aqueous solubility determination

The solubility of starches at 338.2–368.2 K was quantified according to the method of Schoch (1964), which is basically similar to the shake-flask method of Higuchi and Connors (1965). In brief, the procedure can be explained as follows: 2% (w/v) slurries of starch made by dispersing 0.1 gram (MS_0) of starch in 5 mL distilled water were introduced in to centrifugal tubes and equilibrated in a water bath heater equipped with an automatic temperature-controlling system to maintain the temperature within ± 0.2 K. The temperatures designated for this solubility study were 338.2, 348.2, 358.2, and 368.2 K. The average heating rate was 15 K/min as indicated by thermometers mounted in the test tubes. Aluminum foils were used to cover all of the test tubes to prevent water loss. In addition, to avoid sedimentation of the starch granules during heating, periodic mild stirring was performed to the starch slurries using glass stirrers. After a sufficient period of time (>2 h), the saturated solutions were centrifuged at $1500 \times g$ for 30 min, and the mass of the supernatant (MSU) was recorded and was then followed by diluting it with distilled water to make the total volume of the solution was 10 mL. The total quantity of the starch in this solution (MSA) was assessed by phenol-sulfuric acid method (DuBois et al. 1956). Usually the aqueous solubility of the starch is reported as the percentage of the amount of

starch in supernatant to the dry mass of whole starch sample (MS_0) and was calculated according to equation below:

$$PS (\%) = 100 \times MSA/MS_0 \quad (1)$$

However, mass fraction solubility (w_{st}) is preferred in this study due to flexibility for use in the modeling calculation.

$$w_{st} = MSA/MSU \quad (2)$$

Each experiment was carried out in triplicate and the measured mass solubility was reported as the average of them with reproducibility of within $\pm 5.0\%$.

Thermodynamic analysis

Ideal solution approach

The simplest way for estimating the aqueous solubility of starches is by applying the ideal solubility law (Neau et al. 1997). In this case, the solid phase must be solvent free (Peres and Macedo 1996) and the value of activity coefficient becomes unity (Grant and Higuchi 1990). In addition, the affinity between solute molecules and the affinity between solute and solvent molecules are close to each other, and that the molecular volumes of solute and solvent molecules are similar (Neau et al. 1997). Following these approaches, the dissolution of solute in the solvent becomes thermodynamically equivalent to melting of the solute. Accordingly, the shift in free energy of dissolution (ΔG_{dis}) equals the change in free energy of melting (ΔG_f) at the respective temperature. Taking into consideration that the entropy does not change during melting, ΔG_f equals the change in enthalpy of melting (ΔH_f) (Neau et al. 1997). The resulting expression is as follow:

$$\ln(x_2) = -\frac{\Delta H_f}{R} \left(\frac{T_m - T}{T_m \cdot T} \right) + \frac{\Delta C_p}{R} \left(\frac{T_m - T}{T} \right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_m}{T} \right) \quad (3)$$

Equation (3) represents the comprehensive format of the ideal solubility equation, in which x_2 being the mole fraction of solute in the solution at saturated condition, T is the equilibrium temperature, T_m is the melting point of the solute, R is the ideal gas constant, and ΔC_p is the heat

capacity difference of the solute between pure solid and a sub cooled liquid at the respective saturation temperature. Unfortunately, the solute is only thermodynamically stable as a solid at the designated dissolution temperature. Therefore, the ΔC_p is often difficult or even impossible to measure. Thus, an appropriate assumption about ΔC_p value is essential. Neau et al. (1997) suggested that it can be adjusted to zero, which lead to

$$\ln(x_2) = -\frac{\Delta H_f}{R} \left(\frac{T_m - T}{T_m \cdot T} \right) \quad (4)$$

Based on empirical observation, ΔC_p can be better predicted from the entropy of fusion (S_f). Since $\Delta G_f = 0$ at the melting point and $\Delta H_f = T_m \cdot \Delta S_f = T_m \cdot \Delta C_p$, therefore the first two terms in Equation (3) canceled each other out and leads to (Neau et al. 1997)

$$\ln(x_2) = -\frac{\Delta H_f}{RT_m} \ln \left(\frac{T_m}{T} \right) \quad (5)$$

To implement the ideal solubility laws to starches, their enthalpy of fusion and melting temperature have to be available. However, a thorough literature survey unveils the values only for monomers and a few dimmers of sugar unit. Thus, it is necessary to estimate these values for starches.

