The states of water in glutinous rice flour characterized by interpreting desorption isotherm

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Abstract Water content of glutinous rice flour were determined after equilibrium at water activity (a_w) of 0.06–0.98 and temperature of 10, 20 and 30 °C. Distribution of water in different states and its evolution with a_w were characterized using four composite models. Interactions of water molecules with solid matrix and themselves were further evaluated. The Park model was a more realistic and mechanism-based approach for describing water desorption of glutinous rice flour. Increased equilibrium water induced by lowering temperature existed mostly as strongly bound water with only a few parts as weakly bound water. The water-polymer thermodynamic incompatibility predominated the water mobility, and resulted in a rapid decrease of diffusion coefficient at $a_w > \sim 0.7$. Water diffusivity behavior with a_w suggested water clustering at high a_w levels. The Zimm–Lundberg theory, Park model and Brown analysis all revealed that critical a_w of water clustering was of 0.81–0.85, depending on temperature, but gave inconsistent prediction about mean cluster size.

Keywords Glutinous rice four · Isotherm · Desorption · Water state · Clustering · Interaction

Introduction

Sorbed water molecules differ from each other in spatial locations relative to the sorbent surface and themselves. For a multilayer adsorption, the water molecules can locate in different layers, and arrange in different patterns even in same layer. Their different spatial locations make them exist in different states, which can be expressed in terms of their thermodynamic interactions with solid materials, diffusivity and intrinsic mobility in solid matrix, and aggregation behavior with themselves.

State of water in foods can be probed by nondestructive techniques, such as differential scanning calorimetry (DSC) (Furmaniak et al. 2015; Farroni and Buera 2014), Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy (Davis and Elabd 2013) and nuclear magnetic resonance (NMR) spectroscopy (Sun et al. 2010). As a surface phenomenon, water adsorption is a result of sorbent–water and water–water interactions. Logically, with the help of theoretical analysis, one can obtain the information concerning the characteristics of both sorbent and sorbate as well as their interactions from the isotherm data.

Type II isotherm curve in the BET classification is typical for food biopolymer, and can be divided into three regions according to its shape characteristics. The first region locates at lower water activity (a_w) levels, characterizing as a convex curve. This part is usually described using the Langmuir or Freundlich model. The second region locates in middle a_w range and is characterized as a linear or near-linear curve. The linear relationship can be described by the Henry's law. As an upturn curve at high a_w levels, the third region can be described using the Raoult's law (Pascual-Pineda et al. 2014), Kelvin's law (Liu et al. 2013) and Flory–Huggins theory (Chu et al.

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2006). Then, a group of isotherm models (called composite models) have been developed in literatures, in which sorbed water are expressed as the sum of the two or three contributing isotherms. The composite models assume that each contributor follows a specified adsorption mechanism such as the Langmuir adsorption, Henry's or Raoult's law, and that all adsorptions contribute simultaneously and continuously to the overall process of water sorption.

Water molecules prefer to cluster with each other in foods with high water content (Avital et al. 1990; Hernaandez-Munz et al. 2003). Water clustering is one mechanism proposed to interpret the sharp upturn in an isotherm curve. In order to characterize clustering in water-polymer mixture, many qualitative or quantitative approaches have been developed, including thermodynamic analysis, Park isotherm model (Chun and Lee 2015), Brown model, Zimm–Lundberg theory, Flory–Huggins theory and engaged species induced clustering (ENSIC) model (Chu et al. 2006). In food research, the Zimm–Lundberg approach was used in several reports (Avital et al. 1990; Carrillo et al. 1988; Hernaandez-Munz et al. 2003).

The main industrial utilization of glutinous rice flour in China is to produce Tangyuan, a traditional Chinese sweet. Rapid freezing is widely used for industrialization of this indigenous food. Desorption properties of water in glutinous rice flour will determine its transfer during drying and storage of glutinous rice flour, and freezing of Tangyuan.

Water sorption isotherms for rice flour have been determined and their net isosteric enthalpies of sorption have been estimated (Durakova and Menkov 2004; Brett et al. 2009). With the aim of extending our knowledge of water state in glutinous rice flour as a function water activity, after determining moisture contents of glutinous rice flour equilibrated with ten a_w levels at three temperatures, this work aimed to (1) characterize the evolution of water in different states with the help of composite isotherm models, (2) estimate polymer-water thermodynamic non-ideality and water mobility from water diffusion coefficient as a function of water activity, (3) analyze clustering of water and its interactions with solid matrix using the Zimm–Lundberg theory and the Brown model.

