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Raoult's law based food water sorption isotherm

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Abstract

A new model of water sorption isotherm is developed on the basis of Raoult's law. It is assumed that water present in food occurs in two states, as free water with properties of the bulk water and as water of hydration. Hydrated molecules are considered as new entities with molecular weights larger than those of non-hydrated molecules. Hydration reduces the free concentration of water and thus affects water activity in solution.

Application of the developed equation to food sorption data showed that it gives approximation of sorption isotherms much better than that offered by the GAB model. Moreover, it predicts infinite adsorption at $a_w = 1$, the property which is not offered by the GAB equation. The new equation makes it possible to interpolate isotherms at high water activities close to one. The probability that the new equation will fit the food isotherm with small RMS is higher than 90% and substantially exceeds that found for the GAB model. As a two-parameter model it makes substantial improvement over the three-parameter GAB equation. © 2000 Elsevier Science Ltd. All rights reserved.

Notation

a	activity
A	constant
b	constant
c	constant in the GAB model
F, G, H	constants
k	constant in the GAB model
m	mass (g)
M	molecular weight (g/mole)
n	number of molecules
N	number of experimental points
R	residuals (%)
RMS	root mean square (%)
u	water content (g H_2O/g d.m.)
v	variance

Greek symbols

α	constant
χ	constant

Subscripts

c	complex
e	experimental
f	free
h	hydration
m	monolayer
p	predicted
s	solid, solute
t	total
w	water

1. Introduction

Water vapour sorption isotherms have a number of very important applications in food science and technology. They present an equilibrium state of all processes wherein water molecules combine reversibly with food solids. The state of equilibrium have been mathematically described by numerous models (van den Berg & Bruin, 1981). Models, most commonly used to describe sorption of water by foods, are based on surface chemistry adsorption theories.

The food solids are composed of polymeric materials supplemented with small-molecule components such as salts, sugars, organic acids, and flavours. All food solids components undergo hydration in water environment. The hydration properties, in turn affect the interactions of the components with one another, which are pronounced by such food properties as structure, texture and storage life.

All the experimental evidence collected until now show that at least two distinct water environments exist in foods. One of them is similar to bulk water and the other arises from the favourable interactions between water and food constituents. The amount of water whose properties are affected by food components is substantial. For small molecules hydration water can amount to from few to several moles of water per mole of substance. The hydration shell of the hydrated Li^+

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ion is formed by four water molecules (Franks, 1975) while egg phosphatidylcholine is hydrated with 12.4 ± 1 mole of water (Hauser, 1975). About 10 water molecules are associated with phosphatidylcholine headgroups (Crowe, Clegg & Crowe, 1998). Urea is hydrated with seven moles of water and guanidinium ion binds twelve moles of water (Nandel, Verma, Singh & Jain, 1998).

A measurement of unfreezable water showed that substantial amount of water interacts so strongly with other constituents that it is not able to crystallise during cooling. The amount of unfreezable water in plasma proteins is equal to 0.47 g/g, in collagen 0.26 g/g (Simatos, Faure, Bonjour & Couach, 1975). In egg white, bound water is 0.55 g/g, in cornstarch it is 0.35 g/g and in cellulose it is 0.16 g/g (Steinberg & Leung, 1975).

There is no single temperature of freezing of water in foods. The thermodynamic freezing of water in the soybean protein occurs over a range as broad as 40 K (Johari & Sartor, 1998). This is mainly due to perturbations of the ice–water equilibrium by the interactions of water with protein.

The internal dynamics of proteins recovers at hydration level 0.1–0.2 g/g protein. Monoclinic lysozyme is active at level of hydration of 0.2 g/g protein (Nagendra, Sukumar & Vijayan, 1998). This value is much lower than the amount of monolayer capacity (Gregory, 1998). Monolayer coverage for lysozyme is completed at 300 molecules of water per molecule of the enzyme. However, complete hydration occurs at 360–400 water molecules/molecule of lysozyme (Gregory, 1998). Extended chain of lysozyme needs some 1000–1400 water molecules for full hydration (Gregory, 1998). Collagen contains 0.26 g water/g protein which is unfreezable, but the water acquires the same heat of fusion as bulk water at hydration level 0.60 g/g protein. In bovine serum albumin the partial entalphy of water becomes identical to that of free water above 0.54 g/g (Simatos et al., 1975). Full hydration of lysozyme is estimated at 0.45–0.50 g/g protein, but the reduction of water content below 0.75 g/g increases denaturation temperature of the enzyme (Gregory, 1998). The above data are evidence that two different hydration phases occur. By analogy with ion hydration, these phases are denoted as A and B shell. The A shell water is similar to the fraction of non-freezing water. The B shell water differs from the bulk water by melting temperature and heat and entropies of fusion. It continues to a hydration level of about 1.4 g/g which corresponds to the amount of water whose motional correlation times are different from that of bulk water (Gregory, 1998).

