

MOISTURE SORPTION/DESORPTION OF COLLAGEN

by

A. M. MANICH^{1*}, F. MALDONADO¹, J. CARILLA², M. CATALINA¹ AND A. MARSAL¹

¹*Chemical and Surfactant Technology Department*

²*Thermal Analysis and Calorimetry Service*

IQAC (Institute of Advanced Chemistry of Catalonia)

CSIC (Spanish National Research Council)

JORDI GIRONA, 18-26, 08034 BARCELONA, SPAIN

ABSTRACT

Moisture sorption/desorption of two physical forms of collagen (hide powder and leather) was studied. Despite the fact that the testing of sorption/desorption behaviour is time consuming, the application of a Dynamic Vapour Sorption analyzer enabled us to characterize the sorption/desorption behaviour of materials in a relatively short time. Differences in sorption and desorption can be related to the accessibility and internal tortuosity of the materials. BET and GAB models were used to analyze variations in monolayer sorption capacity (internal sorption surface) of different forms of collagen (hide powder and leather). Variations in the energy constants related to primary and secondary sorption were also considered. Given that tests in desorption were performed, the BET and GAB models were also fitted to desorption and the differences observed in the parameters were analyzed. A model of sorption-desorption for porous materials was devised to account for the differences between sorption and desorption.

RESUMEN

Se ha estudiado la sorción/desorción de humedad de dos formas de colágeno (polvo de piel y cuero). Aunque los ensayos de sorción/desorción son muy largos, la utilización de una termobalanza de sorción de vapor ha permitido determinar el comportamiento de sorción/desorción de los materiales con un tiempo de ensayo relativamente corto. Las diferencias en sorción y desorción se pueden relacionar con la accesibilidad y tortuosidad del material. Se han utilizado los modelos de BET y GAB para analizar las diferencias en la capacidad de sorción de la monocapa (superficie interna de sorción) de las diferentes formas estudiadas. Se han analizado las diferencias en las constantes de energía de sorción de la primera capa y de las capas superiores. Los resultados obtenidos en desorción utilizando los modelos de BET y de GAB se han comparado con los obtenidos en los ensayos de sorción. Se ha comprobado que los resultados en desorción se pueden relacionar de manera más lógica con el comportamiento esperado por las distintas muestras analizadas. Los ajustes de los modelos son mejores si en lugar de tomar los valores proporcionados por la balanza DVS se utilizan las estimaciones del contenido de humedad en el equilibrio. Se estudian también los fenómenos de histéresis que se observan en los ensayos de sorción y desorción.

*Corresponding author e-mail: albert.manich@iqac.csic.es

Manuscript received December 15, 2009, accepted for publication March 23, 2010

INTRODUCTION

When collagen is placed in a given atmosphere, it acts as a moisture buffering body that gradually takes up or loses water until reaching equilibrium. This is a dynamic equilibrium that occurs when the number of water molecules evaporating from the specimen in a given time equals the number of water molecules absorbed. It is well known that the moisture content of collagen/leather exerts an influence on its properties.^{1,2,3} This can develop driving forces causing spatial displacement of the substrate⁴ and modify leather properties in an irreversible way by over drying.^{5,6} The property of sorbing moisture is a valuable characteristic of articles in contact with the human body. It avoids problems caused by accumulation of sweat mainly in the feet, which could give rise to microbiological growth on the skin and in shoes.⁷ The sorption of water causes the leather to act as a heat reservoir, protecting the body from sudden changes in external conditions. Moisture content is one of the most important factors in determining the mechanical and electrical properties of the hygroscopic materials. The moisture buffering ability of leather when used in upholstery enhances the indoor air quality of a room.⁸ To conserve parchment, it is necessary to bear in mind its ability to absorb and release water. Moisture content affects its microbial resistance, aspect and durability.⁹ The fibrous structure and the large concentrations of hydrophilic groups of collagen account for its high water sorption capacity. In a study on water-collagen interactions using rat-tail tendons, Pineri et al.¹⁰ described different mechanisms of water fixation. Grigera et al.¹¹ reported two types of water. One type of water is hydrogen-bonded to the macromolecular backbone at well-defined positions and the other type interacts weakly with a number of different sites, forming a multilayer with more liquid-like properties. This is consistent with the view of Caurie,¹² who described three types of water: a) water adsorbed onto the most energetic sites known as strongly bonded primary sites, b) water consisting of weakly bonded secondary molecules, and c) unbonded free liquid water that condenses at saturation pressure.

Sorption isotherms

It is common knowledge that there is a good correlation between the number of water molecules in a monolayer and the number of polar side chains using the classic Brunauer, Emmett and Teller (BET) multilayer sorption equation. This suggests that each polar group initially sorbs one molecule of water followed by multimolecular sorption at a higher humidity. Despite its limitations, the BET equation is still used to calculate monolayer values in very different physicochemical fields, yielding data sorption specific area values. The BET equation is used because of its simplicity and because it has been approved by the International Union of Pure and Applied Chemistry (IUPAC). In 1985, the Commission on Colloid and

Surface Chemistry recommended the so-called BET plot for a standard evaluation of monolayer values in the relative vapour pressure (water activity) interval between 0.05 and 0.30. The Guggenheim, Andersen and de Boer (GAB) sorption equation also provides monolayer sorption values. It has become more popular because the range of the relative vapour pressure interval is much wider than that of the BET equation (from 0.05 to 0.8-0.9).¹³ The BET and the GAB isotherms are closely related since they are based on the same statistical model. The GAB, which is an improvement on the BET model, shares with it the two original BET constants: a) the monolayer capacity X_m , and b) the energy constant C . The GAB model owes its greater versatility to the introduction of a third constant K .

