Measurement of dynamic surface tension to determine critical micellar concentration in lipophilic silicone surfactants

I. Baquerizo [a], M.A. Ruiz [a,*], J.A. Holgado [b], M.A. Cabrerizo [b], V. Gallardo [a]

[a] *Departamento de Farmacia y Tecnología Farmacéutica, Facultad de Farmacia, Campus de Cartuja, Universidad de Granada,*
18071 Granada, Spain
[b] *Departamento de Física Aplicada, Facultad de Ciencias, Campus de Fuentenueva, Universidad de Granada, 18071 Granada, Spain*

Abstract

Silicone surfactants are becoming increasingly important in the pharmaceutical and cosmetic industry, because of their versatility, low cost, and technological advantages. The present study was designed to measure the critical micellar concentration of three non-ionic silicone surfactants, one water-soluble and two lipid-soluble. We measured surface tension with a technique based on drop geometry. Solubility and dispersibility in water were tested in the two lipophilic surfactants with visible and UV light spectrophotometry. The data obtained with all techniques showed a characteristic behavior of lipophilic silicone surfactants, which did not entirely conform to the definition of critical micellar concentration. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Critical micellar concentration; Dynamic surface tension; Silicone surfactant

1. Introduction

One of the advantages of new silicone surfactants is that they can be used in emulsions with a wide variety of lipophilic components. The composition of the oil phase does not interfere with stability, and the resulting mixtures provide an excellent base for the formulation of cosmetic emulsions with different characteristics. A further advantage of these products is that they can be prepared at room temperature [1,2].

The critical micellar concentration (CMC) is a useful measure for pharmacological and technological purposes [3]. The purpose of the present study was to measure the CMC of three silicone surfactants, one water-soluble and two lipid-soluble. Surface tension [4] was measured with a drop geometry technique developed by Cabrerizo et al. [5].

Because no reference values for surface tension were available for lipid-soluble surfactants in previous studies or in the technical information provided by the manufacturer, we also tested a silicone surfactant for which the surface tension was known. The water-soluble nature of this surfactant greatly facilitated CMC measurements. This was done to check the reliability of the technique, and in fact the values we obtained with the drop geometry technique closely matched the reference values given by the manufacturer. However, we emphasize that the supplier's information did not specify the technique used to measure surface tension, the concentration of surfactant tested, or the duration of the analyses.

2. Experimental

2.1. Materials

Abil B 8843 (polysiloxane polyether copolymers) (INCI), from TH Goldschmidt SA (Essen, Germany), was supplied as a pale yellow translucent liquid. This non-ionic, aqueous, external phase surfactant had a surface tension in water at 25°C of 28–31 mN m^{-1}. The relative percentage proportion (wt/wt) of ethylene oxide and polyethylene oxide in this compound was 100/0 (Fig. 1a).

* Corresponding author. Tel.: +34-958-243 904; Fax: +34-958-243 900.

E-mail address: adolfina@platon.ugr.es (M.A. Ruiz).

(a)

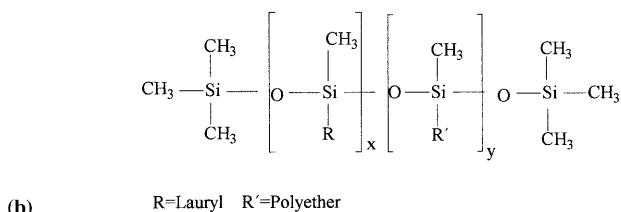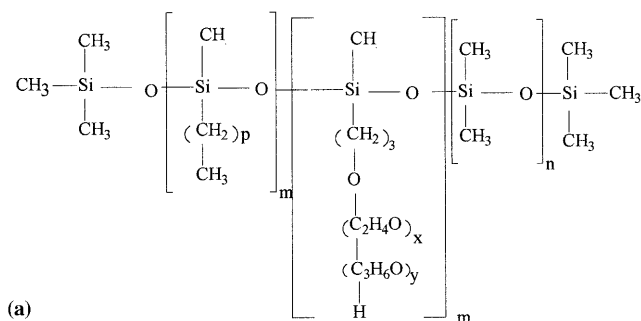**(b)**   R=Lauryl   R′=Polyether

