A Model of Physical Adsorption of Gases*

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Synopsis

Using the Gibbs description of surfaces, a sorption model is developed which describes sorption isotherms for such systems as water in polymers. Moreover, the Freundlich isotherm for monolayer sorption is obtained. The physical interpretation of the constants of the model and the boundary conditions required for application to sorption isotherms are discussed. On basis of the Freundlich isotherm, a multilayer model is proposed to describe the water sorption in polymers. Experimental results within the whole range of relative humidity are found to be in excellent agreement with the multilayer model. Disagreement between model isotherm and experimental data of some polymers at relative humidities above 90% might be due to capillary phenomena not considered in the present model description.

INTRODUCTION

An inhomogeneous surface layer always exists between two adjacent homogeneous phases. This surface layer is created by surface forces characteristic of the physical and chemical properties of the homogeneous phases. Sorption of one type of molecule is said to occur when the concentration of these molecules in the surface layer is higher than those in the homogeneous phases.

A system of two homogeneous phases is considered in the following discussion, each phase containing only one component. No chemical reaction between the components is considered to take place. If one phase is a solid and the second phase a gas, the surface layer would consist only of sorbed molecules of the gas phase. The area of the surface layer is equal to the area of the surface of the solid phase. In highly porous materials such as porous plugs, charcoal, and polymers, for instance, the area of the surface layer is directly proportional to the weight of the solid.

The amount of sorbed gas v referred to a standardized size of the solid in thermodynamic equilibrium is a function of gas pressure p and temperature T:

$$v = v(p,T)$$

Usually the sorption isotherm of a system is measured as a function of pressure at constant temperature:

$$v = v(p)_T$$

Other forms of expressing sorption behavior include sorption isobars (constant pressure),

$$v = v(T)_p$$

and sorption isosteres (constant volume),

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$$p = p(T)_v$$

In general, sorption processes can be characterized by the slope of the corresponding sorption isotherm. Brunauer et al.[1] presented a classification of the physical adsorption of gases which correlates any set of sorption isotherm data to one of five typically shaped isotherms. Adamson[2] gave an extensive discussion of these typical isotherms as shown in Figure 1. An analytical relationship describing the sorption isotherm of a system cannot be derived without a model on a molecular level. All existing models may be classified into two groups: surface models and solution models.[3] Some of these models will be presented below.

Common to all of the surface models is the assumption that the adsorbing phase possesses a surface at which a certain maximum amount of molecules can be adsorbed within one layer. Further sorption resulting in two or more layers is also possible. The surface models differ in their assumptions about the interaction between adsorbent and adsorbate.

If the sorption approaches saturation due to the type 1 isotherm shown in Figure 1, the so-called Langmuir isotherm would be the simplest description of the sorption process. With the Langmuir isotherm it is assumed that a strict monolayer sorption takes place. The molecules are assumed to be adsorbed independently from each other with the same sorption enthalpy for each molecule. Furthermore, the sorption entropy is only related to the permutations of N adsorbed indistinguishable molecules at a total number of S sites.[2] The resulting relationship

$$v = v_m \left[bp/(1 + bp) \right]$$

describes an isotherm concave toward the p-axis and approaches a value v_m at high pressures, corresponding to a completely filled monolayer. The parameter b is a measure of the sorption enthalpy.

Brunauer et al.[1] developed a multilayer model describing S-shaped isotherms corresponding to isotherms of types 2 and 3 in Figure 1. It is assumed that the adsorption process of each layer can be described by the Langmuir equation. The number of layers is assumed to be infinite, and the sorption enthalpy of molecules sorbed in the second and further layers should be equal to the condensation enthalpy of the gas. This BET model yields the relationship

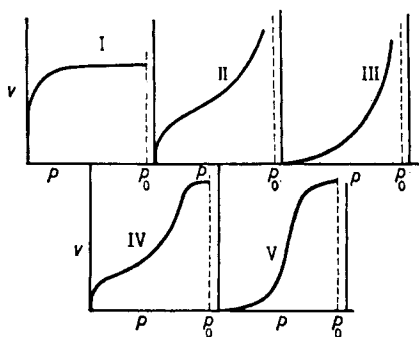$$v = v_m \frac{cx}{(1 - x)[1 + (c - 1)x]}$$

Fig. 1. Typical isotherms for physical adsorption of gases according to Brunauer et al. (Ref. 1).

where v_m is the maximum amount of sorbed molecules in one layer, similar to the Langmuir model, c is a parameter describing the difference between the sorption enthalpy of the first layer and the condensation enthalpy of the gas, and x is equal to p/p_0, while p_0 is the saturation gas pressure.

