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The effect of internal lipids on the water sorption kinetics of keratinised tissues

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Abstract Water has a large influence on the properties of keratinised tissues. The water diffusion properties of keratinised tissues are known to be governed by the cell membrane complex, which is mainly composed of internal lipids. The main aim of this work was to characterise the differences in the water sorption and desorption behaviour of human hair and stratum corneum (SC) both with and without internal lipids. Absorption and desorption curves were obtained using a thermogravimetric balance equipped with a controlled humidity chamber. The results demonstrate that the role of the intercellular lipids in the SC is more marked than in hair, which is likely due to the greater amount of lipids present in its structure. Therefore, lipid structures in the SC are essential both to prevent changes in the water-holding capacity of the skin and to maintain the water permeability of the SC.

Keywords Stratum corneum · Human hair · Internal lipids · Water diffusion

Introduction

Hair is a keratinised fibre with low lipid content (1–9 % dry weight). The role of lipids in human hair is mainly related to its mechanical properties. Despite the low lipid content of hair (especially compared to proteins, which make up <90 % of hair), a number of studies have suggested that hair internal lipids can contribute to physicochemical phenomena such as diffusion, cell cohesion and mechanical strength [1]. However, their presence can also be fundamental in maintaining the internal water content of the fibre. The amount of water in hair plays a crucial role in its physical and cosmetic properties [2].

Analytical and physicochemical studies reveal considerable resemblance between the internal hair lipids and the lipids from the SC of human skin [3–6]. These lipids are rich in ceramides, cholesterol, free fatty acids and cholesterol sulphate [1, 7]. At room temperature, these lipids are ordered as bilayers in a solid crystalline state. It is well known that the permeability of the skin, which prevents water loss and penetration of harmful chemicals from the environment, is localised on the horny layer (SC) of the epidermis [8, 9]. The SC, which is directly responsible for the skin's function as a barrier, is composed of dead keratinised cells embedded in a continuous extracellular lipid structure. The protective mechanical properties of the SC cells are intimately linked to their water content. The intercellular lipids of the SC play an important role in the barrier function of human skin by protecting it from external agents and by controlling transepidermal water loss, thereby maintaining the physiological water content of the skin [6, 10, 11]. Modification of intercellular lipid organisation and composition may impair these properties [12]. Thus, hair internal lipids could enhance barrier function preventing external materials from penetrating the keratin fibres as in the case of skin [13, 14].

Water exerts a large influence on the properties of the keratin tissues. The water diffusion properties of the keratinised tissues are known to be governed by the cell membrane complex (CMC), which is mainly composed of internal lipids. The amount of water in a sample may be expressed in terms of either regain or moisture content.

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Regain refers to the mass of adsorbed water divided by the mass of the dry sample, whereas moisture content is the same mass of adsorbed water divided by the total mass of the sample [15]. A water sorption isotherm is measured by isothermally applying discrete, cumulative humidity changes and monitoring the dynamic and static aspects of sorption, from which diffusion coefficients and equilibrium water contents can be deduced. The moisture sorption isotherm of keratins has been the subject of several studies, and models have been specially developed for describing the moisture sorption and desorption data. The Vrentas and Vrentas model emphasises the role of a glass transition in generating the sigmoidal shape of the adsorption isotherm [16]. The uptake of water by polar polymers has been described by the Flory–Huggins equation [17]. It is a common knowledge that there is a good correlation between the number of water molecules present in a monolayer and the number of polar side chains present using the classic Brunauer, Emmet and Teller (BET) sorption equation [15]. The BET equation is used because of its simplicity and because it has the approval of the International Union of Pure and Applied Chemistry (IUPAC). However, the Guggenheim, Andersen and de Boer (GAB) sorption equation also provides monolayer sorption values and has become more popular because the range of relative vapour pressure intervals is much wider than that of the BET equation [18]. The BET and the GAB isotherms are closely related because they are based on the same statistical model. The GAB model is an improvement on the BET model and shares with it the two original BET constants: (a) the monolayer capacity, *Wm* and (b) the energy constant, *Cg*.