Fig. 1. (a) Chemical formula for Abil B 8843 (polysiloxane polyether copolymers). (b) Chemical formula for Abil WE 09 (cetyl dimethicone copolyol (and) polyglycerol-4-ido-stearate (and) hexyl laurate).
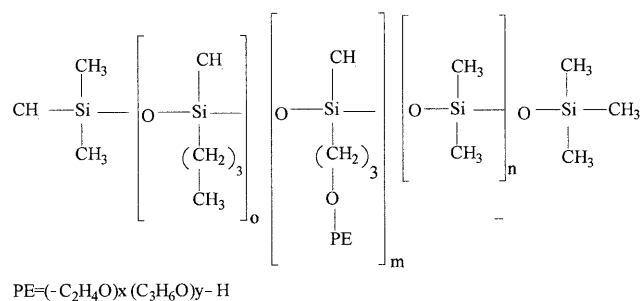

PE=(-C₂H₄O)x(C₃H₆O)y- H

Fig. 2. Chemical formula for Dow Corning Q2-5200 (laurylmethicone copolyol).

Abil WE 09 (cetyl dimethicone copolyol (and) polyglycerol-4-ido-stearate (and) hexyl laurate) (INCI) (also called polysiloxane polyalkyl polyether copolymers) was from TH Goldschmidt SA. This non-ionic, oily,

external phase surfactant was supplied as a pale yellow translucent liquid (Fig. 1b).

Dow Corning Q2-5200 (laurylmethicone copolyol) (INCI) (also known as alkyldimethicone copolyol) was supplied by Dow Corning Ibérica SA (Barcelona, Spain, and Dow Corning Ltd, Brussels, Belgium). This non-ionic, oily, external phase surfactant was supplied as a light straw-colored, translucent liquid (Fig. 2). This compound will be referred to in the text as DC Q2-5200.

Unfortunately, no information on the molecular weight of these compounds was available from the manufacturers.

2.2. Methods

2.2.1. Measurement of dynamic surface tension

The set-up used to measure surface tension in hanging drops is shown in Fig. 3. The hanging drop was formed by injecting the silicone dispersion through a 0.5 mm ID Teflon capillary tube with a microsyringe. The drop was manipulated in a thermostated chamber that kept the drop isolated from the outside environment to avoid contamination, and to maintain constant temperature throughout the experiments.

To facilitate digitalization of the images, the drop was uniformly lit with a diffuser placed between the light source and the chamber. The image analysis segment of the set-up consisted of a Sony CCD IRIS-M370 CE camera (Sony, Tokyo, Japan) equipped with a Leica Apozoom objective (type 40076, Heerbrugg, Switzerland) with a resolution of 752×582 pixels and 256 gray levels. Images were digitalized with a Data Translation DT-3155 card (Marlboro, MA, USA) with a resolution of 768×512 pixels and 256 gray levels. All elements of the set-up except the computer were located on an antivibration table.

The drops were analyzed with the Contact program, which first determined the drop profile by image analysis [6,7] and then used an axiosymmetric drop shape analysis algorithm (ADSA) [8] to fit the outline to the appropriate Laplace equation. The image of the liquid
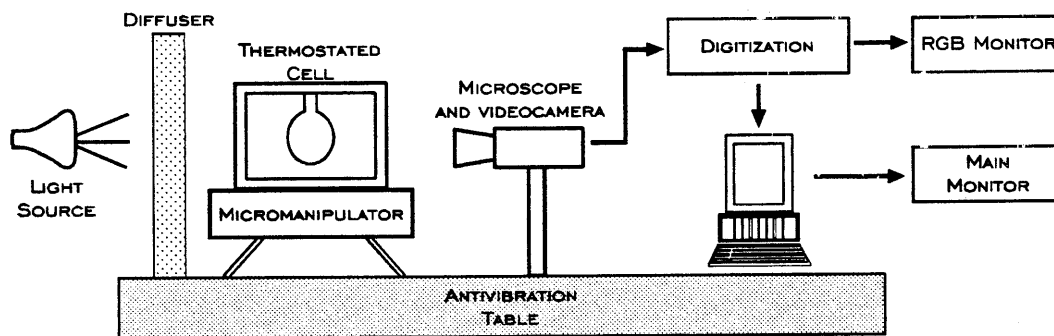

