Flory-Huggins Theory Based Approach for Estimation of Aqueous Solubility of Starch from Various Botanical Sources

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Abstract. Nowadays the importance of starches in industrial application in food, pharmaceutical and cosmetic industries is well recognized. Unfortunately, their thermodynamics aspect has not been well understood. The objective of this study is to develop a simple thermodynamic model for the estimation of aqueous solubility of cereal, tuber and legume starches through Flory-Huggins theory approach. The aqueous solubility of starch was investigated experimentally as the mass percentage of dissolved starch per gram starch using shake-flask method at 338.2 to 368.2 K according to common practice in food science and technology. The solubility of starch was found to increase with the elevation of temperature. In general, starches from tuber exhibit higher aqueous solubility than starches from other sources. The results showed that Flory-Huggins theory is suitable to be used as the basis for the prediction of aqueous solubility of starch from various botanical sources. In most cases, the Flory-Huggins interaction parameters (c_wst) were higher than 0.5 suggesting that water is a poor solvent for starch. The Flory-Huggins interaction parameters were highly dependent on composition, which is in good agreement with previous report for synthetic polymer blends. Therefore, Flory Huggins approach can be used as a useful tool in the prediction of aqueous solubility of starches.

1. Introduction
Starch is a cheap edible natural polysaccharide produced by plants with rich in functional properties. In the recent times, its importance is well recognized, especially in their industrial application in food, pharmaceutical and cosmetic industries. In highly dilute solution, starch is generally used as a texturogen, whereas at low moisture, starch glass is used as a gas barrier in films or controlled delivery devices. In spite of the useful significance of starch in food structuring; its thermodynamics background is scarcely understood [1].

Aqueous solubility can be described as the greatest amount of starch, which can dissolve in a particular volume of water [2]. Collado et al. [3] suggested that starch with low aqueous solubility and stable values are preferred as raw material in the preparation of noodle. In contrast, the rapidly soluble pregelatinised starches are more appropriate in the production of soft foods, such as instant pudding, pie fillings, soups and cake frosting [4]. The aqueous solubility of starch indicates the proof of...
physical interactions between water molecules and the starch chains in both crystalline and amorphous zones. Clearly, when starch granule is heated in excess water, the glycosidic bonds slack with the rise in thermal influence promoting the starch granules to absorb water resulting in irreversible changes (loss of crystallinity), granule swelling, solubilisation of amylose and leaching of amylose out into the water [5,6]. 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 [7].

In this study, we determined the aqueous solubility of starches from different botanical sources (cereal, tuber and legume) easily available in the market and followed by developing a new model based on the well-established Clausius – Clapeyron relation and Flory Huggins theory to estimate the aqueous solubility of starch. The Flory Huggins theory was selected as the fundamental approach in this study as it has been successfully implemented for the prediction of melting point of starches and flours from various botanical sources under low moisture content. Moreover, it would be highly valuable if the proposed model is capable of accurately estimating the aqueous solubility of starch at elevated temperatures that usually implemented during processing of starch-based food.

2. Materials and Method

2.1. Materials

The potato and cassava starches used in this study were respectively obtained from Wako Pure Chemical Industries Ltd. (Tokyo, Japan) and Jiantai Biological Technology Co. Ltd. (Dongguan, China). On the other hand, the corn and wheat starches were procured from Sanwa Cornstarch Co. Ltd. (Kansai, Japan) and Sigma-Aldrich Pte. Ltd. (Singapore), respectively. The commercial mung bean starch (Ton Son Brand) is the product of Sitthinan Co. Ltd. (Thailand), while the adzuki bean starch was supplied by the Hashimoto Food Industry Co. Ltd. (Hokkaido, Japan). The reagent grade sulphuric acid (95.5% v/v) and phenol (80% w/w) were the products of Sigma-Aldrich Pte. Ltd. (Singapore). Lab made distilled water with conductivity of lower than 3 µS.cm⁻¹ was used throughout this study.

