Shape of a Vertical Column of Drops Approaching an Interface

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In a close packed dispersion, a drop at the interface experiences forces from the drops above which affect its shape and rate of coalescence. The shape of a vertical column of two drops approaching either a horizontal plane or deformable fluid-liquid interface is considered here. The surface of the upper drop is sessile and that of the lower drop is defined by the differential equations governing the shape of an annular meniscus with apex. These have been integrated on a digital computer and the areas of the draining films between the two drops and between the lower drop and the interface obtained. The forces pressing on the films may also be obtained when the drop volumes are known and hence the ratio of the coalescence times of the upper and lower draining films. For equisized drops, the results indicate that the lower drop always coalesces with the upper drop before it coalesces with the bulk interface. When the lower drop approaches a deformable interface, the areas of the draining films are almost identical with those associated with a single drop to which the same vertical force is applied through a horizontal surface. Solutions for this case are already available and hence provide an estimate of the areas of the draining films associated with the bottom drop in a vertical column containing several drops.

SCOPE

The coalescence of drops in a close packed dispersion is not well understood. The drops grow in size as they coalesce with each other and finally disappear when they coalesce at the bulk interface. The rate of coalescence depends on the rate of drainage of the intervening fluid films. This increases as the force pressing on the film increases, and it decreases as the area of the film increases. Drops in the dispersion experience forces from the surrounding drops; in particular, drops at the interface experience forces from the drops above. By considering the dynamic equilibrium shape of a column of drops resting on the interface, it is possible to determine the areas of the draining films between a drop and the interface ond between two drops. From the gravitational force pressing on these films, the relative rates of drainage may be obtained. It is thus possible to estimate the relative frequency of coalescence between two drops and between a drop and the bulk interface. This information is invaluable if models which predict the behaviour of close packed dispersions are to be developed.

CONCLUSIONS AND SIGNIFICANCE

The dynamic equilibrium shape of two drops in a vertical column approaching either a horizontal plane or a deformable fluid-liquid interface has been theoretically obtained. The shape of the upper drop is sessile but that of the lower drop is defined by the equations governing the shape of an annular meniscus with apex. These were numerically integrated on a digital computer for a wide range of values of the radius of curvature at the apex of the annular meniscus. From the shape it is possible to obtain the areas of the draining films between the drops and between the lower drop and the plane or deformable interface. The rate of drainage of these films is approximated by the Reynolds' equation which indicates that the coalescence time is proportional to the factor a^2/f, where a is the area of the film and f the force pressing on it. The force f is proportional to the volume of the upper drop for the film between the drops and to the sum of the drop volumes for the lower film. The factor a^2/f has been evaluated for the upper and lower films for a wide range of drop volumes and the ratio of the coalescence times between the drops and between the lower drop and the plane or deformable interface thus obtained. For equisized drops, the lower drop is always more likely to coalesce with the upper drop than with the bulk interface. When the lower drop approaches a deformable interface, the areas of the upper and lower draining films are very close to those for the case in which a force equal to the net weight of the upper drop is applied to the lower drop through a horizontal surface. This infers that the relative coalescence times of the upper and lower films of a drop at the interface in a vertical column of N equisized drops of volume v may be estimated from the areas of the draining films above and below a single drop at the interface subject to a vertical force $(N-1)v\ (\rho_h - \rho_l)g$ applied to the upper film through a horizontal surface.

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Little is known about coalescence in close packed dispersions, but it is now accepted (Barnea and Mizrahi, 1975; Allak and Jeffreys, 1974; Smith and Davies, 1970; Bohnet, 1977) that there is a zone close to the disengaging interface in which forces are transmitted between the drop which do not move relative to each other. Before the drops reach this zone, they move relative to each other, and then momentum is important. Indeed, if the drops are freely suspended, that is, if the net weight of each drop is balanced by the drag force, there are no gravitational forces acting between the drops and the deforming force, when two drops collide, is entirely due to the rate of change of momentum (plus of course electrical and intermolecular forces). This paper is relevant to the coalescence process in the zone close to the disengaging interface.

The effect of a vertical force acting on a single drop at an interface has been discussed by Wood and Hartland (1972) and Hartland and Wood (1973*a*) when the drop approaches a horizontal surface, and by Hartland and Wood (1973*b*) when the drop approaches a deformable interface. Increasing the vertical force increases the coalescence time in all cases.

The two-dimensional case has been discussed by Leidi and Hartland (1976) who were able to compare their results with those when the vertical force arises from the presence of a second drop sitting on the first. These authors also considered the shape of a two-dimensional drop in a horizontal row (Leidi and Hartland, 1975).