The Flory Huggins theory approach

In the solubility study, activities are frequently employed as an alternative to concentrations to counterbalance the deviations from thermodynamic ideality in the liquid phase. In order to facilitate this situation, several thermodynamic approaches have been used to predict the activity coefficient. For instance, the Flory Huggins theory has been successfully employed to estimate solubility of sugar in some cases (van der Sman 2013). For starch–water system where their molecules are highly asymmetric, mass or volume fraction based activity coefficient is much better scaled than mole fraction based activity coefficient especially due to extremely low mole fractions of high-molecular-weight starch dissolved in water (Lindvig et al. 2002). Therefore, volume fraction is preferable due to its temperature

insensitivity (Holten-Andersen and Eng 1988). Volume fractions can be calculated from mass fraction solubility and molar volume of the respective components. The molar volume of water is 18.065 cm³/mol, whereas molar volume of starch is 108.27 cm³/mol (Benczedi et al. 1998).

According to the Flory Huggins theory (Flory 1942), the system of starch–water can be written in term of chemical potential of water and starch as follows:

$$\frac{\mu_w}{RT} = \ln(1 - \emptyset) + \left(1 - \frac{1}{N}\right)\emptyset + \chi \cdot \emptyset^2 \quad (6)$$

$$\frac{\mu_{st}}{RT} = N \left[\frac{\ln(\emptyset)}{N} - \left(1 - \frac{1}{N}\right)(1 - \emptyset) + \chi \cdot (1 - \emptyset)^2 \right] \quad (7)$$

with \emptyset is the volume fraction of dissolved starch and $N = v_{st}/v_w$ is the ratio of the molar volume of starch and water, v_{st} and v_w , respectively. Accordingly, χ is the Flory Huggins interaction parameter, which accounts the summation of excess enthalpic (χ_H) and excess entropic (χ_S) roles to the solute–solvent interaction. Due to their molecular structure, most biopolymers and carbohydrates interact with water through hydrogen bonds, which the original Flory Huggins does not consider (van der Sman 2017). Based on the fact that the molecular size difference between starch and water is extremely large, it is plausible to take infinite value of N for starch–water mixture, which subjects to a consequence that

$$\ln(\emptyset)/N \approx 0$$

$$\left(1 - \frac{1}{N}\right)(1 - \emptyset) \approx (1 - \emptyset)$$

resulting in a simpler form of Flory–Huggins equation:

$$\frac{\mu_{st}}{NRT} = -(1 - \emptyset) + \chi \cdot (1 - \emptyset)^2 \quad (8)$$

Flory Huggins theory permits semi-dilute polymer solutions in the rubbery state to split into a water-rich and polymer-rich phases. However, whether this implies for starch–water mixture systems is still not sure. If it takes place, the thermodynamic condition for the phase transition is that $\mu_w \approx 0$, which is a true estimation for polymers with long chain lengths. In addition, the

long starch molecules are assumed to be flexible and linear chain; and have multiple degrees of freedom (van der Sman 2017). In reality, starch consists of amylose which contains long stiff chain with helical segments and multi branches amylopectin molecules (Eggleston et al. 2018).

Due to the fact that the exact molar weight of starch is not known, it is more comfortable to describe the chemical potential μ_{ust} of the rubbery polymer phase per mole of its monomeric unit (i.e. anhydroglucose). Then, the chemical potential of the starch can be written as (van der Sman and Meinders 2011):

$$\frac{v_{st}}{v_w} \frac{\mu_{st}}{NRT} = \frac{\mu_{ust}}{RT} = -\frac{v_{st}}{v_w} \left[(1 - \emptyset) - \chi \cdot (1 - \emptyset)^2 \right] \quad (9)$$

with $v_{st}/v_w = 5.8$ is the ratio of molar volume of the anhydroglucose and water. In practical applications, the above simplified Flory Huggins correlation can be utilized to predict the aqueous solubility of starch at elevated temperature with the presence of enthalpy of fusion of the repeating unit (ΔH_{fu}) and melting point (T_m) data:

$$-\frac{\Delta H_{fu}}{R} \left(\frac{T_m - T}{T_m \cdot T} \right) = -\frac{v_{st}}{v_w} \left[(1 - \emptyset) - \chi \cdot (1 - \emptyset)^2 \right] \quad (10)$$

