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Manuscript received February 1, 1978; revision received October 16, and accepted October 24, 1980.

Effects of London-van der Waals Forces on the Thinning of a Dimpled Liquid Film As a Small Drop or Bubble Approaches a Horizontal Solid Plane

When a small drop or bubble approaches a solid surface, a thin liquid film forms between them, drains, until an instability forms and coalescence occurs. Lin and Slattery (1982a) developed a hydrodynamic theory for the first portion of this coalescence process: the drainage of the thin liquid film while it is sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. Here the effects of the London-van der Waals forces are included. The resulting theory describes the evolution of the film profile, given only the bubble radius and the required physical properties. The inclusion of a positive disjoining pressure results in better descriptions of the film profiles measured by Platikanov (1964) for air bubbles pressed against glass plates. When the disjoining pressure is negative, an unstable draining film evolves and finally ruptures. Unfortunately, there are no experimental data with which to compare our predicted coalescence times.

JING-DEN CHEN and J. C. SLATTERY

Department of Chemical Engineering
Northwestern University
Evanston, IL 60201

SCOPE

The rate at which drops or bubbles suspended in a liquid coalesce is important to the preparation and stability of emulsions, of foams, and of dispersions; to liquid-liquid extraction; to the formation of an oil bank during the displacement of oil from a reservoir rock. On a smaller scale, when two drops (bubbles) in a liquid phase approach each other or when a drop (bubble) approaches a solid surface, a thin liquid film forms between them, drains, until an instability forms and coalescence occurs. We must understand the factors controlling the rate of coalescence.

Lin and Slattery (1982a,b) considered the early stage of this coalescence process as a drop approaches a solid wall or a fluid-fluid interface. Their results are applicable, when the draining film is sufficiently thick that effects of any electrostatic double layer or of London-van der Waals forces can be neglected.

In what follows, we extend their theory to include the effects of London-van der Waals forces on the drainage process. In order to simplify the problem, we consider only the case of small drops or bubbles approaching a horizontal solid wall. The liquid films are so thin that the Reynolds lubrication theory approximation can be applied.

CONCLUSIONS AND SIGNIFICANCE

This is the first analysis of this problem concerned with the latter stage of the drainage process when the effects of the London-van der Waals forces become significant.

The present theory including the effects of these forces permits a better representation of the film profiles measured by Platikanov (1964) than that given by Lin and Slattery (1982a).

The effects of London-van der Waals forces on the dimpled thinning film are negligible, when the film thickness at the rim is larger than the distance over which these forces are effective. For the 0.1 N KCl solution-air and aniline-air systems, the effects of London-van der Waals forces are negligible at short times and the predictions of the present theory coincide with those given by Lin and Slattery (1982a). At longer times, the present theory is an improvement. For the ethanol-air system, the effects of the London-van der Waals forces are so strong that even at shorter times our film profiles differ from those given by Lin and Slattery (1982a).

Our analysis predicts that the dimpled thinning film approaches with time a flat equilibrium film when there is a positive disjoining pressure attributable to London-van der Waals forces. The thickness of this equilibrium film increases with the disjoining pressure. The time required to reach equilibrium decreases with the disjoining pressure. When there is a negative disjoining pressure due to London-van der Waals forces, the thinning rate at the rim is enhanced, as instability develops, and rupture occurs in a finite time.

When small amounts of surfactant are present, the fluid-fluid interface may remain immobile until late in the drainage process. Lin and Slattery (1982a) gave a good description of the film profiles at short times for the 0.1 N KCl solution-air system, assuming that the interface was immobile. They explained the more rapid drainage observed experimentally at longer times by suggesting that the interface was no longer immobile. The better agreement obtained with the present theory argues against their conclusion.

This work continues to support the conclusion of Lin and Slattery (1982a) that, in the presence of surfactants, the interfacial viscosities will have little effect upon the rate at which a film drains prior to the development of an instability leading to coalescence. As pointed out above, this work suggests that in the presence of surfactants the fluid-fluid interface will be immobile until late in the drainage process. The conclusion follows from the observation that velocity gradients cannot exist within an immobile interface. This does not preclude the possibility that the interfacial viscosities may stabilize a film in the latter stage of the drainage process and in this way retard coalescence.

INTRODUCTION

Coalescence of drops or bubbles in a liquid phase proceeds in three stages. As a bubble approaches a solid surface, a liquid-gas interface or another bubble, a thin liquid film is formed that drains as the two interfaces are forced together. The rate at which this film thins is determined by the rate at which the liquid drains from it. As the thickness of the draining film becomes sufficiently small (about 1,000 Å), the effects of the van der Waals forces and of any electrostatic double layer becomes significant. Depending upon the sign and the magnitude of the disjoining pressure attributable to the van der Waals forces and the electrostatic double layer forces, there may be a critical thickness at which the film becomes unstable, ruptures and coalescence occurs. Comprehensive reviews of thin films are given by Kitchener (1964), Sheludko (1967), and Buscall and Ottewill (1975). Reviews concerned with the drainage and stability of thin liquid films are given by Ivanov and Jain (1979), Jain et al. (1979) and Ivanov (1980).

When a drop or bubble approaches a solid plane, the thin liquid film formed is dimpled (Derjaguin and Kussakov, 1939; Elton, 1948; Evans, 1954; Platikanov, 1964; Hartland, 1969; Aronson and Princen, 1975; Nakamura and Uchida, 1980).

To this point, the only analyses available for this coalescence process have been concerned with the initial stage of the drainage process when the effects of any London-van der Waals forces and of any electrostatic double layer can be neglected.

Frankel and Mysels (1962; also Buevich and Lipkina, 1975) have developed approximate expressions for the thickness of the dimpled film at the center and at the rim as functions of time. Their expression for the thinning rate at the rim is nearly equal to that predicted by the simple analysis of Reynolds (1886) and it is in reasonable agreement with some of the measurements of Platikanov (1964; Lin and Slattery, 1982a). Their predicted thinning rate at the center of the film is lower than that seen experimentally (Platikanov, 1964; Lin and Slattery, 1982a).

