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Publisher Taylor & Francis

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## Tribology Transactions

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713669620>

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First Published on: 01 May 2009

**To cite this Article** Gernon, Michael D., Alford, Daniel, Dowling, Conor M. and Franco, Gerald P. (2009) 'Enhancing Oil/Water Emulsion Stability: The Use of Capillary Contact Angle Measurements to Determine Liquid/Liquid Interfacial Tensions between Aqueous Alkanolamine Solutions and Oils', *Tribology Transactions*, 52:3, 405 — 414

**To link to this Article:** DOI: 10.1080/10402000802687882

**URL:** <http://dx.doi.org/10.1080/10402000802687882>

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# Enhancing Oil/Water Emulsion Stability: The Use of Capillary Contact Angle Measurements to Determine Liquid/Liquid Interfacial Tensions between Aqueous Alkanolamine Solutions and Oils

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*Simple capillary contact angle measurements have been used to determine the liquid/liquid interfacial tension between some aqueous alkanolamine solutions and three organic liquids. Digital photography and constructive geometry techniques were used in order to obtain reproducible contact angle measurements from capillary systems. The relationship of liquid/liquid interfacial tension to emulsion stability was explored, and higher molecular weight alkanolamines were shown to yield aqueous solutions with lower water/oil interfacial tension. The importance of measuring oil/aqueous interfacial tensions as part of an overall emulsion study was demonstrated.*

## KEY WORDS

Interfacial Tension; Interfacial Tension Measurement; Surface Tension; Emulsion; Emulsion Stability

## INTRODUCTION

The determination of liquid/liquid interfacial tensions between aqueous solutions and oils is useful for understanding the stability of oil/water emulsions. The emulsification of a dispersed phase within a continuous phase entails a large increase in the total area of surface contact between the two phases. This increased surface contact increases the internal energy of the system and leads to an inherently unstable situation that attempts to rectify itself by coalescence of the two phases. Various forms of kinetic stabilization can be used to create emulsions that last long enough to be useful, but these methods do not alter the underlying instability of the emulsion. Decreasing the interfacial tension between the two phases increases the inherent (thermodynamic) stability of the emulsion. If the interfacial tension can be lowered to the point where the mixing entropy exceeds the enthalpic surface contact energy, then the emulsion will become inherently stable.

A complete picture of the structure and stability of an oil/water emulsion requires a measurement of the liquid/liquid interfacial tension in the system. A few methods for the measurement of li-

quid/liquid interfacial tension are known, but these methods are either difficult to employ and/or are prone to being inaccurate. All currently known liquid/liquid interfacial tension measurement methods employ some sort of drop shape/weight analysis. For example, Harkens and Humphery reviewed an early use of the drop weight method in 1915 (Harkins and Humphery (1)-(4)). The pendant drop method was employed by Butler to measure the interfacial tension between water, mercury, and benzene (Butler (5)). The pendant drop method was also applied by Donahue and Bartell to measure the interfacial tension between water and a number of organic liquids (Donahue and Bartell (6)). In more recent work, Hool and Schuchardt have developed automated instrumentation for liquid/liquid interfacial tension measurement based on the drop weight method (Hool and Schuchardt (7)).

A number of current approaches to the evaluation of drop shape and/or related contact angles employ digital photography coupled with image expansion techniques (Bhatia, et al. (8)). Digital image manipulation effectively alleviates many of the traditional problems associated with obtaining accurate contact angles from hanging drops, drops on tables, and/or the meniscus within a capillary tube. Drop shape/weight analysis has the advantage of providing for a direct measurement of liquid/liquid interfacial tension while the indirect use of contact angles has the advantage of experimental simplicity and ease of use. The paper by Girifalco and Good provides an excellent example of how a theoretical relationship between surface tension (air/liquid interfacial tension) and liquid/liquid interfacial tension can be developed (Girifalco and Good (9)).

