The influence of ascorbic acid on the rheological properties of the microemulsion region of the SDS/pentanol/water system

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Synopsis

The rheological properties of the microemulsion region of the SDS, pentanol, and water micellar system have been studied experimentally. The W/O and O/W microemulsions behave as typical Newtonian fluids: viscosity remains constant independent of the shear rate. For the bicontinuous system the shear-thinning effect is observed. The addition of ascorbic acid to the system caused a microemulsion viscosity increase, which was the highest in the bicontinuous region and at the lowest temperature.

INTRODUCTION

It is well known that rheology is an excellent tool for obtaining information about changes in colloidal structures and their interactions (1,2). Associated colloid molecules generally form spherical aggregates in the aqueous solution above the CMC concentration value (2). Under appropriate conditions of concentration, salinity, and temperature, in the presence of counterions, these spherical micelles grow in size or change their shape, resulting in the formation of rodlike structures or even long flexible micelles. For the dilute ionic surfactant solution, a simple way to transform spherical micelles to cylindrical micelles is to change the packing parameter, i.e., to decrease the effective headgroup area by adding salt, which diminishes the electrostatic repulsion between the headgroups and allows them to be located closer. With the increasing salt concentration, the cylindrical aggregates grow to flexible wormlike micelles and behave like polymers (3). The formation of such structures modifies the rheological properties of surfactant solutions significantly. This effect is more pronounced in the systems with cationic surfactants than in those containing nonionic and anionic surfactants (3–12).

In emulsions the relationship between structure and rheology has been widely investigated (13–17). As follows from these investigations, the viscosity of a mesophase

structure, such as a lamellar phase, can be many orders of magnitude higher than that of an isotropic swollen micellar phase that can have a composition only slightly different from that of the mesophase. The viscosity of an emulsion is one of the most important factors when it is used as a delivery system in cosmetic and pharmaceutical applications.

The present work is part of our wider studies of the influence of the microenvironment (i.e., type of micellar system) on the activity of antioxidants of varying hydrophobicity (18–23). In this context, it seems interesting to investigate how the addition of bioactive species to the emulsion system changes its rheological properties.

Vitamin C, in the form of L-ascorbic acid (AA), is the most popular antioxidant. It can protect tissues and cells against oxidative damage by free radicals and reactive oxygenderived species (18,24,25,27–31). Vitamin C also improves the elasticity of the skin and reduces wrinkles by its well-known ability to take part in proline and lysine hydroxylation in collagen biosynthesis. Because of its ability to suppress pigmentation of the skin and decomposition of melanin, it can be used as a whitening agent, removing age spots (28-30). For the reasons mentioned above, vitamin C has been used in cosmetic and dermatological products. Because of its hydrophilic character, ascorbic acid has a lower ability to penetrate into the skin. Therefore it is important to select a suitable carrier system to deliver it to the site of action. Microemulsions such as the colloidal drug (e.g., vitamins) delivery systems are preferred because they usually enhance penetration. After application to the skin, the microemulsion components interact with the intercellular lipids of the skin, resulting in changes in their liquid lamellar structure. This effect facilitates drug transport (31-34). Other advantages of microemulsions are thermodynamic stability, simple technology of preparation, and high solubilizing power (35). Although the use of microemulsions seems to be suitable for cosmetic products, it should be noted that they are very often a low-viscosity Newtonian fluid (13). For this reason, they cannot be applied directly to the skin without modifying their viscosity. The usual way to solve this problem is to add suitable thickening agents. But first of all, depending on the final requirements for the product (moisturizing cream, nourishing cream, massage cream) and the skin conditions of the user, the emulsion type and its rheological properties (cream or lotion) should be determined.

In the literature one can find propositions of delivery systems of ascorbic acid and its derivatives, which are most convenient for cosmetics (25,26-34). Spičlin et al. (28,29) proposed as the delivery system for ascorbyl palmitate and sodium ascorbyl phosphate the microemulsion consisting of the medium-chain-length trigliceryde Mygliol 812 as the oil phase, the PEG 8 caprylic/capric glycerides (Labrasol) as the surfactant, the polyglyceryl-6-dioleate Plurol oleique as the cosurfactant, and water. Gallarate et al. (31) in their studies of ascorbic acid stability in emulsified systems for topical and cosmetic use applied O/W microemulsions, O/W and W/O emulsions, and a W/O/W multiple emulsion prepared using the nonionic, skin-compatible emulsifiers dodecylglucoside and cocoamide propylbetaine. As oil they applied isopropyl palmitate or cetearyl octanoate, and 2-ethyl-1,3-hexanediol was chosen as the cosurfactant. The authors underlined the possibility of increasing the stability of AA by choosing an appropriate type of emulsified system in which it is vehicled. The W/O/W multiple emulsion appears to be an interesting topical vehicle for AA, as it provides better stability of the vitamin over time than that given by the W/O emulsion. Han et al. (25) studied the phase behavior of alkanoyl-6-O-ascorbates/water/dodecane mixtures and butyl lactate and butanol as the cosurfactants as far as the application of vitamin derivatives in cosmetics is concerned.



