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The structure elucidation of semisolid w/o emulsion systems containing silicone surfactant

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Abstract

In the course of investigating the effects of silicone surfactant (Abil WE 09®) on the microstructure of semisolid w/o emulsion systems with different water/oil ratios, only dispersed droplets of the internal water phase (1-15 μm size) were discovered in the gel network of white petrolatum. With increasing water content (from 40 to 90% w/w) the degree of dispersity was found to increase (microscopic analysis-polarized light microscopy and TEM). Experiments were also carried out using differential scanning calorimetry (DSC) and rheometry (rotational and oscillatory viscosimetry). The DSC results showed different behaviour of the investigated systems on controlled cooling. In semisolid emulsion systems with droplets small enough and of equal size, a homogeneous nucleation temperature was achieved. In emulsion systems containing a high percentage of water, the assumption that the behaviour of water was like that of the pure (bulk) water was acceptable. All semisolid emulsion systems exhibited pseudoplastic behaviour. Their viscoelastic properties determined using oscillation rheometry correlated well with rotational results.

Key words: Silicone surfactant; Semisolid emulsion system; Transmission electron microscopy; DSC; Rotational rheology; Viscoelasticity

1. Introduction

Nowadays semisolid emulsion systems are very popular formulations, not only for topical delivery (dermal, transdermal), but also for peroral and parenteral administration. Since the structure of a system is responsible for its physical properties (e.g., viscoelasticity) and drug bioavailability, investigations of the structure are essential. The majority of studies have been performed in o/w semisolid emulsion systems (De Vringer, 1986; Eccleston, 1986; Tiddy, 1987), however, few literature data are available concerning w/o systems (Junginger et al., 1983). Recent studies have been focused on the freezing behaviour of water in these systems (Brüggeller, 1982; Motta and Mignini, 1988). The freezing behaviour of emulsified water droplets is affected by several factors,

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especially by the nature and concentration of the surfactant, polydispersity of the internal phase droplets, and salts, dissolved in the aqueous phase (Ganguly, 1992).

Silicone surfactants represent a new group of silicones. They are popular ingredients of cosmetic emulsion systems because of their thermal and chemical stability and lack of physiological effects. Data concerning their use in pharmaceutical systems are sparse (Müller-Goymann, 1992). Their ability to lower surface tension is very similar to that of the well-known organic surfactants. The interfacial tension between water and oils (varying from 35 to 12 mN/m) decreases following the addition of silicone surfactant (to 1–2 mN/m) (Hameyer, 1990). For the silicone part of the molecule, not only hydrophobic, but also lipophobic behaviour is characteristic (Šmid-Korbar et al., 1990). These properties are influenced by different side chains introduced into the molecule. The silicone surfactant used, containing hydrophilic polyether and lipophilic alkyl groups as side chains, is mostly lipophilic. The results of miscibility testing with commonly used components of liquid and semisolid emulsions have confirmed this statement (Gašperlin et al., 1992). Semisolid w/o emulsion systems prepared with silicone surfactant polysiloxane-polyalkylene-polyether copolymer are exceptionally physically stable (Gašperlin et al., 1992). Its stabilizing effect has been explained on the basis of its strong adsorption at the water-oil interface (Fig. 1) (Schefer, 1988) and its polymeric nature (steric efect). The aim of this study was to elucidate the microstructure of semisolid w/o emulsion systems containing silicone surfactant by means of microscopic analysis (polarized light microscopy and TEM), differential scanning calorimetry (DSC) and rheology (rotational and oscillatory viscosimetry).

2. Materials and methods

The silicone surfactant used is a mixture of polysiloxane-polyalkylene-polyether copolymer and nonionic surfactants (Abil WE 09®, T. Goldschmidt, Essen, Germany) (Fig. 1). White petrolatum and purified water met the requirements of DAB 10.

