A survey of temperature effects on GAB monolayer in foods and minimum integral entropies of sorption: a Review

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Abstract

Some aspects of GAB monolayer values in foods were reviewed. Literature data on the stoichiometry of water sorption by proteins and other biopolymers, were re-analyzed and a good linear correlation (r^2 = 0.8431) between the number of polar groups and the GAB monolayer was obtained. This helps to corroborate the hypothesis that each polar group initially adsorbs a water molecule. A survey of GAB monolayers at various temperatures in more than 70 different food products indicated that for most of them - although not all - an increase in temperature produced a decrease in the value of moisture content (g water/100 g solids) corresponding to the monolayer. However, in an appreciable number of cases it was observed that the monolayer remained constant or increased with temperature.

The relationship between the minimum integral entropy (MIE) and the GAB monolayer was studied using literature data. For 38 different food products the regression curve (r^2 = 0.9038) between the moisture content corresponding to MIE and GAB monolayer was close to the 45 ° diagonal, suggesting that GAB values matched the position of minimum integral entropy. However, for a wide variety of other products the moisture of the MIE was located above that of the monolayer.

Key words: GAB monolayer – Water sorption – Isotherms –– Minimum integral entropies – Thermodynamic properties – Temperature effect.

1.Introduction

A fundamental characteristic of food materials which influences almost every aspect of the dehydration process and the storage stability of food products, is its water sorption isotherm. Measurement and modeling of sorption isotherms of food materials has attracted numerous researchers because of their application in relation to the stability and design of food dehydration operations. Comprehensive reviews on sorption behavior of foods have been published and several empirical and semi-empirical equations have been proposed for the correlation of the equilibrium moisture content of food materials (Basu et al., 2006; Peleg, 2020).

Early in 1979, Boquet et al. studied the fitting abilities of various three-parameter literature isotherm equations to describe 39 food isotherms of meats, milk products, proteins, starchy foods and vegetables. The best equation was that of Hailwood and Horrobin (1946), which was developed in attempt to interpret the water sorption isotherms of proteins. The remarkably good ability of Hailwood-Horrobin´s equation to fit experimental sorption data in foods, led Boquet et al. (1979) to call it a "universal" equation to describe the sorption isotherms of water in food. Later, Boquet et al. (1980) were able to demonstrate that Hailwood-Horrobin´s equation was mathematically identical to GAB equation.

In the past, the well-known BET (Brunauer, Emmet and Teller) sorption isotherm was the model that had the greatest application to water sorption by foods and foodstuffs (Labuza,1968; Iglesias and Chirife,1976; Timmermann et al. 2001; Basu et al., 2006). One well familiar constant obtained from BET equation was the monolayer moisture content which, as noted by Timmermann et al. (2001), was found to be a reasonable guide with respect to various aspects of interest in low-moisture foods (Karel, 1973; Iglesias and Chirife, 1982; Iglesias and Chirife, 1984).In the past two decades the Guggenheim, Anderson and de Boer (GAB) isotherm equation was widely used to describe the sorption behavior of many types of foods (Van den Berg, 1981; Basu et al., 2006 ; Quirijins et al., 2005; Lomauro et al., 1985). Having a reasonably small number of parameters (three) the GAB equation has been found to adequately represent the experimental data in the range of water activity of most practical interest in foods. The use of the GAB equation in foods is now almost universally used by laboratories around the world (Singh and Singh, 1996; Quirijns et al. 2005; Peleg 2020).

The thermodynamics of the water vapor-foodstuff equilibrium also provides valuable information into structural matters and energy requirements, but also tools to analyze the consistency of the experimental data (Iglesias et al. 1976; Nunes and Rotstein, 1991). Rizvi and Benado (1984) have reviewed the applicability of thermodynamic properties to dehydrated foods and concluded that thermodynamic calculations yielded important insights regarding the structure of sorbed water.

Stability is greatly influenced by the moisture sorption characteristics of the product. The thermodynamics of water sorption in dried foodstuffs has also drawn interest because some authors suggested that it helps to understand better the stability of reduced moisture foods (Beristain, et al. 2002; Bonilla et al., 2010).

Present review is concerned with some aspects related to the GAB monolayer values and specifically the following: its physical meaning, a survey of literature data on the effect of temperature on monolayers, and a comparison of literature data on location of minimum integral entropy (MIE) and GAB monolayer values in order to verify if both coincide at the same moisture content.

2. Results and Discusion

2.1 The meaning of GAB monolayer value

As mentioned before the Guggenheim, Anderson and de Boer (GAB) isotherm equation has been the most widely discussed moisture sorption model in the literature to describe the sorption behavior of foods (Iglesias and Chirife, 1995; Peleg, 2020; Basu et al. 2006; Timmermann et al. 2001). The GAB model's most familiar presentation is in the form of (eqn 1),

$$\mathbf{M} = \frac{\mathbf{Mo.C.K\,.aw}}{[(\mathbf{1}-\mathbf{K.aw})(\mathbf{1}-\mathbf{K.aw} + \mathbf{C.K.aw})]} \qquad (1)$$

where M is the equilibrium moisture content (g water/100 g dry solids); Mo is the monolayer water content (g water/ 100 g dry solids), a_w is the water activity, and C and K are constants.

Several authors reported that the monolayer value obtained from BET equation is always less than that obtained from the GAB equation (Kaymak-Ertekin and Sultanoglu, 2001; McMinn et al. (2007); Palou et al. 1997). Timmermann et al. (2001) analyzed the dilemma about the differences between the values of BET and GAB monolayer values and demonstrated that GAB monolayer moisture content is more representative than BET´s one.

In a recent review Peleg (2020) stated “that the notion that foods have a physical water monolayer has been widely used in the food literature, but the issue of whether there really exists a water monolayer in foods has never been adequately settled”. It has been suggested, however, that water vapor molecules interact with hydrophilic groups which in foods and biomaterials are abundant. Peleg (2020) stated that this description of the sorption phenomenon is most likely correct although he pointed out that the water monolayer existence is still unproven and perhaps should be treated as a conjecture rather than a hypothesis.

As early as 1945, Pauling advanced that the water sorption monolayer of proteins can be thought in terms of the attachment of one water molecule to each polar group of the side chains of the aminoacids in the protein. In his analysis, Pauling (1945) used BET monolayer values reported by Bull (1944) and the agreement with the number of polar groups of the proteins was roughly satisfactory. Timmermann et al. (2001) noted that in Pauling´s analysis the monolayer values were in most cases lower than the number of polar groups. They replaced BET values by recalculated GAB monolayer values and incorporated casein, a protein not considered by Pauling (1945), and showed that the rough agreement noted by Pauling was now certainly improved.

We used the data collected by Timmermann et al. (2001) and added a few new data on number of polar groups and GAB monolayer values corresponding to insulin, plakaalbumin and wheat and potatoe starch (Mac Laren and Rowen,1951; Timmermann et al., 2001). A good linear correlation between the number of polar groups and the GAB monolayer was found, as shown in **Figure 1.** The obtained linear regression ($r^2 = 0.8431$) was very close to the line of 45 °

indicating a good agreement between number of water molecules calculated to exist in a GAB monolayer, and the number of polar side chains existed. Thus, and in agreement with various works (Gely and Giner, 2000; Quirijins et al. 2005) it may be reasonable to accept that GAB monolayer value provides information about the amount of water that is strongly adsorbed to active sites, suggesting that each polar group initially sorbs one molecule of water. A good linear correlation between the number of polar groups and the GAB monolayer is not perhaps enough to prove a given physical model. Peleg (2020) indicated that the supposition of a critical number of hydrophilic sites would have to be supported by independent physical evidence. However, as stated by Pérez Alonso et al. (2006) the “value of the monolayer is of particular interest since it indicates the amount of water that is strongly adsorbed to specific sites and is considered as the optimum value at which a food is more stable. And this fact has a high practical value regardless of its physical significance.

It is to note that the well known difference between the water sorption behavior of amorphous and crystalline sugars (Iglesias and Chirife, 1978), offers an example that the number of hydrophilic groups alone is insufficient to explain the water sorption pattern.

2.2 Effect of temperature on GAB monolayer values

A review of a large amount of literature data on GAB monolayer values was carried out, but only those articles that reported values at three or more temperatures were chosen for present survey. In most examples shown in the literature the GAB equation has been used independently for each temperature, generating a set of values for C, Mo and k estimated from experimental data for each temperature condition.

