

# Experimental investigations on model emulsion systems stabilized with non-ionic surfactant blends

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## Abstract

We have performed experimental research into model oil-in-water emulsion systems stabilized with non-ionic surfactant blends: thin aqueous films between oil phases and oil drops coalescing against their homophase. Xylene was chosen as the oil phase, and Tween 20 and Span 20, alone or in mixtures at different molar ratios, were used as stabilizers. The roles of the surfactant mole ratio, the electrolyte concentration and pH were studied. It was shown that there is considerable electrostatic repulsion within the aqueous films. The results obtained on thin film stability and on drop lifetime at constant electrolyte concentration indicate that Tween 20 (when present) is the emulsifier that predominantly determines the stability of the systems. This conclusion can be related to the higher surface activity and higher adsorption of Tween as deduced from interfacial tension data. Some evidence of synergism was observed only at an electrolyte concentration of  $10^{-3}$  M (NaCl). We also carried out stability tests on shaken and homogenized batch emulsion systems and the results show good correlation with the data from the model investigations.

*Key words:* Emulsifier blends; Emulsion stability; Mixed surfactants; Non-ionic surfactants; Thin liquid films

## Introduction

Non-ionic surfactants are frequently used as emulsifier ingredients in a large variety of food, cosmetic and pharmaceutical emulsion formulations. The hydrophilic-lipophilic balance (HLB) system has proved useful in choosing the optimal type of emulsifier for a certain application. From the original work of Griffin [1] until the present day [2–6] the HLB concept has always been closely related to the practical use of surfactant mixtures as well as of single emulsifiers.

It has been found empirically that in many applications a blend of two emulsifiers is more

efficient than a single substance at the same HLB value [1,5–8]. A notable detailed study of emulsion stability in the presence of mixed emulsifiers was published by Boyd et al. [7]. In that paper it was shown that maximum stability of Nujol-in-water emulsions stabilized with Tween-Span mixtures is achieved at a certain molar ratio of the two surfactants (1:3 in the case of Tween 20/Span 20). In order to explain their results, the authors discussed possible interactions between the dissimilar surfactant molecules leading to increased surface viscosity and elasticity.

For the time being, however, there is no clearly proven straightforward connection between the properties of the adsorbed interfacial layers of

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mixed surfactants and the emulsion stability. Actually, the discussion of Boyd et al. is based on the measured rheological properties of the Span Tween adsorption layers at the oil/water interface. These correspond to emulsifier concentrations some orders of magnitude higher than those used in their emulsion stability investigations. In a separate paper [9], quite low interfacial viscosities of mixed surfactant layers, not exceeding the viscosities of the layers of individual surfactants, were reported. Furthermore, when dealing with droplet coalescence the hydrodynamics of film formation and thinning should also be accounted for. It has been shown [10] that the hydrodynamic stability of thin emulsion films strongly depends on whether the surfactant is dissolved in the continuous or in the dispersed phase. Thus much more data on the mixed surfactant systems are necessary if one wants to reveal the basic mechanisms of stabilization inside these systems and more generally the HLB scale.

In our investigation we have concentrated on the behaviour and stability of model oil-in-water emulsion systems: thin aqueous films between oil phases and oil drops pressed by the buoyancy against their homophase. We measured the stability of these systems as a function of the surfactant molar ratio. There are reports in the literature [11,12] stating that significant electrostatic charging of the interfaces, caused by adsorption of  $\text{OH}^-$  ions, may exist in similar systems. In order to evaluate the importance of electrostatics we varied in the experiments the electrolyte concentration and pH. The role of the time for surfactant adsorption at the surfaces was also studied.

To estimate the extent to which the model experiments are relevant to real emulsion systems we also carried out simple tests on the separation of shaken and homogenized batch emulsions. The results follow the pattern that is expected from the model investigations. The data are discussed from the viewpoint of the interfacial tension isotherms of the individual emulsifiers and some of their mixtures.

## Materials and methods

### Materials

The complementary emulsifier pair of Tween 20 and Span 20 was used in the experiments. Tween 20 (polyoxyethylene(20) sorbitan monolaurate; HLB, 16.7) is predominantly water soluble and Span 20 (sorbitan monolaurate; HLB, 8.6) is oil soluble [13]. Both surfactants were ICI products for research purposes.

Xylene (isomeric mixture; p.a. grade) was chosen as a model oil phase. Aliphatic hydrocarbons are usually used as substitutes for vegetable oils in similar experimental investigations. We believe, however, that in some investigations xylene may be a better model solvent to represent vegetable oils owing to its higher polarizability.

Tween 20 was always dissolved in the aqueous phase when preparing the solutions. Water purified by a Milli-Q system (Millipore) was used. Span 20 was always dissolved in the xylene phase. Sodium chloride (Merck; analytical grade; heated for 5 h at 450°C) was used for adjusting the necessary electrolyte concentration in the aqueous phase. Hydrochloric acid (p.a. grade) was used in some of the experiments to lower the pH.

Our preliminary experiments revealed that the surfactants, particularly the Tween, are apt to redistribute between the phases and that the redistribution process could affect the emulsion stability [14]. For this reason the experiments were carried out with pre-equilibrated phases. The pre-equilibration procedure was carried out by carefully pouring the phases above one another in a wide flask and gently rotating the flask on a bench shaking machine for more than 24 h. In the preparation and pre-equilibration of the phases, the 1:1 oil:water volume ratio was always sustained. Portions for investigation were carefully withdrawn from the clear bulk phases.