In this article, we have used contact angles measured from the meniscus developed within a capillary tube as the means for calculating liquid/liquid interfacial tensions. A number of detailed theoretical treatments of the capillary rise phenomenon have been published, but none of these provide a good method for conveniently measuring liquid/liquid interfacial tension (Fan, et al. (10)). The method described herein employs an interpretation of capillary data in terms of a triphasic equilibrium at the liquid/glass/air junction. A spherical approximation of the shape of the liquid meniscus within the capillary tube was used as a means of obtaining a more accurate contact angle. Note that a number of textbooks offer a broad coverage of many aspects of interfacial tension and

the stability of colloidal systems (Adamson and Gast (11); Tsujii (12); Hiemenz and Rajagopalan (13); Hunter (14)).

## EXPERIMENTAL SECTION

### Surface Tension Measurements

The air/liquid surface tensions were measured by the maximum bubble pressure method on a Sita online t60 bubble tensiometer. The bubble life was one second. The sample size was less than 4 mL, and a slow bubble rate was used to keep the liquid level constant. Ten bubbles were averaged per reading with five readings taken per sample for a total of 50 readings per sample. All surface tension measurements were taken at 20°C.

### Solution Density Measurement

Solution densities were obtained using an Anton Parr Density Meter (model number DMA 4500). The density meter sample loop was rinsed with IPA and DI water and air-dried between samples. All density measurements were taken at 20°C.

### Contact Angle Determination

The contact angle photos were taken using a 5 megapixel Kodak digital camera. The camera was positioned on a tripod 4 in away from the capillary tube containing the sample. The camera was set in macro mode with flash and spot focus. No zoom was used. The capillary tubes were the Drummond Microdispenser (100–200  $\mu$ L) type. The capillary tubes were dipped into the aqueous phase and withdrawn from the liquid with the top of the capillary sealed. The bottom of the capillary was then capped with a rubber septum and the top opened to the atmosphere. For triphasic contact angles, the oil phase was layered on top of the aqueous phase using an 18 gauge stainless steel flat-tip syringe needle. All contact angle determinations were taken at 20°C.

### Emulsion Stability Measurements

The emulsion stability measurements were started by adding 18 g of the aqueous phase to a 9 dram glass vial. The liquid level was then marked to give a point of reference. Next, 20 mL of the oil phase was layered on top of the aqueous phase, and the vial was shaken vigorously for 30 s. The dispersions were set on a bench, and the time it took for the two mixed phases to separate was measured with a stopwatch. The time necessary for the phase separation to reach within  $1/2$  in of the original reference line was taken as the separation time. The density of the relevant pure phases and solutions at the temperature of the measurement (20°C) is as follows: Soybean (soybean oil, density = 0.919 g/mL), Me Ole (methyl oleate, density = 0.874 g/mL), dodecane (density = 0.750 g/mL), 5% BAE (5% aqueous 2-butylethanolamine, density = 0.99557), 5% BDEA (5% aqueous N-butyl-diethanolamine, density = 0.99942), 5% AMP (5% aqueous 2-amino-2-methyl-1-propanol, density = 0.99704), 5% MAE (5% aqueous methylaminoethanol, density = 0.99728), 5% DGA (5% aqueous diglycolamine, density = 1.00226), 5% MEA (5% aqueous monoethanolamine, density = 0.99955), 5% TEA (5% aqueous triethanolamine, density = 1.00525). All emulsion stability determinations were carried out isothermally at 20°C.

### Drop Weight Measurements

Solution drop weights were obtained with a glass pipette having a known orifice radius at the tip. The aqueous phase was carefully dripped into 20 mL of the oil phase in a 9 dram vial from a point approximately 1" below the surface of the nonpolar phase. The bulb of the pipette was gently squeezed to slowly expel five drops of liquid over a period of 10 s. A constant pressure was maintained on the pipette bulb during dispensing in order to prevent any liquid from being pulled back into the pipette. The drop weights were taken on an analytical balance. All drop weight measurements were made at 20°C.

