



Formation and characterization of three-component-sorbitan monoester surfactant, oil and water-creams

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Abstract

The effect of molecular structure of four sorbitan monoester surfactants (sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate and sorbitan monooleate) on the formation of simple three-component creams is presented. Interfacial properties of the surfactants were determined using a du Nouy tensiometer and rheological properties of selected creams with oscillation stress sweep, creep recovery and viscosity tests. Depending on the composition, sorbitan monolaurate and sorbitan monooleate formed both *o/w* creams and *w/o* creams, while sorbitan monopalmitate and sorbitan monostearate formed only *o/w* creams. Sorbitan monostearate and sorbitan monopalmitate had the smallest *cmc* and A_{cmc} values and they were the most effective surfactants in lowering the interfacial tension. These surfactants formed the most stable and elastic creams with clear linear viscoelastic regions and small compliance values. Sorbitan monolaurate and sorbitan monooleate formed viscous creams without elastic properties.

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1. Introduction

Creams are dispersions of two immiscible liquids, oil and water. With both polar and non-polar regions at the same molecule, a surfactant settles at the interface of oil and water and decreases the interfacial free energy. Stable molecular films of the surfactant molecules at the interfaces form the basis of a homogeneous and stable cream. The molecular struc-

ture of a surfactant affects the rheological properties and the stability of the cream (Barry and Saunders, 1971; Barry and Eccleston, 1973a,b; Eccleston and Beattie, 1988; Korhonen et al., 2000, 2001, 2002). Changes in the rheological properties (recoverable elastic, partly recoverable viscoelastic and unrecoverable viscous behaviour) may signify instability (Zografi, 1982) and provide qualitative and quantitative information of the internal bondings in the cream structure. In addition to rheological measurements, interfacial tension measurements have also been used for the evaluation of emulsion stability (Takamura et al., 1984; Ishii et al., 1988; Krawczyk et al., 1991).

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Sorbitan fatty acid ester surfactants are effective reducers of interfacial tension (Wan and Lee, 1973; Opawale and Burgess, 1998a; Peltonen and Yliruusi, 2000; Peltonen et al., 2001a). At the oil–water interface the hydrocarbon chains of sorbitan monoester molecules orientate to the oil and the sorbitan ring to the aqueous side of the interface (Boyd et al., 1972). The interfacial and molecular properties of sorbitan monoesters have been studied in detail with simple straight-chained hydrocarbon oil–water systems (Peltonen and Yliruusi, 2000; Peltonen et al., 2001a,b,c). It was concluded that the length and double bond in the hydrocarbon chain of sorbitan monoesters affect significantly the interfacial and molecular properties of these surfactants.

The aim of this study was to determine how the molecular structures of four sorbitan monoester (sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate and sorbitan monooleate) surfactants affect the interfacial tension at the oil–water interface, cream-forming properties of different oil/water/surfactant compositions, rheological properties and short-term stability of the creams formed.

2. Materials and methods

2.1. Materials

The surfactants used were non-ionic sorbitan fatty acid esters (Fluka, Switzerland), sorbitan monolau-

rate (Span[®] 20), sorbitan monopalmitate (Span[®] 40), sorbitan monostearate (Span[®] 60) and sorbitan monooleate (Span[®] 80). Sorbitan monolaurate, monopalmitate and monostearate are saturated and sorbitan monooleate unsaturated sorbitan monoesters. Saturated sorbitan monoesters differ from each other in the length of the hydrocarbon chain (Fig. 1a). The unsaturated sorbitan monooleate differs from the sorbitan monostearate with a double bond in the hydrocarbon chain (Fig. 1a). The oil used was isopropylmyristate (Henkel KGAA, Germany), an isopropylester of myristyl acid (Fig. 1b). The surfactants and the oil were used as received without further purification. The water used was purified using the Milli-RO 12 Plus system (Millipore, Molsheim, France).

2.2. Cream preparation

Based on pre-liminary tests, 58 formulations were selected for the cream formation study. The concentration range of surfactant was 0.5–20.0% (w/w) and that of oil (isopropylmyristate) and water 5.0–94.5% (w/w). All the 58 formulations, 100 g each, were prepared with the four surfactants studied. The preparation was performed using a 24-unit reaction block (Reaction block 24.4, H + P Labortechnik GmbH, Oberschleissheim, Germany) which was connected to a warming/cooling unit (Huber CC 250, Peter Huber Kältemaschinenbau, GmbH, Offenburg, Germany) controlled by PC. The water was added in the solution of surfactant and oil in one, two or three stages,

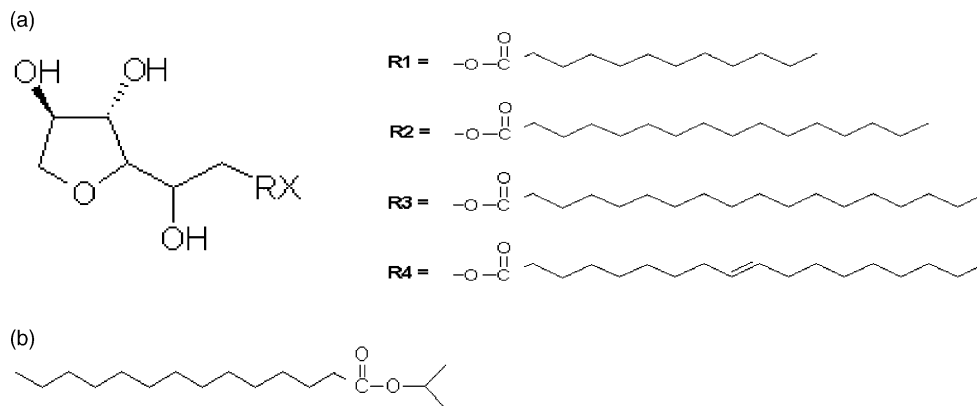


Fig. 1. Structures of sorbitan monoesters (a) and isopropylmyristate (b). R1: sorbitan monolaurate, R2: sorbitan monopalmitate, R3: sorbitan monostearate, R4: sorbitan monooleate.

depending on the vol.% of water. The phases were combined at a temperature of $80 \pm 1^\circ\text{C}$. After each water addition the dispersion was homogenized (speed $25,000\text{ s}^{-1}$) for 15 s (Ultra-Turrax T8, Ika Werke GmbH&Co. KG, Staufen, Germany). The cooling was performed steadily during 90 min from 80 to 30°C . After each lowering of temperature by 5°C the dispersions were homogenized (speed $25,000\text{ s}^{-1}$) for 10 s. The repeatability of the preparation procedure was ensured by preparing the compositions selected in triplicate.