Materials and methods

Materials

Glutinous rice flour was purchased from local market with the composition of 8.08% (dry base, d.b.) protein, 1.11% (d.b.) lipid, 0.92% (d.b.) fiber, 0.90% (d.b.) ash and 88.99% (d.b.) carbohydrate (by difference). The glutinous rice flour was mixed with water to a final moisture content of 45%

(wet base) and conditioned for 3 h before desorption experiments.

Determination of desorption isotherms

Equilibrium moisture content of glutinous rice flour was determined by a gravimetric technique at ten water activity levels. Each flour sample (about 5 g) was placed in a desiccator. Ten types of saturated salt solutions [LiBr, LiCl, CH_3COOK , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, KI, NaCl, KCl and K_2SO_3] were used to maintain ten specified water activity levels inside the desiccators (Greenspan 1977). A test tube containing thymol was placed inside each desiccator with $a_w > 0.75$ to prevent mold growth during storage. The desiccators were placed in temperature-controlled cabinets maintained at 10, 20 and 30 °C (± 1 °C) and the samples were allowed to equilibrate until there was no discernible weight change (± 0.001 g). The equilibrium moisture content was determined by drying in an oven at 105 °C until constant weight. All measurements were done in triplicate.

Composite isotherm models

The following four composite isotherm models were adopted in this work because previous analysis showed that they can give acceptable fitness to isotherm data of glutinous rice flour.

Modified D'Arcy and Watt (MDW) model

The MDW model (Eq. 1) contains three terms on the right of the equation. The first has the form of a Langmuir isotherm and describes the adsorption onto strong sorption sites. The second has the form of the Henry's law and describes adsorption onto weak sorption sites. The third term describes multilayer formation on the secondary sites using the Raoult's law (D'Arcy and Watt 1970).

$$M = \frac{M_L k_L a_w}{1 + k_L a_w} + k_H a_w + \frac{M_b k_b a_w}{1 - k_b a_w} \quad (1)$$

where M is equilibrated water content (kg H_2O per kg dry solid), a_w is water activity, M_L is the Langmuir capacity constant, k_L is the Langmuir adsorption equilibrium constant, k_H is the solubility coefficient of the Henry's law, M_b is the maximum water adsorption at secondary sites, k_b is adsorption equilibrium constants for secondary sites.

Park model

The Park model (Eq. 2) is also based on three sorption terms. Different from the MDW model, the Park model hypothesized that the water molecules adsorbed according

to the Henry's law make clusters, and the clustering reaction of water can be expressed by equilibrium $n\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_n$ (Park 1986).

$$M = \frac{M_L k_L a_w}{1 + k_L a_w} + k_H a_w + k_c a_w^n \quad (2)$$

where k_c is the equilibrium constant for the clustering reaction, and n is the mean number of water molecules per cluster.

Langmuir–Gaussian (L–G) model

The L–G model (Eq. 3) is a two-term isotherm model developed by Liu et al. (2013). The first term describes water adsorption in the pore volume of micropores and the region next to macropore walls using the Langmuir model. The second term describes water vapor condensation in the remnant pore core volume of the macropores based on the Kelvin theory with assuming that the effective pore size follows a Gaussian distribution.

$$M = \frac{M_L k_L a_w}{1 + k_L a_w} + M_{cm} \text{erf} \left(\frac{\mu_1}{RT \ln(1/a_w)} \right) \quad (3)$$

where M_{cm} is the maximum amount of water adsorbed due to capillary condensation, μ_1 is adsorption enthalpy (kJ mol^{-1}), T is temperature (K), R is universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$).

Hailwood–Horrobin (H–H) model

The H–H model (Eq. 4) assumes that the adsorbed water exists in two states: water in simple solution, and water combined to form a monohydrate with a definite unit of the sorbent molecule (Hailwood and Horrobin 1946).

$$M = \frac{18}{W} \frac{k_1 k_2 a_w}{1 + k_1 k_2 a_w} + \frac{18}{W} \frac{k_2 a_w}{1 - k_2 a_w} \quad (4)$$

where W is the molecular weight of dry solids per mole of water sorption sites, 18 is molecule weight of water, k_1 is the equilibrium constant where the hydrate is formed from dissolved water and dry solids, k_2 is the equilibrium constant between dissolved water and water vapor.

The $k_1 k_2$ in the H–H model can be regarded as the k_L , then the first term in the H–H model is actually a modified version of the Langmuir formula, and the $18/W$ means the maximum water amount of the Langmuir adsorption.

