Modified BET Models for Modeling Water Vapor Sorption in Hydrophilic Glassy Polymers and Systems Deviating Strongly from Ideality

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ABSTRACT: The use of two modified BET models for modeling water vapor sorption in various nonideal systems involving strong interactions (textiles, polyamides, polyimide, vinyl polymers, proteins, and related compounds) has been investigated. Contrary to the original BET model derived for multimolecular adsorption and restricted to low water activities only, the three-parameter BET model, which considers sorption on a limited number of sorption layers, allowed the modeling for activities up to 0.9. This model has been shown to be an important extension of the original model but remains limited, due to the divergence of the model for $a \rightarrow 1$. Releasing an other important assumption of the BET model, the GAB model was then investigated and its striking efficiency, in terms of high correlation coefficients and low residual sums of squares, was demonstrated for activities up to 0.95, thus covering all the usual experimental range. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 1415–1430, 1998

Key words: sorption; BET model; GAB model; modeling

INTRODUCTION

Water sorption in polymers is an important factor for many practical applications, because the extent of sorption often determines the polymer properties in working environments. For instance, high water sorption has been related to the degradation of material mechanical strength[1] or the instability of food products.[2] It is also well known that water sorption plays a significant role in the properties of polyimides or thermostable materials used in the microelectronics industry.[3] In addition, the understanding of water sorption isotherms is still a key factor for membrane sys-

tems design including, but not restricted to, food packaging[4] or membrane separation processes.[5] Last, but not least, it also plays a crucial role in biological systems.

Involving strong interactions between penetrant molecules and polymer materials, water sorption in hydrophilic glassy polymers is usually a strongly nonideal process leading to particularly complex isotherms, i.e., sigmoid isotherms also called type II isotherms in reference to the BET classification.[6] Unfortunately, the dual sorption theory,[7] which is one of the most effective theories for describing gas/vapor sorption and permeation in glassy polymers, cannot describe type II isotherms.

According to the original dual sorption theory, the sorption process is considered to follow a dual mode involving vapor dissolution (D) described by Henry's law and vapor adsorption (A) on specific sites (microvoids or holes in the glassy polymer structure). Describing the adsorption process

by Langmuir's theory, the following isotherm can be derived:

$$C = C_D + C_A = k_D p + \frac{C_H' b p}{1 + b p} \qquad (1)$$

The model accounts for isotherms having linear plots at low and high vapor activities, but is incompatible with the inflexion point shown by type II isotherms. Modifications of the original dual sorption theory have attempted to improve its efficiency, especially in the case of water sorption in hydrophilic glassy polymers. Reconsidering the analysis of water transfer in polyacrylonitrile (PAN), Mauze and Stern derived a modified model taking into account the positive deviation from Henry's law at low activities[8]:

$$C = C_D + C_A = [k_D \exp(\sigma C)] p + \frac{C_H' b p}{1 + b p} \quad (2)$$

This four-parameter model allowed the description of the sorption isotherms of water vapor in polyacrylonitrile at different temperatures over the entire activity range. It thus marked a significant improvement compared to the original dual sorption theory whose applicability range was restricted to very low activities only. More recently, Hernandez et al.[9] proposed the dissolution process be described by the Flory–Huggins theory yielding an isotherm equation nonexplicit in C:

$$C = C_D + C_A = \text{FH}(p, \chi) + \frac{C_H' b p}{1 + b p} \qquad (3)$$

with $\text{FH}(p, \chi)$ corresponding to the fraction dissolved according to the Flory–Huggins theory and thus obeying the classic equation:

$$
\begin{aligned}
\ln a &= \ln p/p_o \\
&= \ln C_D + (1 - C_D) + \chi(1 - C_D)^2 \quad (4)
\end{aligned}
$$

This approach remains subject to criticism especially because, according to Flory,[10] the Flory–Huggins theory has been proven to apply well to apolar systems but usually fails for polar systems displaying strong specific interactions. However, the model derived by Hernandez[11] enabled the description, by three parameters only, of water sorption in a polyamide, i.e., the modeling of a type II isotherm corresponding to a system strongly deviating from ideality. Unfortunately, both previous approaches require rather complex numerical analysis involving the mathematical treatment of nonexplicit equations.

More usually, most of the authors dealing with isotherms related to water vapor sorption in hydrophilic glassy polymers have considered the classic Brunauer–Emmett–Teller (BET) model, initially derived to account for adsorption phenomena by a unified theory describing the five isotherms of the BET classification.[6,12] This very simple approach of complex dissolution processes in polymer systems surprisingly performs very efficiently for describing water vapor sorption at low activities. Unfortunately, the classic BET model fails for higher water activities ($a > 0.5$),[13,14] leading most authors to account for water sorption at high activities by another theory like the clustering analysis derived by Zimm[15] and Lundberg.[16]

Extending the first approach by the classic BET model, the present work analyses the ability of two modified BET equations to account for water sorption in various hydrophilic polymers and also in molecules of biological interest. Because they were initially derived for describing adsorption phenomena and are rarely applied to vapor sorption in polymer materials, these three-parameter models will be briefly reviewed.

The two modified BET models will then be critically assessed for describing water vapor dissolution in complex media, and it will be shown that only slight modifications of the classic BET model can lead to very significant improvements for modeling water vapor sorption over all the activity range.

We believe these quite simple modified BET models are of both fundamental and practical interest and can thus be considered as good alternatives to more complex recent approaches like modified dual sorption theories.

THEORETICAL BACKGROUND

Derived by simple extension and generalization of Langmuir's theory of unimolecular adsorption, the classic BET equation[12] is a two-parameter model assuming the condensation of an infinite number of layers from the vapor phase onto the adsorbent surface:

$$C = \frac{a c_p x}{(1 - x)(1 - x + c_p x)} \qquad (5)$$

where $x = p/p_o$ according to the limit conditions imposed by the different assumptions of the model. Among these, two are of particular importance: (1) the number of adsorbed layers is assumed to be infinite; (2) the condensation–evaporation properties of the molecules in the second and higher layers are the same as those of the liquid state ($E_2 = E_3 = \cdots = E_L$).

The above equation can be linearized to lead to a particularly convenient form for testing purposes:

$$\frac{p}{C(p_o - p)} = \frac{1}{ac_p} + \frac{c_p - 1}{ac_p}\frac{p}{p_o} \qquad (6)$$

Accordingly, if the theory is obeyed, a plot of $p/C(p - p_o)$ vs. p/po gives a straight line whose intercept and slope are $1/ac_p$ and $(c_p - 1)/ac_p$, respectively, yielding the values of the parameters of the BET model.

In their original publication[12] Brunauer, Emmett, and Teller also derived a modified model by releasing the first assumption of their classic model and considering a limited number n of adsorbed layers. As expected, the corresponding model yields a three-parameter equation:

$$C = \frac{ac_p x}{(1 - x)}\frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c_p - 1)x - c_p x^{n+1}} \qquad (7)$$

Due to its simplicity, the classic BET equation (two parameters) has been extensively used for modeling water sorption in hydrophilic glassy polymers, and is considered to give good agreement with experimental values for low water activities (i.e., activities between 0 and $0.5^{13,14}$). Small deviations have been reported for very low activities of 0–0.05, but it is difficult to ascribe the problem specifically to any of the different causes of errors that can be related to such low activities.

