Instability of Emulsion Liquid Films Induced by the Transfer of Acetic Acid*

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ABSTRACT

The effect of the transfer of acetic acid on the stability of emulsion films was studied. The water films were stabilized by a surfactant, sodium dodecylbenzenesulfonate, and acetic acid was initially dissolved in the bezene phase, straddling the film. It was found that the mass transfer strongly decreased the lifetime of the films, the effect being less pronounced at higher surfactant concentrations.

INTRODUCTION

The Marangoni–Gibbs instabilities, caused by the transfer of a solute across a liquid/liquid interface, were recognized long ago as one of the major causes of spontaneous emulsification [1]. This effect is of importance for many processes of technological and biophysical significance and have received considerable attention during the last two decades (see e.g. [2,3]). Professor E. Wolfram was one of those who studied the role of the Marangoni–Gibbs instabilities on the wetting in solid/liquid/fluid systems [4].

The theoretical study of Sternling and Scriven [1], although based on a very simplified model, still serves as a background for qualitative explanation of most of the observed pheonomena. Yet the experimentally observed effects are often much more complicated and in many instances are in contradiction with the predictions of the theory [2]. Different kinds of surface motions such as cell convection, oscillation and eruptions have been observed with drops immersed in another liquid and on a flat liquid–liquid interface [2,5].

In some cases it was possible to establish the average size, λ, of the convection cells and to follow its evolution with time [2]. The cells were seen to become quite large (of the order of millimeters). One can assume, therefore,

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*Dedicated to the memory of Professor E. Wolfram

that if there is a second surface, at distances smaller than λ, this could substantially alter the whole process. Such a situation can be created in a liquid film, whose thickness is typically of the order of 100 nm or less. The interaction between the convection cells on either interface of the film, as well as the restrictions imposed by the small thickness and radius of the film, can have many repercussions, but we will put off their discussion until a later theoretical study. Our purpose now is only to demonstrate that the transfer of a solute across the film interfaces can substantially reduce its stability.

We have chosen benzene and water as bulk phases and acetic acid as transferable solute, because instabilities at the interface between bulk phases in this system have been relatively well studied [6,7].

According to the Sternling–Scriven criteria [1] the system should be stable for the transfer of acetic acid from benzene to water [2]. Indeed, no instability has been found for acid concentration in benzene below 0.15 kmol m^{-3} [7], although at 0.3 kmol m^{-3} eruptions have been observed [6]. Adding surfactant has been found to have a very strong effect on the mass transfer coefficient [8,9]: even 10^{-6} kmol m^{-3} of dodecylamine hydrochloride, manoxol and sodium dodecyl sulfate are sufficient to suppress the interfacial convections at 0.98 kmol m^{-3} acid concentration in the benzene phase and to substantially reduce the mass transfer coefficient.

EXPERIMENTAL AND MATERIALS

We measured the lifetime of water films, stabilized by a small amount of sodium dodecylbenzenesulfonate surrounded by benzene solution of acetic acid at different concentrations, c_b. The films were formed in the cell, initially designed for foam films [10] and later adapted for emulsion films [11] (Fig. 1). The film is formed in the capillary 1 (scratched in a vertical direction for better wetting by the water phase) by sucking out the liquid from the biconcave meniscus 2, by means of the micrometric screw 6 and the mercury piston 7. The film was observed from below through the microscopic glass 4 using an Epitip 2 microscope. The measurements were carried out in a thermostated room at $20 \pm 1\,^\circ$C.

Emulsion films are formed in the following way. The bottom part 5 of the cell is filled with the oil (benzene) phase. The tube 3 is filled with the water solution of surfactant and then the lid (holding the capillary 1) is put on top of the bottom part 5. Then, by pushing out the water by means of the screw 6 a biconcave meniscus is formed. A film of fixed radius (in all experiments 10^{-2} cm, controlled visually) is formed by sucking out the water from the meniscus. When the film ruptures, a new film can be formed in the same way without removing the lid.

The cell was treated before use every time with hot chromic acid and then well rinsed with tridistilled water. Tridistilled water (obtained from a quartz
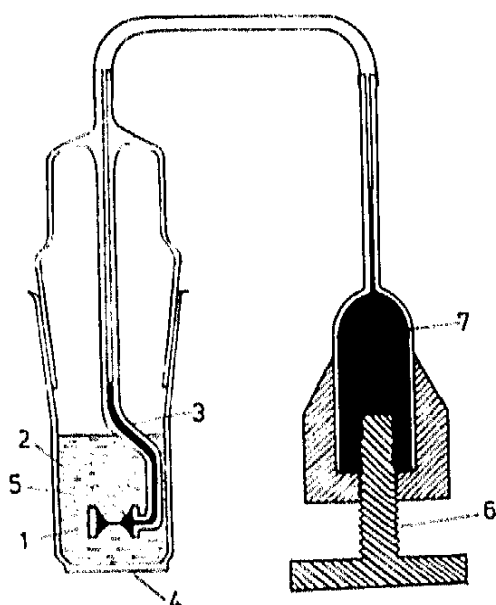
Fig. 1. The cell used for measuring the lifetimes of emulsion films: 1, capillary (film holder); 2, meniscus; 3, tube; 4, optical glass; 5, cell bottom; 6, micrometric screw; 7, mercury piston.

