

A Numerical Study of Surface Tension Auto-Oscillations. Effect of Surfactant Properties

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The effect of the main surfactant properties such as, solubility, surface activity, and diffusion coefficient on the behavior of a system with a surfactant droplet under the free water surface is studied numerically for a semi-infinite model system. The system reveals instability which is manifested by auto-oscillation of the surface tension. The induction time before the beginning of auto-oscillations and amplitude and period of the oscillation are dependent on the surfactant properties. Increase of the above parameters leads to a decrease of the induction time but the degree of their effect is different. The amplitude of the oscillations is mainly dependent on the surfactant solubility.

Introduction

It has been experimentally established that in the system, where under the free water surface a surfactant droplet is formed on the tip of a capillary, long-time regular auto-oscillations of surface tension can take place. At first, the auto-oscillations were revealed by using a diethyl phthalate droplet.¹ Very recently, they were obtained in experiments with aliphatic alcohols.² This phenomenon is different from the known manifestations of instability by the mass transfer. In the present case, the oscillatory behavior evolves by solute transfer from the bulk of the liquid to the liquid–air interface whereas a precondition for the instability of the known oscillatory type is the opposite direction of the solute transfer.^{3,4} That is why a comprehensive theoretical study of the problem is needed.

A qualitative analysis of the system behavior was performed in ref 1. A more detailed theoretical investigation of the phenomenon was started in a recent paper,⁵ where the general regularities of the system behavior were studied by using the surfactant properties chosen close to those for diethyl phthalate. Experimental studies of the auto-oscillations phenomenon in systems with aliphatic alcohols showed that the oscillation characteristics change in the homologous series from nonanol to pentanol.² This result corresponds with the qualitative conclusions about the primary influence of the surfactant properties, such as solubility in water, surface activity and diffusion coefficient, on the system behavior.¹ The present paper is focused on theoretical studies of the direction and extent of this influence on the features of the auto-oscillations.

Theoretical Model and System Parameters

A mathematical model has been proposed that considers the hydrodynamic processes accompanying the mass transfer in a semi-infinite liquid volume with a free upper surface and with a small surfactant droplet in the bulk.⁵ Numerical simulations were performed on the basis of a set of nonlinear non-steady-state Navier–Stokes equations, the continuity equation, and the convective diffusion equation taking into account adsorption at the free water surface. According to the symmetry of the system

under consideration, bipolar coordinates were used for the calculations. The chosen numerical scheme gives an opportunity to follow the general regularities of the system behavior, though it allows only the calculation of a single oscillation.

It was demonstrated by our calculations that in agreement with the experimental data, there exists an induction time at the beginning of the dissolution process when the surface tension in the system remains constant.^{1,2} In this time interval the dominating mechanism of the mass transfer is diffusion whereas the contribution of the convection is negligible. After a specific induction time the convective flux becomes of the same order as the diffusion flux in the region near the symmetry axis. This intensifies the solute transport to the surface in the vicinity of the axis. The concentration gradients on the surface and in the bulk near the surface increase rather strongly. As a consequence, instability arises in the system. At this time the surface adsorption increases very quickly and correspondingly the surface tension decreases. The instability develops initially in the vicinity of the symmetry axis where the concentration gradient has a maximum and then propagates rapidly to more distant regions.

The flow velocity varies along the surface nonmonotonically. It is zero on the symmetry axis, increases with the distance to a maximum in the region close to the axis, and decreases in more distant regions. Such velocity distribution leads to local surface expansion in the vicinity of the axis and to surface contraction in distant regions. Initially, the decrease of the surface adsorption produced by the surface expansion is compensated by the solute flux from the bulk to the surface, but later, when the convective motion propagates in distant regions, the convection brings a more dilute solution to the surface near the symmetry axis so that the normal concentration gradient becomes insufficient to maintain the instability. The instability dies and the convective motion disappears gradually. The adsorption value decreases due to surface expansion near the symmetry axis and partial surfactant desorption in distant regions. As a result, the surface tension increases again and the system returns to a stable state.