However, and most probably because it requires a nonlinear mathematical treatment, the use of the modified BET equation (three parameters) for modeling water sorption in hydrophilic polymers has very rarely been reported in the literature.[17] Another interesting and much more complex approach of multimolecular adsorption was reported by Hill a few years later.[18] Derived from statistical mechanics, it quite surprisingly led to the same set of equations (i.e., the BET equations, two and three parameters).

The release of the second assumption mentioned previously was then discussed by Anderson,[19] de Boer,[20] and Guggenheim,[21] and led to the Guggenheim–Anderson–de Boer (GAB) equation:

$$C = \frac{a_{\text{GAB}}c_{p,\text{GAB}}kx}{(1 - kx)}\frac{1}{1 + (c_{p,\text{GAB}} - 1)kx} \qquad (8)$$

with k being less than 1, assuming the heat of adsorption to be less than the corresponding heat of condensation. Despite having appeared in an article published in 1946, the GAB equation has only rarely been used for modeling water sorption in synthetic or natural polymers. Its use is, for instance, not reported in the famous chapter by Barrie[14] on water in polymers, and the same also holds for the review by Mc Laren and Rowen.[13] Quite recently, however, it has been widely applied to describe water sorption in foods[22] and related natural polymers.[2,23,24] In this article, we show that the GAB equation is very effective for correlating nonideal water sorption in glassy polymers and other materials over the entire activity range, which is not the case for the classic BET model.

METHODS AND PROCEDURES

The sorption data used hereafter were calculated whenever possible from the corresponding values reported in the literature, or obtained from extended sorption isotherm curves when no data tables were available. Even if such values are less accurate than those obtained from direct measurements, they lead to unequivocal results. When the polymer density was available in the reference article, the sorption ratio was calculated as a weight percentage of adsorbed water related to the dry polymer weight, which remains one of the most common ways to define a polymer swelling. However, the lack of polymer densities in the reference publications is quite common. In those cases, the sorption data are reported in units compatible with the reference article (i.e., $\text{cm}^3\,(\text{STP})/\text{cm}^3$ dry polymer or mol % related to the number of moles of accessible amide groups in polyamides). Even if the densities of some polymers have been reported elsewhere,[25] they may not correspond to the samples investigated being dependent on the material history of glassy polymers and especially of glassy semicrystalline polymers. Consequently, the units of the different sorption data used for the present work have not been standardized. The

units describing the different model parameters a and a_{GAB} vary accordingly, and are given in all the tables summarizing the modeling results.

Most of the isotherms reported in the literature have been expressed in terms of pressure and not relative humidity (RH) $x = p/p_o$. The water saturation vapor pressure required for the calculation of RH has been estimated from the corresponding Antoine's relationship using the three parameters reported by Reid et al.[26]

A nonlinear multiparameter regression of experimental data has been performed with a common algorithm based on the Newton–Raphson method. The curve-fitting efficiency has been estimated from the classical correlation coefficient R as well as from the residual sum of squares RSS defined by:

$$\text{RSS} = \sum (y_{\text{exp}} - y_{\text{calc}})^2 \qquad (9)$$

where y_{exp} and y_{calc} are the reported experimental value and the corresponding calculated value, respectively. The RSS values obtained from the regression of a given set of experimental data by different models allow a direct and statistically significant[27] comparison of the respective model efficiencies and have, therefore, been reported in all the tables summarizing the results obtained by the different fittings.

RESULTS AND DISCUSSION

In this section we report and analyze the results obtained by considering more than 40 type II isotherms involving the sorption of water vapor in various synthetic and natural polymers and biomolecules (proteins).

Modified BET Model (Three Parameter BET Model)

Estimation of the Model Parameters

Two different methods have been reported for the estimation of the parameters of the modified BET model.

The first one is due to Brunauer and has been extensively described in his reference book on adsorption phenomena.[6] It consists of assessing the values of the first two parameters a and c_p by linearizing the classical BET equation (two parameters) for the low vapor activities, typically $a < 0.5$ [cf. eq. (6)]. The last parameter, n, is then calculated by nonlinear fitting of the sorption iso-

therm over all the activity range. It must be emphasized that, in this procedure, n is the only parameter to be optimized by nonlinear regression, a and c_p remaining constant and equal to the values obtained by the linearization procedure of the classical equation at low activities.

The second method considers the three parameters of the modified BET model as fitting parameters and yields a nonlinear multiparameter regression. Consequently, it does not involve the use of the two-parameter BET model at low activities, except for obtaining *initial* values for the two parameters a and c_p, allowing a faster convergence of the numerical computing.

Both procedures have first been tested using sorption data for the PAN/H_2O system at different temperatures in the range 20–50°C, as reported by Stannett et al.[28] (Table I). Although both methods are efficient for modeling the isotherm at 50°C (i.e., the only one of all the sorption isotherms investigated in this work, considering activities below 0.65 only), the isotherms corresponding to the lower temperatures cannot be described accurately by the three parameters obtained by the first method. As an example, Figure 1 shows the systematic deviation occurring for almost all the activity range at 30°C; the same trend could also be observed for the other isotherms fitted according to the method reported by Brunauer.

The nonlinear multiparameter regression (method 2), however, allows a quite accurate description of the same isotherm at 30°C (cf. Fig. 1) as well as the other curves corresponding to the other temperatures. As a result, the *total* residual sum of squares values obtained by the multiparameter regression is only 15% of the error corresponding to the first method using n as the only fitting parameter.

Consequently, the nonlinear *multiparameter* regression will be the only method used for the data treatment of all the other isotherms investigated.

Concerning the evaluation of the three-parameter BET model, a final point should be emphasized. The use of sorption data for activities above 0.9 usually leads to a great error of the curve fitting and/or divergence of the numerical resolution. The problem can most probably be ascribed to the divergence of the function $1/(1 - x)$ when the activity tends towards 1 (sorption of liquid water).

Water Vapor Sorption in Natural or Synthetic Polymers

Water sorption in textile fibers is one of the important characteristics of those materials because

Table I   Sorption Isotherms for the System H₂O/PAN at Different Temperatures: Determination of the Parameters of the Modified BET Model

T (°C)	FAR	c_p (adim.)	a (cm³/cm³)	n (adim.)	R	RSS
20	0–0.916	18.26[a]	8.81[a]	9.19[a]	0.9972[a]	5.231[a]
		31.07[b]	7.96[b]	10.53[b]	0.9999[b]	2.093[b]
30	0–0.948	10.05[a]	7.10[a]	16.24[a]	0.9940[a]	22.903[a]
		13.69[b]	8.13[b]	13.59[b]	0.9996[b]	1.575[b]
40	0–0.855	9.61[a]	6.46[a]	14.78[a]	0.9780[a]	36.607[a]
		14.70[b]	7.56[b]	10.39[b]	0.9967[b]	5.519[b]
50	0–0.627	7.67[a]	9.32[a]	9.13[a]	0.9991[a]	0.853[a]
		6.84[b]	9.65[b]	7.89[b]	0.9993[b]	0.684[b]

FAR, fitting activity range.

[a] n has been used as the only fitting parameter according to the method proposed by S. Brunauer[6] (cf. text). Σ RSS a = 65.59.

