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Exploring validity of the macro-micro region concept in the state diagram: Browning of raw and freeze-dried banana slices as a function of moisture content and storage temperature

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State diagram (i.e. 12 micro-regions) of ripe banana was mapped by measuring and modeling its freezing point, glass transition, maximal-freeze-concentration conditions, solids-melting, and BET-monolayer. At 20 °C, the BET-monolayer moisture was observed as 0.044 g/g dry-solids, and decreased with the increase of temperature. Un-freezable water was found as 0.26 g/g sample and the maximal-freeze-concentration temperature (T_m') was observed as −34.5 °C. The freezing point and solids-melting peak were modeled by Chen's and Flory-Huggins models, respectively. Browning of banana stored at different moisture and temperature (i.e. at different micro-regions) were measured as a function of storage time and modeled with first order reaction kinetics. The variation of reaction rate constant was analyzed based on the glass transition, water activity and macro-micro region concepts. At a specific moisture content, reaction rate constant showed a shift (i.e. sample containing freezable water) or change in slope (i.e. sample containing un-freezable water), when plotted as a function of temperature. However, it was difficult to find any validity above or below glass transition (or BET-monolayer) when all data points (i.e. all moisture and temperature) were plotted (i.e. rate constant with moisture or temperature). Arrhenius plot at moisture content 0.04 g/g sample showed two linear regions (i.e. below and above critical temperature 45 °C) with activation energy values of 105.3 and 25.1 kJ/mol, respectively. Universal validation was difficult to achieve, thus the rate constants within different micro-regions were empirically correlated with moisture content, storage temperature, BET-monolayer and glass transition temperature ($p < 0.001$).

1. Introduction

The state diagram is a stability map of different phases and states of a food as a function of water or solids content and temperature; and it is used to determine the possible deterioration or stability when foods are transformed into different phases and states (Rahman, 2004). Most probably, Levine and Slade (1986) presented first state diagram in the food science literature consisting of glass line, freezing curve, and the intersection of these lines. The state diagram was based on the glass transition concept, and White and Cakebread (1966) was the first, who highlighted the importance of the glassy state of foods in determining its stability in relation to the collapse of food powders while raising their temperature. The significant applications of the glass transition concept emerged when its merits are identified and reported in the literature (Levine and Slade, 1986; Slade and Levine, 1988; Roos and Karel, 1991; Rahman, 2006). State diagrams of artificial instant rice (Herawat et al., 2014), pomegranate skin-extract (Al-Rawahi et al., 2013), fish skin gelatin (Rahman et al., 2010; Diaz et al., 2011), date flesh (Guizani et al., 2010), and garlic (Rahman et al., 2005) are published. In the literature, there are negligible state diagrams available, which include freezing point, glass transition, maximal-freeze-concentration conditions, solids-melting, and BET-monolayer.

Over the years, water activity and glass transition are emerged as two most successful theoretical concepts in explaining the food stability during storage and processing. Water activity indicates the binding nature of water molecules (i.e. states of water: bound, free, monolayer, and multi-layers) with the polar sites of the solids

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matrix. Scott (1953) identified that active water is more important to the stability of foods as compared to the total amount of water. The significant progress has been made in the water activity concept for determining the stability of foods. It helps to develop generic rules or limits. For examples, foods are most stable at their “BET-monolayer” or “BET-monolayer water activity” and unstable above or below “BET-monolayer”; a critical water activity limit exists for a specific micro-organism or a class of micro-organism for their growth or toxin production, and biochemical reactions (Scott, 1953; Labuza et al., 1970). Considering bound (i.e. BET-monolayer), adsorbed multi-layer and capillary matrix (i.e. solvent or capillary) water, Labuza et al. (1972) proposed the stability map based on the water activity concept containing growth of micro-organisms and different types of bio-chemical reactions. An updated recent map has been presented by Rahman (2009).

In the literature, numbers of limitations of water activity concept are identified (Rahman, 2010, 2012). One of the major issues of the water activity concept (i.e. BET-monolayer or water binding) is that isotherm is minimally affected by temperature, whereas physico-chemical changes or reactions are strongly affected by temperature (Kurtmann et al., 2009). Considering the limitation of water activity concept, the hypothesis of glass transition concept was proposed. The glass transition concept is based on the molecular mobility in the matrix and it indicates that foods are most stable at or below glass transition. In many cases, the significant decrease in physical and bio-chemical changes did not observe at or below glass transition (Terebiznik et al., 1997; Karmas et al., 1992). It is clear from the literature that all experimental results could not be explained by water activity or glass transition concepts and all foods are not in their glassy or below BET-monolayer (Rahman, 2006, 2009). In addition, all experimental results presented in the literature could not be explained by the above concepts, thus further developments are necessary. However, the limitations of water activity and glass transition concepts would invalid the hypotheses completely rather make it difficult to apply universally (Rahman, 2009, 2010). However, both concepts in combination could be a powerful tool in determining food stability (Chirife et al., 1999; Kurtmann et al., 2009; Zhao et al., 2015). In the literature, numbers of attempts are made to determine stability of foods by applying different types of molecular relaxation. However, molecular relaxation or mobility could provide more insights on the mechanism of stability, but unable to provide any generic trends or rules for stability similar to water activity and glass transition concepts (Rahman, 2010).