Here we do not repeat the whole mathematical formulation of the problem presented elsewhere⁵ but we point out only the main features of the mathematical model. A semi-infinite water

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volume, having a flat nondeformable upper surface in contact with a gas phase and a small spherical surfactant droplet under the surface, was chosen as a model system. It was assumed that the droplet surface is motionless and the surfactant concentration near the droplet surface is constant (and equivalent to the surfactant solubility in water). The viscosity of the gas phase and the intrinsic viscosity of the water surface as well as the evaporation of the surfactant into the gas phase were neglected. It was also adopted that diffusion-controlled adsorption kinetics takes place in the system. For the subsequent analysis we need only a dimensionless form of the equations determining the system behavior, that is the Navier–Stokes equations, the continuity equation, and the convective diffusion equation

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + Pr \Delta \mathbf{v} \quad (1)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (2)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \Delta c \quad (3)$$

where \mathbf{v} is the velocity vector, t is time, p is the pressure in the bulk, Pr is the diffusion Prandtl number (sometimes also named Schmidt number), and c is the concentration, and the dimensionless equations for tangential stress balance and mass balance at the free water surface

$$\frac{\partial v_t}{\partial z} = -Ma \nabla_s \sigma \quad (4)$$

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma v_t - N_D \nabla_s \Gamma) - \frac{1}{N_A} \frac{\partial c}{\partial z} = 0 \quad (5)$$

where v_t is the tangential component of the velocity on the free liquid surface, z is the coordinate normal to the liquid surface, ∇_s is the surface gradient, σ is the surface tension, Γ is the Gibbs adsorption, Ma is the Marangoni number, N_D is the ratio of the surface and bulk diffusion coefficients, and N_A is the ratio of the Henry constant and the characteristic length.

In eqs 1–5 velocity, time, pressure, concentration, surface tension, and adsorption are scaled as D/a , a^2/D , $\rho D^2/a^2$, c_0 , $RT\alpha c_0$, and αc_0 , respectively, where $\alpha = d\Gamma/dc|_{c=0}$ is the Henry constant, $a = \sqrt{h^2 - r_0^2}$ is a characteristic length, h is the immersion depth of the droplet, r_0 is the droplet radius, D is the volume diffusion coefficient, R is the gas constant, T is the temperature, ρ is the liquid density, and c_0 is the solubility of the surfactant in water.

Four dimensionless groups arise from the governing equations and boundary conditions written in a dimensionless form: the ratio of the surface and volume diffusion coefficients, $N_D = D_s/D$; the ratio of the Henry constant and the characteristic length $N_A = \alpha/a$; the diffusional Prandtl number $Pr = \mu/\rho D$; and the Marangoni number $Ma = RT\alpha c_0 a/\mu D$, where μ is the dynamic viscosity of the liquid and D_s is the surface diffusion coefficient.

It is difficult to estimate the actual limits of the N_D value as authentic experimental data of surface diffusion coefficients are practically not available. That is why within this study N_D is maintained constant (equal to unity) except for calculations concerning the influence of the surface diffusion coefficient on the system behavior. The other three characteristic numbers are varied as a consequence of variation of the three system parameters, namely, the surfactant volume diffusion coefficient, solubility, and surface activity coefficient (Langmuir constant).

In a recent paper⁵ the calculations were performed in the assumption that the solute concentration near the surface is small. In this case, Henry's adsorption isotherm can be used

$$\Gamma = Kc \quad (6)$$

with the appropriate expression for the surface tension

$$\sigma = \sigma_0 - \Gamma \quad (7)$$

where K is equal to unity within the scaling chosen for Γ and c . For rather large surfactant concentration the Langmuir isotherm eq 6a has been taken

$$\Gamma = \frac{c}{1 + bc} \quad (6a)$$

with the Szyszkowsky–Langmuir equation for the surface tension

$$\sigma = \sigma_0 + \frac{1}{b} \ln(1 - b\Gamma) \quad (7a)$$

where $b = \alpha c_0/\Gamma_m = K_L c_0$, Γ_m is the saturation adsorption and K_L is the Langmuir constant. With account of eqs 6a and 7a, eq 4 takes the form

$$\frac{\partial v_t}{\partial z} = -Ma \frac{d\sigma}{d\Gamma} \frac{d\Gamma}{dc} \nabla_s c = \frac{Ma}{1 + bc} \nabla_s c \quad (8)$$

The constant b is an additional dimensionless parameter of the system. It disappears in the limit of very small concentrations.