Hartland (1969) developed a more detailed model for the evolution of the thinning film, assuming that the shape of the drop beyond the rim did not change with time and that the configuration of the fluid-fluid interface at the center was a spherical cap. He proposed that the initial film profile be taken directly from experimental data.

Hartland and Robinson (1977) assumed that the fluid-fluid interface consisted of two parabolas, the radius of curvature at the apex varying with time in the central parabola and a constant in the peripheral parabola. A priori knowledge was required of the radial position outside the dimple rim at which the film pressure equaled the hydrostatic pressure.

For the case of a small spherical drop or bubble approaching a solid plane, the development of Lin and Slattery (1982a) is an improvement over that of Hartland (1969) and of Hartland and Robinson (1977). Since the initial and boundary conditions are more complete, less a priori experimental information is required: only the bubble radius and the physical properties. The results are in reasonable agreement with Platikanov's (1964) observations at shorter times. [Since the theory is for small spherical drops, it cannot be compared with Hartland's (1969) data for large drops.] But because their analysis neglects the effects of London-van der Waals forces, it cannot describe as well that portion of Platikanov's (1964) data concerned with the latter stage of the drainage process when these forces become significant.

In what follows, we extend Lin and Slattery's (1982a) theory for the thinning of a dimpled liquid film between a bubble and a solid plane to include the effects of London-van der Waals forces. This is the first analysis of this problem concerned with the latter stage of the drainage process when the effects of these forces are important.

STATEMENT OF PROBLEM

Figure 1 shows a bubble approaching a horizontal solid plane. Our objective is to determine the shape of the thin liquid film separating the bubble from the solid wall as a function of time and radial position.

Lin and Slattery (1982a) made a number of assumptions in considering this same problem in the context of the early stages of the coalescence process.

i) Viewed in the cylindrical coordinate system of Figure 1, the fluid-fluid interface is axisymmetric:

$$z^* = h^*(r^*,t^*) \tag{1}$$

ii) The dependence of h^* upon r^* is sufficiently weak that

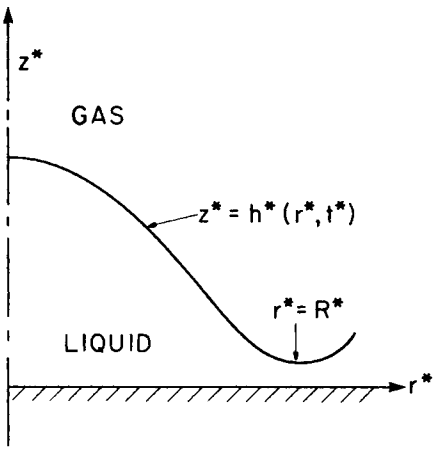

Figure 1. Configuration of a symmetric gas bubble approaching a horizontal solid plane.

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 \ll 1 \tag{2}$$

iii) Let R^* be the rim radius of the bubble:

$$\text{at } r^* = R^* = R^*(t^*): \frac{\partial h^*}{\partial r^*} = 0 \tag{3}$$

The Reynolds lubrication theory approximation applies in the sense that, if

$$h_0^* \equiv h^*(0,0) \tag{4}$$

and

$$R_0^* \equiv R^*(0) \tag{5}$$

we will require

$$\left(\frac{h_0^*}{R_0^*}\right)^2 \ll 1 \tag{6}$$

iv) If there is no surfactant present, the interfacial tension is a constant independent of position on the fluid-fluid interface and the surface viscosities are zero. We will refer to such an interface as being *mobile*.

v) If there is a surfactant present, the tangential components of velocity v^* at the fluid-fluid interface are zero and the interfacial tension gradient required to achieve this condition is very small, which has been verified for the available experimental data by Lin and Slattery (1982a). These interfaces will be termed *immobile*.

vi) Mass transfer at the fluid-fluid interface is neglected.

vii) Viscous effects are neglected within the bubble or drop phase. If the fluid-fluid interface is mobile, only a gas bubble can be considered. If the fluid-fluid interface is immobile, the analysis applies to both a gas bubble and a liquid drop, since it is reasonable to assume that all circulation within a liquid drop would be suppressed.

viii) The pressure p_o^* within the bubble or drop is independent of time and position.

ix) The continuous liquid phase is an incompressible, Newtonian fluid, the viscosity of which is a constant.

x) All inertial effects are neglected.

xi) The effects of gravity and of electrostatic forces are neglected within the draining liquid film. [In contrast with Lin and Slattery (1982a), we will account for the effect of London-van der Waals forces.]

xii) The solid wall is stationary.

xiii) We will assume that pressure within the draining film approaches its local hydrostatic value beyond the rim where the Reynolds lubrication theory approximation (assumption iii) is still valid and that at this point the principle curvatures of the bubbles are constants independent of time. There is a point $r^* = R_h^* > R^*$, where the pressure within the draining film approaches the local hydrostatic pressure in the neighborhood of the bubble and the two principal radii of curvature are constants independent of time,

$$\text{at } r^* = R_h^*: \frac{\partial h^*}{\partial r^*} = \left(\frac{\partial h^*}{\partial r^*}\right)_{t^*=0} \tag{7}$$

$$\text{at } r^* = R_h^*: \frac{\partial^2 h^*}{\partial r^{*2}} = \left(\frac{\partial^2 h^*}{\partial r^{*2}}\right)_{t^*=0} \tag{8}$$

xiv) It has been observed (Platikanov, 1964) that, during the formation of the dimple as the bubble approaches the wall, the thinning rate at the rim is higher than that at the center of the dimple. After the dimple is completely established, the thinning rate at the rim is lower than that at the center. These experimental observations suggest that there is a time at which the thinning rate at the rim is equal to the thinning rate at the center. We will assume that at time $t^* = 0$ in our computations the thinning rate is independent of radial position. We will also assume that for $t^* > 0$ the thinning rate at the center is always greater than the thinning rate at the rim, so long as the effects of any disjoining pressure are negligible.

xv) The bubble or drop is sufficiently small that it may be assumed to be spherical.