Freundlich[4] presented an empirical relationship,

$$v = k(p/p_0)^{1/a}$$

which describes a monolayer sorption similar to the Langmuir isotherm. Sips[5] showed that the Freundlich isotherm can be derived from a model different from the Langmuir model only by the assumption that instead of an equal sorption enthalpy for each molecule, a distribution function of the sorption enthalpy is used. As Sips himself points out,[5] this nonstandard distribution function cannot be correct. Other models, which will not be discussed here, consider the sorbed phase as a liquid film or a van der Waals liquid.[2]

In many cases these models successfully describe the sorption process of certain systems. However, all these models fail in characterizing the sorption of water in polymers and biological macromolecules, especially at relative humidities near saturation. The reasons for this failure are specific to each model. As all of the experimentally determined isotherms of water–polymer systems are typically S-shaped, one would expect a best fit of the experimental data by a multilayer model. Nevertheless, agreement between experimental data and the BET model, for instance, is obtained only at relative humidities below 40%. The disagreement at higher relative humidities might be caused by the unrealistic assumption that even at higher densities of the layers, the water molecules are adsorbed independently of each other.[1] In addition, the number of sorbed layers permitted may be restricted by the network of the polymers.

In contrast to the surface models, the solution models consider adsorbate and adsorbent to be a homogeneous mixture. The activity of the sorbed molecules is obtained as a function of its mole fraction. To determine the entropy of mixing, Flory[6] assumed adsorbent and adsorbate to be a liquid mixture. Because of the enormous difference in the size of water and polymer molecules, the entropy of mixing is not related to the mole fractions, but to the volume fractions of the molecules. The following relationship between water activity a and the volume fractions of water v_1 and polymer v_2 is obtained:

$$\ln a = \ln v_1 + v_2 + \chi v_2^2$$

The interaction parameter χ characterizes the enthalpy of mixing and is assumed to be independent of the volume fractions v_1 and v_2. Other sorption models[3] distinguish strong and weak interactions and take into account interactions between adsorbed molecules.

Solution models characterize the sorption process in water–polymer systems at high relative humidities, in good agreement with experimental results, but fail at water activities of less than about 0.6. This may be attributed mainly to the fact that at low water contents, a polymer cannot be considered as a liquid phase, but forms a solid network.

In the presence of holes within the polymer network, detectable by electron microscopic studies, capillary condensation phenomena can occur. Molecules will condense within these pores at activities less than 1 because of a corresponding gas pressure depression, which is a function of pore size and pore ge-

ometry. The amount of sorbed molecules is thus a function of the pore size distribution and cannot be included generally in all of the sorption models. Assuming a certain geometry of the pores, the pore size distribution is obtained from the amount of gas condensed within the pores as a function of gas pressure. In this paper, a new model of physical sorption will be presented, one which characterizes the sorption of water within polymers over the whole range of relative humidity without taking into account capillary condensation as contained, for instance, in the Kelvin equation.

GIBBS TREATMENT OF BINARY SYSTEMS

A thermodynamic treatment of binary systems of two homogeneous bounded phases is given by Gibbs (see Adamson[2] and Flood,[7] for instance). With reference to Figure 2, phase "a" may be a solid, phase "b" a gas. The area of the surface of contact, C', may be A. Because of surface energies, there will exist an inhomogeneous transition region within the boundaries A' and B'. Outside of A' and B', only the homogeneous phases a and b will exist. At thermodynamic equilibrium the chemical potential of each component, μ_i, is constant. In addition, the boundary surface has a surface tension γ governed by the chemical composition of the contact surface. For uncharged molecules the thermodynamic description of the transition region leads to the following relationship:

$$-S^s \, dT + V^s \, dp - A \, d\gamma = \sum_i N_i^s d\mu_i \qquad (1)$$

where S^s is the entropy within the transition region, V^s is the volume of this region, and N_i^s are the number of moles of each component present in the transition region.

For a theoretical treatment, the surface interactions may be neglected. Thus no transition region will be built up, and the homogeneous phases a and b will stretch to the contact surface C'. Within the volume V^a, given by the boundaries A' and C', there will exist the homogeneous phase a, whereas the homogeneous phase b will be limited to the volume V^b with boundaries B' and C'. From the definition of V^a and V^b, the following relationship results:

$$V^a + V^b = V^s \qquad (2)$$

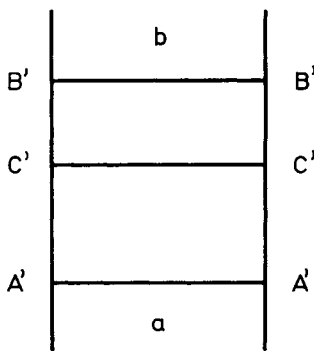For this composite system of two homogeneous phases, thermodynamics yield

Fig. 2. Diagrammatic presentation of the Gibbs boundary surface of a binary system.