Water is a necessary component of the crystallographic until cell in both the A- and B-type structures of starch. Four and 36 water molecules are present in the most recent models of A and B types models of starch, respectively (Imberty & Perez, 1988; Imberty, Buleon, Trau & Perez, 1991). More than 10% of water is necessary for annealing of small amylose chains. The transition of the B-type to the A-type upon heating occurs at water content above 18% (Buleon, Le Bail, Colonna & Bizot, 1998). Starches consist of both crystalline and amorphous regions. The crystalline regions typically exhibit resistance to solvent penetration. Hence, water affects the structure acting as a plasticizer of the amorphous regions. At sufficient water contents, mobility of amorphous regions is initiated and swelling of the polymer is observed.

In such a complex system as flour dough, unfreezable water is 23–24% and at 28% moisture resistance to mixing increases rapidly. This effect is due to possible interactions between gliadin fibrils. The lubricating effect of water is present at 35% moisture (Daniels, 1975). At the same time starch shows no water protons at 2% water content and gluten at moisture lower than 7.5% (Chinachoti, 1998). Since stailing of bread is accompanied by the shift from a mobile to an immobile water fraction it is suggested that water induces reorganisation of amorphous areas and releases constraints present leading to further crystallisation (Slade & Levine, 1991).

Water exerts its solvent properties at water contents higher than the monolayer value. Mobilisation point for sodium chloride in the NaCl–casein system occurs at $a_w > 0.3$ (Gal, 1975; Kinsella & Fox, 1986). The starch sucrose or glucose system shows mobilisation point around $a_w = 0.8$ (Duckworth, 1981) in the starch and β-amylase mixture, the appearance of maltose begins to be noticed when a_w reaches 0.65–0.7. Experiments with dextran and nitroxide probes showed that reaction with ascorbic acid in mechanical mixture was initiated at $a_w > 0.75$ and was strong at $a_w > 0.9$ (Simatos, Le Meste, Petroff & Halphen, 1981).

Caseinate containing nitroxide radicals showed slow motion of the probe at water content below 0.3 g/g d.m. (Le Meste & Duckworth, 1988). At water content higher than 0.25–0.30 g/g d.m. caseinate, both solute diffusivity and protein flexibility is observed. At the water content of 1 g/g dry protein, the mobility of the more mobile spin-labelled side chains and probes was about 10 times lower than those of the same groups of molecules in dilute solution (Le Meste & Duckworth, 1988).

In liquid homogenous solution in the hydration range 0–3 g/g d.m. rotational diffusivity increases linearly with increasing water content (Le Meste & Voilley, 1988). The mobilisation point was below 0.01 g/g d.m. In dextran, gelatine, casein and starch mobilisation point was approximately 0.25 g/g d.m. In caseinates, the paramagnetic probes were immobile at water content below 0.25 g/g d.m. At water content larger than 1 g/g d.m. all probes were mobile (Le Meste, Viguier, Lorient & Simatos, 1990).

Gilbert (1986) suggested that the availability of water is defined by the free energy for the transfer from food matrix to reaction system. This free energy corresponds to the liquefaction of water/water bond formation. The water becomes available for chemical reactions when liquid-like cluster of water molecules is formed.

Water sorption isotherms of mechanical mixtures could not be predicted on the basis of sorption isotherms of individual components (Lewicki, 1997b). Swelling, conformational changes, polymer–polymer interactions, binding of ions, crosslinking and plasticisation of amorphous regions were proposed as the reasons for the observed differences. Simply the mobility of molecules was responsible for the lack of superimposability of experimental isotherms with those predicted.

All the above presented examples show that some water is so strongly bound by food components that water protons give signals representing the rigid phase. The most of hydration water promotes molecular mobility and conformational changes of polymers. However the hydration water has still different properties than the bulk water. Hence, the hydration process reduces the free concentration of water effectively. In the light of this evidence, the surface adsorption theory becomes questionable. Once the molecules can move and polymers can change their conformation and state should the process still be envisaged as the surface adsorption of water molecules or shall it be considered as the dilution process of already existing solution?

Hill (1950) proposed application of solution thermodynamics to the adsorption process. The thermodynamic system considered consisted in non-adsorbed gas being in equilibrium with gas adsorbed on the adsorbent and the diffuse interface placed somewhere between adsorbed and non-adsorbed gas. Hill's theory was modified by Le Maguer (1985) and applied to the sorption isotherm of potato starch. Further application of solution thermodynamics to water sorption isotherms of foods was done by Kumagai, Iwase, Kumagai, Mizuno and Yano (1994). The application of solution thermodynamics to food water sorption isotherms treats the condensed phase as the solution.

Under these circumstances it seems appropriate to use Raoult's law to express water activity in the food system. This approach was used by Bone (1973) to formulate intermediate moisture foods. The solution approach to water state in foods was taken by Ross (1975) to estimate water activity in intermediate moisture foods. Palnitkar and Heldman (1970) proposed the use of Raoult's law for high molecular weight components of food by introduction of effective molecular weight. Chen and Karmas (1980) used effective molecular weight but its use was ambiguous and the method found no use to describe relationship between water activity and water concentration.

The objective of this paper was to develop an equation based on Raoult's law and describing water sorption isotherms of foods in the whole range of water activities.

