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Prevention of model stratum corneum lipid phase transitions *in vitro* by cosmetic additives—Differential scanning calorimetry, optical microscopy, and water evaporation studies

JAIRAJH MATTAI, CLAUDIA L. FROEBE,
LINDA D. RHEIN, F. ANTHONY SIMION, H. OHLMEYER,
DEAN T. SU, and STIG E. FRIBERG, *Colgate-Palmolive Technology Center, 909 River Road, Piscataway, NJ 08854 (J.M., C.L.F., L.D.R., F.A.S., H.O., D.T.S.), and Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13676 (S.E.F.).*

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Synopsis

Two potential moisturizers (maleated soybean oil, identified here as Glyceridacid, and glycerol) were compared for their effects on the liquid crystalline phase of model stratum corneum lipids at 6% and 92% relative humidities (RH) using differential scanning calorimetry (DSC), water evaporation, and polarized light microscopy.

DSC of the model lipid (32% water content) showed a broad endothermic transition at about 52°C, with an enthalpy of 15 J/g lipid. The enthalpy of the transition and water loss from the model lipid were time-dependent; at 6% RH, the enthalpy increased to 43 J/g lipid, with 29.5% water loss by 24 h. This suggests significant crystallization of the model lipid on dehydration, which was confirmed by microscopy. At 92% RH, both the changes in enthalpy and water loss were significantly reduced by 24 h, indicating maintenance of the liquid crystalline phase of the model lipid with very little crystallization. Incorporation of Glyceridacid (5–15 wt%) into the model lipid produced enthalpies between 17–21 J/g lipid after 24 h at 6% RH, with reduced water loss (20–26%). Therefore, Glyceridacid can function as a skin conditioner at low humidity by maintaining the liquid crystalline phase of the model lipid in addition to preventing water loss. Glycerol (10 wt%), a known skin conditioner *in vivo,* inhibited the crystallization of the model lipid, despite almost complete dehydration: enthalpy is 30 J/g lipid after 24 h with few solid crystals present. This suggests an alternative mechanism to humectancy for the moisturizing action of glycerol at low humidity, in agreement with our earlier investigation (4) of the model lipid/glycerol system by microscopy.

The results clearly show the potential of DSC as a quantitative tool to monitor the phase behavior of the model lipid and its alteration by potential moisturizers, under different humidity conditions.

INTRODUCTION

It is well established that the stratum corneum layer of the epidermis is the barrier to water loss from skin and that the decisive influence of intercellular lipids on this barrier

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is now being recognized. Elias *et al.* (1) have proposed that these lipids form multiple layers in a lamellar liquid crystalline arrangement. Friberg and Osborne (2) developed a model stratum corneum lipid system, based on Elias' model, in which neutral and polar lipids are incorporated into a lamellar liquid crystalline host of a fatty acid/soap mixture (pH = 4.5–6). The complete model is a mixture of liquid crystalline and solid phases; the physical state of the lipids in this model system is correlated with the maintenance of proper barrier function (3). A liquid crystalline state permits liquid-like diffusion across the bilayer, while a solid state permits rapid water loss via cracks. It has been proposed (3) that the mixed solid and liquid crystalline states produce the optimal barrier to water loss.

The occurrence of dry skin associated with cold, dry weather may stem from an extensive, elevated level of skin lipids in the solid state. Therefore, a material that maintains a higher proportion of lipid in the liquid crystalline state may be an effective moisturizer. Recently Froebe *et al.* (4) demonstrated that glycerol interacts with the model lipids to maintain the liquid crystalline state even at low relative humidity (RH). Thus glycerol may condition the skin by this alternative mechanism at low RH, since it did not exhibit humectant activity under these conditions.

In the above studies, the liquid crystalline state was observed by polarized light microscopy, while humectancy was determined gravimetrically from water evaporation. To provide a quantitative way of monitoring the liquid crystalline state, we now add the technique of differential scanning calorimetry (DSC), along with optical microscopy, to examine the effects of putative moisturizers at maintaining the liquid crystalline state of model stratum corneum lipids after incubating at 6% and 92% relative humidities for varying periods of time.