Table 1 summarizes data on GAB monolayer values (% dry basis) at several temperatures (mostly in the range 20-50 °C) for more than seventy food items. The raw materials compiled in present work were the following: seeds (various), gums (guar gum, locust bean, tragacanth gum, xanthan gum), maltodextrin, ethnical foods (grape leather (pestil), Gulabjamun mix, Cheese-Puri mix) cassava, cassava bagasse, cassava flour, cocoa beans, fish meal, grape leather, several nuts, mushroom, potato flakes, sweet potato flakes, potatoes, Japanese noodles, loquat fruit, quince fruit, yogurt powder, blueberry powder, blueberry pomace, barley, rice flour, chestnut, cookies, corn snacks, corn, rice crackers, baobab leaf, red peppers, faba bean protein, paprika, "pinhao" flour, mango mix powder, soy protein isolate, apples, cottonseed kernel, cottonseed protein isolate, microencapsulated canola oil, microencapsulated chia oil, microencapsulated natural colorant, microencapsulated paprika oleoresin, microencapsulated beet root juice, microencapsulated Swiss cheese bioaroma powder, fish meal, tamarind seed mucilage, chia seed mucilage, microencapsulated rosemary oil, tea, parmesan cheese, pineapple powders, mushrooms, cookies, casein, bulgur, chitosan, orange juice, cowpeas, and whey protein concentrate.

The effect of temperature on GAB monolayer values for selected products (from data in **Table 1**) is illustrated in **Figures 2** through **9.** The criteria used to group food products in the different figures had two objectives : a) to illustrate that GAB monolayer not always decrease with increasing temperature (as usually stated in literature), but also may remain constant or increase, and b) to avoid overlapping of data that would otherwise occur making the graphs very difficult to interpret.

The monolayer values shown in these figures do not present error bars because the vast majority of surveyed papers did not provide it. Only in a few cases did the authors report error bars for monolayers. For example, Alpízar-Reyes et al. (2016) indicated that relative error bands of GAB monolayers ranged from ± 4.5% to ± 5.9% for tamarind seed mucilage; Escalena-García et al. (2015) indicated values between ± 1.5% to ± 3.0 % for microencapsulated chia oil in whey protein concentrate, and Torres et al. (2012) reported values of ± 1.1% to ±3.2% for several gums (CMC, guar gum, locust bean gum and others).

As frequently reported in literature, GAB monolayer moisture content decreases with increasing temperature for most - but not all - products surveyed. The rate of GAB monolayer change with temperature was found to be strongly dependent on the product. This can be observed by comparing the behavior of sweet potato flakes (**Fig 4**) and paprika (**Fig 7**) which show a steep decline, with others such as malting barley (**Fig 2**), yogurt powder (**Fig 3**), Jasmine rice crackers (**Fig. 4**), , guar gum (**Fig 6**) and Japanese noodles (**Fig 7**) exhibit a more moderate decrease.

Other products show that GAB monolayer was independent (or nearly) of temperature. This is the case for cookies and corn snacks (**Fig 2**), tragacanth gum, locust bean, maltodextrin DE10 (**Fig 5**), microencapsulated paprika oleoresin (**Fig 6**), CMC (**Fig 7**), apple, pineapple powders, cottonseed protein isolate (**Fig 8**),and tea and apples (**Fig 9**). Finally, there are also products in which GAB monolayer increases with increasing temperature, such as fish meal

(**Fig 3**), microencapsulated cheese bioaroma, microencapsulated allspice oil (**Fig 8**) and passion fruit juice microcapsules (**Fig. 9**).

In summary, although in most cases shown in **Table 1** and also in literature (Gely and Giner, 2000; Quirijns et al. 2005; Dominguez et al., 2007) GAB monolayers decrease with increasing temperature, it cannot be taken for granted since as shown here, GAB monolayers can also remain constant or even increase with increasing temperature.

Iglesias and Chirife (1984) analyzed the effect of temperature on BET monolayer values of foods and reported BET values mostly decreased with increasing temperature. They proposed the following empirical model to correlate BET values with temperature:

$$\ln M_{o\mathbf{BET}} = p + a\,.T, \qquad (2)$$

where, $M_{o\mathbf{BET}}$, is BET monolayer moisture content (g water/100 g dry solid), T is temperature (°C), and p and a are constants. Iglesias and Chirife (1984) noted that the relative effect of temperature on BET values was very different for different foods. For example, BET values in some fruits (banana, pineapple, peach) decreased by about 21-35% between 25 and 40 °C, while in eggs the decrease was only 3% over the same temperature Interval. In some cases, equation (1) failed to reproduce the behavior of BET values with temperature. Iglesias and Chirife (1984) suggested that the relative variation of BET values with temperature was dependent on the physicochemical nature of the food as well as the time needed to reach sorption equilibrium. In turn, the equilibrium time dependence was determined by the experimental device utilized to construct the isotherm.

This reasoning can also be applied to the results here reviewed. Most cases shown in **Table 1** were derived from sorption isotherms determined using the known gravimetric method, in which food samples were placed into glass/plastic desiccators containing different saturated salt solutions. Desiccators were then placed in constant temperature incubators at the desired temperature (usually between 20-50 °C) until the equilibrium moisture content was reached. The equilibration time reported ranged between about 15-50 days. Water activity equilibration for these periods of time at relatively high temperatures may cause physical and chemical deterioration of the sample which is reflected in available sorption sites. These reactions may consist in non-enzymatic browning, denaturation, crosslinking and interaction of the native or denatured proteins with oxidized lipids or carbohydrates, as well as structural modifications induced by temperature. Thus, a modification in the availability of hydrophilic sites for water binding by one or several of the above mechanisms, leads to modification of GAB monolayers values when increasing temperature: either a decrease, an increase or a constancy.

Romani et al. (2015) studied the effect of storage time of packed biscuits at 35 °C for up to 92 days, and the adsorption isotherm was determined using a rapid Dynamic Dewpoint Isotherm (DDI), whose equilibration times was far smaller than in the traditional static gravimetric technique. The resulting adsorption isotherms of stored biscuits, observed by means of DDI method, was affected by previous storage time at 35 °C. The monolayer moisture content (BET monolayer in this case) significantly increased from 1.473 to 2.080 g water/100 g db., from the beginning to the end of storage. The authors ascribed the increase of monolayer values during biscuit storage to an increase of active sites for water binding, as a consequence of chemical and physical changes of its main components (egg, starch, sugars, lipid, protein) induced by product ageing.

Iglesias and Chirife (1978) determined the water adsorption isotherms at 30°C of precooked beef previously dried at three different temperatures: 30 °C, 55°C and 70 °C, respectively. They found that the higher the drying temperature the lower was the sorption capacity of dried beef and reported that quantity of water contained in the BET monolayer was affected by the previous drying temperature of 30, 55 or 70 °C reducing from 5.4 to 5.1 and 4.5 (non-fat % dry basis) respectively.

Generally, the GAB model is used independently for each temperature, generating a set of values for C, M_o and K estimated from experimental data for each temperature. Another alternative is the introduction of a temperature dependent expression for the parameters, yielding a bigger amount of constants to be estimated with the whole set of isotherms (Staudt et al.,2013). Accordingly various authors (Martín-Santos et al. 2012; Quirijns et al. 2005; Shirkole et al.,2019) have proposed that M_o was related to temperature by using the following Arrhenius-type equation,

$$M_o = M_o' \exp(\Delta H_m/RT) \tag{3}$$

where M_o' is a pre-exponential factor and ΔH_m is an Arrhenius-type energy factor. However, the complex experimental behavior (decrease, constancy or increase) of GAB monolayers with temperature (Figs. 2 to 10) may not be adequately predicted with eqn. (3).

2.3 Integral entropies of sorption and GAB monolayer

The thermodynamics of water vapor sorption in foods has attracted interest because it may provide a more thorough interpretation of the sorption phenomenon and assists in understanding the mechanism (Beristain et al. 2002). It is well known that the stability of low moisture foods depends on great measure on its moisture sorption characteristics and some researchers considered (Bonilla et al. 2010) that the thermodynamics of water vapor sorption may also propose a scientific criterion for the prediction of the stability and storage life of dehydrated foods. In recent years the study of water sorption thermodynamics in dehydrated products has been the subject of several studies (Pérez-Alonso et al., 2006; Silva et al., 2015; Escalona-García et al, 2015; Faria Freitas et al., 2016; Viganó et al.. 2012; Xiao and Tong, 2013; Moreira et al., 2008) and many others. Various studies reported that a plot of integral entropy curve versus moisture content of various foods showed a well-defined minimum and interpreted that it is the moisture content corresponding to a monolayer, since a complete monolayer corresponds to a small number of configurations of the system (Nunes and Rotstein, 1991, Bertuzzi et al. 2003, Beristain et al.,1994, Xing et al., 2012). Many authors indicated that the decrease in entropy is associated with the loss of mobility of the water molecules followed by an increase in entropy as the water regains mobility by forming several "layers". The integral entropy can be interpreted qualitatively in terms of the order/disorder and randomness of the adsorbed water molecules and could be assumed to coincide with the moisture content required to form a monolayer where strong bonds between the adsorbate and adsorbent occurred. Literature reports used the point of minimum integral entropy as a tool to predict the maximum stability point of dehydrated foods (Bonilla et al., 2010). This will be discussed later in this review.