[b] c_p, a and n have been used as fitting parameters of the nonlinear *multiparameter* regression. Σ RSS b = 9.87 (15% of the Σ RSS a value).

it determines to a great extent the comfort of textiles. For instance, natural textile fibers like wool, silk, or cotton, usually considered as the most comfortable materials, are quite hydrophilic materials compared to most of the synthetic fibers. In Figure 2(a), the sorption isotherms of water vapor in unstretched nylon, silk and wool are given from the data reported by Bull[29] at 25°C. The three-parameter BET model gives quite a good agreement with the experimental data, as shown by the fitting curves in Figure 2 as well as by the correlation coefficients and residual sum of
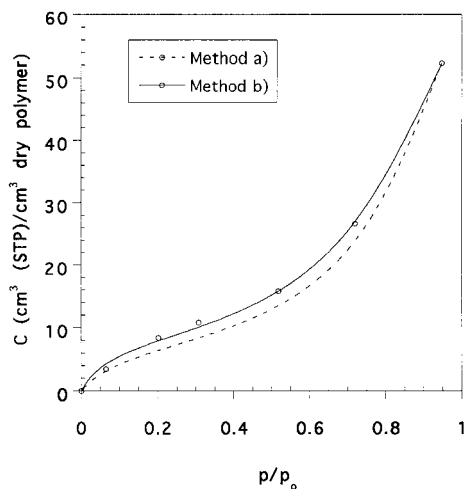

Figure 1   Sorption isotherm for the system H₂O/PAN at 30°C. Modeling by the three-parameter BET model. Method a: n is the only nonlinear fitting parameter according to the method proposed by Brunauer[6] (cf. text). Method b: a, c_p, and n have been used as fitting parameters of the nonlinear *multiparameter* regression (data calculated from Stannett et al.[28]).

squares values reported in Table II. The same also holds for the isotherms curves obtained at 40°C with the same materials. In Figure 2(b), the analysis of the sorption data reported by Rowen and Blaine[30] for three other textile fibers (cellulose acetate, cotton, and viscose) at 25°C shows a very good agreement between experimental and calculated values for cellulose acetate and cotton, whereas a slight deviation occurs for viscose, the correlation coefficient for the last textile remaining, however, quite high (0.9960).

For all the isotherms related to water vapor sorption in textile fibers, the correlation coefficients and the residual sum of squares values show the acceptable efficiency of the three-parameter BET model for accounting for sorption in systems strongly deviating from ideality.

The use of the modified BET model can thus be considered as an interesting extension to the analysis reported by Bull[29] and Rowen and Blaine[30] using the classical BET model limited to the low activity range.

Similarly, the water vapor sorption isotherms in different polyamides (nylons 2, 3, 6, 7, 8, and 11) reported by Puffr and Sebenda[31] can also be described by the modified BET model for activities up to 0.9, as clearly shown by the results reported in Table III. The correlation coefficients are in the very high range ($R > 0.9970$), and the errors are quite low even in the case of nylon 8 where a slight deviation occurs for most of the activity range. Table III also shows the results for regenerated cellulose and yields the same conclusions from data reported by Newns.[32]

Water sorption in thermostable polyimides can dramatically affect their mechanical and electri-
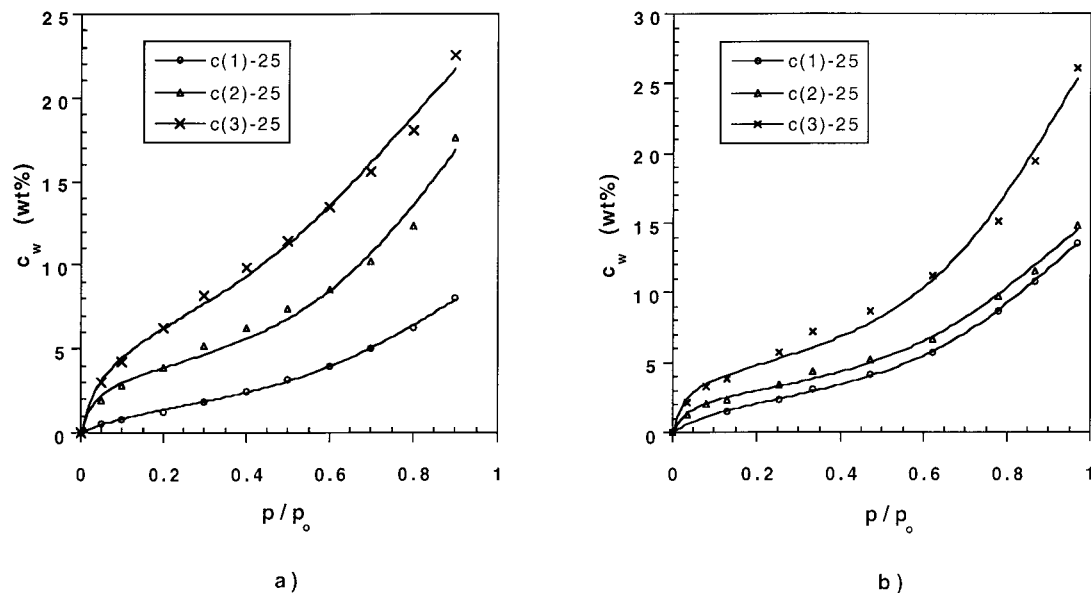
Figure 2 Sorption of water vapor in textiles at 25°C. (a) 1 = unstretched nylon, 2 = silk, 3 = wood (data from Bull[29]); (b) 1 = cellulose acetate, 2 = cotton, 3 = viscose (data from Rowen and Blaine[30]). The curves are the results of the sorption modeling by the three-parameter BET model.

cal properties. The aromatic polyetherimide Kapton is one of the most important commercial polyimides and has been chosen as an example of a thermostable polymer. In contrast to the materials considered previously, thermostable polymers usually have very rigid backbones and their swelling in water vapor is, therefore, quite low (typically a few percent, depending on the polymer structure and temperature). Here again, the three-parameter BET model accurately describes the three isotherms reported by Yang et al.[33] corresponding to different temperatures between 30 and 60°C. To avoid the overlapping of the different curves, only the experimental data and fitting curve corresponding to 45°C have been reported in Figure 3, but the values of the correlation coefficients and residual sum of squares values reported in Table III attest to the striking efficiency of the modified BET model for all of the data fitted.

Comparison of the sorption data of related vinyl polymers, another very important type of polymer, has previously been reported by Peterson.[34] Among other interesting results, the study of water vapor sorption in polyacrylic acid and the corresponding sodium salt revealed, as expected, the pronounced hydrophilic feature of the polyelectrolyte. Type II isotherms have been reported by the previous author to correspond closely to the BET equation (two parameters) up to activities of 0.4–

0.53, depending on the polymer. Table III shows that analysis by the modified BET equation (three parameters) allowed accurate description of both isotherms in the activity range 0–0.9, which covers all the activities investigated during the experiments. However, although the curve fitting (Fig. 4) is good over the entire range of experimental activities for polyacrylic acid, a small deviation occurs for low activities in case of the corresponding sodium polyelectrolyte.

The last part of our investigation deals with natural molecules of biological interest and extends the analysis of Bull,[29] who used the BET model (two parameters), by considering the modified BET model (three parameters) for activities up to 0.9.