Previous studies using high-sensitivity DSC of human as well as porcine stratum corneum (5–7) have shown three broad transitions at 65, 75, and 105°C. These have been attributed to thermal transitions of intercellular lipids, lipid-protein complexes, and intracellular keratin, respectively. If the model lipid system as proposed by Friberg and Osborne (2) is valid, we should expect to see thermal transitions due to the lipids only.

It is well known that lipid transitions are due to changes in hydrocarbon chain packing within the bilayer; endothermic changes are due to changes in packing from an ordered to a more disordered state as more gauche rotamers are formed. These phase transitions are hydration-dependent. For example, at low hydration, where the hydrophilic head groups are not fully hydrated, the hydrocarbon chains are more closely packed and require more energy for melting. Hence the transition will occur at a higher temperature and have a greater enthalpy, as reported earlier for dimyristoylphosphatidylcholine (8).

In the present work, the enthalpy of the phase transition of the model lipid system was quantitatively determined by DSC, at 6% and 92% RH as a function of time and water loss; the phase behavior of the model lipid at these humidities was also tracked by polarizing microscopy, which qualitatively determined the extent of crystal formation in a liquid crystalline matrix. The modification of the phase behavior of the model lipid system by maleated soybean oil, identified here as Glyceridacid, at 5–15 wt% concentration, has also been investigated. Glyceridacid is a modified triglyceride with the chemical name 2-(alkoyloxy)1-[(alkoyloxy)methyl]-ethyl-7-(4-heptyl-5, 6)-dicarboxy-2-cyclohexene-1-yl) heptanoate. It has previously been shown to penetrate the stratum corneum (9), and the skin softening properties of this compound have been reported

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(10). The epidermal lipids were the primary site of action for Glyceridacid as a skin softener (10).

The effects of glycerol on the model lipid were also investigated as a quantitative check on our previous work (4), which showed via microscopy that glycerol is able to maintain the liquid crystalline state of the model lipid at low humidity. This was suggested as an alternative mechanism to humectancy at low humidity for glycerol, which is known to prevent/reverse dry skin *in vivo* (11–13).

MATERIALS AND METHODS

Maleated soybean oil, the fumaric acid adduct of soybean oil, is marketed by Van Dyk (Belleville, NJ) under the tradename Ceraphyl GA.® This substituted triglyceride, identified here as Glyceridacid, was originally marketed by Westvaco under the tradename Glyceridacid 100.® Phosphatidylethanolamine was obtained from Avanti Polar Lipids (Birmingham, AL), while the other lipids shown in Table I and glycerol were obtained from Sigma Chemical Company (St. Louis, MO). All lipids were of the highest grade (98–99%) and used without further purification.

The composition of the model lipid, based on the analysis of stratum corneum lipids by Elias *et al.* (1), is shown in Table I. The procedure for preparing host lipid, and subsequent incorporation of other lipids to form the model lipid at 32% dehydration, is described elsewhere (2,4). The model lipid thus prepared consisted of two phases—a liquid crystalline phase and an excess liquid phase, presumably due to 24% triolein in the model lipid. This two-phase system is not adequate for DSC studies, and we have modified the model lipid system by a reduction of the triolein to 12%, resulting in almost a single phase. The new composition of the model lipid system is shown in Table

Table I
Composition of Model Epidermal Lipid (1) and Modified Model Epidermal Lipid*

Component	Wt% in mixture (model lipid)	Wt% in mixture (modified model lipid)
Free fatty acids	19.0	22.2
Oleic acid	33.1	33.1
Linoleic acid	12.5	12.5
Palmitic acid	36.8	36.8
Palmitoleic acid	3.6	3.6
Stearic acid	9.9	9.9
Myristic acid	3.8	3.8
Phosphatidylethanolamine	5.0	5.8
Cholesterol	14.0	16.4
Cholesterol sulfate	2.0	2.4
Triolein	25.0	12.0
Oleic acid palmityl ester	6.0	7.2
Squalene	7.0	8.3
Pristane	4.0	4.7
Ceramides (type III)	18.0	10.5
Ceramides (type IV)	—	10.5

* Model lipid was prepared containing 32% water.