## RESULTS AND DISCUSSION

### Development of the Measurement Method: The Shape of a Capillary Meniscus

In this paper, contact angles measured in a capillary tube are used to calculate the liquid/liquid interfacial tensions. For the purpose of obtaining the necessary contact angles, a spherical approximation of the shape of a capillary meniscus is employed. A description of the spherical approximation of meniscus shape is given in the Appendix. With the spherical approximation, one can calculate the surface area changes that occur as the shape of the meniscus is altered due to the balance of interfacial tensions. If there was no interfacial tension, then the liquid in a capillary tube would lay flat without a meniscus. The total change in the interfacial surface area between the theoretical flat case, where no interfacial tension exists, and the actual case with a meniscus is used as the basis for calculating the liquid/liquid interfacial tension.

### Development of the Measurement Method: Energy Balance Equation for a Meniscus

The energy balance equation for the change in the interfacial area within a capillary tube is given by Eq. [1] ( $\gamma \equiv$  interfacial tension, G = gas, L = liquid, S = solid,  $\Delta A_{G/S}$  = surface area change of gas/solid interface,  $\Delta A_{L/S}$  = surface area change of liquid/solid interface, and  $\Delta A_{G/L}$  = surface area change of gas/liquid interface):

$$\gamma_{G/S}(\Delta A_{G/S}) = \gamma_{L/S}(\Delta A_{L/S}) + \gamma_{G/L}(\Delta A_{G/L}) \quad [1]$$

Plugging in values for the surface area changes that occur as a meniscus forms yields Eq. [2] ( $r$  = radius of capillary,  $h$  = height of meniscus, and  $\theta$  = contact angle; see Appendix for details):

$$\gamma_{G/S}(2\pi rh) = \gamma_{L/S}(2\pi rh) + \gamma_{G/L}(2\pi hr \tan \theta + 2\pi h^2 - \pi r^2) \quad [2]$$

The spherical approximation of the meniscus shape also provides (see Appendix) Eq. [3]:

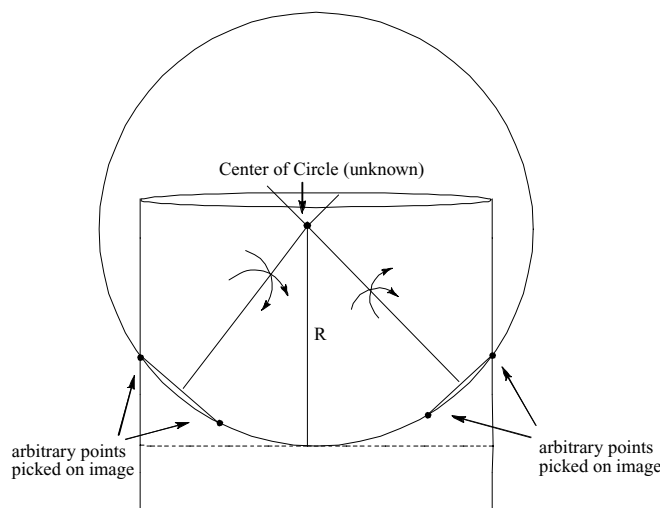
$$h = r \left\{ \frac{1}{\cos \theta} - \tan \theta \right\} \quad [3]$$

A rearrangement of Eq. [2] using Eq. [3] yields Eq. [4]:

$$\begin{aligned} \gamma_{G/S} &= \gamma_{L/S} + \gamma_{G/L} \{ 1/(\cos \theta) - 1/2 \cos \theta / (1 - \sin \theta) \} \\ &= \gamma_{L/S} + \gamma_{G/L} f(\theta) \end{aligned} \quad [4]$$

$$f(\theta) = \frac{1}{\cos \theta} - \frac{1}{2} \left\{ \frac{\cos \theta}{1 - \sin \theta} \right\}$$

It should be noted that both  $h$  and  $r$  have dropped out of Eq. [4].



**Fig. 1**—Two sets of points are selected along the visible arc as shown. A straight line is drawn between the points. Two compass arcs are swung from each point set to an intersection point. The halfway points along the straight segments are marked, and a straight line is drawn from the halfway point through the compass intersection. The point where these two lines intersect is the center of the meniscus circle. The length from the center of the circle to the circumference is measured as  $R$  in the expanded image. The length between the two meniscus edges, again as measured in the expanded image, is  $2r$ . The contact angle is determined from the relationship  $\text{Cos}\theta = r/R$ .