For a vertical force f pressing on a horizontal film of Newtonian fluid with viscosity μ, area a, and uniform thickness δ, the drainage time t for axisymmetric film thinning is given by (Reynolds, 1886; Hartland, 1967)

$$t = \frac{3n^2}{16\pi} \frac{\mu}{\delta^2} \frac{a^2}{f} \qquad (1)$$

where $a = \pi x^2$. If we take proper account of the hydrostatic pressure gradient within the film, exactly the same equation is obtained for a spherical film. The area is now given by $a = 2\pi r^2(1 + \cos\phi)$, where $r = x/\sin\phi$ is the radius of curvature of the film, and ϕ is the inclination of the periphery of the film to the horizontal (Hartland, 1968, 1969).

The force f pressing on the film beneath the upper drop of volume V_1 is $V_1(\rho_h - \rho_l)g$, and on the film beneath the lower drop of volume V_2 is $(V_1 + V_2)(\rho_h - \rho_l)g$. These expressions are true for both plane and spherical films.

Equation (1) suggests that for given values of μ, δ, and n, the coalescence time τ will be proportional to a^2/f. The relative magnitude of this factor for the upper and lower films indicates the relative magnitudes of the coalescence times and hence whether the lower drop is more likely to coalesce with the bulk interface or the upper drop.

In practice, coalescing drop populations contain suspended or dissolved contaminants which tend to concentrate at the interface. During film drainage, these contaminants give rise to surface-tension-gradient induced flows that may significantly alter the rate of coalescence. This effect would manifest itself in Equation (1) through a change in the value of n and perhaps in the initial value of δ. The results presented thus only apply to pure systems.

THEORY

Two cases are considered, as shown in Figures 1*a* and 1*b*, in which the lower drop of volume V_2 approaches either a plane horizontal surface or a deformable fluid-liquid interface. The free surface of the upper drop of volume V_1 is described by the equation for a single three-dimensional sessile drop (Bashforth and Adams, 1883). The shape of that part of the upper drop surrounded by the draining film between the two drops is a spherical cap of radius $R_1 = X_1/\sin\phi_1$. The lengths shown are made dimensionless using the factor $c^{1/2}$, where $c = (\rho_h - \rho_l)g/\sigma$, so that $V_1 = v_1 c^{3/2}$, $V_2 = v_2 c^{3/2}$, $R_1 = r_1 c^{1/2}$, and $X_1 = x c^{1/2}$, where v_1 and v_2 are the actual drop volumes and r_1 and x_1 the actual dimensions of the spherical cap.

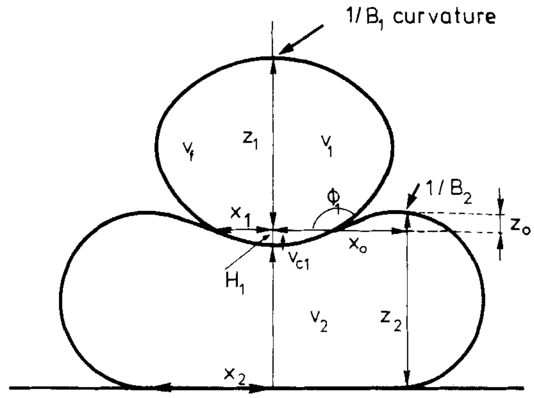

Figure 1a

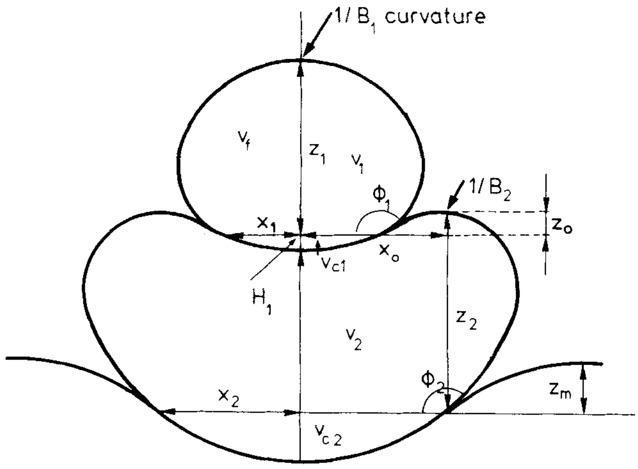

Figure 1b

Fig. 1. Notation for two drops in a vertical column with lower drop approaching (*a*) horizontal plane and (*b*) deformable interface.

The free surface of the lower drop is described by the differential equation governing the shape of an annular meniscus with apex, detailed in the Appendix. To facilitate further discussion, it is useful to introduce the angular inclination of the meniscus to the horizontal θ; this is positive for the outer interface and negative for the inner one. When the drop approaches a plane interface, $\theta = 180$ deg at the edge of the lower draining film, as shown in Figure 1*a*.

When the drop approaches a deformable interface, $\theta = \phi_2$ at the edge of the lower draining film, as shown in Figure 1*b*. The shape of the draining film is that of a spherical cap with radius $R_2 = X_2/\sin\phi_2$, and the shape of the deformable interface is that of an external meniscus (Huh and Scriven, 1969).