The sum of the initial surfactant concentrations of Tween in the aqueous phase and Span in the xylene phase was fixed at  $10^{-4}$  M. In the case of pure Tween, this concentration corresponds to

about twice the CMC [15]. The analysis of the interfacial tension isotherms (see the Discussion section), indicates that the surface activity of Span is lower. Therefore we have chosen emulsifier molar ratios with increasing Span concentration in order to promote the formation of a really mixed adsorption layer. The five different Tween 20/Span 20 molar ratios selected for the experiments were pure Tween, 1:1, 1:3, 1:9 and pure Span.

The initial concentration of emulsifier in practical batch emulsions is chosen in such a way that the final concentration, after some of the emulsifier has adsorbed on the droplet surfaces, is above the CMC. The choice of the initial surfactant concentration close to, but slightly above the CMC in our model experiments ensures that the surface concentration in the thin film and the drop against an interface experiments will be close to the final concentration in real practical batch dispersions. When batch emulsions are prepared with our phases, the final concentration in the solution and on the droplet surfaces will be lower than the one in practical systems, owing to depletion of some of

the emulsifier by adsorption. This, however, was required in order that these emulsions separate in a reasonable period of time, allowing the process of destabilization to be followed.

### Methods

The experimental investigation of thin aqueous films between oil phases was carried out using the set up schematically presented in Fig. 1. The films were formed by an adaptation of the method of Scheludko and Exerowa [16,17] by sucking the aqueous phase from a biconcave meniscus held in a capillary. The glass capillary, inner radius, 1.49 mm, is immersed in the oil phase. The cell is mounted on the table of an inverted metallographical microscope (Eptip 2, Carl Zeiss-Jena). The observations are carried out through the optically clear bottom of the cell by illuminating the film in monochromatic light (wavelength  $\lambda = 546$  nm). The reflected interference picture can be recorded by a video camera. A fibre-optic probe connected to a photomultiplier and recorder allows the scanning

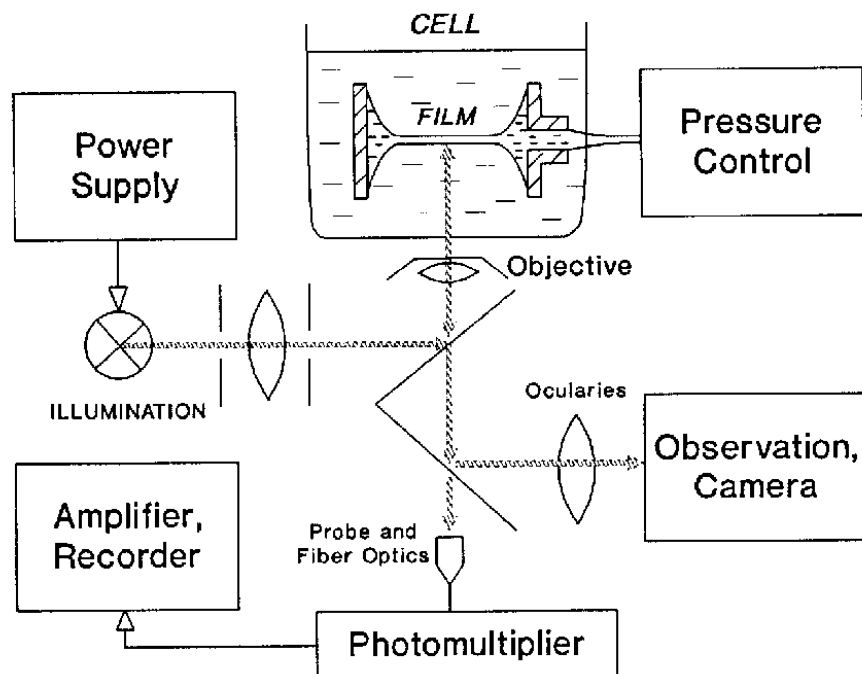


Fig. 1. Basic scheme of the set-up for experimental investigation of thin emulsion films. The films are microscopically observed in reflected monochromatic light.

and registering of the intensity of the reflected light at a given spot [18]. The formulae for calculating the film thickness from the light intensity plot are described in the literature [19].

Usually during the experiments the films were sustained at a constant diameter. This is achieved by keeping the pressure inside the film meniscus constant by a pressure control system comprising two microsyringes and a pressure buffer. The procedure and the adopted scale of film stability are described separately in the following section.

A simple set-up was used for measuring the lifetime of oil drops against a flat homophase (Fig. 2). The drops are formed inside the aqueous phase at the tip of a needle connected to a microsyringe. They are detached by blowing out some of the water phase through a closely situated capillary. The set-up allows ageing of the drop surface for a certain period of time before releasing the drops towards the flat homophase. A detailed description is provided in Ref. 20. A number of similar methods are reported in the literature [21,22].

In the experiments on drop lifetime, the volume of the drop was fixed at  $1 \times 10^{-3}$  ml (corresponding to a radius of  $6.2 \times 10^{-2}$  cm). The final result for each separate system is obtained by averaging the lifetimes of more than 30 drops. The estimated experimental error on the basis of data scattering for these measurements is typically  $\pm 15$  s.

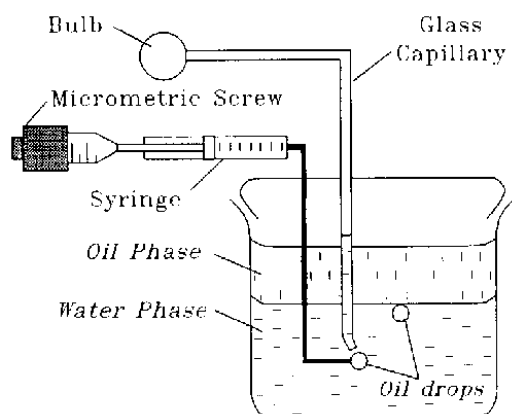


Fig. 2. Scheme of the experimental set-up for measuring the lifetimes of oil drops against a flat homophase.