Temperature has a great impact on rate constants of adsorption. The van't Hoff equation (Eq. 5) is usually employed to describe their dependence on temperature.

$$k = k_0 \exp \left(\frac{Q - L}{RT} \right) \quad (5)$$

where Q and k_0 are the adsorption enthalpy and pre-exponent factor related to various adsorption mechanisms assumed in the above models, respectively; L is the enthalpy of water condensation ($44.03 \text{ kJ mol}^{-1}$).

Regression and statistical analysis

The four composite models were fitted to the isotherm data using STATISTICA Version 12 (StatSoft Inc.) with non-linear optimization on the basis of the program specific Levenberg–Marquardt algorithm. These models were compared using global determination coefficient DC^g .

Determination coefficient at one temperature (DC_T) is defined by (Furmaniak et al. 2015)

$$DC_T = 1 - \frac{\sum_{i=1}^N (M_i^o - M_i^t)^2}{\sum_{i=1}^N (M_i^o - \bar{M}^o)^2} \quad (6)$$

where M_i^o is the observed water content for i -th experimental point, M_i^t is the theoretical value of the water content calculated from models, $\bar{M}^o$ is the average observed water content, and N is the number of points.

The global fitness parameter associated with temperature DC_T^g is the mean square root of DC_T determined for a particular temperature (Furmaniak et al. 2015):

$$DC_T^g = \sqrt{\frac{\sum DC_T^2}{n'}} \quad (7)$$

where n' is the number of temperatures.

The fitness parameter reflecting the goodness of the van't Hoff model, DC_q , and global fitness parameter related to adsorption enthalpy, DC_q^g , were defined similarly using Eqs. (6) and (7), respectively. Global determination coefficient DC^g was calculated using Eq. (8) as Furmaniak et al. (2015) did. $DC^g = 1$ shows the ideal fitness, the lower DC^g value, the worse fitness.

$$DC^g = 1 - \sqrt{(1 - DC_T^g)(1 - DC_q^g)} \quad (8)$$

Results and discussion

Fitting results of the four composite models

Fitting goodness and obtained parameters of the four composite models are listed in Table 1. Adsorption enthalpies calculated using Eq. (5) are also presented. Both DC_T^g and DC^g of the two-term models were smaller than those of the three-term models, suggesting that the Henry term should be included in an isotherm model for glutinous rice flour. Beside absence of the Henry term in the H–H model, its assumption of equal saturated water content of

Table 1 Statistical criterions and best-fit parameters of the four models after fitting to the isotherm data of glutinous rice flour at 10, 20 and 30 °C, and desorption enthalpies from the van't Hoff model

	W	k_1	k_2	$18/W$	$k_L = k_1 k_2$	DC_T	DC_T^g	DC_q^g	DC^g
H–H									
10 °C	241.97	79.77	0.8232	0.0744	65.66	0.9785			
20 °C	266.78	36.65	0.8332	0.0675	30.54	0.9854	0.9846	0.8543	0.9526
30 °C	285.15	19.76	0.8321	0.0631	16.44	0.9899			
Q		49.84	−0.39		49.45				
DC_q		0.9978	0.6808		0.9983				
	M_L	k_L	q_{cm}	μ_1					
L–G									
10 °C	0.1693	5.02	0.2577	0.11		0.9962			
20 °C	0.1664	3.43	0.2435	0.12		0.9978	0.9977	0.9942	0.9963
30 °C	0.1796	2.16	0.2126	0.14		0.9990			
Q		30.06							
DC_q		0.9942							
	M_L	k_L	k_H	M_b	k_b				
MDW									
10 °C	0.0677	35.57	0.1372	0.0073	0.9825	0.9999			
20 °C	0.0548	23.87	0.1329	0.0076	0.9818	0.9999	0.9999	0.9669	0.9978
30 °C	0.0480	13.19	0.1241	0.0081	0.9806	0.9998			
Q		35.28	3.56		0.07				
DC_q		0.9825	0.9467		0.9711				
	M_L	k_L	k_H	n	k_C				
Park									
10 °C	0.0557	77.49	0.1743	17.12	0.2366	0.9998			
20 °C	0.0428	46.61	0.1697	15.55	0.2279	0.9998	0.9998	0.9704	0.9977
30 °C	0.0340	23.91	0.1626	14.10	0.2098	0.9998			
Q		41.97	2.47		4.27				
DC_q		0.9905	0.9756		0.9445				

both strongly bound water and solvent water is another factor responsible for its worse predicting performance than the MDW and the Park models. Determination coefficient can not discern which three-term model (MDW and Park models) is the best-fitness model.