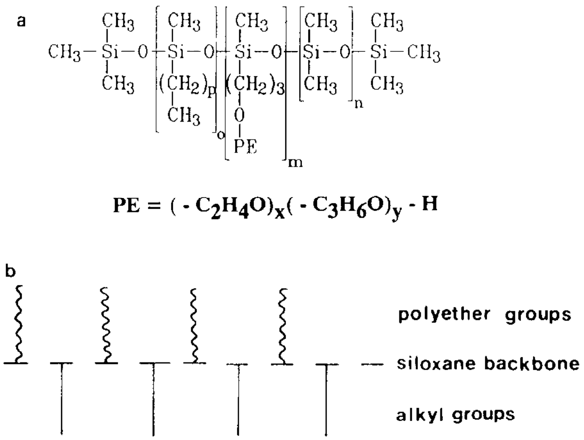

Fig. 1. Chemical structure of the silicone surfactant used (a) and its orientation at the water-oil interface (b).

2.1. Preparation of semisolid emulsion systems

Semisolid emulsion systems were prepared by cold emulsification. The purified water/white petrolatum ratio was modified, whilst the surfactant amount was kept equal in all samples. The compositions of the emulsion systems are listed in Table 1.

2.2. Polarized light microscopy

Each emulsion system was examined using a Carl Zeiss microscope (Jena, Germany) under polarized light immediately after preparation.

Table 1
Compositions of semisolid emulsion systems containing the silicone surfactant tested

Emulsion system	White petrolatum (% w/w)	Purified water (% w/w)	Surfactant (% w/w)
A	55	40	5
B	25	70	5
C	5	90	5

2.3. Preparation of replicas for electron microscopy

Samples for TEM were quickly frozen in freon 22 ($HCClF_2$) and cooled with liquid nitrogen. The frozen samples were placed in a Balzers BSA 202 freeze-etching apparatus. In a high vacuum (10^{-4} Pa) and at an object temperature of −100°C the samples were fractured and shadowed with Pt/C (angle 45°). The replicas were cleaned with purified water. The micrographs were examined and photographed using a Jeol 100 CX electron microscope.

2.4. DSC

A DSC-4 differential scanning calorimeter (Perkin Elmer, Norwalk, CT, U.S.A.) was used. The sample weight was between 5 and 8 mg. Samples were placed in aluminium pans and hermetically sealed. As a reference an empty aluminium pan was used. Water freezing temperatures and enthalpies were determined by cooling the samples from room temperature to −50°C at a cooling rate of 5°C/min. The freezing enthalpies were calculated from thermograms by means of a Perkin-Elmer model 3700 Thermal Analysis Data Station. DSC analyses of the emulsion systems were performed immediately after preparation.

2.5. Rheology

Rotational and oscillation viscometers were used. Viscosity measurements were performed with a PK 1-1.0 cone and plate system (Haake Rotovisco RV 20, Haake, Karlsruhe, Germany) at constant temperature ($T = 23° \pm 0.5°C$). Oscillation experiments were carried out at constant amplitude (0.3) and frequency interval (0.05-100 Hz or 0.31-628.32 s^{-1}) with an MK 25 measuring system (Physica Rheolab MC 20, Physica Messtechnik GmbH, Stuttgart, Germany).

3. Results and discussion

The physical properties of emulsion systems are closely related to their microstructure. The microphotograph of semisolid w/o emulsion sys-