The main aim of this study is to evaluate differences in water sorption and desorption of keratinised tissues (SC and hair) with and without internal lipids. Intercellular lipids have been removed using organic solvent extractions. To this end, sorption isotherms and the kinetics of these processes are discussed in this work.

Methodology

SC isolation

Human skin from various sources, including cosmetic surgery and amputations, has been used for the in vitro assessment of SC properties. However, its availability is limited, and animal skin is therefore frequently used [19, 20]. Porcine skin is a well accepted and readily available model of the human skin barrier and is often used to assess topical and transdermal pharmaceutical formulations either in vivo [21] or in vitro [22]. The porcine SC is known to show both similarities and dissimilarities in structure with human SC. The main difference between the two types of SC is based on the thickness. In a previous study, where the role of the SC thickness in the water permeability through the tissue was evaluated, the suitability of porcine skin for permeation studies was demonstrated [23]. Therefore, pig skin was used in this study. Sections of fresh skin obtained from young pigs, weighing 20–30 kg, were placed in water at 70 °C for 3–4 min, and the epidermis was scrapped off in sheets. To isolate the SC, the epidermal sheets were incubated for 2 h at 37 °C with the epidermal side in contact with a solution of 0.5 % trypsin in PBS at pH 7.4. Trypsin is used to remove adherent cells from the epidermis. After the 2-h treatment, the trypsin was removed by several washes with Milli-Q water [24].

Lipid extraction of human hair and SC

One gram of SC or human hair was submitted to solvent extraction. The internal lipids were extracted at room temperature for 2 h with different mixtures of chloroform–methanol (2:1, 1:1 and 1:2, v/v) (10 mL of the solvent mixture each extraction) and finally extracted with methanol overnight (10 mL) (delipidised SC and hair samples: DL SC and DL HAIR).

Sorption experiments

Absorption and desorption curves were obtained using a thermogravimetric balance equipped with a controlled humidity chamber at a constant temperature (Q5000SA Sorption Analyser, TA Instruments, New Castle, USA). The mass of the analysed keratin samples ranged between 6 and 9 mg. Despite the temperature dependence of water sorption, in this case, all experiments were conducted at 25 °C and a total gas flow of 200 mL min^{-1} following the same procedure:

1. *Initial drying* Temperature 60 °C and 0 % relative humidity (RH) overnight.
2. *Pre stabilisation* Temperature 25 °C, 0 % RH and then initial adsorption kinetics at 5 % RH.
3. *Adsorption curve* The sample previously stabilised at 5 % RH is subjected to progressively increasing by steps of 10 % RH up to a maximum of 95 % RH. The samples remained at each step until its mass reached equilibrium (defined by a change in mass of less than 0.02 % per minute for 10 min).
4. *Desorption curve* The sample stabilised at 95 % RH after the adsorption experiment is exposed to progressively decreasing steps of 10 % RH down to a minimum of 5 % RH. The samples remained at each stage until its mass reached equilibrium (defined by a

change in mass of less than 0.02 % per minute for 10 min).

The high reproducibility of these measurements was established previously in the validation study of this instrument, in which three replicates on a single sample gave consistent sorption isotherms. Due to the long time required to measure a complete isotherm (2.5 days) and the reproducibility of the data generated, only one measurement was taken for each sample.

In this work, the sorption isotherm data were modelled according to the BET and GAB models, in line with other studies [15, 25, 26].

Table 1 shows the sorption isotherms and the parameters used to fit the experimental sorption/desorption data. The goodness of the fit was evaluated by the determination coefficient (R^2).

The absorption/desorption curve of each step was also fitted to a kinetic model that enables numerical values of the rate to be determined using the following kinetic model [15]:

$$R(t) = \frac{Bt^{C}}{A^{C} + t^{C}} \quad (1)$$

where $R(t)$ represents the regain of the sample at time t, B represents the regain at the equilibrium (R_∞), A represents the time of half absorption ($t_{1/2}$) and c represents a power coefficient of each step.