We will adopt these same assumptions and in addition say

xvi) Within the draining liquid film, the mutual force per unit mass b_m^* known as the London-van der Waals force is representable in terms of a scalar potential ϕ^*:

$$b_m^* = -\nabla\phi^* \tag{9}$$

At a planar fluid-fluid interface (Ruckenstein and Jain, 1974)

$$\rho^*\phi^* = \rho^*\phi_0^* = \Phi_B^* + \frac{B^*}{h^{*m}} \tag{10}$$

where ρ^* is the mass density of the liquid film and Φ_B^* is the interaction potential per unit volume of a semi-infinite film liquid in the limit as the fluid-fluid interface is approached. When the film thickness is less than 120 Å, $m \doteq 3$; when the film thickness is larger than 400 Å, $m \doteq 4$ (Churaev, 1974a,b). We speak of

$$\pi^* \equiv -\frac{B^*}{h^{*m}} \tag{11}$$

as the disjoining pressure of a flat film of thickness h^*. When B^* is negative, the interaction potential per unit volume of the continuous phase at the interface is lower than it would be if the continuous phase were semi-infinite. This corresponds to a positive disjoining pressure that acts to repel the fluid-fluid interface from the liquid-solid interface. Because the dependence of h^* upon r^* is weak (assumption ii), we will assume that the local value of interaction energy per unit volume of the liquid at the fluid-fluid interface is equal to that of a flat film of the same thickness.

SOLUTION

The analysis of this problem is very similar to that described by Lin and Slattery (1982a). The only change is the addition of the London-van der Waals mutual force in the equation of motion for the draining liquid film. This can be accomplished simply by replacing p^* in their equation of motion (Lin and Slattery, 1982a Eq. 14) with $(p^* + \rho^*\phi^*)$.

Following this change through their analysis, we find that the differential equation describing the configuration of the fluid-fluid interface becomes

$$-\frac{\partial h}{\partial t'} = \frac{1}{3}h^3\left(\frac{1}{3}\frac{\partial h}{\partial r} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4}\right) + h^2\frac{\partial h}{\partial r}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) - N_{ca}\frac{R_0^*}{h_0^*}\left\{\frac{1}{3}h^3\left[\frac{1}{r}\frac{\partial h}{\partial r}\frac{\partial \phi_0}{\partial h} + \frac{\partial^2 h}{\partial r^2}\frac{\partial \phi_0}{\partial h} + \left(\frac{\partial h}{\partial r}\right)^2\frac{\partial^2 \phi_0}{\partial h^2}\right] + h^2\left(\frac{\partial h}{\partial r}\right)^2\frac{\partial \phi_0}{\partial h}\right\} \tag{12}$$

where

$$h \equiv \frac{h^*}{h_0^*} \qquad r \equiv \frac{r^*}{R_0^*}$$

$$t' \equiv \frac{t^*\mu^*}{\rho^* R_0^{*2} N_{ca}} \left(\frac{h_0^*}{R_0^*}\right)^3 \left(\frac{3-n}{2n}\right)$$

$$\phi_0 \equiv \frac{\phi_0^* \rho^{*2} R_0^{*2}}{\mu^{*2}} \tag{13}$$

and the capillary number N_{ca} is defined as

$$N_{ca} \equiv \frac{\mu^{*2}}{\rho^* R_0^* \gamma_0^*} \tag{14}$$

Here

$$\begin{aligned} &\text{mobile interface:} \quad n = 1 \\ &\text{immobile interface:} \quad n = 2 \end{aligned} \tag{15}$$

μ^* is the viscosity of the liquid film and γ_0^* is the equilibrium interfacial tension.

Substituting Eq. 10 expression in terms of dimensionless variables into Eq. 12, we have

$$-\frac{\partial h}{\partial t'} = \frac{1}{3} h^3 \left(\frac{1}{r^3}\frac{\partial h}{\partial r} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4}\right) + h^2 \frac{\partial h}{\partial r}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) + \frac{mB}{3}\left[\frac{1}{r}\frac{\partial h}{\partial r}\frac{1}{h^{m-2}} + \frac{\partial^2 h}{\partial r^2}\frac{1}{h^{m-2}} - \left(\frac{\partial h}{\partial r}\right)^2 \frac{m-2}{h^{m-1}}\right] \tag{16}$$

where

$$B \equiv \frac{R_0^{*2} B^*}{\gamma_0^* h_0^{*m+1}} \tag{17}$$

Note that, after an application of L'Hospital's rule (Lin and Slattery, 1982a, Eq. 54,)

$$\text{limit } r \to 0:$$

$$-\frac{\partial h}{\partial t'} = \frac{8}{9} h^3 \frac{\partial^4 h}{\partial r^4} + \frac{2m}{3}\frac{B}{h^{m-2}}\frac{\partial^2 h}{\partial r^2} \tag{18}$$

Having been given B and m in the form of the physical properties, we can carry out the integration of Eq. 16.

Our first objective is to calculate the initial configuration of the fluid-fluid interface consistent with assumption xiv. Recognizing that the rate of thinning is dependent of radial position at the initial time, we can use Eq. 16 and 18 to say at $t' = 0$

$$\frac{8}{3}\left(\frac{\partial^4 h}{\partial r^4}\right)_{r=0} + 2mB\left(\frac{\partial^2 h}{\partial r^2}\right)_{r=0} = h^3\left(\frac{1}{r^3}\frac{\partial h}{\partial r} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4}\right) + 3h^2\frac{\partial h}{\partial r}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) + mB\left[\frac{1}{r}\frac{\partial h}{\partial r}\frac{1}{h^{m-2}} + \frac{\partial^2 h}{\partial r^2}\frac{1}{h^{m-2}} - \left(\frac{\partial h}{\partial r}\right)^2\frac{m-2}{h^{m-1}}\right] \tag{19}$$

As discussed by Lin and Slattery (1982a), we require that the result be consistent with

$$\text{at } r = 0: \frac{\partial h}{\partial r} = 0 \tag{20}$$

$$\text{at } r = 0: \frac{\partial^3 h}{\partial r^3} = 0 \tag{21}$$

$$\text{at } r = 1: \frac{\partial h}{\partial r} = 0 \tag{22}$$

and either

$$\text{as } r \to R_h: \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \to \frac{2}{R_b^*}\frac{R_0^{*2}}{h_0^*} \tag{23}$$

for a small bubble freely rising to a solid surface or

$$\text{as } r \to R_h: \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \to -\frac{p_h^* - p_0^*}{\gamma_0^*}\frac{R_0^{*2}}{h_0^*} \tag{24}$$

for a small bubble or drop formed on the tip of a capillary. Here R_b^* is the radius of the nearly spherical drop or bubble and p_h^* is the hydrostatic pressure in the continuous liquid phase.