Probably because of including the Henry term in their isotherm expression, the two three-term models predicted lower Langmuir water contents than the two-term models did (Table 1). The Langmuir water contents predicted by the L–G model were much higher those predicted by the three other models. It is noticeable that the Langmuir term in the L–G model presents two parts of water. However, in the scenario of the MDW and the Park models, the Henry water is also assumed to be sorbed, even though weakly, in the first layer. Therefore, it become understandable that the strongly bound water obtained from the MDW and the Park models was lower than its corresponding parts from the H–H and the L–G models.

For all the four models, the equilibrium constants related to the strong binding were much higher than these related to the weak binding, indicating much faster adsorption of water molecules to the strong sorption sites. Adsorption enthalpy is an important thermodynamic parameter reflecting the state of water. For all the four models, the adsorption enthalpy associated with the strong binding was much higher than that associated with other types of water adsorption.

The mean cluster size of water predicted by the Park model decreased from 17.12 to 14.10 with temperature rising from 10 to 30 °C, which is comparable with the value in flax fibers (18 at 25 °C, Gouanve et al. 2006) but higher than that in starch film (6.3 at 25 °C, Masclaux et al. 2010).

Evolution of water in different states

Contribution of each isotherm component in the composite models to the total water content is presented in Fig. 1. The

Fig. 1 Equilibrated water contents (symbol, circle: 10 °C, square: 20 °C, diamond: 30 °C), predicted total water contents and their contributing isotherms decomposed according to the H–H (a), L–G

(b), MDW (c) and Park (d) models (solid line: 10 °C, dotted line: 20 °C, dashed line: 30 °C)

Langmuir adsorption predicted by the H–H, MDW and Park models approached its maximum with a_w increasing to around 0.1. The Langmuir water decomposed from the L–G model did not reach its saturation even at maximum a_w . Additionally, according to the L–G model, the increasing of water content slowed down as a_w approached its maximum, which is not true for foods, and exposes the intrinsic shortcoming of the L–G model.

The multilayer water predicted by the MDW model and the clustered water predicted by the Park model all kept at a much lower level at low–middle a_w range, and increased rapidly after a critical a_w value was reached. Due to its higher slope, the Henry curve decomposed from the Park model was almost parallel to the total isotherm in the middle a_w regime, which was not the case for the MDW model. The clustered water predicted by the Park model remained to be zero at an a_w lower than ~ 0.75 , and increased sharply with an a_w greater than ~ 0.9 . The Henry water component predicted by the Park model was higher than its counterpart in the MDW model at the expense of clustered water and Langmuir water.

All the four modes predicted that equilibrated water content decreased with temperature increase at same water activity. Deconvolution of the four isotherm models all revealed that the temperature-induced decrease in water content was mostly attributed to the decrease of the strongly bound Langmuir water. When the Henry term was separated in an isotherm model as the case of the MDW and Park models, the decrease of the Henry water also partially contributed to the loss of total water caused by temperature.

Diffusivity under isothermal conditions

The equilibrium isotherms showed a large degree of upturn at high activities (Fig. 1). Two possible interpretations of this sharp upturn are the plasticization of the polymer by the water, and the clustering of water molecules. Clustering causes an increase in the average size of a water cluster and hence reduces the diffusion coefficient, while plasticization allows the polymer chains to move more freely leading to faster diffusion (Chu et al. 2006). Thus the behavior of the

diffusion coefficient can be used to differentiate between plasticization and clustering.

The driving force for the transport of sorbed water through solids is the space gradient of the spreading pressure π . For a spherical body, diffusion velocity of water molecules at radius r is $u = -\frac{1}{f} \frac{d\pi}{dr}$, where f is a coefficient of frictional resistance (Babbitt 1950). Mass density can be expressed as $\rho_s M$, where ρ_s is density of the dry solids. Mass flux, which is the product of velocity and mass density, can be expressed as $J = -\frac{\rho_s M}{f} \frac{d\pi}{dr}$. Under isothermal conditions, $d\pi$ can be expressed as $d\pi = \frac{MRT}{M_w A_0} d \ln a_w$, where M_w is the molecular weight of water, A_0 is the specific surface area of the solid (Aguerre and Suarez 2004). Then the expression for the mass flux is $J = -\frac{\rho_s M^2 RT}{f M_w A_0 a_w} \frac{da_w}{dr}$, and can be reformed as following:

$$J = -\frac{\rho_s M^2 RT}{f M_w A_0 a_w} \frac{da_w}{dM} \frac{dM}{dr} \quad (9)$$

On the other hand, the mass flux of water can also be expressed as Eq. (10) according to the Fick's law.

$$J = -D \rho_s \frac{dM}{dr} \quad (10)$$

where D is diffusion coefficient as a function of water content. Substituting Eq. (10) into Eq. (9), one can obtain Eq. (11).