2.3. Analytical methods

Interfacial tension between the oil and water was measured using a du Nouy tensiometer (KSV Sigma 70, KSV, Finland) with a platinum ring. The measurements were performed as described in the studies of Peltonen and Yliruusi (2000), and Peltonen et al. (2001a). Interfacial tensions were measured for each surfactant. The measurements were started at a surfactant concentration of 0.001 mol/l and the measurements covered the whole determinable range of each surfactant. From the interfacial tension plots the critical micelle concentrations (cmc) were extrapolated at the point of intersection of two linear portions of the interfacial tension versus log concentration plots. The area per molecule at cmc (A_{cmc}) was calculated by means of Gibbs adsorption isotherm

$$\Gamma = - \left(\frac{1}{RT} \right) \left(\frac{d\gamma}{d \ln c} \right) \quad (1)$$

and

$$A_{\text{cmc}} = \frac{1}{\Gamma N} \quad (2)$$

where Γ is the surface excess concentration (number of molecules per surface area), R is the gas constant, T is the temperature, γ is the interfacial tension, c is the concentration and N is the Avogadro's constant. Also the interfacial tensions at cmc (γ_{cmc}) were determined. The measurements ($n = 3$) were performed at room temperature ($22.0 \pm 0.5^\circ\text{C}$).

The type (either o/w or w/o) of the creams was determined with a portable conductivity meter (Scott handylab LF 11, Scott-Geräte GmbH, Mainz, Germany). The conductivities were determined immediately after the cream preparation and two, five and

ten days later. Conductivity determinations were performed in triplicate. Short-term stabilities (at room temperature $22.0 \pm 0.5^\circ\text{C}$ up to 10 days) of the creams were determined visually: the cream was regarded as stable if no phase separation could be detected.

Rheological properties of the creams were determined using a Bohlin CS rheometer (Bohlin Reologi AB, Lund, Sweden, Bohlin CS Rheometer software version 4.03) with a concentric cylinder system (diameter 25 mm). The temperature of the base plate was 25°C . The tests performed were oscillation stress sweep test, creep recovery test and viscosity test. In the oscillation stress sweep test, the stress was increased from 0.025 to 50 Pa, 100 or 150 Pa, depending on the consistency of the cream. The frequency was kept constant (1 Hz). The creep recovery test was performed only for creams with a clear linear viscoelastic region in the oscillation stress sweep test. In the creep recovery test, the sample was exposed to stress for 126 s and the strain recovery was registered up to 224 s. The stress applied was chosen from the linear viscoelastic region of each cream. In the viscosity test, the shear rate was recorded as a function of shear stress. In each determination the stress range started from 0.025 Pa and was continued up to 2 or 153 Pa, depending on the consistency of the cream. Both up- and down-curves were determined. The rheological properties of the creams were determined two days after cream preparation. All the rheological measurements were performed in triplicate from separate samples.

3. Results and discussion

3.1. Interfacial tension

The cmc of sorbitan monolaurate was indeterminate. Sorbitan monolaurate was the only surfactant with no clear break on the interfacial tension versus log concentration plots. In the study of Opawale and Burgess (1998a), it was concluded that this can be due to the affinity of sorbitan monolaurate for the aqueous phase. Of the surfactants used in the present study, sorbitan monolaurate had the shortest hydrophobic hydrocarbon chain, which makes it the most hydrophilic surfactant studied.

Sorbitan monostearate and sorbitan monopalmitate had smaller values of cmc, area per molecule at

Table 1

Critical micelle concentrations (cmc) of solutions of sorbitan monoesters, areas per molecules at cmc (A_{cmc}), interfacial tensions at cmc (γ_{cmc}) and lowerings of interfacial tensions within surfactant concentration range 0.001–0.008 mol/l ($n = 3$)

Surfactant	cmc (mol/l)	A_{cmc} (\AA^2)	γ_{cmc} (mN/m)	Lowering of interfacial tension (mN/m)
Sorbitan monolaurate	–	–	–	9.2 ± 0.7
Sorbitan monopalmitate	0.010 ± 0.000	71 ± 3	2.0 ± 0.0	10.1 ± 0.4
Sorbitan monostearate	0.009 ± 0.000	56 ± 8	2.0 ± 0.0	12.9 ± 0.1
Sorbitan monooleate	0.016 ± 0.001	106 ± 2	5.9 ± 0.1	8.2 ± 0.9

cmc (A_{cmc}) and interfacial tension at cmc (γ_{cmc}) than sorbitan monooleate (Table 1). In addition, sorbitan monostearate and sorbitan monopalmitate lowered the interfacial tension more than sorbitan monolaurate and sorbitan monooleate (Table 1). The differences between the A_{cmc} values were clear. Molecules of sorbitan monostearate with the smallest molecular area are able to pack more tightly at the interfaces and lower the interfacial tension more than the other surfactants studied. The smaller the cmc, the smaller the amount of surfactant that was needed to form micelles. The double bond in the hydrocarbon chain almost doubled the molecular area of sorbitan monooleate as compared to the saturated counterpart sorbitan monostearate (Table 1).

Differences in surface activities of the sorbitan monoesters are primarily derived from the alkyl group (Peltonen and Yliruusi, 2000). Sorbitan monostearate, as well as sorbitan monopalmitate, include long and straight hydrocarbon chains. The increasing chain length promotes the tendency towards the formation of condensed monolayers (Rakshit et al., 1981). The condensed monolayers and the predominant chain–chain interactions of the saturated fatty acids orientate the molecules vertically at the oil–water interfaces (Rakshit et al., 1981). The observation of the more condensed packing of the sorbitan monostearate and sorbitan monopalmitate as compared to the sorbitan monolaurate and sorbitan monooleate is supported by the finding that the former two tolerate compression better and are more readily associated with each other than the other surfactants studied (Peltonen and Yliruusi, 2000). Contrary to the vertical orientation of the surfactants with a long hydrocarbon chain, surfactant molecules with polar groups in the hydrocarbon chain prefer more horizontal orientation at the interfaces (Rakshit et al., 1981). Sorbitan monolaurate has affinity for the aqueous phase (Opawale and Burgess, 1998a) and sorbitan monooleate has a

second polar group, a double bond, in the molecule (Fig. 1a). Thus, the surfactant film of these surfactants tends to be in an expanded horizontal state (Adamson, 1960). In the horizontal orientation the molecules require more space at interfaces leading to a looser packing and weaker chain–chain interactions of the molecules at the interfaces. This was clearly seen from the cmc and A_{cmc} values, and from the interfacial tension-lowering properties of sorbitan monolaurate and sorbitan monooleate (Table 1). The double bond in the sorbitan monooleate molecule decreases the hydrophobic chain–chain interactions (Feher et al., 1977), which can explain the smallest lowering of the interfacial tension by this surfactant.