In order to integrate a finite-difference form of Eq. 19, we replace Eq. 23 or 24 by

$$\text{at } r = 1: \frac{\partial^2 h}{\partial r^2} = C \tag{25}$$

where C is a free parameter, the value of which will be determined shortly.

For each value of C, we can determine for a given value of B a tentative initial configuration of the film by integrating Eq. 19 consistent with Eq. 20 through 22 and 25. The dimensionless radial position at which the pressure gradient becomes negligible is tentatively identified as R_h, subject to later verification that assumption ii is still satisfied at this point.

Equation 16 can be integrated consistent with each of these tentative initial configurations, Eqs. 20, 21, 7 and 8, the latter two boundary conditions first having been made dimensionless. Equation 3 permits us to identify R as a function of time; R_f is the value of R as $t' \to \infty$. We employed the Crank-Nicolson method (Myers, 1971).

In addition to requiring that at time $t^* = 0$ the thinning rate is independent of radial position, assumption xiv demands that for $t^* > 0$ the thinning rate at the center is always greater than the thinning rate at the rim, so long as the effects of any disjoining pressure are negligible. Our numerical computations indicate that for each value of $B \leqq 0$ there is a minimum value of the parameter C for which this condition is satisfied. This also corresponds to the maximum value of h_0^* for which the thinning rate at the center is always greater than the thinning rate at the rim for $t^* > 0$. We will choose this maximum value of h_0^* as our initial film thickness at the center. For sufficiently small $B > 0$, there again is a minimum value of C such that the thinning rate at the center is always greater than the thinning rate at the rim in the early stage of the thinning process where the effects of the disjoining pressure can be neglected.

For a bubble freely rising to the solid surface under the influence of the buoyancy force, R_b^* is measured and R_f^* is determined by (Derjaguin and Kussakov, 1939; Lin and Slattery, 1982a)

$$\text{as } t' \to \infty: R \to R_f = \left[\frac{2}{3}\frac{\Delta\rho^* g^* (R_0^*)^2}{\gamma_0^*}\right]^{1/2} (R_b)^2 \tag{26}$$

For a bubble formed on the tip of a capillary and forced against a solid surface, $p_h^* - p_0^*$ is measured and R_f^* is fixed by (Lin and Slattery, 1982a)

$$\text{as } t' \to \infty: R \to R_f = \left[(R_b)^2 + \frac{2R_b}{p_h N_{ca}}\right]^{1/2} \tag{27}$$

with

$$p_h \equiv \frac{(p_h^* - p_o^*)\rho^* R_0^{*2}}{\mu^{*2}} \tag{28}$$

In both cases, $R_0^* = R_f^*/R_f$.

We can determine h_0^* either from Eq. 23 for a bubble freely rising to the solid surface under the influence of the buoyancy force or from Eq. 24 for a bubble formed on the tip of a capillary and forced against a solid surface.

Having determined R_0^* and h_0^*, we can check whether assumption ii is satisfied at R_h; if it is satisfied here, it will be satisfied everywhere. It is desirable to choose R_h as large as possible, in order to make the pressure gradient at this point clearly negligible. But if R_h is assigned too large a value, assumption ii will be violated.

RESULTS

Figures 2 through 6 show the dimensionless film thickness h as a function of r and t' for $m = 4$ and varying values of B. Notice that

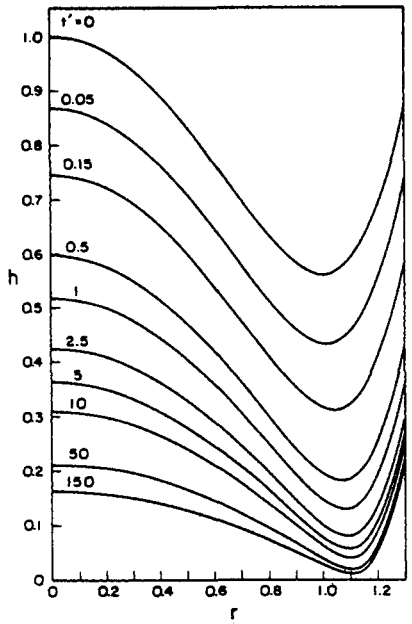

Figure 2. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for $R_h = 1.96$, $B = 0$, $C = 5.05$.

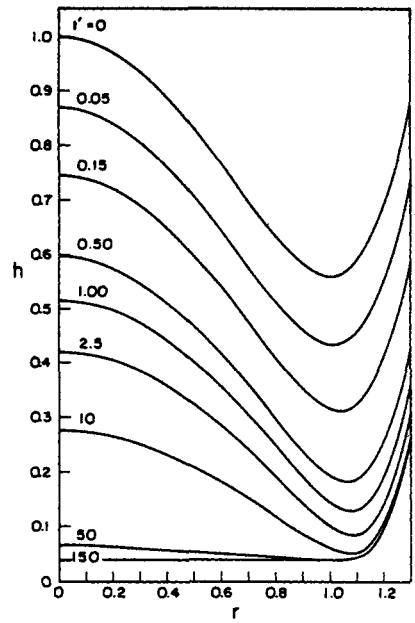

Figure 4. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for $R_h = 1.96$, $B = -3 \times 10^{-5}$, $m = 4$, $C = 5.05$.

a) The initial profiles of Figures 2 through 6 are identical, indicating the absence of the effect of the disjoining pressure. The initial profile of Figure 5 differs from the others, because the disjoining pressure is relatively large.

b) For small t', the film profiles of Figures 2 through 6 are almost identical, suggesting that for sufficiently small values of $|B|$ the effects of the disjoining pressure can be neglected during the early stage of the thinning process.

