The influence of surfactants on the hydrodynamical interaction in emulsion systems

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Abstract: A system of two emulsion droplets is examined as they mutually approach at small separations. The mass transfer of diffusion-controlled surfactants towards the interface is regarded. The cases of a surfactant soluble in only one of the phases as well as in all of them are analysed. Quantitative estimates are presented for the tangential mobility of the droplet/thin layer interface. Different regimes of mass transfer and flow in the drops and a creeping flow and various regimes of mass transfer in the thin layer between them are considered.

Key words: Hydrodynamical interaction, emulsion systems, surfactants.

The hydrodynamical interaction of emulsion droplets at small separations is one of the major factors which determine the properties and the stability of emulsion systems. It is a well known fact that the surfactants strongly influence the tangential mobility of the liquid interfaces and therefore the hydrodynamical behaviour of the fluid particles [1]. In other papers, we have proposed an approach for a quantitative estimation of the basic magnitudes which characterize the interaction in such systems, pure of surfactants—the tangential mobility of the interfaces, the drag force, the energy dissipated in the respective phases [2] and also a comparative analysis of the various terms in the differential equations of motion for an arbitrary mobility of the interfaces [3].

The present study is an extension of this treatment for the practically important case of emulsion systems in the presence of surfactants.

Previous experimental investigations show that if the surfactant is soluble mainly in the layer, it strongly affects the tangential mobility of the interfaces (see for example [4]). The surfactant soluble in the droplets seems to have no significant influence on the drainage of the layer [5]. So far, however, only general qualitative relationships have been established, which permit such a behaviour to be expected [6], and only a few special cases are studied in detail [7–9].

Here we treat different regimes of mass transfer and flow in droplets with a creeping motion and various regimes of mass transfer in the thin layer between them. The point is to obtain quantitative estimates for the tangential mobility of the interfaces. These estimations make things clearer, we believe, as far as the hydrodynamical interaction in emulsion systems with surfactants is concerned.

Formulation of the problem

Two identical droplets with radii $R$ of a liquid with viscosity $\mu$ mutually approach along their common axis. The quantities marked with an asterisk (*) refer to the droplets, and those without an asterisk refer to the layer between them.

The following boundary conditions at the droplet/layer interface are of major interest:

$$ v_t = v_t^* $$

$$ P_{nt} = P_{nt}^* + \nabla \cdot \sigma ; \quad \nabla \cdot \sigma = \frac{\partial \sigma}{\partial t} $$

$$ \nabla \cdot (\Gamma \vec{v}_t) - D^* \nabla^2 \Gamma = - D \frac{\partial c}{\partial n} + D^* \frac{\partial c^*}{\partial n} $$

Here $v_t, v_t^*$ are the tangential velocities; $P_{nt}, P_{nt}^*$ the tangential stress components in a local coordinate...
system \((n, \tau)\), connected with the boundary; \(\sigma\) is the interface tension; \(c, c^*\) are the concentrations of surfactants in the bulk phases. Equation (3) shows that the stationary case with a diffusion controlled bulk flux is dealt with. \(\Gamma\) is the surface concentration of the surfactant; \(D, D^*\) are the bulk diffusion coefficients; \(D_s\) is the surface diffusion coefficient.

Under stationary conditions, the distribution of the surfactants in the bulk of the phases is controlled by the diffusion equations [1]:

\[
v_r \frac{\partial c}{\partial r} + v_z \frac{\partial c}{\partial z} = D \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} \right)
\]

(4)

\[
v_r^* \frac{\partial c^*}{\partial r} + v_z^* \frac{\partial c^*}{\partial z} = D^* \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c^*}{\partial r} \right) + \frac{\partial^2 c^*}{\partial z^2} \right).
\]

(5)

Because of the axial symmetry of the model, a cylindrical coordinate system \((r, \varphi, z)\) is convenient.

The following effective quantities are introduced: \(H_f, R_f\) = effective dimensions of the thin liquid layers; \(H^*, R^*\) = dimensions of the effective zones in the droplets; \(U, U^*\) = characteristic velocities in the layer and at the layer/droplet interface (Fig. 1); \(\Delta c_r, \Delta c_z\) = characteristic changes in the surfactant concentration along the \(r, z\)-axes for the thin layer; \(\Delta c_r^*, \Delta c_z^*\) = characteristic changes in the surfactant concentration along the \(r, z\)-axes for the droplets; \(\delta, \delta^*\) = normal dimensions of the effective zones within which the main concentration changes in the layer and in the droplets appear.

The aim is to determine how the tangential mobility of the interface \(U^*\) is connected with the rest of the effective magnitudes as well as with the system's parameters.

**Surfactant soluble in the thin layer**

As was already mentioned in [2], \(R^* \sim R_f\). Then, for \(R_f < R\), the estimates have been obtained:

\[
v_r = v_r^* \sim U^*
\]

(6a)

\[
P_m = \mu \frac{U - U^*}{H_f}
\]

(6b)

\[
P_{m*} = \mu^* \frac{U^*}{H^*}
\]

(6c)

The use of (6), the effective quantities, already introduced and the interface tangential force balance (2) lead to:

\[
\mu \frac{U - U^*}{H_f} \sim \mu^* \frac{U^*}{H^*} + \frac{\partial \sigma}{\partial c} \frac{\Delta c_r}{R_f}
\]

(7)

where

\[
\Delta_r \sigma \sim \frac{\partial \sigma}{\partial r} = \frac{\partial \sigma}{\partial c} \frac{\partial c}{\partial r} \sim \frac{\partial \sigma}{\partial c} \frac{\Delta c_r}{R_f}.
\]

(8)

The separate terms of the surfactant mass balance may be treated in a similar manner:

\[
\frac{\Gamma U^*}{R_f} - D^s \left( \frac{\partial c^*}{\partial c} \right) \frac{\partial c^*}{\partial c} \sim \Delta c^*_z
\]

(9)

Here

\[
\nabla^2 \Gamma \sim \frac{\partial c^*}{\partial c} \sim \frac{\partial c^*}{\partial c} \frac{\Delta c^*_z}{R_f}.
\]

(10)

The estimation (8) indicates that the sole reason for not having constant \(\sigma\)-values is the change of the concentration in the layer immediately adjacent to the surface (in the subsurface layer) due to the drainage of