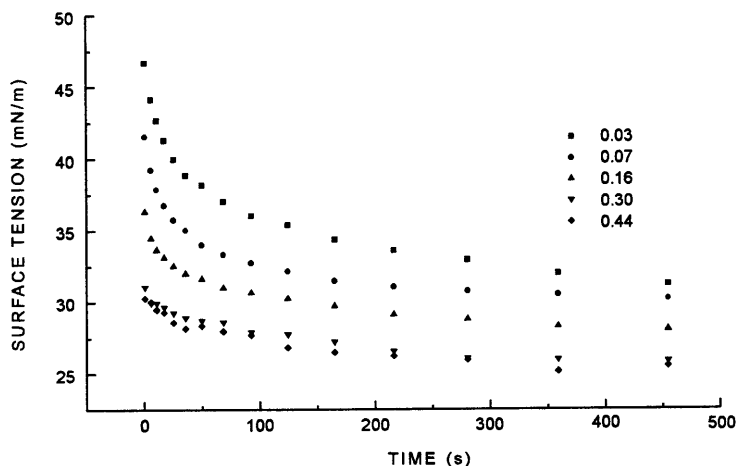Fig. 3. Scheme of the set-up used to measure surface tension in hanging drops.

Fig. 4. Changes in surface tension at different concentrations (wt/vol) of the silicone surfactant Abil 8843 at $25 \pm 0.2°C$ as a function of time.

drop was acquired from the camera and stored in digital form in computer. An edge-detection algorithm was then used to find the contour of the drop in the image, and an edge-linking algorithm was used to ensure that the contour used by the program precisely matched that of the image. Once the drop profile was obtained, a numerical method was used to find the theoretical drop profile that best fit the empirical profile. This involved selection of some experimental points on the contour and adjusting them to the values predicted by the Laplace equation. The interphase parameters of the liquid drop were then found from the fitted theoretical profile.

Differences in dynamic surface tension with each concentration of surfactant were calculated with the Contact program from digitalized images obtained for 0–10 000 s.

2.2.2. Measurement of equilibrium surface tension

Equilibrium surface tension was calculated with the slope method of Cabrerizo et al. [5] as reported previously [9]. For each concentration we first calculated the derivative of dynamic surface tension with respect to time at each point on the experimental time curve. The lowest value of the derivative was found for each concentration, and the cut-off value was estimated as the largest minimum. The cut-off value for each concentration was on the order of 0.001 mN m^{-1} s^{-1}. Values below this point appeared only sporadically, and were taken to reflect equilibrium.

2.2.3. Determination of solubility and dispersibility

Ultraviolet and visible light spectrophotometry (Perkin–Elmer UV–Vis spectrometer with Lambda 2 version 5.1 software (Perkin–Elmer Corp, Analytical Instruments, Norwalk, CT)) were used to select six wavelengths (maximal absorption: 525, 445 and 405 λ with visible light, and 265, 242 and 229 λ with UV

light). The different concentrations of the two silicone-based surfactants were tested at each of these wavelengths. The concentrations of each surfactant were prepared by adding different volumes of sample to double-distilled water in transparent flasks, so that the density of each solution could be checked. The sample dispersions were homogenized by ultrasound; this was especially necessary for W/O emulsifiers DC Q2-5200 and Abil WE 09, because of their poor solubility and high viscosity.

3. Results and discussion

3.1. Dynamic surface tension

To verify the efficacy of the hanging drop method we previously measured the dynamic surface tension of the non-ionic water-soluble silicone surfactant Abil B8843 at five concentrations (Fig. 4) and compared the results with the values provided by the manufacturer. The experimental curves showed that surface tension decreased with time, and reached equilibrium relatively quickly (400–600 s) because of the water-soluble nature of this compound. Equilibrium was reached much sooner at higher concentrations, whereas lower concentrations required longer times for the surface tension to decrease. The equilibrium surface tension was 25–32 mN m^{-1}; these values were very close to the 28–31 mN m^{-1} range given by the manufacturer.