A pressure balance on a control surface passing through the apex of the upper drop, the surfaces of the draining film, and the apex of the annular meniscus enable the equilibrium position of the edge of the draining film between the two drops to be located:

$$\frac{2}{B_1} + Z_1 - \frac{4 \sin\phi_1}{X_1} = Z_o + \frac{1}{B_2} \quad (2)$$

This enables the area A_1 of the draining film between the drops to be obtained from

$$A_1 = 2\pi R_1^2(1 + \cos\phi_1) \quad (3)$$

The volume of the upper drop is given by

$$V_1 = V_f + V_{c1} \quad (4)$$

where V_f is the volume of the free part of the drop and V_{c1} is the volume of the spherical cap:

$$V_{c1} = (\pi R_1^3/3)(2 + 3\cos\phi_1 - \cos^3\phi_1) \quad (5)$$

The volume of the lower drop depends on whether it is approaching a plane or a deformable interface. For the plane interface, the volume is given by

$$V_2 = V_o - V_i - V_{c1} \quad (6)$$

in which V_o is the volume of revolution of the outer meniscus between the apex of the annular meniscus and the edge of the draining film beneath the lower drop (that is, between $\theta = 0$ and 180 deg), and V_i is the volume of revolution of the inner meniscus between the apex of the annular meniscus and the edge of the draining film beneath the two drops (that is, between $\theta = 0$ and $\phi_1 - 180$ deg. The area of the draining film beneath the lower drop is

$$A_2 = \pi X_2^2 \quad (7)$$

For the deformable interface, the volume of the lower drop is given by

$$V_2 = V_o - V_i - V_{c1} + V_{c2} \quad (8)$$

in which V_i and V_{c1} are defined as above, V_o is now the volume of revolution of the outer meniscus between $\theta =$ 0 and ϕ_2, and V_{c2} is the volume of the spherical cap enclosed by the draining film beneath the lower drop:

$$V_{c2} = (\pi R_2^3/3)(2 + 3\cos\phi_2 - \cos^3\phi_2) \quad (9)$$

where $R_2 = X_2/\sin\phi_2$ is the radius of the spherical cap.

To locate the edge of the draining film beneath the lower drop, a second pressure balance is needed on a control surface passing through the apex of the annular meniscus, the surfaces of the draining film, and the horizon of the external meniscus:

$$\frac{1}{B_2} + Z_2 = \frac{4X_2}{\sin\phi_2} + Z_m \quad (10)$$

The area of the draining film is given by

$$A_2 = 2\pi R_2^2(1 + \cos\phi_2) \quad (11)$$

As described in the Appendix, tables have been produced for different values of X_o and radius of curvature at the apex B_2, from which the critical parameters of the annular meniscus Z_o, Z_2, ϕ_1, ϕ_2, V_o, V_i and X_2 may be obtained.

CALCULATION OF EQUILIBRIUM SHAPE

The equilibrium shape of a drop of volume V_1 resting on a second drop of volume V_2 approaching a horizontal plane is defined by the parameters B_1, X_1, and ϕ_1 for the upper drop and B_2, X_o, Z_o, X_2, and Z_2 for the lower drop. When the lower drop approaches a deformable interface, the parameters ϕ_2 and Z_m must also be specified. These parameters and the volumes V_1 and V_2 were determined as follows:

1. A value of B_1 is chosen. This determines the profile of the upper drop through the tables, giving the shape of a sessile interface (Hartland and Hartley, 1976).
2. A value of ϕ_c is chosen [which must be greater than the value of ϕ_c for a single drop approaching its homophase. This was discussed by Princen (1963) and tabulated by Hartland and Hartley (1976)]. The corresponding values of Z_1, X_1 and V_f are then read off from the sessile drop tables at the specified values of B_1.
3. The volume of the spherical cap enclosed by the upper draining film may be obtained from Equation (5) and hence the drop volume V_1 from Equation (4). The area of the draining film follows from Equation (3).
4. A value of X_o is chosen such that $X_o \geqq X_1$, and the values of B_2 and Z_o are obtained by quadratic interpolation in the tables giving the shape of an annular meniscus (described in the Appendix), using the values of X_1 and ϕ_1 which lie on the inner part of the profile. (No interpolation is required for ϕ_1, but the value of X_1, read off from the sessile drop tables, does not occur uniquely in the annular meniscus tables.)
5. The equilibrium values B_2 and Z_o are those which satisfy Equation (2) in which B_1, Z_1, X_1, and ϕ_1 are known. They are determined by varying the value of X_o and using quadratic interpolation to find the correct value.
6. When the lower drop approaches a plane interface, knowledge of B_2 and X_o enables the value of X_2 to be found at $\theta = 180$ deg from the computer program for the annular meniscus. The area of the lower draining film follows immediately from Equation (7). The volumes of revolution of the outer and inner meniscis, V_o and V_i, may also be calculated at $\theta = 180$ deg and $\phi_1 - 180$ deg, respectively. These enable the volume V_2 of the lower drop to be obtained from Equation (6).
7. When the lower drop approaches a deformable interface, knowledge of B_2 and X_o enables Z_2 and X_2 to be calculated at different values of $\theta = \phi_2$ from the computer program for the annular meniscus. The values of X_2 and ϕ_2 yield Z_m from the tables, giving the shape of an external meniscus (Hartland and Hartley, 1976). Only those values of Z_2, X_2, ϕ_2, and Z_m which satisfy Equation (10) are correct, and ϕ_2 must be adjusted until this is so. The area of the lower draining film then follows immediately from Equation (11). If we use the equilibrium value of ϕ_2, the volumes V_o and V_{c2} may be obtained from the computer program and Equation (9) respectively and hence the volume of the lower drop V_2 from Equation (8).
8. Steps 1 to 7 were repeated for many values of B_1 in the range $\log_{10}B_1$, -0.5 to 2.0. For each value of B_1, steps 2 to 7 were repeated for values of ϕ_1 in the range $\phi_{min} < \phi_1 \leqq 180$ deg in 5 deg steps, where ϕ_{min} is the value of ϕ_1 when the volume of the lower drop is infinite (corresponding to an infinite meniscus).