The thermodynamic analysis of sorption needs the knowledge of isotherms at different temperatures; and three isotherms in the range 20 - 40 °C or 25 – 45 °C have been mostly used. The analysis of the thermodynamic functions of water sorption in foods have been described in detail by many authors (Xing et al. 2012; Beristain et al., 1994, Kumagai et al., 1994) and includes the Gibbs free energy (ΔG),

$$\Delta G = \Delta G_o + R\,T\,\ln(a_w) \qquad (4)$$

where T is the absolute temperature (K); R, the universal gas constant (J mol^{-1} K^{-1}); and aw is the water activity. A change on free energy as a result of water sorption is usually accompanied by changes on both the enthalpy and the entropy. Both differential and integral enthalpies (ΔH), and entropy (ΔS) may then calculated. Sorption enthalpy is a molar differential quantity derived from the temperature dependence of the isotherm, in contrast to the integral enthalpy which is the average energy for all the water molecules already bound at that level. The respective differential and integral entropies are obtained from the differential and integral enthalpies, respectively. Pérez Alonso et al. (2006), Tolaba et al. 2007, Domínguez et al. (2007), Bonilla et al. (2010) and Rodríguez-Bernal et al. (2015) -among others- described the calculation of differential and integral thermodynamic functions in water sorption in foodstuffs.

As indicated by Bonilla et al. (2010) changes in the integral entropy have been calculated from,

$$(\Delta S_{int})_T = \frac{-(\Delta H_{int})_T - \Delta G)}{T} \quad (5)$$

A large number of literature studies reported a minimum of integral entropy versus moisture content and were reviewed to verify whether or not such minimum actually occurs close to the GAB monolayer. Only those studies that reported both the integral minimum entropy and the GAB values were chosen for this review, and about fifty eligible articles with appropriate data were used.

As mentioned above, the net integral entropy of water adsorption usually decreases gradually with increasing moisture content to a minimum value around the monolayer moisture content, and then increases with further increase in moisture content. Although the value of minimum entropy may be unique, there are food products with zones in which this minimum does not vary appreciably in a defined range of moisture (Beristain and Azuara, 1990). For example, Rascón et al. (2015) indicated that for paprika oleoresin encapsulated in Capsul (modified starch) this zone begins at moisture contents of 5.89 g water/100 g soluble solids and ends at 6.94 g water/100 g soluble solids. Bonilla et al. (2010) reported that for whey protein microcapsules at 25 °C moisture content at minimum integral entropy was 6.38 % (dry solids) but the moisture content range where integral entropy remained more or less constant was 5.10 – 6.52 % (dry basis).

Figure 10 shows a plot of the moisture corresponding to MIE versus the GAB monolayer, for 39 pairs of values obtained from literature. Since these values were in most cases reported at 3 temperatures (mostly 25-45 °C), a mean value was used here. It can be seen that there is a linear relationship between both parameters and the regression line is close to the 45 ° diagonal

(**Fig. 10**) with a quite acceptable correlation coefficient (r^2 = 0.9089). The relationship between the moisture content of both variables is given by equation (6),

$$[\Delta S_{int}]_{min} = 0.8935.\ \text{GAB value} + 0.8523 \qquad (6)$$

which indicates that the GAB monolayers are close to the moisture of MIE zone. Delgado et al. (2014) noted that in some cases the thermodynamic analysis was not in accordance with the monolayer obtained with the GAB model, generally the minimum integral entropy point being higher than the GAB monolayer. This behavior was also observed in several products examined in the present review. Thirty-one pairs of literature values (not included in those showed in Figure 10) were plotted in **Figure 11**. The regression line is now far from the 45 ° diagonal and the dispersion of the data is reflected in a lower value of r^2 (0.8024). The relationship between the moisture content of both variables is given by equation (7),

$$[\Delta S_{int}]_{min} = 1.448.\ \text{GAB} + 1.466 \qquad (7)$$

which indicates that for these products the moisture at minimum integral entropy if considerably higher than GAB monolayer.

Some authors considered the minimum integral entropy to be the point of maximum stability (Pérez-Alonso et al., 2006). However, when the moisture at the point of the minimum integral entropy is considerably higher than GAB monolayer, there is uncertainty regarding the validity of minimum entropy as a point of stability.

At this stage we prefer not to consider stability aspects since “stability” is the sum of many changes such as microbial spoilage, oxidative, enzymatic and nonenzymatic reactions, texture, crispness and other physical changes (stickiness, collapse, crystallization) associated with the glass transition (Roos, 1995). In turn, these changes depend on food moisture content in different ways. Nevertheless, some general comments on stability needs to be made.

There is no direct reason to explain why in a group of foods (**Figure 10)** the moisture at the minimum integral entropy point is close to the GAB monolayer, but in another group of foods and foodstuffs (**Figure 11**) the moisture at MIE is considerably higher than GAB monolayer. Admittedly, foods are heterogeneous mixtures of biopolymers, water and solutes. Therefore the positive or negative correlation between moisture of MIE and GAB monolayer are probably due to differences in composition and structure of food systems examined. According to Viganó et al. (2012) foods with the same chemical composition and different microstructure could show different moisture sorption behavior influencing the results. They studied the thermodynamics of water sorption by pineapple powders produced by vibro-fluidized drying (VFD), spray drying (SD), freeze drying (FD) or vacuum drying (VD) and reported that the moisture (and hence a_w) at the minimum integral entropy depended on the drying method utilized; for example, it was 6.8 % (db.) for VD and dramatically increased to 18.9 % for VFD. They stated this difference is due to changes produced in the product microstructure during dehydration; and that powders produced by SD and VFD are more stable at changing a_w because they presented minimum entropy at higher moisture contents. However, this statement should be taken with caution as it was not confirmed experimentally. The GAB monolayer was less sensible than MIE to these microstructural changes. Comparing VFD and VD the GAB monolayer changed by about 67 % while the MIE suffered a 178 % change.

Sánchez-Saenz et al. (2011) studied the encapsulation of allspice oil in a mixture of whey protein concentrate, mesquite gum and maltodextrin, and reported that conditions of maximum stability (minimum integral entropy) for microcapsules corresponded to a_w = 0.713 at 25 °C, or 0.657 at 35°C. It must be noted that aw 0.713 at 25 °C may allow growth of xerophilic fungi during storage, albeit slowly. Similarly, Bonilla et al. (2010) encapsulated canola oil in soy protein isolate and reported that at 35 °C the moisture condition for stability (minimum integral entropy) corresponded to a_w = 0.71 ; again, this a_w will also allow growth of some xerophilic fungi. Azuara-Nieto and Beristain (2007) reported that minimum integral entropy predicted that at 30°C the maximum stability of powder whey protein will occur when stored at aw =0.50, but they did not substantiate experimentally this statement.

More research is needed to determine whether the thermodynamic approach helps to predict storage stability of foods and foodstuffs. Some works cited in this review experimentally confirmed the relationship between MIE and stability of the studied products. But in others this was not the case, or it was not experimentally confirmed.

3. Conclusions

Re-examination of old data on the stoichiometry of water sorption in proteins but with addition of some new values for other biopolymers, confirmed there is a good correlation (r^2 = 0.8413) between the number of water molecules calculated to exist in a GAB monolayer and the number of polar groups. This reconfirms the old Pauling´s hypothesis that each polar group initially sorbs one molecule of water.

A literature survey performed for more than 70 different food items allowed to collect GAB monolayer values at different temperatures. Although the decrease of GAB values with increasing temperature is the behavior usually reported in literature, it cannot be taken for granted since as shown here the monolayer can also remain constant or even increase with increasing temperature.

The study of the relationship between the minimum integral entropy (MIE) and the GAB monolayer indicated that for 38 different foods a good agreement was observed between the moisture content corresponding to the minimum integral entropy and the GAB monolayer. However, for other foods the regression curve between both parameters indicated that the moisture content corresponding to the minimum integral entropy was considerably higher than GAB monolayer. The results of this review may help to support the use of GAB monolayer value as an adequate moisture content for many aspects of food stability. Also, it may promote additional research about the relation between the GAB monolayer and the minimum integral entropy, as well as the real role of the latter in the prediction of stability of low-moisture foods.