The results presented in ref 5 were obtained for the following values of the system parameters: solubility of the surfactant in water $c_0 = 6.7 \times 10^{-6}$ mol/cm³, Henry constant $\alpha = 6.9 \times 10^{-4}$ cm ($\Gamma_m = 5.3 \times 10^{-10}$ mol/cm², $K_L = 1.3 \times 10^6$ cm³/mol), diffusion coefficients in the volume D and in the surface D_s both 5×10^{-6} cm²/s, droplet radius $r_0 = 1$ mm, and capillary immersion depth $h = 1$ cm. The maximum values of the adsorption 2 orders less than the saturation adsorption Γ_m were calculated so that the use of eqs 6 and 7 should be appropriate. Indeed, the verifying calculations by using eqs 6a and 7a instead of eqs 6 and 7 led, practically, to the same results. Only a 10-fold increase of the surfactant solubility led to noticeable deviations in the calculations on the basis of eqs 6 and 7. In the present study the surfactant solubility was varied within many orders so that all results presented here were obtained by using eqs 6a and 7a.

The values of the diffusion coefficient for the surfactants most frequently used varies within limits narrow enough.⁶ That is why the influence of the diffusion coefficient was studied here by choosing three values 2×10^{-6} , 5×10^{-6} , and 8×10^{-6} cm²/s. Usually, the parameter of the Langmuir isotherm Γ_m changes also insignificantly.⁶ So, a constant value of $\Gamma_m = 5.3 \times 10^{-10}$ mol/cm² was used, as in the previous calculations.⁵ The Langmuir constant K_L and the surfactant solubility c_0 can change in broader limits. In the present calculations K_L was varied from 1.3×10^4 to 1.3×10^{10} cm³/mol and c_0 from 6.7×10^{-10} to 6.7×10^4 mol/cm³. The values of the droplet immersion depth and the droplet radius remained the same as in ref 5: $h = 1$ cm, $r_0 = 1$ mm.

Results and Discussion

Effect of Solubility. The solubility of the surfactant in water is included only in one of the characteristic dimensionless groups, namely in the Marangoni number that increases with

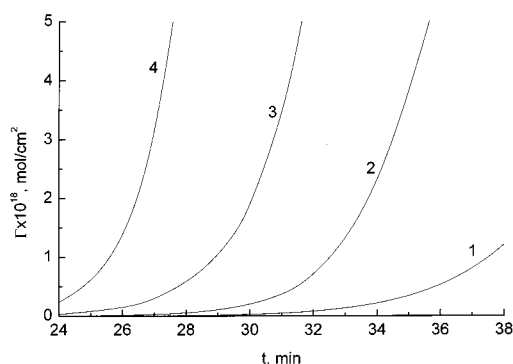


Figure 1. Surface adsorption vs time during the induction time at a distance of $r = 0.5$ cm from the symmetry axis: (1) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $K_L = 1.3 \times 10^6$ cm³/mol; (2) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $K_L = 1.3 \times 10^8$ cm³/mol; (3) $c_0 = 6.7 \times 10^{-4}$ mol/cm³, $K_L = 1.3 \times 10^6$ cm³/mol; (4) $c_0 = 6.7 \times 10^{-4}$ mol/cm³, $K_L = 1.3 \times 10^8$ cm³/mol.

TABLE 1: Dependence of the Calculated Characteristic Parameters of the System on the Surfactant Solubility

solubility of surfactant in water, mol/cm ³	induction time, s	oscillation amplitude, mN/m ($r = 1$ cm)	max. surf. velocity, cm/s ($r = 1$ cm)
$K_L = 1.3 \cdot 10^6$ cm ³ /mol			
6.7×10^{-10}	8400	0.000 86	0.03
6.7×10^{-8}	4406	0.021	0.26
6.7×10^{-6}	2772	0.25	1.3
6.7×10^{-4}	1962	3.1	6.5
$K_L = 1.3 \cdot 10^8$ cm ³ /mol			
6.7×10^{-8}	3518	0.024	0.26
6.7×10^{-6}	2398	0.26	1.3

c_0 and also in the dimensionless parameter b of the Szyszkowsky–Langmuir equation. The value bc in eq 8 approaches the order of unity only in the last stage of the instability development and is much smaller than unity during the foregoing diffusion stage. Therefore, it does not influence the system behavior during the stable initial stage and at the beginning of the instability development; in particular, it does not influence the value of the induction time.