RESULTS AND DISCUSSION

The equilibrium parameters, drop volumes, and areas of the draining films were calculated as described above for many different values of B_1 in the range $-0.5 < \log_{10}B_1 <$ 2 and several different values of ϕ_1 for the two cases when the lower drop is approaching a plane or a deformable interface. When the lower drop approaches a horizontal plane, no solutions exist if $Z_2 < H_1 + Z_o$, which is the case for some values of ϕ_1 when $\log_{10}B_1 = 2$. The drop volume V_1 is then very large, but a considerable part of

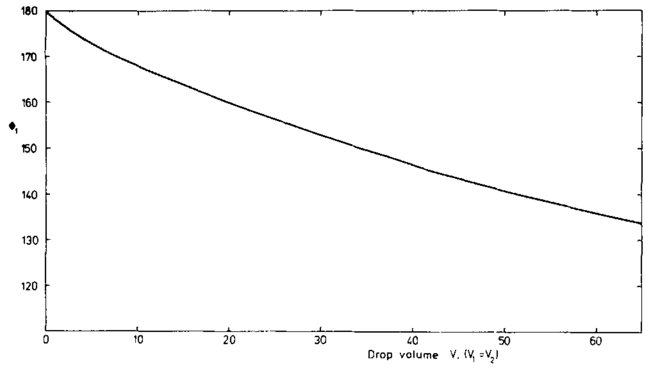

Fig. 2. Variation of inclination of edge of upper draining film ϕ_1 with drop volume V for equisized drops approaching a horizontal plane.

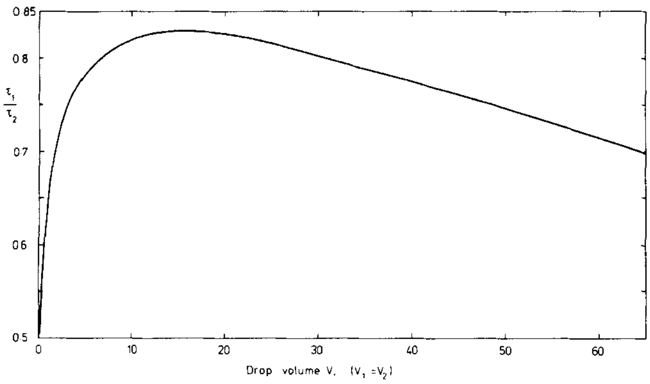

Fig. 4. Variation of ratio of coalescence times τ_1/τ_2 for upper and lower films with drop volume V for two equisized drops approaching a horizontal plane.

this is contained in the spherical cap of volume V_{c1}. Further quadratic interpolation yields the equilibrium parameters and areas when the drop volumes are equal ($V_1 = V_2 = V$). Figure 2 shows the variation of the inclination of the periphery of the upper draining film ϕ_1 with V when the lower drop approaches a horizontal plane. For very small drops, $\phi_1 = 180$ deg, so the upper film is also plane and horizontal. As V increases, the value of ϕ_1 decreases.

Figure 3 shows the variation of ϕ_1 and ϕ_2 with V when the lower drop approaches a deformable interface. For very small drops, $\phi_1 = \phi_2 = 180$ deg. As V increases, ϕ_2 decreases sharply, but ϕ_1 decreases only slightly to a minimum of about 175 deg at $V \simeq 9$ and then increases, becoming greater than 180 deg when $V \gtrsim 19$. In other words, the upper film is almost plane and horizontal over a wide range of V. When V is large, the spherical cap bounded by the film penetrates the upper drop rather than the lower drop. The upper drop then encompasses the lower drop rather than the more usual case depicted in Figure 1*b*.