The energy constants should not be overlooked. They determine the details of the sigmoidal shape of the isotherms, i.e. the form of the normalised X/X_m vs. water activity a_w plot. Thus, C determines the shape of the "knee" at the lower activity range. C is proportional to the ratio between the attachment rate constant and the escape rate constant per unit pressure for the primary sites.¹³ Constant K for the GAB model determines the profile at the higher water activity range, regulating the upswing after the plateau following the "knee" at the medium water activity range. Higher values of K establish a more pronounced upswing. K is related to the attachment rate constant and the escape rate for all higher layers in the system.¹⁴ The lower the value of K , the less structured the state of the sorbate in the multilayers above the monolayer, which is less structured than in the pure liquid state. K increases with stronger interactions between sorbate and sorbent.¹³

The shape of the isotherm reflects the manner in which the water is bonded to the system. In the field of water vapour sorption by a solid sorbent, moisture sorption hysteresis gives rise to two different paths between sorption and desorption. The extent of hysteresis is related to the nature and state of the components of the sample, reflecting their potential for structural and conformational rearrangements, which alter the accessibility of the water to the energetically favourable polar sites. The general shape of the equilibrium water sorption isotherm for collagen can be described by a Type II or Type III isotherm with a small amount of water that persists at a very low relative humidity and a large amount of water at a high relative humidity.¹⁶ Table 1 shows the sorption isotherms and the parameters used to fit the experimental sorption/desorption data. The basic mechanism of equilibrium depends on the balance between the rate of attachment and detachment of water molecules in the sorbed material. The monolayer moisture content calculated from the equilibrium sorption isotherms is essential for the physical and chemical stability of dehydrated materials. At lower water activities water is held by strong hydrophilic sites. When sorbed, water molecules

TABLE 1

BET and GAB models. Parameters used to fit the experimental sorption data

Model	Mathematical equation
BET (21) GAB (22)	$X = X_m C a_w / [(1-a_w)(1-a_w + C a_w)]$ $X = X_m C K a_w / [(1- K a_w)(1- K a_w + C K a_w)]$
Parameter	Definition
a_w	Water activity expressed as vapour relative pressure p/p_0 , where p_0 is the saturated vapour pressure.
X	Equilibrium moisture content at a_w in g sorbed/100g of sorbent on dry basis.
X_m	Monolayer moisture content in g sorbed/100g of sorbent on dry basis d.b.
C	Energy constant related to the difference between the free enthalpy of the water molecules in the pure liquid state and in the monolayer. This is proportional to the rate between both the attachment and the escape rate constants for the primary sites.
K	Ratio between the standard vapour pressure of the liquid and the vapour pressure of the sorbate in the secondary (upper) layers. Proportional to the rate between the attachment rate constant and the escape rate for all higher layers.

can become attached to additional water molecules that are transformed into less firm sorption sites. When the water activity is increased, sorption enters a second region, where sorbed water is more loosely held by hydrogen bonds. This “multilayer region” can be considered a transition phase between the initial and final regions of the isotherm. The least firmly bonded water is produced when the water activity attains the highest levels. In this region, “condensed water” is mechanically entrapped within the voids of the fibre, and has many of the characteristics of liquid water. According to Dent¹⁴ it is possible to calculate the fractions of the total sorption as a function of water activity a_w : variation of empty sites, monolayer moisture content, “primary” and “secondary” water bonded molecules, and the ratio between them.

OBJECTIVE

The main aim of this study is to evaluate the influence of the presentation form and treatments induced in collagen/leather in the surface sorption area, the moisture level at which the monolayer is reached, the moisture holding capacity at saturation, and the hysteresis, by assessing the sorption/desorption isotherms. The results yielded by the BET and GAB models in sorption and desorption are compared using the data provided by the Sorption Analyzer and those given by the predicted sorption values at equilibrium.

MATERIALS

Sorption/desorption tests were performed on fibrous collagen material supplied in powder form and leather. The hide powder provided by the British Leather Confederation (BLC, Northampton, UK) meets the specifications of the Official Hide Powder of the Society of Leather Technologists and Chemists (SLTC). The batch supplied (ref. B34, April 2008) had the following characteristics: ash content 0.36%, pH 6.5, moisture 12.5%.

Three samples were prepared from this material:

- A:** Hide powder humidified and air-dried
- B:** Hide powder humidified and lyophilized exceeding sample A in porosity.
- C:** Hide powder first treated with 24% of sodium dodecyl sulphate (SDS) anionic surfactant from Aldrich and then with 140% of nonylphenol polyethylene oxide with 10 mol EO (NFOE10) nonionic surfactant from Marchon Surfac according to the procedure described by Maldonado et al.¹⁷ resulting in a sample with approximately 38% of hide powder, 9% SDS and 53% NFOE10. The treatment with surfactants was carried out at pH 3.0 and 25°C.

Leather samples were as follows:

D: Bovine leather from Curtidos Mare Nostrum, 1.1 to 1.3 mm in thickness subjected to a conventional chromium tanning process fatliquored with a mixture of resin and sulphited oil and retanned with a Chromium/Mimosa/Melamine mixture.

E: Bovine leather from Curtidos Badía, 1.6 mm in thickness subjected to conventional chromium tanning and finishing process including a hydrophobic treatment during fatliquoring based on Densodrin CD from BASF.

F: Sample E previously dried at 102°C for 5 hours to remove all water.

All six samples were conditioned in a standard atmosphere.¹⁸

METHODS

Sorption and desorption curves were obtained in the Q5000SA Dynamic Vapour Sorption DVS Analyzer from TA Instruments. Sample weights were between 11 and 16 mg.

Measuring procedure:

1. Initial Drying: temperature 60°C, relative humidity 0%, time 1 h.
2. Pre-stabilization: temperature 25°C, relative humidity RH 0% and then, initial adsorption kinetics at RH 5%.

TABLE 2

Moisture content at the end of each step of sorption and desorption X_e and at equilibrium X_∞ in % on dry basis of hide powder samples A, B and C according to the relative humidity (water activity) of the step.