Nonlinear regression produced the best estimates of the model parameters B, A and c, which enabled us to calculate the asymptotic regain at the equilibrium R_∞ and the half absorption time $t_{1/2}$ and rate $v_{1/2}$. The nonlinear regression required unbiased initial estimates of the model parameters, which were provided by the linear regression between $t/R(t)$ and t. This linear region was fit to a straight line $t/R(t) = \alpha + \beta t$, where α/β and $1/\beta$ are the initial estimators of A and B, respectively [15].

Table 1 BET and GAB model and parameters used to fit the experimental sorption data

Model	Mathematical equation
BET	$W = Wm\ Cg\ a_w/[(1 - a_w)(1 + (Cg - 1)\ a_w)]$
GAB	$W = Wm\ Cg\ K\ a_w/[(1 - Ka_w + Cg\ K\ a_w)]$

Parameter	Definition
a_w	Water activity expressed as vapour relative pressure p/p0, where p0 is the saturated vapour
W	Equilibrium moisture content at a_w in g sorbed/100 g of sorbent on dry basis
Wm	Monolayer moisture content in g sorbed/100 g of sorbent on dry basis
Cg	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 of 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 for all higher layers

Diffusion coefficient calculations

The diffusion coefficient was obtained using the method applied by Vickerstaff [27] to study the diffusion of dyes within fibres. This diffusion appears to be well represented by an expression derived from Fick's equation applied to moisture diffusion. This expression yielded satisfactory results for the early stages of moisture absorption, as in the case of dye diffusion. If the fraction of absorbed water is plotted against the square root of the absorption time, the points should be linear:

$$R(t)/R_\infty = \sqrt{D_A}\sqrt{t}$$

The slope is considered to be the square root of the *apparent diffusion coefficient*, D_A, of the water. If the apparent diffusion coefficient is measured over the sample's mass instead of the sample's surface, it is measured in min^{-1}.

Results

The water management properties of SC and human hair were monitored by dynamic vapour sorption [28]. Water uptake and desorption isotherms for SC and human hair were evaluated using software supplied by TA Instruments. The moisture content was plotted against the relative humidity to create the isotherms (Fig. 1). The shape of the isotherm reflects the manner in which water is bound by the system. Both keratinised tissues studied exhibited the classic Type II sigmoidal adsorption and desorption isotherm, typical for hygroscopic materials, when water is scarcely attracted to the product. The sigmoidal nature of the isotherms has been described by numerous models and is considered to consist of three components. At low RH values (0–15 %), the monolayer adsorption onto the internal surface of the fibre is the dominant process; between 15 and 70 % RH, polylayer water formation in the transient fibre microcapillaries occurs, and above 70 % RH, capillary condensation becomes increasingly dominant [29]. The isotherms for the two keratinised tissues are quite different, with much higher water absorption at 95 % RH for SC than for human hair. The human hair isotherm shows a small amount of water at a very low relative humidity and an increase at a high relative humidity. For SC,

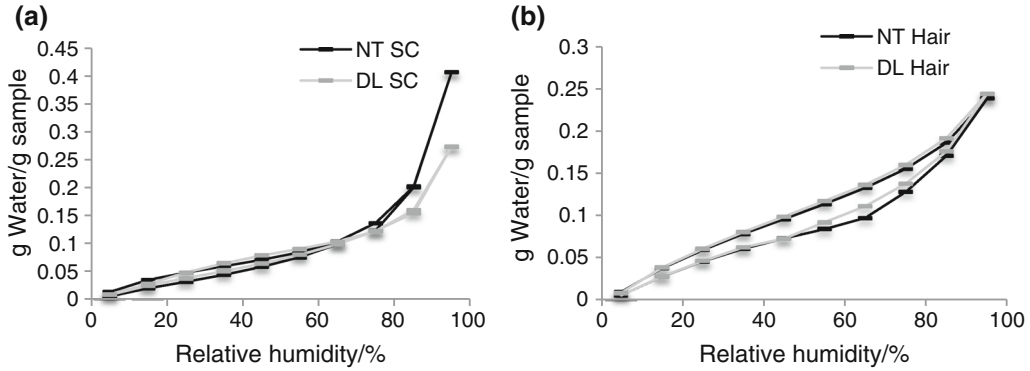

Fig. 1 Water sorption isotherms for SC (**a**) and human hair (**b**) with and without internal lipids