Surface tension was then measured in the non-ionic lipid-soluble silicone surfactants Abil WE 09 and DC Q2-5200 at different concentrations in double-distilled water (Figs. 5 and 6). Abil WE 09 is a combination of cetyl-dimethicone copolyol with organic and inorganic emulsifiers (polyglyceryl-4-isostearate and hexyl laurate), i.e. it is a modification of dimethicones in which propylene oxide, ethylene oxide and carbohydrate

chains replace the methyl radicals. The solubility and dispersibility characteristics are influenced by three main factors: the degree of polymerization increases the hydrophobic capacity of the polymethyl silicone chain, the proportion of ethylene moieties influences hydrophilic capacity, and the proportion of propylene oxide affects hydrophobic capacity [10]. The high-carbon-number carbohydrate chains reduce solubility in water, as do the associated non-ionic emulsifiers, which are markedly hydrophobic.

Fig. 7 shows the absorbance of Abil WE 09 at different wavelengths of visible and UV light. Solubility increased to a concentration of approximately 0.5% (wt/vol), and remained unchanged thereafter, indicating that the additional surfactant present in higher concentrations formed part of the lipophilic aggregate formed on the surface of the solution.

Despite the predominantly hydrophobic structure of Abil WE 09, we found that surface tension of aqueous solutions decreased as concentration of the surfactant increased (Fig. 5). The effects of the decrease in surface tension probably reflected only the degree of polymerization of ethylene oxide and propylene oxide.

Compound DC Q2-5200 is a member of the third generation silicone surfactants [11] which do not require complementary emulsifiers or additives. This compound consists of a hydrophobic dimethicone skeleton, a lauryl radical (dodecyl) chain of 12 carbon atoms (making it hydrophobic), and a polyester chain, which is responsible for its partial dispersibility and hence the main cause of the decrease in surface tension in water (Fig. 6). At high concentrations of DC Q2-5200, the data showed some irregularity; this discrepancy was probably due to the accumulation of lipophilic surfactant at the interface.

This effect was also seen in the spectrophotometric data (Fig. 8): at high concentrations the curve did not show a further increase, but instead revealed a notable
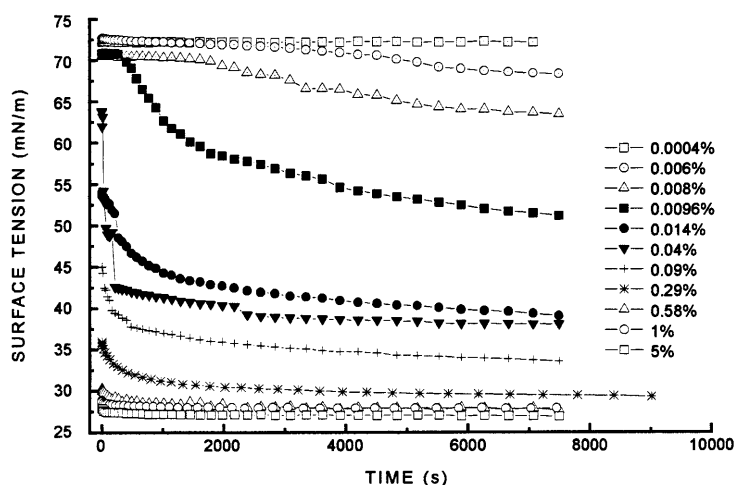

Fig. 5. Changes in surface tension at different concentrations (wt/vol) of the silicone surfactant Abil WE 09 at $25 \pm 0.2°C$ as a function of time.
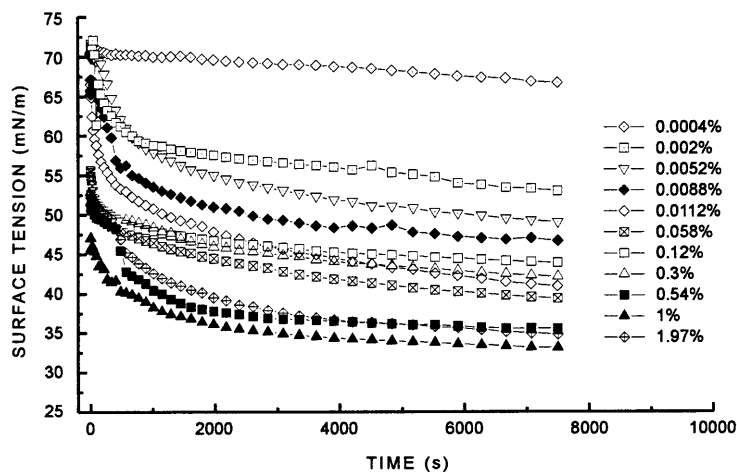