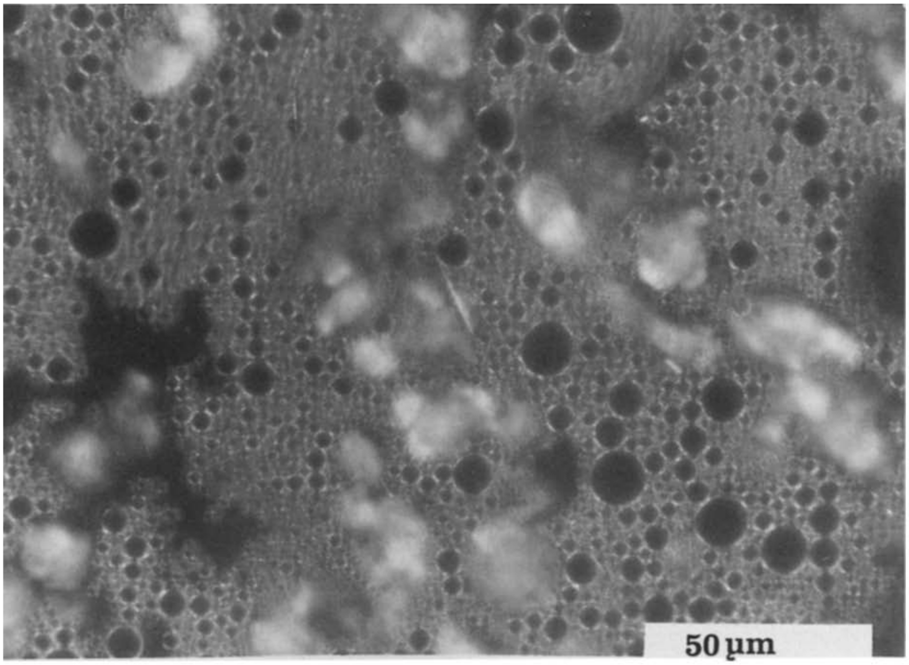

Fig. 2. Microphotograph of semisolid w/o emulsion system (B) in polarized light.

tems containing silicone surfactant showed a gel network consisting of white petrolatum and water droplets as internal phase (Fig. 2). No ordered structures such as liquid crystals were confirmed using transmission microscopy (Fig. 3). Again, only dispersed droplets of internal water phase (1–15 μm size) were found in the gel network of white petrolatum. With increasing water content (from 40 to 90% w/w) the degree of dispersity was also found to increase. At least two parameters are responsible for the physical stability of such a concentrated emulsion system (C, containing 90% w/w of water): first, the degree of dispersity of the internal phase; and second, for the surfactant, the strength of its interfacial film caused by its very strong adsorption at the water/oil interface and the steric stabilization due to its polymeric character, respectively.

The incorporation and distribution of internal water phase and its interactions with other components in the semisolid emulsion system were also studied by means of DSC. On heating no differences in thermal effects were noted. However, different behaviour was observed during controlled cooling from room temperature to −50°C caused only by freezing of water. Regarding the composition of emulsion systems, freezing of water was observed in within the interval from −20 to −40°C. With increasing water content the freezing peaks shift from −40 to −20°C (Fig. 4). In system A (40% w/w of water) the freezing peak appeared at about −40°C. This temperature is known to be the homogeneous nucleation

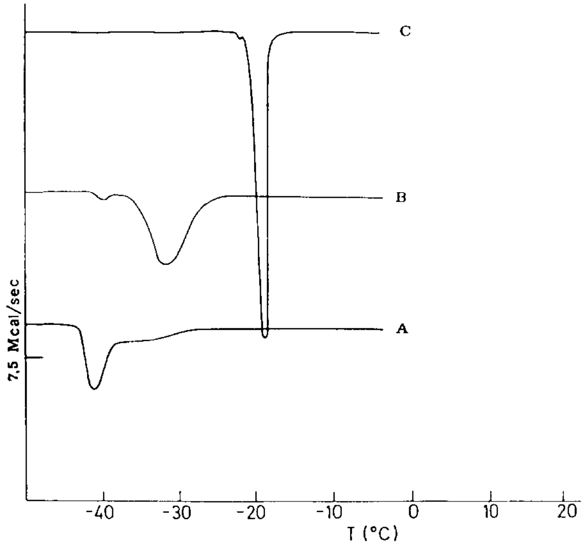

Fig. 4. Thermograms of emulsion systems containing silicone surfactant (A–C) immediately after preparation.

