Volume 122, February 2014

ISSN 0260-8774

ELSEVIER

journal of
food engineering

CrossMark

A BET approach to multilayer adsorption in swelling products

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ARTICLE INFO

ABSTRACT

An equation for multimolecular sorption is presented. It is based on the BET model with the assumption that the adsorbing surface can be divided in two regions:

A region that supports only a limited number of adsorbed layers due to geometric restrictions, and another region that can adsorb an unlimited number of layers. The proposed equation is applicable to type 2 and 3 isotherms (BDDT classification), and was successfully used to fit water sorption equilibrium data of some foodstuff from literature for the water activity range 0.05–0.90, and a temperature range from 10 to 70 °C.

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1. Introduction

Design and operation of many processes during the elaboration of food products, requires the evaluation of drying times, shelf life of packaged foodstuffs or water activity of mixed products such as dehydrated sausages, soups and juices. For these purposes it is necessary to know the equilibrium relationship between moisture content and water activity and its dependence on temperature. Foodstuffs usually present isotherms with a sigmoid-shaped behavior, characteristic of the multilayer adsorption.

The first successfully multilayer sorption equation, a generalization of Langmuiŕs theory, was developed by Brunauer et al. (1938), but its ability to fit experimental data is restricted to water activities from 0.05 to 0.35. This limitation was associated to the simplifying assumptions adopted during the development of the model (Pickett, 1945; Horiuti and Nakamura, 1967).

Pickett (1945) and Anderson (1946) developed new isotherm equations modifying some of the simplifying assumptions made by Brunauer et al. (1938). Anderson's equation, better known in the literature as GAB isotherm (van den Berg, 1981), was used to fit sorption isotherms up to water activities of 0.9 in some cases (Bizot, 1983; Lomauro et al., 1985), whereas Pickett equation was found valid for water activities lower than 0.8 (Kutarov and Robens, 2012).

To evaluate the adsorbent surface area in planar surfaces, the usual approach consists of assuming that the adsorbed molecules are flat (Pfeifer et al., 1989), but such assumption is not appropriate for rough surfaces. As it will be shown a better approach is obtained considering the molecules of adsorbate as spheres of given volume. Thus, the classical BET model is extended to rough surfaces, and the resulting isotherm used to evaluate the ability to fit equilibrium data for water sorption in foods.

It is well known that there are large differences in the values for surface area measured in food products using nitrogen and water as adsorbates (Labuza, 1968). Food–water sorption isotherms are Type II, typically associated to non porous adsorbents (Gregg and Sing, 1982), but the differences in surface area with nitrogen and water is usually interpreted as a proof of microporous structures and, in consequence, isotherms should be Type I (Hellman and Melvin, 1950; Andrieu and Stamatopoulos, 1986).

This contradiction must be avoided taking into account that polymeric food constituents, such as starches, and proteins suffer volume changes during loss or regain of moisture. Such volume changes can be associated to the collapse or creation of transient pore structures, sterically limited in absence of gelation, that modifies the accessible number of active sites (Aguerre et al., 1989a).

It is the purpose of the present work to extend the applicability of the BET model to higher values of water activity. An equation for multimolecular adsorption is presented based on the assumption

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that the development of the multilayer region must be geometrically restricted during the sorption. The ability of this equation to describe hygroscopic equilibrium data of several foods was evaluated.

1.1. Model developing

Brunauer et al. (1938) carried out an isotherm equation for multimolecular adsorption by extending Langmuir treatment of monomolecular adsorption with the aid of a few simplifying assumptions. These authors developed an equation (actually named BET equation) that was derived from a model of an adsorption surface divided into n segments, having 1, 2, 3, ..., i number of layers of adsorbed molecules. According to this model, condensation and evaporation occurs at the top of these surfaces, i.e. between the uncovered surface s_0 and the first layer, s_1:

$$a_1 \frac{P}{P^\dagger} s_0 = b_1 s_1 \exp\left(-\frac{E_1}{RT}\right) \tag{1a}$$

where a and b, are the condensation and evaporation coefficients, E is the heat of adsorption, R the gas constant, $P^\dagger$ is a pressure reference and T the temperature. Between any successive layers, the equilibrium can be expressed as:

$$a_i \frac{P}{P^\dagger} s_{i-1} = b_i s_i \exp\left(-\frac{E_i}{RT}\right) \tag{1b}$$