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I. This modification of the triolein content is reasonable since about 12% triolein was found in the lipids of the outer stratum corneum by Lampe *et al.* (14). Glyceridacid and glycerol were added directly to the model lipid (32% water content) in constricted tubes, followed by the usual mixing procedure described previously (2,4).

Lipid samples were examined by polarized light microscopy at 6% and 92% RH. Samples of the lipids (60–100 mg) were spread on microscope slides in uniform layers, 0.5-mm thick and 0.5-cm^2 and placed in constant-humidity chambers; photomicrographs were taken at the initial time and after 6 h, 24 h, and 48 h of exposure to 6% RH or 92% RH. This technique detects both solid crystal and liquid crystalline phases.

DSC studies were performed at 6% and 92% RH. 10–15-mg samples of the model lipid or model lipid plus additive were weighed accurately into DSC pans and placed in the constant-humidity chambers for 6, 24, and 48 hours. Samples were reweighed to determine water loss, the pans were hermetically sealed, and DSC was run at 5°C/min from 10–110°C using a DuPont 9900 differential scanning calorimeter.

RESULTS AND DISCUSSION

STUDIES WITH MODEL LIPID ALONE

DSC of modified model stratum corneum lipids (32% hydrated) showed a broad endothermic transition, with an onset temperature of 30°C and a final temperature of 70°C (Figure 1a). (The DSC curve is the first heating run following sample preparation.) This corresponds to a transition from a liquid crystalline phase, observed by x-ray diffraction and microscopy (2), via the melting of lipid domains, to an unknown phase not determined in the present study. The transition maximum is quite broad but is centered at about 52°C. This transition parallels the broad and overlapping transition of intercellular lipids observed at a maximum of 65°C for human as well as porcine stratum corneum (5–7). After incubation for 6, 24, and 48 h at 6% RH (Figures 1b, 1c, and 1d), the DSC transitions show substantial changes, with emergence of some sharper transitions overlapping the broader transition. There was also an increase in cooperativity of the transition, as it sharpened and shifted to higher temperatures. These changes are consistent with dehydration of the lipids, as observed for phospholipids (8). In contrast, minor changes in the transition shape occurred after 6 h at 92% RH, while after 24 h, the transition sharpened, with a maximum at 52°C and with little change on further incubation (data not shown).

Table II summarizes the corresponding enthalpy data, from triplicate measurements, for the model lipid, under different incubation times and RH. Despite the broadness of the transition, there was very good reproducibility for transition enthalpies. At 6% RH, the transition enthalpies were 15 ± 1, 21 ± 1, 43 ± 1, and 52 ± 1 J/g after 0, 6, 24, and 48 h incubation (Table II), with corresponding water losses of 18.2 ± 0.1, 28.6 ± 0.5, and 29.5 ± 1.1% (Table III). The more than doubling of the enthalpy at longer incubation times indicates that a large fraction of the hydrocarbon chains in the lipid bilayers has crystallized into a more ordered state, such as in a solid crystalline form, resulting in a greater enthalpy for the transition. At about 29% dehydration, most of the lipids are fully dehydrated, resulting in increased enthalpy changes as the hydrocarbon chains are packed more closely for maximum Van der Waals interaction.

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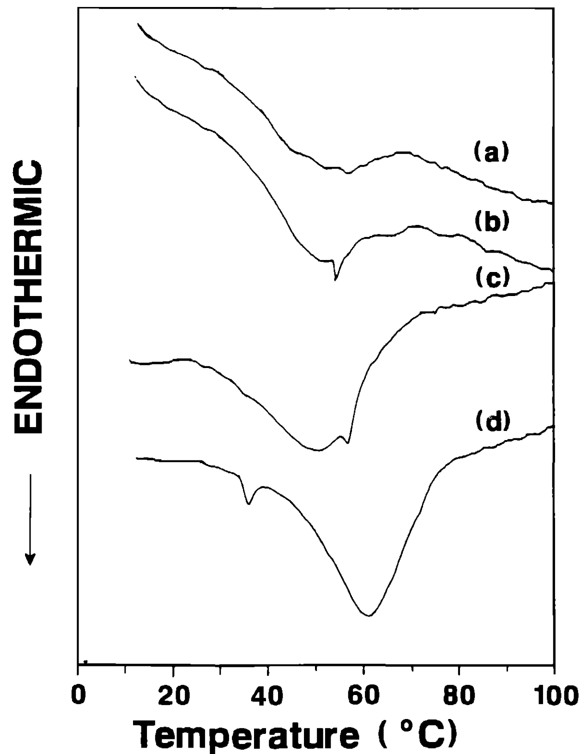

Figure 1. Differential scanning calorimetry of model lipid incubated for 0 h (a), 6 h (b), 24 h (c), and 48 h (d) at 6% RH.

