DRAINAGE OF EMULSION AND FOAM FILMS IN SCHELUDKO-EXEROWA CELLS

J. Coons^{*}, P. Halley **, S. McGlashan^{**}, and T. Tran-Cong^{***}

*Los Alamos National Laboratory, P.O. Box1663, MS C930 Los Alamos, NM 87545, USA

**Department of Chemical Engineering, University of Queensland, St. Lucia, QLD 4072, Australia

***Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia

<u>Summary</u> Here the Maney-Tsekov-Radoev (MTR) drainage theory in the form of a semi-empirical equation is shown to be the most consistent with existing drainage time data from emulsion and foam films.

INTRODUCTION

Thin liquid films (TLFs) are fundamental components in a variety of industrial processes including foam manufacturing, oil exploration, and the growth of bio-organisms. Improved understanding of the drainage is essential for accurate predictions of the stability and lifetime of a film. Numerous fundamental studies of thin films have been conducted in specially designed capillary cells, referred to as Scheludko-Exerowa cells, in which a biconcave foam or emulsion film is created by suspension of a thin film across the capillary. A foam film is surrounded by a gas and an emulsion film is surrounded by an immiscible liquid. The capillary tube is permeable to permit the drainage and thinning of the film. Coupled with optical probes, the film thickness can be measured with high precision. In this paper, predictions of drainage times from the lubrication theory of Reynolds [1] and the theory of Manev et al [2], referred to as the Manev-Tsekov-Radoev (MTR) theory, are compared to experimental measurements obtained from numerous investigators. The objective of the comparison is to determine the extent to which drainage theory is consistent with the body of thin film measurements. MTR theory is represented with the original equation derived by Manev et al and a semi-empirical equation recently described by Coons et al [3]. It is shown that the semi-empirical MTR equation is most consistent with available data, and the Reynolds equation and theoretical MTR equation provide effective upper and lower bounds of drainage times, respectively.

THEORY

Reynolds [1] simplified the Navier-Stokes equations to describe the flow of a viscous liquid being squeezed between two rigid surfaces. In a geometry analogous to a TLF, each surface is circular and the film has the shape of a cylinder. The film thickness decreases with time as a consequence of a force acting between the film surfaces. Application of lubrication theory where the surfaces are nearly plane parallel and no slip occurs at the interfaces leads to the Reynolds equation for the film thinning velocity.

$$V_{\rm Re} = -dh/dt = 2h^3 \Delta P/3 \mu R^2$$

h is the average film thickness, ΔP is the average radial pressure drop across the film, R is the film radius, and μ is the bulk viscosity of the film. In a Scheludko-Exerowa cell, a cylindrical film forms in the center of the biconcave film spanning the capillary tube. The liquid pressure at the perimeter of the film is reduced due to the interfacial curvature. The reduced pressure causes the film to drain and the film thickness decreases. As the thickness approaches a few hundred nanometers, long range van der Waals forces become significant. These forces are attractive in nature and act to increase the intrafilm pressure. Under the conditions described, the average pressure drop in a TLF is given by the following expression.

$$\Delta P = 2\sigma \left(\frac{R_c}{R_c^2 - R^2}\right) + \frac{A}{6\pi h^3}$$

A is the Hamaker constant, R_c is the radius of the capillary tube, and σ is the interfacial tension. In a free standing TLF, the interfaces are not rigid and the non-uniform film pressure causes the interface to deform. Hence, the interfaces bounding TLFs become corrugated and nonparallel as thinning proceeds. Radoev et al [4] was the first to report the size and behavior of the hydrodynamic corrugations. They found that the amplitude is proportional to the radius of the film and independent of the film thickness. The drainage theory of Manev et al [2] assumes that the local film thickness is a homogeneous function of the average film thickness and the pressure drop across a corrugated film is directly proportional to the driving pressure divided by the square root of the eigenvalue of the dominant waveform. These assumptions lead to the following expression for the thinning velocity.

