INTERACTIONS OF NONIONIC AND ANIONIC SURFACTANTS WITH COLLAGEN

Jiří Krejčí Rahula Janiš Iva Doležálková Jaroslava Kucejová Pavlína Vltavská Markéta Jančíková Tomas Bata University in Zlin Nám. T.G.M 275, 762 72, Zlin Czech Republic

ABSTRACT

Anionic surfactants are being used as the main active ingredient in cleaning products intended for industrial or personal use. Another ingredients included in cleanser systems because of their synergistic effect are nonionic surfactants. Taking into account that surfactants can induce a skin irritation, their interactions with skin components need to be evaluated.. The aim of this study was to assess a sorption of anionic surfactant sodium dodecyl sulphate (SDS), nonionic surfactant Igepal CA 720 (Ig) and their mixtures on collagen fibres - the major skin proteins. During the interaction, the amount of bound surfactant (Q_i) and the swelling degree of collagen fibres (α_m) were determined. It was confirmed, that the effect of surfactant on skin depends on pH value. At pH = 6 large amount of anionic surfactant Ig. Using a mixture of both surfactants, the amount of surfactants bound was only 0,3 mmol/g. Addition of nonionic surfactant did not lead to a reduction of SDS detergent efficacy, but caused a significant decrease in SDS irritation potential as demonstrated by determination of the swelling degree. Presence of nonionic surfactants in the mixture decreased collagen swelling and therefore improved barrier function of skin.

Keawords: nonionic and anionic surfactants, collagen, swelling degree of collagen fibres

1. INTRODUCTION

The basic function of the skin is the protection of the body against environmental influences and the skin structure is highly adapted to this purpose. The uppermost layer of the skin - stratum coneum consists of corneocytes and lipid molecules that form bilayer structures [1]. These structures serve as the main barrier to the diffusion of substances into the skin and are also responsible for the high water impermeability [2]. Collagen fibres are the major component of the lower part of the skin - dermis. In comparison with keratine, which is the major component of epidermis, collagen is more reactive and hydrophilic. The presence of water and various chemicals can induce physical changes in collagen fibres that can affect the skin condition.

Surfactants are commonly used in personal care products as a part of various cleansing and washing products. Their primary aim is the removal of soils and excess sebum, however it is also well understood that the use of surfactants can result in unfavorable removal of intercellular lipids, which can lead to reduced skin barrier function. Moreover, surfactants are able to penetrate into the deeper layers of the skin and react with keratine and collagen [3].

A heterogenous system of collagen-ionic surfactants was investigated by many authors. Maldonado et al. [3] assume two-stage sorption. Interactions in the first stage proceeds on the basis of electrostatic forces, in the second stage decisive hydrophobic interactions occur between already bound molecules of ionic surfactants and free molecules in solution.

Nonionic surfactants react only in the presence of the ionic ones. According to Henriquez et al. [4] the decisive role in ionic surfactants binding is played by hydrophobic interactions. Under isoelectric conditions low sorption occurs and interactions are not cooperative. Together with sorption a mild swelling of collagen fibres occurs at concentrations near the c.m.c. Krejčí et al. [5] studied the interaction of anionic surfactant mixture with collagen fibres at various mixture composition and ionic strenghts. Changes in the mixture composition after sorption depend on the surfactant nature as well as on interactions of surfactants in mixed micelles. But these changes are not very significant.

The aim of our study was to describe a binding of the mixture of anionic surfactant sodium dodecyl sulfate and nonionic surfactant Igepal CA 720 to collagen fibres.

2. MATERIAL AND METHODS

Collagen was obtained from beef Achilles' tendons by Křivinka method [6]. Both surfactants, SDS and Igepal CA 720, were of 99% purity and were employed without further treatment. Both surfactants were used either alone or in mixture defined by molar fraction of SDS (x_{SDS}) and Britton-Robinson buffer (pH=6 or pH=4) was used to dissolve surfactants. The exact procedure for surfactant-collagen reaction and the calculation of the bound amount of surfactants (Qt) and mass swelling degree (α m) was described in Křivinka et al. [6]. The composition of surfactant mixture prior and after the reaction was determined by standard spectrophotometric method of methylene blue for SDS and by UV spectrophotometric method (λ =221.5) for Igepal.