Indeed, the Clausius–Clapeyron relation still applies, but now with the use of enthalpy of fusion per mole of the repeating unit ΔH_{fu} . In the investigation of the melting point depression of starch, food scientists generally use this form of the Flory Huggins theory (Eckelt et al. 2008). However, for accurate prediction of aqueous solubility of starch, more rigorous use of Flory-Huggins theory is preferred.

$$\frac{\mu_{st}}{RT} = \ln(\emptyset) - (N - 1)(1 - \emptyset) + \chi \cdot N \cdot (1 - \emptyset)^2 \quad (11)$$

$$-\frac{\Delta H_{fu}}{R} \left(\frac{T_m - T}{T_m \cdot T} \right) = \ln(\emptyset) - (N - 1)(1 - \emptyset) + \chi \cdot N \cdot (1 - \emptyset)^2 \quad (12)$$

Flory postulated that the crystalline part of a polymer does not imbibe water (Flory 1949). In fact, the starch crystal phase contains structural water, which does not redound to the chemical potential of liquid water μ_w . Therefore, the volume fraction of the starch in the rubbery phase (\emptyset) can be calculated using:

$$\emptyset = \frac{(1 - \varepsilon) \left(\frac{w_{st}}{\rho_{st}} \right)}{\left(\frac{w_w - w_{wx}}{\rho_w} \right) + (1 - \varepsilon) \left(\frac{w_{st}}{\rho_{st}} \right)} \quad (13)$$

with ε is the degree of crystallinity, while w_w and $w_{st} = 1 - w_w$ are respectively the mass fraction of water and starch. The ρ_w and ρ_{st} represent the mass densities of water and starch, respectively. Surprisingly, Limbach and Ubbink (2008) found that the density of polysaccharides is evidently independent of the molar weight and looks to stand for the whole class of polysaccharides. van der Sman (2008) suggested to take the value $\rho_{st} = 1550 \text{ kg/m}^3$. The amount of structural water w_{wx} can be computed as

$$w_{wx} = \frac{1}{3} \frac{M_w}{M_{st}} \varepsilon \cdot w_{st} \quad (14)$$

M_w and M_{st} represent the molar weight of water and anhydroglucose. The factor 1/3 indicates the most possible ratio of the number of structural water molecules to the anhydroglucose molecules in a single lattice unit cell. Alternatively, the (\emptyset) can be easily estimated from the curve fitting of the volume fluctuations obtained from the amorphous starch-water systems data (Benczedi et al. 1998).

$$\emptyset = 1 - 1.386 (1 - w_{st}) + 0.399(1 - w_{st})^2 \quad (15)$$

In the absent of particular attractive interactions between polymer and solvent, one might assume that the value of χ always positive (repulsive), in which case the best solvent one could expect for would be athermal, i.e. with $\chi = 0$. In reality, the predominantly good solvents for normally used polymers possess χ values upward of 0.3 (Brandrup et al. 1999). This is exceptional because $\chi = 0.5$ has been well-recognised as the limiting value for a marginal solvent (Milner et al. 2009). Theoretically, the Flory-Huggins interaction parameter (χ_{wst}) decreases linearly with the increases of temperature following the correlation (Farhat and Blanshard 1997):

$$\chi(T) = \frac{C \cdot v_i}{RT} \quad (16)$$

with C and v_i are respectively the energy of interaction per solvent molecule and molar volume of the solvent. Surprisingly, van der Sman (2017) found that analysis reveals that the interaction

parameter between polyols, sugars and polysaccharides and water is indeed temperature independent. This result is in good agreement with van der Sman and Meinders (2011) who observed that the interaction parameter of polysaccharides (maltodextrins and starch) and water is temperature independent. However, this parameter is composition dependent for maltodextrins with degree of polymerization larger than 2 (van der Sman 2017):

$$\chi_{wst} = \chi_0 + (\chi_1 - \chi_0) \cdot \Phi^2 \quad (17)$$

with $\chi_0 = 0.5$ for all maltodextrins and polysaccharides, especially ungelatinised starch and gelatinized starch in the semi-dilute regime. The χ_1 is the Flory Huggins interaction parameter in the concentrated regime and being largely dependent on the molar weight M_s (van der Sman 2017). The inclusion of composition dependent on χ_{wst} is an effort to widen the application of Flory Huggins theory to the semi-dilute regime (van der Sman and Meinders 2011).