$$V = V_{\rm Re} l^{3/2}$$

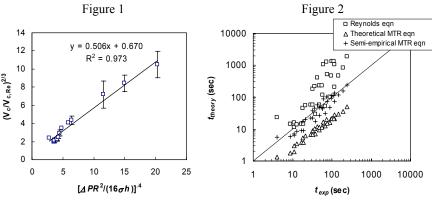
MTR theory provides the following theoretical expression for *l*, the number of domains or extrema in the film.

$$l = \left[\frac{\Delta P}{h\sigma} \left(\frac{R}{4} \right)^2 \right]^{2/5}$$

Use of the above expression for the number of domains in the MTR thinning velocity equation is referred to as the theoretical MTR equation. As is shown in Figure 1, a comparison has been reported [3] between the theoretical domains and the thinning velocity ratio at the critical point of rupture using the data of Radoev et al [4]. The data suggest a different proportionality, which is adequately represented by the following semi-empirical equation.

$$l = \frac{1}{2} \left\{ \left[\frac{\Delta P}{h\sigma} \left(\frac{R}{4} \right)^2 \right]^{2/5} + \frac{4}{3} \right\}$$

This semi-empirical form of the MTR equation provides significantly different thinning velocities in comparison to the theoretical MTR equation. Both equations predict that thick films drain in accordance to Reynolds equation. However, the thickness at which the thinning velocity deviates from the Reynolds equation differs. The semi-empirical MTR equation predicts this deviation will occur slightly prior to the theoretical MTR equation, i.e. at larger film thicknesses. However, shortly after this Reynolds thickness is traversed, the theoretical MTR equation predicts faster thinning velocities in comparison to the semi-empirical form. It has also been shown [3] that the theoretical MTR expression for the number of domains goes to 2/3 when ΔP is dominated by the van der Waals term, which leads to sub-Reynolds thinning velocities. Under the same conditions, the semi-empirical MTR equation goes to unity suggesting that the film drains in accordance with the Reynolds equation. The condition of the driving pressure being dominated by the van der Waals component leads to the lowest possible Reynolds thickness for a given film. A major conclusion of the MTR theory is that no TLF is able to drain to the point of rupture and maintain a thinning velocity consistent with Reynolds equation [3].



RESULTS

The purpose of this paper is to compare predictions of the Reynolds, theoretical MTR, and semi-empirical MTR equations to experimental measurements on thin films from the literature. All films were studied under conditions in which the interfaces were tangentially immobile. Drainage time between two thicknesses was calculated by integration of the following equation.

$$t_d = \int_{h_{-}}^{h_{\text{max}}} \frac{dh}{V}$$

Further details including the physicochemical properties are provided elsewhere [5]. Results are shown in Figure 2.

CONCLUSIONS

The semi-empirical form of the MTR equation was found to be more accurate in predicting the drainage times of a variety of emulsion and foam films. This reinforces the validity of the drainage theory proposed by Manev et al [2].

References

- [1] Reynolds, O.: On the Theory of Lubrication and Its Application to Mr. Beachamp Tower's Experiments, including an Experimental Determination of the Viscosity of Olive Oil, *Philos. Trans. R. Soc. London*, **177**, 157-234, 1886.
- [2] Manev, E., R. Tsekov and B. Radoev: Effect of Thickness Non-Homogeneity on the Kinetic Behaviour of Microscopic Foam Films, *J. Dispersion Sci. Technol.*, **18**, 769-788, 1997.
- [3] Coons, J.E., P.J. Halley, S.A. McGlashan and T. Tran-Cong: Review of Drainage and Spontaneous Rupture in Free Standing Thin Films with Tangentially Immobile Interfaces, *Adv. Colloid Interface Sci.*, **105**, 3-62, 2003.
- [4] Radoev, B.P., A.D. Scheludko and E.D. Manev: Critical Thickness of Thin Liquid Films: Theory and Experiment, J. Colloid Interface Sci., 95, 254-265, 1983.
- [5] Coons, J.E., P.J. Halley, S.A. McGlashan and T. Tran-Cong: A Bounding Analysis of Spontaneous Rupture in Thin Films. I. Film Drainage, *in preparation*.