Figure 4 shows the ratio of the coalescence times for the upper and lower films when both drops have the same volume and the lower drop approaches a horizontal plane. The ratio is always less than one and passes through a maximum at $\tau_1/\tau_2 \simeq 0.83$ when $V \simeq 16$. For smaller values of V, the ratio rapidly falls and approaches 0.5 when V is very small. [The coalescence time is assumed to be proportional to the factor A^2/F, as indicated by Equation (1)].

Figure 5 shows the ratio of the coalescence times when both drops have the same volume and the lower drop approaches a deformable interface. The ratio is always less than one and passes through a maximum at $\tau_1/\tau_2 \simeq 0.29$ when $V \simeq 16$ (as when the lower drop approaches a horizontal plane). For smaller values of V, the ratio falls and approaches 0.125 when V is very small. The ratio is always less than when the lower drop approaches a horizontal plane as the lower drop sinks into the deformable interface, thus increasing the area of the lower film.

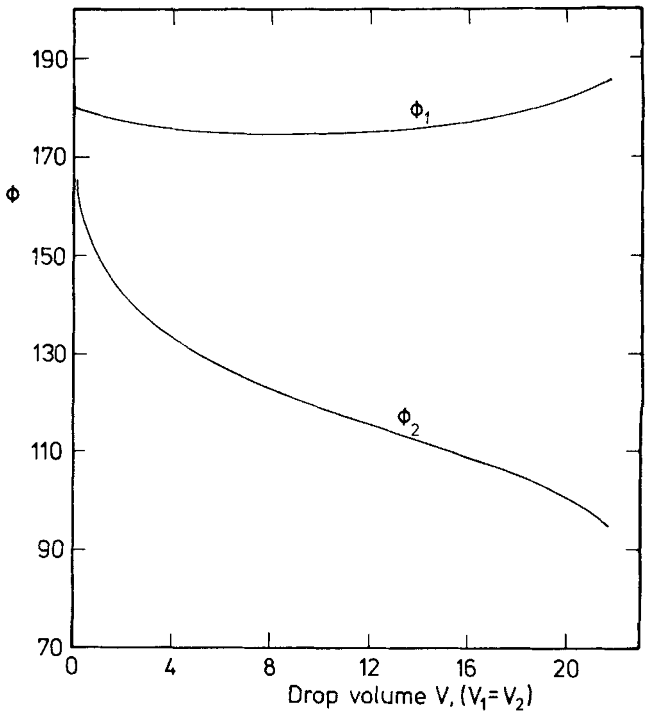

Fig. 3. Variation of inclination of edge of upper and lower draining films ϕ_1 and ϕ_2 with drop volume V for equisized drops approaching a deformable fluid-liquid interface.

Limiting Case of Small Drops

Very small drops retain their spherical shape, and capillary pressures are large compared with hydrostatic pressures. The film between equisized drops thus becomes plane, with area given by (Frankel and Mysels, 1962)

$$a_1 = \frac{2\pi}{3} w^4 \frac{\Delta\rho g}{\sigma} \tag{12}$$

where $\Delta\rho = \rho_h - \rho_l$ is the density difference between the phases.

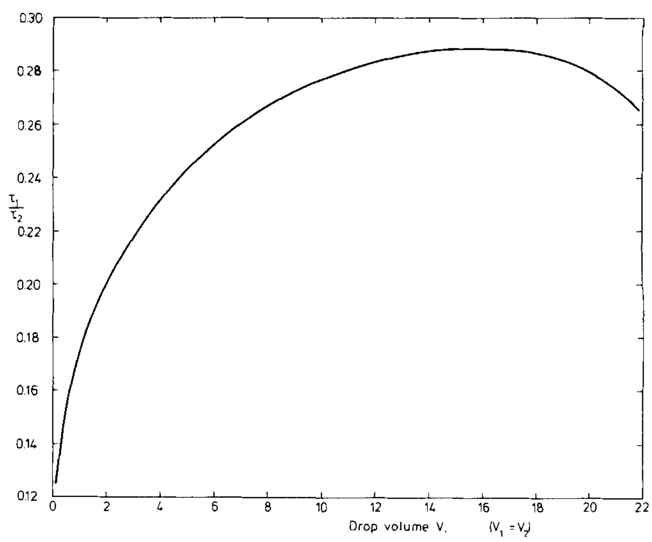

Fig. 5. Variation of ratio of coalescence times τ_1/τ_2 with drop volume V for two equisized drops approaching a deformable fluid-liquid interface.