$$-(S^a + S^b)dT + (V^a + V^b)\, dp = \sum_i N_i\, d\mu_i \tag{3}$$

S^a and S^b are the entropies of the homogeneous phases a and b within the volumes V^a and V^b, respectively; N_i is the number of moles of component i in both phases. Substracting eqs. (3) and (1) by taking into account eq. 2, and under isothermal conditions ($dT = 0$),

$$-(d\gamma)_T = \sum_i \Gamma_i (d\mu_i)_T \tag{4}$$

which is known as the Gibbs adsorption isotherm. The Gibbs surface excess Γ_i denotes the difference per unit area between the number of moles of component i in the transition region and the homogeneous phases with the same total volume as the transition region:

$$\Gamma_i = n_i^s - n_i = (N_i^s - N_i)/A \tag{5}$$

The surface of separation C' may be chosen in such a way that the Gibbs surface excess of one component vanishes. Thus the Gibbs adsorption isotherm may be rewritten for a k-component system:

$$-(d\gamma)_T = \sum_{i=1}^{k-1} \Gamma_i (d\mu_i)_T \tag{6}$$

This choice of C' is very useful to gravimetric sorption measurements at a solid–gas interface. Without any restriction, the solid (phase a) may be assumed to be permeable to the gas (phase b) and may swell when adsorption takes place. The boundaries A' and C' are chosen such that the volume V^a includes exactly the "dry" solid without any adsorbate, in accordance with the determination of the "dry weight" of the adsorbent. B' is determined by the requirement that the volume V^s includes adsorbent and adsorbate in sorption equilibrium, corresponding to a measurement of the "wet weight" of the adsorbent. Because of these definitions, the volume $V^b = V^s - V^a$ is composed of the volume of the adsorbate and a volume V which is equal to the volume change of the adsorbent caused by swelling. The weight of the solid is the same in both measurements, and the Gibbs surface excess of the solid vanishes. In a binary system the Gibbs adsorption isotherm is then written

$$-(d\gamma)_T = \Gamma(d\mu)_T \tag{7}$$

Γ is the Gibbs surface excess of the gas and μ its chemical potential.

MONOLAYER MODEL

In water–polymer and many other similar systems, the density of the adsorbate is much higher than the density of the gas. Thus the amount of gas n in volume V^b is negligible compared to the amount of adsorbate n^s, and the Gibbs surface excess of the gas is thus equal to the experimentally determined amount of adsorbate. Using the chemical potential of a gas at a temperature T below its critical temperature,

$$\mu = \mu_0(p_0, T) + RT \ln p/p_0 \tag{8}$$

where p_0 is the saturation pressure of the gas at temperature T and R is the gas constant, it follows from eq. (7) that

$$-(d\gamma)_T = n^s RT(d \ln p/p_0)_T \qquad (9)$$

In the following a strict monolayer adsorption caused by a lowering in surface tension is assumed. Describing the monolayer as a two-dimensional gas, the lowering of surface tension results in a two-dimensional film pressure,[2] Π_1:

$$\Pi_1 = \gamma_0 - \gamma_1 \qquad (10)$$

where γ_0 and γ_1 is the surface tension of free and filled surfaces, respectively. In the case of an ideal two-dimensional gas, the following equation of state is obtained

$$\Pi\sigma = RT \qquad (11)$$

where $\sigma = 1/n^s$ is the area per mole of sorbed molecules. Taking into account cohesive interactions between sorbed molecules, the equation of state may be written[8]

$$\Pi\sigma = RTa \qquad (12)$$

where the parameter a gives a measure of the cohesive forces. Using this equation of state, the following relationship results:

$$-\left(\frac{\partial\gamma_1}{\partial n^s}\right)_T = RTa \qquad (13)$$

Combining eqs. (9) and (13) results in the total differential:

$$d \ln(n^s) = a \, d \ln(p/p_0) \qquad (14)$$

Integration of this equation leads to an adsorption isotherm equivalent to the Freundlich isotherm:

$$n^s = k(p/p_0)^{1/a} \qquad (15)$$

where k is the integration constant. With the boundary condition of a completely filled layer ($n^s = n_m$) at saturation ($p = p_0$), it follows that

$$k = n_m \qquad (16)$$

Normalizing the size of the adsorbing area by the unit weight of the solid, the amount of gas adsorbed per unit weight of the solid becomes v. The integration constant is then equal to the amount of gas in a completely filled monolayer per weight unit of the solid, v_m. The sorption isotherm can be written

$$v = v_m(p/p_0)^{1/a}. \qquad (17)$$

Rearranging, the following relationship results:

$$\ln v = \ln v_m + (1/a) \ln(p/p_0)$$

where the constants v_m and a may be determined from a $\ln v$ versus $\ln(p/p_0)$ plot of experimental data.

While v_m is directly proportional to the area of the surface, v is directly proportional to the area of the filled surface, and the difference $v_0 = v_m - v$ is directly proportional to the area of free surface. Therefore, the following equation holds:

$$v = v_0 \frac{(p/p_0)^{1/a}}{1 - (p/p_0)^{1/a}} \qquad (18)$$

describing the thermodynamic equilibrium between free and filled surface at monolayer sorption.

The parameter a describes the change in surface tension by adsorption. Assuming the change in molar surface energy of sorbed molecules, $e_1 = (\gamma_0 - \gamma_1)/n_m^s$, to be independent of temperature within a suitable temperature interval, the following relationship holds:

$$RTa = (\gamma_0 - \gamma_1)/n_s^s = e_1 = \text{const}$$

The parameters a_1 and a_2 are inversely related to the temperatures T_1 and T_2 of the corresponding sorption isotherms

$$a_1/a_2 = T_2/T_1 \tag{19}$$

It should be pointed out that adsorption will occur whenever the gain in Gibbs surface free energy (= surface tension) is negative, corresponding to a positive value of a. As v_m is always positive, the amount of adsorbed gas v increases monotonically with gas pressure p. In a v versus p/p_0 plot, the curve obtained is thus convex for $a > 1$, linear for $a = 1$, and concave for $a < 1$. In case of $a = 0$, v vanishes for all gas pressures $p < p_0$. Only at $p = p_0$ does v become abruptly equal to v_m. Such an adsorption without any gain in surface energy takes place in the case of condensation or sublimation of a gas.