Being s_{i-1} and s_i the surfaces at the top of the respective $i-1$ and i layers. Considering that $\Delta S_i = R \ln(b_i/a_i)$ is the sorption entropy of the i-layer, Eq. (2) can be written in a more convenient form:

$$\frac{P}{P^\dagger} = \frac{b_i s_i}{a_i s_{i-1}} \exp\left(-\frac{E_i}{RT}\right) = \frac{s_i}{s_{i-1}} \exp\left(-\frac{\Delta G_i}{RT}\right) \tag{2}$$

where ΔG_i is the sorption free energy of the i-layer. Assuming that the free energy of sorption for the i-layer differs from the free energy of bulk water by a certain amount, it can be written in general that:

$$\Delta G_i = \Delta G_L + \Delta G_i^e \tag{3}$$

where ΔG_i^e differentiates the state of the adsorbed molecules from that of the molecules in pure liquid. Replacing Eq. (3) into Eq. (2), it results:

$$\frac{P}{P^\dagger} = \frac{s_i}{s_{i-1}} \exp\left(-\frac{\Delta G_L}{RT}\right) \exp\left(-\frac{\Delta G_i^e}{RT}\right) \tag{4}$$

and given that $P_0 = P^\dagger \exp(-\Delta G_L/RT)$, it results:

$$x = \frac{P}{P_0} = \frac{s_i}{s_{i-1}} \exp\left(-\frac{\Delta G_i^e}{RT}\right) \tag{5}$$

where a_w is the water activity. Hence, the fraction of surface occupied by 1st, 2nd, ..., ith layer follows the relation:

$$s_i = s_{i-1} x \exp\left(\frac{\Delta G_i^e}{RT}\right) = s_{i-1} x h_i \tag{6}$$

where $h_i = \exp(\Delta G_i^e/RT)$ and $h_1 = \exp(\Delta G_1/RT) = C$ is a constant of BET equation.

Then, from Eq. (6) it can be found:

$$s_i = s_{i-1} x h_i = s_{i-2} x^2 h_{i-1} h_i = \cdots = s_1 x^{i-1} \prod_{j=2}^{i} h_j = C s_0 x^i \prod_{j=2}^{i} h_j \tag{7}$$

he monolayer capacity, N_m, is:

$$N_m = \frac{1}{\sigma} \sum_{i=0}^{\infty} s_i = \frac{1}{\sigma}\left(s_0 + s_1 + \sum_{i=2}^{\infty} s_i\right) = \frac{s_0}{\sigma}\left(1 + Cx + \sum_{i=2}^{\infty} Cx^i \prod_{j=2}^{i} h_j\right) \tag{8}$$

where σ is the cross-section area of water molecule. Similarly the total number of molecules, N_k, that form a k adsorbed layer is:

$$N_k = \frac{1}{\sigma} \sum_{i=k}^{\infty} s_i = \frac{1}{\sigma}\left(\sum_{i=k}^{\infty} C s_0 x^i \prod_{j=2}^{i} h_j\right) \tag{9}$$

and the total number of molecules, N, that form the adsorbed film is:

$$N = \sum_{k=1}^{\infty} N_k = \frac{1}{\sigma} \sum_{k=1}^{\infty} \sum_{i=k}^{\infty} s_i$$
$$= \frac{C s_0}{\sigma}\left[x + \sum_{i=2}^{\infty} x^i \prod_{j=2}^{i} h_j + \sum_{k=2}^{\infty} \sum_{i=k}^{\infty} x^i \prod_{j=2}^{i} h_j\right] \tag{10}$$

Thus

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} x^i \prod_{j=2}^{i} h_j + \sum_{k=2}^{\infty} \sum_{i=k}^{\infty} x^i \prod_{j=2}^{i} h_j\right]}{1 + C\left(x + \sum_{i=2}^{\infty} x^i \prod_{j=2}^{i} h_j\right)} \tag{11}$$

Eq. (11) is therefore the isotherm equation for multilayer adsorption that takes into account the variation of the free energy of adsorption with successive layers. For $h_j = 1$ (free energy of the adsorbed multilayer equal to the free energy of bulk liquid water), Eq. (11) reduces to BET equation. Furthermore, if for the second and higher layers the free energy of the sorbed substance differs from that of pure liquid water in a constant amount ($h_j = k$), Eq. (11) reduces to GAB equation (Aguerre et al., 1989b).