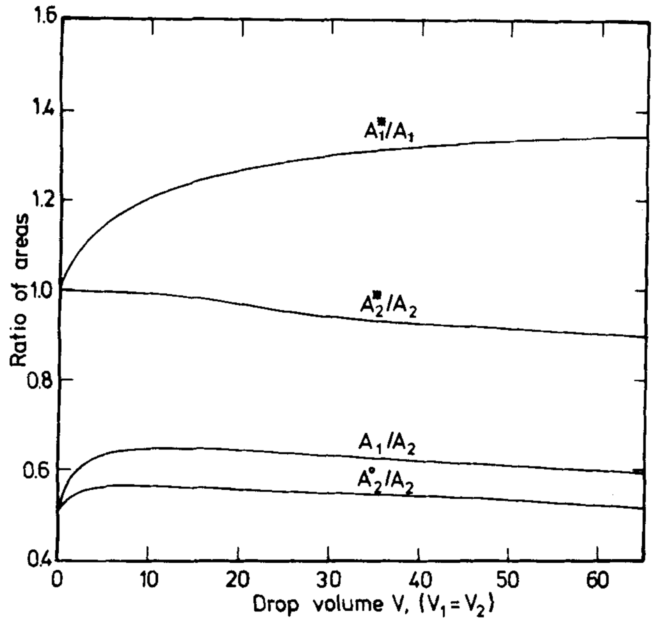

Fig. 6. Comparison of areas of upper and lower draining films for two equisized drops of volume V approaching a horizontal plane with those for a single drop trapped between two horizontal surfaces, subject to an applied force V (equal to the net weight of the upper drop). The areas for the single drop are denoted with an asterisk. Also shown is the ratio A_1/A_2 for a column of two drops and the ratio $A_2°/A_2$, in which $A_2°$ is the area beneath a single drop with no applied force.

When the lower drop approaches a horizontal plane, the capillary pressure within the draining film is $2\sigma/w$, but the net weight of the two drops pressing on the film becomes $(8\pi/3)w^3\ \Delta\rho g$. Therefore, the area of the lower film is

$$a_2 = \frac{4\pi}{3} w^4 \frac{\Delta\rho g}{\sigma} \tag{13}$$

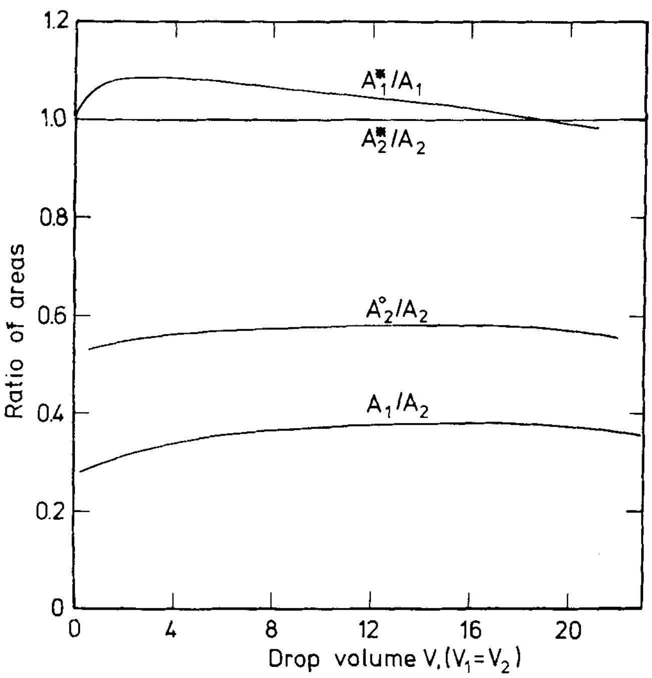

Fig. 7. Comparison of areas of upper and lower draining films for two equisized drops of volume V approaching a deformable interface with those for a single drop with a force V applied to the upper surface through a horizontal surface. The areas for the single drop are denoted with an asterisk. Also shown is the ratio A_1/A_2 for a column of two equisized drops and the ratio $A_2°/A_2$ in which $A_2°$ is the area of the film beneath a single drop with no applied force.

When the lower drop approaches a deformable interface, the capillary pressure within the film is reduced to σ/w, and the net weight of the two drops is still $(8\pi/3)w^3\Delta\rho g$. The area of the film is

$$a_2 = \frac{8\pi}{3} w^4 \frac{\Delta\rho g}{\sigma} \tag{14}$$

A comparison of the values of a^2/f for the upper and lower films shows that for small drops the ratio of the coalescence times $\tau_1/\tau_2 = 0.5$ when the lower drop approaches a horizontal plane but $\tau_1/\tau_2 = 0.125$ when the lower drop approaches a deformable interface. These are precisely the limits observed in Figures 4 and 5 for the ratios of τ_1/τ_2 calculated from the dimensionless area of the draining film and the dimensionless force acting on them.