Fig. 6. Changes in surface tension at different concentrations (wt/vol) of the silicone surfactant Dow Corning Q2-5200 at $25 \pm 0.2°C$ as a function of time.
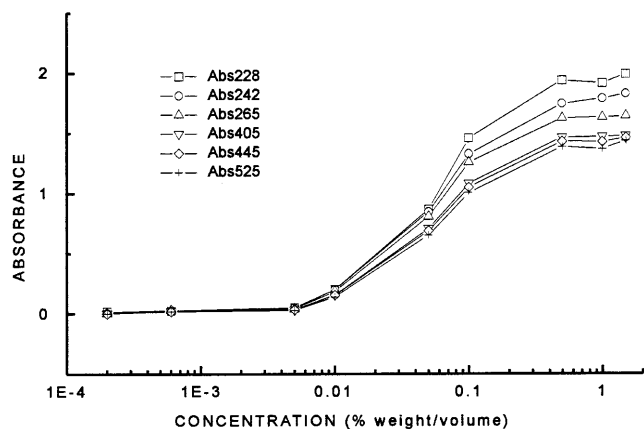
Fig. 7. Spectrophotometric absorbance of Abil WE 09 at different wavelengths of UV and visible light as a function of concentration.
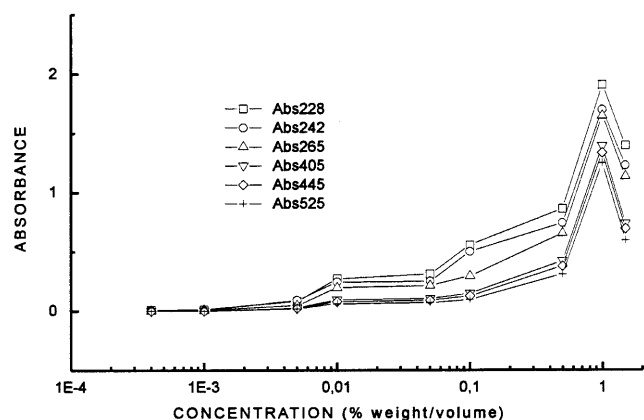

Fig. 8. Spectrophotometric absorbance of DC Q2-5200 at different wavelengths of UV and visible light as a function of concentration.

decrease in dispersability, which in turn affected the CMC.

In general, surface tension decreased more markedly with time in Abil WE 09 than in DC Q2-5200 (Figs. 5 and 6).

3.2. Critical micellar concentration

The slope method was used to calculate equilibrium surface tension for different concentrations of Abil WE 09 (Fig. 9) and DC Q2-5200 (Fig. 10). The resulting curves were used to determine the CMC.

The time to equilibrium for Abil WE 09 was variable, ranging from about 300 s at higher concentrations to more than 1 h at lower concentrations. This behavior was also shown by DC Q2-5200, which reached equilibrium after approximately 1000 s at higher concentrations, but needed more than 2 h to reach equilibrium at the lowest concentrations.

When equilibrium surface tension was plotted against concentration of the surfactant, the resulting curve

showed three distinct parts. The first part represented the range of lower concentrations at which surface tension remained more or less constant. The surface tension in this part of the curve was similar to that of the solvent (in this case water, with a surface tension of 72.78 mN m^{-1}). The second part reflected a rapid decrease in surface tension with increasing concentration, as a result of adsorption. The rate of decrease in surface tension was therefore dependent on the amount of surfactant adsorbed and the hydrophilic nature of the surfactant molecule. The third section of the curve represented a region where surface tension again remains more or less constant regardless of concentration, indicating that once maximum adsorption has been reached, the unadsorbed portion forming micelles in solution. Critical micellar concentration is that concentration at which surface tension is lowest, and at which micelles begin to form. In other words, it is the transition point between the second and third regions of the curve. The curve for Abil WE 09 clearly shows three different regions (Fig. 9); however, formation of micelles and the appearance of turbidity begin before the transition point (CMC) is reached, as will be explained below.

The concentration–surface tension plot for DC Q2-5200 (Fig. 10) did not show the ideal behavior seen with Abil WE 09. This was because of its hydrophobic structure, which made it poorly soluble in water and led to the accumulation of hydrophobic micelles (Fig. 8).