Table II
Enthalpy Values for Model Lipid, Model Lipid Plus 5%, 10%, and 15% Glyceridacid, and Model Lipid Plus 5% and 10% Glycerol, Incubated for Different Periods of Time at 6% and 92% Relative Humidities

	Enthalpy (J/g lipid or J/g (lipid + additive)					
		Model lipid + Glyceridacid			Model lipid + glycerol	
Time	Model lipid	5%	10%	15%	5%	10%
0 h	15 ± 1	13	11	8	14	13
6 h at 6% RH	21 ± 1	15	15	12	17	20
24 h at 6% RH	43 ± 1	21	22	17	38	30
48 h at 6% RH	52 ± 1	35	28	23	45	35
6 h at 92% RH	20 ± 2	15	13	13	15	14
24 h at 92% RH	20 ± 1	17	15	15	—	15
48 h at 92% RH	24 ± 1	17	16	18	19	13

The transition enthalpies exhibited a small change from 15 ± 1 J/g lipid at 0 h, to 20 ± 2, 20 ± 1, and 24 ± 1 J/g lipid after 6, 24, and 48 h of incubation at 92% RH (Table II). The corresponding water losses were 13.3 ± 0.5, 21.6 ± 0.2 and 24.9 ± 0.4%, respectively, after 6, 24 and 48 h (Table III). Thus, despite 25% of initial weight

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Table III
Percent Water Loss From Model Lipid, Model Lipid plus 5%, 10%, and 15% Glyceridacid, and Model Lipid Plus 5% and 10% Glycerol, Incubated for Different Periods of Time at 6% and 92% Relative Humidities

	% Water loss					
		Model lipid + Glyceridacid			Model lipid + glycerol	
Time	Model lipid	5%	10%	15%	5%	10%
0 h	—	—	—	—	—	—
6 h at 6% RH	18.2 ± 0.1	11.3	10.7	11.7	17.9	19.0
24 h at 6% RH	28.6 ± 0.5	25.8	19.9	20.8	29.0	27.8
48 h at 6% RH	29.5 ± 1.1	27.7	25.7	23.8	30.5	27.9
6 h at 92% RH	13.3 ± 0.5	6.3	6.0	6.1	8.9	1.3
24 h at 92% RH	21.6 ± 0.2	13.9	10.7	11.3	11.8	+1.8
48 h at 92% RH	24.9 ± 0.4	17.8	15.0	15.4	11.2	+1.5

loss due to water, the model lipid is maintained to a large degree in the liquid crystalline state at 92% RH, with minor changes in hydrocarbon chain-packing in the bilayer. Previous studies on the phase behavior of phospholipids show transition enthalpies and temperatures to increase rapidly with dehydration, attaining maximum values at very low hydration, as the lipid molecules become fully dehydrated (8). At 25% water loss, corresponding to 7% hydration, the model lipids are apparently sufficiently hydrated to prevent crystallization, with its concomitant large increase in enthalpy.

These results are confirmed by polarized light microscopy. Figures 2a and 3a show photomicrographs of the model lipid at 100× magnification at the initial time and after 24 h at 6% RH. At the initial time (Figure 2a), the pattern is characteristic of a liquid crystal. After 24 h (Figure 3a), significant crystal formation has occurred, with a solid-crystal network of large plate-like crystals after 48 h (data not shown). At 92% RH, crystallization of the model lipid is far less dramatic than that observed at 6% RH; the photomicrographs reveal largely liquid crystalline structures even after 48 h incubation (data not shown). This is to be expected, as the water loss from the model lipid