The diffusion equation in the dimensionless form (eq 3) does not contain the dependency on c_0 . The convective term is small in the initial stage and the concentration field formed only due to diffusion should be independent of the solubility. According to eq 8, the same dimensionless concentration gradient causes larger values of the surface velocity at larger Marangoni numbers. This motion extends to the bulk due to viscous stress (eq 1) and the bulk velocities are also larger at larger c_0 . That means, in the case of larger solubility of the surfactant, the convective flux increases more quickly and the instability should arise at smaller values of the dimensionless surface concentration and, consequently, in shorter times. The induction time should decrease correspondingly. The numerical simulation confirms this conclusion (Table 1).

At the beginning of the droplet dissolution the dimensionless concentration distribution as well as the dimensionless surface adsorption is independent of the solubility of the surfactant until the convection is still weak and the convective mass transfer is negligible in comparison with the diffusion mass transfer. On the other hand, the dimensional concentration and adsorption are scaled as c_0 and αc_0 , respectively, so that they are proportional to the solubility and therefore, larger for the same time moment when the solubility is larger (Figure 1). The velocity of the liquid motion (dimensionless as well as dimensional) is also larger when the solubility is larger (Figure 2), as discussed above. Consequently, the convective fluxes

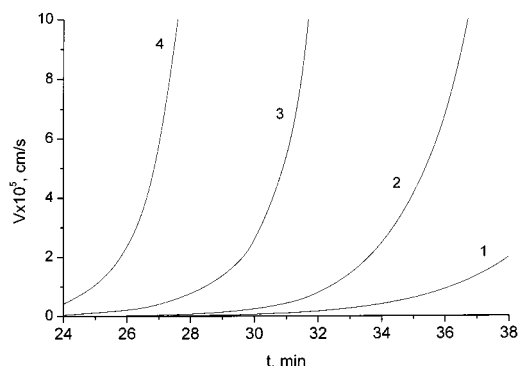


Figure 2. Surface velocity of the liquid vs time during the induction time at a distance of $r = 0.5$ cm from the symmetry axis: (1) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $K_L = 1.3 \times 10^6$ cm³/mol; (2) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $K_L = 1.3 \times 10^8$ cm³/mol; (3) $c_0 = 6.7 \times 10^{-4}$ mol/cm³, $K_L = 1.3 \times 10^6$ cm³/mol; (4) $c_0 = 6.7 \times 10^{-4}$ mol/cm³, $K_L = 1.3 \times 10^8$ cm³/mol.

increase more rapidly, and the convection begins to influence the concentration field earlier. The dimensionless concentration fields commence to differ; particularly, the dimensionless concentration values in the region close to the surface as well as the dimensionless adsorption values begin to be larger if the solubility is larger.

According to the larger values of the velocity and the dimensionless concentration gradients in systems that contain a more soluble surfactant, the convective flux reaches the same order as the diffusion flux in a shorter time. That means, the instability arises earlier. It should be emphasized, however, that at the same time the dimensionless concentrations are larger in the convective stage for the more soluble surfactants but, according to the decrease of the induction time, the dimensionless concentrations are lower at the moment of the beginning of the instability.

An example of the change in the system behavior due to change of the solubility is given in Figure 3. The exact values of the parameters characterizing the system behavior are compiled in Table 1. It is important that in the system with 2 order larger solubility the instability arises at dimensionless surface concentrations approximately 1 order smaller. For example, the maximum dimensionless concentrations for systems 1 and 2, presented in Figure 3, are 2.19×10^{-3} and 3.96×10^{-4} , respectively. However taking into account the concentration scale, the real concentration values are larger for larger solubilities; i.e., in this case the change in the surface tension (oscillation amplitude) is also larger (Figure 3a, Table 1).

As the surface velocity during the instability development is larger when the surfactant solubility is larger (Figure 3b), the surfactant spreads over the surface more quickly, and consequently, the surface tension decreases more rapidly (Figure 3a). On the other hand the larger surface velocity causes larger surface extension and therefore the instability fades in more short time (Figure 3a). So it could be expected that the oscillation period decreases when the solubility increases.

When the solubility is 6.7×10^{-10} mol/cm³, the calculated oscillation amplitude decreases to less than 0.001 mN/m at the distance to the symmetry axis $r = 1$ cm. So it can be concluded that at small enough solubility, the oscillation practically cannot be revealed in the experimental observation because of a very small oscillation amplitude and a very large oscillation period.

