



Role of macromolecules in the safety of use of body wash cosmetics



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ABSTRACT

One of the most challenging problems related to the use of surfactants in body wash cosmetics is their potential to cause skin irritations. Surfactants can bind with proteins, remove lipids from the epidermal surface, contribute to the disorganization of liquid crystal structures in the intercellular lipids, and interact with living skin cells. These processes can lead to skin irritations and allergic reactions, and impair the epidermal barrier function.

The present study is an attempt to assess the effect of polymers and hydrolysed proteins present in the formulations of model body wash cosmetics on product properties. Special attention was given to the safety of use of this product type. The study examined three macromolecules: polyvinylpyrrolidone (PVP), hydrolysed wheat protein (HWP) and polyvinylpyrrolidone/hydrolysed wheat protein crosspolymer (PVP/HWP). The addition of the substances under study was found to improve the foaming properties of body wash cosmetics, increase their stability during storage, and contribute significantly to an improvement in the safety of product use by reducing the irritant potential. The strongest ability to reduce the skin irritation potential was determined for the formula enriched with the PVP/HWP crosspolymer.

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1. Introduction

Due to their amphiphilic structure and a range of unique properties associated with it, surfactants (surface active agents) have found a variety of applications in many branches of industry. They are used, for example, in the detergent, cosmetics, petrochemical and pharmaceutical industries, in agriculture and in medicine [1–6]. Surfactant molecules consist of two parts: hydrophilic (showing affinity to polar substances) and hydrophobic (having affinity to non-polar substances). The bipolar structure of surfactant molecules is responsible for their surface activity. Due to their adsorption capacity and ability to reduce surface tension at the interface between phases, surfactant molecules make it possible to combine two immiscible substances, e.g. water and oil (emulsification, solubilization), disperse air bubbles in the liquid phase (foam formation) and wet the hydrophobic surface by water (process of soil removal). It is due to these properties that surfactants have a broad array of applications in cosmetics and household chemicals [1–4]. The main activity of surfactants in these products is the washing effect [1–6].

Body wash cosmetics and detergents are typically aqueous (10–20%) solutions of surfactants enriched with various substances in order to enhance the washing effect, achieve an appropriate consistency (viscosity), colour, fragranciness or product preservation [4–6]. Despite a number of benefits, surface active agents also possess a range of unfavourable characteristics. With respect to cosmetics and detergents that are in frequent contact with the skin, one of the greatest disadvantages of surfactants is their potential to cause skin irritations and allergies [7,8]. The literature data [7–23] suggest that the highest irritant potential is associated with ionic surfactants which are used in many products as the primary washing agent [2–6].

The irritant potential of washing products is a consequence of diverse types of interactions between surface active agents and the skin. Above all, surfactants exhibit an ability to bind to proteins which are present in the stratum corneum (SC). The interaction leads to degradation of the protein structure and to protein denaturation, culminating in the process referred to as SC swelling [7–23]. The activity is attributed primarily to anionic surfactants, such as sodium lauryl sulphate [10,11,14,16,18] and sodium laurate [21], due to relatively strong electrostatic interactions occurring between this group of surfactants and proteins. Non-ionic surfactants interact with the SC proteins primarily through relatively weak hydrogen bonding interactions, which is why their protein denaturing ability, and hence their capacity to cause skin irritations

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via this mechanism, is limited [7,8,21]. Surfactants can also cause solubilization of epidermal and intercellular lipids, resulting in the disintegration of the liquid crystal structure of the intercellular cement and damage to the skin's barrier function. The processes can ultimately facilitate the penetration of various substances (surfactants included) into the intercellular cement structure, and increase transepidermal water loss (TEWL) [7,8,20,21]. Another mechanism of contact between surfactants and the skin involves surfactant interactions with living cells of the dermis, corneocytes and Langerhans cells which participate in immune processes. Cell damage can accelerate proliferation, dilation of blood vessels or aggregation of blood cells [7,8,21].

Numerous studies [7–23] provide evidence showing that interactions occurring between surfactants and the SC depend primarily on the time of contact, surfactant concentration and structure. In the homologous series, the strongest interactions are noted for molecules containing 12 carbon atoms in the hydrophobic chain and at concentrations immediately below the critical micelle concentration (CMC). At concentrations not exceeding the CMC, the protein binding capacity rises along with the increase in surfactant concentration. Above the CMC, the interactions are not directly proportional, and their nature depends on the type of the surface active agent. Studies [7–23] point out the considerable role of surfactant monomers (the form which occurs in solutions at concentrations below the CMC) in triggering skin irritations. Owing to their small size, monomers easily enter through the pores into the SC, bind to the surface proteins and interact with the intercellular cement. The process is much more difficult for micelles, which are larger in size. After reaching the CMC, however, the irritant potential of surfactants does not remain constant. Repulsive forces existing between the hydrophilic parts of surfactants in micelles make micellar aggregates thermodynamically unstable which constantly disintegrate, releasing free monomers into the solution. When the CMC is exceeded, a state of equilibrium is achieved between surfactant molecules in micelles and monomers in the bulk phase. It has been suggested that an increased irritant potential observed after the formation of micelles in the solution is linked to monomers released from them or to emerging submicellar structures which are similar in size to skin pores [7].