$$D = \frac{RT}{f M_w A_0} \frac{M^2}{a_w} \frac{da_w}{dM} \quad (11)$$

For glutinous rice flour, value of ρ_s was evaluated using $\rho_s = (1 - M) / \left(\sum_1^4 m_i / \rho_i \right)$ from its components masses m_i and their mass densities ρ_i . Mass densities for (poly) saccharide, protein, ash and fat are 1550, 1330, 2440 and 930 kg m⁻³, respectively (van der Sman 2008). Using the m_i values as stated in *Materials* section, ρ_s was calculated to be 1.5234 kg m⁻³. A_0 was calculated using the BET model at $a_w < 0.45$, being 2.6929, 2.4274 and 2.2258×10^5 m² kg⁻¹ at 10, 20 and 30 °C, respectively. f was calculated using Eq. (12) derived by Skaar and Babiak (1982).

$$f = \frac{\delta}{\mu_w} \exp \left(\frac{E_D - E_\mu}{RT} \right) \quad (12)$$

where δ is the mean spacing between water adsorbed molecules (3.0×10^{-10} m, Aguerre and Suarez 2004), μ_w is viscosity of free liquid water (1.3063, 1.0042 and 0.8012 mPa s at 10, 20 and 30 °C, respectively, Li and Ge 2011), E_μ is the activation energy for the variation of water viscosity with temperature (17.45 kJ mol⁻¹, calculated using the above data), and E_D is the activation energy for the variation of the diffusion coefficient with temperature,

Fig. 2 Evolution of water diffusion coefficients as a function of activity for water desorption of glutinous rice flour at 10, 20 and 30 °C

$= 0.5E_H$ (Aguerre and Suarez 2004). E_H is the desorption energy of the monolayer water, and calculated using the BET model at $a_w < 0.45$ being 33.4 kJ mol⁻¹.

The park model was adopted to calculate da_w/dM term in Eq. (11). Finally, the D values were computed using Eq. (11), and plotted in Fig. 2.

Diffusion coefficient of water during isothermal situations increased with water activity, and reached its maximum at a a_w of ~ 0.7 , then decreased rapidly when further increasing a_w . In the a_w range of ~ 0.6 to ~ 0.8 , variation of diffusivity was mild. Similar trend and same order of magnitude of water diffusivity were observed for corn, potato and native manioc starches (Aguerre and Suarez 2004). Decreasing diffusivity at high a_w levels suggested that water aggregation might have occurred.

Thermodynamic non-ideality factor and intrinsic mobility

For a binary system where the chemical potential is the true driving force for the mass transport process, the diffusion coefficient as determined based on the assumption of the Fick's law can be written as the product of two factors (Eq. 13): an intrinsic mobility (D') and a thermodynamic non-ideality factor (L) defined as Eq. (14) (Doghieri et al. 1999).

$$D = D' L \quad (13)$$

$$L \equiv \left(\frac{\partial \ln(a_w)}{\partial \ln(M)} \right)_{T,P} = \left(\frac{M \partial a_w}{a_w \partial M} \right)_{T,P} = \frac{M}{a_w} \frac{da_w}{dM} \quad (14)$$

Thermodynamic factor is indicative of the strength of polymer-penetrant thermodynamic interactions. Mobility coefficient is a purely kinetic parameter and is inversely proportional to the resistance to molecular motion in the polymer-penetrant mixture.

Thermodynamic factor for glutinous rice flour was calculated using Eq. (14) with the Park isotherm model being applied

Fig. 3 Variation of thermodynamic non-ideality factor (a) and water mobility (b) with water activity at three temperatures

to estimate the derivative term, and presented in Fig. 3a. As observed by Doghieri et al. (1999), in the case of vapor sorption in a hydrocarbon polymer, the thermodynamic factor is lower than unity if the polymer-penetrant interactions are unfavorable, and higher than unity if favorable. As seen from Fig. 3a, the polymer-water interactions in glutinous rice flour were unfavorable when a_w was higher than ~ 0.75 .