From their study on the temperature dependence of χ for five blend compositions in the H88/D78 systems, Krishnamoorti et al. (1994) found that at each composition χ is roughly linear with T^{-1} , but with slope and intercept that vary with composition:

$$\chi(\Phi, T) = \frac{A(\Phi)}{T} + B(\Phi) \quad (18)$$

This form sufficiently represents $\chi(\Phi, T)$ over the attainable range of temperature (the single phase region) for all systems with the exception of the H78/DPEB system, for which χ is fundamentally independent of temperature. Krishnamoorti et al. (1994) ended up with a conclusion that the composition and temperature dependency of χ_{wst} may follow an empirical equation:

$$\chi(\Phi, T) = \beta(T) + \frac{\gamma(T)}{\Phi \cdot (1 - \Phi)} \quad (19)$$

in which both $\beta(T)$ and $\gamma(T)$ conform the independent relationships of the form $A/T + B$. On the other hand, Nedoma et al. (2008) observed that χ exhibits linear correlation with $(2\Phi - 1)$. They suggested that of $(2\Phi - 1)$ is the most comfortable measure of blend composition as it becomes zero for symmetric blends with $\Phi = 0.5$, and most determination of χ in the literature are conducted

using symmetric blends. Then, they suggested the following correlations to show the influence of temperature, composition and molecular weight on χ :

$$\chi(\Phi, T) = A(T) + B(T) \cdot \frac{(2\Phi - 1)}{N_{ave}} \quad (20)$$

$$A = -0.00662 + \frac{10.6}{T} - \frac{3040}{T^2} \quad (21)$$

$$B = -0.722 + \frac{638}{T} - \frac{229000}{T^2} \quad (22)$$

$$N_{ave} = 4 \left[\frac{1}{N_{st}^{1/2}} + \frac{1}{N_w^{1/2}} \right]^2 \quad (23)$$

Unfortunately, the molecular weight and the number of anhydroglucose per chain of the starch are not exactly known (van der Sman and Meinders 2011). For that reason, the $B(T)/N_{ave}$ can be lumped and Equation (20) can be simplified to:

$$\chi(\Phi, T) = A(T) + B'(T) \cdot (2\Phi - 1) \quad (24)$$

By taking into consideration that χ_{wst} is independent of temperature (van der Sman 2017), the values of β and γ of Equation (19) and A and B' of Equation (24) were kept constant at all temperatures studied.

In this work, the combined Clausius–Clapeyron and Flory Huggins correlation was used to fit the experimental aqueous solubility data. The constants (β and γ) of Krishnamoorti et al. (1994) equation or A and B' of Nedoma et al. (2008) equation) of the Flory Huggins interaction parameter were acquired through a non-linear curve fitting optimization process using Auto2fit software version 3.0 (CPC-X software). The optimization employed the Levenberg–Marquardt algorithm, which is an iterative process that finishes when the calculation reaches convergence. We used 5000 iterations with convergence tolerance of 1.0×10^{-6} .

Computational validation

The experimental aqueous solubility data of various starches was fitted to Equations (12) (19), and (24), by which the constants of the proposed model were optimized. Then, the back-calculated aqueous solubility values were employed to calculate the individual relative deviation (IRD) and mean relative deviation (MRD) values, which indicate thoroughness of the model. The values

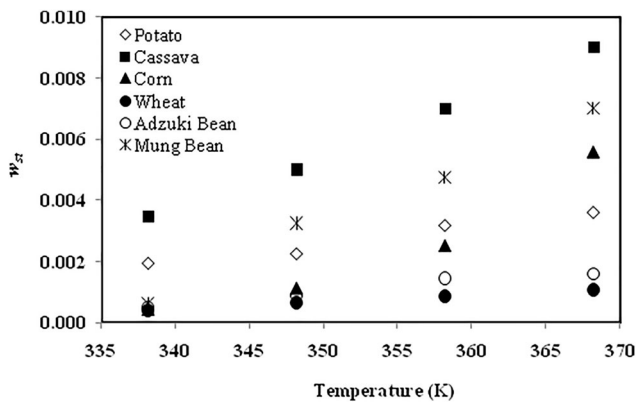


Figure 1. Mass fraction aqueous solubility of various starches.