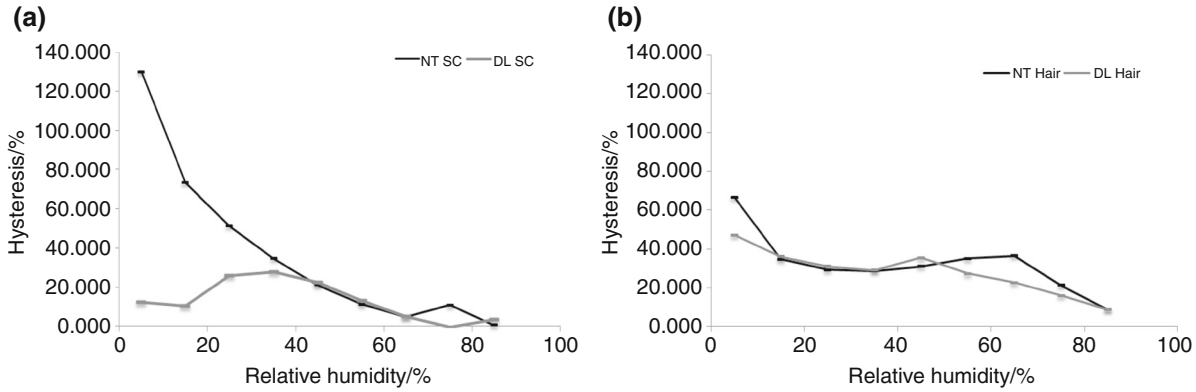

Fig. 2 Effects of relative humidity on hysteresis between sorption and desorption isotherms for SC (**a**) and human hair (**b**) with and without internal lipids

there is a low to moderate amount of water absorbed from 0 to 60 % RH; above 60 % RH, the amount of water uptake increases exponentially [30].

Moisture sorption hysteresis results when there are distinct paths for sorption and desorption. The extent of hysteresis is associated with the nature and state of the components of the sample. These components may alter the accessibility of water to the energetically favourable polar sites [31, 32]. The moisture isotherms showed distinct hysteresis between sorption and desorption cycles for both keratinised samples, indicating different structural changes of the keratinised tissues caused by interactions with water. In agreement with other authors, a slight hysteresis was found in the SC sample, and the isotherm for human hair behaved with the characteristic hysteresis similar to that observed in wool and porcupine quills [30].

Generally, the hysteresis is calculated as the difference between the desorbed water mass and the absorbed water mass at the same relative humidity [33]. However, this type of measurement could include the moisture contents of the fibres. In our study, the degree of the hysteresis was calculated according to the following equation that evaluates the extent of specific structural changes [33]; the calculated data are plotted against humidity in Fig. 2.

$$\text{Hysteresis}\,(\%) = 100 \times (M_{(\text{total during desorption})} - M_{(\text{total during sorption})})/M_{(\text{total during sorption})}$$

For both untreated keratinised samples, SC and hair, the extent of hysteresis clearly decreases with increasing relative humidity. This behaviour suggests that the keratinised tissues' structure changes significantly either when moisture adsorbs onto the dry tissue or when the moisture desorbs from the tissue. These structural changes become less significant after some moisture has been absorbed on the keratinised tissue. When increasing the relative humidity (in the RH range of 30–95 %), the hysteresis of SC was lower than that shown by human hair. This difference can be explained by the pore sizes of hair, which are most likely larger than that of SC. The pore size of SC suppresses capillary condensation, making the isotherms nearly reversible. Hair is a mesoporous material, and capillary condensation can occur at higher relative humidity resulting in hysteresis [33]. This result can also be

Table 2 Maximum moisture regain, total time to reach equilibrium (t_T) and apparent diffusion coefficient (D_A) for SC and human hair with (NT) and without (DL) internal lipids