RH/% or $100 \times a_w$	Sample A		Sample B		Sample C	
	X_e	X_∞	X_e	X_∞	X_e	X_∞
Sorption test:						
5	1.57	2.31	2.31	2.49	0.79	0.81
15	5.02	5.81	6.04	6.22	2.39	2.44
25	8.07	8.71	9.05	9.28	3.87	3.94
35	11.13	11.23	11.87	11.89	5.42	5.49
45	14.37	14.45	14.82	14.85	7.12	7.22
55	17.86	17.88	18.00	18.01	9.15	9.16
65	21.74	21.75	21.77	21.77	11.83	11.84
75	26.51	26.52	27.04	27.05	15.87	15.88
85	32.97	32.99	34.17	34.19	22.59	22.62
95	45.65	45.77	47.06	47.17	39.30	39.42
Desorption test:						
85	34.70	34.68	35.90	35.89	22.99	22.92
75	28.79	28.76	29.92	29.88	16.37	16.37
65	24.53	24.23	25.58	25.33	12.50	12.48
55	21.03	20.78	22.07	21.84	9.84	9.82
45	17.86	17.59	18.86	18.64	7.85	7.81
35	14.82	14.50	15.77	15.55	6.08	6.06
25	11.76	11.42	12.68	12.43	4.57	4.54
15	8.39	8.01	9.21	8.97	3.06	3.03
5	4.14	3.58	4.64	4.36	1.36	1.34

TABLE 3

Moisture content at the end of each step of sorption and desorption X_e and at equilibrium X_∞ in % on dry basis of leather samples D, E and F according to the relative humidity (water activity) of the step.

RH/% or 100×aw	Sample D		Sample E		Sample F	
	X_e	X_∞	X_e	X_∞	X_e	X_∞
Sorption test:						
5	2.06	2.24	1.79	1.93	0.93	0.99
15	4.67	4.89	4.61	4.81	2.77	2.86
25	6.77	6.80	6.82	7.16	4.85	5.36
35	8.68	8.76	8.77	8.87	6.94	7.16
45	10.65	10.78	10.62	10.77	8.96	9.25
55	12.81	12.94	12.39	12.54	11.05	11.33
65	15.20	15.31	14.18	14.29	13.36	13.55
75	18.11	18.21	16.43	16.55	16.22	16.37
85	22.13	22.24	20.57	20.68	20.45	20.53
95	30.15	31.99	29.66	30.96	28.97	30.01
Desorption test:						
85	25.33	24.78	24.92	24.50	24.32	23.94
75	21.72	21.19	21.40	20.98	20.91	20.50
65	18.75	17.74	18.73	18.29	18.29	17.85
55	16.44	16.05	16.50	16.04	16.14	15.65
45	14.31	13.84	14.44	13.98	14.10	13.57
35	12.24	11.82	12.42	11.94	12.08	11.58
25	10.08	9.68	10.30	9.86	9.98	9.52
15	7.63	7.24	7.72	7.37	7.44	7.08
5	4.37	3.83	4.14	3.76	3.88	3.51

- Sorption steps: the sample previously stabilized at 5% RH is subjected to sorption tests that progressively increase from 15% to 95% in steps of 10% RH. The sample is stabilized at 95% RH after the last step.
- Desorption steps: the sample stabilized at 95% RH after the sorption kinetics is subjected to desorption tests that progressively decrease from 85% to 5% in steps of 10% RH. The sample is stabilized at 5% RH after the last step.
- Final step conditions: each step lasts a maximum time of 500 min. However, if the variation in weight is lower than 0.02% for 10 min, the step is concluded.

Based on the moisture content at the end of each step, the

software provided by TA Instruments fits the BET and GAB models to the experimental data. Although the final moisture content is close to that of the equilibrium, it does not coincide with it. It is therefore recommendable to estimate the moisture content at each step when equilibrium is reached.

RESULTS

The moisture content of the samples at the end of each step when equilibrium is reached can be estimated by using a methodology devised by the authors (19). Tables 2 and 3 show the moisture content in % on dry basis at the end of each step (X_e) yielded by the DVS analyzer as a function of water activity or relative humidity. Tables 2 and 3 also show the values of the moisture content estimated at equilibrium X_∞ .

Modelling the Sorption/Desorption Processes

The BET and GAB fits were obtained by using the values of sorption provided by the DVS. To obtain the BET fit, a non-linear regression of the inverse of equation (20) was carried out using the initial estimators given by the linear regression $a_w/[1-(a_w)X]=A+B \times a_w$ being $C=1+B/A$ and $X_m=1/(C \times A)$. The value of a_w at which the monolayer moisture content X_m was reached, was obtained from $a_w(X_m) = (\sqrt{C} - 1)/(C - 1)$.

The calculation of the GAB fit was made following the methodology described by Timmermann.¹³ The first estimators of the GAB parameters were derived through the polynomial regression $a_w/X = c + b \times a_w + a \times a_w^2$, the estimators of X_m , C and K being those obtained from the equations $f = b^2 - 4ac$, $K = (b + \sqrt{f})/(2c)$, $C = 2 + b/(aK)$ and $X_m = 1/\sqrt{f}$. The estimators were used to carry out the non-linear regression of the inverse model of equation.²¹ Thereafter, a second non-linear regression using the results obtained by the first non-linear regression as initial estimators was used to obtain the model parameters of equation.²¹ The GAB sorption model enabled us to predict the moisture sorbed at saturation ($a_w=1$), which represents the moisture holding capacity of the sample X_s , whenever K is

lower than 1. The holding capacity of samples A, B and C was 53.62, 56.45 and 59.35 %, respectively. That of samples D, E and F was 35.09, 34.82 and 34.38 %, respectively. When the GAB model was fitted to desorption, the moisture holding capacity X_d was considered. The results of sorption and desorption are shown in Table 4.

The application of the same methodology to the sorption/desorption estimated at equilibrium gave the corresponding parameters of the BET and GAB models. The moisture holding capacity X_e at equilibrium for hide powder samples A, B and C was 54.38, 56.77, 59.76 %, respectively. That of samples D, E and F was 38.02, 36.87 and 36.03 %. The moisture holding capacity at equilibrium X_e was considered when the GAB model was fitted to desorption. The results are given in Table 5.