In Figure 5(a), the water vapor sorption isotherms of six different proteins (Zein, egg albumin, α and β-pseudoglobulin, salmin, and collagen) are reported together with the modeling results corresponding to 25°C. The less hydrophilic proteins (i.e., Zein and egg albumin) lead to moderate water sorption and show excellent correlation by the modified BET model over the activity range of 0–0.9 (Table III). Of even more interest, the relative errors (Table III) remain low even for the most hydrophilic proteins where sorption ratios vary quite considerably over the entire activity range; the extreme variations being due to

Table II Parameters of the Three-Parameter–Modified BET Model for Water Vapor Sorption in Textiles and Proteins

	Ref.	FAR	c_p (adim.)		a (wt %)		n (adim.)		R		RSS	
			25°C	40°C	25°C	40°C	25°C	40°C	25°C	40°C	25°C	40°C
Proteins												
Zein	29	0–0.90	24.86	22.23	3.40	3.20	9.68	9.17	0.9960	0.9977	1.749	0.835
Egg albumin	29	0–0.90	23.01	19.15	4.97	4.79	11.00	10.23	0.9942	0.9951	6.398	4.636
α and β-Pseudoglobulin	29	0–0.90	29.15	23.79	6.01	5.84	11.18	10.46	0.9929	0.9953	11.577	6.707
Salmin	29	0–0.90	9.70	14.09	8.41	7.51	24.67	35.11	0.9989	0.9960	9.402	30.328
Collagen	29	0–0.90	32.51	18.73	8.82	8.72	9.49	8.63	0.9962	0.9970	10.787	7.525
Elastin	29	0–0.90	31.80	17.30	5.73	5.74	8.75	7.83	0.9925	0.9966	8.129	3.304
Serum albumin	29	0–0.90	28.28	23.92	5.53	5.38	11.34	10.31	0.9959	0.9913	5.696	10.362
γ-Pseudoglobulin	29	0–0.90	29.03	22.78	5.95	5.86	11.20	10.29	0.9932	0.9929	10.851	10.292
Gelatin	29	0–0.90	59.00	31.88	7.35	7.26	11.92	10.48	0.9902	0.9898	24.87	10.479
Textiles												
Unstretched nylon	29	0–0.90	6.59	5.11	1.78	1.78	9.72	9.19	0.9994	0.9989	0.079	0.137
Silk	29	0–0.90	28.04	20.62	3.55	3.44	10.43	9.49	0.9930	0.9941	3.608	2.590
Wool	29	0–0.90	17.58	14.13	6.13	5.89	7.01	6.78	0.9974	0.9981	2.433	1.617
Viscose	30	0–0.97	33.05	—	4.28	—	11.58	—	0.9960	—	5.142	—
Cotton	30	0–0.97	25.16	—	2.74	—	10.13	—	0.9984	—	0.700	—
Cellulose acetate	30	0–0.97	8.48	—	2.41	—	10.97	—	0.9998	—	0.059	—

FAR, fitting activity range.

Table III   Parameters of the Three-Parameter–Modified BET Model for Water Vapor Sorption in Synthetic Polymers

	Ref.	FAR	T (°C)	c_p (adim.)	a (adim.)	n (adim.)	R	RSS
Polyamides[a]								
Nylon 2	31	0–0.87	20	14.21	22.74 (mol %)	8.36	0.9986	27.14
Nylon 3	31	0–0.82	20	14.59	23.88 (mol %)	16.09	0.9981	81.04
Nylon 6	31	0–0.83	20	6.83	25.65 (mol %)	8.7	0.9997	4.69
Nylon 7	31	0–0.87	20	7.80	15.82 (mol %)	11.2	0.9978	20.56
Nylon 8	31	0–0.81	20	13.14	11.21 (mol %)	24.5	0.9974	36.37
Nylon 11	31	0–0.87	20	7.64	9.87 (mol %)	6.5	0.9986	2.50
Other polymers								
Regenerated cellulose	32	0–0.92	15	16.82	6.64 (wt %)	8.40	0.9983	2.530
Kapton polyimide	33	0–0.95	30	20.51	0.68 (wt %)	6.45	0.9992	0.015
	33	0–0.92	45	9.62	0.70 (wt %)	6.13	0.9994	0.009
	33	0–0.76	60	6.45	0.78 (wt %)	6.05	0.9990	0.010
Polyacrylic acid	34	0–0.95	26	105	4.45 (wt %)	48.0	0.9971	27.80
Sodium polyacrylic acid	34	0–0.96	26	3.19	28.42 (wt %)	16.75	0.9966	341.2

FAR, fitting activity range.
[a] a is given in mol % corresponding to mol/100 of accessible amide groups.[31]

salmin and collagen with maximum water vapor sorption ratios of 70% and almost 40%, respectively. The same conclusions hold for the related isotherms at 40°C. However, similar analysis of sorption data for four other quite hydrophilic bio-molecules (elastin, serum albumin, γ-pseudoglob-ulin, and gelatin) yields significant errors, as shown by the curves in Figure 5(b) as well as the R and RSS values reported in Table II (for instance, at 25°C, correlation coefficients less than

0.9960 and ΣRSS = 49.54). Here again, the most important deviations occur for the most hydro-philic material (gelatin, R = 0.9902 and RSS = 24.87 for a swelling value of roughly 40% for x = 0.9 at 25°C). Moreover as already mentioned in a previous subsection, only activities in the range 0–0.9 could be considered with the three-parame-ter BET model; the addition of values obtained
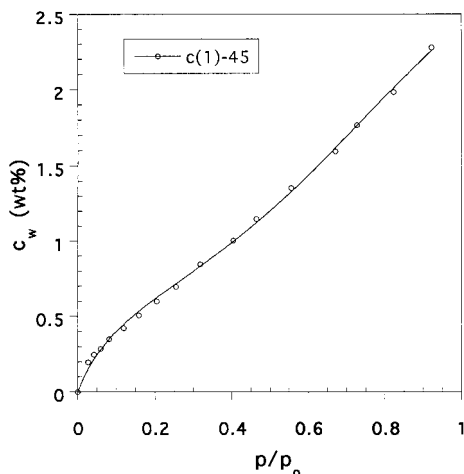

Figure 3   Sorption of water vapor in polyimide Kapton at 45°C (data from Yang et al.[33]). The curve is the result of the sorption modeling by the three-parameter BET model.
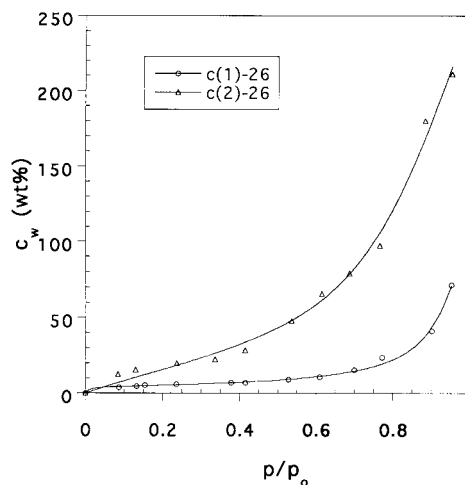