still) was used as the water phase. The benzene (initially analytical grade) was purified by washing it with concentrated sulfuric acid and 30% solution of KOH, drying it with solid KOH and then distilling it. The solvents, benzene and water, were prepared in such a way as to become mutually saturated before use. The acetic acid and surfactant used (sodium dodecylbenzenesulfonate), both analytical grade, were used without further purification.

RESULTS AND DISCUSSION

The surfactant concentration in the water phase, c_s, was chosen high enough ($c_s \geq 10^{-4}$ kmol m^{-3}) to ensure the formation of relatively thick (yellow in reflected white light) films, which were stable in the absence of mass transfer (they lived longer than 900 s). The solute (acetic acid), with concentration c_b, was added to the benzene phase. For each set of concentrations, c_s and c_b, the lifetimes τ of 30 films were measured (τ is defined as the time which elapses between the formation and the rupture of the film). These data were used to calculate the integral distribution curves (as described in [12]) and to obtain from them the lifetime $\tau_{1/2}$, at which 50% of the films rupture. Figure 2, where N is the number of films which have survived time τ, shows an example of such a curve for $c_b = 0.3$ kmol m^{-3} and $c_s = 10^{-4}$ kmol m^{-3}. Since the curves were not always smooth, we also calculated the average lifetime, $\bar{\tau}$, for each series of experiments. With only one exception ($c_b = 0.1$ kmol m^{-3}, $c_s = 3.16 \times 10^{-4}$ kmol m^{-3}), τ_1 and $\bar{\tau}$ practically coincide. The results are shown in Table 1 and Fig. 3.

Several conclusions can be drawn from these results. It is clear that the solute transfer promotes film rupture. There are two distinct ranges in terms
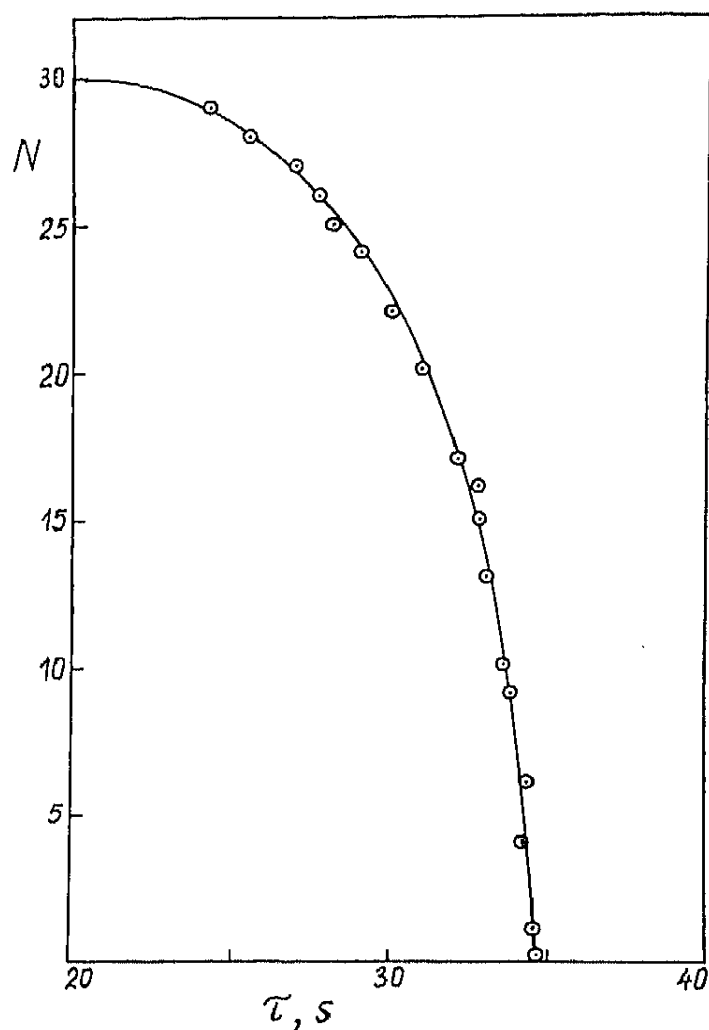
Fig. 2. An integral distribution curve for the number, N, of films having survived time τ ($c_b = 0.3$ kmol m^{-3}, $c_s = 10^{-4}$ kmol m^{-3}).