It is assumed that every activity which increases the size of micelles, stabilizes them and reduces the number of free monomers can produce a decrease in the irritant potential of surfactants [7–23]. The most common strategy employed in industrial practice to reduce the irritant potential of surfactants is using their mixtures [7,8,21]. An addition of cationic, non-ionic and amphoteric surface active agents to anionic surfactant solutions has been shown to contribute to an increase in size and stabilization of micelles [1,7,8,12,15–17,20,21,23]. The permanence and stability of anionic surfactant micelles are small because of electrostatic repulsion of hydrophilic parts. An addition of a different type of surfactant reduces repulsive forces acting between the hydrophilic heads, thus stabilizing micelles and preventing micellar disintegration. Since the size of micelles increases as well, the penetration of aggregates deep into the epidermis is markedly impeded. A similar effect can be demonstrated by macromolecules (polymers, proteins and hydrolysed proteins) or refatting agents [1,7,8,12,15–17,20,21,23]. Their interactions with surfactants lead to an increased size of micellar aggregates and micellar stabilization through the incorporation into their structures and formation of complexes with surfactants (the mechanism underlying the process is discussed below).

A very important aspect in the process of formulating cosmetics is the selection of ingredients, so that the use of any given ingredient aimed at improving a specific product property does not have an adverse effect on other functional properties. Regarding the safety of use, the widely applied solution in the form of surfactant

mixtures (e.g. anionic and non-ionic) can contribute to limiting interactions between surfactants and proteins but, at the same time, has a capacity to increase the quantity of lipids washed away from the skin due to the strong potential of non-ionic surfactants to emulsify fatty substances. The present study explores the possibilities for incorporating macromolecules into the formulations of model body wash cosmetics as additives enhancing the safety of product use, taking into account the effects on other aspects related to product use (functionality). The study assessed the impact of polymer type on the irritant activity of model cosmetics (zein number, change in the pH of bovine serum albumin solution) as well as basic determinants of the quality of body wash cosmetics including foaming properties, viscosity, turbidity and stability.

2. Materials and methods

2.1. Materials

Raw materials used in the commercial cosmetics were used to develop the body wash gels: *Sodium Laureth-2 Sulfate* (SLES, trade name Brensurf 25; supplier Brenntag, Poland), *Cocamidopropyl Betaine* (Dehyton K, BASF, Germany), *Citric Acid* (Citric Acid, Chempur, Poland), *Polyvinylpyrrolidone*; average molecular weight 50,000 Da (Luviskol K30, BASF, Germany), *Polyvinylpyrrolidone/Hydrolysed Wheat Protein Crosspolymer*; average molecular weight 40,000 Da (Hydrotriticum PVP, Croda, UK), *Hydrolysed Wheat Protein*; average molecular weight 20,000 Da (Gludain AGP, BASF, Germany), *Sodium Chloride* (Sodium Chloride, Chempur, Poland), *Sodium Benzoate* and *Potassium Sorbate* (Euxyl K712, Schuelke & Mayr, Schuelke Poland), MiliQ water.

In the physico-chemical tests were used: zein from corn (Zein, Sigma-Aldrich, USA), Albumin (Albumin Bovine fraction V, Bioshop, Canada), potassium sulfate (Chempur, Poland), copper sulfate pentahydrate (Chempur, Poland), sulfuric acid 98% (Chempur, Poland), Tashiro indicator (Chempur, Poland), sodium hydroxide, citric acid (Chempur, Poland). All reagents were analytical grade.

2.2. Methods

2.2.1. Viscosity measurements

A Fungilab Expert (Fungilab, Spain) rheometer was used. Measurements were carried out at 22 °C with a rotary speed of the spindle of 10 rpm. Viscosity values presented in the figures below represent average values obtained from five independent measurements.

2.3. Determination of the foaming properties

The method of measurement was in line with Polish Standard PN-ISO 696:1994P (Surface active agents – Measurement of foaming power – Modified Ross-Miles method). The foam volume produced by 500 mL of samples solutions (1 wt%) falling from a height of 450 mm into a cylinder (1000 mL) containing 50 mL of the same solution was measured. Measurements were carried out at 22 °C. The final result was the arithmetic mean of five independent measurements. Foam stability was calculated from the equation:

$$\text{Foam stability} = \frac{V_{10}}{V_1} \times 100\%$$

where: V_{10} – foam volume after 10 min, V_1 – foam volume after 1 min.

2.4. Determination of the turbidity

The test was performed using a HACH 2100 AN turbidity analyzer (turbidimeter). The sample was transferred to a cuvette,

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