Two types of batch emulsion stability experiment were carried out. The first type of batch emulsions were produced by dispersing by shaking the pre-equilibrated water and xylene phases in graduated test tubes. Four millilitres of each phase were poured into test tubes with an inner diameter of 10 mm. Three subsequent cycles of 20 vigorous shakes by hand with two rest intervals of 5 min between the cycles were applied in each experiment. Immediately after the third cycle the process of emulsion destabilization was monitored by recording the volume of the xylene layer separated on top of the emulsion. The final results on the rate of oil separation were calculated by averaging the data of more than five independent experiments for each resolution curve.

The second type of batch emulsions were dispersed with the use of a laboratory-type rotating blade homogenizer. The samples consisted of 50 ml of each phase, pre-equilibrated and roughly dispersed by hand before the homogenization. They were treated for 2 min at approximately 1200 rev  $\text{min}^{-1}$  and for 1 min at about 3600 rev  $\text{min}^{-1}$ . Immediately after the homogenization the emulsions were transferred into graduated cylinders with an inner diameter of 28 mm, and the process of separation was monitored. The results presented are averaged over two independent experimental runs (four runs in the case of systems containing  $10^{-3}$  M electrolyte).

Samples of the shaken and the homogenized emulsions were investigated microscopically. The samples were observed in a Bürker cytometer cell, 0.1 mm in depth, without dilution. The emulsion type was determined on the basis of the difference in the refractive indices obtained by the Becke method [23]. The average size of the homogenized droplets was estimated by counting the diameters of more than 150 droplets for each sample.

The experiments were conducted at  $22 \pm 1^\circ\text{C}$ . The cells and all instrumental glassware were cleaned before each experiment in concentrated chromic acid for not less than 24 h, after which they were rinsed and immersed in deionized water for not less than 12 h, and then vacuum dried.

### Procedure for rating the film stability

The thin film thickness and stability measurements were performed on films with diameters 220–240  $\mu\text{m}$ . After loading the cell with the phases, 30 min were allowed for the formation of an adsorption layer at the surfaces and 10 min were allowed for relaxation of the adsorption layer after each film rupture.

During the evolution of a thin liquid film, many phenomena might take place: dimple formation and flow-out, thinning of the plane-parallel film, transition to a black film, etc. [10]. The films could rupture during any of the stages of thinning or remain stable. After the formation of the films their outgrowth was observed; if the films were unstable (rupturing during a certain stage of thinning) their lifetimes were measured. If stable equilibrium films (with constant thickness) formed, their responses to the increase in the film diameter were studied. In all cases where equilibrium films were reached, the film thickness was measured.

In order to estimate the stability of the films we have adopted a six-degree stability scale based on the film behaviour throughout the experimental observations.

(5) Very stable: the formed sturdy equilibrium films hardly rupture even on a drastic increase of the film diameter.

(4) Stable: long-living equilibrium films form, but they easily rupture on an increase of the film diameter.

(3) Transitional: the films rupture during the thinning process, occasionally forming equilibrium films.

(2) Unstable: the films always rupture at a certain stage of thinning but the thinning process lasts for more than 30 s.

(1) Very unstable: the films exist for less than 30 s.

(0) Extremely unstable: the films exist for less than 3 s.

The film stability data were obtained by observing the behaviour of more than 20 independently formed films in the case of stable films or measuring

the lifetimes of more than 30 films in the case of unstable films. Each data point on the film thickness is a result of averaging the outcome of five or more independent experimental runs.

### Results

The data for the equilibrium film thickness are presented in Fig. 3. It is seen that the films without added electrolyte are thicker than 100 nm. The addition of  $10^{-3}$  M electrolyte decreases the thickness to 30–50 nm. The data on solutions containing 0.1 M electrolyte are not shown in the figure as all these films were quite unstable. In the cases where the evolution of these films with high electrolyte concentration could be followed, black film formation was observed before rupturing. The thicknesses of the black films determined by the interferometric measurements were in the  $12 \pm 3$  nm range. The measured thicknesses are similar to those reported by other authors for emulsion films stabilized with non-ionic surfactants in the presence of electrolyte [17,24].

It is also seen that in general the thickness increases with increase in the Span 20 molar fraction. No substantial change in the thickness is registered when  $10^{-4}$  M hydrochloric acid is added to the aqueous phase.

In Figs. 4 and 5, results are presented for the emulsion film stability measurements. The influence of both the surfactant molar ratio and the electrolyte concentration is shown. The data in Fig. 4 cover the cases where only NaCl is used as electrolyte; the data in Fig. 5 are for solutions to which  $10^{-4}$  M HCl is added.