c) For sufficiently large t', the effect of the disjoining pressure becomes dominant when $|B| > 0$.

d) As $|B|$ increases for $B < 0$, the thickness of the film at the rim increases. Since a larger rim thickness offers smaller resistance to flow, the film drains faster and has a smaller center thickness.

e) As $|B|$ increases for $B < 0$, less time is required for the dimpled film to become flat and the thickness of the final film is larger. At $t' = 150$, the profiles in Figures 3 and 4 are almost flat, but the one in Figure 2 is still dimpled. In Figure 5, the film profile is almost flat at $t' = 10$.

f) For sufficiently small values of $B > 0$, the effects of the disjoining pressure can be neglected during the early stage of the thinning process and there is a minimum value of C for which assumption xiv is satisfied. In Figure 6, for $t' < 2.5$ the film profiles are almost identical to those in Figures 2 through 4, although the rim thickness reduces to zero at $t' \doteq 6.73$.

This problem is highly nonlinear and its solution must be developed numerically. There have been several recent investigations of the stability of solutions for nonlinear problems (Chapman and Proctor 1980; Barratt and Sloan 1981; Jones 1981; Neitzel and Davis 1981). We favor the approach taken by Neitzel and Davis (1981), who conducted numerical experiments. They developed an accurate, numerical solution for their two-dimensional, unsteady-state

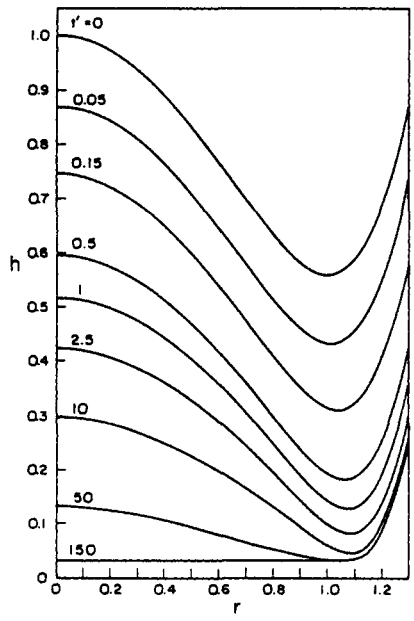

Figure 3. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for $R_h = 1.96$, $B = -10^{-5}$, $m = 4$, $C = 5.05$.

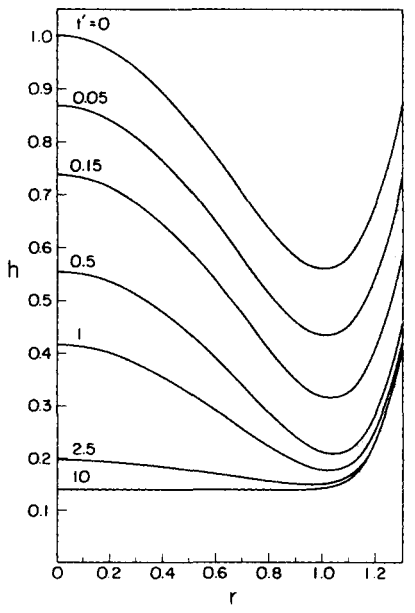

Figure 5. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for $R_h = 1.96$, $B = -0.005$, $m = 4$, $C = 5.05$.

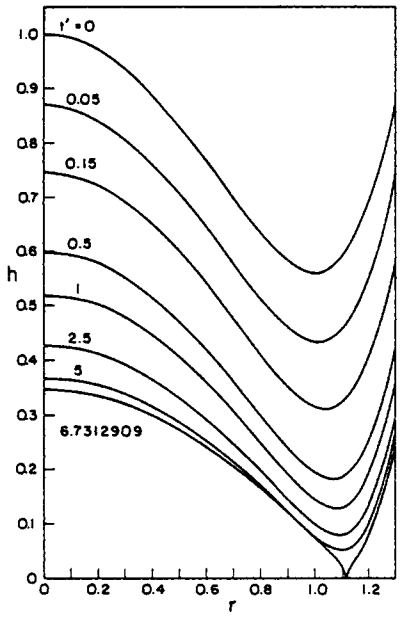

Figure 6. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for $R_h = 1.96$, $B = 10^{-5}$, $m = 4$, $C = 5.05$.

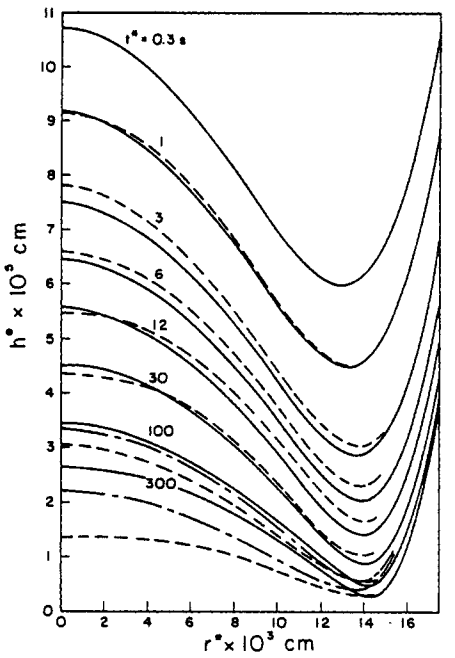

Figure 7. Comparisons of the film profiles calculated using the present theory ($R_h = 1.96$, $B = -10^{-5}$, $m = 4$, $C = 5.05$, — · —) and Lin and Slattery's theory (1982a, $R_h = 1.96$, $B = 0$, $C = 5.05$, ——) with those measured by Platikanov (1964, - - -) for 0.1 N KCl solution-air interface. Here t^* represents Platikanov's experimental time scale, and $t^* = 0.30$ s corresponds to our $t' = 0$.

problem. They imposed no external disturbances to trigger instability; the small round-off and truncation errors were sufficient, presumably constituting small disturbances. The instabilities developed automatically as a function of time in their numerical solution. In order to reduce the number of variables to be studied, they did not investigate all forms of instabilities, confining their attention to axisymmetric solutions.