2.2. Aqueous solubility experiment

The aqueous solubility of starches at 338.2 – 368.2 K was examined following the method of Schoch [8], which is fundamentally identical to the shake-flask method firstly developed by Higuchi and Connors [9]. In essence, the method can be explicated as follows: 2% (w/v) starch slurries prepared by dispersing 0.1 gram (MS₀) of starch in 5 × 10⁻⁵ m³ distilled water were put in to centrifugal glass tubes and incubated in an automatically controlled water bath heater to maintain the temperature within ±0.2 K. The temperatures investigated in this solubility study were 338.2, 348.2, 358.2, and 368.2 K. All of the test tubes were covered by aluminum foils to avoid the loss of water. In addition, periodic mild stirrings were performed to the starch slurries using glass stirrers to ensure no serious sedimentation of starch granules. After 7,200 seconds incubation, the supernatant (MSU) was separated from the saturated solutions via centrifugation at 1500 ×g for 30 min. Schoch [8] mentioned that 7,200 seconds incubation is already sufficient for the starch to dissolve in water. The mass of the supernatant (MSU) was written down and it was added with distilled water to make the total volume of the solution was 1 × 10⁻⁵ m³. The total quantity of the starch in this solution (MS₄) was analysed by phenol-sulphuric acid method [10]. 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 (MS₀) and was calculated according to equation below:

\[ PS (%) = 100 \times \frac{MS_A}{MS_t} \] (1)

Each experiment was carried out in triplicate and reported aqueous solubility value was the average of them with reproducibility of within ±5.0%
2.3. Flory – Huggins theory approach

Based on the Flory Huggins theory [11], the starch – water system can be expressed in term of chemical potential of starch as follows:

\[
\frac{\Delta H_{fu}}{R} \left( \frac{T_m - T}{T_m \cdot T} \right) = \ln(\varnothing) - (N - 1)(1 - \varnothing) + \chi \cdot N \cdot (1 - \varnothing)^2
\]

(2)

Obviously, the Clausius – Clapeyron relation still applies, but now with the utilisation of enthalpy of fusion per mole of the repeating unit \( \Delta H_{fu} \). The \( \chi \) in equation (2) is the Flory Huggins interaction parameter, \( T \) is the absolute temperature of the system, \( T_m \) is the melting point of the starch, \( R \) is ideal gas constant and \( N \) is the is ratio of the molar volume of starch and water. In addition, \( \varnothing \) is the volume fraction of the dissolved starch. The value of \( \varnothing \) can be related with mass fraction aqueous solubility according to the following equation [12]:

\[
\varnothing = 1 - 1.386 \left( 1 - w_{st} \right) + 0.399 \left( 1 - w_{st} \right)^2
\]

(3)

The accuracy of the proposed model was evaluated using the mean relative deviation (MRD):

\[
MRD = \frac{\sum_{t}^{N_d} \times \left( \left| w_{st}^{Cal} - w_{st}^{Obs} \right| \right) / w_{st}^{Obs}}{N_d}
\]

(4)

Where \( N_d \) is the number of data point in each set of experiment. \( w_{st}^{Cal} \) and \( w_{st}^{Obs} \) represent the calculated and observed aqueous solubility.

3. Results and Discussion

3.1. Effect of botanical source on aqueous solubility of starch

The necessary physicochemical properties of starches investigated in this work are presented in Table 1. It was observed that starch derived from different botanical sources has different type of crystallinity, melting point and enthalpy of fusion of its anhydroglucose unit. These properties are believed to affect the aqueous solubility of the starch [7].

| Starch Source        | X-Ray Diffraction Type | \( \Delta H_{fu}, \) J.mol\(^{-1} \) | \( Tm, \) K   | References |
|----------------------|------------------------|-----------------------------------|--------------|------------|
| Wheat                | A                      | 37300                             | 483.2        | [13]       |
| Corn                 | A                      | 42300                             | 460.2        | [14]       |
| Potato               | B                      | 20.00                             | 441.2        | [14]       |
| Cassava              | A                      | 38200                             | 527.2        | [15]       |
| Mung bean            | CA                     | 47880                             | 508.2        | [16]       |
| Adzuki bean          | A                      | 68040                             | 476.2        | [17]       |