It is seen from Fig. 4 that the stability generally increases in two cases: (i) upon increase of the relative proportion of Tween 20; (ii) upon decrease of the electrolyte concentration. The same trends are observed in Fig. 5. Comparing the heights of the bars in the two figures leads to the conclusion that in most cases the addition of hydrochloric acid decreases the stability. A particular case of very low film stability is observed in the system containing only Span at pH 4 and a 0.1 M electro-

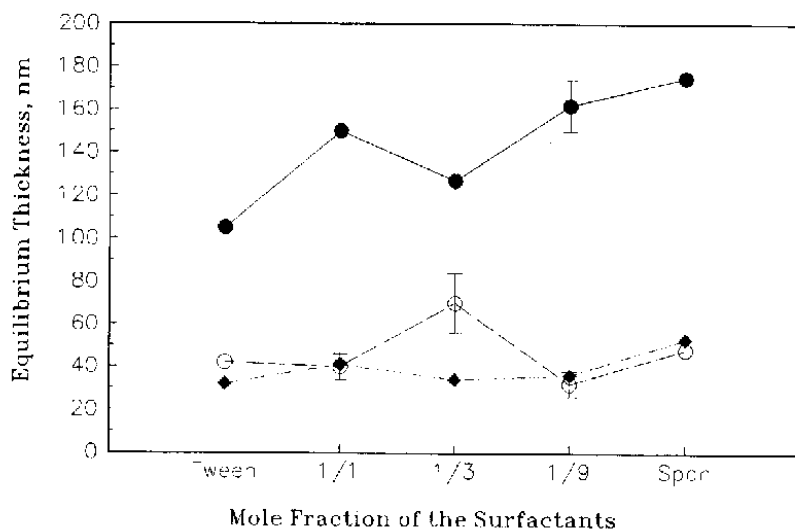


Fig. 3. Results from interferometric measurements of the equilibrium thickness of aqueous films as a function of the surfactant molar ratio. The electrolyte concentration corresponding to the different data points is as follows: ●, no electrolyte added; ○,  $10^{-3}$  M NaCl; ◆,  $10^{-3}$  M including  $10^{-4}$  M HCl.

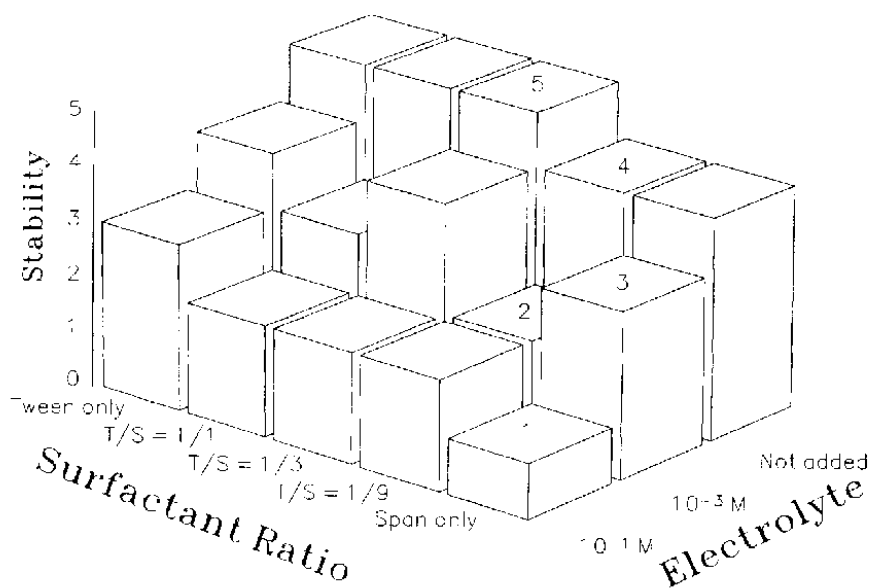


Fig. 4. Results from the investigation on the stability of aqueous films as a function of surfactant molar ratio and electrolyte concentration. The numbers on the vertical axis coincide with the described rating of the stability (see the Procedure for Rating the Film Stability section).

lyte concentration. The films from that system are the only ones registered as "extremely unstable" (see Methods section), i.e. the film evolution after its formation could hardly be observed due to its almost immediate rupture.

No real synergistic effects can be seen in either

of the figures as none of the surfactant mixtures shows a higher stability than the pure Tween. It is notable, however, that the stability of the 1:3 Tween/Span blend for some electrolyte-containing systems is higher than that of the neighbouring 1:1 and 1:9 blends (Figs. 4 and 5). The film

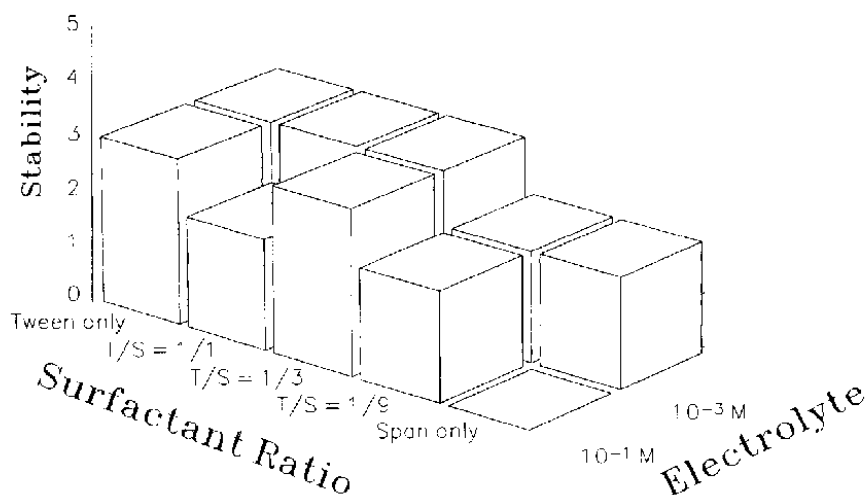


Fig. 5. Results from the investigation on the stability of aqueous films at a decreased pH as a function of surfactant molar ratio and electrolyte concentration. The electrolyte comprises NaCl and 10<sup>-4</sup> M hydrochloric acid. The numbers on the vertical axis coincide with the described rating of the stability (see the Procedure for Rating the Film Stability section).

thickness recorded at 10<sup>-3</sup> M NaCl is also higher for the 1:3 molar ratio than for the 1:1 and 1:9 molar ratios (Fig. 3).