3.2. Formation and stability of three-component creams

The types and the short-term stabilities of the three-component creams are presented in Figs. 2–5. Sorbitan monolaurate and sorbitan monooleate formed both o/w and w/o creams, sorbitan monopalmitate and sorbitan monostearate only o/w creams. Each surfactant formed o/w creams at small concentrations of oil (right corners in the ternary plots) (Figs. 2–5). As the concentration of oil was increased, o/w creams were formed only at small surfactant concentrations. Sorbitan monolaurate could bind the largest amount of oil (84%) to the inner phase (Fig. 2). With saturated sorbitan monoesters the capacity to bind oil as an inner phase decreased as the chain length of the hydrophobic hydrocarbon chain increased (Figs. 2–4). Sorbitan monolaurate and sorbitan monooleate formed w/o creams with rather equal concentrations of oil and water (middle part of the ternary plots) (Figs. 2 and 5). Sorbitan monooleate formed w/o creams at a lower concentration of surfactant than sorbitan monolaurate. The short-term stabilities of the w/o creams were poor, all of them remaining stable for less than

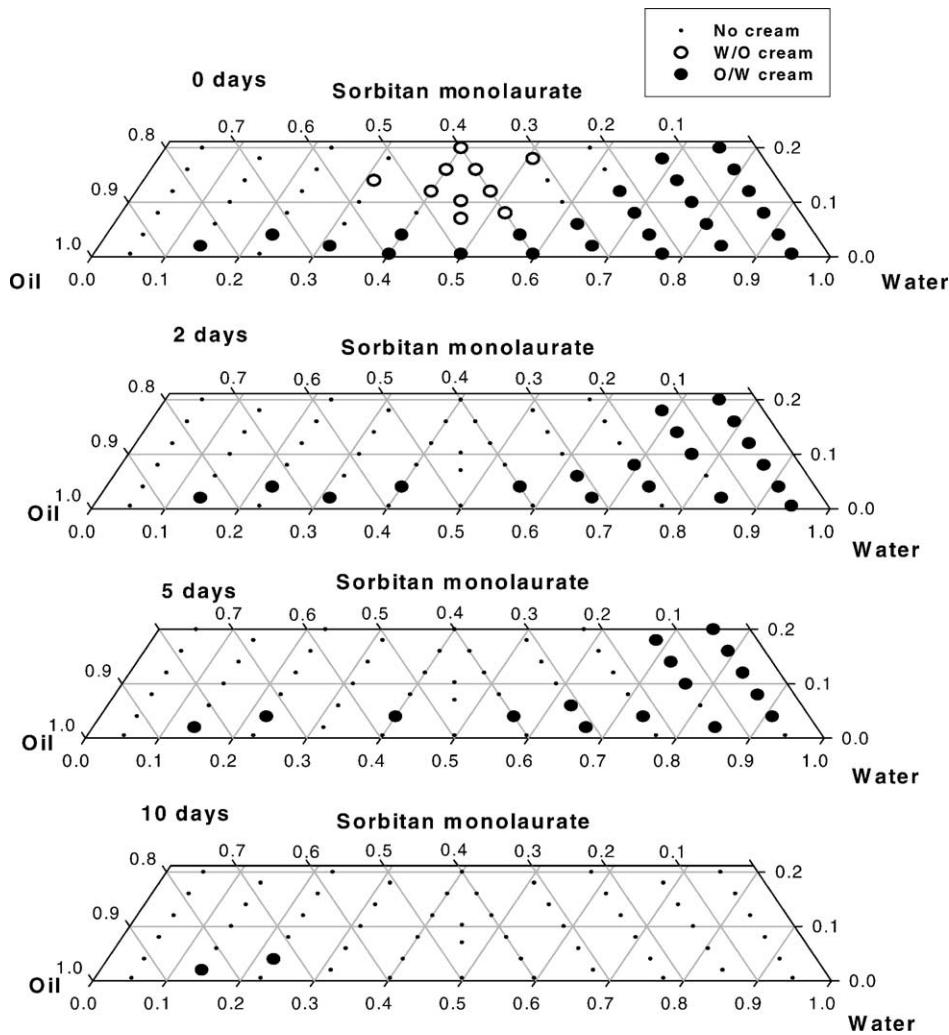


Fig. 2. Formation and short-term stabilities of creams using sorbitan monolaurate as the surfactant. Maximum concentration percentage (w/w) of the component at the corner of component name.

2 days. On the contrary, several o/w creams remained stable for up to 10 days with all the other surfactants but sorbitan monooleate (Figs. 2–5). After 10 days of storage, sorbitan monostearate (Fig. 4) had the highest number of homogeneous cream formulations. These creams contained small amounts of oil and more than 2% of the surfactant.

According to the supplier of surfactants, the HLB values of the sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate and sorbitan monooleate were 8.4, 7.6, 4.2 and 4.9, respectively. The HLB values of the surfactants did not explain

the types of the creams formed. The lipophilic sorbitan fatty acid ester surfactants should enhance the forming of w/o emulsions (Rowe et al., 2003). Theoretically, the Bancroft's rule states that the phase in which the surfactant is more soluble tends to be the dispersion medium (Becher, 1957), and the Oriented Wedge Theory states that the surfactant portion with the greater cross sectional area will be settled to the external part of the droplet interface (Autian, 1966). In the present study, w/o creams were formed only in the presence of sorbitan monolaurate and sorbitan monooleate. The different cream-forming properties