Figures 2 through 5 represent the evolution of stable draining films. Figure 6, in which the disjoining pressure is negative, shows the evolution of a draining film and its subsequent rupture. This rupture may or may not be the result of the development of an instability. A numerical experiment such as this will not distinguish between the case of a unique solution and the stable member of a family of solutions. It is furthermore important to recall that we have limited our attention here to axisymmetric solutions. We have not investigated the likely development of non-axisymmetric instabilities. All we can say is that the predicted dimensionless coalescence time 6.73 . . . is an upper bound, since the development of non-axisymmetric instabilities would result in a smaller value. Unfortunately, there are no experimental data available with which to compare this prediction.

We have compared these computations with data for three systems exhibiting positive disjoining pressures studied by Platikanov (1964). He formed a small bubble on the tip of a capillary and forced it against a glass plate. The bubble was assumed to be a hemisphere (outside the immediate neighborhood of the draining film) whose radius R_b^* was the same as the radius of his capillary, 0.24 cm. Since he did not measure the bubble pressure $p_h^* - p_o^*$ and since he observed that it was difficult to maintain the rim radius R^* at a constant value for long periods of time, we matched his reported value for the rim radius R^* with an average of R (calculated using equally spaced times in the interval corresponding to his observations) to determine $R_0^* = R^*/R$. Because his first measurements in all three cases were taken after our $t' = 0$ (the time at which the rate of thinning is independent of radial position), we related our time scale to his by matching his initial measurement of film thickness at the rim. As we shall demonstrate, we found it satisfactory to identify $R_h = 1.96$ for all of these systems. Since the film thickness is large, we used $m = 4$ to describe the fully retarded London-van der Waals interaction potential in the film (Churaev, 1974a). For the 0.1 N KCl solution-air system and for the ethanol-air system, the value of B was chosen to give values for the equilibrium flat film thickness that were in good agreement with the reported experimental values. Because no value was given for the aniline-air system, the value of B was determined by comparing our calculated film thickness at the center and at the rim with the experimental data. The resulting values of B^* have the right order of magnitude (Churaev, 1974a).

0.1 N KCl Solution-Air

Platikanov (1964) reports observations for an air bubble forced against a glass plate through a continuous 0.1 N KCl solution: $\gamma_0^* = 7.27 \times 10^{-2}$ N/m and $\mu^* = 1.0 \times 10^{-3}$ Pa·s. KCl was added in order to eliminate any positive electrostatic disjoining pressure (Platikanov, 1964 footnote 10).

Since it is very difficult to produce and maintain uncontaminated aqueous solutions, we follow the suggestion of Platikanov (1964) in assuming that some surface-active material is present and $n = 2$.

Figure 7 compares our computations ($R_h = 1.96$, $B = -10^{-5}$, $m = 4$, $C = 5.05$), Lin and Slattery's (1982a) computations ($R_h = 1.96$, $B = 0$, $C = 5.05$), and Platikanov's (1964) data. The experimental values of t^* are shown. Platikanov (1964) reported that $R^* = 1.4 \times 10^{-2}$ cm for $t^* = 1$ to 300 s. We find that at our $t' = 0$ [Platikanov's (1964) $t^* = 0.30$ s] when the thinning rate is independent of position

$$R_0^* = R^*/1.1 = 1.273 \times 10^{-2} \text{ cm}$$
$$h_0^* = h^*(0,0) = 1.068 \times 10^{-4} \text{ cm}$$
$$B^* = -6.234 \times 10^{-29} \text{ J·m}$$

and

$$\left(\frac{h_0^*}{R_0^*}\right)^2 = 7.04 \times 10^{-5}$$

which means that the Reynolds lubrication theory approximation (assumption iii) is applicable. The first reported experimental data are for a later time (his experimental $t^* = 1$ s) at which the centerline film thickness is 9.1×10^{-5} cm. Notice that the thinning rate is still nearly independent of radial position for his initial profile.

At $r = R_h = 1.96$,

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 = 4.98 \times 10^{-3}$$

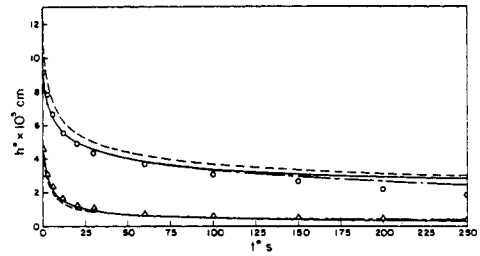

Figure 8. Comparisons of the predictions of the present theory (— · —), Lin and Slattery's theory (1982a, ——), and Frankel and Mysels' theory (1962, $n = 2$, - - -) with Platikanov's (1964) experimental h^*_{center} (○) and h^*_{rim} (△) for 0.1 N KCl solution-air interface. Here t^* represents Platikanov's experimental time scale.

which means that assumption ii is still satisfied at this point.

Figure 7 shows that at short times ($t^* < 30$ s) when the film thickness is larger than the distance over which the London-van der Waals forces are effective, our predictions are identical with those of Lin and Slattery (1982a). But at long times ($t^* > 100$ s) our theory predicts larger rim thicknesses, smaller center thicknesses, and more rapid drainage than that of Lin and Slattery (1982a). This is attributable to the London-van der Waals component of the positive disjoining pressure, the effect of which is more pronounced at longer times when the film thickness is smaller.

Platikanov (1964) observed that after a long period of time the dimple completely disappeared and a 300 Å equilibrium film was formed. From our computations, we find that the dimpled thinning film assumes a uniform thickness of 317 Å when $t' \doteq 320$ [Platikanov's (1964) $t^* = 3{,}795$ s].

Figure 8 shows that the present theory is an improvement over that given by Frankel and Mysels (1962).

Aniline-Air

Platikanov (1964) studied an air bubble forced against a glass plate with aniline as the continuous phase:

$$\gamma_0^* = 3.7 \times 10^{-2}\ \text{N/m and } \mu^* \doteq 4.48 \times 10^{-3}\ \text{Pa·s.}$$

Because of the likely presence of contaminants, we again assumed an immobile interface with $n = 2$.