The sorption surface area

The sorption surface area S can be calculated through equation $S = 0.01 X_m L n / M$ (22), where S is the area (m^2/g), L the surface covered by a water molecule ($10.6 \times 10^{-20} m^2$), M the molecular weight of water (18 g/mol) and n Avogadro's number (6.022×10^{23}).

TABLE 4

Monolayer capacity X_m , constants C and K for BET and GAB models fit to the moisture content given by the DVS and determination coefficient R^2 .

Sample	BET Model			GAB Model				
	Ref.	X_m	C	R^2	X_m	C	K	R^2
Sorption tests:								
A		14.89	2.123	99.907	13.11	4.325	0.771	99.878
B		11.19	4.642	99.976	12.19	6.013	0.793	99.976
C		6.43	2.514	99.970	5.61	4.090	0.908	99.981
D		7.13	7.182	99.997	8.43	8.040	0.768	99.876
E		8.18	4.998	99.960	7.38	10.979	0.793	99.340
F		8.32	2.256	99.996	7.84	4.363	0.785	99.774
Desorption tests:								
A		11.29	10.144	99.973	13.50	10.887	0.754	99.876
B		11.94	11.102	99.986	13.73	13.001	0.761	99.816
C		4.87	6.836	99.952	5.58	6.376	0.907	99.989
D		8.77	17.029	99.955	11.08	15.608	0.692	99.932
E		9.24	14.068	99.981	11.09	16.014	0.688	99.873
F		9.11	12.914	99.984	10.80	15.433	0.692	99.833

TABLE 5

Monolayer capacity X_m , constants C and K of BET and GAB fits using the sorption/desorption values at equilibrium X_∞ and determination coefficient R^2 .

Sample	BET Model			GAB Model			
Ref.	X_m	C	R^2	X_m	C	K	R^2
Sorption tests:							
A	10.22	5.204	99.985	12.26	5.584	0.785	99.923
B	10.76	5.360	99.982	12.00	6.478	0.797	99.980
C	6.46	2.574	99.969	5.57	4.294	0.909	99.981
D	6.95	8.389	99.999	7.86	9.868	0.798	99.704
E	8.14	5.535	99.947	7.13	13.089	0.810	99.117
F	8.58	2.335	99.940	7.44	5.305	0.803	99.627
Desorption tests:							
A	11.84	7.663	99.997	13.40	9.765	0.760	99.869
B	12.01	9.991	99.995	13.63	12.213	0.764	99.831
C	4.87	6.704	99.951	5.55	6.365	0.908	99.987
D	8.80	13.393	99.991	9.85	17.148	0.743	99.710
E	9.12	12.244	99.980	10.17	16.573	0.727	99.692
F	8.98	11.242	99.975	9.97	15.567	0.727	99.700

Selecting the best model and procedure

Hide powder sample B was obtained from sample A after wetting and lyophilization. Consequently, it follows that the monolayer sorption capacity of sample B will exceed that of sample A. Sample C was obtained by subjecting sample A to a surfactant treatment, and its collagen content is approximately 38% of that of sample A. Thus, it follows that the monolayer capacity of sample C will be approximately 38% of that of sample A. The higher monolayer capacity of sample B is observed in desorption test and the differences in the estimation of monolayer capacity between the BET and GAB models in desorption are lower when moisture contents used are those estimated at equilibrium. Under these conditions, the monolayer capacity of sample C best approximates the collagen content of the sample. For comparison, models were fitted to desorption using the moisture content at equilibrium. The GAB model was preferred to the BET model because it enabled us to manage the evolution of secondary sorbed water. Consequently, the influence of the sample type and treatment on the sorption/desorption isotherms was evaluated using the GAB model with the estimated moisture content at equilibrium. The estimation of monolayer capacity, sorption surface area and energy constants for primary and secondary sorbed layers was based on the desorption isotherms.

DISCUSSION

The monolayer moisture content

As regards the results given by the GAB model in desorption using the moisture content of the samples at equilibrium, sample C shows the lowest monolayer sorption capacity followed by that of the leather samples D (1.2 mm in thickness) and E and F (1.6 mm in thickness). The highest monolayer capacities are those of hide powder samples A and B, the latter lyophilized. The monolayer capacity of sample C is 41% of that of sample A, which resembles the collagen content of sample C, which is approximately 38% of sample A.

Energy constant C of primary sorbed monolayer

Hide powder samples show low values of constant C , the lowest being that of the hide powder treated with surfactant (sample C) and the highest that of the lyophilized one (sample B). Leather samples show a higher constant. Leathers subjected to hydrophobic treatment show a constant lower than that of the leather without this treatment. Drying of the hydrophobic sample additionally decreases the constant. The evolution of the energy constant C as a function of moisture holding capacity X_i is plotted in Figure 1. The evolution of C seems to be consistent with the binding energy of primary sites. The surfactant treatment enabled the sample to sorb a large

amount of moisture at higher water activities, resulting in a maximum moisture holding capacity despite the low content of collagen (38%). The presence of surfactant accounts for the low value of the energy constant. Higher constants are those of the hide powder samples, which because of their morphology, show a higher moisture escape rate from primary sites than the leather samples. Lyophilization caused sample B to be more accessible to moisture, increasing its monolayer capacity and the energy constant. Leather samples show higher constants. Sample D (conventionally tanned 1.2 mm in thickness) shows the highest sorption capacity at saturation followed by the thickest leather E (hydrophobically treated) which shows a lower energy constant followed by that of sample F.

Energy constant K of secondary upper sorbed layers

It is well known that the higher the constant, the higher the relationship between the attachment rate of moisture on subsequent secondary layers and their escape rate. This results in a higher number of sorbed layers. This can be clearly seen in Figure 2, which plots the relationship between K and the number of sorbed layers at saturation X_1/X_m . The thickest leather samples E and F subjected to hydrophobic treatment give the same lowest K value followed by the thinner leather sample D, which is conventionally tanned. Leather samples yield K values lower than 0.75, which correspond to a maximum number of sorbed layers at saturation lower than 4. Hide powder samples A and B show values of K exceeding 0.75 and the number of sorbed layers is slightly higher than 4. Lyophilization favoured an increase in K and, consequently, in the sorption capacity of the sample. Finally, the hide powder sample treated with surfactant yields the highest value of constant K , exceeding 0.9, which enables the sample to absorb more than 10 layers at saturation. The relationship between the number of maximum sorbed layers and constant K is in line with the relationship: $X_m/X_1 = 1.014 - 1.014 \times K$ with a correlation coefficient of 0.9997.

