Gluplexes

NATIVE WHEAT PROTEIN COMPLEXES FOR USE IN SURFACTANT BASED SYSTEMS

INTRODUCTION
Proteins in detergency

Despite the increasing availability of highly skin-compatible surfactants that still retain excellent detergent properties, the adverse reactions potentially caused by these ingredients have never been underestimated by dermatologists and cosmetic scientists, and the subject persists as one of the key topics in cosmetology.

The mechanisms of the adverse effects produced by surfactants upon contact with skin and hair are not fully elucidated, but general agreement exists that penetration of surfactant within the keratin matrix of the stratum corneum or cuticle cells of the hair fibers is the first step of the tissue damage. Only monomeric surfactants can penetrate, while the hydrated micelles are too large to enter the tight network of keratin; thus, the concentration of tenside monomers (and hence the critical micelle concentration, CMC) should be related to the skin and hair damage.

Addition of protein substances to cleansing formulations is known to improve their skin and eye tolerability and to reduce the adverse effects of intense and repeated detergency (dehydration, roughness, impairment of the skin barrier function). The principal mechanism invoked to explain their protection effects is based on the formation of complexes between proteins and surfactants within the detergent formulation, which produce larger micelles and consequent lowering of the CMC of the system.

Protein derivatives used with this purpose are usually prepared by partial hydrolysis of plant reserve proteins or animal scleroproteins; the hydrolytic cleavage make them water soluble and suitable for use in liquid products, but causes a reduction of their ability to bind surfactants and decreases their foaming properties as well.

Native, non-hydrolyzed vegetable protein derivatives have been recently developed as active ingredients for detergency, with the aim to enhance their skin protecting performances. Water solubility and stability are obtained by means of complexation with surfactants, a special process that preserves their molecular size and structure. The beneficial effects of these new derivatives have been tested by monitoring two important biophysical indicators of the skin damage on detergency: the Transepidermal Water Loss (TEWL, indicator of the skin barrier function) and the Electric Capacitance (EC, indicator of the hydration of the horny layer).

NATIVE PROTEINS – SURFACTANT COMPLEXES
Mechanism of complexation

The binding of ionic surfactants to proteins is made possible by cooperative, noncovalent bonds, which can replace the intra- and intermolecular forces stabilizing the 3D conformation of the protein. This results in reversible unfolding of the protein coil (to a variable degree), while the surfactant molecules turn from a hydrated or micellar form into a bound...
species (Figure 1). A new species (complex) is formed: water solubility and surface hydrophobicity of proteins are greatly increased.

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Protection efficacy in vivo test – comparison with various protein hydrolysates

Epicutaneous tests were made to compare the ability of native wheat proteins and various protein hydrolysates to protect the skin from acute irritancy effects of surfactants. The occlusive patch test methodology was adopted as exposure model. 15 volunteers were involved in the test. The Transepidermal Water Loss was used as indicator of the skin damage. Evaluations were made at 24 hours intervals after patch removal, with a Tewameter® TM210 (Courage+Khazaka electronics, Germany). Measurements values are expressed as the % changes versus controls. It can be observed that all proteins restrain the TEWL increase caused by Sodium Lauryl Sulfate and that the new native wheat proteins derivatives (GLUPLEX) show the best performance (Figure 2).
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Protection efficacy in vitro test – comparison with various protein hydrolysates

Similar results were obtained by an alternative in vitro test, based on the swelling response of a collagen membrane. Principle of the method is that the amount of water absorbed by an insoluble collagen film immersed in a detergent preparation is predictive of its in vivo irritancy. Collagen membrane stripes are immersed in phosphate buffer solutions containing pure surfactant(s) alone and added with equal amount of different protein derivatives; the test samples are incubated in close containers at 50°C for 24 hours and the water uptake is measured.

Sodium Lauryl Sulfate (SLS) and Sodium Laureth Sulfate (SLES) were used as control tensides. The new native wheat protein derivatives (GLUPLEX) were compared with: keratin hydrolysate (average molecular weight 3000 Daltons), collagen hydrolysate (2000D), wheat protein hydrolysate (2200D). It can be observed that all protein derivatives reduce the water uptake caused by surfactants and that the new derivatives show the best performance (Figure 3).

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Protection efficacy in vivo test – quantitative evaluation

In order to quantitate the protective potential of native wheat proteins at different ratios with surfactants, the patch test methodology and TEWL measurements have been applied. In this test the surfactant’s concentration was brought to a high value (5%), to maximize the irritation response, and the exposure time was reduced to 8 hours. Native wheat protein content ranges from 0.5 to 5%. 15 volunteers were involved in this test.