	Regain at 95 % RH/%	t_T/min	D_A/min^{-1}
NT SC	40.68	3658.59	0.0154 ± 0.005
DL SC	27.35	2840.61	0.0615 ± 0.031
NT HAIR	23.90	4340.70	0.0177 ± 0.007
DL HAIR	24.46	4520.78	0.0151 ± 0.007

Table 3 Parameters of the adjustments of models BET and GAB for SC and human hair with (NT) and without (DL) internal lipids

Models	Parameters	NT SC	DL SC	NT HAIR	DL HAIR
BET	*Wm*	0.0460	0.0572	0.0649	0.0674
	Cg	9.182	4.525	6.032	6.821
	R^2	0.98	0.96	0.98	0.99
GAB	*Wm*	0.0423	0.0663	0.0710	0.0727
	Cg	4.689	4.192	7.736	8.042
	K	0.939	0.759	0.769	0.768
	R^2	0.99	0.99	0.99	0.99

explained molecularly; the greater the change induced in the substrate by water absorption, the greater the hysteresis [34]. The presence of lipids in the SC makes the adhesion of water on the SC more difficult, and the modification induced by water absorption is less relevant than that observed on hair, resulting in lower hysteresis.

In addition, the degree of hysteresis shows that when the lipids are extracted from both keratinised tissues, the greatest changes are found in the SC sample. These differences in the degree of hysteresis mainly occur at low humidity (5–35 % RH). High hysteresis is found in the SC sample at low humidity, which can be attributed to the high binding energy of the first water molecules that absorbs. These molecules would be difficult to desorb, giving rise to a high sorption hysteresis. When the lipids are extracted from the SC tissue, a decrease in the sorption hysteresis at low RH is observed. This decrease can be attributed to an important modification of the SC integrity due to the lipid extraction.

As previously mentioned, the maximum moisture regain indicates an important difference between the two keratinised tissues. Much greater overall water absorption at 95 % RH was observed in the SC than in the human hair samples. Furthermore, when the lipids are extracted from SC and hair, the resultant modified samples revealed changes in their sorption properties (Fig. 1; Table 2). While a slightly increase in the water absorbed and desorbed is found when lipids are extracted from the hair fibres, the lipid-depleted SC exhibits a significantly reduced water content. It is well known that depleting the SC lipids disrupts the skin's barrier function by altering the formation of bilayers in the intercellular lipid spaces, which reduces the water retention characteristics of the SC [35]. Furthermore, the reduced water uptake capacity can also be attributed to the loss of moisturising factors (NMFs). NMFs play a central role in maintaining the water content of the SC. NMF is commonly claimed to increase the water content in the SC an thereby protect the skin from dryness [b]. NMFs, together with the extracellular lipid matrix, facilitate the maintenance of sufficient concentrations of water in the SC [35].

To better evaluate the differences in the sorption process, the moisture absorbed and desorbed in each RH step of the isotherm was calculated (Fig. 3) by fitting the sorption results to a kinetic model that considered that the sample was kept at each RH until it reached equilibrium ($t = \infty$). Evaluation of the moisture absorbed and