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Table 1 –Literature data on GAB monolayer values in foods and foodstuffs at various temperatures

Product	Composition/ Description	Adsorption/ Desorption	Temperature, °C	GAB, monolayer, % dry basis	Reference
Camellia oleífera seeds	Shelled	Adsorption	20	2.60	Xing et al., 2012
			30	3.10	
			40	2.65	
	Unshelled Equil. time 15-21 days	Adsorption	20	2.91	
			30	2.97	
			40	2.73	
Gum arabic		Adsorption	25	8.11	Pérez Alonso et al., 2006
			35	9.97	
			40	11.0	
Mezquite gum (1)		Adsorption	25	8.35	
			35	7.32	
			40	5.72	

Maltodextrin, DE10		Adsorption	25	7.35	
			35	6.99	
			40	6.96	
Cassava bagasse	Composition: Carbohydrates 72.8%; Fat 6.2% ; Ash 11.6% ; Protein 9.4% Equil. time 28 days	Adsorption	20	5.61	Carregari Polachini et al. 2016
			30	5.24	
			40	4.64	
			50	4.03	
			55	3.86	
			65	3.65	
			70	3.49	
			75	3.40	
			80	3.27	
Cassava		Adsorption	30	6.16	Kohua et al. (2012)
			45	5.59	
			60	3.66	
		Desorption	30	6.96	
			45	5.36	
			60	4.21	

Encapsulated Swiss cheese bioaroma powder	Encapsulated in MD DE20 and Capsul	Adsorption	15	13.76	Silva et al. (2015)
			25	17.8	
			35	24.0	
			45	32.0	
Microencapsulated chia oil	Encapsulants: WPC and Mesquite gum Equil. time 20-25 days	Adsorption	25	6.32	Escalona-Garcia et al. 2016
			35	5.58	
			40	5.18	
Cocoa beans		Desorption	30	6.06	Koua et al. (2016)
			45	5.35	
			60	5.08	
Microencapsulated natural colorant	Encapsulants Arabic gum: Maltodextrin Equil. time 20-25 days	Adsorption	20	6.34	Pavón-García et al. (2011)
			35	3.78	
			40	2.83	
	Mesquite Gum: Maltodextrin Equil.time 20-25 days	Adsorption	20	6.77	
			35	3.70	
			40	2.83	
Microencapsulated paprika oleoresin	Encapsulant: Starch Capsul Equil. time 40-55 days	Adsorption	25	6.50	Rascón et al. (2015)
			35	6.40	
			45	6.39	
Microencapsulated	Encapsulant : Arabic	Adsorption	25	4.69	Guadarrama-Lezama et al.

beetroot juice	gum		35	4.30	(2014a)
			40	3.64	
Fish meal	From anchovy Time to equil. 21 days	Sorption	25	6.03	Vivanco and Taboada (1998)
			35	5.45	
			45	4.22	
Grape leather *(pestil)*	Grape juice and starch Time to equil. 21 28 days	Adsorption	15	10.34	Kaya and Kahyaoglu (2005)
			25	13.98	
			35	8.39	
Gulabjamun mix	Mix of: milk powder, refined wheat flour, semolina, baking powder, citric acid	Sorption Time to equil. 40 days	10	3.17	Pushpadass et al. (2013)
			25	3.14	
			40	3.10	
Gums (several)	CMC Time to equil. 56 days	Adsorption	20	9.1	Torres et al. (2012)
			35	8.1	
			50	7.7	
			65	6.9	
	Guar gum		20	3.2	
			35	2.8	
			50	2.5	
			65	2.0	
	Locust bean		20	4.1	

			35	3.8	
			50	3.4	
			65	3.0	
	Tragacanth gum		20	5.0	
			35	4.9	
			50	4.5	
			65	3.8	
	Xanthan gum		20	7.7	
			35	7.4	
			50	7.0	
			65	6.1	
Macadamia nuts		Adsorption	25	1.43	Dominguez et al. (2007)
			35	1.35	
			45	1.02	
Microencapsulated canola oil	Encapsulant : Whey protein concentrate	Adsorption	15	5.44	Bonilla et al. (2011)
			25	4.37	
			35	3.98	
	Encapsulant : Soy protein Isolate	Adsorption	15	5.68	
			25	4.88	
			35	4.43	
	Encapsulant : Mesquite Gum	Adsorption	15	6.61	
			25	5.56	

			35	5.04	
Mesquite gum (2)		Desorption	25	10.59	Beristain et al. (1999)
			35	8.08	
			45	6.27	
Oyster mushroom *(Pleurotus ostreatus)*		Adsorption	25	5.2	Pascual-Pineda et al. (2020)
			35	4.5	
			45	3.9	
Parmesan cheese (grated)		Sorption	16	5.71	Faria Freitas et al. (2016)
			24	4.92	
			32	4.86	
			40	4.52	
			48	4.36	
			56	4.76	
			64	4.13	
Pineapple powder (freeze dried)	Added with maltodextrin	Adsorption	20	6.8	Viganó et al. (2012)
			30	6.0	
			40	6.2	
			50	6.2	
Potato flakes	Equil. time. 15 days	Adsorption	15	4.75	Carvalho Lago and Zapata Noreña (2015)
			20	4.27	
			25	3.96	
			30	3.42	

Sweet potato flakes	Equil. time 15 days	Adsorption	15	10.35	Carvalho Lago and Zapata Noreña (2015)
			20	9.46	
			25	7.57	
			30	6.37	
Potato	Equil. time 21 days	Adsorption	30	6.16	McMinn and Magee (2003)
			45	5.26	
			60	3.66	
		Desorption	30	6.96	
			45	5.59	
			60	4.21	
Tamarind seed mucilage	Equil. time 21-25 days	Adsorption	20	9.99	Alpizar-Reyes et al. (2016)
			30	11.32	
			40	11.99	
Chia seeds mucilage	Equil. time 20-25 days	Adsorption	25	7.93	Velazquez-Gutiérrez et al. (2014)
			35	5.33	
			40	4.05	
Loquat fruit	Equil. time 56 days	Sorption	20	16.3	Moreira et al. (2008)
			35	13.6	
			50	12.1	
			65	9.9	
Quince fruit	Equilib. time 56 days	Sorption	20	11.5	Moreira et al. (2008)
			45	8.02	

			65	4.35	
Dehydrated yacon bagasse	Protein 2.32 %, Lipids 0.35 %; Ash 4.0%; Fiber 22.2 %; CH 67.4 %	Sorption	20	1.2	Carvalho Lago and Zapata Noreña (2015)
			30	1.0	
			40	0.7	
			50	0.6	
Yogurt powder, spray dried	Added with sugar and maltodextrin before drying	Sorption	20	4.88	Seth et al. (2018)
			30	4.54	
			40	3.86	
			50	3.52	
Cheese-Puri mix	Prepared from wheat flour, cheddar cheese, milk powder	Adsorption	25	2.05	Thanuja and Ravindra (2012)
			35	2.50	
			45	2.49	
Blueberry juice powder	Added with whey protein isolate	Adsorption	20	10.5	Tao et al. (2017)
			35	8.7	
			50	8.6	
Blueberry fruit (mashed)		Adsorption	20	9.6	Tao et al. (2017)
			35	7.2	
			50	6.3	
Blueberry pomace		Adsorption	20	4.5	Tao et al. (2017)
			35	4.2	
			50	4.1	
Cassava flour	Equil. time 19-25 days	Adsorption	25	7.31	Ayala-Aponte (2016)

			30	7.28	
			35	6.32	
Malting barley		Desorption	20	10.18	Gely and Pagano (2012)
			30	9.29	
			40	8.51	
			50	8.13	
Rice flour	DVS: very short equil. time	Adsorption	5	7.9	Sandoval et al. (2011)
			23	7.3	
			45	6.6	
Chestnut		Desorption	20	6.08	Vázquez et al. (2001)
			30	6.05	
			40	6.02	
			50	6.00	
Cookies	Adsorption	“Habaneras”	25	4.58	Palou et al. (1997)
			35	4.53	
			45	4.15	
		“Ricanelas”	25	4.09	
			35	4.09	
			45	3.91	
		“Animalitos”	25	4.41	
			35	4.11	

			45	3.97	
Corn snacks	Adsorption	Doritos	25	3.26	Palou et al. (1997)
			35	3.06	
			45	3.00	
		Tostitos	25	3.71	
			35	3.77	
			45	3.45	
Jasmine rice crackers		Sorption	30	5.94	Siripatrawan and Jantawat (2006)
			45	5.60	
			60	5.01	
Kuka (baobab leaf)	Equil. time 15-18 days	Adsorption	34	4.83	Ajisegiri et al. (1994)
			37	3.94	
			45	3.68	
		Desorption	34	9.35	
			37	8.41	
			45	5.78	
Macadamia in-shell nuts	Equil. time 42 days	Adsorption	10	4.14	Palipane and Driscoll (1993)
			20	3.85	
			30	3.60	
			40	3.37	
		Desorption	10	5.56	
			20	4.94	

			30	4.42	
			40	3.92	
Red peppers	Equil. time.>21 days	Adsorption	30	9.96	Kaymak-Ertekin and Sultanoglu (2001)
			45	9.95	
			60	8.6	
		Desorption	30	11.3	
			45	9.0	
			60	6.7	
Sesame seed (whole)	Equil. time 28 days	Sorption	15	3.09	Kaya and Kahyaoglu (2006)
			25	2.66	
			35	1.89	
Dehulled sesame seed	Equil. time 28 days	Sorption	15	2.44	
			25	2.62	
			35	2.15	
Dehulled-roasted sesame seed	Equil. time 28 days	Sorption	15	1.82	
			25	1.64	
			35	1.74	
Faba bean protein		Adsorption	25	5.52	Alpízar-Reyes et al. (2018)
			35	4.55	
			40	4.32	
Microencapsulated chili extract	Equil. time 15-20 days	Adsorption	25	12.49	Guadarrama-Lezama et al. (2014b)
			35	10.58	

