

An Equation for Fitting Moisture Sorption Isotherms of Food Proteins

B. Ali Asbi and Ion C. Baianu*¹

A simple four-parameter equation was proposed that could be used to predict the sorption isotherm of water in food protein systems. Analysis of 15 sets of food protein data was fitted with this equation, and the results showed very good agreement between predicted and observed values within the a_w range from 0.05 to 0.9. The application of this new model in describing moisture sorption isotherms of type II in the BET classification was shown to be an improvement compared with other two-parameter equations reported in the literature.

INTRODUCTION

A food moisture sorption isotherm describes the relationship between the moisture content in food and the relative humidity of the air with which the food is in equilibrium at constant temperatures and pressures. The so-called water activity, a_w , which is defined thermodynamically as

$$a_w = p/p^0 \quad (1)$$

where p and p^0 are the water vapor pressures in the food and that of the pure water, respectively, is related to the equilibrium relative humidity (ERH) by

$$\text{ERH} = 100a_w \quad (2)$$

A plot of moisture content of foods (on a dry basis) against a_w is, therefore, a typical and practical procedure for pictorially representing the sorption isotherms.

The knowledge of moisture sorption isotherms, usually in graphical form, has found applications in two major areas in food technology: First, microbial growth, enzymatic reactions, nonenzymatic browning, and lipid oxidations are some of the deteriorative mechanisms that are known to be dependent on water activity (Scott, 1957; Acker, 1969; Rockland and Nishi, 1980). These undesirable reactions would therefore be more rapid away from the optimum moisture content of the food required for storage stability of dehydrated and intermediate moisture foods (as well as for packaging requirements and design).

The second major application of moisture sorption isotherms is in food engineering in which the accurate computation of equilibrium moisture content values permits the process of optimization of drying as a food unit operation, namely the calculations of drying times and efficiency in energy utilization (Bruin and Luyben, 1980).

Because of the importance of water activity, the accurate prediction of sorption isotherms in food systems has always been actively investigated by food scientists, chemists, and physicists. Recently, Van der Berg and Bruin (1981) reviewed more than 70 model equations that have been proposed in the literature to mathematically describe the sorption isotherms found in foods, macromolecules, polymers, etc. These are equations that have been derived either from first principles of thermodynamics or statistical mechanics or have been based entirely on empirical and semiempirical considerations. While there are equations that have proved to be relatively successful, many of the others adequately describe only parts of the sorption iso-

therms. The more successful models have the main disadvantage of having to rely on optimization techniques that are usually computer-assisted evaluations of the parameters (e.g., D'Arcy and Watt, 1970).

It is the objective of this paper to propose a model equation that has the characteristics of being both simple and practical, i.e. has the main advantage of not requiring any computer assistance, and at the same time remains accurate in the prediction over a wide range of a_w values. It is also very desirable that the new model would exhibit a better performance than other equally simple equations that have so far been employed in the literature for the description of water sorption behavior in foods.

METHODS OF ANALYSIS

The shape of a typical food sorption isotherm is generally sigmoidal or of type II in the BET classification (Brunauer, 1945). It has been shown to be possible, therefore, to divide the sorption isotherm curve into three regions that may correspond to the relative binding state of water in foods (Van den Berg and Bruin, 1981). An equation to describe the moisture content in these three regions will thus be

$$n = n_I + n_{II} + n_{III} \quad (3)$$

where n is the moisture content in grams/100 g of solids and the subscripts I-III represent the three different parts of the sorption curve, respectively.

The first and second regions of the sorption isotherm have been described respectively as strongly bound water and weakly bound water, and thus it is not surprising that adsorption theories borrowed from surface chemistry have been applied quite extensively and successfully in these regions. The classical example is the so-called BET equation (Brunauer et al., 1938), but such adsorption models will satisfactorily predict sorption isotherms only up to an a_w of about 0.5.

To keep our model simple we approximate the sorption characteristics of water in the first and second regions by

$$n = n_I + Ca_w \quad (4)$$

where n_I and C are constants. This is a linear relationship, and thus we will not expect it to accurately describe the moisture content of foods at very low a_w values. This is acceptable since for most practical purposes the range of $0 < a_w < 0.1$ is usually of little significance to the food scientist.

In the third part of the sorption isotherm, water behaves more or less like free water in bulk solution, and therefore several model equations had been based on solution theories to evaluate the sorption isotherm in this region. In a nonideal solution, our proposed model to describe this third part of the sorption behavior is as follows:

$$n = Aa_w^B \quad (5)$$

Department of Food Science, University of Illinois, Urbana-Champaign, Illinois 61801.

¹Present address: Physical Chemistry & NMR Laboratories, 567 Bevier Hall, 905 S. Goodwin Ave., University of Illinois, Urbana, IL 61801.