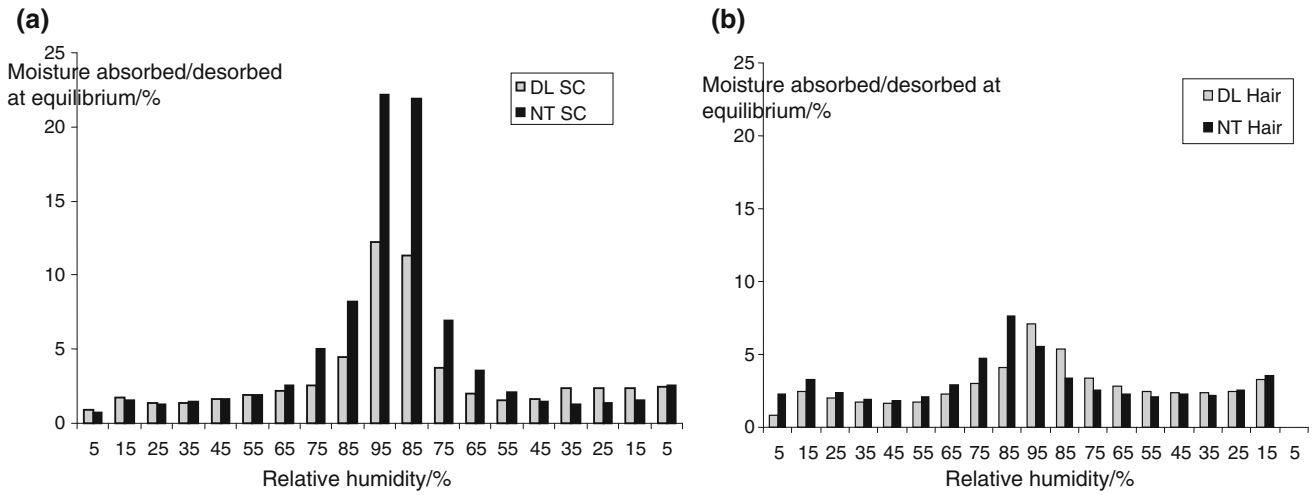

Fig. 3 Moisture absorbed/desorbed at equilibrium in regain (%) for SC (**a**) and human hair (**b**) with and without internal lipids

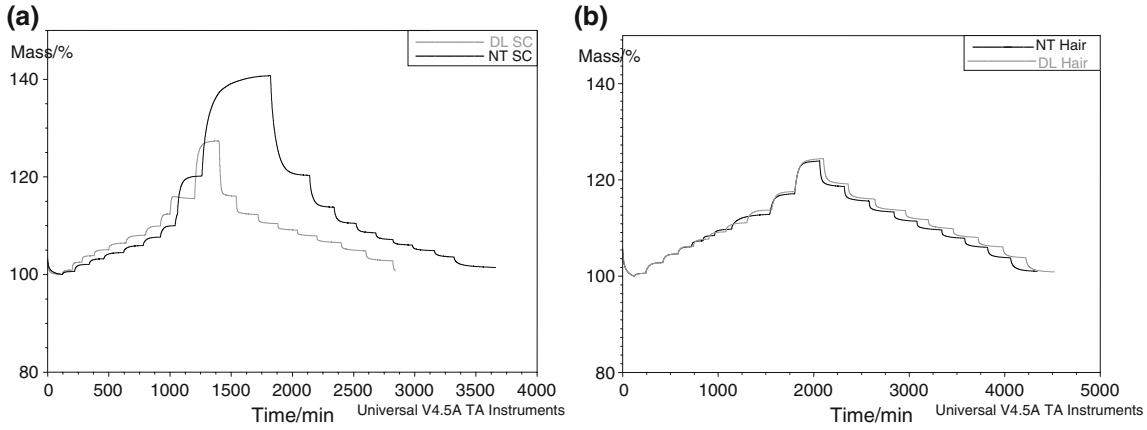

Fig. 4 Moisture uptake as a function of time for SC (**a**) and human hair (**b**) with and without internal lipids