Hysteresis between sorption and desorption

Hysteresis is related to the potential for structural and conformational rearrangements that alter the accessibility of energetically polar sites.²² Figure 3 illustrates a possible explanation of the alteration of the moisture accessibility of sorption sites into a porous material. This can account for hysteresis and for the differences in the estimation of monolayer sorption capacity between sorption and desorption. The diffusion process begins with the penetration of moisture passing through the entrance of a pore. The molecules are attached to sorption sites close to the entrance. Subsequent molecules have two options: a) to be attached onto primary sorbed molecules forming a secondary sorbed layer or b) to reach the inner sorption sites, increasing the primary sorbed monolayer. In sorption, primary and secondary sorbed molecules at the entrance can obstruct the penetration of water molecules to the inner part of the pore, resulting in a decreased estimation of monolayer capacity and a lower moisture content

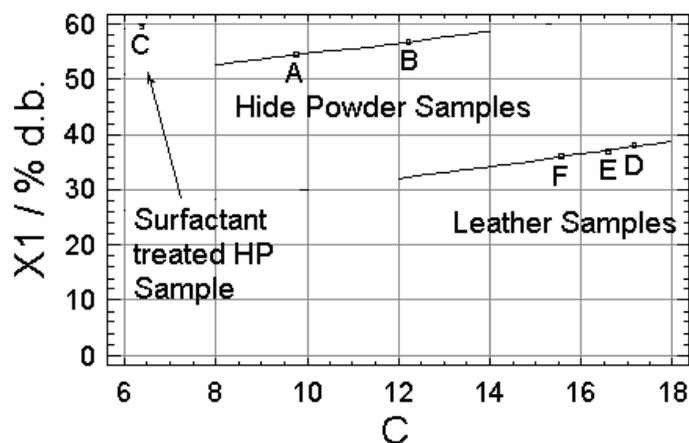


Figure 1. Energy constant C for primary sorption sites and moisture holding capacity X_1 at saturation according to sample reference.

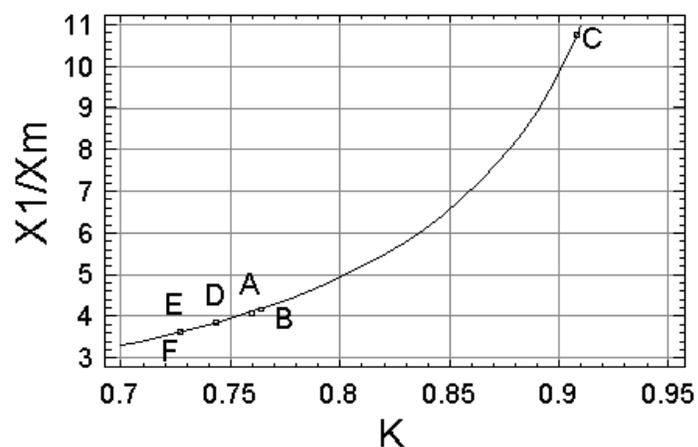


Figure 2. Relationship between the number of maximum sorbed layers X_1/X_m at saturation and constant K of GAB model according to sample type.

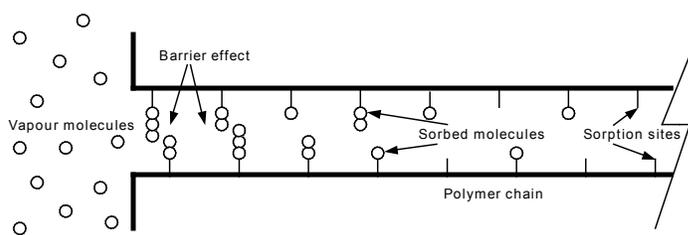


Figure 3. Physical picture of moisture sorption in a pore to explain the differences in monolayer capacity between sorption and desorption.

at all water activities. Moisture sorption and desorption is a dynamic equilibrium and with time some of the secondary sorbed molecules near the entrance can migrate to inner sites, contributing to an increase in the monolayer and to a better balance of the moisture content between the cover and the core of the sample. At saturation, when the equilibrium is attained, the sample reaches its moisture holding capacity and the monolayer is complete.