In solids with a large specific surface area for sorption, there are extended structures of cracks and micropores that justify it. In these cases it is necessary to take into consideration geometric restrictions that limit the number of adsorbed layers supported, as the most relevant aspect.

Taking into account the BET assumptions, $h_j = 1$, and in addition assuming that the total surface area available for sorption is formed by two types of surfaces or regions: (a) a region representing a fraction, α, of the total adsorbing surface that only adsorbs a limited number of adsorbate layers, i.e. internal surface such as pores; (b) the remainder fraction, $1 - \alpha$, of the total adsorbing surface, where unlimited sorption may occur, i.e. external surface and macropores where large values of n are required to fill them. From Eq. (11) it can be written:

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} x^i + \sum_{k=2}^{n} \sum_{i=k}^{\infty} x^i\right]}{1 + C\left(x + \sum_{i=2}^{\infty} x^i\right)} + (1 - \alpha)$$
$$\times \frac{C\left[x + \sum_{i=2}^{\infty} x^i + \sum_{k=n+1}^{\infty} \sum_{i=k}^{\infty} x^i\right]}{1 + C\left(x + \sum_{i=2}^{\infty} x^i\right)} \tag{12}$$

whose solution is:

$$\frac{N}{N_m} = \frac{Cx(1 - \alpha x^n)}{(1 - x)(1 - x + Cx)} \tag{13}$$

where the parameters C, N_m, n and α can be obtained by non-linear regression analysis using the experimental values of equilibrium moisture content (N) versus water activity (a_w). Eq. (13) resembles the Pickett equation (1945) and reduces to it when $\alpha = 1$.

2. Results and discussion

The applicability and accuracy of the new isotherm was evaluated using experimental data of several materials obtained from the literature. The goodness of fit was evaluated using the mean relative percentage deviation modulus, $E\%$, defined as:

$$E\% = \frac{100}{p} \sum_{i=1}^{p} \frac{|N_i - N_{pi}|}{N_i} \tag{14}$$

Table 1
Estimated parameters of Eq. (13) fitted to experimental data of various materials.