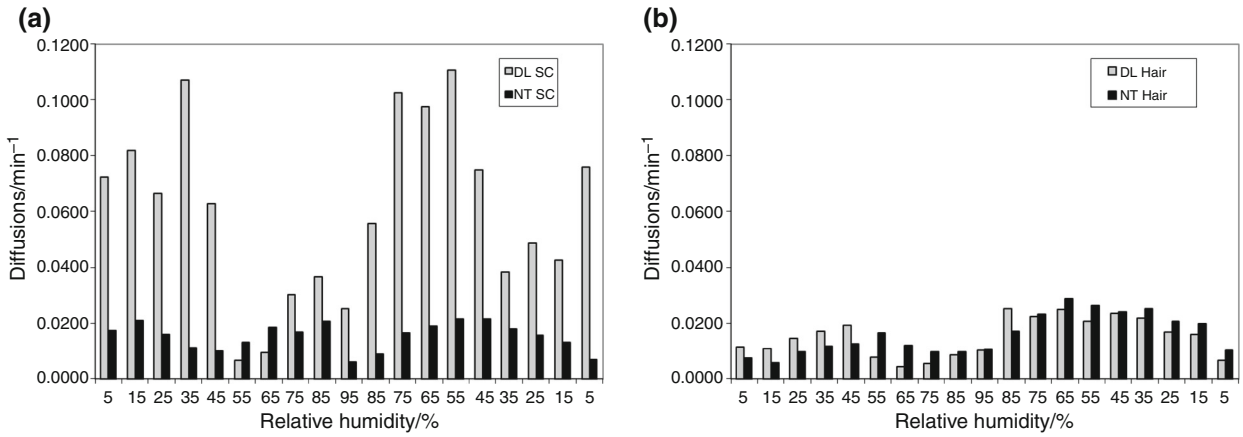

Fig. 5 Diffusion coefficients (min^{-1}) for SC (**a**) and human hair (**b**) with and without internal lipids

desorbed over the total range of relative humidity demonstrated that lipid extraction again led to more significant changes for the SC tissue than in the hair fibres (Fig. 3). When lipids are extracted from the hair fibres, a small reduction in the absorbed water was found only at the initial humidity steps. However, when lipids are depleted from the SC, a clear decreased capacity to absorb water was found in almost all of the humidity's steps evaluated, especially at high humidity. These results confirm the important role of the lipids in maintaining the water levels in the SC, which is directly related to a proper SC function as a barrier.

In this work, BET and GAB equations were used to model the moisture sorption isotherms. The BET model is one of the most widely used theoretical models to describe sorption isotherms because it ensures a good fit for a great variety of products with low water activity. The model is restrictively applicable within the 0.05–0.45 a_w range. Besides, the GAB model was considered an important improvement on the BET equation, and its application has shown a good fit up to an a_w of 0.9 [36, 37]. Both isotherms (BET and GAB) are closely related as they follow from the same statistical model. The regression of the experimental sorption data using the BET and GAB models yielded values of *Wm*, the monolayer capacity, and *Cg* and *K*, the energy constants [18]. The values obtained are shown in Table 3. To evaluate the efficiency of each model, the coefficient of correlation was also reported. These coefficients show that although both models fitted well ($R^2 > 0.96$), the more extended range of application of the GAB equation over the BET equation makes it the most adequate to describe the adsorption isotherms. The GAB model produces the best fit throughout the entire range of water activity. The monolayer capacity values and the energy constants confirm the differences in the water sorption between the two keratinised tissues evaluated in this work. The results further confirmed the damaging effects due to the lipid extraction on both keratinised tissues. The different modelled parameters evaluated were hardly influenced by lipid extraction from the hair fibres. The energy constant, *Cg*, of the primary sorbed monolayer slightly

increases after the hair lipid extraction, which means that there is a certain increase in the binding energy where water interacts with the fibres. When the lipids were extracted from the SC, an increase in the monolayer capacity (*Wm*) was observed, which indicated that water molecules could penetrate more easily through the primary layers of the damaged tissue. In addition, the LD SC showed a decrease in both energy constants. These results indicate that water is more easily released from the lipid-depleted SC.

The kinetics of moisture sorption were evaluated for all of the keratinised tissues studied. The time versus mass change (%) profile of the full sorption/desorption is shown in Fig. 4. For a given water absorption event, the time taken by the sample to reach equilibrium can be used to evaluate the sample state. There are significant differences in the rate at which SC and human hair reached equilibrium (Fig. 4; Table 2). Even though lower amounts of water were absorbed, hair fibres reached equilibrium much more slowly than SC tissues. Differences in the keratinised structure of SC and hair were also confirmed by evaluation of the diffusion coefficients (*D*) (Table 2). Usually, there is an inverse relationship between the time parameter (t_T) and the diffusion coefficient, i.e. more time is needed to reach equilibrium for tissues with low water permeability, i.e. low diffusion coefficients. However, this trend was not observed when comparing the untreated SC and hair. Contrary to our expectations, hair required a much longer time to reach equilibrium but still had a greater diffusion coefficient. These differences in the absorption/desorption kinetics could be due to the following factors: different morphological structure or/and different protein/lipid chemical compositions. The higher proportion of lipids in the SC, which favours a crystalline state of the lipids in the CMC, could lead to a slower rate of water penetration (lower diffusion) through the lipid bilayer of the SC relative to the hair fibres.