for IRD and MRD were computed using Equations (25) and (26):

$$IRD = 100 \times \left(|w_{st}^{Cal} - w_{st}^{Obs}| \right) / w_{st}^{Obs} \quad (25)$$

$$MRD = \sum_1^N IRD / N_d \quad (26)$$

where N_d was the number of data points in each set.

Results and discussion

Effect of type of botanical sources on starch solubility

The aqueous solubilities of starch from various botanical sources at various temperatures are presented in Figure 1, while the physicochemical properties of the starches are tabulated in Table 1. These aqueous solubility values are within the range of acceptable aqueous solubility of starches from various botanical sources reported in the literature (Das et al. 2015). As expected, all starches were less soluble below the gelatinization temperature (T_{gel}). In addition, the solubility of all of the starches increases as the temperature increases (Alam and Hasnain 2009). This increase in solubility is basically induced by the interruption of hydrogen bonds, which allows more extensive interactions between starch chains within the amorphous and crystalline regions (Zhang et al. 2018). From Figure 1, we notice that the starch granules hold their integrity when heated in excess water up to their gelatinization temperatures and break of their granular structure thereafter. This condition triggers the starch granules to absorb more water and promote

granule swelling, which lead to the solubilization and leaching out of amylose and results in enhanced solubilities (Alam and Hasnain 2009).

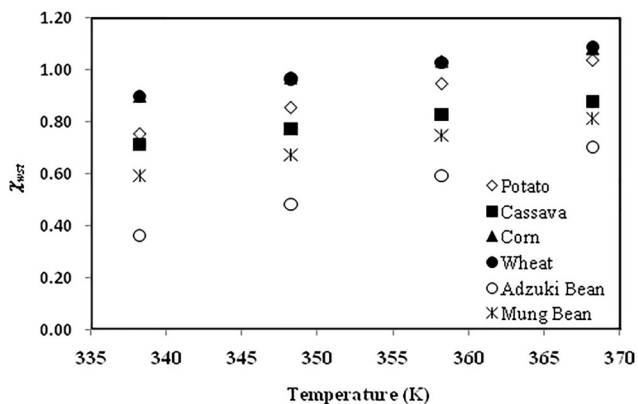
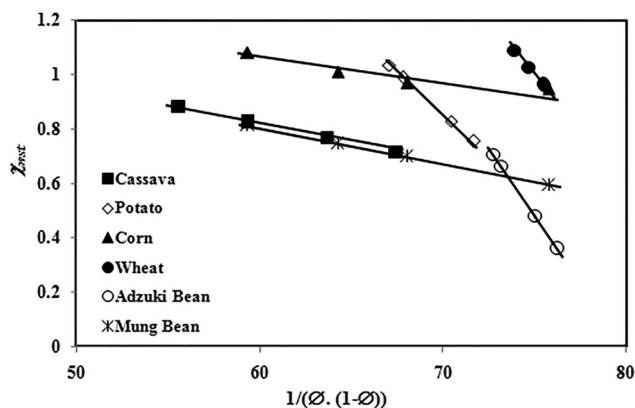
The differences in aqueous solubility of the six starches investigated at elevated temperatures could be attributed to the different morphology, granule size, molecular structure, crystallinity, amylose to amylopectin ratio, chain length distributions, protein and lipid content and botanical source (Fan et al. 2016). It is common that starch with B-type crystal polymorph exhibits higher aqueous solubility than the A-type and C-type starches (Crochet et al. 2005). Exceptionally, although cassava starch exhibits A-type X-ray diffraction pattern it shows the highest solubility at all temperatures compared to other starches. This is because the nonglucosidic portion (protein and lipid content) of cassava starch is extremely low. Therefore, amylose does not form complexes with lipids in cassava starch. Theoretically, starches with smaller granule size and/or lower molecular weight have higher aqueous solubility and vice versa (Goering and de Haas 1972). Mung bean and potato starches show their high solubility due to low molecular weight and low protein and lipid content. The presence of considerable amount specific proteins and lipid in wheat, corn and adzuki bean starches is likely to lower their aqueous solubility (Zhang and Hamaker 2003).