The differential thermodynamic potentials of sorption may be defined by the following relationships:

$$\Delta\overline{G} = RT \ln(p/p_0)$$

$$\Delta\overline{H} = -RT^2 \frac{d \ln(p/p_0)}{dT} \tag{20}$$

$$\Delta\overline{S} = -R \ln (p/p_0) - RT \frac{d \ln(p/p_0)}{dT}$$

Inserting the sorption equation results in

$$\Delta\overline{G} = e_1 \ln(v/v_m)$$

$$\Delta\overline{H} = \overline{G} + e_1 T \frac{d \ln v_m}{dT} - T \ln(v/v_m) \frac{de_1}{dT}$$

$$\Delta\overline{S} = e_1 \frac{d \ln v_m}{dT} - \ln(v/v_m) \frac{de_1}{dT} \tag{21}$$

These relationships should be discussed only for one special case, which is realistic for many systems at values of v/v_m greater than about 0.05: the term $\ln(v/v_m)(de_1/dT)$ should be negligible compared to $e_1(d \ln v_m/dT)$. Then $\Delta\overline{S}$ is independent of the amount of sorbed gas, whereas $\Delta\overline{H}$ increases monotonically with v parallel to $\Delta\overline{G}$. In contrast, adsorption of the Langmuir type is characterized by constant $\Delta\overline{H}$, whereas $\Delta\overline{S}$ decreases with increasing v. Thus, in this particular case, one may distinguish in an elegant way between the two models, although they have very similarly shaped isotherms. According to this discussion, and contrary to that by Roginski,[9] an experimentally proven dependency of the sorption enthalpy on the amount of sorbed molecules does not necessarily lead to the assumption of a heterogeneous surface.

Two objections against the Freundlich isotherm are mentioned in the litera-

ture,[2,10] citing that this formula is entirely empirical. The Freundlich relationship, unlike the Langmuir one, neither approaches Henry's law at low gas pressures nor does it exhibit saturation (a limiting value of sorption capacity) at infinite gas pressures. In the low-pressure region, at the corresponding low concentrations, the adsorbed molecules behave like an ideal two-dimensional gas with a molar surface energy of RT.[2] Thus the model-independent molar surface energy RTa within the whole pressure range may be improved by introducing a factor f:

$$e_1 = RTaf \tag{22}$$

with the boundary conditions

$$\lim_{p \to 0} f = 1/a$$

$$\lim_{p \to p_0} f = 1$$

With this more realistic description of the monolayer surface energy, a linear region results for the Freundlich isotherm at low gas pressures. The deviation of the term af from unity characterizes the nonideal behavior of the adsorbate.

In the high-pressure region, adsorption at temperatures above and below the critical temperature T_c of the gas must be distinguished. For $T < T_c$, the gas pressure cannot increase to infinity. At pressures $p = p_0$, the molecules are present in a condensed state. Thus the chemical potential of the adsorbate cannot be described by eq. (8). Moreover, the density of the adsorbate is not much higher than that of the corresponding liquid. Therefore, the Gibbs surface excess may not be equalized to the amount of adsorbate n^s. At temperatures $T > T_c$, the density of the gas in the high-pressure region is also not negligible compared with the density of the adsorbate. Thus the application of the Freundlich isotherm is strictly limited to a pressure region where the density of the gas is small enough to equalize the Gibbs surface excess with the amount of adsorbate. At larger pressures, more realistic assumptions have to be used to develop a sorption model starting from the Gibbs adsorption equation [eq. (4)]. This will be done in a future paper.

MODIFIED MULTILAYER MODEL

Multilayer adsorption has to be considered in general. The number of layers allowed to be adsorbed is taken to be n. This number n may become infinite. In addition, a model describing multilayer sorption must contain the corresponding monolayer isotherm for $n = 1$. Allowing for a finite number of sorbed layers, n, and employing the Langmuir isotherm for each layer, Dent[11] recently developed a modified multilayer model for the sorption of vapors by polymers. Utilizing assumptions similar to those of the BET model, another modified sorption model is presented in this paper. In contrast to the BET model and its modification by Dent, the Freundlich isotherm rather than the Langmuir isotherm is applied to each of the layers with the present model. The film pressure of the first layer may possess the value Π_1, while all succeeding layers are assumed to be adsorbed with a different but constant film pressure Π_2 as a

consequence of cohesive interactions between molecules in higher layers, which are different than those between the molecules sorbed in the first layer:

$$\Pi_1 = \gamma_0 - \gamma_1$$

$$\Pi_i = \gamma_{i-1} - \gamma_i, \quad i > 1 \tag{23}$$

Adsorption at the ith layer is assumed to take place only on that part of the surface which is covered by $(i - 1)$ layers. Desorption from the ith layer is assumed to take place only at that part of the surface where the $(i + 1)$th to nth layers are uncovered. As illustrated in Figure 3, the multilayer is broken down into a part of uncovered surface v_0, a part of surface covered by a monolayer v_1, a part covered by a double layer v_2, and so on. The adsorbed molecules contributing to thermodynamic equilibrium are filled in. The equilibrium between v_0 and v_1 is given by the Freundlich isotherm [eq. (16)]:

$$v_1 = v_0 x$$

$$x = \frac{(p/p_0)^{1/a}}{1 - (p/p_0)^{1/a}}$$

and

$$a = e_1/RT = \Pi_1 \sigma / RT \tag{24}$$

Similarly, the following relation holds for all succeeding layers:

$$v_i = v_{i-1}y, \quad i > 1$$

with

$$y = \frac{(p/p_0)^{1/b}}{1 - (p/p_0)^{1/b}}$$

and

$$b = e_2/RT = \Pi_2 \sigma / RT \tag{25}$$

From eqs. (24) and (25) it follows that for v_i

$$v_i = v_0 x y^{i-1}, \quad 1 \leq i \leq n \tag{26}$$

The total size of surface v_m is given by

$$v_m = \sum_{i=0}^{n} v_i \tag{27}$$

while the amount of adsorbate v is related to v_i by

$$v = \sum_{i=1}^{n} i v_i \tag{28}$$
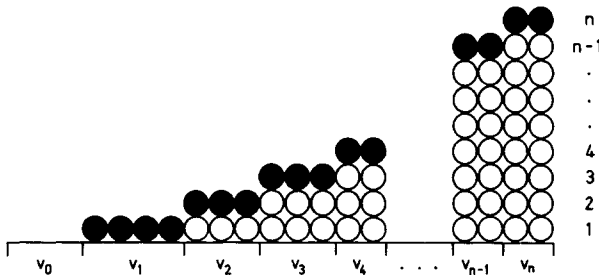

Fig. 3. Diagrammatic presentation of multilayer sorption.

Then

$$\frac{v}{v_m} = \frac{v_0 x \sum_{i=1}^{n} i y^{i-1}}{v_0 \left(1 + x \sum_{i=1}^{n} y^{i-1}\right)} \tag{29}$$

leads to the final result:

$$v = \frac{v_m x [1 - (n+1)y^n + n y^{n+1}]}{(1-y)[1-y+x(1-y^n)]} \tag{30}$$

The variables are the size of the surface v_m, the maximum number of layers n, and the parameters x and y, which are related to the molar surface energies by eqs. (24) and (25). With a monolayer the sum in eq. (29) up to $n = 1$ yields the Freundlich isotherm.

The four parameters may be estimated from experimental data by the following procedure: at very low gas pressures ($p \ll p_0$), only monolayer adsorption is assumed to take place. Thus, from a $\ln v$ versus $\ln(p/p_0)$ plot of experimental data, the constants v_m and a can be determined. At saturation ($p = p_0$), eq. (30) yields by use of the rule of l'Hospital:

$$\lim_{p \to p_0} v = v_m n \tag{31}$$

Using the experimentally determined amount of gas sorbed at $p = p_0$ and the known value v_m results in the number of layers n. The parameter b may then be derived by a least-squares analysis of the experimental data employing eq. (30). If there is any water sorbed by capillary phenomena, which may occur at relative humidities above 85%, both parameters n and b have to be determined by a least-squares analysis using only experimental data which do not include the effects of capillary phenomena.

A finite number of layers might be caused by two reasons. First, when sorption is taking place at two parallel walls, the maximum number of sorbed layers is given by the size of sorbed molecules and the distance between these two walls. The second reason might be that with increasing distance from the surface, the gain in surface energy of a layer decreases, so that e_{n+1} vanishes for the $(n + 1)$th layer. Thus sorption in the $(n + 1)$th is due to a "normal" condensation of the gas occurring only at $p = p_0$, whereas v_{n+1} vanishes for all $p < p_0$. Of course, n is not a constant value describing the number of sorbed layers at the whole surface, but represents a suitable mean value.

As in the discussion of the temperature dependence of the Freundlich parameter a, one may at this point assume temperature-independent changes of surface energies e_1 and e_2, within a suitable temperature interval. Thus, similar to eq. (19), the following relationships between the temperatures T_1 and T_2 and the parameters a_1, a_2, or b_1, b_2, respectively, hold:

$$a_1/a_2 = T_2/T_1$$

$$b_1/b_2 = T_2 T_1 \tag{32}$$

In Figures 4–6 typical isotherms are presented using the multilayer relationship (30) for various values of the parameters a, n, and b. As can be seen from Figure
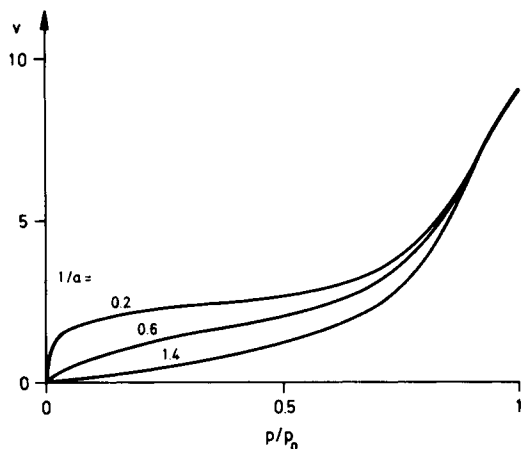
Fig. 4. Effect of the parameter a on the shape of the multilayer isotherm calculated by means of eq. (30).
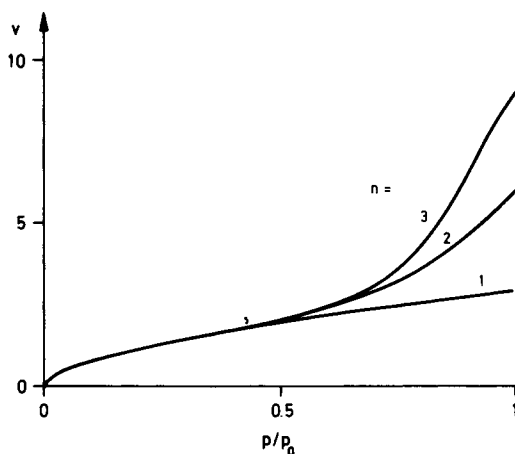

Fig. 5. Effect of the parameter n on the shape of the multilayer isotherm calculated by means of eq. (30).

4, at low vapor pressures a convex curve results for $a > 1$ and a concave curve for $a < 1$, corresponding to the Freundlich type of monolayer sorption. The amount of sorbed gas at $p = p_0$ is directly proportional to n (see Fig. 4), whereas the curvature at intermediate gas pressures is predominated by the parameter b. As can be seen from Figs. 4–6, the new multilayer model describes any of the five typical sorption isotherms presented by Brunauer et al. (see Fig. 1), depending on the choice of the parameters.

Although the construction of the modified multilayer model is very similar to that of the BET model, a four-parameter relationship results, in contrast to the two parameters of the BET model. It should be pointed out that the BET model implicitly contains two additional "parameters," which are assumed to be independent of the system under consideration. These are the number of sorbed layers (being infinite) and the sorption enthalpy of the additional layers (being equal to the condensation enthalpy of the gas). As will be shown later describing the sorption of water in polymers, the number of sorbed layers may
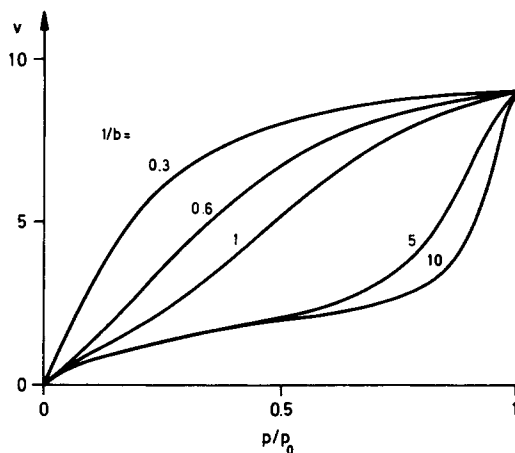
Fig. 6. Effect of the parameter b on the shape of the multilayer isotherm calculated by means of eq. (30).

be assumed to be $n = 2$ for any polymer. In addition, the change of the surface energy at sorption in the second layer can be assumed to be $1/b = 3.8$, independent of the system under consideration, without affecting the good agreement between experimental data and model calculations. Thus the modified model can be considered as a refined two-parameter relationship similar to the BET model.

APPLICATION OF THE MULTILAYER MODEL TO EXPERIMENTAL DATA

Since the experimentally determined partial entropy of sorption is independent of the water content for many polymers,[12] at least at low vapor pressures, and with respect to the discussion of the partial thermodynamic potentials obtained for a Freundlich sorption process, one might reasonably describe the sorption of water in polymers using the modified model presented in this paper. To characterize water sorption in polymers with this multilayer model, first the existence of the underlying assumptions should be checked. The experimental data[12,13] were obtained for binary water–polymer systems by gravimetric determination of the amount of adsorbant. Thus the Gibbs sorption equation presented in eq. (7) is still applicable to the data without any restriction.

A swelling factor of 10 vol %, common to many polymers, and a density of the adsorbed water of 1 g/cm³ will result in a volume V^b of $(10+v)$ mm³/100 mg dry polymer, where v is the water content of the polymer in wt. % referred to the dry polymer. While the maximum density of vapor at a pressure p and at temperatures less than 50°C is $(p/p_0) \times 10^4$ mg/mm³, the amount of vapor n_g within a volume V^b is

$$n_g \leq (10 + v) \frac{p}{p_0} \times 10^{-4} \tag{33}$$

where n_g is given in wt. % referred to the dry polymer. The vapor pressure p corresponds to a water content v. As can be seen from eq. (33), n_g is negligible compared with v. Thus the Gibbs surface excess is equivalent to the water content v.