The curve for Abil WE 09 (Fig. 9) suggested that the CMC (27 mN m^{-1}) was approximately 0.5%. At higher concentrations there were no significant changes in surface tension, although we did note a slight tendency toward a decline.

The findings for DC Q2-5200 (Fig. 10) suggested that the CMC was to the right of the steeply declining portion of the curve, at a surface tension of 35.50 mN m^{-1}. This value yields a CMC of 1.0%. The variations in surface tension seen at higher concentrations were probably caused by rapid saturation of the surfactant. An initial minimum appeared at a concentration of 0.05%, followed by an increase, then a second decrease at a concentration of 1.0%, which reflected the point of maximum solubility-dispersibility (Fig. 8). The first minimum, which appeared consistently in the same range of concentrations in our assays with DC Q2-5200, may reflect the presence of impurities in our samples.

In both silicone-based surfactants we found that micelles (aggregates that were easily visible on the surface) did not form at the same surface tension as that at which turbidity appeared. A possible explanation for this result was suggested by Ananthapadmanabhan et al. [12] who noted that the transition point in

the surface tension–surfactant concentration curve indicated the start of micelle formation. However, in silicone-based surfactants the point at which micelle formation began cannot be clearly established. Some solutions became turbid at concentrations below the CMC. These authors also found that solutions at concentrations higher than the CMC in fact behaved as dispersions.

Therefore, in practical terms our values for CMC can be taken to represent the concentration at which the surfactant fulfils its purpose, i.e. reduces surface tension to the lowest value possible. This may be termed 'relative CMC', to clarify the fact that this concentration does not strictly satisfy the classic definition of CMC.

In Abil WE 09, turbidity first appeared at a concentration below 0.01%; at concentrations above this value aggregates formed and became increasingly larger with increasing concentration. Turbidity also increased, and the dispersion appeared milky at a concentration of 0.5% (the same concentration at which surface tension was lowest), becoming increasingly opaque as concentration increased (Fig. 7). In DC Q2-5200 turbidity first appeared at a concentration above 0.001%, and increased steadily. The dispersion appeared milky at a concentration of 0.5%, and became increasingly opaque as the concentration approached 1% (the concentration at which surface tension was lowest). However, at concentrations higher than 1%, turbidity decreased. Aggregates became visible at concentrations as low as 0.001%, and increased in size as concentration increased (Fig. 8).

In conclusion, we found that the method used gave reliable measurements of surface tension in silicone surfactants, based on the comparison of our values for
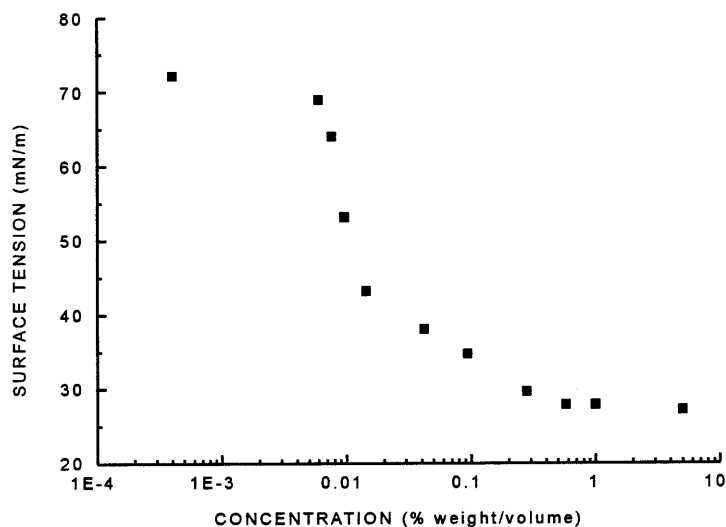

