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Surface tension reduction in air-water systems containing nonionic surfactant – comparison of mass transfer limited models

Introduction

Surface tension reduction in systems containing surfactants occurs as a result of enhancement in surfactant surface concentration Γ . This enhancement occurs with finite rate, which depends on:

- the surfactant transport from the bulk solution to the subsurface region,
- the rate of surfactant adsorption at the interface,
- possible changes of interfacial surface.

Although the process is widely discussed in literature, it is commonly assumed that the interfacial area is constant and the process can be divided into two steps [Sosnowski, 2006]:

1. diffusional transport of surfactant from the bulk phase to subsurface region close to the interface,
2. adsorption from subsurface region to the interface (this stage is described by kinetic equation, typically by Langmuir equation).

What is also commonly assumed, is the fact that the second step is infinitely fast as compared with transport step. This allows to simplify the description of discussed phenomenon as being controlled by diffusion only. In this way, it is stated that surface tension can be reduced as fast as the rate of surfactant diffusional transport from the solution to the interface it enables.

Basic drawback of diffusion-limited model is not taking into account hydrodynamic effects. In systems where convection appears the assumptions of diffusion-limited model are not fulfilled. This happens in industrial systems as well as in several experimental setups (such as for example during the measurement of dynamic surface tension with the aid of maximum bubble pressure technique). In bubble tensiometers, employing this measurement technique, bubbles appear at the tip of capillary and detach from it with high frequency mixing intensively the solution, which is currently tested.

Another problem, which is not addressed by diffusion-limited model, is the influence of changes of interfacial surface on the obtained experimentally values of dynamic surface tension. Such situation occurs at the time of bubble formation in surfactant solutions for example during measurements with the use of maximum bubble pressure method.

In this study, a proposition of non-diffusional description of surface tension reduction in dynamic conditions in systems containing nonionic surfactant Tween80 is presented. Proposed macroscopic model exploits the conception of mass transfer coefficient in liquid phase. In addition, changes in interfacial surface (surface of a growing bubble in maximum bubble pressure method) are taken into account in the model. Obtained results were compared with asymptotic solution of Ward and Tordai equation and experimental results.

Materials and Methods

Dynamic surface activity of the Tween80 (*Sigma-Aldrich*) solutions was studied with the aid of bubble tensiometer BP2 (*Krüüss*, Germany) equipped with a hydrophobised glass capillary (inner diameter of 0.241 mm) and a special testing cell which holds about 5–6 ml of liquid. Some preliminary research was done with Tween80 solutions of various concentrations (results not published yet) and it was concluded that smaller volume of testing cell had no significant effect on obtained dynamic surface tension results. The BP2 experimental device enabled measurements of surface tension changes during the formation of a fresh air-water interface which is represented by growing air bubble in the tested solution. The time range

of surface formation extended from 10 ms to 20–30 s in every single experiment. All experiments were run in triplicate in constant temperature of 25°C assured by the external thermostat.

Polysorbate 80 (POE (20) sorbitan monooleate, Tween 80, molecular weight 1310 g/mol) is a non-ionic surfactant with excellent emulsifying and wetting properties. Nonionic surfactants are widely used as model systems for solubilization of drugs and as model adsorbents for investigation of the interfacial phenomena [Bąk, 2013]. Dixit et al. [2012] used Tween80 as model surfactant in studies with maximum bubble pressure method.

Surfactant solutions studied in this work were in concentrations of 0.01, 0.1 and 1.0 mg/ml. The lowest concentration is below CMC, which for Tween80 is equal 0.016 mg/ml [Bąk, 2013], in other two cases the concentration is higher than CMC.

As already mentioned in Introduction section, in this study, model calculations were made for diffusion limited mass transport from the bulk solution to the gas/liquid interface and mass transport described by macroscopic model.