### Development of the Measurement Method: Isolating the Liquid/Liquid Interfacial Tension

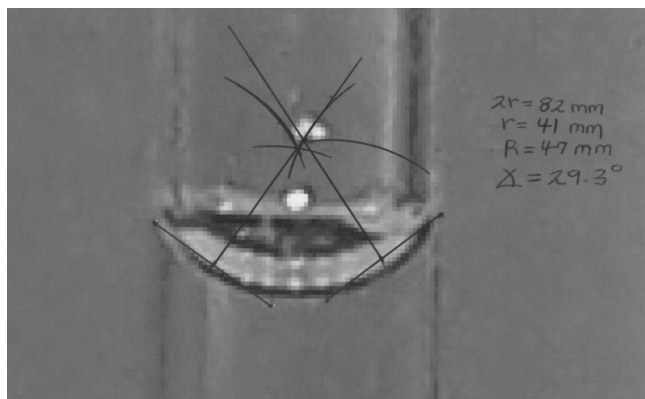
Consider the contact angle for an aqueous solution of interest in contact with air. From Eq. [4] above:

$$\gamma_{\text{Air/Glass}} = \gamma_{\text{Solution/Glass}} + f(\theta)\gamma_{\text{Air/Solution}} \quad [5]$$

Consider the contact angle for an oil of interest in contact with air. From Eq. [4] above:

$$\gamma_{\text{Air/Glass}} = \gamma_{\text{Oil/Glass}} + g(\theta)\gamma_{\text{Air/Oil}} \quad [6]$$

Now consider a similar contact angle measurement for a system wherein the oil (nonpolar liquid) of interest is layered directly on



**Fig. 2**—Calculation of the contact angle for DI water (deionized water) in contact with air inside a capillary tube.

**TABLE 1**—ROOM TEMPERATURE LIQUID/AIR SURFACE TENSIONS IN MILLINEWTONS PER METER (EQUIVALENT TO DYNES/CM)

Concentration (% wt/wt)	BAE	BDEA	AMP	DGA	MAE	MEA	TEA
0.5	59.8	60.1	70.4	72.1	70.7	72.3	70.2
1.0	52.8	54.8	68.8	70.9	69.7	72.3	70.1
5.0	37.9	41.0	60.6	68.0	64.6	70.6	66.6
50	29.8	33.4	41.3	55.6	46.0	60.7	54.8

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

BDEA = N-butyl-diethanolamine (available as Synergex<sup>®</sup> T from Taminco, Allentown, PA).

AMP = 95% (aq) solution of 2-amino-2-methyl-1-propanol (available from Dow Chemicals, Midland, MI).

MAE = Methylaminoethanol (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

DGA = Diglycolamine (product of Huntsman Corporation, Salt Lake City, UT).

MEA = Monoethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

TEA = Triethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

top of the aqueous solution of interest in a capillary tube. The corresponding energy balance equation for the new interface is given by Eq. [7]:

$$\gamma_{\text{Oil/Glass}} = \gamma_{\text{Solution/Glass}} + h(\theta)\gamma_{\text{Oil/Solution}} \quad [7]$$

Combining Eqs. [5], [6], and [7] provides the necessary relationship for obtaining the interfacial tension between the nonpolar liquid and the aqueous solution (designated  $\gamma_{\text{Oil/Solution}}$ ), as given by Eq. [8]:

$$\begin{aligned} \gamma_{\text{Oil/Glass}} - \gamma_{\text{Solution/Glass}} &= h(\theta)\gamma_{\text{Oil/Solution}} \\ &= f(\theta)\gamma_{\text{Air/Solution}} - g(\theta)\gamma_{\text{Air/Oil}} \end{aligned} \quad [8]$$

The rearrangement of Eq. [8] yields Eq. [9]:

$$\gamma_{\text{Oil/Solution}} = 1/h(\theta)\{f(\theta)\gamma_{\text{Air/Solution}} - g(\theta)\gamma_{\text{Air/Oil}}\} \quad [9]$$

$f(\theta)$  is the geometric term of Eq. [4] with the contact angle between the aqueous solution and air.