Two series of experiments on lifetimes of oil drops against a homophase interface were conducted. In the first series the drops were released from the needle tip immediately after their formation. The data on the lifetimes of these drops as a function of surfactant molar ratio and electrolyte

concentration are presented in Fig. 6. In the second series of experiments the drops were allowed to relax in the aqueous solution for 10 min before detaching them from the needle. In this way a better adsorption layer of surfactant is expected to form at the drop interfaces. The results from that series of experiments are presented in Fig. 7. Comparing Figs. 6 and 7 it is easy to determine that the lifetime of the drops increases after the

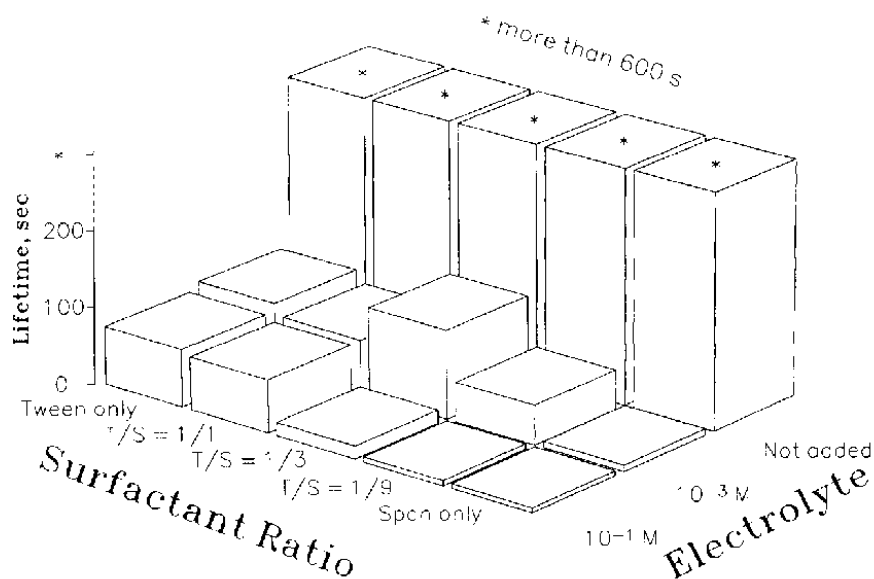


Fig. 6. Lifetimes of oil drops released against the flat homophase immediately after their formation.

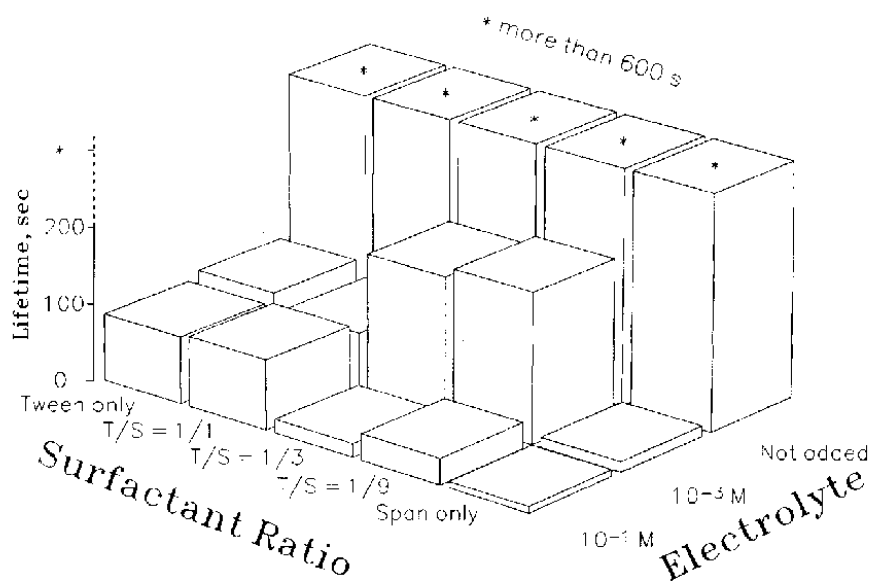


Fig. 7. Lifetimes of oil drops released against the flat homophase after 10 min of contact with the aqueous phase.

surface has been allowed to adsorb surfactant (either Tween or Span) before releasing the drops.

It is also evident from Figs. 6 and 7 that the results for the drops against an interface stability generally follow the same pattern as in the thin film stability experiments: (i) the lifetime decreases with increase in the electrolyte concentration; (ii) the Tween-containing systems are more stable than the Span-containing systems. A kind of synergistic effect is observed in the systems, whose aqueous phase contains  $10^{-3}$  M electrolyte. The effect is less pronounced in Fig. 6; actually it falls there within the limits of the estimated experimental error. After allowing a better saturation of the surfaces, as shown in Fig. 7, the 1:3 and the 1:9 Tween/Span mixtures have a definitely increased stability compared with the pure Tween or Span systems.

Visual and microscopical investigations of the shaken and homogenized batch emulsions showed that all these are of the oil-in-water type. Therefore all the studies on aqueous films between oil phases are relevant to the batch emulsions obtained. The droplet diameters in the shaken systems were above  $100 \mu\text{m}$ . The sizes of the emulsion drops in the homogenized systems a few minutes after their

formation were in the  $25 \pm 6 \mu\text{m}$  range for the pure Tween and  $32 \pm 12 \mu\text{m}$  for the pure Span.