Table I. Values of Parameters of the Equation (6) for Various Food Proteins (25 °C) Based on the Adsorption Data of Bull (1944)

proteins	parameters			
	n_I	C	A	B
collagen	4.736	26.200	25.452	7.316
gelatin	4.129	24.051	53.525	12.423
egg albumin				
lyophilized	1.987	16.650	22.042	8.884
unlyophilized	2.276	17.440	24.871	9.758
coagulated	1.990	14.350	12.720	6.635
β -lactoglobulin				
lyophilized	1.540	18.714	30.190	10.468
crystallized	1.672	19.691	35.837	10.527
serum albumin	2.510	18.570	28.040	10.190
pseudoglobulin ^a				
γ	2.570	20.122	34.701	10.891
α and β	2.788	19.949	33.292	10.744
C zein	1.560	10.280	10.372	5.660
B zein	1.685	10.351	9.295	6.810
salmin	3.813	14.241	53.070	3.646
elastin	3.198	13.902	6.863	2.278
lysozyme ^b	1.6	17.6	15.3	9.837

^aPseudoglobulins are impure globulin proteins, and C and B zein are zein protein fractions, the preparation of which is described by Bull (1944). ^bData of Lioutas et al. (1986).

The derivation of the power law equation (5) is based on the observation that in the range of high a_w the hydration of proteins has an exponential dependence on a_w due to the ability of each water molecule to form hydrogen bonds with up to four neighboring water molecules. This proposition will therefore lead to the following general equation to account for the overall moisture sorption isotherm curve:

$$n = n_I + Ca_w + Aa_w^B \quad (6)$$

In our study on food proteins we have made use of the adsorption data published by Bull (1944) because it is still one of the most complete sets of tabulated data for proteins available in the literature. The fitting performance of our equation to these data is compared with those in the literature (Iglesias and Chirife, 1982). The equations that describe best the sorption isotherms of the proteins were selected so that they are also in a simple form; thus, we considered three two-parameter equations (k_1 and k_2 are constants). Bradley's equation (Bradley, 1936):

$$\ln(1/a_w) = k_1 k_2^n \quad (7)$$

Henderson's equation (Henderson, 1952):

$$n = [k_1 \ln(1 - a_w)]^{k_2} \quad (8)$$

Oswin's equation (Oswin, 1946):

$$n = k_1 [a_w / (1 - a_w)]^{k_2} \quad (9)$$

RESULTS AND DISCUSSION

In order to utilize the proposed new equation, the following procedure is observed. To determine the four constant parameters in eq 6, two graphical plots are required. For $n \ll n_{III}$, eq 6 is reduced to the linear form as in eq 4, and thus a plot of n against a_w , which is the actual sorption isotherm itself, should give an intercept equal to n_I and a slope equal to C .

With the first two parameters known, it becomes possible to evaluate A and B simply by rearranging (6):

$$\ln[n - n_I - Ca_w] = \ln n_{III} \quad (10)$$

$$= \ln A + B \ln a_w \quad (11)$$

A graphical plot of $\ln n_{III}$ against $\ln a_w$ would therefore give the slope as B and the intercept as $\ln A$.

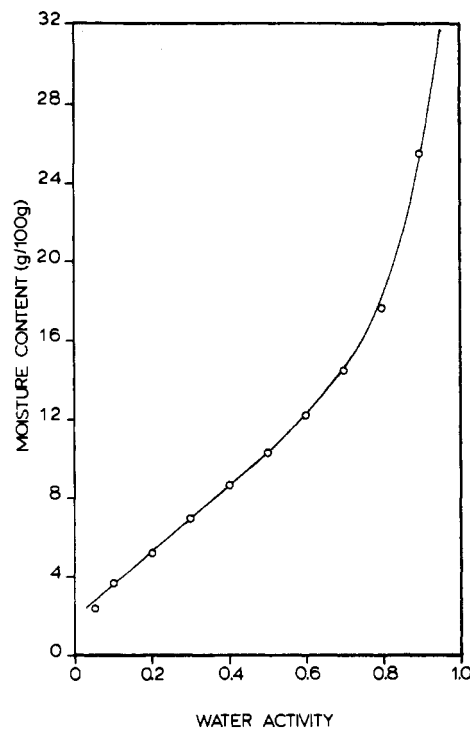


Figure 1. Moisture sorption isotherm of lyophilized egg albumin at 25 °C from data of Bull (1944). Observed values (O) vs. calculated values (—) obtained from eq 6.

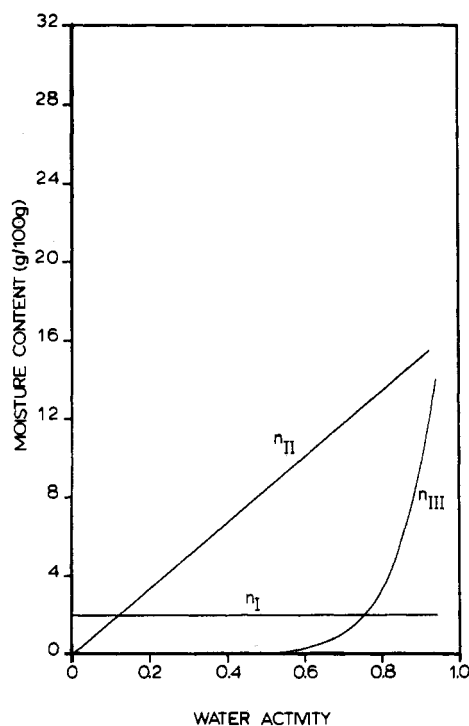


Figure 2. Components of eq 6 that describe the sorption isotherm for the lyophilized egg albumin system at 25 °C.