Effect of composition and temperature on Flory Huggins interaction parameters

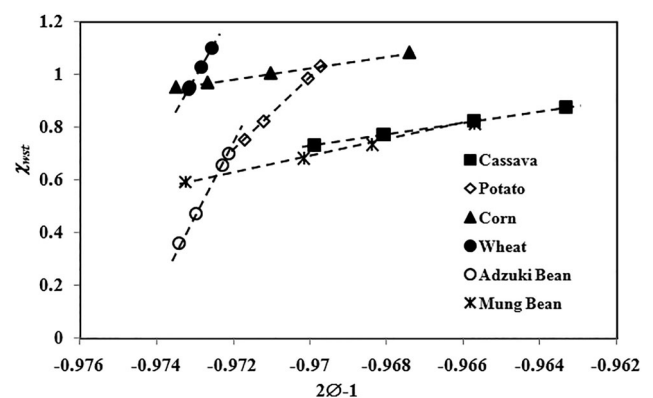
The optimized Flory-Huggins interaction parameters of starch–water system (χ_{wst}) in this study are shown in Figure 2. In most cases, the values of χ_{wst} were higher than 0.5 suggesting that water is a poor solvent for starch (van der Sman and Meinders 2011). As depicted in Figure 2, the values of χ_{wst} slightly increase with the increasing temperature. This phenomenon indicates that starch–water systems exhibit lower critical solution temperature (LCST) behavior (Nedoma et al. 2008). As a result, the χ_{wst} should merely depend on the composition in these systems (Krishnamoorti 1999). However, this result is not surprising since most (if not all) past studies on LCST polymer blends have also indicated similar observation (Reichart et al. 1997).

Table 1. Physicochemical properties of starches.

Starch (type)	Size μm	Crystallinity %	Amylose%	Protein %	Lipid %	T_{gel} K	ΔH_{fu} J/mol	T_m K	MW g/mol	Ref.
Corn (A)	13.5	27.0	23.0	0.40	0.60	339.00	42300	460.2	1.80×10^8	Donovan and Mapes (1980); Zhang et al. (2017)
Wheat (A)	18.6	29.9	19.4	0.20	0.08	326.30	37300	483.2	1.78×10^8	Lelievre (1974); Tetchi et al. (2007)
Potato (B)	44.5	23.0	20.1	0.10	0.10	334.20	56700	441.2	9.40×10^7	Donovan and Mapes (1980); Zhang et al. (2017)
Cassava (A)	16.0	35.0	20.0	0.08	0.01	334.77	38200	527.2	1.30×10^8	Garcia et al. (1996); Tetchi et al. (2007); Aldana and Quintero (2013)
Mung Bean (C _A)	22.1	29.1	24.6	0.13	0.06	343.31	47880	508.2	4.61×10^7	Califano and Anon (1990); Phrukkiwattanakul et al. (2014)
Adzuki Bean (A)	32.0	27.4	28.8	0.10	0.60	330.03	68040	476.2	1.48×10^8	Biliaderis et al. (1980); Tjahjadi and Breene (1984)

**Figure 2.** Flory Huggins interaction parameters of various starches–water system.**Figure 3.** Plot of χ_{wst} versus $1/(\phi \cdot (1-\phi))$.

Later, our modeling calculations also confirmed that the Flory-Huggins interaction parameter is strongly dependent on composition at a given temperature range. Following the Flory Huggins theory, the composition is expressed as the volume fraction of dissolved starch (ϕ). Figure 3 presents the correlation between χ_{wst} versus $1/(\phi \cdot (1-\phi))$ according to the correlation of Krishnamoorti et al. (1994), whereas and Figure 4 depicts correlation between χ_{wst} versus