As mentioned above, more significant differences in the sorption kinetics are found when the lipids are extracted from the SC tissue than from the hair fibres. The lipid extraction procedure led to a clear reduction in the water content on the SC resultant tissue which can be related to a significant decrease on the time needed to reach equilibrium. These results indicate that the SC integrity was substantially modified, demonstrating that the water affects the structure of molecular components in SC [38]. The diffusion coefficients, which show the moisture penetration velocity, were calculated as described in the experimental section at each level of RH (Fig. 5). The mean values of the diffusion coefficient are also summarised in Table 2. Accordingly, the diffusion coefficients increased in the lipid-depleted SC. The diminution of the water content due to the lipid extraction showed the important role of water in maintaining the SC in stable conditions [39]. The change in the content of lipid components in the SC strongly relates to its barrier function [40].

On the contrary, the mean value of the diffusion coefficient for the lipid-extracted hair fibres slightly decreased. For hair fibres, perhaps an intercellular adhesion following the lipid removal could explain the obtained results.

Evaluation of the diffusion coefficients at each individual RH was also investigated (Fig. 5). For the SC, an increase in the diffusion coefficient occurred at almost all humidity levels. However, when the lipids were removed from the hair fibres, the diffusion coefficients increased during the absorption process but decreased during the desorption process. These results indicated that water is more strongly bound in the lipid-extracted hair fibres, resulting in a decrease in the desorption rate of the water. This result is in agreement with the GAB results, where an increase in the energy constant Cg after the lipid extraction was found, indicating a certain increase in the binding energy at the sites of water interactions with the lipid-extracted fibres.

These results are similar to those from other authors where the essential role of the stratum corneum lipids on the conservation of the stratum corneum structural integrity has been described [13]. When the lipids are removed from the SC structure, the resultant sample had clearly modified permeability, as shown by a significant increase in its diffusion coefficient. The stabilisation of the lipid lamellar structures is essential to regulate the water content of the keratinised tissues.

Conclusions

The role of the lipids in the stratum corneum and human hair was studied by absorption and desorption experiments. The shape of the equilibrium water sorption isotherms of both of these keratinised tissues could be described by a Type II isotherm with a small amount of water persisting at a very low relative humidity and an increase at a high relative humidity. A characteristic hysteresis between uptake and desorption, as observed with other keratinised tissues, was obtained. More significant hysteresis was observed in the human hair than in the SC. The degree of hysteresis showed that when the lipids were extracted from both tissues, the greatest impact was on the SC sample. Lower water content was achieved for human hair than for SC. In addition, while a slight increase in the water absorbed and desorbed was found when lipids were extracted from the hair fibres, the water content of the lipid-depleted SC was found to be significantly reduced.

Significant differences in the rate at which SC and human hair reached equilibrium were found. SC diffusion coefficients were lower than those obtained for hair fibres. The increased amount of lipids in the SC compared to human hair could account for lower water permeability. More significant differences in the sorption kinetics were found when the lipids were extracted from the SC tissue than from the hair fibres. Diffusion coefficients for the

extracted hair fibres increased in the absorption process and decreased in the desorption process, indicating an increase in the binding energy at sites where water interacted with the lipid-extracted fibres. In addition, when the SC lipids were extracted, a significant increase in the SC permeability, as demonstrated by an increase in the diffusions coefficients, was observed. These results demonstrated the essential role of the intercellular lipids in regulating the water content, which directly affect the SC barrier function. Lipid structures in the SC are essential in maintaining the water-holding capacity of the skin and in regulating the water permeability of the SC.

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