2. The model

It is assumed that hydration of food components reduces the concentration of water with properties of the bulk water. Moreover, it is assumed that hydration of molecule forms a complex with properties different than those of a molecule and the bulk water. According to this model, food consists in free water with properties of the bulk water, and hydrated dry matter. Hence, water in food is divided into two fractions: free water and water in hydration shells. Thus,

$$m_t = m_f + m_h \tag{1}$$

and the hydrated dry matter is present in the amount

$$m_c = m_s + m_h \tag{2}$$

with molecular weight:

$$M_c = M_s + 18.016n. \tag{3}$$

With these assumptions water activity can be expressed with Raoult's law in the following form:

$$a_w = \frac{(m_f/18.016)}{(m_f/18.016) + (m_c/M_c)}. \tag{4}$$

The above equation fulfils the following boundary conditions:

$$a_w = 0, \quad m_f = 0,$$
$$a_w = 1, \quad m_f \to \infty.$$

Assuming

$$\frac{m_h}{m_t} = \chi \tag{5}$$

and combining Eq. (5) with Eq. (1) the amount of free water is

$$m_f = (1 - \chi)m_t. \tag{6}$$

Substitution of Eq. (6) into Eq. (4) yields:

$$a_w = \frac{m_t(1-\chi)/18.016}{(m_t(1-\chi)/18.016) + (m_c/M_c)}. \tag{7}$$

Rearranging Eq. (7) gives:

$$a_w = \frac{m_t}{m_t + (18.016 m_c/((1-\chi)M_c))}. \tag{8}$$

Since m_c and M_c are not known, Eq. (8) is written as

$$a_w = \frac{m_t}{m_t + \alpha}, \tag{9}$$

where

$$\alpha = \frac{18.016 m_c}{(1-\chi)M_c} \tag{10}$$

Eq. (9) solved for α yields

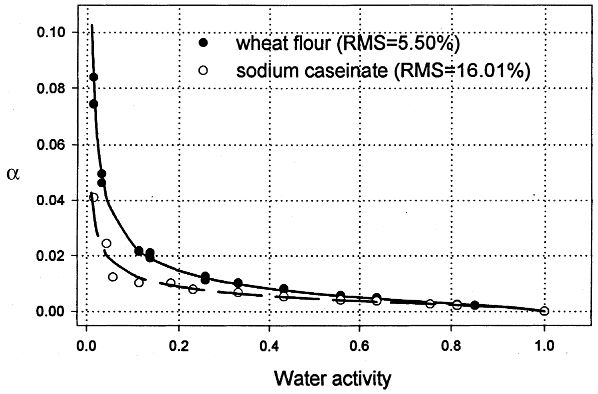

Fig. 1. Relationship between α and water activity for wheat flour and sodium caseinate.

$$\alpha = m_t\left(\frac{1}{a_w} - 1\right). \tag{11}$$

Water content is usually expressed as

$$u = \frac{m_t}{m_s}. \tag{12}$$

For $m_s = 1$, Eq. (11) can be written as

$$\alpha = u\left(\frac{1}{a_w} - 1\right). \tag{13}$$

Having water sorption isotherm α at a given water activity can be calculated and the relationship $\alpha = f(a_w)$ can be found for a selected food product. It is important to notice, that for $a_w = 1$, $\alpha = 0$. This point is in agreement with the boundary conditions and should be included into calculations. Example of a relationship between α and a_w is presented in Fig. 1.

The relationship between α and a_w is very well approximated by the following equation

$$\alpha = A\left(\frac{1}{a_w} - 1\right)^b. \tag{14}$$

Combining Eq. (14) with Eq. (13) and solving for water content the following is obtained

$$u = A\left(\frac{1}{a_w} - 1\right)^{b-1}. \tag{15}$$

This is the food water sorption isotherm derived on the basis of Raoult's law.

Derived equation is like the Oswin (1946) equation, however substantial differences occur in analysis of sorption data. These are

- the Oswin equation is an empirical one, and it is a frequency curve derived by Pearson. Equation presented in this paper is derived on the basis of the Raoult' s law and parameter α has a physical meaning. When an amount of hydration water increases α also increases, and for the system in which there is no free water α approaches infinity. Moreover, in the system in which hydration does not occur (no solutes) $\alpha = 0$.
- the parameters in the Oswin equation are found by plotting log u vs $\log((1/a_w) - 1)$ (Oswin, 1946). This procedure excludes point at $a_w = 1$, hence there is no possibility to extrapolate data to high water activities. Parameters A and b in Eq. (15) are obtained by approximate solution of Eq. (14) with the criterion either the highest coefficient of determination or the least standard error of estimation. This procedure allows to include the point $\alpha = 0$; $a_w = 1$ into calculations, hence the data at high water activities can be interpolated.

3. Application to sorption data

Water sorption isotherms of 38 products and 31 model mechanical mixtures (Table 1) were described by the derived equation. For comparison, two three-parameter models were used in the analysis. The model developed by Anderson (1946), De Boer (1953) and Guggenheim (1966) known as the GAB model is described by the following equation:

$$u = \frac{u_m k c a_w}{(1 - k a_w)[1 + (c - 1) k a_w]}. \tag{16}$$

Equation developed by Lewicki (1998) is also a three-parameter model

$$u = F\left[\frac{1}{(1 - a_w)^G} - \frac{1}{1 + a_w^H}\right]. \tag{17}$$

The Table Curve 2D software (curve fitting software with built-in and user-defined equations, Jandel Sci.) was used to fit tested equations to experimental isotherms. The goodness of fit was measured by calculation of residuals (R) and root mean square (RMS) expressed in per cent. Statistical measures were calculated from the following equations:

$$R = \frac{u_e - u_p}{u_e} 100, \tag{18}$$

$$\mathrm{RMS} = 100\sqrt{\frac{\sum\left((u_e - u_p)/u_e\right)^2}{N}}. \tag{19}$$

Residuals and RMS were calculated using Excel software (Microsoft).