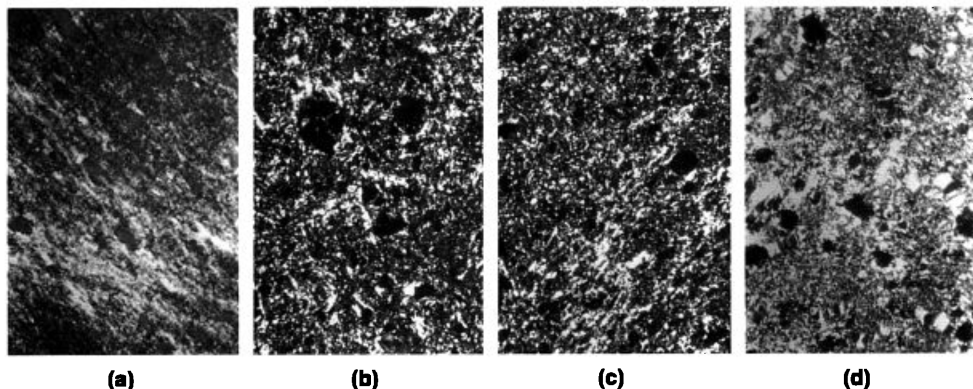

Figure 2. Model lipid with 0% (a), 5% (b), 10% (c), and 15% (d) Glyceridacid viewed under polarized light at 100× magnification, at the initial time.

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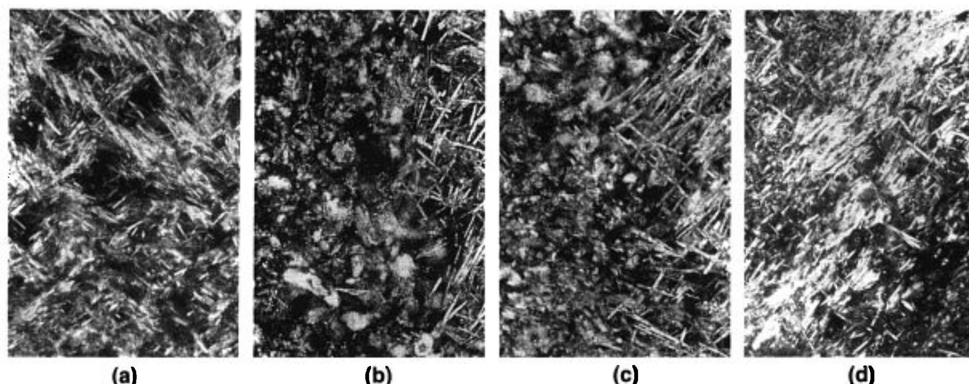

Figure 3. Model lipid with 0% (a), 5% (b), 10% (c), and 15% (d) Glyceridacid after 24-h exposure to 6% RH, viewed under polarized light at 100× magnification.

is suppressed at high humidities. The liquid crystal state, which is highly dependent on water content, is therefore maintained.

STUDIES WITH MODEL LIPID CONTAINING GLYCERIDACID

Incorporation of 5–15% Glyceridacid into the hydrated model lipid resulted in a reduction in intensity of the DSC transition, with a shift to lower transition temperature (Figure 4b); after equilibration for 6 h at 6% RH, the original shape of the transition was recovered [compare Figures 4a (model lipid) and 4c (model lipid plus Glyceridacid)], with subsequent sharpening of the transition on further incubation for 24 and 48 h (Figures 4d and 4e). However, the transition enthalpies were considerably reduced compared to the model lipid (Table II); the values ranged from 8 J/g lipid at 0 h to 23 J/g (lipid + Glyceridacid) after 48 h at 6% RH for the 15% Glyceridacid sample. Clearly, at 6% RH, Glyceridacid prevented the hydrocarbon chains from crystallizing and thus maintained the liquid crystalline phase even at low hydration, a behavior similar to that observed with glycerol (4). In addition, the percent water loss at both low and high RH values (Table III) is significantly lower compared to the model lipid for all incubation times. Comparable enthalpy and water loss data were obtained for the 10% Glyceridacid sample. At 5% concentration of Glyceridacid, the enthalpy of the transition was 21 and 35 J/g (lipid + Glyceridacid) after 24 and 48 h, respectively, with some increase in water loss. There is some crystallization of the model lipid after 48 h at 6% RH, although the liquid crystalline state is largely maintained.