The outcome of the stability measurements of shaken batch emulsions as a function of time  $t$  is presented in Figs. 8(a)–8(c). The volume fraction of emulsified (non-separated) xylene,  $\Phi_e$ , is plotted in these graphs:  $\Phi_e(t) = 1 - V_s(t)/V_i$ , where  $V_s(t)$  and  $V_i$  are respectively the volumes of the demulsified and the initially dispersed xylene phases.

Comparing the rate of emulsion breakdown and the volume of the remaining non-separated emulsion from the graphs, the already formulated rules of decreasing stability with addition of electrolyte and increasing the molar part of Span are seen to be valid. The only exception is observed in the case of the  $10^{-3}$  M electrolyte, where the curve for the 1:3 Tween/Span mixture represents a higher stability than those for the 1:1 mixture and the system without electrolyte. Still the stability of that emulsion is lower than that of the system containing only pure Tween. Thus these results comply with the expectations based on the model film and drop experiments.

The results from the tests on the stability of homogenized emulsion systems are presented in Figs. 9(a)–9(c). The systems with high electrolyte



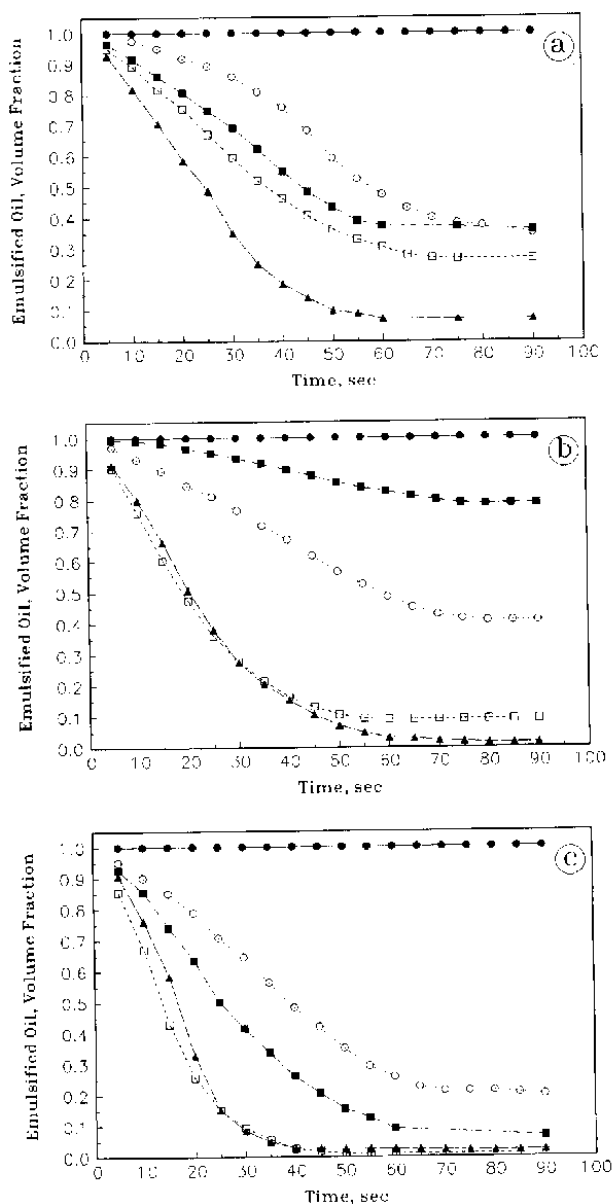


Fig. 8. Volume fraction of emulsified oil in shaken batch emulsions as a function of time for three different electrolyte concentrations in the aqueous phase: (a) no electrolyte added; (b)  $10^{-3}$  M NaCl; (c)  $10^{-1}$  M NaCl. The data points correspond to the following molar ratios of the surfactants: ●, pure Tween; ○, 1:1 Tween/Span; ■, 1:3 Tween/Span; □, 1:9 Tween/Span; ▲, pure Span.

concentration showed a very rapid separation, demulsifying in less than 30 min. Thus the addition of electrolyte to these emulsions drastically decreases the stability. As in the previous cases,