Figure 4   Sorption of water vapor in vinyl polymers at 26°C. 1 = polyacrylic acid, 2 = sodium polyacrylic acid (data calculated from Peterson[34]). The curves are the results of the sorption modeling by the three-pa-rameter BET model.
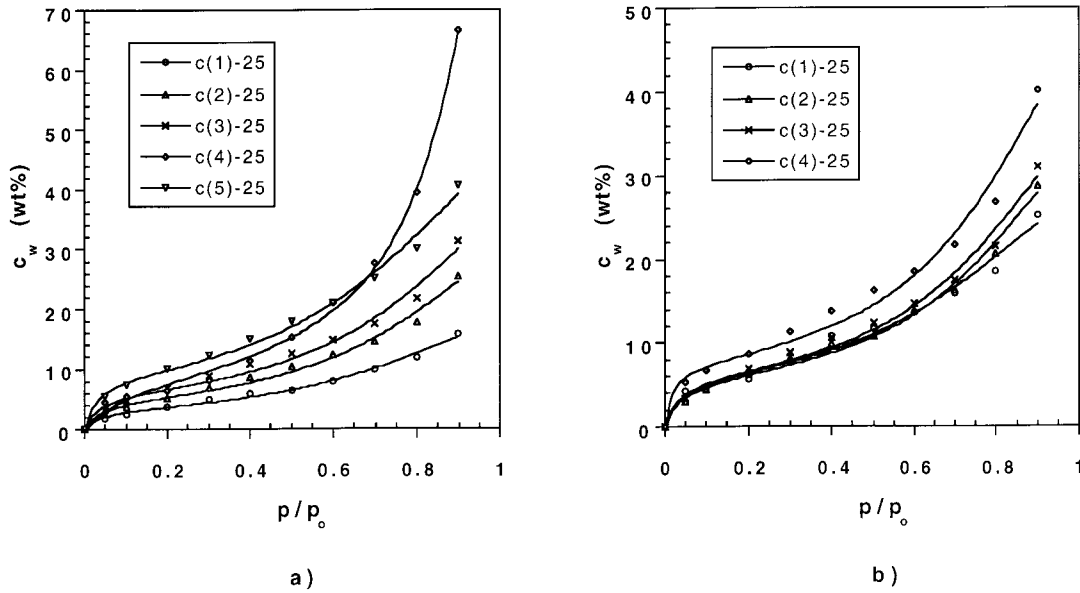
Figure 5 Sorption of water vapor in proteins at 25°C. (a) 1 = zein, 2 = egg albumin, 3 = α and β-pseudoglobulin, 4 = salmin, 5 = collagen. (b) 1 = elastin, 2 = serum albumin, 3 = γ-pseudoglobulin, 4 = gelatin (data from Bull[29]). The curves are the results of the sorption modeling by the three-parameter BET model.

for higher activities resulted in a very poor fitting efficiency or, for most of the cases, the divergence of the numerical resolution.

GAB Model

Estimation of the Model Parameters

Three methods have been reported for determining the three parameters of the GAB model.

The first method proposed by Bizot[22] and also used by Roos[2] for modeling water vapor sorption in foods or related products is worthy of mention. Bizot[22] proposed eq. (8) to be rewritten as:

$$Y = \frac{x}{C} = \alpha x^2 + \beta x + \gamma \qquad (10)$$

where $\alpha = k(1 - c_{p,\mathrm{GAB}})/(a_{\mathrm{GAB}}c_{p,\mathrm{GAB}})$, $\beta = (c_{p,\mathrm{GAB}} - 2)/(a_{\mathrm{GAB}}c_{p,\mathrm{GAB}})$, and $\gamma = 1/(a_{\mathrm{GAB}}c_{p,\mathrm{GAB}}k)$. The model parameters can then be calculated from α, β, and γ by the following relationships:

$$a_{\mathrm{GAB}}^2 = -\frac{1}{4\alpha\gamma - \beta^2} \qquad (11)$$

$$k = -\frac{\beta - (1/a_{\mathrm{GAB}})}{2\gamma} \qquad (12)$$

$$c_{p,\mathrm{GAB}} = \frac{1}{k\gamma a_{\mathrm{GAB}}} \qquad (13)$$

The obvious advantage of Bizot's method is that only a quadratic regression of the plot $Y = x/C$ vs. x is required for calculating the parameters of the GAB model, thus allowing the modeling by most of the graphic softwares available (Cricket Graph, etc.).

The second method, proposed by Delwiche et al.,[24] consists of a multiple linear regression of eq. (8) rewritten in the form:

$$\frac{1}{C} = \beta_{-1}\frac{1}{x} + \beta_0 + \beta_1 x \qquad (14a)$$

or following the parameter notations of Bizot:

$$\frac{1}{C} = \gamma\frac{1}{x} + \beta + \alpha x \qquad (14b)$$

This method avoids using a nonlinear fitting program provided that a multiparameter multivariable linear fitting program is available. The three parameters of the GAB model have then to be calculated by the relationships (11), (12), and (13) in the same way as for Bizot's procedure.

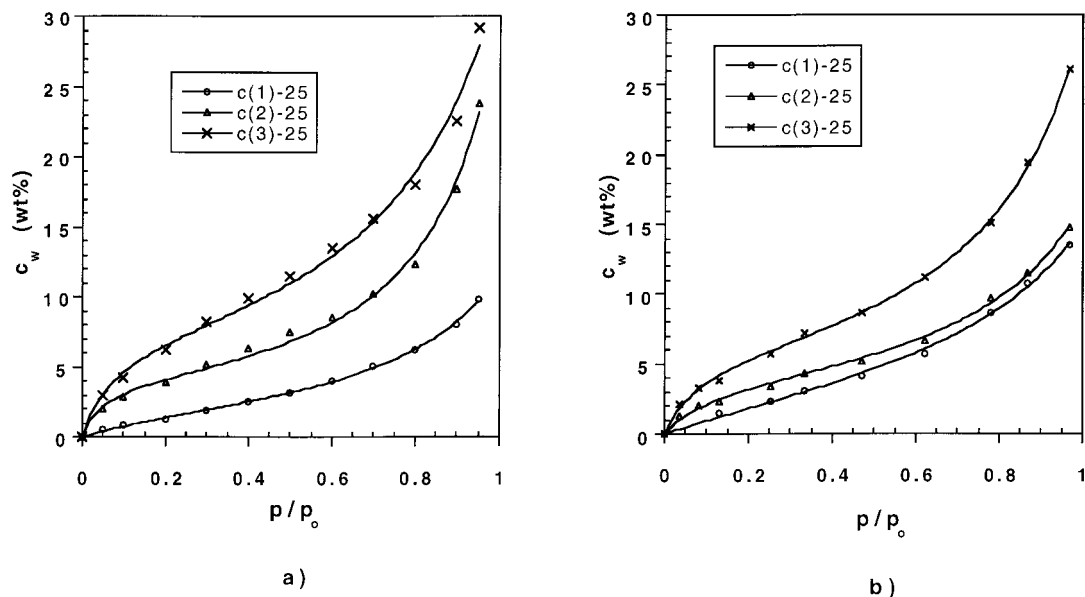The last method is the quite classical nonlinear

Figure 6   Sorption of water vapor in textiles at 25°C. (a) 1 = unstretched nylon, 2 = silk, 3 = wool (data from Bull[29]); (b) 1 = cellulose acetate, 2 = cotton, 3 = viscose (data from Rowen and Blaine[30]). The curves are the results of the sorption modeling by the GAB model.

multiparameter regression. Because of the efficiency of this method as clearly shown by the previous results, this approach has been followed for calculating the three parameters of the GAB model for all the isotherms discussed previously. It leads straight to the three parameters of the model, without requiring their calculation from intermediate parameter values in contrast to both of the methods mentioned previously .