Effect of Surface Activity. The surface activity of the solute can be characterized by the parameter $\alpha = \Gamma_m K_L$. In our study it was changed by the change of the Langmuir constant. The surface activity influences two of the dimensionless groups: the

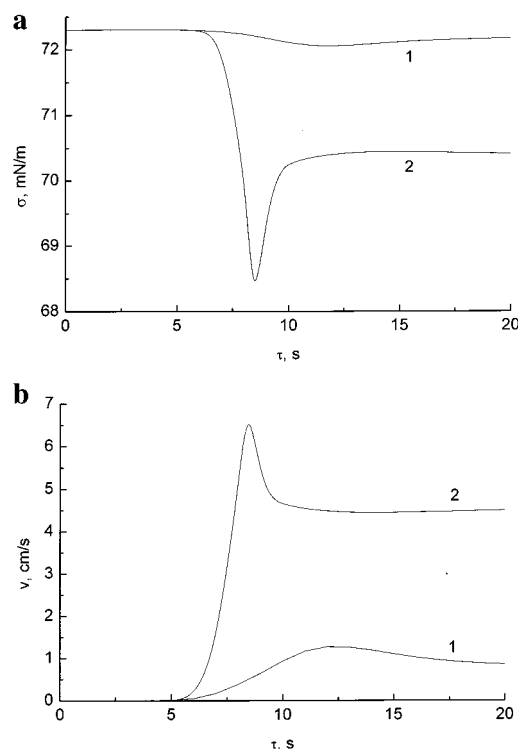


Figure 3. (a) Surface tension vs time after the onset of instability at a distance of $r = 1$ cm from the symmetry axis for $K_L = 1.3 \times 10^6$ cm³/mol ($\tau = t - t_0$, t is the time after onset of the droplet dissolution): (1) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $t_0 = 46$ min 5 s; (2) $c_0 = 6.7 \times 10^4$ mol/cm³, $t_0 = 32$ min 35 s. (b) Surface velocity vs time after the onset of instability at a distance of $r = 1$ cm from the symmetry axis for $K_L = 1.3 \times 10^6$ cm³/mol ($t = t - t_0$, t is the time after onset of the droplet dissolution): (1) $c_0 = 6.7 \times 10^{-6}$ mol/cm³, $t_0 = 46$ min 5 s; (2) $c_0 = 6.7 \times 10^4$ mol/cm³, $t_0 = 32$ min 35 s.

Marangoni number (Ma) and the ratio of the Henry constant and the characteristic length (N_A). The Langmuir constant is also included in the parameter b , the effect of which on the system behavior has already been discussed. The increase in the surface activity leads to an increase of the Marangoni number, and from this point of view, its influence is similar to the influence of the surfactant solubility. On the other hand, according to eq 5, an increase of the surface activity leads to a decrease of the dimensionless normal diffusion flux to the surface at a constant normal concentration gradient and, consequently, to a decrease of the surface concentration and the surface concentration gradient. During the induction time when convection is negligible, both effects have the same magnitude but an opposite direction and should eliminate each other. In this case, the system behavior is determined by the effect of the surfactant's surface activity on the value of the normal concentration gradient.

The performed calculations show that the surface activity of the surfactant does practically not influence the bulk concentrations during the diffusion stage. At the same time, as the dimensionless flux to the surface decreases if the surface activity increases, also the dimensionless values of the adsorption and consequently the concentration near the surface decrease; i.e., the dimensionless normal concentration gradient increases with increasing surface activity, as also is seen in Figure 4.

This conclusion results also from the following argument. If the surface activity increases, a larger amount of the solute molecules accumulates on the surface (the dimensional adsorption is larger) and creates near the surface a lack of the dissolved surfactant molecules. Thus, the positive influence of the

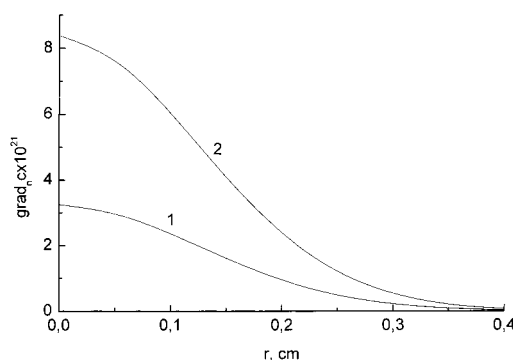


Figure 4. Dimensionless normal concentration gradient vs distance to the symmetry axis at 10 min after the beginning of the droplet dissolution for $c_0 = 6.7 \times 10^{-6}$ mol/cm³: (1) $K_L = 1.3 \times 10^6$ cm³/mol; (2) $K_L = 1.3 \times 10^8$ cm³/mol.