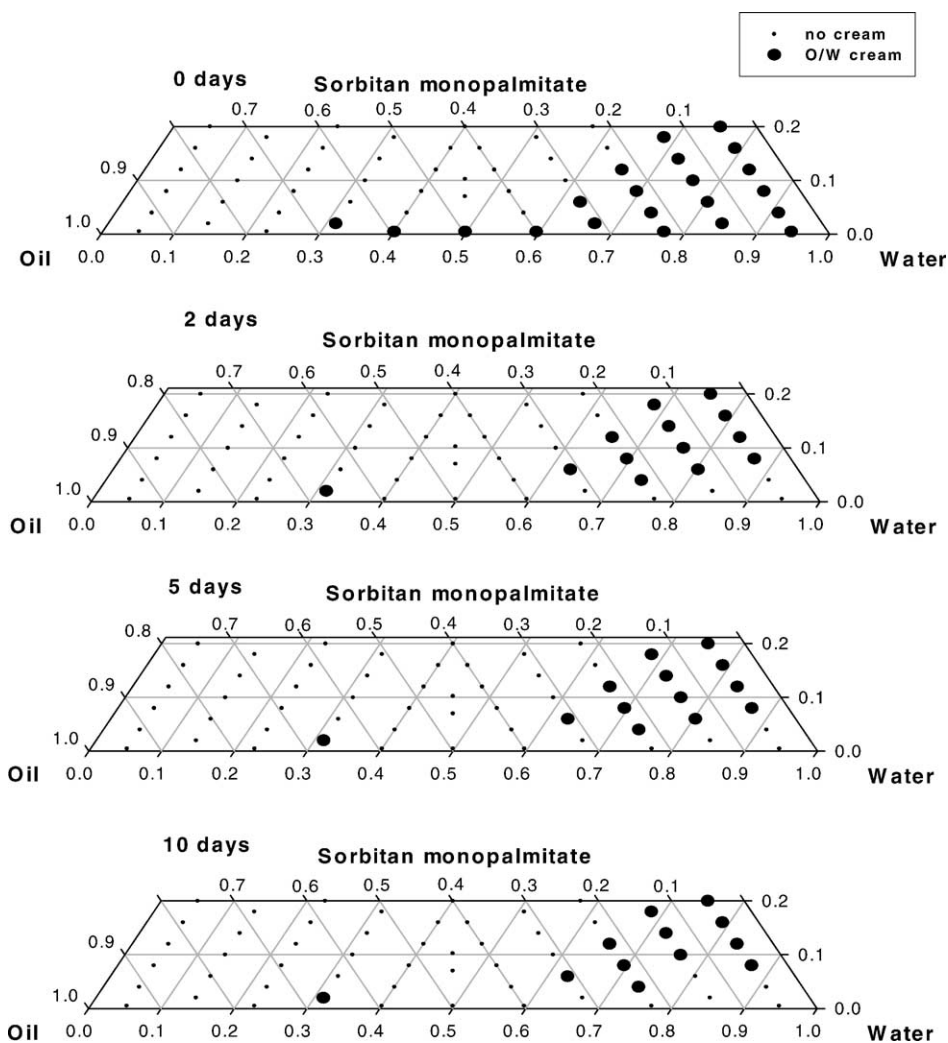


Fig. 3. Formation and short-term stabilities of creams using sorbitan monopalmitate as the surfactant. Maximum concentration percentage (w/w) of the component at the corner of component name.

of the surfactant pairs sorbitan monolaurate and sorbitan monooleate, and sorbitan monopalmitate and sorbitan monostearate, were noticed also in a previous study (Korhonen et al., 2002). The short hydrocarbon chain of sorbitan monolaurate and the double bonded hydrocarbon chain of sorbitan monooleate make these surfactants more polar than the longer hydrophobic alkyl chains containing sorbitan monopalmitate and sorbitan monostearate. As stated earlier in the present study, the hydrocarbon tails of sorbitan monolaurate and sorbitan monooleate did not settle straight to-

wards the oil phase; due to the decreased chain-chain interactions they settled more horizontally at the interfaces (Adamson, 1960). The formation of w/o creams with quite equal volumes of the inner and outer phases can be caused by the increased amount of interfaces as compared to the o/w creams in the right corners of the ternary plots (Figs. 2 and 5). As the concentration of surfactant increased, as compared to the o/w creams in the lowest part in the ternary plots (Figs. 2 and 5), it is possible that the hydrophobic tails of the surfactant molecules no longer had

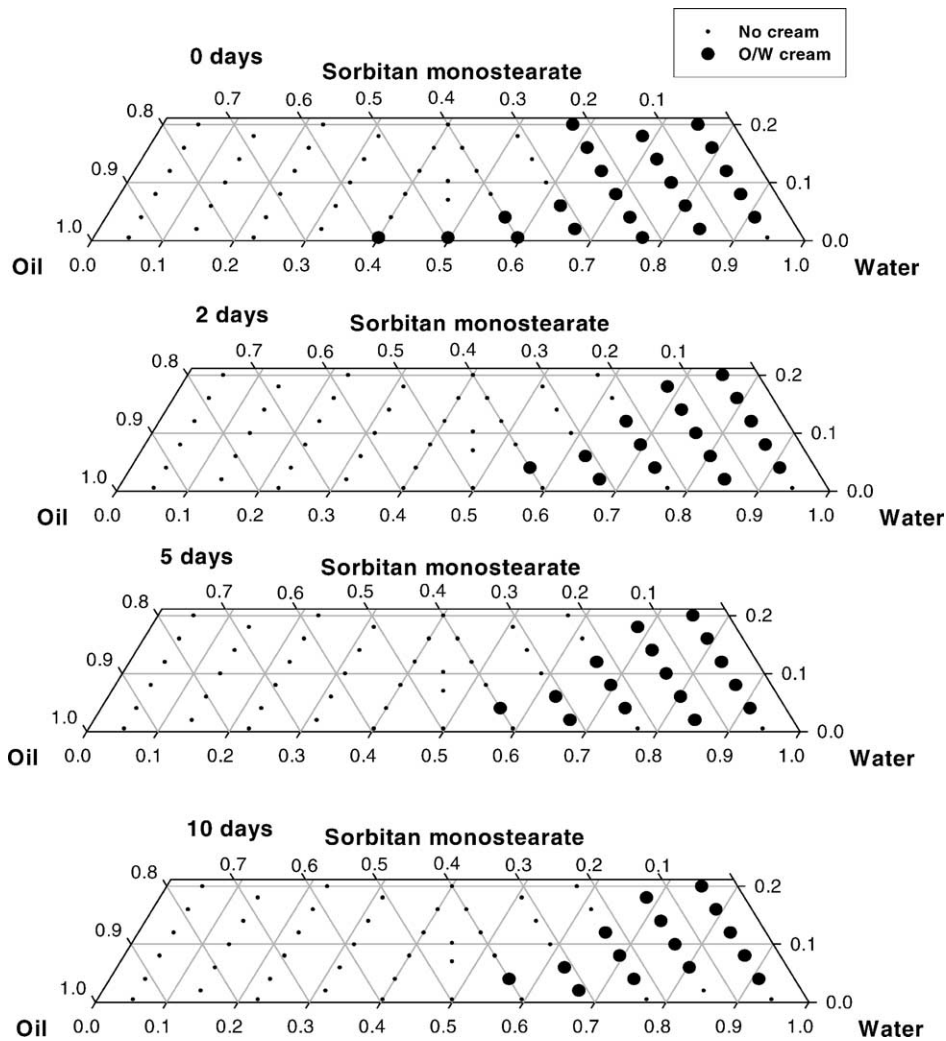


Fig. 4. Formation and short-term stabilities of creams using sorbitan monostearate as the surfactant. Maximum concentration percentage (w/w) of the component at the corner of component name.

enough space to orientate inside the droplets. This probably caused the conversion of o/w creams to w/o creams.