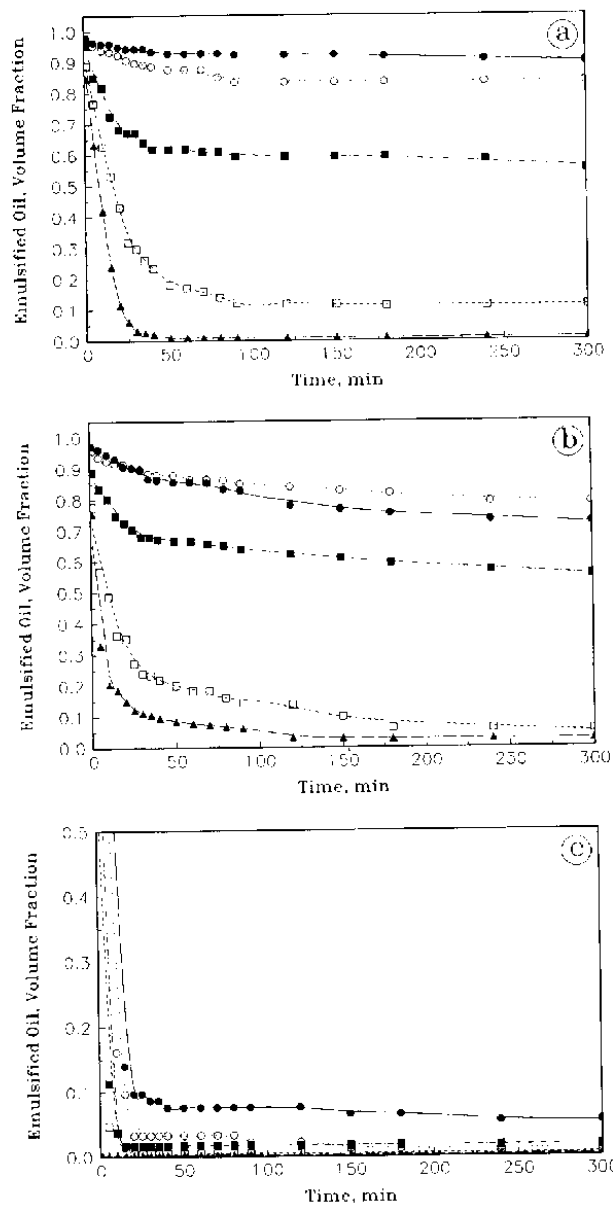


Fig. 9. Volume fraction of emulsified oil in homogenized batch emulsions as a function of time for three different electrolyte concentrations in the aqueous phase: (a) no electrolyte added; (b)  $10^{-3}$  M NaCl; (c)  $10^{-1}$  M NaCl. The points correspond to the following molar ratios of surfactants: ●, pure Tween; ○, 1:1 Tween/Span; ■, 1:3 Tween/Span; □, 1:9 Tween/Span; ▲, pure Span.

the rate of emulsion breakdown at a fixed electrolyte concentration increases with the increasing molar fraction of Span in the mixture, reaching a maximum at the systems stabilized with Span only.

Again there is an exception in the case of the  $10^{-3}$  M electrolyte where the curve for the 1:1 surfactant mixture presents a slightly higher volume of emulsified phase than the curve for the pure Tween.

The time scales in Figs. 8 and 9 are rather different owing to the much higher rate of creaming and coalescence in the shaken systems. If, however, we compare the amount of oil that remains emulsified after the fast creaming and coalescence process has been accomplished, it is seen that at the same surfactant and electrolyte concentrations a smaller volume portion of oil remains emulsified in the homogenized emulsions in comparison with the shaken ones (this is especially evident in the case of pure Tween).

### Discussion

The aqueous films are quite thick in the absence of electrolyte (Fig. 3). It should be expected that such a long-range repulsion between the film surfaces results from electrostatic interactions. This assumption is supported by the reduced film thickness at  $10^{-3}$  M of electrolyte and black film formation at high electrolyte concentrations ( $10^{-1}$  M). It is known that the oil/water interfaces are negatively charged, possibly due to the adsorption of  $\text{OH}^-$  ions at the interfacial boundary [11]. The existence of a significant  $\zeta$  potential in mineral and cottonseed oil emulsions stabilized by Spans and Tweens has been reported by Becher and Tahara [12]. Our own investigations [12(a)] have shown that  $\zeta$  potentials as large as  $-70$  mV can exist for xylene drops in water in the presence of Span 20/Tween 20. The  $\zeta$  potentials we measured demonstrate an increase with the increase in Span concentration, analogously to the observed trends in film thicknesses.

The electrostatic repulsion is undoubtedly significant for the behaviour of the investigated model systems. Comparing Figs. 4–7 it is natural to conclude that the reduced film and drops against an interface stability at increased electrolyte concentrations is a result of the suppressed electro-

static repulsion (we assume that other effects, like salting out of the surfactant by increased NaCl concentration, are negligible). The above conclusions are also expected to be applicable to the observed increase in coalescence rate of batch emulsions on increasing the electrolyte concentration (Figs. 8 and 9). However, one cannot conclude that the electrostatic repulsion is the only important factor of stabilization as there are at least two pieces of evidence against such a conclusion: (i) the fact that the Span-containing systems, although exhibiting a greater electrostatic repulsion, are distinctively less stable; (ii) the observation that the HCl-containing films are less stable although their thickness is approximately the same. Therefore the influence of other factors on film stability should also be accounted for.

It would be hard to discuss the factors of stabilization further without introducing some additional data on the interfacial properties of the Tween/Span systems. In a separate study, the interfacial tension isotherms of pure Tween 20, pure Span 20 and their mixtures were measured by the du Nouy ring pull-out method [25]. It was found that the pure Tween is much more surface active at lower concentrations. For example, at a concentration of  $10^{-5}$  M the adsorption layer of pure Tween is almost completed ( $\Gamma/\Gamma_\infty=0.97$ , where  $\Gamma$  is surface concentration and  $\Gamma_\infty$  is saturated surface concentration), while the adsorption layer of pure Span is still quite unsaturated ( $\Gamma/\Gamma_\infty=0.28$ ). At the surfactant concentration of  $10^{-4}$  M, which we have chosen in our study, the surface activity and the adsorption of Span are expected to increase significantly and to be comparable with those of Tween. To promote a really mixed layer, the 9:1 Span/Tween mixture was included in the experimental scheme. In spite of that, higher adsorption of Tween is probably existent in most of the cases studied. In consequence, the properties and the stability of the systems should be expected to depend on the presence of Tween, mainly.