Rahman (2006) combined glass transition and water activity concepts in the state diagram by drawing BET-monolayer line. Rahman (2009) advanced the state diagram by proposing the macro-micro region concept in determining the stability of foods. He hypothesized 13 micro-regions having the highest to lowest stability based on the locations from the glass and BET-monolayer lines. For example, region-1 (relatively non-reacting zone, below the BET-monolayer line and glass line) is the most stable and region-13 (highly reacting zone, far from BET-monolayer line and glass line) is the least stable. The stability decreased as the zone number increased. Advantages of macro-micro region concept are as follows: (1) stability rules could be developed for each micro-region (i.e. narrow moisture and temperature range) as compared to the macro-region (i.e. broad moisture and temperature region), and (2) the states or phases of the materials could be identified in each micro-region. A reference point could also be identified where BET-Monolayer line and glass line intersect and any location in the state diagram could be assessed in relation to the reference point (Rahman, 2010, 2015). In order to test the hypothesis of macro-micro region concept, browning of raw and freeze-dried banana during storage was considered in this study.

In order to test the validity of the water activity and glass transition concepts, most of the reported experiments were designed by considering three options. In the first method, sample(s) at a specific moisture content was stored at one or few selected temperature (Terebiznik et al., 1997; Mazzobre et al., 1997a, 1997b; Sa and Sereno, 1999; Karmas et al., 1992; Lievonen et al., 1998). In the second method, samples at different moisture contents were stored at a constant temperature (Selim et al., 2000; Buera et al., 1995; Bell, 1996; Bell and Hageman, 1994; Chen et al., 1999).

In the third approach, samples at specific moisture (i.e. dried sample) were placed at different water activity for equilibration process by maintaining a constant temperature (Moraga et al., 2011; Syamaladevi et al., 2011). The property was measured with time as the equilibration process was continued. Moraga et al. (2011) stored freeze-dried apple and banana at different relative humidity (i.e. a_w: 0.11–0.68) in glass jars by maintaining their temperatures at 20 °C. After equilibration, they measured the rate of color (L-value) and mechanical structure (i.e. puncture force) changes. In a first step, they determined two critical water activity values, one from the water activity value $(a_c)_1$ at 20 °C from the plot of glass line *versus* water activity (i.e. validity of the glass transition concept); and another one $(a_c)_2$ at the BET-monolayer value from the plot of equilibrium moisture content *versus* water activity (i.e. validity of the water activity concept). In the second step, they plotted rate as a function of water activity and determined an experimental critical water activity when a change of slope was observed. This experimental critical water activity (i.e. point of a change in slope in the plot of rate *versus* a_w) was compared with the $(a_c)_1$ and $(a_c)_2$ for determining the validity of the theoretical concepts. Moraga et al. (2011) concluded that both glass transition and water activity concepts need to be considered for explaining mechanical structural changes since experimental critical water activity [$(a_c)_e = 0.33$, for both apple and banana] was much higher than the $(a_c)_1$ (i.e. 0.04, for apple and 0.23, for banana). However, only water activity concept needs to be used to explain the color change since experimental critical water activity [$(a_c)_e = 0.43$, for both apple and banana] was closer to the $(a_c)_2$ (i.e. 0.37, for apple and 0.45, for banana). Similarly, Syamaladevi et al. (2011) measured the anthocyanin (i.e. color pigment) stability of fresh-frozen (i.e. fresh moisture; and −20, −35 and −80 °C) and freeze-dried raspberry (i.e. 23 °C and a_w: 0.11–0.75). They analyzed data by first order reaction kinetics and tested validity of the glass transition and water activity concepts by plotting rate constant as a function of (T-T_g) or a_w. They observed a change in slope at (T-T_g) = 50 °C and water activity at 0.43.

The major flaws in the experimental design of Moraga et al. (2011) and others were: (i) only one temperature was considered, thus the real effects of the temperature was missing, and (ii) the change of the properties was measured with the varied moistures during the equilibration period (i.e. water activity from initial to final state), and this was not the reaction rate (i.e. rate constant) at a fixed moisture or water activity. In addition, the rational of defining $(a_c)_1$ and $(a_c)_2$ was not clearly identified. In the case of freeze-dried sample, Syamaladevi et al. (2011) considered whether the change of slope matched the T-T_g at zero. However, the real effects of moisture and temperature could not be identified since the experiments were conducted only at one temperature. The values of T-T_g were varied since T_g increased with the increase of moisture contents.

In order to check the validity of water activity and glass transition concepts, it is necessary to conduct the reaction rate or change at a fixed moisture and stored at a specific temperature (i.e. isothermal conditions). In addition, stored temperature should be varied for each experiment (i.e. moisture or water activity needs to be fixed). In the literature, availability of these types of experiments