In earlier studies, interfacial elasticity, compressibility and reversible expandability of surfactant monolayers were properties connected to stable emulsions (Opawale and Burgess, 1998b; Kanouni et al., 2002). In the present study, the smallest cmc, A_{cmc} and γ_{cmc} values and the most effective ability to lower the interfacial tension of sorbitan monostearate (Table 1), due to the most stable interfacial monolayer formation, supported its ability to form the most

stable creams at the smallest surfactant concentrations. Likewise, the corresponding values of sorbitan monopalmitate supported the formation of stable creams. The longer hydrocarbon chain of sorbitan monostearate and sorbitan monopalmitate (18 and 16 carbons, respectively) than that of the used oil (isopropylmyristate, 14 carbons in the hydrocarbon chain) enabled the penetration of the oil molecules between the surfactant molecules (Stokes and Evans, 1997). This made the packing at the interfaces tighter due to the increased hydrocarbon volume at the interfaces, which also supports the stability of the creams. On the

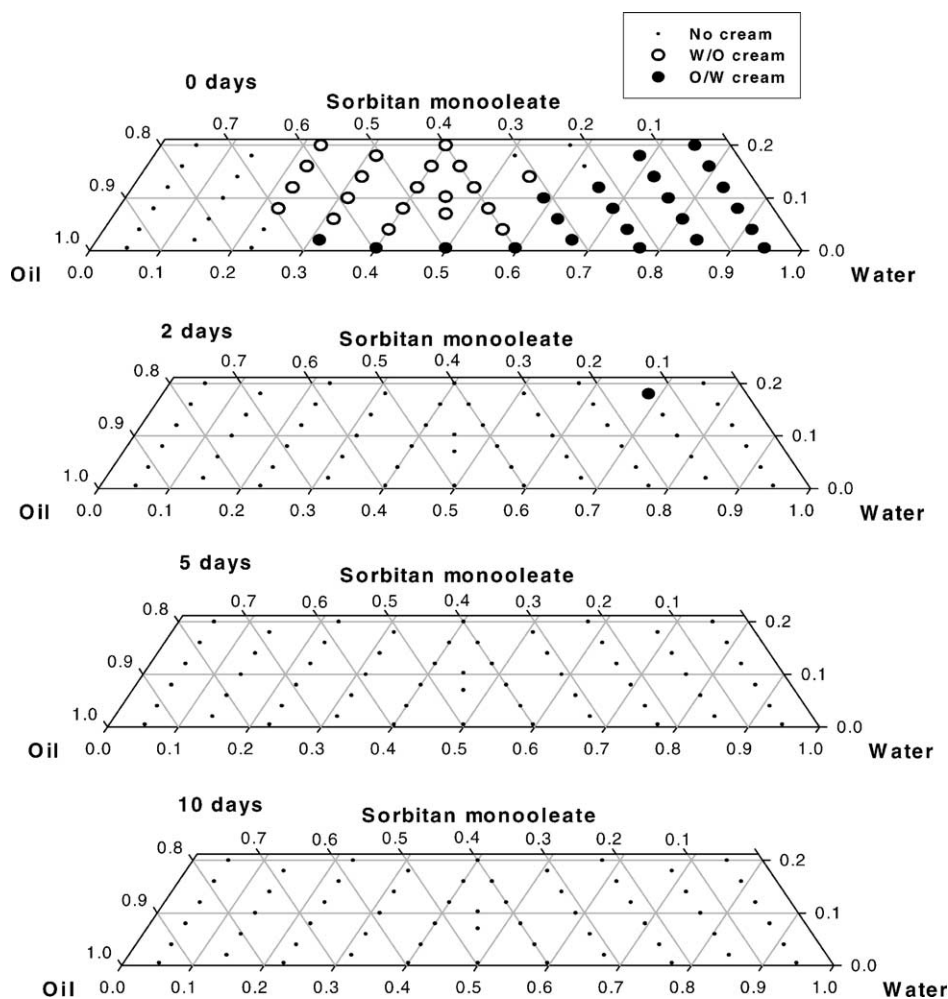


Fig. 5. Formation and short-term stabilities of creams using sorbitan monooleate as the surfactant. Maximum concentration percentage (w/w) of the component at the corner of component name.

contrary, because the chain length of isopropylmyristate exceeds that of sorbitan monolaurate (12 carbons in the hydrocarbon chain), the penetration of the hydrocarbon chains of the oil between the hydrocarbon chains of the sorbitan monolaurate was negligible (Stokes and Evans, 1997). This was also the case with sorbitan monooleate as the double bond decreases the hydrophobic chain–chain interactions between the adjacent surfactant molecules and oil molecules (Feher et al., 1977). Gullapalli and Sheth (1999) have shown that a surfactant blend containing at least one surfactant with a similar hydrocarbon chain length as the oil used produces emulsions with a maximum stability.

3.3. Rheological properties

Rheological properties were tested from new, comparable cream formulations prepared with similar amounts (mol) of each surfactant (Table 2). The oscillation stress sweep test (Fig. 6) showed that creams containing sorbitan monopalmitate and sorbitan monostearate formed clearly more consistent creams than those containing sorbitan monolaurate and sorbitan monooleate. The formulation containing sorbitan monostearate was very elastic and it had a wide linear viscoelastic region. The storage modulus value of the cream containing sorbitan monopalmitate was

Table 2
Compositions percentage (w/w) of creams selected for the rheological studies

Component	Cream containing sorbitan monolaurate	Cream containing sorbitan monopalmitate	Cream containing sorbitan monostearate	Cream containing sorbitan monooleate
Surfactant	14.5	16.9	18.1	18.0
Oil	13.8	13.8	13.8	13.8
Water	71.7	69.3	68.1	68.2

The amount 0.042 mol of the surfactants was equal in all creams. The creams formed were o/w creams ($n = 3$).

small and the linear viscoelastic region was clearly narrower than that of the cream containing sorbitan monostearate (Table 3). The end point of the linear viscoelastic region was determined as the stress when the storage modulus (G') value was dropped 10% from the linear level. The more viscous behaviour of the cream with sorbitan monopalmitate as surfactant was also seen from the value of loss tangent in the linear viscoelastic region (Table 3). However, based on the values of loss tangent, both creams could be classified as elastic ($\tan \delta < 1$) (Gasparlin et al., 1998). The smaller the ratio of G''/G' ($\tan \delta$), the more rubbery or elastomeric is the behaviour (Ferry, 1980). The creams containing sorbitan monolaurate or sorbitan monooleate were viscous without linear viscoelastic regions (Fig. 6).