Therefore, in addition to maintaining the liquid crystalline state of the model lipid, Glyceridacid is also able to reduce water loss. Thus Glyceridacid is able to maintain the lamellar liquid crystalline state by two mechanisms.

Note the DSC curves of the model lipid at 0 h, prepared at different times, show minor variation in the shape of the transition (compare Figures 1a and 4a); however, the enthalpy of the transition is not affected.

The above results are in good agreement with optical microscopy data. Figures 2b, 2c, and 2d and Figures 3b, 3c, and 3d show photomicrographs of the model lipid with 5%, 10%, and 15% Glyceridacid after 0 and 24 h, respectively, at 6% RH. At 0 time, the

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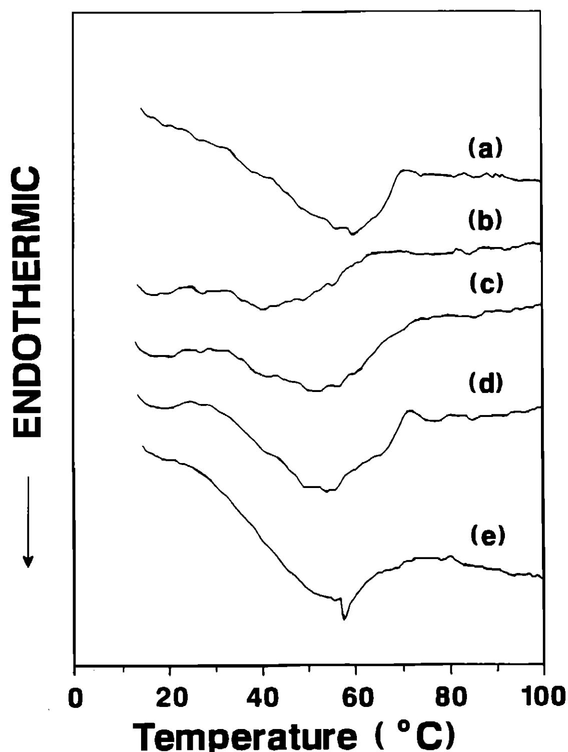

Figure 4. Differential scanning calorimetry of model lipid plus 15% Glyceridacid incubated for 0 h (b), 6 h (c), 24 h (d), and 48 h (e) at 6% RH. Model lipid incubated for 0 h (a) included for comparison.

liquid crystalline phase is clearly present. After 24 h, Glyceridacid samples (5% and 10%) exhibited co-existing liquid crystalline and crystalline phases, with a greater proportion of crystalline characteristics. This contrasts with much greater crystallization of the model lipid alone after 24 h (compare Figure 3a with Figures 3b and 3c). The 15% Glyceridacid sample showed more liquid crystalline character, along with finer crystals (Figure 3d). By 48 h, the samples containing 5 and 10% Glyceridacid exhibited many small crystals against a liquid crystal background, while the 15% Glyceridacid sample exhibited a roughly half-liquid/half-solid, crystal material (data not shown).

Glyceridacid, at 5%, 10%, and 15% of the model lipid, is capable of preventing solid crystallization of the model lipid that normally accompanies water loss at low humidity. This is in excellent agreement with the quantitative results obtained by DSC above.

Glyceridacid is able to maintain the liquid crystalline state of the model lipid at low humidities by incorporating into the bilayer structure; this is as a result of its similarity to other lipids of the model lipid system in having a hydrophobic (fatty acyl chain) and a hydrophilic (glycerol headgroup) moiety. The bulky cyclohexene ring containing trans carboxylic acid of Glyceridacid will reduce lateral chain-packing and Van der Waals interaction within the bilayer, and this will increase lipid fluidity or reduce lipid crystallization. Therefore, lower transition enthalpies will be observed. Glyceridacid also reduced water loss from the model lipid. Water acts by hydrating the polar head groups of the lipids, thus increasing their size; this affects the hydrocarbon portion of the bilayer by reducing their lateral interaction and thus increasing their fluidity (8).