We carried out an application of this model to the adsorption data of various food proteins as compiled by Bull (1944), and the results of the analysis are shown in Table I. A plot for a selected protein is depicted in Figure 1, which illustrates very reasonable agreement between the calculated and observed values. In Figure 2 the components of the three portions of the isotherm equation are shown.

In order to evaluate the goodness of fit of the model as applied to the experimental sorption data, a mean relative percentage deviation modulus E_{av} (%) was used, which is

Table II. Comparison of Goodness of Fit for Different Models in the Prediction of Sorption Isotherms of Food Proteins at 25 °C Based on the Adsorption Data of Bull (1944)

proteins	eq 6		other eq ^a		
	a_w range	E , %	eq	a_w range	E , %
collagen	0.10–0.90	0.78	Oswin	0.1–0.8	1.30
gelatin	0.05–0.95	1.25	Oswin	0.1–0.8	1.92
egg albumin					
lyophilized	0.05–0.95	2.39	Oswin	0.1–0.8	3.17
unlyophilized	0.10–0.95	1.39	Henderson	0.1–0.8	2.58
coagulated	0.10–0.90	1.42	Bradley	0.1–0.8	2.82
β -lactoglobulin					
lyophilized	0.10–0.90	1.75	Henderson	0.1–0.8	1.95
crystallized	0.05–0.95	2.81	Henderson	0.1–0.8	3.15
serum albumin	0.10–0.95	1.59	Oswin	0.1–0.8	1.36
pseudoglobulin					
γ	0.05–0.95	2.44	Henderson	0.1–0.8	2.76
α and β	0.10–0.95	1.19	Henderson	0.1–0.8	2.54
C zein	0.10–0.90	2.02	na ^c		
B zein	0.10–0.90	2.76	na ^c		
salmin	0.05–0.80	2.74	d		
elastin	0.05–0.80	3.94	d		
lysozyme ^b	0.0–0.95	1.67	na ^c		

^aIglesias and Chirife (1982). ^bData of Lioutas et al. (1986). ^cna = not available. ^dNot fully satisfied by any two-parameter equation.

an average of the relative percent difference between the calculated and observed values. The modulus is defined as

$$E_{av} (\%) = 100[(n_c - n_o)/n_o]/N \quad (12)$$

where n_c and n_o are, respectively, the calculated and observed values and N is the number of data points. This statistical evaluation is an indication of the overall degree of success of the model equation in fitting the experimental data points (Iglesias and Chirife, 1982).

A comparison is also made between the new model proposed and those sorption isotherm models found in the literature. We have restricted our study to two-parameter equations for reasons which have been discussed previously. Iglesias and Chirife (1982) recently compiled and determined the model equations that describe the food proteins selected in this study. In Table II we have compared the performance of such models in fitting the experimental sorption isotherm data.

CONCLUSION

From Table II it is obvious that the new model proposed (eq 6) has a better overall performance than the other model equations (Bradley, Oswin, Henderson). Statistically the mean percentage deviation is lower for the predicted values computed by eq 6 than those calculated by the other models. In addition, the new proposed eq 6 shows a remarkably high degree of accuracy since it covers a much wider range of a_w values, in certain cases even from as low as 0.05 up to as high as $0.95a_w$.

It is also noteworthy that no accurate mathematical description of the isotherm could be found for salmin and elastin as examined by Iglesias and Chirife (1982), who

investigated several two-parameter equations including those mentioned in this paper. Bull (1944) reported that even the simple BET theory deviated strikingly for the salmin data. Our new proposed model, however, appears to work reasonably well although the range of the fit is less wide than for the other proteins, but the mean percentage deviation still remains acceptable. The fitting data for the zein proteins by other two-parameter equations were not available, however, and so no comparison could be made with the proposed model. However, it is obvious that the new equation (6) shows reasonable agreement in its prediction for the sorption properties of the zeins.

The analysis carried out above has shown the excellent potential of the application of eq 6 in accurately describing water sorption behavior of foodstuffs. Although the main group of food components studied was proteins, it is very likely that a similar high agreement between predicted and observed data would be found for other food groups, especially if the sorption curves are sigmoidal in shape and have a very narrow n_1 region.

In summary, the primary steps in the application of the new proposed model involve a simple graphical procedure in which two plots are made to evaluate the four parameters. The main advantages of this procedure over other two-parameter sorption isotherm equations are its simplicity and accuracy over a wide range of a_w values. For these reasons, the application of such a model would be quite attractive in the food processing industry.

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