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Publication Date
1965-12-01

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Berkeley, California

AEC Contract No. W-7405-eng-48

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December, 1965

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Abstract

A unified treatment of Levich's three mechanisms of retardation of drop motion by a surface-active agent is presented.

Levich[1,2] has explained how the motion of a falling drop can be retarded by differences of surface tension between the front and the rear of the drop caused by differences in the surface concentration of a surface-active agent. The motion of the surface of the drop tends to increase the surface concentration at the rear of the drop. This effect is counterbalanced by surface diffusion and by exchange of surface-active agent between the interface and the bulk solution. This exchange involves an adsorption at the front of the drop and a desorption at the rear of the drop, and it may be opposed by slow diffusion into the bulk of the solution or by slow adsorption-desorption kinetics.

These three factors - surface diffusion, slow diffusion in the bulk, and slow adsorption kinetics - are treated separately by Levich. It is found here that the three effects can be treated simultaneously with no additional assumptions. The resulting retardation coefficient then reflects the relative importance of these three effects.

where the prime denotes differentiation with respect to r. Substitution into the equations of motion (4) gives

$$
\begin{aligned}
\frac{\partial p}{\partial r} - \rho g \cos\theta &= -\mu U \cos\theta \ [F'' + 2F'/r + 4(G - F)/r^2] \\
&= -\mu U \cos\theta \ (F'' + 4F'/r), \\
\text{and} \quad \frac{\partial p}{\partial \theta} + \rho g r \sin\theta &= \mu r U \sin\theta \ [G'' + 2G'/r - 2(G - F)/r^2] \\
&= \mu r U \sin\theta \ (\tfrac{1}{2} r F''' + 3F'' + 2F'/r) .
\end{aligned}
\quad (7)
$$

By differentiating the first of equations (7) with respect to θ and the second equation with respect to r and subtracting the resulting two equations we obtain

$$
\frac{1}{2} r^4 \frac{d^4 F}{dr^4} + 4r^3 \frac{d^3 F}{dr^3} + 4r^2 \frac{d^2 F}{dr^2} - 4r \frac{dF}{dr} = 0 .
\quad (8)
$$

This is a form of Euler's equation and has the general solution

$$
F = A_1 + A_2 r^2 + A_3 r^{-1} + A_4 r^{-3}.
\quad (9)
$$

From the general solution for F and the continuity equation (6), one can construct the velocity distribution outside the drop

$$
\begin{aligned}
v_r &= -\left[U - (\tfrac{3}{2} U - v_0) \frac{R}{r} + (\tfrac{1}{2} U - v_0) \frac{R^3}{r^3} \right] \cos\theta , \\
v_\theta &= \left[U - (\tfrac{3}{4} U - \tfrac{1}{2} v_0) \frac{R}{r} - (\tfrac{1}{4} U - \tfrac{1}{2} v_0) \frac{R^3}{r^3} \right] \sin\theta ,
\end{aligned}
\quad (10)
$$

so as to satisfy the conditions (1) at infinity and the condition (2) on the surface of the drop. Equations (7) can then be integrated to yield the pressure distribution.

$$
p - p_0 = \rho g r \cos\theta + \mu \cos\theta \ (\tfrac{3}{2} U - v_0) \frac{R}{r^2} .
\quad (11)
$$

In a similar fashion one can construct the velocity distribution inside the drop

$$v_r' = v_o \left(1 - r^2/R^2\right) \cos\theta \; ,$$

$$v_\theta' = v_o \left(-1 + 2r^2/R^2\right) \sin\theta \; ,$$

(12)

so as to satisfy the condition that the velocity should be finite at $r = 0$ and the conditions

$$v_r' = v_r, \qquad v_\theta' = v_\theta \qquad \text{at } r = R$$

(13)

on the surface of the drop. Here primes refer to the fluid inside the drop. The equations of motion then yield the pressure distribution.

$$p' - p_o' = \rho'gr \cos\theta - 10\mu'v_o \cos\theta \; r/R^2 \; .$$

(14)

The two constants U and v_o are to be determined from the force balance at the interface, but this must be postponed until the surface tension and concentration distributions are known.

Surface Concentration

Conservation of surface-active agent in the interface is expressed by the equation

$$j_n = \text{div}_s \left(\underline{v}_t \Gamma\right) - \text{div}_s \left(D_s \; \text{grad}_s \; \Gamma\right)$$

(15)

where

$$v_t = v_o \sin\theta \; .$$

Let

$$\Gamma = \Gamma_o + \Gamma'$$

(16)

where Γ' is the deviation from the average surface concentration and is assumed to be small compared to Γ_o. This assumption allows us to write

$$\text{div}_s \; \underline{v}_t \Gamma = \left(\Gamma_o + \Gamma'\right) \text{div}_s \; \underline{v}_t + \underline{v}_t \cdot \text{grad}_s \Gamma'$$

$$\approx \Gamma_o \; \text{div}_s \; \underline{v}_t = \left(2v_o\Gamma_o/R\right) \cos\theta \; .$$

(17)

Rather than try to solve the equation of convective diffusion for the concentration of the surface-active agent in the bulk solution, we follow Levich and express the normal flux in terms of the thickness δ of the Nernst diffusion

layer

$$j_n = D(c_b - c_s)/\delta = (D/\delta)(\Gamma_o - \Gamma_s)/(\partial\Gamma/\partial c)_{eq}. \tag{18}$$

For small deviations from equilibrium we can express the concentration difference in terms of the difference of surface concentrations and take $(\partial\Gamma/\partial c)_{eq}$ to be constant.