The results of the creep recovery tests supported the results of the oscillation stress sweep tests. The compliances (J) of the cream containing sorbitan monostearate were very low, clearly lower than with the cream containing sorbitan monopalmitate (Fig. 7 and Table 3). If the sample is tested in the linear viscoelastic region, the elements that cause an elastic response will give an equal contribution both in the creep and the recovery phase (Schramm, 1994). In the cream with sorbitan monostearate as surfactant the instantaneous recovery was about 50% higher than the instantaneous strain at the beginning of the creep phase (Fig. 7), although the stress (40 Pa) used was clearly in the linear viscoelastic region (up to 102 Pa). Instantaneous elastic deformation represents the breaking of the bonds that are stretched elastically; the rest of

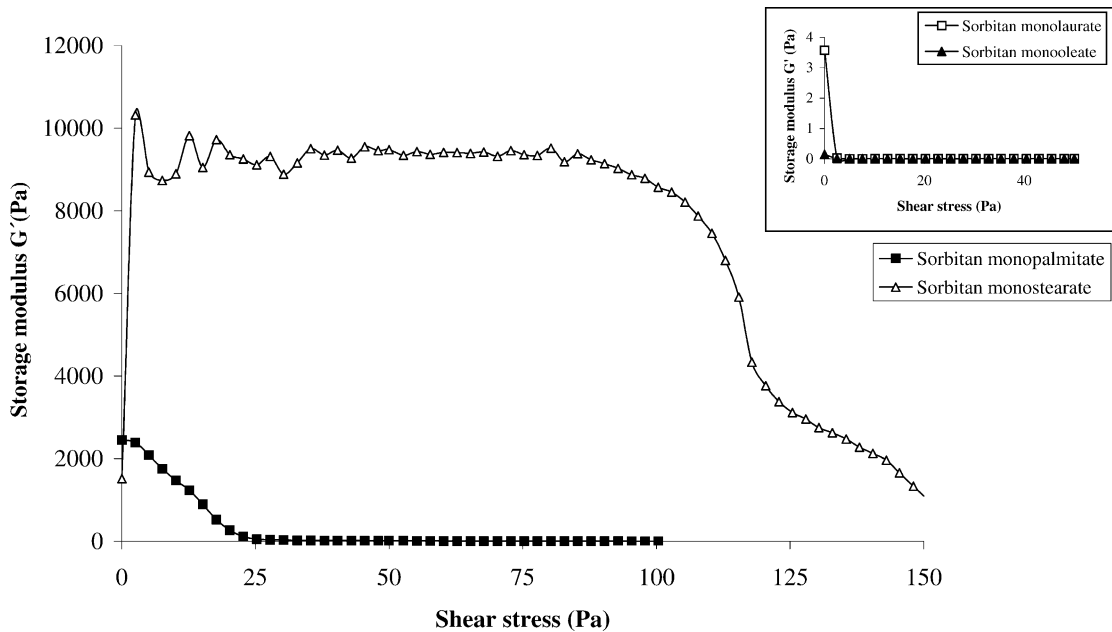


Fig. 6. Storage modulus values for creams containing sorbitan monoesters (sorbitan monolaurate/sorbitan monopalmitate/sorbitan monostearate/sorbitan monooleate) in the oscillation stress sweep test. Note the different scaling of axes ($n = 3$).

Table 3

Storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta = G''/G'$) values in linear viscoelastic regions, and end point values of linear viscoelastic regions in oscillation stress sweep tests. Compliance (J) values at time points 3 s, 126 s (at the end of creep phase) and 224 s (at the end point of recovery phase) in creep recovery tests. Shear rate values at the maximum applied shear stress and yield points in viscosity tests ($n = 3$)

Test	Cream containing sorbitan monolaurate	Cream containing sorbitan monopalmitate	Cream containing sorbitan monostearate	Cream containing sorbitan monooleate
Oscillation stress sweep				
G' (Pa)	–	2000 ± 700	9500 ± 1100	–
G'' (Pa)	–	1300 ± 600	1900 ± 500	–
$\tan \delta$	–	0.6 ± 0.1	0.2 ± 0.1	–
End point of linear viscoelastic region (Pa)	–	6.0 ± 0.0	102 ± 0	–
Creep recovery				
J at time point 3 s ($\times 10^{-3} \text{ Pa}^{-1}$)	–	1.9 ± 0.5	0.3 ± 0.0	–
J at time point 126 s ($\times 10^{-3} \text{ Pa}^{-1}$)	–	8 ± 4	0.7 ± 0.3	–
J at time point 224 s ($\times 10^{-3} \text{ Pa}^{-1}$)	–	5 ± 4	0.3 ± 0.2	–
Viscosity				
Shear rate (s^{-1}) at maximum shear stress	380 ± 1	120 ± 40	1.0 ± 0.9	160 ± 2
Yield point (Pa)	–	29.3	75.3	–

the creep curve represents the breaking and reforming of secondary bonds and viscous flow (Barry and Warburton, 1968; Davis, 1969). After the instantaneous recovery neither the cream containing sorbitan monostearate nor that containing sorbitan monopalmitate

showed practically any additional recovery. Neither of the curves followed the Burger model presented in a previous study (Korhonen et al., 2002).

Viscosity tests showed the thixotropic behaviour of each cream. The most thixotropic cream was the

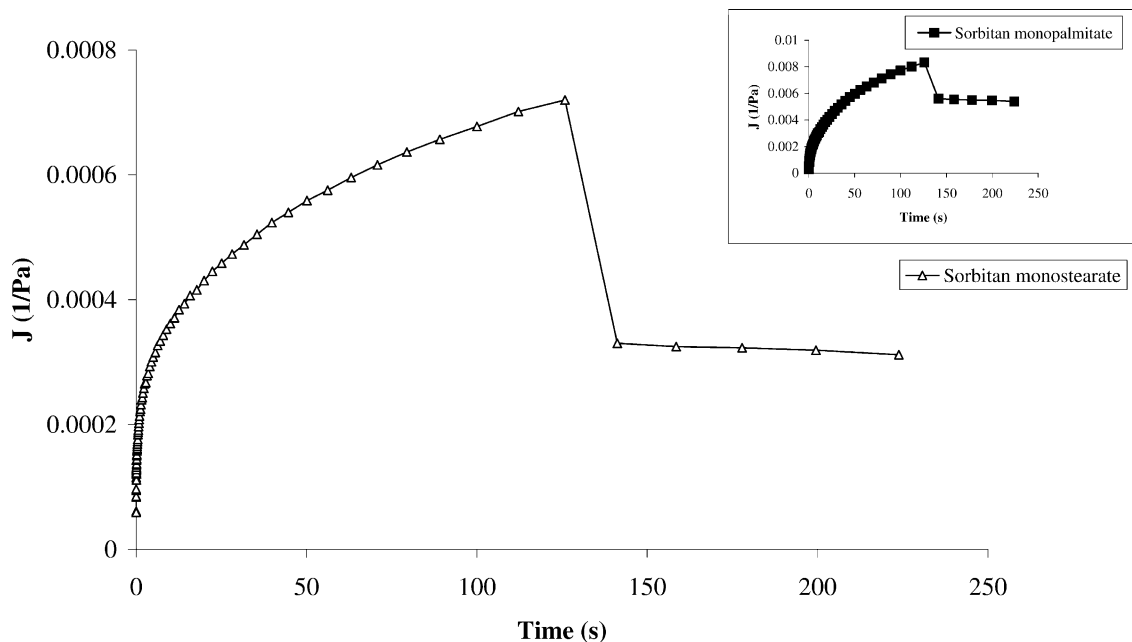


Fig. 7. Creep and recovery compliances of creams containing sorbitan monostearate and sorbitan monopalmitate in the creep recovery test. Note the different scaling of axes ($n=3$).