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Imokawa *et al.* (15,16) have shown that stratum corneum lipids are important in the water-holding function of the stratum corneum. In addition, a number of pseudoceramides have been synthesized by Imokawa *et al.* (17); topical application of these pseudoceramides significantly improved dry skin conditions, and this was accompanied by recovery in the water content of the stratum corneum. Based on our *in vitro* studies, Glyceridacid is also predicted to behave like the pseudoceramides in improving dry skin and recovering the water content of the stratum corneum.

Photomicrographs of the samples were also taken at 100× after 6, 24, and 48 h of exposure at 92% RH (Figures 5b, 5c, and 5d for the 24-h exposure). Crystallization of the lipid is far less dramatic than that observed at very low humidity. These photographs reveal largely liquid crystalline structures, even for the control material.

One unusual feature occurred in both the 10% Glyceridacid and 15% Glyceridacid samples after 48 h at 92% RH: flat, plate-like crystals with sharp right-angle contours appear mingled with the liquid crystalline phase. These crystals are unlike the fine, needle-shaped solid crystals that precipitated from the model upon loss of water. Furthermore, the crystals are more numerous in the 15% Glyceridacid sample than in the 10% Glyceridacid sample. This dose-dependence would indicate that Glyceridacid, either alone or in combination with one or more components of the model, separates from the gross structure. This formation was not apparent in samples exposed to low humidity; perhaps the simple crystallization of lipid upon dehydration is so rapid as to pre-empt the slow formation of this unidentified crystal form. These phenomena are under further investigation to define the compositions of the different solid crystals.

STUDIES WITH MODEL LIPID CONTAINING GLYCEROL

The DSC curve for the model lipid plus 5% glycerol (Figure 6b) is similar to that of the model lipid (Figure 6a) and was slightly changed after 6 h at 6% RH (Figure 6c); however, further incubation for 24 and 48 h induced the formation of a higher-temperature phase at a maximum of 70–75°C (Figures 6d and 6e). While we do not know the nature of this phase, we speculate that it is due to lateral phase separation of lipids induced by glycerol. Because of the broadness of the transitions, deconvolution of

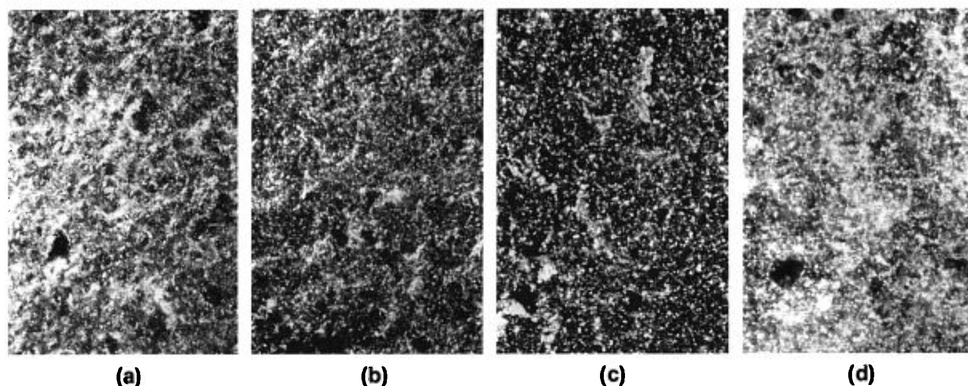

Figure 5. Model lipid with 0% (a), 5% (b), 10% (c), and 15% (d) Glyceridacid after 24-h exposure at 92% RH, viewed under polarized light at 100× magnification.

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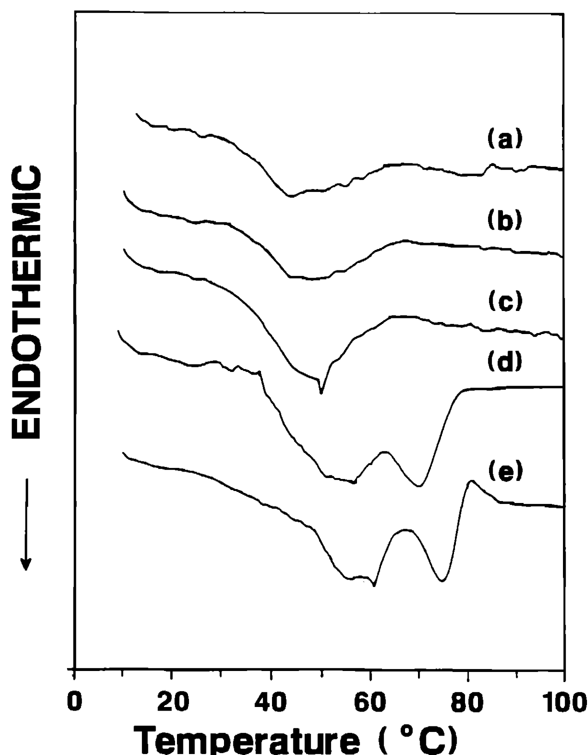