Considering the application of analysed equations to sorption data the following assumptions were made

- fits with RMS ⩾ ± 25% were considered as loaded with too large error to be accepted,
- for the GAB model being a modification of the multilayer adsorption developed by Brunauer, Emmett and Teller (1938) some other limits were applied. The value of $k > 1$ is not feasible from the thermodynamic as well as mathematical point of view.

Table 1
Products tested for the goodness of fit of predicted sorption isotherms

Product	Water activity range	Source
Apple cellular fiber	0.11–0.98	Labuza (1985)
Avicel PH 101 MCC	0.11–0.90	Wolf et al. (1984)
Beef	0.03–0.85	Own results
Carrageenan	0.11–0.98	Labuza (1985)
Carrot	0.022–0.90	Own results
Caseinate, sodium salt	0.022–0.865	Own results
Caseinate, sodium salt	0.015–0.813	Own results
Caseinate, sodium salt	0.022–0.865	Own results
Casein	0.20–0.90	Bizot (1983)
Cellulose, powdered	0.022–0.865	Own results
Cellulose, powdered	0.11–0.98	Labuza (1985)
Cellulose, powdered	0.015–0.813	Own results
Citrus pulp fiber	0.11–0.98	Labuza (1985)
Coffee	0.05–0.95	Bizot (1983)
Corn bran flour	0.11–0.98	Labuza (1985)
Gelatin	0.11–0.98	Labuza (1985)
LM pectin	0.11–0.98	Labuza (1985)
Macaroni	0.015–0.813	Own results
Mushroom (*Boletus edulis*)	0.03–0.85	Own results
Oat bran flour	0.11–0.98	Labuza (1985)
Onion	0.03–0.85	Own results
Pea flour	0.03–0.85	Own results
Polyglicine	0.1–0.9	Bizot (1983)
Potato flakes	0.03–0.85	Own results
Rice	0.015–0.813	Own results
Rice bran flour	0.11–0.98	Labuza (1985)
Soy bran flour	0.11–0.98	Labuza (1985)
Starch gel, potato	0.033–0.980	Bizot, Buleon, Mouhouo-Riou and Multon (1985)
Starch gel, potato	0.055–0.973	Own results
Starch, potato	0.112–0.903	Bizot (1983)
Starch, potato	0.015–0.813	Own results
Starch, potato	0.022–0.865	Own results
Starch, potato	0.022–0.865	Own results
Tomato powder	0.05–0.80	Own results
Wheat bran flour	0.11–0.98	Labuza (1985)
Wheat flour	0.015–0.851	Own results
Wool	0–0.95	Bull (1944)
Yeast (*Saccharomyces cerevisiae*)	0.03–0.748	Own results
Model		
Caseinate: Cellulose = 1:1	0.022–0.865	Own results
Caseinate: Cellulose = 1:2	0.022–0.865	Own results
Caseinate: Cellulose = 2:1	0.022–0.865	Own results
Starch:Caseinate:Cellulose:Glucose:Citric acid:Salts = 1:1:1:0.5:0.3:0.2	0.022–0.865	Own results
Starch:Caseinate:Cellulose = 1:1:1	0.022–0.865	Own results
Starch:Caseinate:Glucose = 1:1:1	0.022–0.865	Own results
Starch:Caseinate:NaCl = 50:33:17	0.022–0.865	Own results
Starch:Caseinate = 1:1	0.022–0.865	Own results
Starch:Caseinate = 1:1	0.022–0.865	Own results
Starch:Caseinate = 1:3	0.022–0.865	Own results
Starch:Caseinate = 2:3	0.015–0.813	Own results
Starch:Caseinate = 2:3	0.022–0.865	Own results
Starch:Caseinate = 2:8	0.015–0.813	Own results
Starch:Caseinate = 2:8	0.022–0.865	Own results
Starch:Caseinate = 3:1	0.022–0.865	Own results
Starch:Caseinate = 3:2	0.015–0.813	Own results
Starch:Caseinate = 3:2	0.022–0.865	Own results
Starch:Caseinate = 8:2	0.015–0.813	Own results
Starch:Caseinate = 8:2	0.022–0.865	Own results
Starch:Caseinate = 8:2	0.022–0.865	Own results
Starch:Cellulose:Glucose = 1:1:1	0.022–0.865	Own results

Table 1 (Continued)

Product	Water activity range	Source
Starch:Cellulose = 1:1	0.022–0.865	Own results
Starch:Cellulose = 1:2	0.022–0.865	Own results
Starch:Cellulose = 2:3	0.015–0.813	Own results
Starch:Cellulose = 2:8	0.015–0.813	Own results
Starch:Cellulose = 3:2	0.015–0.813	Own results
Starch:Cellulose = 8:2	0.015–0.813	Own results
Starch:Citric acid = 1:1	0.022–0.865	Own results
Starch:Glucose = 1:1	0.022–0.865	Own results
Starch:Glutamic acid = 4:1	0.022–0.865	Own results
Starch:NaCl = 4:1	0.022–0.865	Own results

Moreover, to keep the error of u_m within ± 15% the value of c must be greater than 5.5 (Lewicki, 1997a). Hence, fits with $k > 1$ or $c < 5.5$ were considered as not fulfilling theoretical requirements, regardless of the calculated RMS.