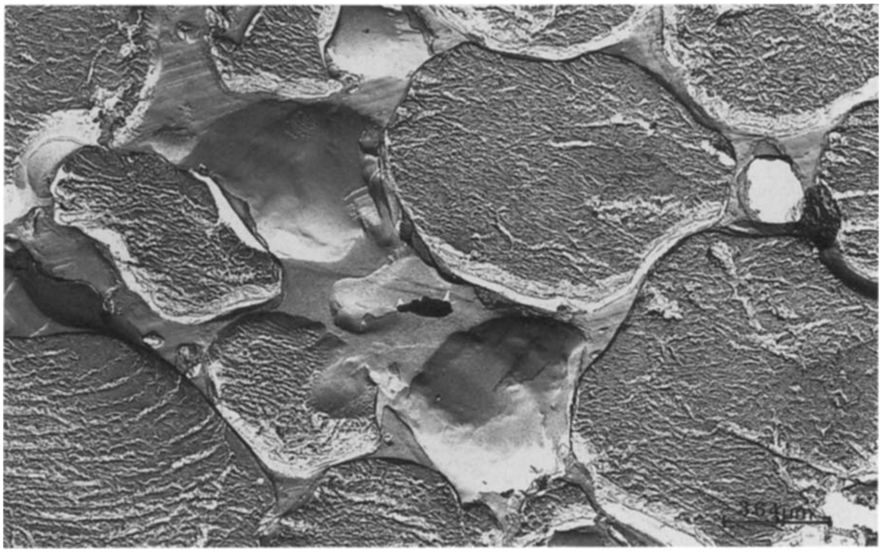

Fig. 3. TEM microphotograph of semisolid w/o emulsion system (B).

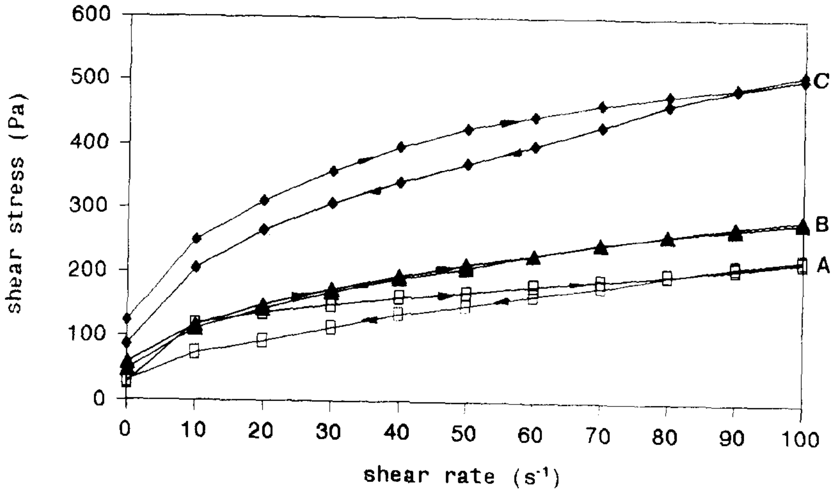

Fig. 5. Rheograms of semisolid emulsion systems (A–C) immediately after preparation.