TABLE 1

Lifetime, τ_1 (s), and average lifetime, $\bar{\tau}$, for water films, stabilized with sodium dodecylbenzene-sulfonate of concentration c_s (kmol m^{-3}), sandwiched between phases, containing acetic acid of concentration c_b (kmol m^{-3})

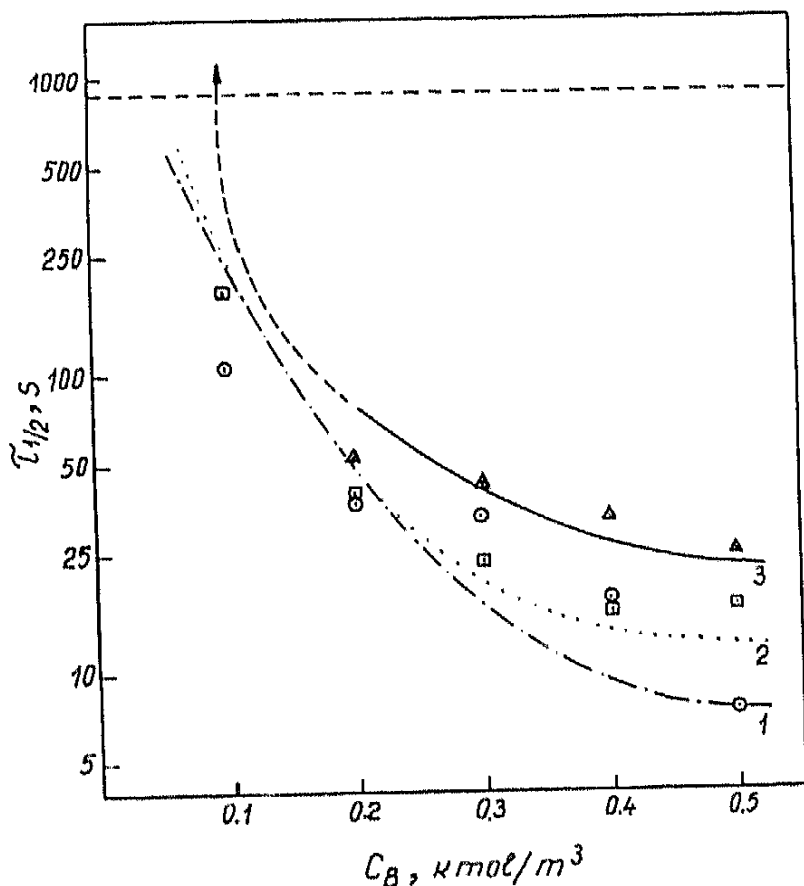| c_s (kmol m^{-3})	c_b (kmol m^{-3})										
	0	0.1		0.2		0.3		0.4		0.5	
	$\bar{\tau}$	$\bar{\tau}$	τ_1	$\bar{\tau}$	τ_1	$\bar{\tau}$	τ_1	$\bar{\tau}$	τ_1	$\bar{\tau}$	τ_1
1×10^{-4}	>900	111.6	10.80	34.3	36.0	31.2	32.4	17.9	17.4	8.4	7.4
3.16×10^{-4}	>900	280.0	190.0	39.0	38.6	23.8	23.5	16.0	15.9	16.2	16.2
1×10^{-3}	>900	>900	>900	57.8	53.5	43.2	43.0	32.8	32.8	30.4	24.8

Fig. 3. Lifetime, $\tau_{1/2}$, as a function of the concentration c_b, of acetic acid in the benzene phase at different surfactant concentrations c_s: 1 (○), 10^{-4} kmol m^{-3}; 2 (□), 3.16×10^{-4} kmol m^{-3}; 3 (△), 10^{-3} kmol m^{-3}. The horizontal dashed line at 900 s indicates the limit above which the films are considered as infinitely stable. The dashed portion and the arrow on curve 3 indicates that at $c_b < 0.2$ kmol m^{-3} the films are infinitely stable.

of the solute concentration: a drastic initial decrease in lifetime at $c_b < 0.2$ kmol m^{-3} followed by a slower but still noticeable decrease in the film stability. As one would expect, the increase of the surfactant concentration, c_s, stabilizes the film, but this effect is much less pronounced than in the case of an interface — as already pointed out in the Introduction, even 10^{-6} kmol m^{-3} in the latter case completely damps out the surface convections. One more difference with respect to the interface between two bulk phases is the fact that we observed instabilities in films even at low solute concentrations, at $c_b = 0.1$ kmol m^{-3}, whereas with this direction of mass transfer the interfaces become unstable only at $c_b > 0.15$ kmol m^{-3} (see above). We did not observe spontaneous emulsification or movement of the meniscus interface (without a film being formed in the meniscus) at any of the acetic acid concentrations used. The present study is not sufficient to draw any definitive conclusions, but all the facts taken together lead us to think that although the phenomenon we observed is likely to have fundamentally the same origin as the instabilities at a single interface, it may have some peculiarities of its own, connected with the finite thickness of the liquid layer.

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