Substituting Eqs. (11) and (14) into Eq. (13), following equation can be obtained to calculate water mobility.

$$D' = \frac{RTM}{fM_w A_0} \quad (15)$$

The calculated mobility as a function of water activity for glutinous rice flour is shown in Fig. 3b. In the a_w range of 0 to ~ 0.1 , water mobility increased with a_w . In the a_w range of ~ 0.1 to ~ 0.9 , slower increase in water mobility was observed. When a_w was higher than ~ 0.9 , water mobility increased sharply. The trend of the mobility with water activity can be phenomenally explained from variation of amount of the Langmuir water, Henry water and the clustered water with the consideration of much lower mobility of the Langmuir water and higher mobility of other two types of water. Theoretically, mobility increase is usually explained as the result of swelling and/or plasticization of polymer after water absorption. Water absorption might have induced swelling of the glutinous rice flour particles (Malumba et al. 2013). According to the reported glass transition temperature as a function of water content for rice flour (Nithya et al. 2015), water plasticization effect might have occurred at $a_w > 0.9$. Both swelling and plasticization can result in an increase of total free volume in the flour matrix; therefore, the mobility of the sorbed molecules increased with water activity.

The critical water activity above which the mobility increased rapidly was coincident with that above which clustered water predicted by the Park mode increased rapidly (Fig. 1). Similar observations are documented in previous reports (Farroni and Buera 2014; Sun et al. 2010),

even through applied isotherm models and mobility probing techniques are different from ours.

Equation (13) suggests that the behavior of diffusivity is a result of the competing water activity dependence of D' and L . Although D' was an increasing function of water activity, the measured diffusion coefficient decreased significantly at $a_w > \sim 0.75$. This indicated that the thermodynamic non-ideality has offset the effects of plasticization and finally dominated the diffusion of water in glutinous rice flour as water activity reached to high levels.

Zimm–Lundberg analysis

For a binary solvent (1) + polymer (2) system which is far from critical conditions, Zimm (1953) derived the following approximate solution (Eq. 16) for the KB integral (G_{ij}) on the basis of the Kirkwood–Buff (KB) theory. The KB integral G_{ij} between components i and j , defined as the spatial integral over the pair correlation function, gives a measure of the tendency of molecules j to cluster around a central molecule i .

$$G_{11} \approx -v_1 \phi_2 \left(\frac{\partial(a_1/\phi_1)}{\partial a_1} \right)_{P,T} - v_1 \quad (16)$$

where a_1 is the activity of component 1; v_1 is the partial molar volume per molecule of species 1; ϕ_1 , ϕ_2 is volume fraction of component 1, 2, respectively.

Zimm (1953) and Zimm and Lundberg (1956) introduced the notion of “cluster integral” G_{11}/v_1 to characterize the solvent clustering in the system. They called G_{11}/v_1 a “cluster integral”, because the quantity $\phi_1 G_{11}/v_1$ is the mean number of type 1 molecules in excess of the mean concentration of type 1 molecules in the neighborhood of a given type 1 molecule; thus, it measures the clustering tendency of the type 1 molecules (Zimm 1953). For a water + polymer system, cluster integral is expressed as:

$$\frac{G_{ww}}{v_w} = -(1 - \phi_w) \left(\frac{\partial(a_w/\phi_w)}{\partial a_w} \right)_{P,T} - 1 \quad (17)$$

The sum $\phi_w G_{ww}/v_w + 1$, therefore, is the mean cluster size. In this study, the determination of the MCS was deduced using the Park model. Considering $\phi_w = \frac{M/\rho_w}{1/\rho_s + M/\rho_w}$, one can obtain the mean cluster size of water molecules based on the Park model (Gouanve et al. 2006):

$$MCS_{\text{Park}} = \frac{\rho^2}{M^3(1 + \rho/M)^2} \left[\frac{M_L k_L a_w}{(1 + k_L a_w)^2} + k_H a_w + k_c n a_w^n \right] \quad (18)$$

where $\rho = \rho_w/\rho_s$, ρ_w is density sorbed water, dependent on water content. Determined ρ_w values of water adsorbed on low-protein fraction of wheat flour at different water contents (Gur-Arieh et al. 1967) were adopted in this study, and fitted to the Peleg-Fermi model. The final formula was expressed as Eq. (19) with $R^2 = 0.968$.

$$\rho_w = \frac{0.528}{1 + \exp[(M - 0.115)/0.019]} + 0.967 \quad (19)$$

MCS_{Park} was calculated using Eq. (18) combined with Eq. (19) with neglecting the temperature dependence of ρ_s and ρ_w . Results are shown in Fig. 4. MCS_{Park} kept almost constant then increased sharply with a_w increase. The critical a_w values where the MCS_{Park} reached to unity were about 0.85, 0.83 and 0.81 at 10, 20 and 30 °C, respectively. Water molecules are randomly mixed within the solid matrix when water activity is lower than the critical values, and begin to cluster when water activity is higher than the critical values (Chu et al. 2006). At maximum a_w values involved in this study, water molecules formed clusters with an average number of about three. Water clustering occurs frequently in polymers of low polarity because water molecules bound to the polymer compete efficiently with polymer polar sites to

Fig. 4 Mean cluster size of water at various water activities for glutinous rice flour at three temperatures as indicated

“capture” new water molecules (Le Gac et al. 2014). Insolubility of starch granules may have act as “low polarity” and induced water clustering.