Results of curve fitting are collected in Table 2. Tomato powder sorption isotherm could not be described by any of the tested equations with sufficient accuracy. Dried onion and mechanical mixture of starch and sodium chloride water sorption isotherms could be only described by the developed equation. Neither GAB nor Lewicki's equations could describe these isotherms with sufficient accuracy.

The following number of fits fulfilling above-mentioned assumptions was obtained out of 69 analysed isotherms: the GAB model – 56; Lewicki's equation – 65 and the developed equation – 68, which is 81%, 94% and 99%, respectively. Hence, the probability of receiving fit with RMS < ±25% is around 80% for the GAB model, and higher than 90% for two other analysed equations.

Further analysis of GAB, Lewicki's and the new equation was done for only those isotherms, which fulfilled the assumed limits.

Residuals calculated by Eq. (18) express the difference between experimental and predicted values at a point. The frequency of residuals is presented in Fig. 2. The relationship between frequency and the level of residuals is well described by the Pearson distribution. The most frequent residuals are collected in Table 3.

Analysis of cumulative frequency of residuals (Fig. 3) shows that the probability to obtain fit of water sorption isotherm within a given range of residuals is very different for analysed equations. For Eq. (17) and $-5 \leqslant R \leqslant +5\%$ the probability is 65.2%, for the GAB model it is 42.6% and for the developed equation it is 43.1%. If the range of residuals is extended to $-10 \leqslant R \leqslant +10\%$ the respective probabilities are 84.0%, 74.0% and 70.5%.

The frequency of RMS for analysed equations is presented in Fig. 4. The most frequent RMS for Eq. (17) is ±2.24%, for the GAB model it is ±9.47% and for the new equation it is ±4.66%. Cumulative frequencies of RMS for the analysed equations are presented in Fig. 5. The highest probability to fit experimental data with small RMS gives Lewicki's equation (Table 4). Smaller probability is quaranted when the new equation is used. The least probability is expected when the GAB model is applied. Since Raoult's law based equation has only two parameters its applicability to food water sorption isotherms seems to be very good, and makes substantial improvement over the GAB equation.

Results presented in this paper are different from those published by Lomauro, Bakshi and Labuza, (1985a,b). Analysis of over 300 isotherms showed that the GAB model gave the highest percentage of fits with mean relative deviation modulus less than five. That was from 42.9% for meats to 100% for nuts and oilseeds. The Oswin equation, which was also analysed by Lomauro and co-workers, was not as good as the GAB equation. The percentage of fits with means relative deviation modulus less than 5 were from 0 for milk products to 93.8% for nuts and oilseeds.

Equation derived in this paper and based on Raoult's law takes into account, besides the experimental points, a point $\alpha = 0$; $a_w = 1$. This makes a substantial difference over the procedure proposed by Oswin (1946) or Lomauro et al. (1985a) and probably increases goodness of fit to analysed isotherms.

Equations analysed in this paper contain two or three parameters. It was interesting to see how precision of parameters estimation influences total variance of calculated water content. It was assumed that standard deviation of each parameter is equal to ±5% of the estimated value. The principle of variance additivity was used in this analysis (see Appendix A) and the results are presented in Fig. 6. It is evident that the GAB model needs a high precision of the parameters estimation if a fit with small RMS is expected. Standard deviation of predicted water content is strongly dependent on water activity and at $a_w > 0.8$ it is larger than ±10%. Eq. (17) yields standard deviation, which is little dependent on water activity, and approaches ± 10% at water activities close to one. The developed equation yields results similar to those obtained for Lewicki's equation but at $a_w > 0.9$ estimated water content is loaded with larger error than that calculated for Eq. (17).