$g(\theta)$  is the geometric term of Eq. [4] with the contact angle between the oil and air.

$h(\theta)$  is the geometric term of Eq. [4] with the contact angle between the aqueous solution and the oil.

**TABLE 2**—ROOM TEMPERATURE LIQUID/AIR SURFACE TENSIONS IN MILLINEWTONS PER METER (EQUIVALENT TO DYNES/CM)

Oil	Surface Tension (dynes/cm)
Soybean Oil	54.8
Methyl Oleate	34.6
Dodecane	39.3

Note: The soybean oil (SB), methyl oleate (MeOle), and dodecane (DOD) were obtained from Sigma-Aldrich Chemical Company.

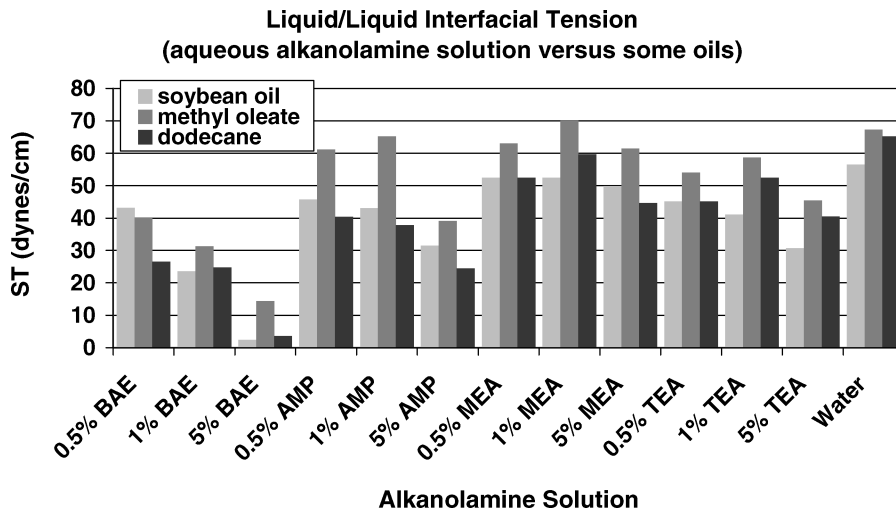


Fig. 3—The liquid/liquid interfacial tension of some aqueous alkanolamine solutions at 0.5%, 1%, and 5% concentrations versus three organic liquids. Acronyms are as given in Table 1.

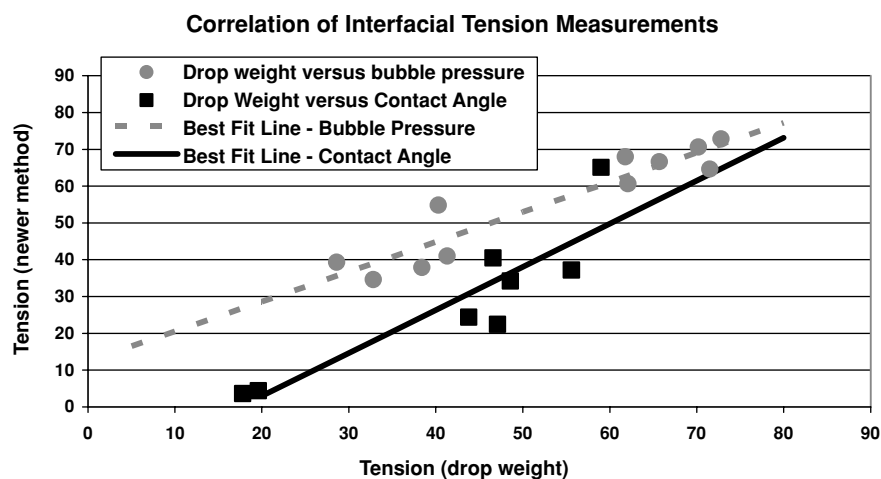


Fig. 4—Correlation of interfacial tension measurements made by drop weight with measurements made by maximum bubble pressure (air/liquid, circles) or capillary contact angle (liquid/liquid, squares).