Material	T (°C)	C	N_m (%, d.b.)	α	n	R^2	$E\%$ Eq. (14)	References
Champignon mushroom (*Agaricus bisporus*) (a)	30	2.42	20.28	0.8478	1.41	0.9999	0.19	Shivhare et al. (2004)
	40	2.36	18.52	0.8556	1.37	0.9971	1.49	
	50	2.61	15.59	0.8588	1.50	0.9975	1.91	
	60	1.79	17.80	0.9037	1.26	0.9985	1.78	
	70	1.64	15.68	0.8945	1.30	0.9981	2.71	
Pea, dried (s)	27	11.63	4.52	0.7181	6.38	0.9997	2.26	Kumar and Balasubrahmanyam (1986)
Cashew kernel (s)	27	47.98	2.01	0.8484	9.82	0.9933	6.28	
Field beans, split (s)	27	13.18	6.86	0.6213	1.18	0.9915	3.81	
Fried bengal gram (s)	27	13.72	4.14	0.9852	8.06	0.9942	5.86	
Green gram split (s)	27	42.07	6.13	0.7952	3.47	0.9976	2.59	
Kesari gram, split (s)	27	29.43	4.46	0.5124	2.49	0.9993	2.05	
Lentil, split (s)	27	18.42	7.21	0.7506	1.79	0.9989	1.67	
Pleorotus flabellatus (s)	27	9.68	5.41	0.4405	13.58	0.9979	4.78	
Pleorotus sajor-caju (s)	27	28.91	5.09	0.7805	5.75	0.9989	2.89	
Red gram split (s)	27	7.15	31.91	0.9168	0.16	0.9959	2.35	
Sesame, whole (s)	27	29.00	2.86	0.8956	3.13	0.9947	3.74	
Casein (a)	25	12.04	5.74	0.9864	3.72	0.9981	0.97	Bizot (1983)
Casein (d)	25	9.72	7.96	0.8923	2.34	0.9994	0.77	
Dextrin (a)	10	12.02	13.01	0.8752	0.99	0.9993	0.98	
Potato starch (a)	20	8.57	8.03	0.9230	3.47	0.9997	1.21	
Coffe (a)	20	2.21	3.23	0.8784	14.94	0.9999	3.62	
Cinnamon (a)	25	20.18	6.26	0.9999	3.63	0.9999	0.19	Wolf et al. (1973)
Cardamom (a)	25	25.30	6.02	0.6734	2.64	0.9997	0.67	
Lentils (a)	25	17.67	6.95	0.8701	3.63	0.9999	0.76	
Coriander (a)	25	10.95	5.87	0.7814	2.21	0.9998	0.84	
Nutmeg (a)	25	26.93	4.57	0.8170	2.82	0.9997	0.86	
Chamomile (a)	25	16.78	6.07	0.5010	4.67	0.9998	0.94	
Ginger (a)	25	15.23	7.30	0.8049	2.29	0.9992	1.11	
Anis (a)	25	15.03	4.32	0.9900	9.42	0.9997	1.15	
Horseradish (a)	25	17.02	6.80	0.6437	5.00	0.9998	1.31	
Thyme (a)	25	23.39	4.77	0.6729	4.43	0.9997	1.44	
Cheese, Emmenthal (a)	25	9.68	3.42	0.9604	13.25	0.9996	1.66	
Clove (a)	25	29.72	4.25	0.6638	3.08	0.9990	1.45	
Joghurt (a)	25	5.18	5.15	0.9421	19.53	0.9968	8.07	
Savory (a)	25	28.36	6.61	0.8497	3.44	0.9986	1.97	
Huhn (a)	45	6.89	5.39	0.9253	10.93	0.9998	1.99	
Laurel (a)	25	17.58	4.38	0.8125	5.95	0.9984	2.37	
Marjoram (a)	25	20.24	4.94	0.4006	2.91	0.9981	2.37	
Pears (a)	25	1.64	12.31	0.9200	7.96	0.9997	2.65	
Avocado (a)	25	10.55	3.52	0.9900	10.13	0.9991	3.43	
Celery (a)	25	5.39	7.06	0.8406	9.09	0.9996	3.43	
Pineapple (a)	25	0.46	26.24	0.9688	2.63	0.9998	3.95	
Eggplant (a)	25	6.56	7.76	0.4396	7.96	0.9991	4.00	
Forelle (a)	45	6.63	5.12	0.9185	12.79	0.9991	4.86	
Fennel (a)	25	0.33	70.06	0.9777	0.22	0.9979	7.60	
Banane (a)	25	0.41	18.65	0.6432	3.87	0.9975	9.06	
Radish (a)	25	1.86	10.71	0.9901	7.98	0.9957	13.20	
Mint (a)	25	12.69	7.42	0.6493	1.90	0.9998	0.88	
Para nut (a)	25	26.85	1.81	0.7100	4.10	0.9997	0.90	
Pekan nut (a)	25	13.60	1.95	0.9869	4.90	0.9996	1.38	
Rice, rough (d)	40	3.12	11.30	0.9148	1.45	0.9997	0.56	Iguaz and Vírseda (2007)
	50	2.60	11.02	0.9264	1.34	0.9986	1.68	
	60	1.94	11.20	0.9520	1.39	0.9980	1.67	
	70	1.56	11.72	0.9508	1.28	0.9978	2.10	
	80	1.40	10.94	0.9544	1.45	0.9988	2.17	
Meat, raw minced (s)	10	11.41	6.48	0.9807	10.71	0.9988	2.42	Motarjemi (1988)
	30	7.82	5.99	0.9711	10.20	0.9986	4.91	
	50	13.67	4.78	0.9746	12.80	0.9995	1.54	
Lard (s)	25	13.96	0.36	0.6626	4.10	0.9997	1.07	
Mullet roe, unsalted (a)	25	3.14	7.37	0.7957	0.65	0.9998	0.73	Chau et al. (1982)
Mullet, white muscle (a)	25	9.46	7.12	0.9681	4.86	0.9993	1.73	
Cod, unsalted (a)	25	13.02	7.78	0.6336	3.67	0.9953	4.79	Doe et al. (1982)