The two important parameters characterizing a water clustering process are the critical water activity of clustering and the size of the cluster. Critical water activities for glutinous rice flour are slightly higher than that for bread (0.75, Avital et al. 1990), gliadin film (0.65, Hernandez-Munz et al. 2003) and mechanical mixed Hylon 7-sucrose blend (0.7, Carrillo et al. 1988). The MCS_{Park} values for glutinous rice flour at the maximum water activities are comparable with the results (from 2 to 4, depending on materials) in the above reports.

Figure 4 shows that water molecules preferred to cluster at higher temperature. Similar trend was observed by Yang et al. (1985) for Kapton polyimide in glass state, and Rawat and Khali (1998) for wood equilibrated at a_w levels of up to 0.98. According to the park model, water molecules prefer to cluster at lower temperature (Table 1), which was contradictory to the prediction from the Zimm–Lundberg method (Eq. 18). This contradictory observation might be due to the assumptions of the Zimm–Lundberg clustering model: Additivity of water and polymer specific volumes and thermodynamic equilibrium of water-polymer system. Relaxation of polymers may take many months. Therefore, water sorption data, which are typically obtained within a several days, may not represent the equilibrium state (Authelin et al. 2014).

Comparing Fig. 2 with Fig. 4 suggests that the critical a_w for water clustering was not coincident with the a_w beyond which the diffusivity decreased. Similar deviation was also reported (Chu et al. 2006; Davis and Elabd 2013). This suggests that the beginning of diffusivity decrease does not mean that water clustering will occur immediately.

Brown analysis

Brown (1980) proposed a different procedure of water clustering analysis, which combines conventional Flory–Huggins solution theory and Zimm–Lundberg cluster theory. In Brown’s approach, the total amount of sorbed water is considered to consist of two types: water sorbed by a normal random mixing and water sorbed in the form of clusters. Brown’s method links the volume fraction of sorbed water ϕ_w to the water activity with the following relation.

$$\frac{1}{\phi_w} = \frac{K_1}{a_w} - K_2 \quad (20)$$

where K_1 and K_2 are constants. Equation (20) represents the Henry’s law for $K_2 = 0$, the Langmuir type behavior for negative K_2 values and a clustered isotherm for positive

K_2 values. The intersection of the $1/\phi_w \sim 1/a_w$ straight line with the $1/\phi_w$ axis gives the critical value ϕ_c where clustering of water molecules sets in through Eq. (21) (Pissis and Kyritsis 2013). After ρ_w being calculated by Eq. (19), critical water content M_c can be computed from ϕ_c and ρ_w .

$$\phi_c = \frac{1}{K_2} \quad (21)$$

The Brown analysis allows a unique definition of the Flory–Huggins interaction parameter (χ). Under infinite dilution conditions ($\phi \rightarrow 0$), Eq. (20) can be expressed in terms of the Henry's law $1/\phi_H = k_1/a_w$, and the Flory–Huggins equation reduces to $a_w \approx \phi \exp(1 + \chi)$. The Henry's law is a limiting approximation of the Flory–Huggins theory, then one can extract the following χ expression for infinite dilution conditions ($\phi \rightarrow 0, \phi_H \rightarrow 0$) (Pissis and Kyritsis 2013).

$$\chi \approx \ln K_1 - 1 \quad (22)$$

At any water activity, the experimental sorption can be compared to that predicted by the Henry's law isotherm to provide a ratio, N_e , which is defined as the 'enhancement number', and can be calculated from Eq. (23) (Karad and Jones 2005). N_e is an indication for the deviation from the Henry type of sorption.

$$N_e = \frac{\phi_w}{\phi_H} = \frac{K_1}{K_1 - K_2 a_w} = 1 + K_2 \phi_w \quad (23)$$

It can be seen from Eq. (20) that the derivative within the brackets in Eq. (17) is equal to $-K_2$. The mean cluster size for this case (MCS_B) is given by

$$MCS_B = 1 + K_2 \phi_w - K_2 \phi_w^2 \quad (24)$$

In order to further investigate water clustering in glutinous rice flour, reciprocal water volume fraction was plotted against reciprocal water activity. The Brown plot (not shown) exhibited nonlinear behavior in the whole a_w range. Karad and Jones (2005) applied the Brown model to their isotherm data at higher water activities. Isotherm data at the three higher activities for glutinous rice flour were used to

determine parameters K_1 and K_2 in Eq. (20). The Brown analysis is usually applied to rubbery polymers. While Brown (1980) himself did applied Eq. (20) to model water adsorption of glassy polymers. Here, the Brown model was also applied to analyze water desorption of glutinous rice at the three lower water activities. The values of χ , N_e and MCS_B were calculated using Eqs. (22), (23) and (24), respectively. All the resulted values are collected in Table 2.