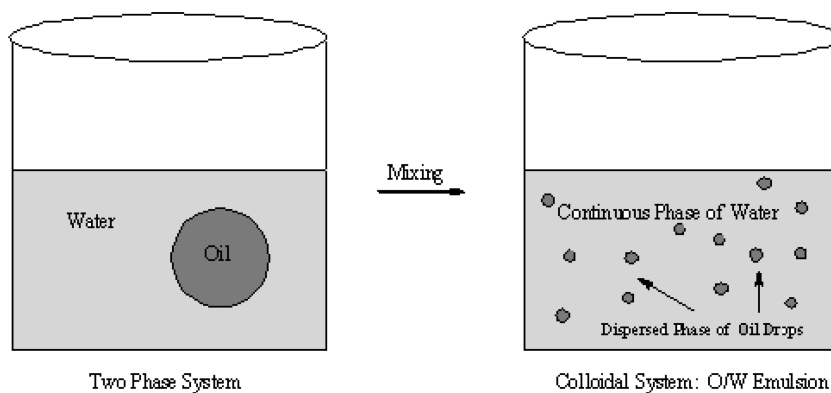


Fig. 5—Oil in water emulsions are created by mixing a two-phase system of oil in water until the oil phase becomes finely dispersed throughout the water phase.

TABLE 3—REPRESENTATIVE LINES FROM THE EXCEL SPREADSHEET USED TO CALCULATE THE INTERFACIAL TENSIONS BETWEEN AQUEOUS SOLUTIONS OF SOME ALKANOLAMINES AND VARIOUS OILS

Aq	Oil	$\theta$ Aq	$\theta$ Oil	$\theta$ Aq/Oil	$f(\theta)$	$g(\theta)$	$h(\theta)$	$\gamma_{\text{Air/Solution}}$	$\gamma_{\text{Air/Oil}}$	$\gamma_{\text{Oil/Solution}}$
Water	SB	29.3	52.8	43.0	0.293	0.168	0.217	72.8	54.8	55.6
1% BAE	MeOle	35.8	52.8	49.5	0.256	0.168	0.184	52.8	54.8	23.2
1% AMP	MeOle	38.3	52.8	51.2	0.242	0.168	0.176	68.8	54.8	42.3

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

AMP = 95% (aq) solution of 2-amino-2-methyl-1-propanol (available from Dow Chemicals, Midland, MI).

SB = Soybean oil.

MeOle = Methyl oleate.

### Development of the Measurement Method: Accurate Measurement of a Contact Angle

Digital photography was employed as a means of capturing and expanding an accurate image of the meniscus of interest. With an

enlarged image of the meniscus, standard techniques of constructive geometry could be applied to determine the contact angle (Fig. 1). An example of a contact angle calculation is given in Fig. 2.