			40	7.70	
Paprika		Adsorption	30	10.04	Shirkole et al. (2019)
			40	7.54	
			50	4.42	
			60	3.78	
Pinhao flour (seeds of Araucaria angustifolia)	Equil. time 30-40 days	Adsorption	10	6.60	Cladera-Olivera et al. (2011)
			20	6.04	
			30	5.77	
			40	5.17	
Rosemary oil microencapsulated with Arabic gum		Adsorption	15	12.42	Silva et al. (2014)
			25	11.52	
			35	10.29	
			45	8.42	
Mango mix powder (mixed with MD DE 17-20)	Equil. time 28-35 days	Adsorption	20	5.53	Cano-Higuita et al. (2013)
			30	4.33	
			40	3.45	
			50	2.79	
Japane noodles (Udon)		Desorption	20	7.88	Inazu et al. (2001)
			30	7.38	
			40	6.83	
Soy Protein Isolate		Adsorption	15	5.68	Bonilla et al. (2010)
			25	4.88	

			35	4.43	
Whey protein Concentrate		Adsorption	15	5.44	
			25	4.37	
			35	3.98	
Mesquite gum		Adsorption	15	6.61	
			25	5.56	
			35	5.04	
Tea	Equil. time 3-17 days	Adsorption	25	4.40	Arslan and Togrul (2006)
			35	4.20	
			45	4.19	
Orange juice, s. dried		Adsorption	20	12.6	Sormoli and Langrish (2014)
			30	10.9	
			40	10.2	
			50	9.8	
Pistacho nuts paste	Equil. time 50-60 days	Adsorption	20	2.23	Maskan and Gogüis (1997)
			30	2.18	
			40	2.43	
Green beans			20	7.09	Samaniego-Esguerra et al. (1991)
			30	6.51	
			40	5.31	
Casein acid, from buffalo milk		Adsorption	25	5.60	Sawhney et al. (2011)
			35	4.70	

			45	4.55	
Bulgur	Equil. time 7 days	Adsorption	20	5.03	Erbas et al. (2015)
			30	3.69	
			40	2.55	
Apples, Golden delicious	Equil. time 9-16 days	Desorption	30	12.1	Mbarek and Mihoubi (2018)
			40	12.9	
			50	12.2	
			60	12.6	
Cottonseed Protein Isolate		Adsorption	15	3.93	Tunc and Duman (2007)
			25	3.61	
			35	3.47	
			45	3.29	

Equil. = Equilibrium

Figure captions

Figure 1. Comparison of GAB monolayer values with number of polar groups in various proteins and potato and wheat starch.
Data points correspond to: Collagen, Gelatin, Seroalbumin, Wool, Lactoblob. crist., Idem freeze dried, Egg albumin coagulated, Egg albumin freeze dried, Egg albumin not f. dried, c-zein, b-zein, Salmin, Casein, Insulin, Plakalbumin, Wheat Starch, Potato Starch. (from Timmermann et al., 2001; McLaren and Rowen, 1951).

Figure 2. Effect of temperature on GAB monolayer value.
Cookies and corn snacks: from data reported by Palou et al. (1997); Blueberry juice powder: from data reported by Tao et al. (2017); Cassava flour: from data reported by Ayala-Aponte (2016); Malting barley: from data reported by Gely and Pagano (2012).

Figure 3. Effect of temperature on GAB monolayer value.
Cocoa beans: from data reported by Koua et al. (2016); Fishmeal: from data reported by Vivanco and Taboada (1998); Parmesan cheese: from data reported by Faria Freitas et al. (2016); Yogurt powder: from data reported by Seth et al. (2018); Loquat fruit: from data reported by Moreira et al. (2008); Quince fruit: from data reported by Moreira et al. (2008).

Figure 4. Effect of temperature on GAB monolayer value.
Potato: from data reported by McMinn and Magee (2003); Potato flakes: from data reported by Carvalho Lago et al. (2013); Sweet potato flakes: from data reported by Carvalho Lago et al. (2013); Jasmine rice crackers: from data reported by Siripatrawan and Jantawat (2006); Corn: from data reported by Gely and Giner (2006); Macadamia nuts: from data by Domínguez et al. (2007).

Figure 5. Effect of temperature on GAB monolayer value.

C. oleifera seeds, unshelled: from data reported by Xing et al. (2012); C. oleífera seeds, shelled: from data reported by Xing et al. (2012); Gum arabic: from data reported by Pérez-Alonso et al. (2006); Mesquite gum (1): from data reported by Pérez-Alonso et al. (2006); Maltodextrin DE10: from data reported by Pérez-Alonso et al. (2006); Locust gum: from data reported by Torres et al. (2021); Tragacanth gum: from data reported by Torres et al. (2012); Mesquite Gum (2): from data reported by Beristain et al. (1999).

Figure 6. Effect of temperature on GAB monolayer value.

Microencapsulated chia oil: from data reported by Escalona-García et al. (2016); Microencapsulated paprika oleoresin: from data reported by Rascón et al. (2015); Microencapsulated beetroot juice: from data reported by Guadarrama-Lezama et al. (2014); Microencapsulated canola oil : from data reported by Bonilla et al. (2011); CMC: from data reported by Torres et al. (2012); Guar gum : from data reported by Torres et al. (2012)

Figure 7. Effect of temperature on GAB monolayer value

Mango mix powder (mixed with MD): From data reported by Cano-Higuita et al. (2013); Japanese noodles: from data reported by Inazu et al. (2001); Paprika: from data reported by Shirkole et al. (2019); Potato flakes: from data reported by Carvalho-Lago et al. (2013); CMC: from data reported by Torres et al. (2012); Blueberry pomace: from data reported by Tao et al. (2017)

Figure 8. Effect of temperature on GAB monolayer

Microencapsulated allspice essential oil (1) with WPC 66 %+ Mesquite gum 17 %+ MD 17 % : from data reported by Sánchez-Sáenz et al. (2017); Microencapsulated allspice essential oil (2) with WPC 17 %+ Mesquite gum 17 %+ MD 66 %: from data reported by Sánchez-Saenz et al (2017); Apple (Golden Delicious): from data reported by Mbarek and Mihoubi (2018); Cottonseed kernel: from data reported by Tunc and Dumar (2007); Cottonseed Protein Isolate: from data reported by Tunc and Dumar (2007); Pineapple powder (freeze-dried): from data reported by Viganó et al. (2012); Pineapple powder (vacuum dried): from data reported by Viganó et al. (2012).

Figure 9. Effect of temperature on GAB monolayer

Tea: from data reported by Arslan and Togrul (2006); Orange juice (spray-dried): from data reported by Sormoli and Langrish (2014); Safflower petal: from data reported by Kaya et al. (2007); Apples (Golden delicious): from data reported by Mbarek and Mihoubi (2018); Bulgur: from data reported by Erbas et al. (2015); Pistachio nuts paste: from data reported by Maskan and Gogüis (1997) ; Passion fruit juice microcapsules: from data reported by Carrillo-Navas et al. (2011).

Figure 10. Correlation between moisture content of minimum integral entropy (MIE) and GAB monolayer

Borocotó fruit, medium phase; from data of Rodríguez-Bernal et al. 2015) - *Camelia Oleifera* shelled (from data of Xing et al. 2012); *C. oleífera* unshelled; (from data of Xing et al., 2012); Arabic gum (from data of Xing et al.(2012); Paprika oleoresin encapsulated in modified starch,(from data of Rascón et al. (2015); Muitle extract microencapsulated in Arabic gum, mesquite gum and maltodextrin (from data of Pavón-García et al. 2015); Xanthan gum (from data of Torres et al. 2012); Macadam nut (from data of Domínguez et al. (2007); Mesquite gum (from data of Bonilla et al. 2010); Millet grains, var. Exborno, adsorption (from data of Aviara et al. 2016); Millet grains var. Ex Borno, desorption (from data of Aviara et al. 2016) ; Millet grains var. Sosat C88, adsorption (from data of Aviara et al., 2016); Whey protein isolate (from data of Bonilla et al. 2010); Oyster mushroom, freeze-dried (from data of Pascual-Pineda et al. 2020) ; Parmesan cheese,grated, storage & drying (from data of María-Freites et al. 2016); Pineapple powder spray-dried, and vacuum dried (from data of Viganó et al. 2012); Sweet potato flakes (from data of Carvalho-Lago et al. 2013); Yogurt freeze-dried (from data of Azuara-Nieto and Beristain, 2006); Sesame seed dehulled and roasted (from data of Kaya and Kahyaoglu, 2006); Cocoa beans (from data of Kohua et al. 2016); Mango pulp, spray dried with maltodextrin or skimmed milk, (from data of Cano-Higuita et al. 2013); Pullulan (from data of Xiao and Tong, 2013); Pullulan:Alginate 60:40, (from data of Xiao and Tong 2013) ; Pullulan:Alginate 40:60, (from data of Xiao and Tong 2013); Alginate (from data of Xiao and Tong 2013); Faba bean protein (from data of Alpízar-Reyes et al. (2018); Sugar beet root (from data of Iglesias et al. (1976); Yogurt, concentrated and freeze-dried conc. (from data of Azuara and Beristain, 2006); Sweetened yogurt, spray-dried (from data of Seth et al. (2018); Potato, desorption (data from McMinn and Magee, 2003).