Figure 1 shows the observed aqueous solubility of starches at elevated temperature and their comparison with the calculated values obtained from the modeling using combined Clausius – Clapeyron relation and Flory Huggins theory approaches. The increment of temperature remarkably escalated the aqueous solubility. Refer to their crystalline structure, B – type starch is more soluble than A – type and C– type starches [18]. Although being classified as A – type starch, the solubility of cassava starch is the highest at all temperature amongst the starches studied in this work. Potato starch with a higher enthalpy of fusion of its anhydroglucose unit is slightly less soluble than cassava starch. It can also be seen that the other starches were markedly less soluble, especially at lower temperature below their gelatinization temperature. In general, starches with lower molecular weight exhibit higher
aqueous solubility than those of higher molecular weight. In addition, the degree of branching of the amylopectin in the starch granule may also affect the leaching of amylose to water which greatly contributes to solubility. The X-Ray diffraction of the starch granule represent its granule morphology, especially the arrangement birefringence pattern in a radial direction or the degree of order in starch granules. In general, starch molecules consist of amorphous and crystalline parts, which the crystallites are formed by short, external chain segment of amylopectin with a degree of polymerisation of about 10 – 20 glucosyl units. Usually two chain combines into a double-helix having 4 – 6 nm length with 6 glucose residues per turn of each strand and a pitch of approximately 2.1 nm. In the A - type starch crystal, the double-helices are highly packed in to a monoclinic unit cell containing 8 water molecules, while in B - type starch crystal the double-helix are packed in a hexagonal unit cell with 36 water molecules. That is why the B - type starch is theoretically more soluble than other type or starches. In addition, the presence of specific proteins in wheat and adzuki bean starches was likely to lower their aqueous solubility [7].

![Figure 1. Effect of temperature on the aqueous solubility of various starches at atmospheric condition](image)

It is also obviously displayed in Figure 1 that the calculated aqueous solubility values are in accordance with the experimental data. Most of the experimental solubility data coincide with the full lines, which represent the calculated aqueous solubility. These results denote that the combined Clausius – Clapeyron relation and Flory Huggins theory approaches are adequate to be used as the basis for the thermodynamic modeling of aqueous solubility of starch.

3.2. Effect of temperature on Flory Huggins interaction parameter

Figure 2 depicts the Flory Huggins interaction parameters at elevated temperatures for all of the starches. It is evident that in most cases, the Flory-Huggins interaction parameters ($\chi_{sw}$) were higher than 0.5 suggesting that water is a poor solvent for starch [19].

As seen in Figure 2, the Flory Huggins interaction parameters slightly increase with the increase in temperature. This phenomenon indicates that starch – water systems exhibit lower critical solution temperature (LCST) behaviour [20]. This result is in contradiction with literature where the interaction parameter between carbohydrates and water was reported to be temperature independent [21]. However, this finding is in good agreement with previous report for synthetic polymer blends [20, 22]. However, the value of the Flory-Huggins interaction parameters also does not necessarily concur to the mass fraction solubility of the starch as the mass fraction solubility also depends on the melting point and heat of fusion.
4. Conclusion
The aqueous solubility of starches from six different botanical sources (cereal, tuber and legume) at elevated temperatures (338.2 to 368.2 K) has been investigated. The aqueous solubility of all of those starches escalates with temperatures. The aqueous solubility of the starch is strongly depending on its botanical source, which indicates to the uniqueness of the starch. The Flory Huggins based solubility model has been proven its capability for the prediction of aqueous solubility of those starches. The Flory Huggins interaction parameter is found to be sturdily dependent on composition rather than the temperature. Therefore, Flory Huggins approach can be used as a useful tool in the prediction of aqueous solubility of starches.

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Figure 2. Effect of temperature on the Flory Huggins interaction parameter

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**Figure 2.** Effect of temperature on the Flory Huggins interaction parameter
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