TABLE 4—ANGLES (IN DEGREES) MEASURED IN CAPILLARY TUBES OF RADIUS 1 MM

Lower Phase	Upper Phase	Contact Angle	Lower Phase	Upper Phase	Contact Angle	Lower Phase	Upper Phase	Contact Angle
DI Water	air	29	0.5% MEA	SB	48	5% BAE	MeOle	47
SB	air	53	0.5% TEA	SB	46	5% BDEA	MeOle	35
MeOle	air	47	1% BAE	SB	50	5% AMP	MeOle	49
Dod	air	41	1% BDEA	SB	50	5% MAE	MeOle	54
0.5% BAE	air	32	1% AMP	SB	51	5% DGA	MeOle	51
0.5% BDEA	air	36	1% MAE	SB	48	5% MEA	MeOle	50
0.5% AMP	air	39	1% DGA	SB	54	5% TEA	MeOle	48
0.5% MAE	air	32	1% MEA	SB	48	DI Water	Dod	48
0.5% DGA	air	34	1% TEA	SB	46	0.5% BAE	Dod	37
0.5% MEA	air	35	5% BAE	SB	46	0.5% BDEA	Dod	51
0.5% TEA	air	36	5% BDEA	SB	56	0.5% AMP	Dod	42
1% BAE	air	39	5% AMP	SB	55	0.5% MAE	Dod	42
1% BDEA	air	40	5% MAE	SB	57	0.5% DGA	Dod	46
1% AMP	air	44	5% DGA	SB	52	0.5% MEA	Dod	53
1% MAE	air	37	5% MEA	SB	51	0.5% TEA	Dod	58
1% DGA	air	38	5% TEA	SB	45	1% BAE	Dod	50
1% MEA	air	41	DI Water	MeOle	43	1% BDEA	Dod	45
1% TEA	air	36	0.5% BAE	MeOle	43	1% AMP	Dod	45
5% BAE	air	39	0.5% BDEA	MeOle	45	1% MAE	Dod	46
5% BDEA	air	40	0.5% AMP	MeOle	50	1% DGA	Dod	47
5% AMP	air	45	0.5% MAE	MeOle	42	1% MEA	Dod	52
5% MAE	air	40	0.5% DGA	MeOle	48	1% TEA	Dod	54
5% DGA	air	40	0.5% MEA	MeOle	47	5% BAE	Dod	47
5% MEA	air	40	0.5% TEA	MeOle	44	5% BDEA	Dod	49
5% TEA	air	32	1% BAE	MeOle	44	5% AMP	Dod	44
DI Water	SB	43	1% BDEA	MeOle	40	5% MAE	Dod	47
0.5% BAE	SB	57	1% AMP	MeOle	56	5% DGA	Dod	46
0.5% BDEA	SB	49	1% MAE	MeOle	50	5% MEA	Dod	46
0.5% AMP	SB	48	1% DGA	MeOle	47	5% TEA	Dod	54
0.5% MAE	SB	54	1% MEA	MeOle	51			
0.5% DGA	SB	48	1% TEA	MeOle	50			

Note: All angles have been rounded to the nearest whole number.

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

BDEA = N-butyl-diethanolamine (available as Synergex<sup>®</sup> T from Taminco, Allentown, PA).

AMP = 95% (aq) solution of 2-amino-2-methyl-1-propanol (available from Dow Chemicals, Midland, MI).

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MEA = Monoethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

TEA = Triethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

TABLE 5—LIQUID/LIQUID INTERFACIAL TENSIONS (DYNES/CM) BETWEEN AQUEOUS SOLUTIONS OF DIFFERENT ALKANOLAMINES AT THREE DIFFERENT AQUEOUS CONCENTRATIONS (21 SOLUTIONS TOTAL) AND THREE DIFFERENT TYPES OF OIL (63 COMBINATIONS TOTAL)