Figure 9 compares our computations ($R_h = 1.96$, $B = -3 \times 10^{-5}$, $m = 4$, $C = 5.05$), Lin and Slattery's (1982a) computations ($R_h =$ 1.96, $B = 0$, $C = 5.05$), and Platikanov's (1964) data at longer times. At shorter times, the present theory coincides with that of Lin and Slattery (1982a), who also give a comparison with Platikanov's (1964) data. The experimental values of t^* are shown. Platikanov (1964) reported that $R^* = 1.6 \times 10^{-2}$ cm for $t^* = 1$ to 900 s. We find that at our $t' = 0$ [Platikanov's (1964) $t^* = 2.06$ s]

$$R_0^* = R^*/1.1 = 1.455 \times 10^{-2}\ \text{cm}$$
$$h_0^* = 1.39 \times 10^{-4}\ \text{cm}$$
$$B^* = -2.72 \times 10^{-28}\ \text{J·m}$$

and

$$\left(\frac{h_0^*}{R_0^*}\right)^2 = 9.13 \times 10^{-5}$$

consistent with the Reynolds lubrication theory approximation (assumption iii). At $r = R_h = 1.96$,

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 = 6.46 \times 10^{-3}$$

which shows that assumption ii was not violated.

We predict that the dimpled thinning film attains a uniform thickness of 544 Å at $t' \doteq 150$ [Platikanov's (1964) $t^* \doteq 11{,}956$ s].

The present theory is superior to that given by Frankel and Mysels (1962) as shown in Figure 10.

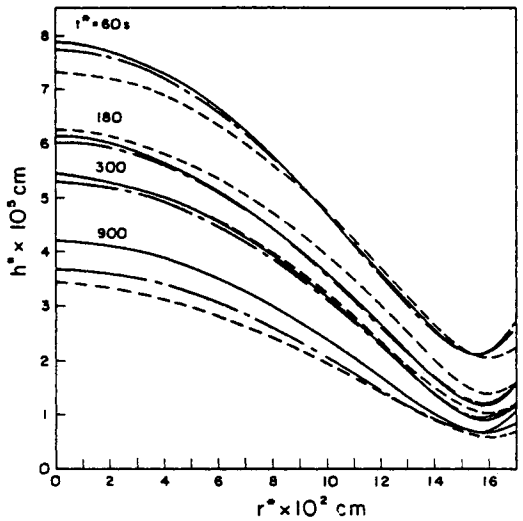

Figure 9. Comparisons of the film profiles calculated using the present theory ($R_h = 1.96$, $B = -3 \times 10^{-5}$, $m = 4$, $C = 5.05$, — · —), and Lin and Slattery's theory (1982a, $R_h = 1.96$, $B = 0$, $C = 5.05$, ——) with those measured by Platikanov (1964, - - -) for aniline-air interface. Here t^* represents Platikanov's experimental time scale, and $t^* = 2.06$ s corresponds to our $t' = 0$.

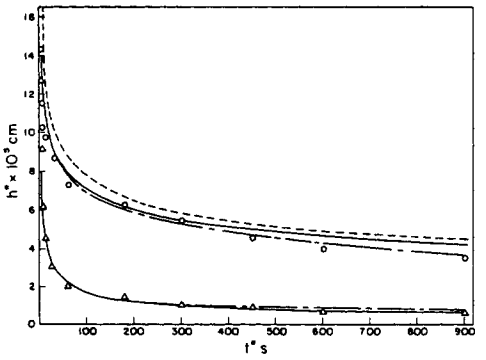

Figure 10. Comparisons of the predictions of the present theory (— · —), Lin and Slattery's theory (1982a, ——), and Frankel and Mysels' theory (1962, $n = 2$, - - -) with Platikanov's (1964) experimental h^*_{center} (○) and h^*_{rim} (△) for aniline-air interface. Here t^* represents Platikanov's experimental time scale.

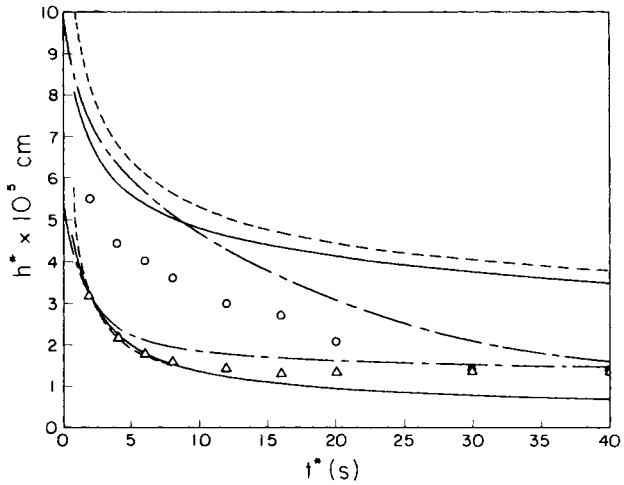

Figure 11. Comparisons of the predictions of the present theory ($R_h = 1.96$, $B = -0.004$, $m = 4$, $C = 4.5$, — · —), Lin and Slattery's theory (1982a, $R_h = 1.96$, $B = 0$, $C = 5.05$, ——), and Frankel and Mysels' theory (1962, $n = 1$, - - -) with Platikanov's (1964) experimental h^*_{center} (○) and h^*_{rim} (△) for ethanol-air interface. Here t^* represents Platikanov's experimental time scale.

Ethanol-Air

Platikanov (1964) observed an air bubble forced against a solid surface through a continuous phase of ethanol:

$$\gamma_0^* = 2.23 \times 10^{-2}\ N/m \text{ and } \mu^* = 1.20 \times 10^{-3}\ Pa{\cdot}s.$$

Since pure ethanol was used, we could expect a mobile interface for which $n = 1$.