Table 2
Constants in analyzed equations

Product	Equation							
	GAB			Eq. (17)			Eq. (15)	
	u_m	k	c	F	G	H	A	b
Apple cellular fiber	No solution			0.1989	0.5149	4.3814	0.0955	0.2611
Avicel PH 101 MCC	0.0390	0.7895	9.47	0.0975	0.2698	0.7333	0.0540	0.5657
Beef	0.0377	0.9812	14.47	0.0602	0.7576	0.6169	0.0758	0.4942
Carrageenan	0.1162	0.9035	42.12	0.3850	0.2985	0.7215	0.2220	0.5838
Carrot	No solution			0.2115	0.4483	3.0198	0.0971	0.1955
Caseinate, sodium salt	0.0607	0.8110	6.86	0.1249	0.3738	0.7095	0.0807	0.4908
Caseinate, sodium salt	0.0510	0.8853	15.56	0.1047	0.4724	0.4360	0.0873	0.5850
Caseinate, sodium salt	0.07801	0.7541	7.63	0.1820	0.2622	0.7571	0.0958	0.5048
Casein	0.0858	0.6540	7.12	0.2276	0.1345	0.9299	0.0959	0.6060
Cellulose, powdered	0.0342	0.8489	11.91	0.1057	0.2236	0.8127	0.0549	0.5826
Cellulose, powdered	0.0285	0.7294	12.30	0.0715	0.2234	0.6476	0.0373	0.5830
Cellulose, powdered	0.0187	0.8750	15.26	0.0399	0.4424	0.4812	0.0311	0.5739
Citrus pulp fiber	0.0435	0.9422	19.35	0.1238	0.4170	0.6027	0.0902	0.5252
Coffee	No solution			0.1509	0.3776	9.6308	0.0440	0.2284
Corn bran flour	0.0432	0.9237	56.18	0.1338	0.3642	0.5131	0.0933	0.5701
Gelatin	0.0923	0.9380	114.06	0.2752	0.3981	0.5763	0.1958	0.5456
LM pectin	0.0828	0.9541	7.26	No solution			0.1427	0.4377
Macaroni	0.0426	0.9071	10.61	0.0859	0.5098	0.5628	0.0715	0.4802
Mushroom (*Boletus edulis*)	No solution			0.0653	0.8038	0.2979	0.0799	0.5421
Oat bran flour	0.0354	0.9288	43.20	0.1156	0.3507	0.3852	0.0854	0.6070
Onion	No solution			No solution			0.0982	0.2990
Pea flour	0.0539	0.8489	53.18	0.1223	0.3869	0.2825	0.0978	0.6679
Polyglicine	0.0883	0.6268	5.55	0.2153	0.1328	0.9649	0.0835	0.5745
Potato flakes	0.0545	0.8937	43.78	0.1163	0.4712	0.2971	0.1042	0.6308
Rice	0.0571	0.6770	9.20	0.2116	0.1923	0.7401	0.1085	0.5001
Rice bran flour	0.0378	0.9843	42.89	0.0724	0.7012	0.1515	0.0960	0.4696
Soy bran flour	0.0392	0.9488	123.06	0.1013	0.4592	0.3120	0.0881	0.5461
Starch gel, potato	0.0633	0.8976	42.27	0.2067	0.2894	0.5150	0.1263	0.6020
Starch gel, potato	0.0643	0.8484	29.13	0.2079	0.2351	0.6069	0.1177	0.6299
Starch gel, potato	0.0986	0.7567	8.37	0.2521	0.2100	0.7940	0.1249	0.5785
Starch gel, potato	0.0942	0.7293	10.75	0.2213	0.2500	0.6484	0.1222	0.5656
Starch gel, potato	0.0871	0.7453	17.42	0.2199	0.2376	0.5572	0.1234	0.6233
Starch gel, potato	0.0961	0.7306	13.61	0.2436	0.2216	0.6287	0.1283	0.5840
Wheat bran flour	No solution			0.0801	0.6860	0.2209	0.0960	0.4696
Wheat flour	0.0810	0.7358	17.40	0.2041	0.2322	035634	0.1144	0.6054
Wool	0.0733	0.7819	16.13	0.2087	0.2121	0.6456	0.1056	0.6157
Yeast (*Saccharomyces cerevisiae*)	No solution			0.0592	0.9699	0.1393	0.0878	0.5851
Model								
C:Cel = 1:1	0.0445	0.8146	17.20	0.0877	0.3063	0.5341	0.0556	0.5832
C:Cel = 1:2	0.0361	0.8042	17.20	0.0877	0.3063	0.5341	0.0556	0.5832
C:Cel = 2:1	0.0500	0.8232	13.90	0.1167	0.3400	0.5633	0.0767	0.5624
S:C:Cel:G:CA:Salts = 1:1:1:0.5:0.3:0.2	No solution			0.0832	0.6083	1.2530	0.0638	0.2666
S:C:Cel = 1:1:1	0.0553	0.7970	16.07	0.1348	0.2974	0.5549	0.0834	0.5804
S:C:G = 1:1:1	No solution			0.0446	0.9028	0.0555	0.0725	0.5648
S:C:NaCl = 50:33:17	No solution			0.0556	1.2602	0.1110	0.0835	0.6248
S:C = 1:1	0.0703	0.7779	18.96	0.1753	0.2757	0.4788	0.1089	0.6405
S:C = 1:1	0.0747	0.7827	11.04	0.1846	0.2843	0.6525	0.1063	0.5335
S:C = 1:3	0.0654	0.8036	20.50	0.1587	0.3077	0.4903	0.1029	06190
S:C = 2:3	0.0686	0.7828	14.14	0.1614	0.3005	0.5631	0.1007	0.5805
S:C = 2:3	0.0693	0.8154	16.51	0.1637	0.3288	0.5281	0.1076	0.5932
S:C = 2:8	0.0662	0.8143	14.15	0.1498	0.3486	0.5359	0.1011	0.5749
S:C = 2:8	0.0621	0.8515	17.11	0.1403	0.3875	0.4903	0.1025	0.5810
S:C = 3:1	0.0844	0.7374	20.45	0.2180	0.2243	0.5390	0.1210	0.6250
S:C = 3:2	0.0707	0.7929	30.34	0.1747	0.2915	0.4295	0.1139	0.6589
S:C = 3:2	0.0744	0.7645	10.43	0.1734	0.2836	0.6521	0.1012	0.5306
S:C = 8:2	0.0808	0.7453	14.78	0.1985	0.2502	0.5882	0.1135	035769