There are many theoretical indications that Tween 20 should be a better stabilizer of the studied oil-in-water systems than Span 20. Owing

to its higher adsorption at the investigated bulk concentration, the Tween should promote a larger Gibbs elasticity  $E_G$ :

$$E_G = -\Gamma_0 \frac{\partial \gamma_0}{\partial \Gamma_0} = kT \frac{\Gamma_0}{1 - \Gamma_0/\Gamma_\infty}$$

where  $\gamma_0$  and  $\Gamma_0$  denote respectively the equilibrium interfacial tension and surface concentration,  $\Gamma_\infty$  is the saturated surface concentration,  $k$  is the Boltzmann constant and  $T$  is the temperature (the last equality above holds for the Langmuirian adsorption isotherm, by which the data for the Tween are matched well). It has been shown [10,26] that the higher Gibbs elasticity decreases the rate of interdroplet film thinning and the probability of rupture. The lower interfacial tension in the Tween-containing systems is also a favourable factor for the film stability, since it reduces the capillary pressure of the droplets and consequently the driving pressure of film thinning. The voluminous water-penetrating polyoxyethylene chains of the Tween should promote possible steric repulsion between the film surfaces [27].

The above conclusion is supported by the experimental evidence connecting model or batch emulsion stability and surfactant type or molar ratio. Without exception the systems containing only Tween are more stable than those containing only Span. In the case of mixed surfactants (except when synergistic effects are observed) the stability generally decreases in the order of increasing Span concentration in the mixture. According to Bancroft's rule [10] and the HLB scale [3,6] one should expect Span 20 to be a better stabilizer of water-in-oil than of oil-in-water emulsions. We, however, have not registered phase inversion in the pure Span systems. This can be connected with the electrostatic repulsion within the thin films. According to Becher [28], about 85 vol% of oil are required for inversion to occur for Span 20 at low concentrations. Furthermore, as shown recently [29], the Bancroft rule may sometimes not hold for emulsifier concentrations below the CMC.

The observed synergistic effects (Figs. 6, 7 and 9(b)) or traces of such effects (Figs. 4 and 8(b)) in our experiments at pH 7 are not very pronounced and concern only systems containing  $10^{-3}$  M electrolyte. Most of them are encountered at a Tween 20/Span 20 molar ratio of 1:3, corresponding to that reported by Boyd et al. [7] and Shah [8] although this does not seem to be a general rule (see Figs. 7 and 9(b)). It will be hard to determine the origin of these effects on the basis of the data reported in this work. The data on film thickness (Fig. 3) indicate a larger electrostatic repulsion for the 1:3 system. Conversely we have already seen (see the above discussion) that electrostatic interactions are not the only factor of stabilization, especially at a fixed electrolyte concentration. If any specific interactions between the adsorbed molecules are responsible for the synergistic effects, as suggested by Boyd et al., a more comprehensive experiment able to evaluate the role of the steric repulsion forces is required. It is also hard to estimate the scope of the importance of possible synergism in real practical emulsion systems which will generally have larger surfactant concentrations and smaller droplet sizes. One conclusion, however, that follows from our results is that synergistic effects may be operative only at certain regions of electrolyte and surfactant concentrations and pH. From a practical viewpoint this means that the postulated empirical rule [5] that "blends of emulsifiers are nearly always much more effective than any single chemical composition" should be applied with caution and checked for any particular case.

The difference in the rate of separation of the shaken and homogenized systems can be attributed to the much higher rate of creaming of the larger drops of the shaken emulsion. After the creaming is accomplished, the amount of separated oil in the homogenized emulsion systems is larger than in the shaken ones. Probably this is a result of the smaller drop sizes of the former, since there are theoretical predictions [26,30] stating that films between smaller drops thin much faster and are subjected to higher capillary (driving) pressures.

Another possible reason for the higher degree of separation of the homogenized dispersion is the bigger depletion of the emulsifier due to the adsorption on the widely developed surface of the smaller drops.

From a methodological point of view it is noteworthy that the experimental results on thin liquid films and lifetime of single drops against a flat interface (model emulsions) at least in our case match well the outcome of the batch emulsion stability tests. This experimental finding is not obvious from theoretical considerations if one bears in mind the difference in the drop sizes and the capillary pressures typical for the model and for the batch systems. Thus model experiments are proven to be applicable and useful for detailed studies of batch emulsion stability.

### Conclusions

The results from thin aqueous film and drops against an interface experiments in model emulsion systems containing Tween 20–Span 20 blends indicate the following.

(1) Electrostatic interactions in the studied model systems with thin aqueous films exist and are important for their stability. Increase in the electrolyte concentration leads to a smaller film thickness and decreased stability.

(2) Tween 20 is the better stabilizing agent, thanks to its higher adsorption, higher Gibbs elasticity, preferential solubility in the continuous phase and voluminous molecule. Its replacement with Span 20 decreases the stability.

(3) Evidence of synergistic effects was found only in some of the drop against an interface experiments with surfactant blends and only at an electrolyte concentration of  $10^{-3}$  M NaCl. In the thin film investigations at the same electrolyte concentration, traces of such effects were also observed.

(4) The addition of hydrochloric acid generally decreases the stability; the effect is much more pronounced with Span 20.

(5) The ageing of the surfaces increases the

stability, probably as a result of the formation of better adsorption layers.

The observed trends in the stability of model systems correlate very well with the tests on shaken and homogenized batch emulsions. In particular, traces of enhanced stability in the presence of mixed surfactants were again observed only in batch emulsions containing  $10^{-3}$  M electrolyte. Thus, although synergism in the blended emulsifier systems is possibly existent, this phenomenon seems to be not very pronounced and restricted to certain ranges of electrolyte concentrations and pH.

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