Figure 6. Differential scanning calorimetry of model lipid plus 5% glycerol incubated for 0 h (b), 6 h (c), 24 h (d), and 48 h (e) at 6% RH. Model lipid incubated for 0 h (a) included for comparison.

the separate phases was not possible. For these incubation times, the enthalpy of the main lipid transition was obtained by extrapolating the y-axis to intercept the temperature axis, cutting out the area for the transition, weighing this area, and comparing it with the weight of the total area, whose enthalpy is known. The enthalpy of the model lipid plus 5% glycerol at 6% RH after 6, 24, and 48 h is comparable to that of the model lipid without glycerol (Table II). Therefore, the liquid crystalline phase is not maintained at 5% glycerol concentration under low humidity conditions. Addition of 10% glycerol did not induce the higher temperature phase (at 70–75°C) even after 48 h at 6% RH (data not shown), but this phase was observed after 48 h at 92% RH. However, the liquid crystalline phase is partially maintained after 24 and 48 h at 6% RH (Table II), as indicated by the lower enthalpy of the model lipid plus glycerol compared to that of the control. At 92% RH, both 5% and 10% glycerol maintained the liquid crystalline phase of the model lipid, as observed from the enthalpy changes in Table II. Water loss from the model lipid was not affected by 5% or 10% glycerol at 6% RH (Table III) and was also noted previously (4). At 92% RH, 5% glycerol significantly reduced water evaporation from the model lipid, while humectancy of glycerol was observed at 10% concentration after 24 and 48 h (Table III) and was also observed previously (4).

These quantitative results are in good agreement with our recent study of the model lipid/glycerol system by optical microscopy (4); glycerol prevented crystallization of the model lipid at low humidity without preventing water loss. Therefore, glycerol, at 10%

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concentration or greater, functions as a skin conditioner at low humidities by this mechanism, while at high humidities, it acts as a humectant.

CONCLUSIONS

In the present investigation, we showed that DSC can be used as a quantitative tool to measure the changes in transition enthalpies of model stratum corneum lipids as the liquid crystalline phase is dehydrated under low-humidity conditions. DSC can also quantitatively measure the changes in enthalpy induced by dehydration or addition of a potential cosmetic ingredient.

DSC results suggest that Glyceridacid can be considered a potential moisturizer because it maintained the liquid crystalline state of the model lipid and prevented water evaporation; the enthalpy values showed small changes with time at low RH, and water loss was reduced compared to the model lipid alone. The results are consistent with previous observation on the skin-conditioning benefit of Glyceridacid (10). Glycerol is also considered a potential moisturizer at 10% concentration and at low humidity, since it maintained the liquid crystalline phase of the model lipid (although water loss was not prevented). This suggests an alternative mechanism for the action of glycerol at low humidity. The results are in agreement with previous findings of the model lipid/glycerol system, observed by polarized light microscopy (4). The ability of additives to maintain the liquid crystalline phase was dose-dependent. Glyceridacid was more effective at lower doses than glycerol. The results also showed at least two mechanisms by which additives can prevent crystallization of lipids: preventing water loss and interacting with the bilayer structure, thus fluidizing the lipid chains. While Glyceridacid is proposed to act by both mechanisms, glycerol functions mainly via the latter mechanism.

In our future research, we will utilize the DSC technique, together with water evaporation and optical microscopy studies, to examine the effects of a range of moisturizers/humectants on the phase behavior of model stratum corneum lipids. We will then determine the relevance of the findings to *in vivo* skin moisturization.

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