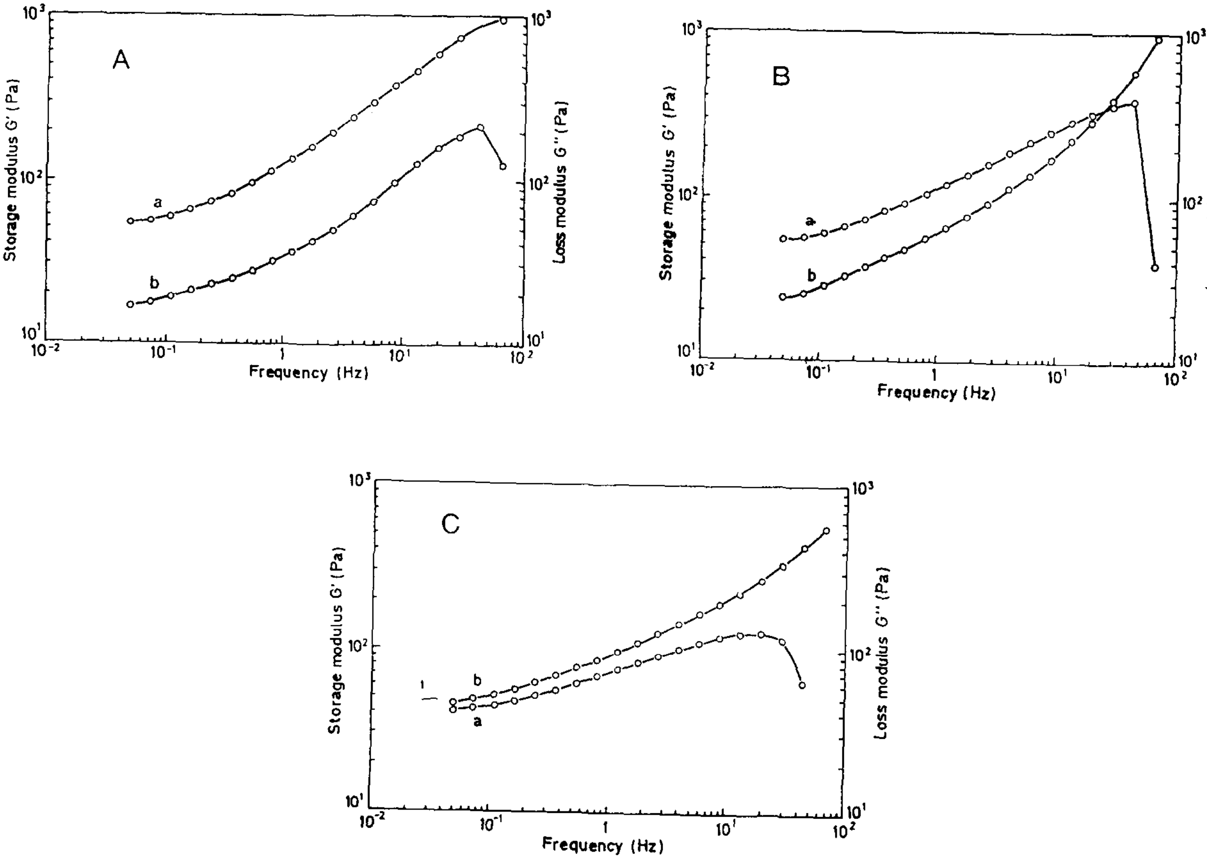

Fig. 6. Loss (a) and storage (b) moduli of semisolid emulsion systems containing silicone surfactant (A–C) as a function of oscillatory frequency.

temperature (Brüggeller, 1982), also achieved in w/o emulsion systems when droplets are small enough and of equal size. The freezing peak at about −20°C, observed in system C (90% w/w of water), was identical to that of bulk purified water, used as reference. The contention that, in w/o systems containing a high percentage of water, the behaviour of water is like that of the pure (bulk) water is acceptable. Two peaks were observed in system B: the peak at −27°C represented the crystallization of droplets in the emulsion similar to bulk water; the second peak at lower temperature indicated the homogeneous nucleation of ice in the remaining droplets. In those emulsion systems in which the concentration of surfactant vs that of water was raised, water freezing at homogeneous nucleation temperature occurred. This water appeared to be incorporated into micellar aggregates (possibly bound water), indicating a different state in comparison to the bulk water.

Rotational viscosity measurements of semisolid w/o emulsion systems containing silicone surfactant were performed under isothermic conditions. All three systems (A–C) demonstrate pseudoplastic behaviour (Fig. 5). On analysis of rheograms it was found that system A with the lowest water content (40% w/w) was thixotropic, undoubtedly due to the influence of white petrolatum and its structure, respectively. System B (containing 70% w/w of water) was thixotropic at shear rates lower than 70 s^{-1}, whereas at higher rates negative thixotropy (rheopexy) was evident. In system C (containing 90% w/w of water) rheopexy was expressed over the entire range of shear rates employed.

The viscoelastic properties of semisolid w/o emulsion systems were determined using oscillation viscosimetry at constant amplitude and different frequencies. These experiments allow one to draw a distinction between the elastic and plastic behaviour of a semisolid system, expressed as G' (storage modulus-elastic behaviour) and G'' (loss modulus-plastic behaviour). Viscous behaviour (Fig. 6) is dominant over the whole frequency range in system A. System B demonstrates a crossover point at about 30 Hz; plastic behaviour is expressed at lower frequencies and an elastic nature at higher frequencies. System C is elastic over the entire frequency range. These observations correlate well with rotational experiments: system A is predominantly thixotropic, system B thixotropic and rheopexic and system C entirely rheopexic.

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