The negative K_2 , indicating a Langmuir adsorption at lower a_w , and positive K_2 , suggesting a Zimm–Lundberg isotherm are in line with our analysis using the Park model. The Flory–Huggins parameter χ was larger than 0.5, indicating a repulsive interaction between water and polymer material (Radosta et al. 1989). Then water–water interaction was predominant, and water molecules preferred to form clusters in glutinous rice flour at high activities. This conclusion was consistent with the results of the Zimm–Lundberg analysis. The water activities corresponding to the M_c values at 10, 20 and 30 °C were also in good agreement with the critical water activities determined from the Zimm–Lundberg analysis.

The MCS_B values at maximum a_w were around 2, which are lower than that obtained from the Zimm–Lundberg analysis (~ 3 , Fig. 4). The mean cluster size predicted from the Park model was several times higher than the results from the Brown analysis and the Zimm–Lundberg analysis. Similar discrepancy was also reported by Gouanve et al. (2006) for flax fibers. These contradictory results suggested that mean cluster size was sensitive to the model selected to fit isotherm data. Recently, direct measurements from FTIR-ATR spectroscopy show that water clusters are the prevalent population of water in some glassy polymers, where the Zimm–Lundberg model predicts only water monomers (Davis and Elabd 2013). Gouanve et al. (2006) concluded that the average size of the water cluster determined by the Zimm–Lundberg method should be considered only as a first approximation. According to our point of view, the different scenarios of the Zimm–Lundberg theory and the Park model should also respond for their inconsistent predictions. The Zimm–Lundberg theory assumes that all water molecules aggregate to form clusters

Table 2 Values for characteristic parameters from the Brown analysis for glutinous rice flour

	K_1	K_2	R^2	χ	M_c	a_w	ϕ_w	N_e	MCS_B
$a_w = 0.06\text{--}0.23$									
10 °C	0.73	−7.45	0.9866			0.2338	0.097	0.28	0.35
20 °C	1.00	−9.05	0.9940			0.2311	0.076	0.31	0.36
30 °C	1.57	−8.79	0.9964			0.2161	0.064	0.44	0.47
$a_w = 0.75\text{--}0.98$									
10 °C	5.85	3.81	0.9325	0.77	0.25	0.9817	0.386	2.47	1.90
20 °C	6.98	4.28	0.9599	0.94	0.23	0.9789	0.368	2.58	2.00
30 °C	7.73	4.96	0.9818	1.05	0.20	0.9730	0.344	2.71	2.12

when water activity is higher than a critical value. In contrast, the Park model assumes that only part of water takes part in water clustering. Assuming the cluster sizes of the Langmuir water and Henry water are unity, water content-weighted average size of water cluster in glutinous rice flour at maximum activities was calculated to be 6.1, 7.1 and 8.0 at 10, 20 and 30 °C, respectively.

Conclusion

In summary, the Henry term is necessary to be incorporated in a composite isotherm model in order to get a perfect modeling of water desorption for glutinous rice flour. Statistical criteria itself can not discern the most suitable isotherm model. Additional diffusivity analysis disclosed that the Park model can describe water desorption of glutinous rice flour both phenomenally and theoretically. Decomposition of the Park model revealed that (1) the Langmuir water adsorption completed when a_w reached to ~ 0.05 ; (2) the Henry water developed with a_w in almost parallel to the total water isotherm within the middle a_w region; (3) water molecules began to cluster when $a_w > \sim 0.75$; (4) temperature-induced decrease of water was mainly due to the decrease of the Langmuir water and partially to the decrease of the Henry water.

Water mobility in glutinous rice flour increased rapidly when a_w was higher than ~ 0.9 . The increasing mobility was overwhelmed by the strong water–water interaction when a_w was higher than ~ 0.75 . Water diffusivity behavior with a_w suggested that water clustering had occurred in glutinous rice flour at high a_w levels. Water cluster analysis using the Zimm–Lundberg theory revealed that water molecules started to aggregate at critical a_w values of 0.81–0.85 dependent on temperature, which were coincident with the results of the Park model and the Brown analysis. The predicted mean cluster size values from the Zimm–Lundberg analysis were comparable to the values from the Brown model, but much lower than those from the Park model.

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