a: Adsorption, d: desorption, s: sorption.

where N_i and N_{pi} are the experimental and predicted moisture contents, respectively, and p the number of data. It is generally considered that $E\%$ values below 10% give a reasonable good fit for practical purposes (McLaughlin and Magee, 1998; Lopes Filho et al., 2002).

The results of the fitting procedure of the Eq. (13) to the experimental data of the equilibrium water content versus water activities are presented in Table 1, which shows the values of the fitting parameters calculated by non-linear regression. The adequacy of

Eq. (13) was evaluated by the determination coefficient (R^2) and the magnitude of the mean relative percentage deviation modulus that are also reported.

In Figs. 1 and 2 it can be seen the ability of the proposed equation to fit experimental water sorption data on some foodstuffs at different temperatures.

The n parameter resulted from the present analysis is lower than 5 for 70% of tested products, indicating therefore the
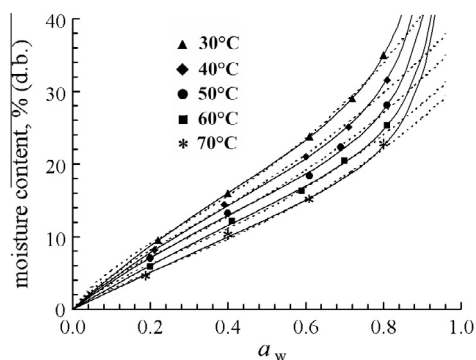
Fig. 1. Influence of temperature on adsorption isotherms of champignon mushroom (*Agaricus bisporus*). Solid line, Eq. (13); Dotted line, Pickett equation.
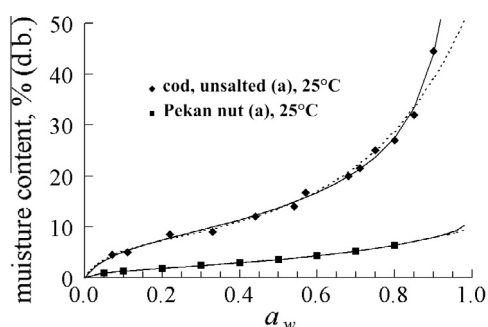

Fig. 2. Adsorption isotherms of cod and Pekan nut. Solid line, Eq. (13); Dotted line, Pickett equation.

complexity of the different adsorbents and the existence of a microporous structure, that involves the major part of the adsorbent surface (high α values).

The Pickett equation fitting is also plotted in Figs. 1 and 2, where it can be seen a worse adjustment with the experimental data at high water activities than the one obtained with Eq. (13). The Pickett assumption of limited sorption in the surface of the adsorbent is responsible for the observed lack of fitting at high water activities.

3. Conclusions

A sorption isotherm was derived assuming the development of a pore structure during sorption that provokes geometric restrictions. It was found that the assumption of only two different regions of sorption, although arbitrary, leads to simple isotherm equation. Eq. (13) can be useful for describing the water sorption in foods, given that it predicts infinite sorption at $x = 1$ for $\alpha < 1$; most food products have isotherms given by Eq. (13); two of the equation parameters have the same meaning as in the BET model.

Fruit, milk products, starchy-foods, proteins, meat, spices, nuts and oilseeds and some vegetables were modelled by Eq. (13), covering a range of a_w from 0.03 to 0.90, approximately; The ability of Eq. (13) to correlate a great variety of food materials is related with the tendency of most foods to present lower sorption capacity than the one predicted from BET theory, for high water activity.

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