Water Sorption in Natural or Synthetic Polymers

To allow the comparison between both modified BET models, the same systems as described previously were considered, and the efficiency of the GAB model was evaluated in terms of the activity range allowing an accurate modeling as well as quantitative fitting parameters (correlation coefficients R and residual sum of squares RSS).

In contrast to the three-parameter BET model, which was limited to activities up to 0.9, the GAB model allowed the accurate description of water vapor sorption in six different textile fibers at 25°C up to activities as high as 0.95, which, in fact, corresponds to the highest value of the experimental range (Fig. 6).

For most of the textile fibers (i.e., unstretched nylon, silk, viscose, and cotton), the correlation coefficients R of the GAB model are equal or superior to those corresponding to the modified BET

model, whereas a broader activity range could be taken into account. The sorption isotherms corresponding to water vapor sorption in unstretched nylon, silk, and wool at a higher temperature (40°C) could also be fitted by the GAB model over the activity range of 0–0.95 with a striking efficiency (see Table IV).

The same conclusions can be drawn from the GAB modeling of water vapor sorption in the different polyamides mentioned previously (i.e., nylons 2, 3, 6, 7, 8, and 11). The correlation coefficients obtained were particularly high (R in the range 0.9992–0.9999) except for nylon 11 where the R value is only 0.9968. In Figure 7, the sorption isotherm corresponding to nylon 8, which had led to a significant deviation during the modeling by the first modified BET model (R = 0.9974 and RSS = 36.37), is shown and the modeling curve obtained by the GAB model as well as the fitting efficiency parameters (R = 0.9992 and RSS = 10.84) demonstrate the superiority of the model derived by Guggenheim, Anderson, and de Boer in that particular case.

Moreover, compared to the first modified BET model (BET three parameters) which, in the case of water sorption in polyamides, was restricted to activities strictly less than 0.9 (Table III), the GAB model could usually account for the sorption properties for activities up to 0.95, as reported in

Table IV   Parameters of the GAB Model for Water Vapor Sorption in Textiles and Proteins

|	Ref.	FAR	$c_{p,\text{GAB}}$ (adim.)		a_{GAB} (wt %)		k (adim.)		R		RSS	
			25°C	40°C	25°C	40°C	25°C	40°C	25°C	40°C	25°C	40°C
Proteins												
Zein	29	0−0.95	19.53	16.60	3.99	3.88	0.85	0.83	0.9978	0.9986	1.819	0.885
Egg albumin	29	0−0.95	17.86	13.62	5.79	5.88	0.87	0.84	0.9981	0.9990	4.270	1.723
α and β-Pseudoglobulin	29	0−0.95	21.42	16.23	7.01	7.13	0.87	0.85	0.9981	0.9992	6.038	1.957
Salmin	29	0−0.95	9.40	5.65	8.80	9.30	0.97	0.96	0.9993	0.9983	17.296	34.99
Collagen	29	0−0.95	20.15	12.66	10.90	11.28	0.82	0.79	0.9994	0.9995	2.923	2.051
Elastin	29	0−0.95	26.96	14.82	6.49	6.87	0.85	0.81	0.9943	0.9960	11.904	6.702
Serum albumin	29	0−0.95	16.66	16.95	6.89	6.52	0.85	0.85	0.9996	0.9983	1.009	3.757
γ-Pseudoglobulin	29	0−0.95	24.70	18.98	6.66	6.75	0.89	0.87	0.9970	0.9972	10.461	7.776
Gelatin	29	0−0.95	45.68	25.21	8.06	8.31	0.90	0.87	0.9963	0.9968	21.454	14.232
Textiles												
Unstretched nylon	29	0−0.95	4.17	3.22	2.63	2.88	0.79	0.75	0.9994	0.9997	0.128	0.055
Silk	29	0−0.95	22.26	16.87	4.08	4.04	0.87	0.85	0.9974	0.9977	2.651	1.918
Wool	29	0−0.95	16.13	12.01	7.33	7.52	0.78	0.75	0.9964	0.9981	5.792	2.445
Viscose	30	0−0.97	14.00	—	6.06	—	0.80	—	0.9995	—	0.640	—
Cotton	30	0−0.97	11.20	—	4.02	—	0.76	—	0.9988	—	0.510	—
Cellulose acetate	30	0−0.97	2.79	—	4.91	—	0.71	—	0.9991	—	0.306	—

FAR, fitting activity range.
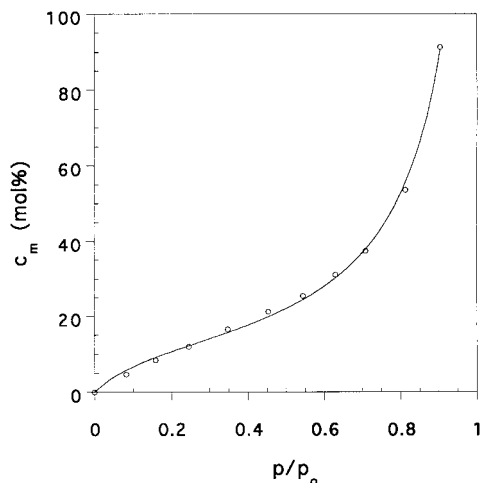
Figure 7 Sorption of water vapor in nylon 8 at 20°C (data from Puffr and Sebenda[31]). The curve is the result of the sorption modeling by the GAB model.

Table V. The same trend could also be observed for the GAB modeling of water vapor sorption in a related polymer (regenerated cellulose at 15°C).

However, GAB analysis of the different sorption isotherms related to the thermostable polyimide Kapton led to higher errors, expressed in terms of residual sum of squares, than the first modified BET model over the same activity range. Consequently, the correlation coefficients ob-

tained by the GAB model are slightly inferior but, nevertheless, remain quite high ($R > 0.9980$).

Although the GAB model leads to a significant improvement (error reduced by almost 50%) in the modeling of water vapor sorption in polyacrylic acid, i.e., one of the commercially most important vinyl polymers, it also failed to accurately account for the sorption properties in the corresponding sodium salt ($R = 0.9944$ and RSS $= 562$). Consequently, considering the deviation also encountered with the three-parameter BET model, it seems that neither modified BET model can account for water sorption in sodium polyacrylic acid, most probably due to the very strong interactions involved by the sodium *polyelectrolyte*.

Compared to the three-parameter BET model, the GAB analysis of water vapor sorption in molecules and polymers of biological interest was not limited to activities less than or equal to 0.90. It seems that the weighing factor k plays a significant role in avoiding the numerical divergence at very high activities.

As a result, the sorption properties over the entire activity range investigated experimentally could be described by the GAB model, usually with a high accuracy, as shown by the R and RSS values reported in Table IV.