Figure 11. Correlation between moisture content of minimum integral entropy (MIE) and GAB monolayer

Green coffee beans (data from Beristain et al. 1994 ; Green coffee beans (data from Estrada Bahen, 2019); dehydrated yacon bagasse (data from Carvalho Lago et al. 2015);Tarragon (data from Kahyaoglu,, 2007); Winged bean seed (data from Fasina et al. 1999); Soya bean (data from Aviara et al. 2004); Sesame seed, whole (data from Kahyaoglu, 2006); Sesame seed dehulled (data from Kahyaoglu (2006); Red onion microcapsules in maltodextrin (data from Pascual-Pined et al. ,2018); Millet grain flour germinated (data from Sharama et al. 2018); Millet grain flour non-germinated (data from Sharama et al. 2018); Encapsulated canola oil in soy protein isolate (data from Bonilla et al. 2010); Encapsulated canola oil in mesquite gum (data from Bonilla et al, 2010); Tragacanth gum (data from Torres et al.,2012); Encapsulated natural colorant in Arabic gum 50% + Maltodextrin 50% (data from Pavón-García et al. 2011); Encapsulated natural colorant in Mesquite gum 50 %+ Maltodextrin 50 % (data from Pavón-García et al. 2011); Defatted sesame meal (data from Al-Mahasneh , 2007); Arabic gum 17%+ Mesquite gum 66%+ Maltodextrin 17% (data from Pérez-Alonso et al. 2006); Alfalfa pellets (data from Fasina et al. 1997); Mesquite gum (data from Pérez-Alonso et al. 2006); Microencapsulated allspice essential oil in whey protein conc.- Mesquite gum & maltodextrin, (data from Sánchez-Saenz et al. 2007); Sweet potato flakes (datfrom Fasina et al.2006); Red onion microcapsules (data from Pascual-Pineda et al. 2018) ; Soybean TGX (from data of Aviara et al. 2004); Winged bean seed (data from Fasina et al. 1999) ; Pestil (grape leather), (data from Kaya and Kahyaogluom, 2005); Beet root microcapsules in Arabic gum, (data from Guadarrama-Lezama et al., 2014); Pineapple powder with maltodextrin, vibro fluidized bed (data from data of Viganó et al., 2012); Canola oil microencapsulated with soy protein isolate, whey protein concentrate, or mesquite gum (data from Bonilla et al., 2010); Microcapsules passion fruit juice in arabic gum 17%+mesquite gum 66%+

maltodextrin 17% (from data of Carrillo-Navas et al (2011) ; Microcapsules passion fruit juice in arabic gum 17%+mesquite gum 17%+maltodextrin 66% (from data of Carrillo-Navas et al (2011).

Figure 1

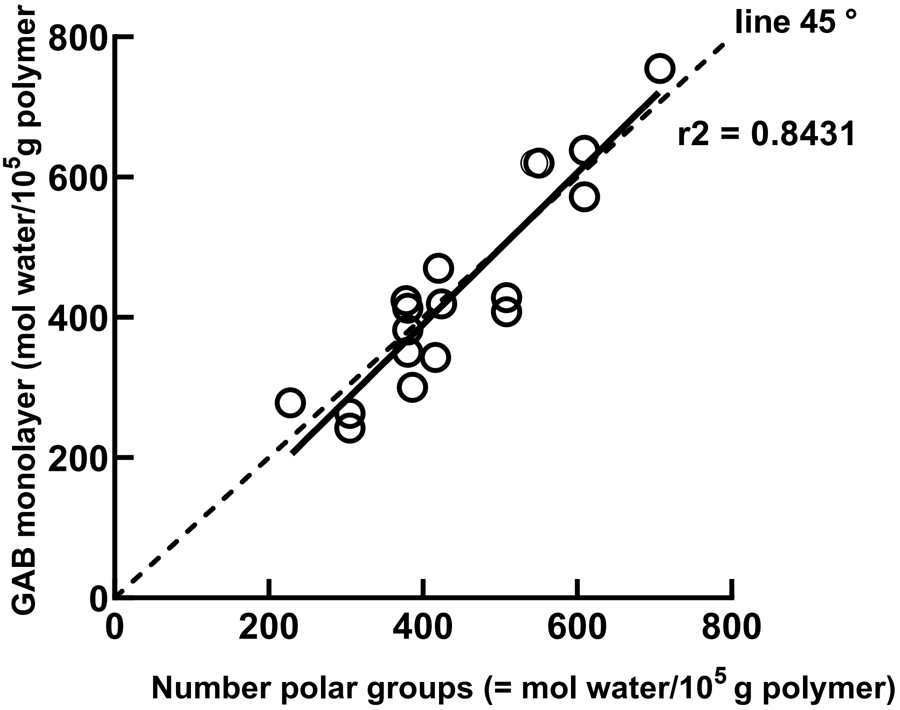

line 45 °
r2 = 0.8431
GAB monolayer (mol water/10^5 g polymer
0
200
400
600
800
Number polar groups (= mol water/10^5 g polymer)
0
200
400
600
800

Figure 2

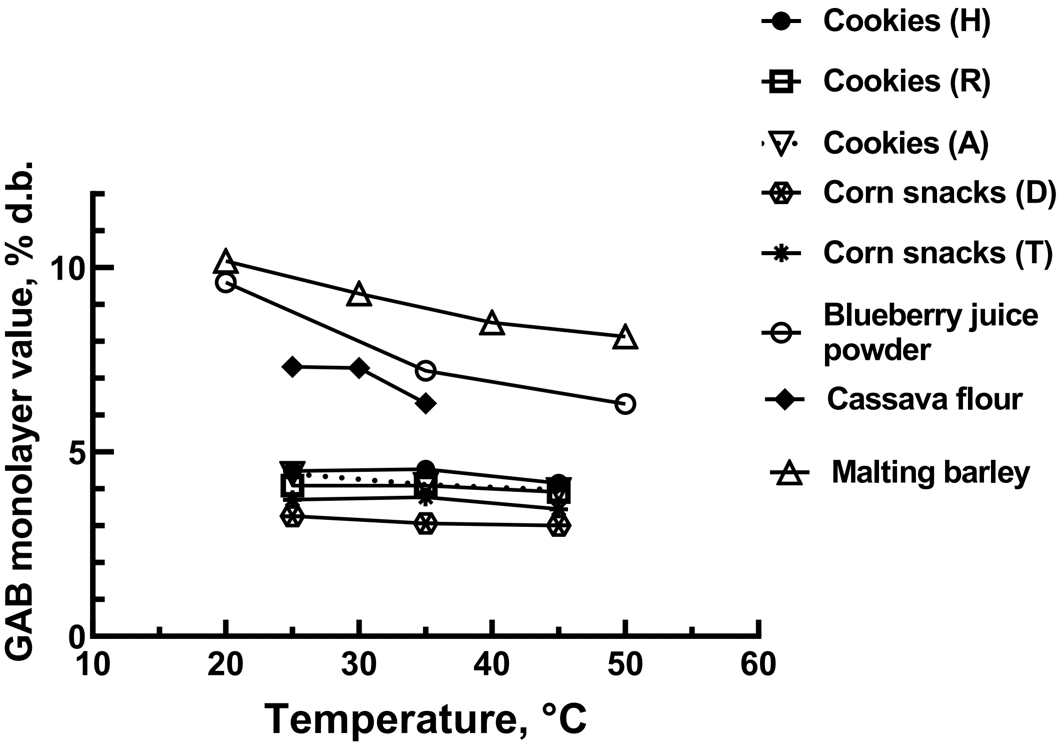
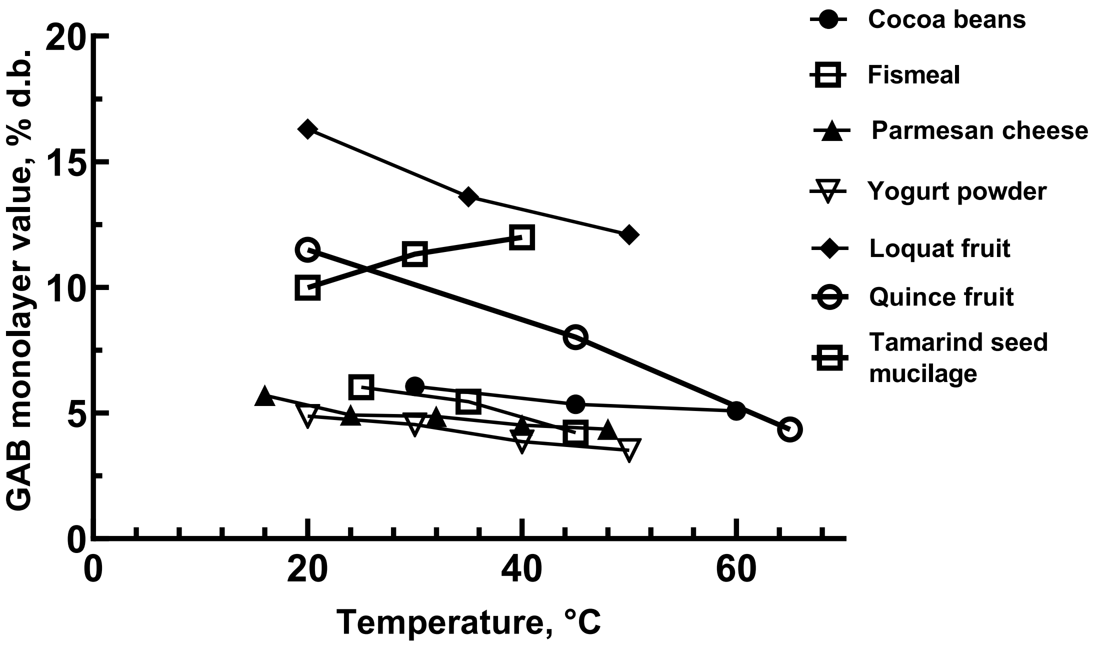