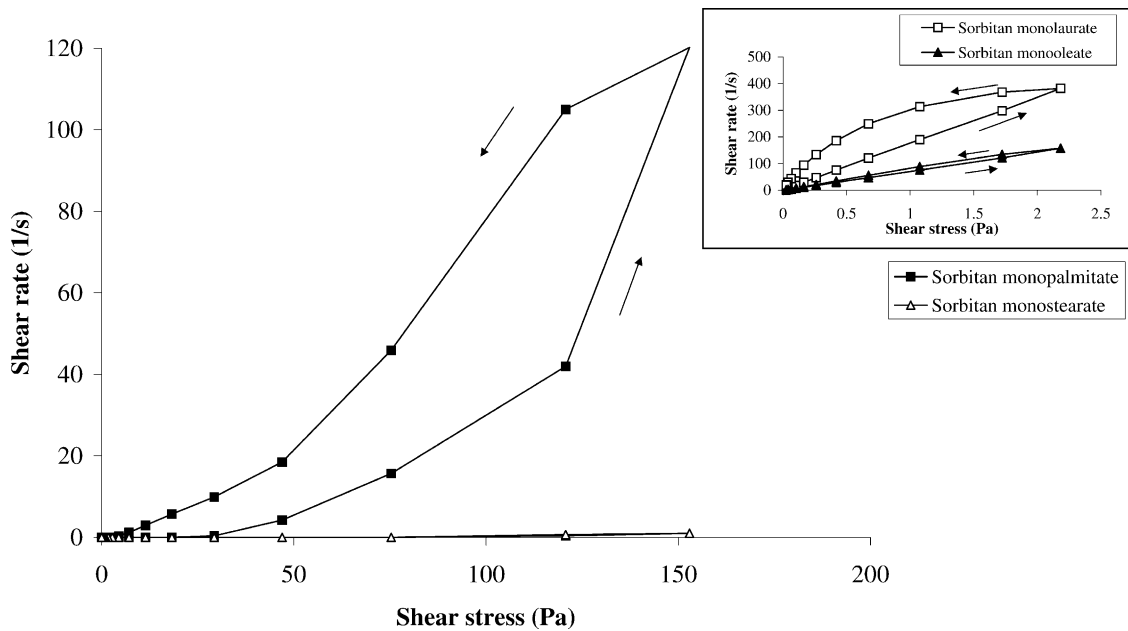


Fig. 8. Viscosity curves of creams containing sorbitan monoesters (sorbitan monolaurate/sorbitan monopalmitate/sorbitan monostearate/sorbitan monooleate) in the viscosity test. Note the different scaling of axes ($n = 3$).

cream containing sorbitan monopalmitate with pseudoplastic behaviour in the up-curve (Fig. 8). The very beginning of the down-curve corresponded the dilatant behaviour, the rest of the curve pseudoplastic behaviour (Fig. 8). Cream formulations containing sorbitan monolaurate and sorbitan monooleate as surfactants exhibited Newtonian flow indicating up-curves. The Newtonian flow indicated that the droplets did not aggregate to any significant extent by the impact of stress applied (Sherman, 1967). The cream containing sorbitan monostearate had clearly the highest yield point (Table 3). Creams containing sorbitan monolaurate and sorbitan monooleate did not have yield points (Fig. 8), as could be expected also from the results of the oscillation stress sweep test.

Sorbitan monostearate with the longest saturated hydrocarbon chain formed the most elastic structure for the cream. Sorbitan monopalmitate with a two carbons shorter hydrocarbon chain formed a clearly less elastic, but still linearly viscoelastically behaving structure for the cream. Corresponding findings that the increasing chain length of surfactant, up to a certain limit, produces more consistent creams have been made also in earlier studies (Barry and Eccleston, 1973a,b; Barry and Saunders, 1971;

Eccleston and Beattie, 1988; Korhonen et al., 2002). Because of the simple three-component formulations, viscoelastic properties of the creams were concluded to be mainly due to the interfacial properties of the surfactants. Smaller cmc and A_{cmc} values and the more effective lowering of interfacial tension increased the viscoelastic nature of the creams containing sorbitan monostearate and sorbitan monopalmitate. Also the longer hydrocarbon chain of surfactant than of oil increased the viscoelastic nature of these creams by tightening the packing of the molecules and increasing chain–chain interactions at the interfaces (Stokes and Evans, 1997). On the contrary, the looser packing of the molecules at the interfaces (Carlotti et al., 1995) and decreased hydrophobic chain–chain interactions between the adjacent surfactant molecules and oil molecules (Feher et al., 1977) decreased the consistency of the cream containing double bonded sorbitan monooleate. The most elastic structures of creams containing sorbitan monostearate and sorbitan monopalmitate explain also the most stable creams. It is generally concluded that the viscoelastic nature of a cream is a good indicator of stability (Förster and Herrington, 1997; Zografis, 1982; Gasperlin et al., 1998).

4. Conclusions

The length and double bond of the hydrocarbon chain caused clear differences in the interfacial, cream-forming and rheological properties of the surfactants studied. Sorbitan monostearate and sorbitan monopalmitate lowered the interfacial tension the most. Sorbitan monolaurate and sorbitan monooleate formed both w/o creams and o/w creams, sorbitan monostearate and sorbitan monopalmitate only o/w creams. Sorbitan monostearate formed the most elastic structure for the cream. Sorbitan monopalmitate formed a linearly viscoelastically behaving cream which, however, was not as elastic as the cream containing sorbitan monostearate. Sorbitan monolaurate and sorbitan monooleate formed viscous creams without elastic properties.