In Figure 8(a), we report the experimental re-

Table V Parameters of the GAB Model for Water Vapor Sorption in Synthetic Polymers

	Ref.	FAR	T (°C)	$c_{p,\text{GAB}}$ (adim.)	a_{GAB} (adim.)	k (adim.)	R	RSS
Polyamides[a]								
Nylon 2	31	0–0.87	20	8.22	39.32 (mol %)	0.76	0.9998	3.393
Nylon 3	31	0–0.91	20	7.48	30.69 (mol %)	0.89	0.9999	5.170
Nylon 6	31	0–0.98	20	4.35	37.72 (mol %)	0.77	0.9999	4.825
Nylon 7	31	0–0.95	20	5.97	19.89 (mol %)	0.86	0.9996	8.187
Nylon 8	31	0–0.90	20	8.04	13.15 (mol %)	0.95	0.9992	10.842
Nylon 11	31	0–0.95	20	8.84	11.58 (mol %)	0.78	0.9968	10.359
Other polymers								
PAN	28	0–0.99	20	31.21	8.67 (cm^3/cm^3)	0.86	0.9987	6.828
	28	0–0.95	30	7.14	11.28 (cm^3/cm^3)	0.84	0.9996	1.644
	28	0–0.86	40	8.80	9.87 (cm^3/cm^3)	0.83	0.9993	1.225
	28	0–0.63	50	6.39	10.74 (wt %)	0.90	0.9989	1.008
Regenerated cellulose	32	0–0.92	15	9.89	9.31 (wt %)	0.75	0.9997	0.414
Kapton polyimide	33	0–0.95	30	13.50	0.99 (wt %)	0.63	0.9981	0.037
	33	0–0.92	45	6.76	1.14 (wt %)	0.60	0.9983	0.026
	33	0–0.76	60	5.79	1.07 (wt %)	0.71	0.9988	0.012
Polyacrylic acid	34	0–0.95	26	22.45	5.14 (wt %)	0.97	0.9982	16.84
Sodium polyacrylic acid	34	0–0.96	26	0.37	164.4 (wt %)	0.70	0.9944	561.7

FAR, fitting activity range.
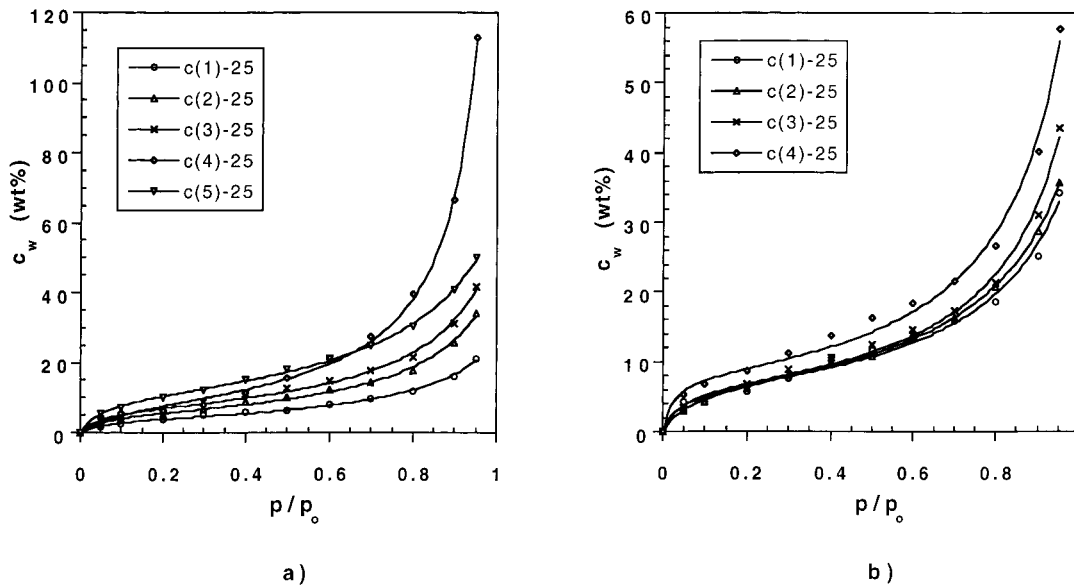[a] a is given in mol % corresponding to mol/100 mol of accessible amide groups.[31]

Figure 8 Sorption of water vapor in proteins at 25°C. (a) 1 = zein, 2 = egg albumin, 3 = α and β-pseudoglobulin, 4 = salmin, 5 = collagen. (b) 1 = elastin, 2 = serum albumin, 3 = γ-pseudoglobulin, 4 = gelatin (data from Bull[29]). The curves are the results of the sorption modeling by the GAB model.

sults as well as the modeling curves corresponding to water vapor sorption in six proteins (Zein, egg albumin, α and β-pseudoglobulin, salmin, and collagen at 25°C). These proteins have already been considered in Figure 5 over an activity range of 0–0.9 only, due to the divergence of the numerical resolution corresponding to the three-parameter BET model at very high activities.

If the fitting efficiency of the GAB model is slightly superior to that of the three-parameter BET model, the major advantage of the model derived by Anderson et al. is its ability to account for the different isotherms over all the activity range investigated during sorption experiments. The same conclusions also hold for the related sorption properties at higher temperature (40°C).

Moreover, the fitting errors corresponding to the treatment of sorption data isotherms related to four other hydrophilic proteins (elastin, serum albumin, γ-pseudoglobulin, gelatin) we had previously reported for the three-parameter BET model, could be significantly reduced by using the GAB model over a broader activity range [cf. Table IV and Fig. 8(b)]. However, it should be emphasized that both modified BET models were only moderately successful for description of water sorption in gelatin, i.e., one of the most hydrophilic compounds investigated in this work (GAB model: $R = 0.9963$, RSS

$= 21.45$, and three-parameter BET model: $R = 0.9902$, RSS $= 24.87$).

Comparison of the Performance of the Different BET Models

The above discussion has already referred to some of the advantages of the approach derived by Guggenheim, Anderson, and de Boer for accounting for water sorption in highly nonideal systems. However, in this part, the ability of both models to describe type II isotherms will be discussed in a more quantitative manner.

Comparison of the Residual Sums of Squares

One of the common ways for assessing the relative performances of given models consists in comparing the residual sums of squares obtained with the same sets of experimental values. As previously discussed, the three-parameter BET model and the GAB model have usually not been tested on the same range of values. From a qualitative point of view, the model derived by Anderson et al. has proved its superiority over a broader activity range (usually covering all the experimental activity range).

In Table VI, we report the residual sums of squares corresponding to both models and each

Table VI Comparison of the Efficiencies of the Three-Parameter BET Model and the GAB Model for the Analysis of More Than 40 Isotherms for Water Vapor Sorption in Hydrophilic Glassy Polymers and Proteins

	Σ RSS 3 Parameters BET Model	Σ RSS GAB Model
Proteins	89.46 (25°C)	77.17 (25°C)
	84.47 (40°C)	74.07 (40°C)
Textiles	12.02 (25°C)	10.03 (25°C)
	4.34 (40°C)	4.42 (40°C)
Polyamides	172.3	42.77
Other polymers	40.23	28.03
	Σ = 402.8	Σ = 236.5

series of polymers or proteins investigated in this work. For the calculations, only the polyelectrolyte (sodium polyacrylic acid), having led to obvious deviations with both models, has been excluded. The results reported in Table VI thus reflect the modeling efficiency of 18 isotherms for proteins, 9 isotherms for textiles, 6 isotherms for polyamides, and 9 isotherms for the subclass entitled "Other Polymers," i.e., more than 40 different type II isotherms.