Cookies (H)
Cookies (R)
Cookies (A)
Corn snacks (D)
Corn snacks (T)
Blueberry juice powder
Cassava flour
Malting barley
GAB monolayer value, % d.b.
0
5
10
10
20
30
40
50
60
Temperature, °C

Figure 3



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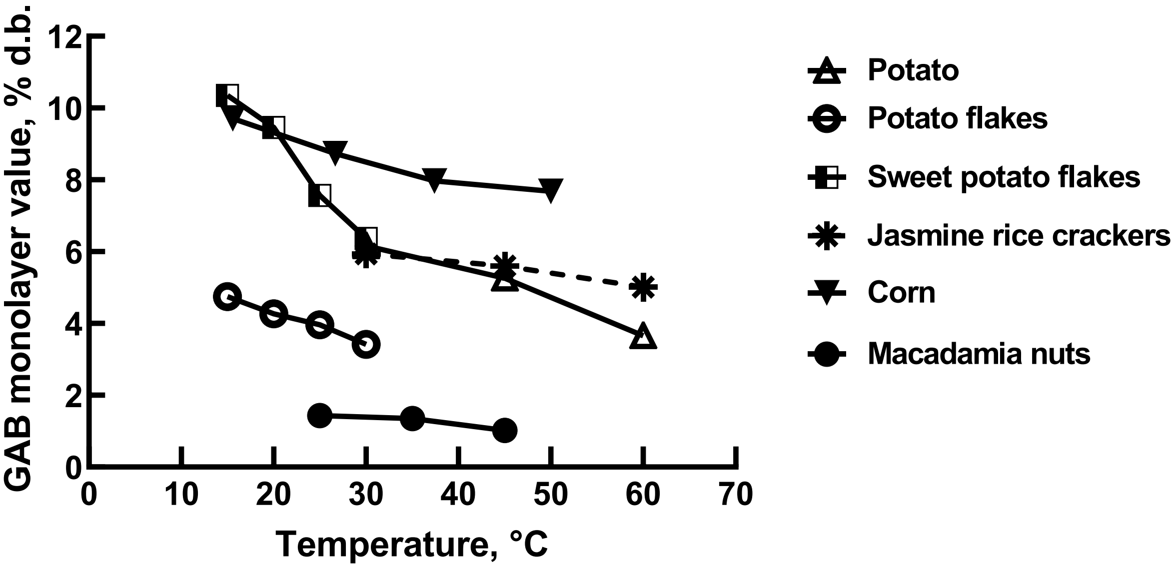

Figure 5

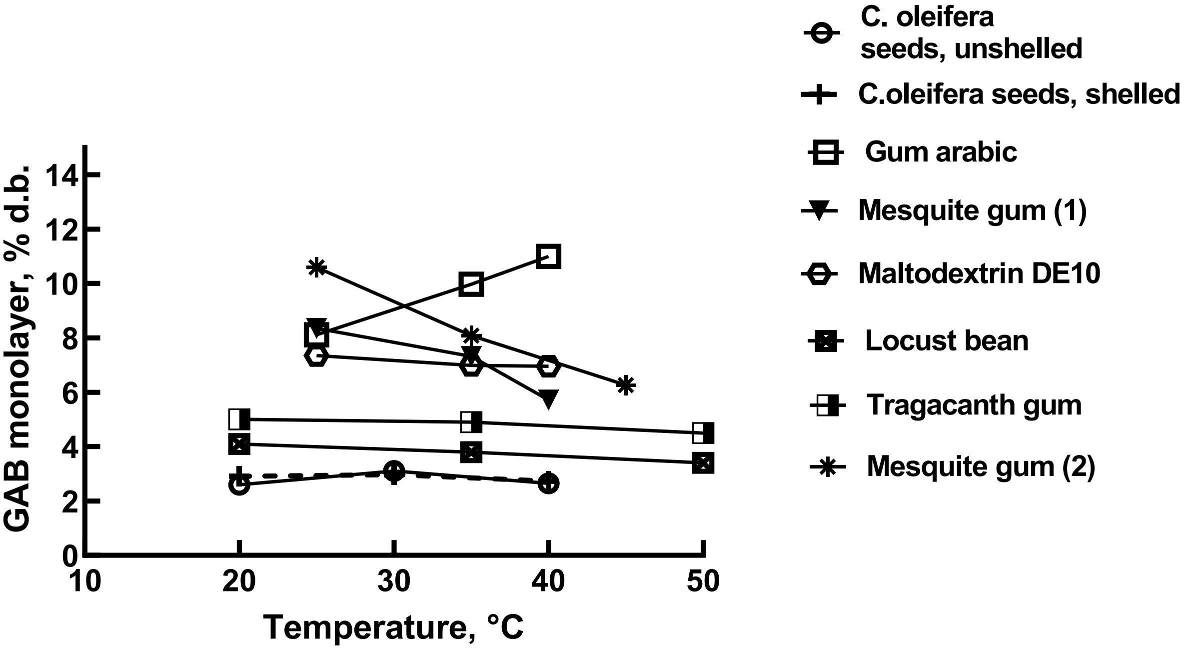

Figure 6

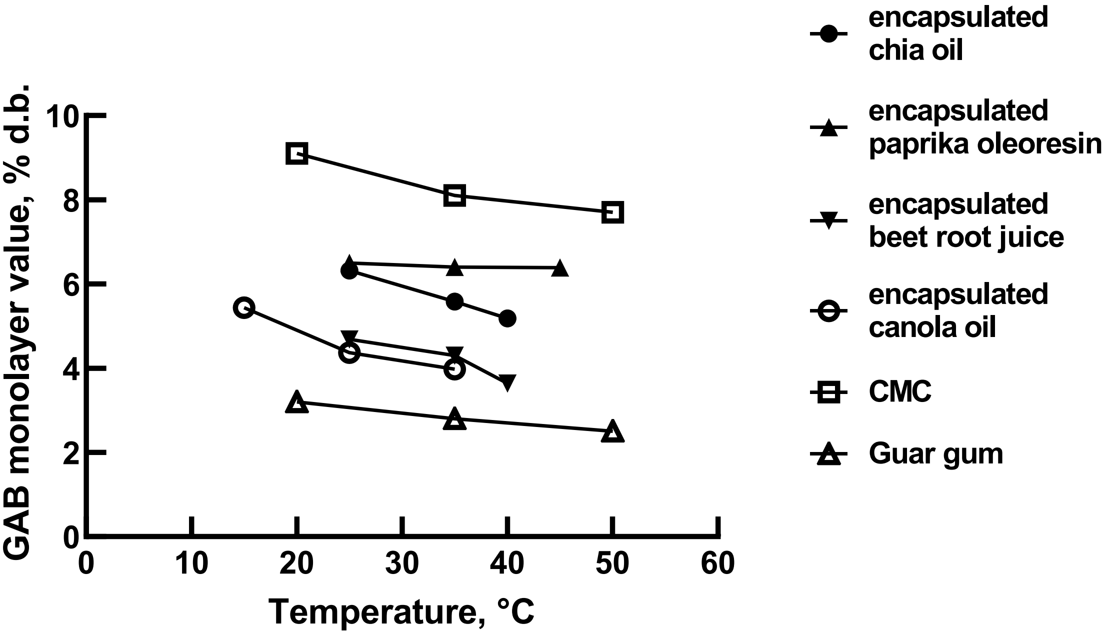
GAB monolayer value, % d.b.
10
8
6
4
2
0
0
10
20
30
40
50
60
Temperature, °C
encapsulated chia oil
encapsulated paprika oleoresin
encapsulated beet root juice
encapsulated canola oil
CMC
Guar gum