Comparison with Film Areas when Force is Applied through Horizontal Plane

The areas of the upper and lower draining films may be compared with those resulting when the force on the lower drop is applied through a horizontal surface. Figure 6 shows the comparison when the lower drop of volume V approaches a horizontal plane and a vertical force $F_1 = V$ is applied to the upper surface. The areas of the upper and lower films for the drop trapped between two horizontal surfaces are indicated with an asterisk. For very small drops there is no difference between the areas in the two cases, and the ratios A_1^*/A_1 and A_2^*/A_2 are equal unity. As the drop volume V increases, the ratio A_1^*/A_1 becomes considerably greater than one and the ratio A_2^*/A_2 slightly less than one. The ratio of the areas of the upper and lower films A_1 and A_2 when the force on the lower drop is applied through an upper drop is also shown for comparison, as is the ratio A_2°/A_2 in which A_2° is the area of the film beneath a single drop with no applied force.

Figure 7 shows the comparison when the lower drop approaches a deformable interface. For very small drops, there is again no difference between the areas in the two cases. As the drop volume V (and applied force $F_1 = V$) increases, the ratio A_1^*/A_1 becomes slightly greater than one and passes through a maximum of about 1.085 when $V \simeq 3$. The ratio then decreases steadily and becomes less than one when $V \gtrsim 19$. The ratio A_2^*/A_2 is equal to unity for all V. This is because the angle ϕ_1 is always close to 180 deg (as shown in Figure 3) when the force on the lower drop is applied through an upper drop. When the force is applied through a horizontal surface, the inclination at the edge of the upper draining film is always exactly 180 deg. The small difference between the angles in the two cases is compensated by a corresponding difference in the two values of X_1. The ratio of the areas of the upper and lower draining films A_1 and A_2 when the force on the lower drop is applied through an upper drop is also shown for comparative purposes, as is the ratio A_2°/A_2 in which A_2° is the area of the film beneath a single drop with no applied force.

The fact that the ratio A_2^*/A_2 equals unity and the ratio A_1^*/A_1 is close to unity over a wide range of V means that applying the force to the lower drop through a horizontal surface provides a good model for when the force is applied through an upper drop, at least when both drops have the same volume. It suggests that the area of the draining film beneath a column of N equisized drops of volume V may be estimated from that beneath a single drop of volume V to which a force $(N - 1)V$ is applied through a horizontal surface. This information is already available as the effect of an applied force F on a drop of volume V has been obtained (Hartland and Wood, 1973*b*). In this way, the tedious calculation of the shape of each successive drop in a column of N drops to yield the area beneath the bottom drop may be avoided.

ACKNOWLEDGMENT

The work described in this paper was supported by the Schweireischer Nationalfonds zur Föderund dev Wissenschaftlichen Forschung.

NOTATION

a = area of draining film
A = ac = dimensionless a
a_1 = area of upper draining film
A_1 = a_1c = dimensionless a_1
a_2 = area of lower draining film
A_2 = a_2c = dimensionless a_2
b = radius of curvature at apex of annular meniscus (in Appendix)
B = $bc^{1/2}$ = dimensionless b
b_1 = radius of curvature at apex of upper drop
B_1 = $b_1c^{1/2}$ = dimensionless b_1
b_2 = radius of curvature at apex of annular meniscus
B_2 = $b_2c^{1/2}$ = dimensionless b_2
c = $(\rho_h - \rho_l)g/\sigma$ = constant characterizing physical properties
f = force pressing on draining film
F = $fc^{1/2}/\sigma$ = dimensionless f
g = acceleration due to gravity
h_1 = vertical distance from edge of draining film to bottom of upper film
H_1 = $H_1c^{1/2}$ = dimensionless h_1
n = number of immobile surfaces
N = number of drops in a vertical column
r = radius of curvature of draining film
R = $rc^{1/2}$ = dimensionless r
s = arc length measured from apex of annular meniscus
S = $sc^{1/2}$ = dimensionless s
t = drainage time
v = volume of drop
V = $vc^{3/2}$ = dimensionless v
v_c = volume of spherical cap enclosed by draining film
V_c = $v_cc^{3/2}$ = dimensionless v_c
v_f = free drop volume
V_f = $v_fc^{3/2}$ = dimensionless v_f
w = radius of spherical drop
x = horizontal distance from axis of symmetry
X = $xc^{1/2}$ = dimensionless x
x_o = horizontal distance from axis of symmetry to apex of annular meniscus
X_o = $x_oc^{1/2}$ = dimensionless x_o
z = vertical distance measured from apex of annular meniscus
Z = $zc^{1/2}$ = dimensionless z
z_o = vertical distance from apex of upper drop to edge of upper draining film
Z_o = $zc^{1/2}$ = dimensionless z_o
z_m = height of horizon of external meniscus above periphery of draining film
Z_m = $z_mc^{1/2}$ = dimensionless z_m