Figure 11 compares the film thickness at the center and at the rim as measured by Platikanov (1964) with the predictions of the present theory ($R_h = 1.96$, $B = -0.005$, $m = 4$, $C = 5.05$), of Lin and Slattery (1982a) ($R_h = 1.96$, $B = 0$, $C = 5.05$), and of Frankel and Mysels (1962). Platikanov (1964) reported that $R^* = 1.25 \times 10^{-2}$ cm for $t^* = 4$ to 30 s. We find that at our $t' = 0$ [Platikanov's (1964) $t^* = 0.1$ s]

$$R_0^* = R^*/1.01 = 1.238 \times 10^{-2}\ \text{cm}$$
$$h_0^* = 1.000 \times 10^{-4}\ \text{cm}$$
$$B^* = -7.28 \times 10^{-27}\ \text{J·m}$$

and

$$\left(\frac{h_0^*}{R_0^*}\right)^2 = 6.52 \times 10^{-5}$$

consistent with the Reynolds lubrication theory approximation (assumption iii). At $r = R_h = 1.96$,

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 = 4.67 \times 10^{-3}$$

indicating that assumption ii was satisfied.

Platikanov (1964) suggested that the rapid rate of thinning was attributable to a positive disjoining pressure. He observed that after $t^* = 30$ s the dimple disappeared and a 1,400 Å equilibrium film was formed. Our computations predict that the dimpled thinning film attains a uniform thickness of 1,407 Å at $t' \doteq 8$ [Platikanov's (1964) $t^* \doteq 100$ s].

ACKNOWLEDGMENT

The authors are grateful for financial support by the U.S. Department of Energy (Contract No. DE-AC19-79BC10068).

NOTATION

b_m^* = mutual force per unit mass
B^* = parameter in Eq. 10
B = defined by Eq. 17
C = parameter in Eq. 25
g^* = magnitude of the acceleration of gravity
h^* = film thickness
h = dimensionless film thickness defined by Eq. 13
h_0^* = film thickness at $t^* = 0$ and $r^* = 0$
h_{center}^* = film thickness at $r^* = 0$
h_{rim}^* = film thickness at the rim
m = parameter in Eq. 10
n = defined by Eq. 15
N_{ca} = capillary number defined by Eq. 14
p^* = pressure in liquid film
p_h^* = hydrostatic pressure in the continuous liquid phase
p_h = dimensionless hydrostatic pressure, defined by Eq. 28
p_o^* = pressure within the bubble or drop
r^* = cylindrical coordinate
r = dimensionless cylindrical coordinate defined by Eq. 13
R^* = rim radius of the bubble or drop
R = dimensionless rim radius defined as R^*/R_0^*
R_b^* = radius of the bubble or drop
R_b = dimensionless radius of the bubble or drop defined as R_b^*/R_0^*
R_f^* = dimple radius as $t' \to \infty$ or just prior to the development of an instability and coalescence
R_f = dimensionless dimple radius as $t' \to \infty$ or just prior to the development of an instability and coalescence, defined as R_f^*/R_0^*
R_h^* = radial position where the pressure p^* within the draining film approaches the local hydrostatic pressure in the neighborhood of the bubble or drop
R_h = dimensionless radial position where the pressure p^* within the draining film approaches the local hydrostatic pressure in the neighborhood of the bubble or drop, defined as R_h^*/R_0^*
R_0^* = rim radius of the bubble or drop at $t^* = 0$
t^* = time
t' = dimensionless time defined by Eq. 13
v^* = velocity vector
z^* = cylindrical coordinate

Greek Letters

γ_0^* = equilibrium surface tension
μ^* = bulk viscosity of liquid film
ρ^* = density of liquid film
$\Delta\rho^*$ = density difference between the two fluid phases
ϕ^* = potential energy per unit mass of the liquid film
ϕ_0^* = ϕ^* evaluated in the limit as the fluid-fluid interface is approached
ϕ_0 = dimensionless quantity defined by Eq. 13
ϕ_B^* = potential energy per unit volume of the semiinfinite film liquid in the limit as the fluid-fluid interface is approached
π^* = disjoining pressure, defined by Eq. 11

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Manuscript received October 8, 1981, and accepted February 22, 1982.

Stripping of Carbon Dioxide from Monoethanolamine Solutions in a Packed Column

A procedure using only fundamental physico-chemical data is developed for the design and analysis of packed columns used for solvent recovery in gas purification processes involving chemical reaction. The results of 173 experiments on the mass transfer performance of a pilot-scale regenerator stripping CO_2 from loaded monoethanolamine solutions are reported and compared with model predictions. Anomolous responses of the overall mass transfer coefficient to changes in process conditions are observed and explained by the process model which is found to predict correctly both the magnitude of the coefficient and its response.

R. H. WEILAND
Department of Chemical Engineering
Clarkson College of Technology
Potsdam, NY 13676

M. RAWAL
Combustion Department
Australian Iron and Steel Pty. Ltd.
Wollongong, NSW 2500, Australia

R. G. RICE
Department of Chemical Engineering
Louisiana State University
Baton Rouge, LA 70803

SCOPE

The literature on gas absorption into chemically-reactive solution is vast and the fundamentals of the process are well understood. Most gas purification plants, however, require the solvent to be regenerated, yet the stripping operation has been studied hardly at all despite the fact that it is the major cost component in impurity removal processes. Recently, Astarita and Savage (1980a) have shown that the theory of absorption can be applied to desorption with only mild restrictions. Desorption is considerably more complicated, however, because in stripping one must account always for the reversibility of the chemical reactions so that chemical thermodynamics invariably enters into the calculations.

Sufficient appears to be known to permit the design of packed *absorbers* from first principles. Here we examine the design of packed strippers using fundamental physico-chemical data as our primary basis, and a detailed procedure for the design of new columns and the analysis of existing ones emerges. Then we present an extensive set of measurements of mass transfer coefficients obtained in a pilot-scale regenerator using the carbon dioxide—aqueous monoethanolamine system. These results are compared with theoretical predictions. The effect of several operating variables on stripping column performance are evaluated and the sometimes counterintuitive results are explained through a detailed analysis of the way in which a change to one variable can simultaneously affect several others.

CONCLUSIONS AND SIGNIFICANCE

The two-film model of Whitman (1923) forms the basis of a procedure for the design of packed regeneration columns used

Correspondence concerning this paper should be addressed to R. H. Weiland.