Table 2 (Continued)

Product	Equation							
	GAB			Eq. (17)			Eq. (15)	
	u_m	k	c	F	G	H	A	b
S:C = 8:2	0.0793	0.7742	25.11	0.1986	0.2682	0.4726	0.1224	0.6459
S:C = 8:2	0.0725	0.7876	8.65	0.1686	0.2982	0.7029	0.0964	0.5074
S:Cel:G = 1:1:1	0.0217	0.9842	18.48	0.0379	0.7240	0.3072	0.0466	0.4632
S:Cel = 1:1	0.0525	0.7704	14.27	0.1297	0.2658	0.5956	0.0747	0.5762
S:Cel = 1:2	0.0397	0.8182	16.20	0.0949	0.3265	0.5418	0.0618	0.5643
S:Cel = 2:3	0.0425	0.7891	20.70	0.1094	0.2977	0.4974	0.0698	0.6088
S:Cel = 2:8	0.0319	0.8281	16.63	0.732	0.3585	0.5113	0.0507	0.5760
S:Cel = 3:2	0.0544	0.8481	16.96	0.1223	0.3892	0.4949	0.0890	0.5713
S:Cel = 8:2	0.0652	0.8234	19.83	0.1519	0.3475	0.4830	0.1047	0.5964
S:CA = 1:1	No solution			0.0444	1.1183	0.3103	0.0579	0.5776
S:G = 1:1	0.0329	0.9382	20.00	0.0544	0.6526	0.1937	0.0602	0.6170
S:Glut. acid = 4:1	0.0582	0.8422	38.71	0.1365	0.3645	0.3505	0.1034	0.6461
S:Nacl = 4:1	No solution			No solution			0.10165	0.5687

C – caseinate, CA – citric acid, Cel – cellulose, G – glucose, Glut. acid – glutamic acid, and S – potato starch.

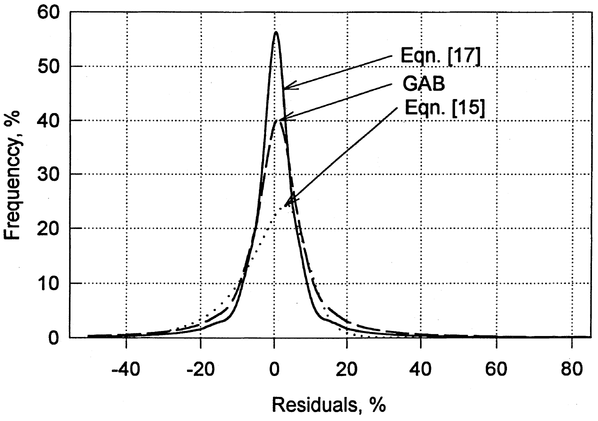

Fig. 2. Frequency of residuals for analysed equations.

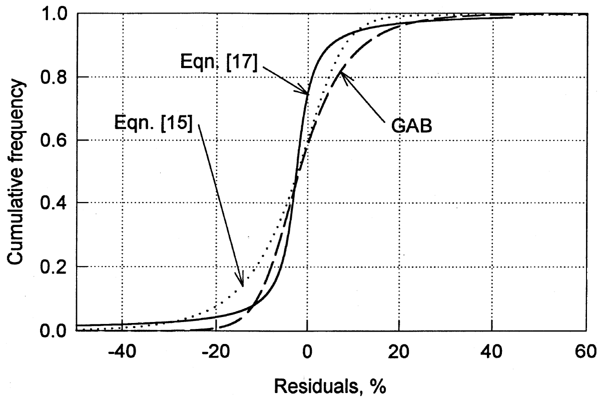

Fig. 3. Cumulative frequency of residuals for analysed equations.

Table 3
Frequency of residuals

Equation	Residuals (%)	Frequency (%)
Eq. (15)	3.02	24.2
Eq. (17)	0.33	56.3
GAB	0.90	40.2

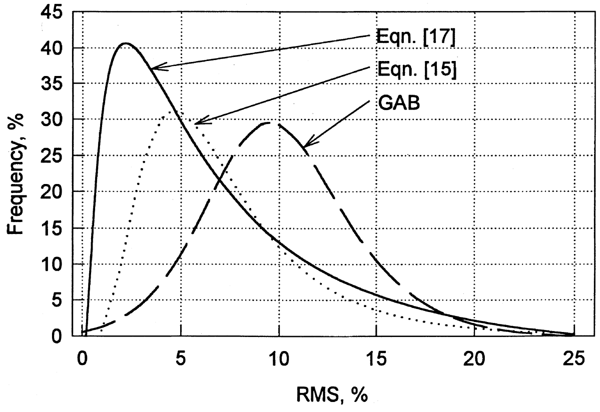

Fig. 4. Frequency of RMS for analysed equations.