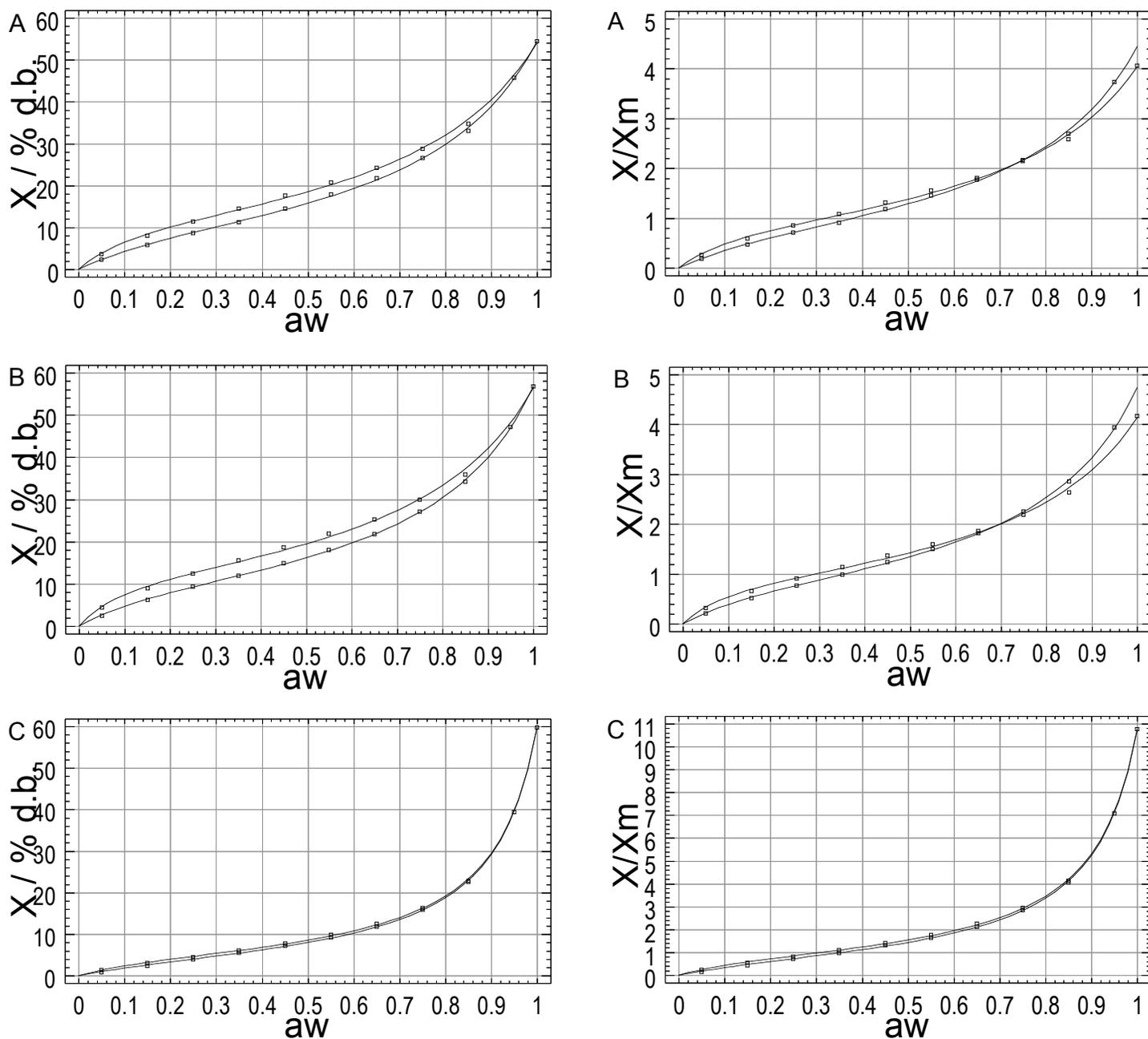


Figure 4: Moisture sorption/desorption X in g of moisture per 100 g of dry sample vs. water activity (left), and in normalized plot X/X_m (number of sorbed layers) vs. water activity (right), of hide powder samples A, B (lyophilized) and C (surfactant treated).

In desorption, the secondary sorbed molecules near the entrance will be the first to be desorbed, being progressively followed by the more internally secondary sorbed molecules. When desorption begins, the number of primary sorbed molecules is the highest. This reduces the desorption amount per unit of decrease in water activity, resulting in higher values than in sorption at the same level of water activity. This accounts for the differences between the normalized curves X/X_m of sorption and desorption. At saturation, the number of layers reached in sorption is higher than in desorption although the moisture holding capacity is the same.

The left side of Figure 4 plots the moisture content X of the hide powder samples as a function of water activity a_w in sorption and in desorption measured in % of water on dry basis. The right side plots the normalized form (X/X_m) of moisture content (number N of sorbed layers) vs. water activity. Figure 5 shows the same plots for leather samples. The curves that reach the highest value at $a_w = 1$ are those of sorption $N_s = X_s/X_{mS}$ whereas the other ones, which at $a_w = 1$ are below, are those of desorption $N_D = X_D/X_{mD}$, which rise above the curves of sorption at low values of water activity. The curve on the left side enables us to estimate