Figure 7

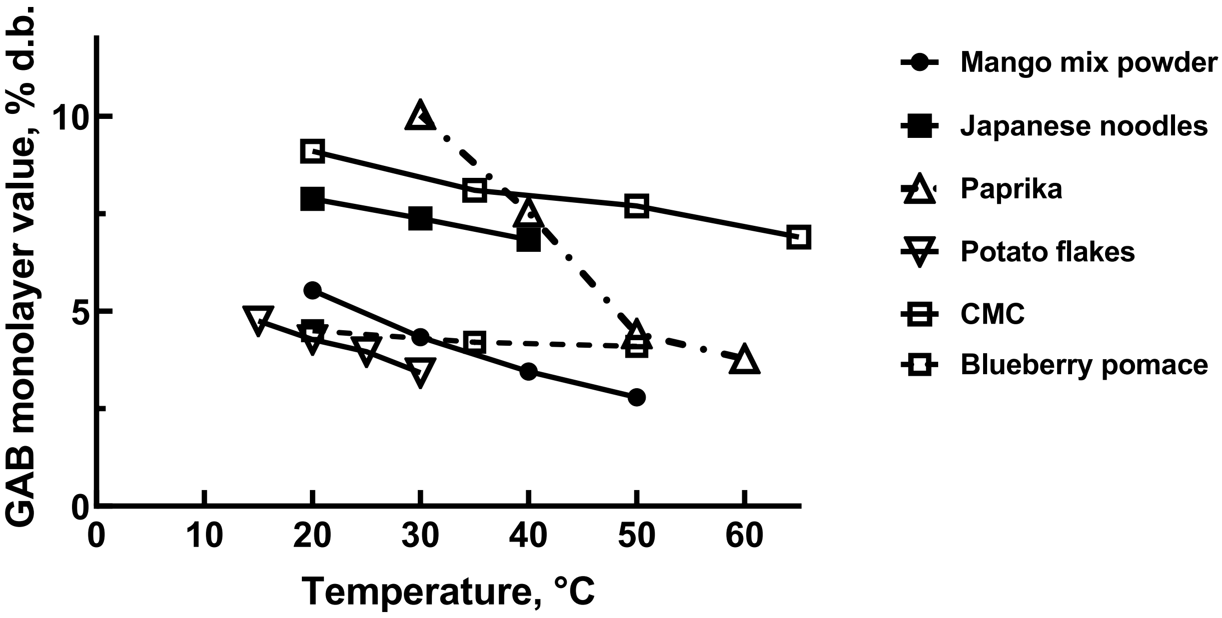
GAB monolayer value, % d.b.
10
5
0
0
10
20
30
40
50
60
Temperature, °C
Mango mix powder
Japanese noodles
Paprika
Potato flakes
CMC
Blueberry pomace

Figure 8

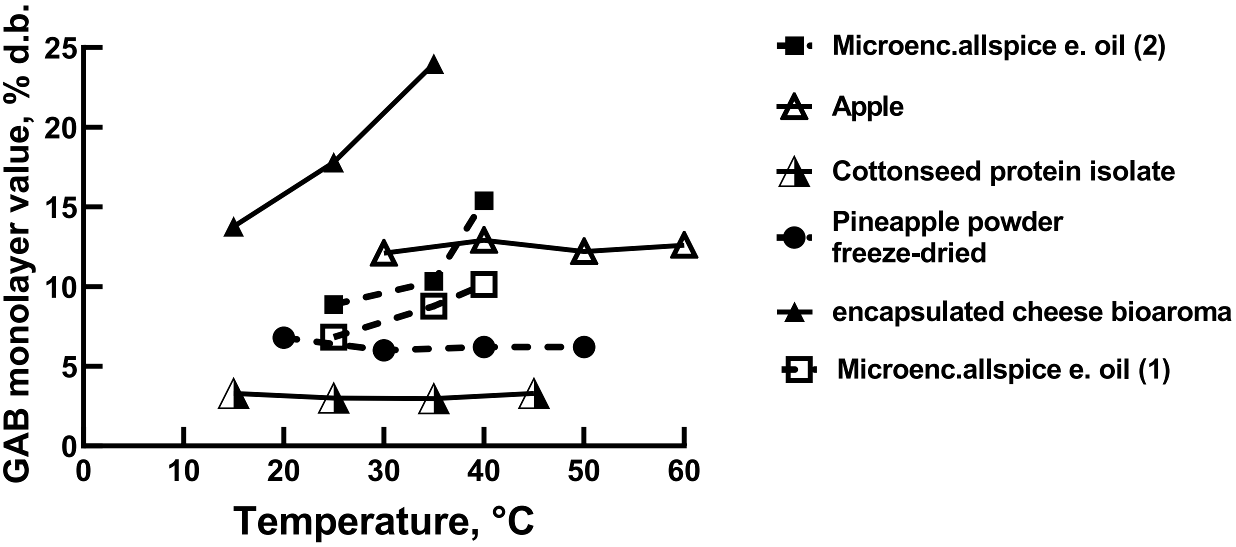

Figure 9

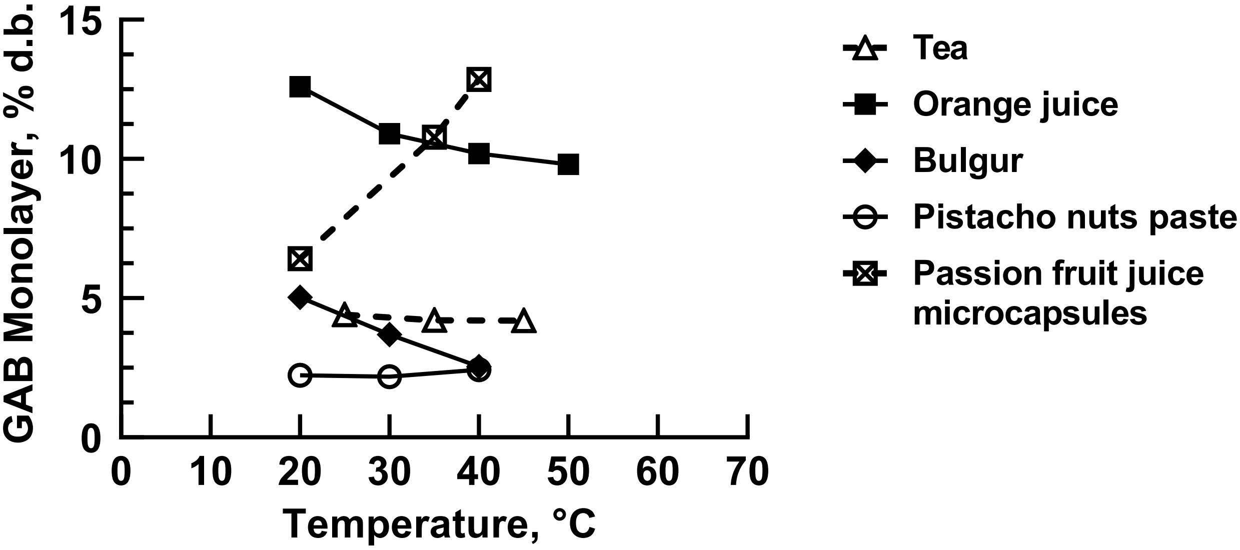

Figure 10

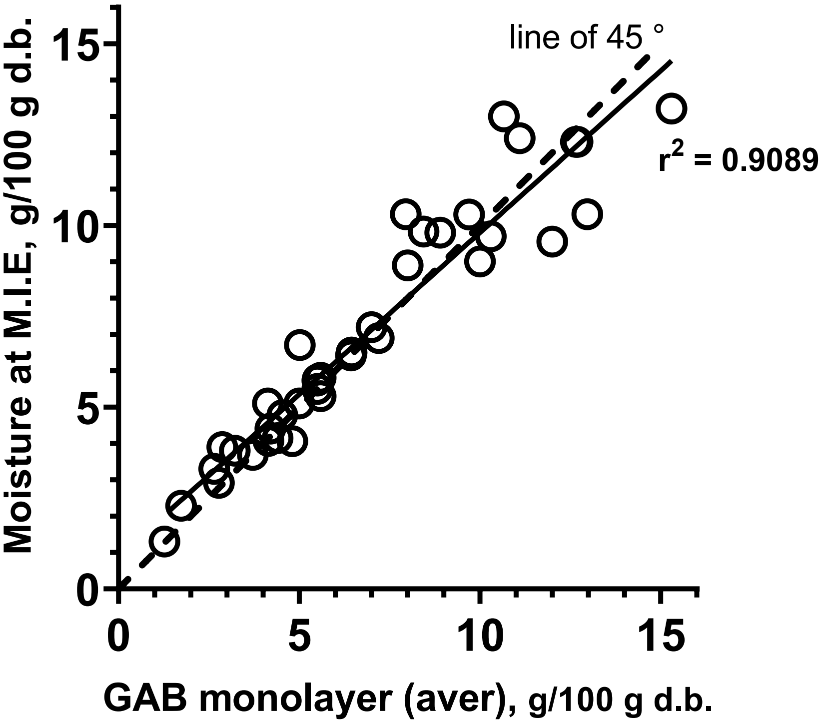

Figure 11