Figure 1. Solubilization of ascorbic acid in a microemulsion region formed by water, pentanol, and SDS.

1-pentanol	H ₂ O	Microemulsion type
(wt %)	(wt %)	(wt %)
89	5	W/O
77	17	W/O
75	19	W/O
65	29	W/O
50	44	W/O
39	55	W/O
22	72	Bicontinuous system
7	87	O/W
5	89	O/W
3	91	O/W
1	93	O/W
0	94	Micellar solution

Table I
Composition (Percentage by Weight) and Type of the Examined Samples

In all samples the SDS content was 6% by weight.

They concluded that alkanoyl-6-O-ascorbates are more stable in surfactant aggregates than in the aqueous solution.

The systems mentioned above contain many ingredients that improve their properties. They are rather not suitable for basic studies. We propose as the model system that consisting of SDS, pentanol, and water. The first reason for investigating this system is that it contains a very well pronounced microemulsion region (18,36,37). This region includes an inverse micellar solution, which is the basis for W/O microemulsions, a bicontinuous part, and the aqueous micellar solution that forms the basis for the O/W microemulsions. The second reason is that ascorbic acid can be solubilized up to 60% by weight into a microemulsion (18). Therefore, in our opinion, this system can serve as a model for studying an effect of AA on the rheological properties of various types of microemulsion.

Understanding the rheology of the antioxidant-containing emulsions is useful not only



Figure. 2. Influence of temperature on the viscosity of the microemulsion region of the SDS/pentanol/water system.

Table II Temperature Influence on Viscosity of Water				
Temperature	Data 1 (mN · s/m ²) (mPa · s)	Data 2 (mN · s/m ²) (mPa · s)	Data exp. (mN · s/m ²) (mPa · s)	
15°C	1.404		1.11	
22°C	0.958	1.005*	0.931	
30°C	0.807	0.801	0.812	
40°C	0.656	0.656	0.664	

* 20°C: data 1-(40); data 2-(41); data exp.-measured values.

in various pharmaceutical and cosmetic formulations, where processing variables can result in a change of dispersed phase volume, size distribution, and particle-particle interaction as well as particle deformability, but also in studying the naturally occurring processes. Micelles can be considered as a simple model of the cell membranes present in the biological system (18,25,38,39).

EXPERIMENTAL

The sodium dodecyl sulphate, L-ascorbic acid, and 1-pentanol used were supplied by Fluka Chemie and RdH Laborchemicalien GmbH & Co. KG. Water was doubly redistilled.



Figure 3. Flow curves for (a) W/O microemulsion, (b) bicontinuous system, and (c) O/W microemulsion.

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Figure 4. Influence of ascorbic acid concentration on the viscosity of the microemulsion region of the SDS/pentanol/water system: (a) temperature 15°C, (b) temperature 22°C, (c) temperature 30°C, and (d) temperature 40°C.

The microemulsion was prepared by titration of pentanol and sodium dodecyl sulphate mixtures of various weight ratios by ascorbic acid water solution. This mixture was vigorously mixed to obtain a clear and highly stable microemulsion.

To determine the influence of ascorbic acid on the rheology of SDS/pentanol/ H_2O microemulsions, samples with 6% SDS (percentage by weight) and increasing contents of ascorbic acid were examined (along a dashed line corresponding to 6% SDS in the phase diagram) (Figure 1 (18,37); Table I).



All rheological measurements were conducted with a Bohlin Rheometer CVO 50 with a PC computer and thermostat RTE 111 M (Spectro-Lab). The double-gap measuring system DG 24/27 consists of a hollow cylinder, which is lowered into a cylindrical groove

in the outer cylinder. The sample of microemulsion is contained in the double annular gap between them. The time of measurement was 1957 s, shear stress σ was changed in the range of $3.24 \cdot 10^{-2} - 64$ mPa, and shear rate $\dot{\gamma}$ was changed from 2.5 to 5.0 s⁻¹.

RESULT AND DISCUSSION

VISCOSITY OF MICROEMULSION FORMED IN THE SDS/PENTANOL/WATER SYSTEM

The viscosity of the studied system as it goes from the isotropic phase through a lamellar mesophase regime and again to an isotropic phase at high water content is presented in Figure 2.