Fig. 9. Equilibrium surface tension at different concentrations (wt/vol) of the silicone surfactant Abil WE 09.
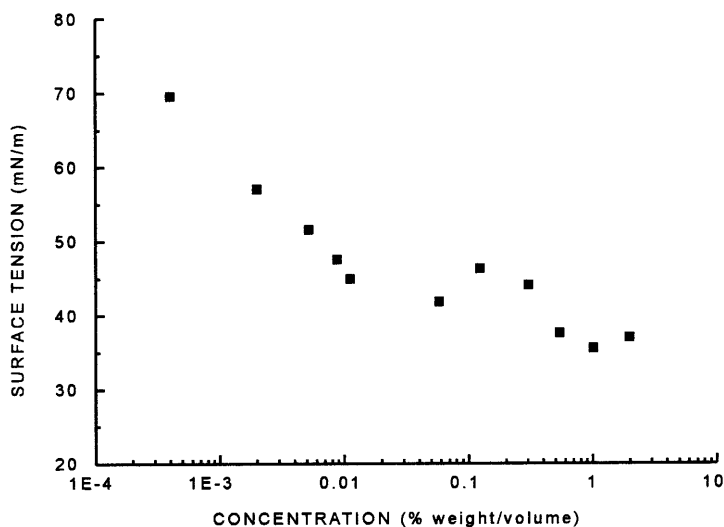

Fig. 10. Equilibrium surface tension at different concentrations (wt/vol) of the silicone surfactant Dow Corning Q2-5200.

a water-soluble surfactant with those provided by the manufacturer. Two hydrophobic silicone surfactants showed a clear decrease in surface tension to values below that of water, probably as a result of the degree of polymerization of ethylene oxide. The values we found for relative CMC were 0.5% (wt/vol) for Abil WE 09 and 1.0% (wt/vol) for DC Q2-5200. The unusual behavior of the surface tension–concentration curve in these surfactants was probably caused by their silicone content and poor solubility in water. We therefore use the term 'relative CMC' to denote the concentration at which increasing concentration of the surfactant led to no further decrease in surface tension, although it did not coincide with the concentration at which micelles or turbidity first became apparent.

Acknowledgements

References

[1] D. Schäfer, Siloxanos organomodificados para formulaciones cosméticas. In: Tego cosmetic. Jornada técnica. Evolución de la química de la silicona y su aplicación cosmética, TH Goldschmidt, Barcelona, 1990, pp. 11–16.

[2] J. Del Arco Ortiz de Zárate, M.A. Arruza Olaechea, M.A. De Diego Rica et al., Formulación Magistral de Medicamentos, Colegio Oficial de Farmacéuticos de Bizkaia, 1993, pp. 149–167.

[3] A. Le Hir, Farmacia Galénica, Masson, Barcelona, 1995, pp. 157–158.

[4] F. Puisieux, M. Seiller (Eds.), Galénica. Agents de surface et emulsions (les systémes dispersés, I). In: Galenica 5, Technique et Documentation, Lavoisier, Paris, 1983, pp. 109–116.

[5] M.A. Cabrerizo-Vilchez, Z. Policova, D.Y. Kwok, P. Chen, A.W. Neumann, The temperature dependence of interfacial tension of aqueous human albumin solution/decane, Colloids Surf. B 5 (1995) 1–9.

[6] P. Cheng, D. Li, L. Boruvka, Y. Rotenberg, A.W. Neumann, Automatio of axisymmetric drop shape analysis for measurements of interfacial tensions of aqueous human albumin solution-decane, Colloids Surf. 43 (1990) 151–167.

[7] J.A. Holgado, Analisis Digital de Interfases Curvas, Thesis, Departamento de Física Aplicada, Universidad de Granada, Granada, 1996.

[8] Y. Rotenberg, L. Boruvka, A.W. Neumann, Determination of surface tension and contact angle from the shapes of axisymmetric fluid interfaces, J. Colloid Interface Sci. 93 (1993) 169–177.

[9] P. Chen, S. Lahooti, Z. Policova, M.A. Cabrerizo-Vilchez, A.W. Neumann, Concentration dependence of the film pressure of human serum albumin at the water/decane interface, Colloids Surf. B 6 (1995) 279–289.

[10] A. Nieto, A. del Pozo, A. Roda, Nuevas Tendencias de Formulación de Preparados Tópicos, vol. 331, Emulsiones, Acofar, 1995, pp. 40–42.

[11] J. Carbajo, M.L. Espejo, Las siliconas: el futuro cosmético, Farmacéutico 99 (1991) 53–65.

[12] K.P. Ananthapadmanabhan, E.D. Goddard, P. Chandar, A study of the solution, interfacial and wetting properties of silicone surfactants, Colloids Surf. 44 (1990) 281–297.