It has been found a significant decrease of the irritation potential for both surfactants up to a surfactant/protein ratio of 10:1 (5% surfactant, 0.5% protein) (Figure 4).
In order to test the performances of the new protein derivatives in a real use situation, the collagen membrane test was applied to realistic detergent preparations containing increasing amounts of Native Wheat Protein – Surfactant Complex. Two simple bubble bath formulations with different irritation potential (A more irritant than B in a traditional patch test) were used. Some reduction in the collagen film swelling (predictive parameter of in vivo irritancy) was obtained at a surfactant-protein ratio of 10 : 1. The protection was comparatively more effective for the formulation with the higher content of sodium laureth sulfate and the higher irritation potential (Figure 5).

**Table 1**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formula A</th>
<th>Formula B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Laureth Sulfate 70%</td>
<td>25.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Cocamidopropylamine Oxide 30%</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Disodium Laureth Sulfosuccinate 40%</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>Disodium Cocoamphodiacetate 30%</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Pearlescent 35% (Sodium Laureth Sulfate, Glycol Distearate)</td>
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</tr>
<tr>
<td>Cocamide DEA</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>PEG-7 Glyceryl cocoate</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Glycerine</td>
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<td></td>
</tr>
<tr>
<td>Citric acid</td>
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<td>0.1</td>
</tr>
<tr>
<td>Preservatives, dyes, water</td>
<td>to 100%</td>
<td>to 100%</td>
</tr>
</tbody>
</table>

**Figure 5**

Collagen membrane test. Water uptake for formulations A and B (1% active washing substance for both), alone and in presence of increasing amounts of native wheat proteins (0.1 to 0.4%). Solutions were prepared in phosphate buffer 1mM pH 6.0. Incubation at 50°C for 24 hours. Each solution was tested in triplicate and the mean value was taken as the measurement value.
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Washing test – comparison with mild tensides

The forearm washing test was adopted as a more realistic exposure model respect to the soap chamber test, to evaluate the time course of the skin barrier function and the skin hydration upon cumulative exposure to detergents. 20 volunteers were subject to cycles of two daily washings (immersion of the forearm in a thermostated bath at 37°C) of 5 minutes for 3 weeks with the test solutions. One forearm was exposed to 1% Sodium Lauryl Sulfate (SLS); the opposite forearm was exposed to 1% SLS + 1% Cocamidopropyl betaine (10 subjects), or 1% SLS + 1% Native Wheat Proteins (10 subjects). TEWL was measured with a Tewameter® TM210; skin hydration was evaluated with a Corneometer® CM825 (Courage+Khazaka electronics, Germany).

On repeated exposure to the highly irritant SLS surfactant, an increase of the transepidermal water loss and a reduction of the water content in the skin are produced. These adverse effects, indicators of a progressive skin damage, are successfully counteracted by a mild tenside (Cocamidopropyl betaine) and by the large protein molecules contained in GLUPLEX. Native wheat proteins were found to prevent skin dehydration more efficiently then Cocamidopropyl betaine (Figure 6).

The measurement values are calculated as % change = \([\frac{X_{TR}}{X_{CTRL}}_T - \frac{X_{TR}}{X_{CTRL}}_B]\) \times 100, where:

- \(X_{TR}/X_{CTRL}\)_T = value ratio for treated and control sites at time T
- \(X_{TR}/X_{CTRL}\)_B = baseline value ratio for treated and control sites.
CONCLUSIONS
Formulating with Gluplexes

Gluplexes (Native wheat protein – surfactant complexes) should be considered protein additives for detergent formulations. Their major performance is the reduction of surfactant irritancy. Since they contain native, long chain wheat proteins, they are preferred to protein hydrolysates when a higher protection against the basic tensides of the formulation is needed. Due to the presence of complexed tensides, they retain an effective surface activity and in some product categories (cleansing lotions, freshening towelettes, toothpastes, mouth washers ...), where the concentration of the tensides is usually low (0.5-2%) they can replace the basic surfactants, resulting washing and foaming properties comparable to that of the correspondent tenside, but far lower irritation potential.

GLUPLEX Native Protein Surfactant Complexes

- 5% minimum protein content
- 5 - 8% surfactant content
- Compatible with surfactant solutions
- Fully water miscible
- Provides reduction of surfactant irritancy
- Improves foam properties
- Substantive to skin and hair
- Gluplex LES - Sodium laureth sulfate complex
- Gluplex AC - Potassium cocoate complex
- Gluplex OS - Sodium olefin sulfonate complex
- Gluplex LS - Sodium lauryl sulfate complex

REFERENCES

- Teglia A, Mazzola G, Secchi G. Relationship between chemical characteristics and cosmetic properties of protein hydrolysates. XVIIIth IFSCC Congress, Yokohama 1992; A207


• Steinhardt J, Scott JR, Birdi KS. Differences in the solubilizing effectiveness of the sodium dodecyl sulfate complexes of various proteins. Biochemistry 1977; 16(4):718-725