Except for the set of textile data where the RSS values obtained by both models are quite similar, the error corresponding to the GAB model is usually significantly less than the error for the three-parameter BET model. Compared to the error corresponding to the three-parameter BET model, the GAB model error is decreased by 15% for proteins, 30% for the subclass entitled "Other Polymers," and 75% for the set of nylon polyamides.

The range of activities covered by the GAB model is systematically equal or superior to that for the three-parameter BET model.

The previous comparison of the residual sums of squares demonstrates the superiority of the GAB model to account for water sorption in the complex systems investigated in this work.

Influence of Temperature on Sorption Properties

According to Brunauer,[6] an adsorption model should not only describe the adsorption properties of a given system at a given temperature but also account for their variations with temperature. From the assumptions made for deriving both modified BET models,[6,19] the parameters a, n, and k are supposed to vary only slightly with temperature, whereas the variation of c_p should be described by an Arrhenius type law.

The modeling of water vapor sorption in poly-

acrylonitrile and polyimide Kapton at different temperatures allows a further assessment of the performance of both models to account for water sorption in complex media.

According to the values reported in Table VII, the parameters a, n, and k vary with temperature only slightly.

In Figure 9(a), the Arrhenius plots corresponding to the c_p parameters obtained by both models for water sorption in polyacrylonitrile (PAN) also show the expected trend, despite a certain scattering of the data points, which is quite common for parameters derived by optimization especially when the experimental data are relatively scarce. The activation energies corresponding to the sorption process are 8.4 kcal/mol and 8.7 kcal/mol according to the parameters of the three-parameter BET model and GAB model, respectively. In Figure 9(b), the corresponding plots are reported for the system H_2O/Polyimide Kapton. This thermostable polymer induces a low water sorption compared to PAN, and the data points are less scattered and lead without ambiguity to sorption activation energies of 5.6 kcal/mol and 4.2 kcal/mol for the three-parameter BET model and GAB model, respectively. As expected, the values of activation energies found for the thermostable and thus rigid polymer are less than those calculated for PAN.

Although the three-parameter BET model and the GAB model have been used here for modeling phenomena rather different from adsorption processes for which they were initially derived, the parameters corresponding to water sorption in complex systems follow quite well the trends previously described for adsorption phenomena. However, the ability of both models to account for the influence of temperature on sorption properties appears to be quite similar for the two sys-

Table VII Influence of Temperature on Water Sorption Model Parameters

		Three-Parameter BET Model			GAB Model		
	T (°C)	c_p	a	n	$c_{p,\text{GAB}}$	a_{GAB}	k
PAN[a]	20	31.07	7.96	10.53	31.21	8.67	0.86
	30	13.69	8.13	13.59	7.14	11.28	0.84
	40	14.70	7.56	10.39	8.80	9.87	0.83
	50	6.84	9.65	7.89	6.39	10.74	0.90
Kapton[b]	30	20.51	0.68	6.45	13.50	0.99	0.63
	45	9.62	0.70	6.13	6.76	1.14	0.60
	60	6.45	0.78	6.05	5.79	1.07	0.71

[a] Experimental data from Stannett et al.[28]
[b] Experimental data from Yang et al.[33]

tems investigated and, consequently, does not allow any further discrimination between the two modified BET models investigated in this work.

CONCLUSION

The results of an analysis of more than 40 type II isotherms have demonstrated the ability of two modified BET models to account for water vapor

Figure 9 Influence of temperature on water vapor sorption: Arrhenius plots ln c_p versus $1/T$ for the c_p parameters obtained by the three-parameter BET model (M1) and the GAB model (M2). (a) System $H_2O/$ Polyacrylonitrile; (b) system $H_2O/$polyimide Kapton.

sorption in systems strongly deviating from ideality.

The three-parameter BET model, considering sorption on a limited number of layers, provides a good extension of the first BET model, which is restricted to low activities only. However, the sorption properties at very high activities ($a > 0.9$) could not be well described by the three-parameter model, most probably due to the model divergence for $a = 1$ corresponding to pure liquid water.

The GAB model represents a good alternative and is usually accurate for activities up to 0.95.

The striking efficiency of the GAB model makes it the model of choice for describing water vapor sorption in complex systems.

Moreover, from analysis of the influence of temperature on sorption properties of two particular systems involving polymers inducing high and low water sorption, respectively, the variation of the parameters was shown to be compatible with the two theories.

In conclusion, and without claiming that either of the models investigated truly describes the physics of such complex sorption processes, the GAB model is a simple model that allows the accurate description of the type II isotherms corresponding to water vapor sorption in hydrophilic glassy polymers and related compounds, usually for all the activity range investigated experimentally. This is clearly an advantage compared to the most common approach using the classic BET model.

Last, but not least, to avoid the use of a complex fitting program, the method proposed by Bizot[22] and briefly described earlier facilitates the determination of the GAB parameters, allowing water vapor sorption modeling in complex media by
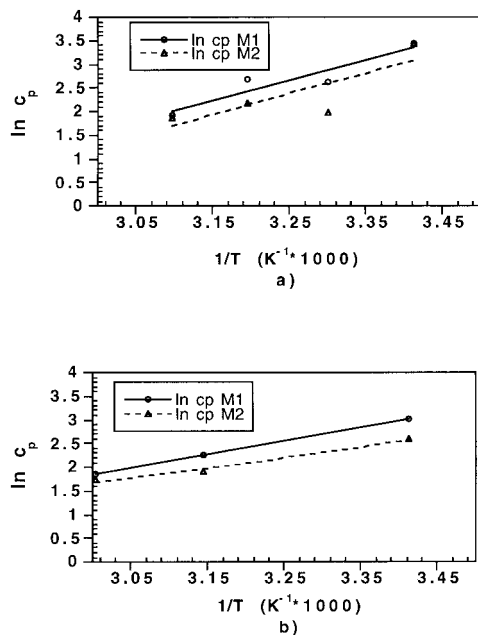
most of the Graphics softwares commercially available.

NOMENCLATURE

a	parameter of the BET model
a_{GAB}	parameter of the GAB model
b	hole affinity constant (original dual sorption theory)
C	solubility
C_A	solubility related to the adsorption process
C_D	solubility related to the sorption process
C'_H	hole saturation constant (original dual sorption theory)
c_p	parameter of the BET model
$c_{p,GAB}$	parameter of the GAB model
E_L	heat of liquefaction
k	correction factor of the GAB model
k_D	Henry's law dissolution constant
n	number of adsorbed layers
p	pressure
p_o	saturation vapor pressure
RSS	residual sum of squares
x	relative humidity ($=p/p_o$)
α	first parameter of Bizot's method
β	second parameter of Bizot's method
β_{-1}	first parameter of Delwiche's method
β_0	second parameter of Delwiche's method
β_1	third parameter of Delwiche's method
γ	third parameter of Bizot's method
σ	plasticizing constant
χ	Flory–Huggins interaction parameter

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