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References

- Adamson, A.W., 1960. *Physical Chemistry of Surfaces*. Interscience Publishers Inc., New York, pp. 124–138.
- Autian, J., 1966. Emulsions. In: Martin, E.W. (Ed.), *Pharmaceutical Dispensing*, 6th ed. Mack Publishing Company, Pennsylvania, pp. 223–258.
- Barry, B.W., Eccleston, G.M., 1973a. Influence of gel networks in controlling consistency of o/w emulsions stabilised by mixed emulsifiers. *J. Texture Studies* 4, 53–81.
- Barry, B.W., Eccleston, G.M., 1973b. Oscillatory testing of o/w emulsions containing mixed emulsifiers of the surfactant/long chain alcohol type: influence of surfactant chain length. *J. Pharm. Pharmacol.* 25, 394–400.
- Barry, B.W., Saunders, G.M., 1971. The self-bodying action of alkyltrimethylammonium bromides/cetostearyl alcohol mixed emulsifiers; influence of quaternary chain length. *J. Colloid Interface Sci.* 35, 689–705.
- Barry, B.W., Warburton, B., 1968. Some rheological aspects of cosmetics. *J. Soc. Cosmet Chemists* 19, 725–744.
- Becher, P., 1957. *Emulsions: Theory and Practice*. Reinhold Publishing Corporation, New York, pp. 85–133.
- Boyd, J., Parkinson, C., Sherman, P., 1972. Factors affecting emulsion stability, and the HLB concept. *J. Colloid Interface Sci.* 41, 359–370.
- Carlotti, M.E., Pattarino, F., Gasco, M.R., Cavalli, R., 1995. Use of polymeric and non-polymeric surfactants in o/w emulsion formulation. *Int. J. Cosmetic Sci.* 17, 13–25.
- Davis, S.S., 1969. Viscoelastic properties of pharmaceutical semisolids. I: Ointment bases. *J. Pharm. Sci.* 58, 412–417.
- Eccleston, G.M., Beattie, L., 1988. Microstructural changes during the storage of systems containing cetostearyl alcohol/polyoxyethylene alkyl ether surfactants. *Drug. Dev. Ind. Pharm.* 14, 2499–2518.
- Feher, A.I., Collins, F.D., Healy, T.W., 1977. Mixed monolayers of simple saturated and unsaturated fatty acids. *Aust. J. Chem.* 30, 511–519.
- Ferry, J.D., 1980. *Viscoelastic Properties of Polymers*, 3rd ed. John Wiley & Sons Inc., New York, pp. 33–55.
- Förster, A.H., Herrington, T.M., 1997. Rheology of siloxane-stabilized water in silicone emulsions. *Int. J. Cosmetic Sci.* 19, 173–191.
- Gasperlin, M., Tusar, L., Tusar, M., Kristl, J., Smid-Korbar, J., 1998. Lipophilic semisolid emulsion systems: viscoelastic behaviour and prediction of physical stability by neural network modelling. *Int. J. Pharm.* 168, 243–254.
- Gullapalli, R.P., Sheth, B.B., 1999. Influence of an optimized non-ionic emulsifier blend on properties of oil-in-water emulsions. *Eur. J. Pharm. Biopharm.* 48, 233–238.
- Ishii, F., Takamura, A., Ogata, H., 1988. Compatibility of intravenous fat emulsions with prodrug amino acids. *J. Pharm. Pharmacol.* 40, 89–92.
- Kanouni, M., Rosano, H.L., Naouli, N., 2002. Preparation of a stable double emulsion ($W_1/O/W_2$): role of the interfacial films on the stability of the system. *Adv. Colloid Interface Sci.* 99, 229–254.
- Korhonen, M., Niskanen, H., Kiesvaara, J., Yliruusi, J., 2000. Determination of optimal combination of surfactants in creams using rheology measurements. *Int. J. Pharm.* 197, 143–151.
- Korhonen, M., Hellen, L., Hirvonen, J., Yliruusi, J., 2001. Rheological properties of creams with four different surfactant combinations—effect of storage time and conditions. *Int. J. Pharm.* 221, 187–196.
- Korhonen, M., Lehtonen, J., Hellen, L., Hirvonen, J., Yliruusi, J., 2002. Rheological properties of three component creams containing sorbitan monoesters as surfactants. *Int. J. Pharm.* 247, 103–114.
- Krawczyk, M.A., Wasan, D.T., Shetty, C.S., 1991. Chemical demulsification of petroleum emulsions using oil-soluble demulsifiers. *Ind. Eng. Chem. Res.* 30, 367–375.
- Opawale, F.O., Burgess, D.J., 1998a. Influence of interfacial properties of lipophilic surfactants on water-in-oil emulsion stability. *J. Colloid Interface Sci.* 197, 142–150.
- Opawale, F.O., Burgess, D.J., 1998b. Influence of interfacial rheological properties of mixed emulsifier films on the stability of water-in-oil-in-water emulsions. *J. Pharm. Pharmacol.* 50, 965–973.
- Peltonen, L., Yliruusi, J., 2000. Surface pressure, hysteresis, interfacial tension, and cmc of four sorbitan monoesters at water-air, water-hexane, and hexane-air interfaces. *J. Colloid Interface Sci.* 277, 1–6.
- Peltonen, L., Hirvonen, J., Yliruusi, J., 2001a. The behavior of sorbitan surfactants at water-oil interface: straight chain hydrocarbons from pentane to dodecane as an oil phase. *J. Colloid Interface Sci.* 240, 272–276.

- Peltonen, L., Hirvonen, J., Yliruusi, J., 2001b. The effect of temperature on sorbitan surfactant monolayers. *J. Colloid Interface Sci.* 239, 134–138.
- Peltonen, L., Karjalainen, M., Hirvonen, J., Yliruusi, J., 2001c. Four sorbitan monoesters: XRPD and DSC studies on bulk material and ellipsometric studies on Langmuir-Blodgett monolayers. *STP Pharm. Sci.* 11, 283–287.
- Rakshit, A.K., Zografi, G., Jalal, I.M., Gunstone, F.D., 1981. Monolayer properties of fatty acids. II. Surface vapor pressure and the free energy of compression. *J. Colloid Interface Sci.* 80, 466–473.
- Rowe, R.C., Sheskey, P.J., Weller, P.J., (Eds.), 2003. *Handbook of Pharmaceutical Excipients*, 4th ed. Pharmaceutical Press, London, pp. 591–595.
- Schramm, G., 1994. *A Practical Approach to Rheology and Rheometry*. Gebrueder HAAKE GmbH, Karlsruhe, pp. 93–111.
- Sherman, P., 1967. Rheological changes in emulsions on aging. III. At very low rates of shear. *J. Colloid Interface Sci.* 24, 107–114.
- Stokes, R.J., Evans, D.F., 1997. *Fundamentals of Interfacial Engineering*. Wiley-VCH, Inc., New York, pp. 201–270.
- Takamura, A., Ishii, F., Noro, S., Tanifuji, M., Nakajima, S., 1984. Study of intravenous hyperalimentation: effect of selected amino acids on the stability of intravenous fat emulsion. *J. Pharm. Sci.* 73, 91–94.
- Wan, L.S.C., Lee, P.F.S., 1973. Influence of nonionic surfactants on the interfacial tension in an oil/water system. *Can. J. Pharm. Sci.* 8, 136–139.
- Zografi, G., 1982. Physical stability assessment of emulsions and related disperse systems: a critical review. *J. Soc. Cosmet. Chem.* 33, 345–358.