The main theoretical method for analyzing diffusion-controlled mass transport to freshly formed interfaces is the Ward and Tordai equation [1946] which describes the time dependence of surface concentration $\Gamma(t)$ [mol/m²]:

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} - 2 \sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} c_s d(\sqrt{t-\tau}) \quad (1)$$

where: c_0 – the bulk surfactant concentration [mol/m³], D – the surfactant diffusion coefficient [m²/s], c_s – the concentration in the subsurface [mol/m³], t – the surface lifetime [s] and τ – a dummy variable of integration. Owing to the convolution integral in the Eq. (1) to account for back diffusion, this equation cannot be solved analytically and as a consequence experimental results cannot be easily fitted to this equation. That is why asymptotic solutions are often applied, which for $t \rightarrow 0$ is called short time approximation [Eastoe and Dalton, 2000]:

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} \quad (2)$$

To link surface concentration with surface tension, Frumkin equation of state was used:

$$\gamma(t) = \gamma_0 + RT\Gamma_m \ln \left(1 - \frac{\Gamma(t)}{\Gamma_m} \right) \quad (3)$$

where: $\gamma(t)$ – the dynamic surface tension [N/m], γ_0 – the surface tension of the solvent [N/m], R – the gas law constant [J/(mol K)], T – the absolute temperature [K], Γ_m – the maximum surface concentration of surfactant [mol/m²].

Calculations for macroscopic model was performed with the use of equation describing convection mass transfer of surfactant in liquid phase:

$$\frac{dc_s}{dt} = \frac{k_c}{\delta} c_0 - c_s \left(\frac{k_c}{\delta} - \frac{1}{A} \frac{dA}{dt} \right) \quad (4)$$

where: c_s – surfactant concentration in the subsurface [mol/m³], k_c – mass transfer coefficient [m/s], δ – subsurface thickness [m], c_0 – the bulk surfactant concentration [mol/m³], A – surface of a growing bubble [m²] which is changing with time. Mass transfer coefficient was calculated from the correlation for moving in liquid gas bubbles of diameter $d < 0.1$ cm [Perry, 1999].

An assumption was made that the adsorption at the interface is instan-

taneous and that the equilibrium is according to *Langmuir* isotherm:

$$\frac{\Gamma(t)}{\Gamma_m} = \frac{Kc_s}{1 + Kc_s} \quad (5)$$

where: $\Gamma(t)$, Γ_m and c_s – as described above [mol/m^2], K – adsorption constant [m^3/mol]. To link surface concentration with surface tension, *Frumkin* equation of state was used – Eq. (3).

All the physicochemical data, necessary for model calculations, were taken from works by *Bąk* [2013] and *Amani et al.* [2011].

Results and Discussion

Fig. 1. presents experimental results compared to calculations made according to asymptotic solution of *Ward and Tordai* equation (Eq. (2)).

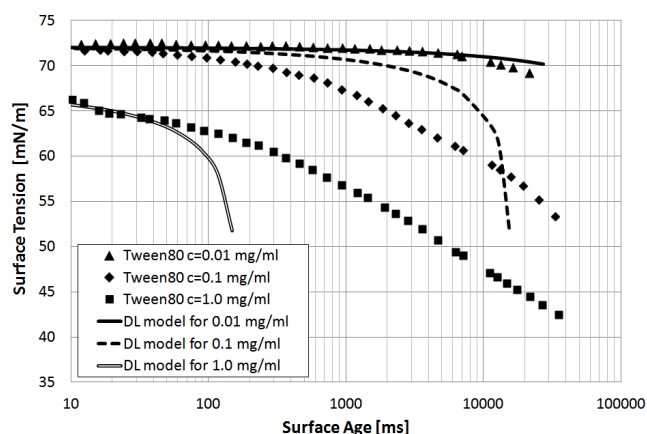


Fig. 1. Relationship between surface tension and surface age for *Tween80* solutions in 25°C – comparison of experimental results (average for $n=3$, SD not shown for sake of clarity) and short time approximation of diffusion-limited model