Experimental data of water sorption on homogeneous cellulose acetate (CA) membranes at 35 and 45°C, as well as the differential thermodynamic functions determined from experimental data by use of eq. (19), have been published recently by the authors.[13] The corresponding experimental results, the values of the model parameters obtained with these data, and the sorption isotherms calculated by means of eq. (30) using the model parameters are presented in Figure 7. As is obvious from this figure, the water sorption isotherm of a homogeneous CA membrane can be rendered by the model relationship in excellent agreement with the experimental data and within the whole range of relative humidity. It might thus be concluded that all the water within a homogeneous CA membrane interacts strongly with the polymer. The polar OH- and COOH-groups, as well as both the O atoms of the cellobiose bond and the O atoms within the rings of the β-glucoside units, might be considered as the corresponding sorption sites. Treating the sorbed water molecules as a two-dimensional gas ascribes two degrees of freedom to them regarding their translational motion. This freedom of motion in two dimensions can be identified with a motion of the sorbed molecules between sorption sites. A motion out of the plane (third dimension) is statistically insignificant and thus negligible. This view is supported by independent calorimetric investigations of water sorption by CA membranes.[14]

The limited number of about two layers of sorbed molecules ($n \simeq 1.9$) might be a consequence of the short-range forces responsible for the water sorption such as dipole–dipole interactions between polar groups of the polymer chains and the water molecules. The action of short-range forces is supported by the values
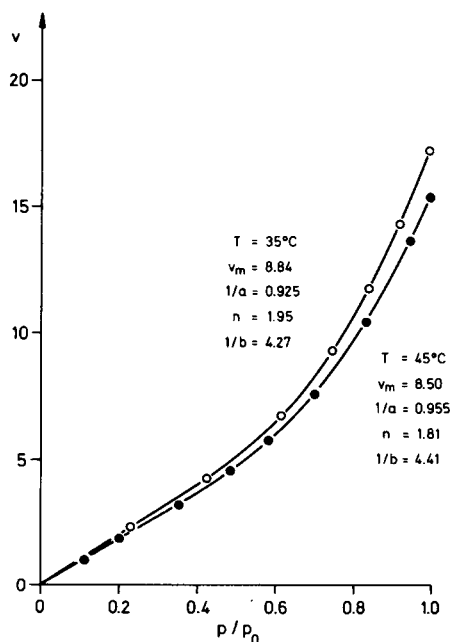

Fig. 7. Sorption isotherms of a homogeneous CA membrane at 35°C (○) and 45°C (●) calculated by use of eq. (30) and the parameter values v_m, n, $1/a$, and $1/b$ specified in the figure. The points represent the experimental data (Ref. 13). v and v_m are given in wt. % referred to the dry weight of the membrane.

of the surface energies of the first and second layer, as the surface energy of the second layer of sorbed molecules is found to be much smaller than the surface energy of the first layer. The parameters a and b, related to the surface energy of the corresponding layer, satisfy eq. (32). Therefore, the surface energies may reasonably be assumed to be independent of temperature within the temperature interval considered. The thermodynamic potentials $\Delta\bar{G}$, $\Delta\bar{H}$, and $\Delta\bar{S}$ might well be obtained from eqs. (20) and (30) if eq. (30) is rearranged to fit the multilayer model relationship numerically:

$$p = p(v)_T$$

The corresponding result (Fig. 8) is in good agreement with experimental values.[13]

Clearly the sorption model presented in this paper does not require the existence of a two-dimensional geometric surface within the membrane, but rather considers a distribution of the sorbed water within the entire bulk phase of the polymer. This picture is in no way identical with the existence of a real solution. The existence of a real solution requires certain degrees of freedom for both the solvent and solute molecules. In contrast, with the present sorption model only the water is considered to move in a plane, whereas the polymer is taken to be equivalent to a rigid matrix.

Water is dissolved in asymmetric CA membranes at relative humidities above 85% by capillary condensation.[13,14] For this reason, only experimental data of water sorption obtained at relative humidities below 85%[13] can be used to determine the model parameters. The experimental data, as well as the resulting isotherms, are presented in Figure 9. Excellent agreement exists between calculated and experimental data at relative humidities below 85%. The disagreement between calculated and measured water content at higher relative humidities might be due to capillary phenomena excluded in the multilayer description.