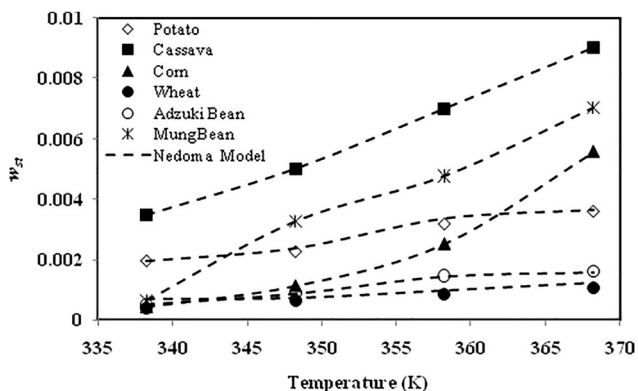
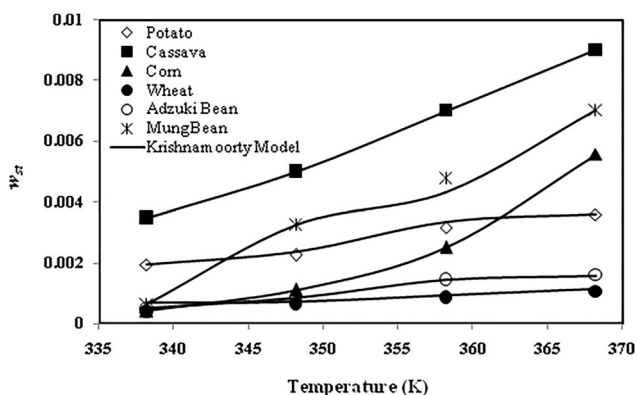
**Figure 4.** Plot of χ_{wst} versus $(2\phi-1)$.

$(1-\phi)$ suggested by Nedoma et al. (2008). Both figures exhibit excellent linear correlations with different value of slopes. The correlation between χ_{wst} and $1/(\phi \cdot (1-\phi))$ has negative value of slopes, whereas the $(1-\phi)$ and χ_{wst} are very well correlated with positive value of slopes. It can also be clearly observed that the slopes are dependent on the botanical source of the starch.

Table 2 presents the optimized constants of Flory Huggins interaction parameters dependency on composition and temperature calculated using correlation of Krishnamoorti et al. (1994) and Nedoma et al. (2008). We kept the constants of Equations (19) and (24) to be temperature independent as suggested by van der Sman and Meinders (2011) and let them to be merely composition dependent. As seen in Table 2, the average MRD values are less than 2% for all constants of both equations suggesting that they are valid at all temperatures for the respective starch. Our results agree well with Krishnamoorti et al. (1994) that the values of $\beta(T)$ and $\gamma(T)$ for starch–water system do not follow the $A/T+B$ relationship because their χ is essentially

Table 2. Constants of Flory Huggins interaction parameters.

Starch (type)	Equation of Krishnamoorti et al. (1994)			Equation of Nedoma et al. (2008)		
	β	γ	MRD (%)	A	B'	MRD (%)
<i>Cereal</i>						
Corn (A)	1.6795	-0.0096	1.8908	22.1029	21.7276	2.1169
Wheat (A)	6.6555	-0.0754	1.5611	247.0232	252.8623	1.8814
Average MRD			1.7260			1.9992
<i>Tuber</i>						
Potato (B)	5.0897	-0.0605	1.9780	138.4204	141.6760	2.0158
Cassava (A)	1.6609	-0.0141	0.2859	22.2892	22.2693	0.7232
Average MRD			1.1320			1.3695
<i>Legume</i>						
Mung Bean (C _A)	1.6033	-0.0133	0.8062	28.8401	29.0227	0.7391
Adzuki Bean (A)	7.8791	-0.0986	2.6969	159.1402	265.8490	2.8280
Average MRD			1.7516			1.835

**Figure 5.** Comparison of experimental and calculated mass fraction aqueous solubility of various starches using χ correlation of Krishnamoorti et al. (1994).**Figure 6.** Comparison of experimental and calculated mass fraction aqueous solubility of various starches using χ correlation of Nedoma et al. (2008).

independent of temperature. It is also surprising that lumping of the $B(T)/N_{ave}$ in Equation (20) to B' in Equation (24) does not reduce the accuracy of the equation. In addition to the successful removal of temperature dependence on χ_{wst} , the use of B' is simpler and may open widely further application of Flory Huggins approach in starch-water system model development.