TABLE 2: Dependence of the Calculated Characteristic Parameters of the System on the Surfactant Activity

Langmuir const, cm ³ /mol	induction time, s	oscillation amplitude, mN/m ($r = 1$ cm)	max. surf. velocity, cm/s ($r = 1$ cm)
$c_0 = 6.7 \times 10^{-8}$ mol/cm ³			
1.3×10^{10}	3483	0.024	0.26
1.3×10^8	3518	0.024	0.26
1.3×10^6	4406	0.021	0.26
1.3×10^4	8440	0.002	0.04

surfactant activity is larger than the negative one, and at the same time, the velocities as well as the dimensional adsorption values in a system with larger surface activity of the surfactant are larger (Figures 1 and 2). However, the destabilizing effect of the surface activity is obviously smaller than the effect of the surfactant solubility (Figures 1 and 2).

A variation of the Langmuir constant in rather wide limits (1.3×10^{10} to 1.3×10^6 cm³/mol) does nearly not influence the oscillation amplitude and the maximum surface velocity (Table 2). Only if the Langmuir constant decreases to 1.3×10^4 cm³/mol does the normal concentration gradient near the surface strongly decrease, leading to a significant deceleration of the mass transfer to the surface. Therefore, the convection in the system grows very slowly and the induction time increases much more considerably than within the limits of 1.3×10^{10} to 1.3×10^6 cm³/mol. For low Langmuir constants, e.g., 1.3×10^4 cm³/mol, the oscillation amplitude decreases also significantly (Table 2).

Effect of the Diffusion Coefficient. Apart from the ratio of the surface and volume diffusion coefficients, the volume diffusion coefficient is included in the Marangoni number and in the diffusion Prandtl number. The influence of a change of the Prandtl number on the system stability is not obvious. To clarify this question, the simulation was performed for two systems that differ only in the Prandtl number while the other dimensionless numbers remain constant. The main characteristics of the systems are presented in Table 3 (simulations 2 and 3). It is seen that the change in the induction period as well as in the oscillation amplitude are rather small. The influence of the diffusion coefficient by the Prandtl number is not essential in the chosen interval of the diffusion coefficient variation.

An increase of the volume diffusion coefficient leads to a decrease of the Marangoni number with the consequence that the system becomes more stable and the dimensionless induction time increases. However, the dimensional induction period decreases with increasing diffusion coefficient as far as the time is scaled by a^2/D . The oscillation amplitude and maximum

TABLE 3: Influence of the Diffusion Coefficients on the System Behavior ($K_L = 1.3 \times 10^4 \text{ cm}^3/\text{mol}$, $c_0 = 6.7 \times 10^{-6} \text{ mol/cm}^3$)

simulation	vol diffusion coeff, cm^2/s	diffusion Prandtl no.	ratio of diffusion coeffs	induction time, s	oscillation amplitude, mN/m ($r = 1 \text{ cm}$)	max. velocity, cm/s ($r = 1 \text{ cm}$)
1	8×10^{-6}	1.25×10^3	1	1776	1.31	7.1
2	5×10^{-6}	2×10^3	1	2723	1.29	6.2
3 ^a	5×10^{-6}	1×10^3	1	2727	1.24	4.8
4	2×10^{-6}	5×10^3	1	6299	1.09	4.6
5	2×10^{-6}	5×10^3	5	6299	1.09	4.6
6	2×10^{-6}	5×10^3	1000	6316	1.08	4.6

^a In simulation 3, the value of the Prandtl number is taken to be two times less than in simulation 2 by a formal change of the solvent density.

TABLE 4: Comparison of Theoretical and Experimental Parameters of the Oscillations of Surface Tension for the Droplet Radius $r_0 = 1 \text{ mm}$

surfactant	density, kg/m^3	diffusion coeff, $10^{-10} \text{ m}^2/\text{s}$	solubility in water, mol/m^3	Langmuir const, m^3/mol	droplet immersion depth, mm	induction time, s	
						exp	calc
diethyl phthalate	1118	5.72	6.7	1.3	6.2	720	846
octanol	827	6.67	3.4	3.23	5.65	460	587
heptanol	822	7.18	14	0.62	10.1	278	1940
hexanol	819	7.81	58	0.23	9.25	66	1383

surface velocity increase if the diffusion coefficient increases, but their change is rather small within the chosen interval of the diffusion coefficient variation (Table 3).