As one may notice, satisfactory fitting of model predictions to experimental results is observed for *Tween80* solutions of 0.01 mg/ml in the whole range of surface age values. For other two concentrations, satisfactory fitting occurs only for surface age up to ca. 100 ms for 0.1 mg/ml solution and for surface age up to ca. 60 ms for 1.0 mg/ml solution. Besides, for 1.0 mg/ml solution the diffusion-limited model cannot give surface tension values for surface age higher than 150 ms, which is a serious limitation of the model. However, obtained results may suggest that for the shortest surface ages diffusion-limited model describes properly, at least to certain extent, observed phenomena.

Fig. 2 presents experimental results compared to calculations made according to proposed in this work macroscopic model (Eqs (3)-(5)).

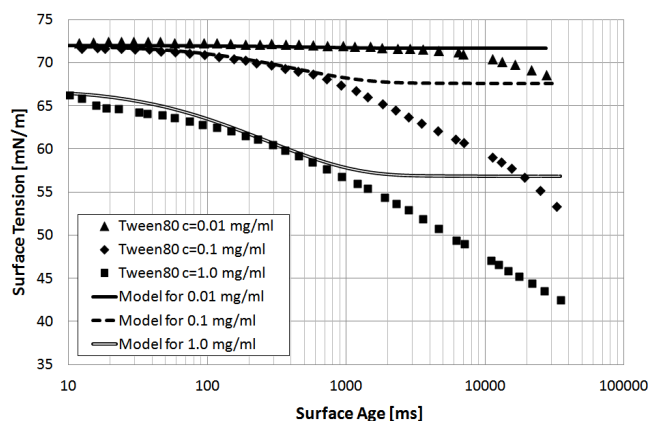


Fig. 2. Relationship between surface tension and surface age for *Tween80* solutions in 25°C – comparison of experimental results (average for $n=3$, SD not shown for sake of clarity) and macroscopic model

Again it can be seen, that the fitting depends on the concentration of surfactant solution. Comparing to diffusion-limited model, for 0.1 and 1.0 mg/ml solutions, macroscopic model gives results closer to experimental points for broader range of surface age – up to ca. 1000 ms for both concentrations. Apart from that, no limitations were observed in terms of surface tension calculations for the 1.0 mg/ml solution.

Macroscopic model somehow predicts reaching equilibrium in surface tension, however much faster and for higher surface tension values, than it can be observed experimentally. The discrepancy between model and experimental curves may be explained by the presence of micelles in tested solutions with concentrations of 0.1 and 1.0 mg/ml (concentrations > CMC). Neither of discussed in this work models takes into account the behaviour of micellar solutions. The importance of micellar structures, present in subsurface region, for adsorption dynamics has been demonstrated for example during research of pulmonary surfactant system in alveoli, where such surfactant reservoirs exist close to air/water interface and strongly participate in surface tension reduction in dynamic conditions of breathing cycle [Parra and Perez-Gil, 2015].

Conclusions

In this work, a concept of non-diffusional description of surface tension reduction in dynamic conditions in systems containing non-ionic surfactant *Tween80* is presented. Proposed macroscopic model exploits the conception of mass transfer coefficient in liquid phase. In addition, changes in interfacial surface (surface of a growing bubble in *Maximum Bubble Pressure method*) are taken into account in the model. Obtained results were compared with asymptotic solution of *Ward and Tordai* equation and experimental results. For model considerations, the case of mass transfer limited process with instantaneous adsorption was assumed.

For both models, satisfactory fitting of theoretical calculations to experimental results is achieved only for limited range of surface age. On the one hand, the presence of micells in solutions above CMC may be responsible for noticed deviations.

It is also probable that the discussed process is not fully mass transfer limited and that the rate of adsorption has finite values and has to be included in model considerations. However, presented in this work preliminary results of application of macroscopic conception are quite promising. Development of the model will be the topic of future work.

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