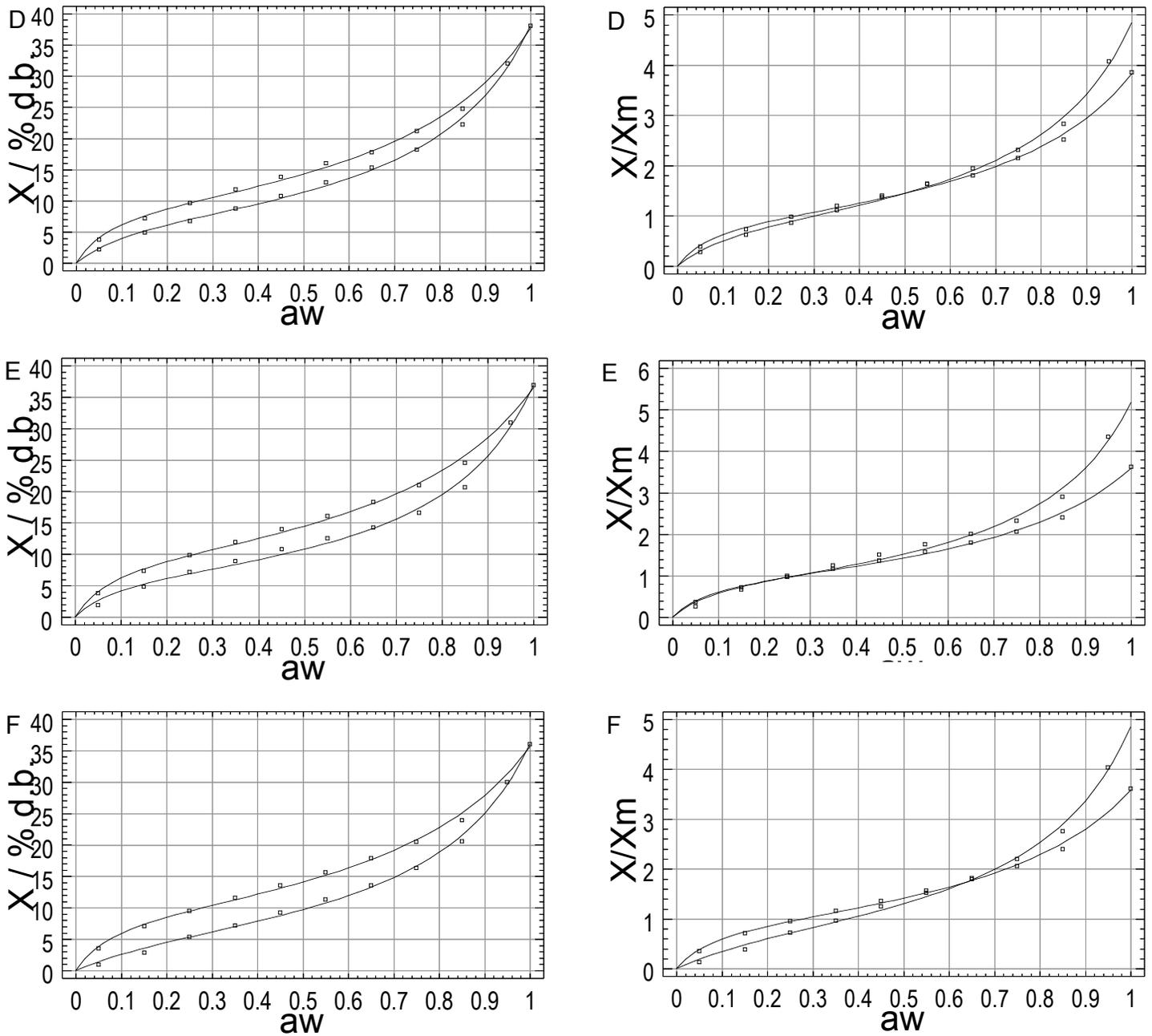


Figure 5: Moisture sorption/desorption X in g of moisture per 100 g of dry sample vs. water activity (left), and in the normalized plot X/X_m (number of sorbed layers) vs. water activity (right), of leather samples D, 1.2 mm in thickness conventionally tanned, E, 1.6 mm in thickness subjected to hydrophobic treatment, and F is obtained from E after dry treatment in an oven at 102°C for 5 hours.

the moisture holding capacity X_f . The hysteresis between sorption and desorption can be measured by the difference in moisture content between desorption and sorption at a water activity of 0.5: $\Delta X_{0.5} = X_{0.5D} - X_{0.5S}$.

The curves on the right side estimate the hysteresis between sorption and desorption from the perspective of the primary sorbed layer. The monolayer capacity measured in sorption X_{mS} is normally lower than that measured in desorption X_{mD} owing to the obstructive effect of the secondary

sorbed molecules. As observed on the right side of Figures 4 and 5, the higher the differences between X_{mD} and X_{mS} , the lower the water activity at which the number of sorbed layers in sorption NS equals that of desorption ND . Based on these results, two additional estimations of hysteresis can be made although they are more directly related to the monolayer content. The results of $\Delta X_{0.5}$, X_{mS}/X_{mD} and $(aw)_{NS=ND}$ are shown in Table 6. There is a clear relationship between the variation in monolayer capacities X_{mS}/X_{mD} and the level of water activity at which the

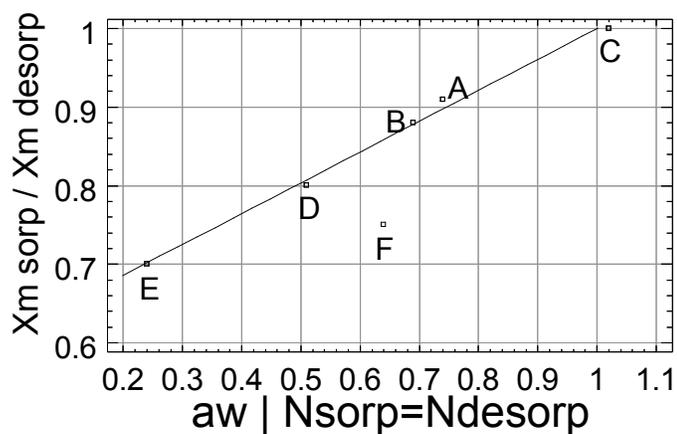


Figure 6. Relationship between hysteresis of collagen samples measured by the rate between monolayer capacities X_{mS}/X_{mD} in sorption and desorption and the level of water activity at which the content of sorbed layers in sorption and in desorption is the same $(aw)_{NS=ND}$.

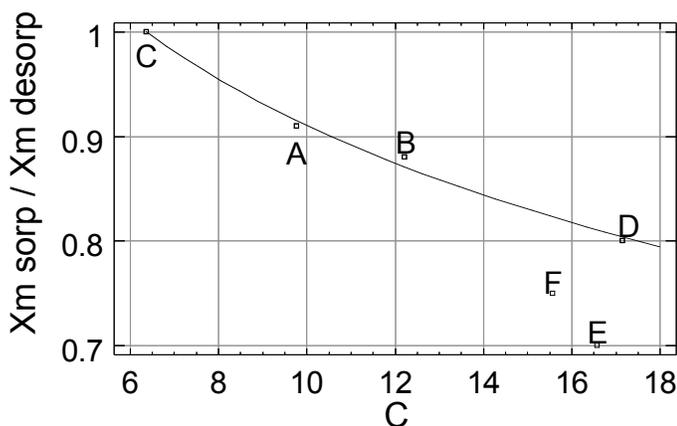


Figure 7. Relationship between hysteresis of the monolayer measured by the rate between monolayer capacities X_{mS}/X_{mD} in sorption and desorption and the energy constant C of the primary layer.