Greek Letters

ϕ = inclination of drop surface to horizontal at edge of draining film
θ = angle of inclination of annular meniscus to horizontal
δ = film thickness
ρ_h = density of heavy phase
ρ_l = density of light phase
$\Delta\rho$ = $\rho_h - \rho_l$ = density difference
σ = interfacial tension
τ = coalescence time
μ = viscosity

Subscripts

1 = upper drop
2 = lower drop
h = heavy
l = light

Superscripts

o = single drop
$*$ = single drop with applied force

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APPENDIX

Annular Meniscus with Apex

Consider the annular meniscus with an apex, shown in Figure A1, in which the radius of curvature at the apex is b and the distance of the apex from the axis of symmetry is x_o. The excess pressure inside the surface at this point is σ/b, and the increase in hydrostatic pressure difference over a height z is $z(\rho_h - \rho_l)g$. Equating the excess pressure within the surface at the height z to the stress due to the interfacial curvature at this point gives

$$\frac{d\theta}{ds} + \frac{\sin\theta}{x} = \frac{\sigma}{b} + z(\rho_h - \rho_l)g \qquad \text{(A1)}$$

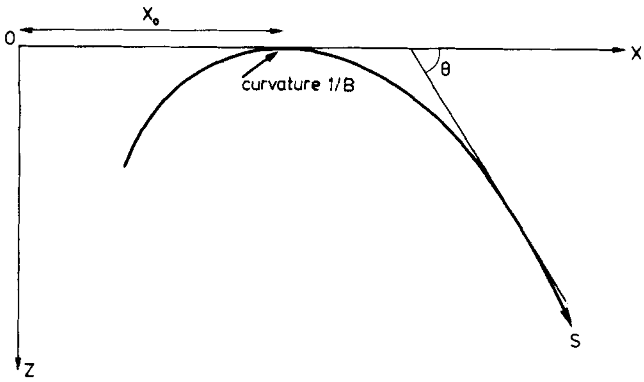

Fig. A1.

In dimensionless form, this becomes

$$\frac{d\theta}{dS} = \frac{1}{B} + Z - \frac{\sin\theta}{X} \qquad (A2)$$

in which $S = sc^{1/2}$, $X = xc^{1/2}$, $B = bc^{1/2}$, and $Z = zc^{1/2}$, where $c = (\rho_h - \rho_l)g/\sigma$. The distance of the apex from the axis of symmetry is $X_o = x_o c^{1/2}$.

Furthermore, the variables X, Z, S, and θ are related geometrically by

$$\frac{dX}{dS} = \cos\theta; \quad \frac{dZ}{dS} = \sin\theta \qquad (A3)$$

and the variation with S of the volume of revolution $V = vc^{3/2}$ and surface area of revolution $A = ac$ are given by

$$\frac{dV}{dS} = \pi X^2 \sin\theta \qquad (A4)$$

$$\frac{dA}{dS} = 2\pi X \qquad (A5)$$

At the apex, the boundary conditions are

$$X = X_o; \quad \frac{d\theta}{dS} = \frac{1}{B} \qquad (A6)$$

and

$$\theta = S = Z = V = A = 0 \qquad (A7)$$

Written in the above form, the equations apply to both the outer and inner interfaces of the meniscus.

For the outer interface, $X > X_o$ and θ, S, Z, V and A are positive. For the inner interface, θ and S are negative, $X < X_o$ and Z, V and A are positive.

These equations have been integrated using a Runge-Kutta technique with a stringent error control (Hartland and Hartley, 1976) for twenty values of X_o between 0.1 and 10 and forty values of B between 0.01 and 100. Tables have been produced accurately to six figures of the values of X, Z, S, A, and V at 5 deg intervals in θ between 0 and 270 deg. More values at different initial values of X_o and B and at any value of θ can be produced at will from the computer program.

Manuscript received July 5, 1977; revision received March 17, and accepted April 24, 1978.

A New Thermodynamic Representation of Binary Electrolyte Solutions Nonideality in the Whole Range of Concentrations

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A system of equations based on the ionic atmosphere theory of Debye and Huckel, Born model contribution, and local compositions of the nonrandom two-liquid (NRTL) model is developed to represent isothermal activity coefficients, in the whole range of concentrations, for solutions in an undissociated solvent of a partially or completely dissociated electrolyte.

The physical constants and the four adjustable parameters necessary to represent the osmotic coefficient, for fifteen strong aqueous electrolytic solutions, are given at 298.15°K and atmospheric pressure. Vapor-liquid equilibrium, for the hydrochloric acid-water system at 298.15°K, is represented for acid compositions ranging from infinite dilution to 18 M using a known dissociation constant and six parameters.

SCOPE

Properties of very concentrated electrolyte solutions which are the bases of fluid phase equilibria calculation are needed in chemical engineering applications, especially in the design of separation processes. The purpose of this work is to represent vapor-liquid equilibria of binary systems, especially water-inorganic acid or salt mixtures, in a very large range of concentrations using analytical equations for the activity coefficients in the

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