4. Conclusions

Equation derived in this work and based on Raoult's law gives approximation of food water sorption isotherms much better than that offered by the GAB model. Moreover, it predicts infinite adsorption at $a_w = 1$, the property which is not offered by the GAB equation. The equation allows to predict water adsorption at a_w close to one, because a point $\alpha = 0$, $a_w = 1$ is included into calculations. This is a two-parameter equation and the error the parameters are loaded with affects estimated water content practically independently of water activity. As a two-parameter equation, the derived equation makes substantial improvement over the three-parameter GAB model.

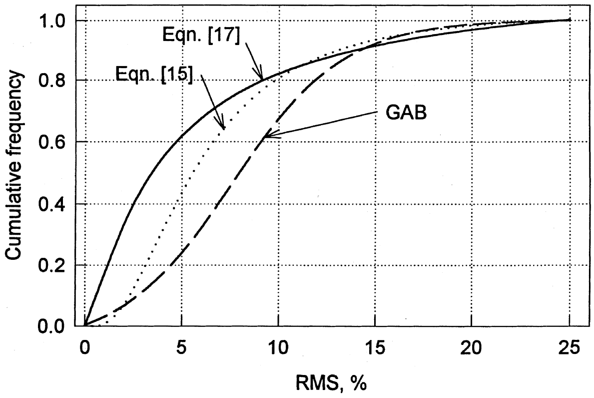

Fig. 5. Cumulative frequency of RMS for analysed equations.

Table 4
Probability to fit water sorption isotherm with assumed RMS

Equation	Probability (%)		
	$-2.5 \leqslant$ RMS $\leqslant 2.5$	$-5 \leqslant$ RMS $\leqslant 5$	$-10 \leqslant$ RMS $\leqslant 10$
Eq. (15)	12.4	43.9	80.8
Eq. (17)	40.4	62.1	82.3
GAB	8.9	24.2	67.6

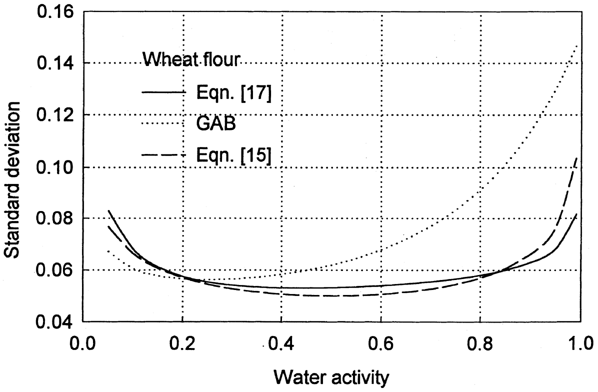

Fig. 6. Relationship between predicted water content and water activity for analysed equations. Parameters estimated with ± 5% error.

Appendix A

Considering the equation developed by Lewicki (1997b) the variance of u is equal to

$$v(u) = \left(\frac{\partial u}{\partial F}\right)^2 v(F) + \left(\frac{\partial u}{\partial G}\right)^2 v(G) + \left(\frac{\partial u}{\partial H}\right)^2 v(H),$$

where

$$\frac{\partial u}{\partial F} = \frac{1}{(1-a_\mathrm{w})^G} - \frac{1}{1+a_\mathrm{w}^H},$$

$$\frac{\partial u}{\partial G} = -\frac{F\ln(1-a_\mathrm{w})}{(1-a_\mathrm{w})^G},$$

$$\frac{\partial u}{\partial H} = \frac{Fa_\mathrm{w}^H \ln a_\mathrm{w}}{\left(1+a_\mathrm{w}^H\right)^2}.$$

For the GAB model the variance of u is given by

$$v(u) = \left(\frac{\partial u}{\partial u_\mathrm{m}}\right)^2 v(u_\mathrm{m}) + \left(\frac{\partial u}{\partial c}\right)^2 v(c) + \left(\frac{\partial u}{\partial k}\right)^2 v(k),$$

where

$$\frac{\partial u}{\partial u_\mathrm{m}} = \frac{cka_\mathrm{w}}{(1-ka_\mathrm{w})[1+(c-1)ka_\mathrm{w}]},$$

$$\frac{\partial u}{\partial c} = \frac{u_\mathrm{m}ka_\mathrm{w}}{[1+(c-1)ka_\mathrm{w}]^2},$$

$$\frac{\partial u}{\partial k} = \frac{u_\mathrm{m}a_\mathrm{w}}{(1-ka_\mathrm{w})^2} + \frac{u_\mathrm{m}(c-1)a_\mathrm{w}}{[1+(c-1)ka_\mathrm{w}]^2}.$$

For Eq. (15) developed in this work the variance of u is expressed by the following equation

$$v(u) = \left(\frac{\partial u}{\partial A}\right)^2 v(A) + \left(\frac{\partial u}{\partial b}\right)^2 v(b),$$

where

$$\frac{\partial u}{\partial A} = \left(\frac{1}{a_\mathrm{w}} - 1\right)^{b-1},$$

$$\frac{\partial u}{\partial b} = A\left(\frac{1}{a_\mathrm{w}} - 1\right)^{b-1} \ln\left(\frac{1}{a_\mathrm{w}} - 1\right).$$

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