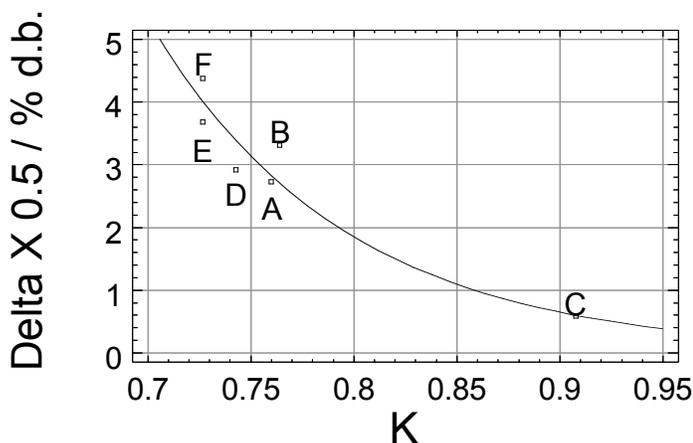


Figure 8. Relationship between hysteresis in humidity content between sorption and desorption at a water activity of 0.5 $\Delta X_{0.5}$ and the constant K of secondary layers.

number of sorbed layers equals that of desorption $(aw)_{NS=ND}$ (see Figure 6). Hide powder and leather samples are on a straight line except sample F dried at 102°C for 5 hours. Both parameters can account for hysteresis linked to the monolayer. Figure 7 shows the relationship between the monolayer capacity rate X_{mS}/X_{mD} and the energy constant of the monolayer C . The higher the hysteresis (lower values of X_{mS}/X_{mD}) the greater the energy constant of the primary sorbed molecules. Although the hydrophobic treatment of samples E and F does not affect the energy constant, it increases the effect of hysteresis. This is expected since hydrophobicity may obstruct both sorption and desorption of water molecules linked to the monolayer.

Figure 8 plots the differences in humidity content between sorption and desorption at water activity of 0.5 ($\Delta X_{0.5}$) and the constant K of secondary layers. It can be observed that the lower the energy constant K (lower number of sorbed layers), the higher the hysteresis. This is probably due to the secondary layers. Samples subjected to a hydrophobic treatment show the lowest values of K and the highest hysteresis.

Water activity corresponding to the monolayer moisture content and sorption surface area

Water activity at which the moisture content of the sample is that of the monolayer ($a_{w,m}$) can be graphically measured on the right side of Figures 4 and 5. This can be determined from the BET model by $(\sqrt{C-1})/(C-1)$ and from the GAB equation by $(\sqrt{C-1})/[K(C-1)]$. Up to this level of water activity, moisture is strongly linked to the sorbent and can be regarded as a hydrated form of the sorbent. It is not possible to degrade the sorbent by hydrolysis and/or by microbiological activity. This level of water activity can be considered as an upper limit for an adequate long-term storage of the sorbent. Water activities corresponding to the monolayer and sorption surface area are shown in Table 7.

CONCLUSIONS

In the light of our findings, the following conclusions may be drawn:

- Moisture sorption/desorption tests can be performed in a limited range of time by setting conditions to shorten the trials. Nevertheless, it is recommendable to estimate the moisture content at equilibrium.
- GAB model in desorption yielded more consistent results in monolayer capacity of hide powder and leather samples. The application of the estimated values of moisture content at equilibrium decreased the differences in the estimation of monolayer capacities between the BET and the GAB methods.

TABLE 6

Hysteresis measured through the differences in humidity content between sorption and desorption at a water activity of 0.5 $\Delta X_{0.5}$ (Figs 4&5 left side), relationship between monolayer capacities X_{mS}/X_{mD} and water activity $(aw)_{NS=ND}$ at which the number of sorbed layers in sorption N_S equals that in desorption N_D .

Parameter	A	B	C	D	E	F
$\Delta X_{0.5}$	2.72	3.31	0.58	2.91	3.68	4.37
X_{mS}/X_{mD}	0.91	0.88	1.00	0.80	0.70	0.75
$(aw)_{NS=ND}$	0.74	0.69	1.02	0.51	0.24	0.64

TABLE 7

Sorption surface area S (m^2/g) determined through the monolayer capacity X_m and water activity $(aw)_m$ at which the monolayer is reached.

Parameter	A	B	C	D	E	F
S	475.2	483.4	196.8	349.3	360.7	353.8
$(aw)_m$	0.32	0.29	0.31	0.26	0.27	0.28

- GAB model enabled us to estimate the moisture holding capacity, which can reach values close to 60% on dry basis for hide powder samples and close to 40% for leather samples. The sample forms and the treatments applied can modify the moisture holding capacity by 20% on dry basis.
- The energy constant of the primary sorbed monolayer was influenced by the sample forms and by the treatments applied. Leather samples showed the highest values of the constant (higher than 15) although hydrophobic and drying treatments slightly decreased it. As regards hide powder, the energy constant ranged between 9 and 13, the highest being that of the lyophilized hide powder sample. The surfactant treated hide powder sample showed the lowest value of the constant, lower than 7.
- The energy constant of the secondary upper layers showed a good relationship with the number of sorbed layers, being influenced by the sample form and by the treatments applied. Leather samples sorbed less than 4 layers of water molecules and their constant was below 0.75, the lowest being those of the thickest and hydrophobic treated leathers. Hide powder samples sorbed more than 4 layers of water molecules, the constant exceeding 0.75. The surfactant treated hide powder sample sorbed more than 10 water molecule layers and the constant was higher than 0.9.

- Hysteresis between sorption and desorption can be measured by differences in moisture content between desorption and sorption at a water activity of 0.5 or between the estimated monolayer capacities in sorption and in desorption. The former is better related to the energy constant of secondary upper layers. Hysteresis increased as the constant decreased. The lower the number of sorbed layers, the higher the hysteresis, the highest being that of the hydrophobic treated leather samples. As regards the relationship between monolayer capacities in sorption and desorption, the hysteresis increased with the energy constant of the primary layer. Leather samples showed higher hysteresis than hide powder samples and the surfactant treated sample showed practically no effect of hysteresis.

- The sample type and the treatments applied considerably influenced the sorption-desorption behaviour of the samples.

ACKNOWLEDGEMENTS

The authors are indebted to the Spanish Project MAT2007-66569-C02-02 for funding. They are also indebted to Ms. A. Lopez and C. Ferrero for their assistance in the experimental work and to Mr. George von Knorring for improving the final version of the manuscript.

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