Table I summarizes the values of the model parameters characterizing water sorption of various polymers. As capillary condensation of water can appear
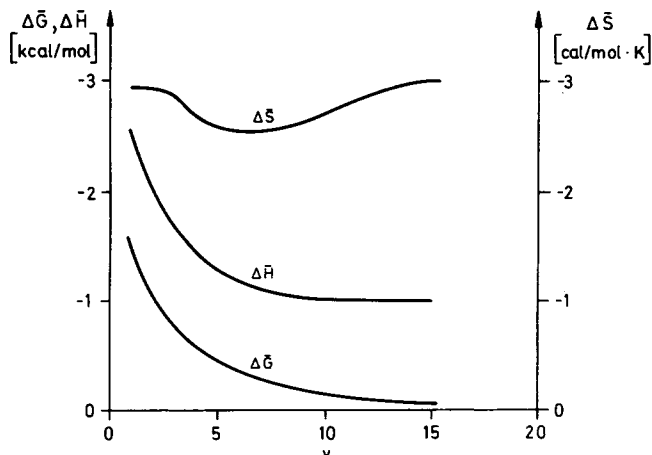

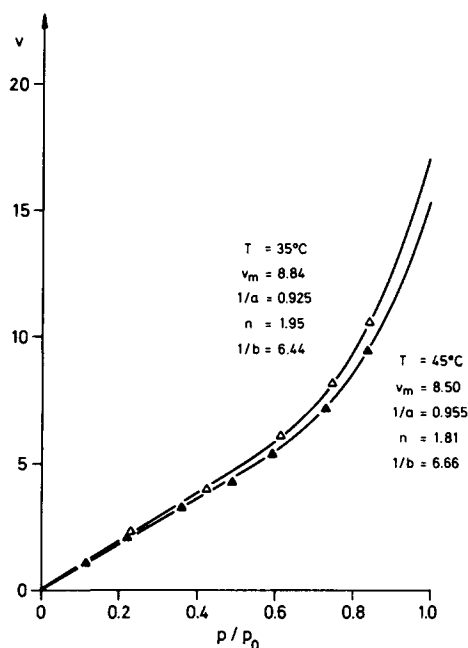Fig. 8. Differential thermodynamic potentials of water sorbed in a homogeneous CA membrane.

Fig. 9. Sorption isotherms of an asymmetric CA membrane at 35°C (△) and 45°C (▲) calculated by use of eq. 30 and the parameter values v_m, n, $1/a$, and $1/b$ specified in the figure. The points represent the experimental data (Ref. 13). v and v_m are given in wt. % referred to the dry weight of the membrane.

TABLE I

Polymer	T, °C	v_m (wt. %)[a]	$1/a$	n	$1/b$
Cellophane	50	12.53	0.55	1.98	3.76
Cellulose-2-acetate	50	10.47	0.84	1.77	3.48
Ethyl-Cellulose	50	2.26	1.00	1.96	3.38
Fibrolan	30	14.88	0.55	2.17	4.18
Nylon 6,6	30	4.00	0.69	1.84	3.37

[a] Referred to the dry weight of the polymer material.

with these polymers at relative humidities above 90%, only experimental data obtained at relative humidities below 90% have been used to determine the parameter values.[12]   Figure 10 shows the experimental data and the isotherms calculated by means of eq. (30).   Certainly the multilayer model characterizes water sorption of polymers and yields calculated sorption isotherms for all systems analyzed in excellent agreement with the experimentally determined ones at relative humidities below 90%.   The difference between calculated and experimentally determined sorption isotherms at relative humidities above 90% might again be due to capillary condensation of water within pores of the polymers, as discussed in connection with the water sorption of asymmetric CA membranes.

As can be seen from Table I, the determination of the model parameters results in about two layers ($n \simeq 2$) of sorbed water for all polymers considered.   Also, the fourth parameter, b, does not vary too much with altering the polymer; a
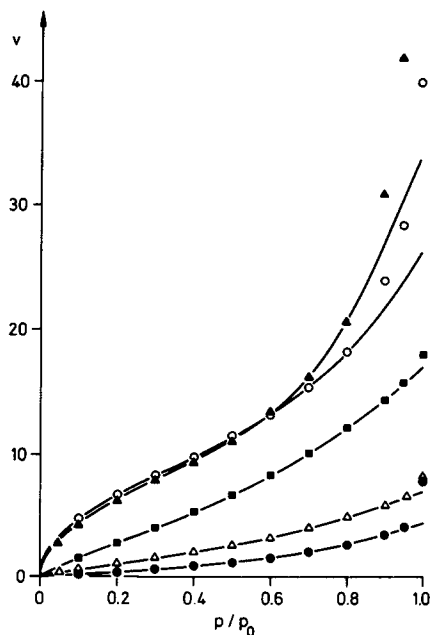
Fig. 10. Sorption isotherms of cellophane (O), cellulose-2-acetate (■), Fibrolan (▲), ethyl-cellulose (●), and nylon 6,6 (△) calculated by use of eq. (30) and the parameter values v_m, n, $1/a$, and $1/b$ specified in Table I. The points represent experimental data taken from the literature (Ref. 12). v and v_m are given in wt. % referred to the dry weight of the membrane.

constant value of $1/b = 3.8$ might thus be used to estimate the water sorption isotherms of the different polymers without any important influence on the shape of the resulting sorption isotherm. The finite value of $n \simeq 2$ for the number of sorbed water layers in polymers as well as the low surface energy of the second layer compared to the surface energy of the first layer are quite consistent with the concepts of the short-range action of the dipole–dipole forces between water molecules and polar groups of the polymer backbone in water–polymer systems. The good agreement between model calculations and experimentally determined water sorption isotherms of different polymers, as well as with the thermodynamic potentials, justifies the application of the model presented in preference to other models to characterize water sorption in polymers more accurately.

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