The simulation shows that also the ratio of the surface and volume diffusion coefficients (i.e., the surface diffusion coefficient) does nearly not affect the system behavior. Even a unlikely high value of $N_D = 1000$ leads only to a small change in the induction time and the oscillation amplitude.

Comparison with Experiments. The simulation concerns a model system that deviates from the real systems because of its infinite dimensions. So it is very important to understand what is the correlation between the calculated and the real characteristics of the system.

It has been shown⁵ that during the induction period, surfactant is present mainly in the vicinity of the symmetry axis and its concentration in distant regions is negligible. Therefore, the value of the adsorption as well as the concentration near the surface in the vicinity of the symmetry axis cannot be considerably affected by the extent of the system, especially by small droplet immersion depths. Therefore, the values of the induction time calculated on the basis of the proposed model system should have only small differences from those observed in the experiments.

Recently auto-oscillations of the surface tension have been studied systematically for diethyl phthalate and aliphatic alcohols.^{1,2} It has been experimentally established that induction time and oscillation period decrease in the homologous series of the alcohols from nonanol to pentanol. The solubility of the substances in water increases in this series whereas their surface activity decreases. According to the above theoretical conclusions, an increase in the solubility should lead to a decrease in the induction time and oscillation period in this series. At the same time they should increase with a decrease of the surface activity. However, it is important to note that for these substances the product of solubility and surface activity is nearly constant, i.e., the surface activity decreases to the same degree as the solubility increases. As mentioned above, the effect of the solubility on the system behavior is stronger than the effect of the surface activity. Thus, in the homologous alcohol series the decrease of induction time and oscillation period from nonanol to pentanol is in line with the theoretical conclusions presented here. For a quantitative comparison of the theoretical and experimental results, the simulations have been performed with system parameters corresponding to the experimental conditions (Table 4).

The calculated values of the induction time for diethyl phthalate and octanol are in good agreement with the experiments. Small differences may be caused by the fact that the experimental measurements were started at once after the droplet formation, but it takes 2–3 min to form the droplet and dissolution takes place already during this time. Besides, the droplet diameter was not strictly controlled in the experimental observations but its increase leads to a decrease of the induction time, especially at a small droplet immersion depth. For example, the induction time calculated for an octanol droplet with a radius of 1.5 mm is 460 s; i.e., it is equal to the experimental induction time. The last circumstance shows also the importance of the control of the droplet dimensions.

The induction times calculated for heptanol and hexanol are much larger than that observed in the experiments. That confirms the assumption that for the theoretical considerations of these substances also the buoyancy force should be taken into account because of their small density and quite high solubility in water.² It was shown in ref 2 that the density difference of the saturated octanol solution in water and pure water is about $9 \times 10^{-5} \text{ g/cm}^3$, whereas for the saturated pentanol solution this difference is about $4 \times 10^{-3} \text{ g/cm}^3$. Thus, in the system with a pentanol droplet the buoyancy force is 2 orders larger than in the system with an octanol droplet and may affect significantly the system behavior.

Obviously, the oscillation amplitude depends rather strongly on the system extent. In the accepted model the surfactant spreads over an unlimited area so that the simulations should give reduced amplitude values. Indeed, the oscillation amplitudes calculated for octanol and diethyl phthalate are approximately 1 order less than those experimentally observed. The theory should give more correct approximations to the experimental results for the case, when the measuring distance is much less than the diameter of the used measuring cell. So far, experimental data are not available for such conditions.

Conclusions

The mathematical simulation performed for the auto-oscillations of the surface tension in systems containing a surfactant droplet allows a better understanding of the influence of the surfactant properties on the system behavior. An increase in the solubility of the surfactant, the Langmuir constant, and the volume diffusion coefficient leads to a decrease in the induction time and the oscillation period. The surface diffusion coefficient

does not noticeably influence the system behavior. The oscillation amplitude and the maximum surface velocity depend mainly on the solubility of the surfactant in water. They increase with increasing solubility.

A comparison of the results of the simulations with the experimental data shows that the proposed model provides good agreement with the experimental values of the induction time for substances the saturated solutions of which have only small differences in density to water. For surfactants having a density more different from the water density and solubility sufficiently large, the buoyancy force should be taken into account by theoretical consideration. Because of the infinite extension of the surface in the proposed model the calculated values of the oscillation amplitude are about of 1 order less than those obtained in the experiments.

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