In series with the mass transfer resistance in the solution there may be a resistance at the interface associated with the kinetics of adsorption. For small deviations from equilibrium we take this to be a linear relationship

$$j_n = -\alpha(\Gamma - \Gamma_s) . \tag{19}$$

These two expressions (18) and (19) can be combined to eliminate Γ_s:

$$j_n = -\alpha D\Gamma'/[D + \alpha\delta(\partial\Gamma/\partial c)_{eq}] . \tag{20}$$

This equation (20) can be combined with the interfacial material balance (15) to yield a differential equation for Γ':

$$-\frac{\alpha D\Gamma'}{D + \alpha\delta(\partial\Gamma/\partial c)_{eq}} = \frac{2v_o\Gamma_o}{R}\cos\theta - \frac{D_s/R^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Gamma'}{\partial\theta}\right) \tag{21}$$

with the solution

$$\Gamma' = -Kv_o\cos\theta \tag{22}$$

where

$$K = \frac{2\Gamma_o R}{2D_s + \alpha DR^2/[D + \alpha\delta(\partial\Gamma/\partial c)_{eq}]} . \tag{23}$$

Force Balance at the Interface

The force balance at the interface can be expressed as

$$\left.\begin{array}{l} p' + \tau'_{rr} - p - \tau_{rr} = 2\sigma/R \\[2mm] \tau'_{r\theta} - \tau_{r\theta} + \text{grad}_s\sigma = 0 \end{array}\right\} \text{ at } r = R \tag{24}$$

where

$$\tau_{r\theta} = -\mu\left[r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial\theta}\right] \text{ and } \tau_{rr} = -2\mu\frac{\partial v_r}{\partial r} . \tag{25}$$

Substitution of the expressions for the velocity components and the pressure and the expression

$$\sigma = \sigma_o + \frac{\partial \sigma}{\partial \Gamma} (\Gamma - \Gamma_o) \tag{26}$$

with $\partial \sigma / \partial \Gamma$ taken to be constant allows us to determine the constants:

$$p'_o = p_o + 2\sigma_o/R, \tag{27}$$

$$U = \frac{\mu + \mu' + \gamma}{2\mu + 3\mu' + 3\gamma} \frac{2(\rho' - \rho)gR^2}{3\mu}, \tag{28}$$

$$v_o = \frac{(\rho' - \rho)gR^2}{3(2\mu + 3\mu' + 3\gamma)} = \frac{\frac{1}{2}\mu U}{\mu + \mu' + \gamma}, \tag{29}$$

where

$$\gamma = -\frac{1}{3} K \frac{\partial \sigma}{\partial \Gamma}. \tag{30}$$

The Retardation Coefficient

For large values of the retardation coefficient γ, equation (28) reduces to Stokes law, and for small values it reduces to the Hadamard-Rybczyński formula.

When one of the three effects treated above predominates over the others, the expression for γ reduces to the appropriate formula of Levich. For large values of the surface diffusion coefficient D_s or small values of the solubility of the surface-active agent in the bulk solution, we have

$$\gamma_3 = -\frac{\Gamma_o R}{3D_s} \frac{\partial \sigma}{\partial \Gamma}. \tag{31}$$

Levich's value seems to be too large by a factor of 2 in this case. When surface diffusion is negligible and the adsorption resistance is small compared to the mass-transfer resistance in the solution we have

$$\gamma_2 = -\frac{2\Gamma_o \delta}{3 DR} \left(\frac{\partial \Gamma}{\partial c}\right)_{eq} \frac{\partial \sigma}{\partial \Gamma}. \tag{32}$$

When surface diffusion is negligible and the adsorption resistance is large

compared to the mass-transfer resistance in the solution we have

$$r_1 = -\frac{2\Gamma_o}{3dR}\frac{\partial\sigma}{\partial\Gamma}.$$

(33)

Finally, we might notice that with the assumption of the Nernst diffusion layer it makes no difference whether the surface-active agent is soluble in the outer fluid or in the fluid inside the drop.

Acknowledgment

This work was supported by the United States Atomic Energy Commission.

Nomenclature

c_b - concentration in the bulk of the solution.

c_s - concentration in the solution near the interface.

D - diffusion coefficient in the bulk fluid.

D_s - diffusion coefficient for surface diffusion.

F - expresses radial dependence of v_r.

g - gravitational acceleration.

G - expresses radial dependence of v_θ.

j_n - normal flux of surface-active agent into the interface.

K - constant (see equation (23)).

p - pressure.

r - radial coordinate measured from the center of the drop.

R - radius of the drop.

U - rate of fall of the drop.

v_o - tangential velocity at the equator of the drop.

v_r - radial velocity component.

v_θ - velocity component in θ-direction.

α - coefficient in linear expression of adsorption kinetics.

γ — retardation coefficient.

Γ — surface concentration.

Γ_o — average surface concentration.

Γ' — deviation from the average surface concentration.

Γ_s — surface concentration in equilibrium with c_s.

δ — thickness of Nernst diffusion layer.

θ — angular coördinate measured from the front of the drop.

μ — viscosity of the outer fluid.

μ' — viscosity of fluid inside drop.

ρ — density of the outer fluid.

ρ' — density of fluid inside drop.

σ — surface tension.

τ_{rr} — component of the viscous stress tensor.

$\tau_{r\theta}$ — component of the viscous stress tensor.

div_s — surface divergence.

grad_s — surface gradient.

References

1. Veniamin G. Levich. <u>Physicochemical Hydrodynamics</u>. Englewood Cliffs: Prentice-Hall, Inc., 1962. Sections 73, 74, and 75.

2. A. Frumkin and V. Levich. "O vliyanii poverkhnostno-aktivnykh veshchestv na dvizhenie na granitse zhidkikh sred." <u>Zhurnal Fizicheskoĭ Khimii</u>, <u>21</u>, 1183-1204 (1947).