3. RESULTS AND DISCUSSION

The chosen methods allowed the evaluation of interactions of collagen with surfactants either alone or in 1:1 mixture ($x_{SDS} = 0.5$). Results are expressed as sorption isotherms and mass swelling degree of collagen fibres. Sorption isotherms of SDS in pH=4 and pH=6 are compared in Fig. 1.



Figure 1. Sorption isotherms of SDS to collagen fibre at ph=4 and pH=6

As expected, the amount of bound surfactant (Q_t) was higher at lower pH due to higher charge density of collagen fibres, that resulted in higher level of primary and secondary sorption. The Q_t values are in accordance with the values commonly reported for protein-anionic surfactant interactions [3,5]. No binding was observed with nonionic surfactant Igepal, which is also supported by other studies [3]. Dependence of the mass swelling degree α_m on pH is indicated in Fig.2. Taking into account equilibrium concentration (C_R) of surfactant and the corresponding amount of bound surfactant, in acid environment steep decrease in α_m occurred in the first stage (primary sorption), then a gradual increase in α_m was observed due to anionic surfactant sorption.



Figure 2. Changes in the mass swelling degree (α_m) in SDS-collagen system at pH=4 and pH=6

Sorption isotherms of individual surfactants in SDS-Igepal mixture (1:1) at different pH are compared in Fig. 3. The measuring method enabled us to determine individual isotherms for each surfactant in the mixture separately. It is evident, that sorption of both surfactants in the mixture is higher at pH=4 when compared to pH=6. Nevertheless, the total amount of bound surfactants is about 50% lower than the Q_t of SDS alone. Similarly, at pH=6 the total amount of bound surfactants in mixture did not exceed 20% of Q_t acquired for SDS.



Figure 3. Sorption isotherms of SDS and Igepal in SDS-Igepal mixture (1:1) at pH=4 and pH=6

The changes in mass swelling degree of collagen fibres after interactions with surfactant mixture are shown in Fig. 4. These changes in α_m values showed a similar trend as changes in α_m values measured for SDS alone, although the swelling degree of collagen in the presence of surfactant mixture did not raised gradually in the higher equilibrium concentrations of surfactants. After interaction of surfactant mixture, the values of α_m remained at the level of values reported for collagen fibres in physiological environment.



Figure 4. Changes in the mass swelling degree (α_m) of collagen in SDS-Igepal mixture (1:1) at pH=4 and pH=6

4. CONCLUSION

Mixture of anionic and nonionic surfactants has the ability of sorption to collagen fibres in both acidic environment and the environment near the isoelectric point. Total amount of bound surfactants is significantly lower than the amount of bound anionic surfactant alone. Nonionic surfactant added to the reaction mixture prevented the collagen fibres from swelling and therefore its addition could be suitable in various cleansing formulations intended for products coming into contact with human skin.

5. ACKNOWLEDGEMENT

This work was supported by the project of the Czech Ministry of Education, Youth and Sports No. MSM 708 835 2101.

6. REFERENCES

- [1] Tagahami H.: Stratum corneum as a barrier in the skin. Jpn. J. Dermatol. 108, 713-727, 1990.,
- [2] Dykes P.: Surfactants and the skin. Int. J. Cosmet. Sci. 20, 53-61, 1992.,
- [3] Maldonado F., Almeda M., Otero A. and Costa-Lopez J.: The binding of surfactants to collagen, J. Protein Chem. 10, 189–192, 1992.
- [4] Henriquez M., Lissi E., Abuin E. and Cifferi A.: Assembly of amphiphilic compounds and rigid polymers, Interaction of sodium dodecyl sulfate with collagen. Macromolecules 27, 6834–6840, 1994.
- [5] Krejčí J.: Interaction of mixture of anionic surfactants with collagen. Int. J. Cosmet. Sci. 29, 121-129, 2007.,
- [6] Křivinka M., Vinklárek Z. and Krejčí J.: Heterogenous surfactant-collagen interaction. Tenside Surfactants Detergents 34, 22–27, 1997.