Model validation with experimental data

The aqueous solubilities of starch obtained from back calculation using Equation (12) and the optimized constants of Flory Huggins parameter are compared with those obtained from experiments. For comparison purpose, both Equations (19) and (24) were used in Flory Huggins parameter calculation. The modeling results are given in Figures 3 and 4.

It is clearly seen in Figure 5 and 6 that Flory Huggins based aqueous solubility model performs excellent estimation of aqueous solubility of all starches under study. No matter either using χ correlations by Krishnamoorti et al. (1994) or by Nedoma et al. (2008), Flory Huggins based aqueous solubility model fits the experimental data very well. Table 2 provides the mean relative deviations (MRD) of the calculated aqueous solubility of various starches from their experimental values. In general, the MRD values were lower than 2% for all starches. Calculation of aqueous solubility of starch using χ correlations by Krishnamoorti et al. (1994) resulted in a slightly higher MRD than that of using χ correlations by Nedoma et al. (2008). In addition, the Equation (24) developed by Nedoma et al. (2008) offers simpler and faster calculations than Equation (19) to obtain comparable results. Therefore, as supported by the fact that starch-water systems exhibit lower critical solution temperature (LCST) behavior, the composition dependent and temperature independent approaches used in the χ correlations are exactly correct. Although the Flory Huggins theory was originally developed to hold only in the concentrated regime, our results finally confirmed that it is also applicable to the

semi-dilute regime. Therefore, Flory-Huggins theory is suitable to be used as the basis for the prediction of aqueous solubility of starch from various botanical sources.

Conclusion

The aqueous solubility of cereal, tuber and legume starches at elevated temperatures (338.2 to 368.2 K) has been studied. The aqueous solubility of all of those starches increases with temperatures. It is observed that the solubility of starch is strongly affected by its botanical source, which contributes to the uniqueness of the starch. The Flory Huggins based solubility model has been developed and proven its accuracy for the estimation of aqueous solubility of those starches. Composition exhibits stronger effect on the Flory Huggins interaction parameter than the temperature. Therefore, Flory Huggins approach can be used as a powerful tool in the estimation of aqueous solubility of starches.

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Nomenclature

A, B, B'	the constants of the model
C	energy of interaction per solvent molecule
IRD	individual relative deviation
MRD	mean relative deviations
M_{st}	molar weights of anhydroglucose, g/mol
M_w	molar weights of water, g/mol
N	the ratio of the molar volume of starch and water
N_{st}	the number of repeat units (anhydroglucose) per chain of the starch
N_w	the number of repeat units of water
R	ideal gas constant, 8.31 J/mol.K
T	temperature, K
T_m	melting point of the solute, K
v_i	molar volume of solvent, cm ³ /mol
v_{st}	molar volume of starch, cm ³ /mol
v_w	molar volume of water, cm ³ /mol
w_w	mass fraction of water

w_{wx}	amount of structural water
w_{st}	mass fraction solubility of starch
w_{st}^{Cal}	mass fraction solubility of starch calculated from the model
w_{st}^{Obs}	mass fraction solubility of starch obtained from experiment
β, γ	the constants of the model
χ	Flory Huggins interaction parameter
χ_0	Flory Huggins interaction parameter in the semi dilute regime
χ_1	Flory Huggins interaction parameter in the concentrated regime
χ_{wst}	Flory Huggins interaction parameter for starch--water system
x_2	mole fraction of starch in solution at saturation
ε	the degree crystallinity, %
ΔC_p	heat capacity difference of the solute between pure solid and a subcooled liquid at the dissolution temperature, J/mol. K
ΔG_{dis}	free energy of dissolution, J/mol
ΔG_f	free energy of melting, J/mol
ΔH_f	enthalpy of fusion at the melting point temperature, J/mol
ΔH_{fu}	enthalpy of melting per mole of the repeating unit, J/mol
ΔS_f	entropy of fusion at the melting point temperature, J/mol. K
\emptyset	volume fraction of dissolved starch
ρ_w	mass densities of water and starch, kg/m ³
ρ_{st}	mass densities of starch, kg/m ³
μ_w	chemical potential of water, J/mol
μ_{st}	chemical potential of starch, J/mol
μ_{ust}	chemical potential of the rubbery starch phase per mole of anhydroglucose, J/mol

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