Microemulsion viscosity increases with increasing water content in the system beginning with the value characteristics for pentanol (4.65 mPa \cdot s for 15°C; 2.99 mPa \cdot s for 30°C) (40). In an inverse micellar solution, the basis for W/O microemulsion, it reaches a plateau at the value of water concentration, depending on the temperature (40 wt % of water for 15°C; 10 wt % of water for 40°C), which finishes at 72 wt % of water content (in a bicontinuous part of the phase diagram). Next, the viscosity of the aqueous micellar solution that forms the basis for the O/W microemulsion decreases and finally reaches the value close to that characteristic for water (Table II).

As expected, the increase in the temperature of the system ($15^{\circ}C$, $22^{\circ}C$, $30^{\circ}C$, and $40^{\circ}C$) caused the microemulsion's viscosity to decrease. These data are in accordance with the well known theoretical fact that the viscosity of material is usually found to decrease with an increase in temperature, assuming no physical/chemical changes are being induced by the applied heat energy (42,43).

Figure 3 presents three examples of so-called flow curves: Figure 3a for the water-in-oil microemulsion (6% SDS, 65% pentanol, 29% water), Figure 3b for the bicontinuous system (6% SDS, 22% pentanol, 72% water) and Figure 3c for the oil-in-water micro-emulsion (6% SDS, 1% pentanol, 93% water).

For W/O and O/W microemulsions the measured viscosity of fluid remains constant independent of the shear rate. These systems demonstrate Newtonian behavior (Figures 3a and 3c). For the bicontinuous system, viscosity decreases as the shear rate is increased—shear thinning behavior (Figure 3b). One can notice that the experimental viscosity values are changing in the same manner as those typical for the emulsion system described by Israelachvili (13). The fact outlined above that the bicontinuous phase exhibits non-Newtonian behavior is connected with the large-scale structure in a material. From the statistical picture of a bicontinuous microemulsion, the structure behaves similarly to a highly crosslinked polymer, and consequently rheology similar to that of swollen gels might be expected. However, the microemulsion structure is rapidly fluctuating so that it flows easily, and although snapshots of a polymer gel and a bicontinuous phase might be topologically similar, their dynamic behavior is not at all so (44,45).

INFLUENCE OF ASCORBIC ACID (AA) ON THE RHEOLOGICAL PROPERTIES OF THE MICROEMULSION REGION OF THE SDS/PENTANOL/WATER SYSTEM

As follows from our own experiments, ascorbic acid is dissolved/solubilized up to 60%

in the microemulsion region of the SDS/pentanol/water system (18). The % content of ascorbic acid in the sample ought to be understood as a percent of the total microemulsion weight in this sample. The addition of AA to the system caused reduction of the microemulsion region in the phase diagram. Ascorbic acid serves as a competitive organic anion to the surfactant, changing the W/O microemulsion system towards an O/W one. Figure 4 illustrates the influence of ascorbic acid on the rheological properties of the surfactant system.

The ascorbic acid addition to the system (2%, 10%, 20%, 60% of the microemulsion weight) caused the increase in the microemulsion viscosity, the highest in the bicontinuous region (see Figure 4a for 15°C, Figure 4b for 22°C, Figure 4c for 30°C, and Figure 4d for 40°C). One can notice the decrease in the W/O microemulsion region with the increasing AA concentration, which is consistent with the phase diagram described earlier. As we have already mentioned, the phenomenon of viscosity increasing occurs because the AA presence in the system changes its microstructure. The ascorbic acid, being an electrolyte, causes formation of bigger surfactant aggregates, which contain some amount of the continuous phase. As a result, the volume of the dispersed phase increases, resulting in an increase in the total viscosity of the colloidal system (42).

The temperature dependence of viscosity is more clearly seen in Figure 5, where an example for the ascobic acid concentration equal to 20% is presented. There is a great consistency in the results presented above with those discussed earlier (Figure 2) and with the typical viscosity/temperature curves for microemulsions known from data in the literature (13,42,45).



Figure 5. Influence of temperature on the viscosity of the microemulsion region of the SDS/pentanol/water system (20% ascorbic acid).

CONCLUSION

From the investigations carried out it can be stated that:

1. The W/O and O/W microemulsion region of the SDS/pentanol/water system behaves as a typical Newtonian fluid: viscosity remains constant for all the shear rates.

2. The ascorbic acid addition to the system causes the viscosity of the microemulsion to increase. The largest η increases were observed in the bicontinuous region and at the lowest investigated temperature. The ascorbic acid presence in the system changes its microstructure, which causes changes in the colloidal system's viscosity.

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