(Aq) Solution	Oil	$\gamma_{\text{Oil/Solution}}$ (dynes/cm)	(Aq) Solution	Oil	$\gamma_{\text{Oil/Solution}}$ (dynes/cm)	(Aq) Solution	Oil	$\gamma_{\text{Oil/Solution}}$ (dynes/cm)
DI H <sub>2</sub> O	SB	56.5	0.5% MEA	Dod	61.4	1% TEA	Dod	43.2
DI H <sub>2</sub> O	MeOle	67.3	0.5% TEA	Dod	65.0	5% BAE	SB	2.4
DI H <sub>2</sub> O	Dod	65.1	1% BAE	SB	23.5	5% BDEA	SB	4.0
0.5% BAE	SB	43.2	1% BDEA	SB	21.4	5% AMP	SB	31.5
0.5% BDEA	SB	40.1	1% AMP	SB	38.8	5% MAE	SB	28.4
0.5% AMP	SB	45.7	1% MAE	SB	29.3	5% DGA	SB	38.8
0.5% MAE	SB	47.4	1% DGA	SB	52.4	5% MEA	SB	41.2
0.5% DGA	SB	56.3	1% MEA	SB	44.1	5% TEA	SB	30.7
0.5% MEA	SB	52.4	1% TEA	SB	33.7	5% BAE	MeOle	14.4
0.5% TEA	SB	45.1	1% BAE	MeOle	31.3	5% BDEA	MeOle	11.4
0.5% BAE	MeOle	40.2	1% BDEA	MeOle	26.8	5% AMP	MeOle	39.1
0.5% BDEA	MeOle	47.5	1% AMP	MeOle	60.4	5% MAE	MeOle	40.4
0.5% AMP	MeOle	61.1	1% MAE	MeOle	43.8	5% DGA	MeOle	51.1
0.5% MAE	MeOle	45.1	1% DGA	MeOle	55.1	5% MEA	MeOle	53.0
0.5% DGA	MeOle	68.6	1% MEA	MeOle	61.1	5% TEA	MeOle	45.4
0.5% MEA	MeOle	63.0	1% TEA	MeOle	50.3	5% BAE	Dod	3.6
0.5% TEA	MeOle	54.0	1% BAE	Dod	24.7	5% BDEA	Dod	4.4
0.5% BAE	Dod	26.5	1% BDEA	Dod	19.9	5% AMP	Dod	24.4
0.5% BDEA	Dod	43.5	1% AMP	Dod	34.2	5% MAE	Dod	22.5
0.5% AMP	Dod	40.3	1% MAE	Dod	28.9	5% DGA	Dod	34.2
0.5% MAE	Dod	35.5	1% DGA	Dod	44.3	5% MEA	Dod	37.2
0.5% DGA	Dod	54.6	1% MEA	Dod	50.4	5% TEA	Dod	40.5

Note: The calculation of the liquid/liquid interfacial tension is by Eq. [9]. The use of Eq. [9] is illustrated in Table 3.

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

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TEA = Triethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

### Using the Method; Liquid/Liquid Interfacial Tension Measurements

The air/liquid surface tensions of aqueous solutions of some alkanolamines at room temperature (20°C) are given in Table 1 (note that the surface tension of pure water is 72.8 dynes/cm at 20°C):

The air/liquid surface tensions of some oils at room temperature (20°C) are given in Table 2.

An Excel spreadsheet is employed to calculate the geometric terms  $f(\theta)$ ,  $g(\theta)$ , and  $h(\theta)$  from the relationship (see Eq. [4]):

$$f(\theta), g(\theta), \text{ and } h(\theta) = (1/\cos\theta) - \cos\theta/(1 - \sin\theta)$$

The measured capillary contact angles are obtained for the aqueous solution, oil, and mixed solution/oil, respectively. Within the same spreadsheet, the values of  $f(\theta)$ ,  $g(\theta)$ , and  $h(\theta)$  can be combined with the solution/air and oil/air surface tensions to yield the solution/oil interfacial tension via Eq. [9].

Some representative lines from a spreadsheet used to calculate solution/oil interfacial tensions are given in Table 3.

The contact angle data collected from the capillary tube experiments are collated in Table 4.

### Using the Method; Compilation of Liquid/Liquid Interfacial Tension Measurements

The liquid/liquid interfacial tensions (dynes/cm) between aqueous solutions of seven different alkanolamines at three different aqueous concentrations (21 solutions total) and three different nonpolar liquids (63 total combinations) along with base data for DI water (deionized water) are compiled in Table 5.

#### Trends in Liquid/Liquid Interfacial Tension

The variation of liquid/liquid interfacial tension for the aqueous alkanolamine solutions examined herein at three different concentrations (0.5%, 1%, and 5%) versus soybean oil, methyl oleate, and dodecane is presented in Fig. 3. It can be seen that alkanolamines like BAE and to a lesser extent AMP and TEA show a marked decrease in liquid/liquid interfacial tension with oils, especially at higher concentrations. The alkanolamine MEA shows almost no variation in liquid/liquid interfacial tension with concentration. The greater the decrease in interfacial tension between an oil and an aqueous solution with increasing solute concentration, the more pronounced the surfactant-like properties of the solute. Thus, N-alkylalkanolamines (AAAs) like BAE can be assumed to have substantially greater surface-active effects than simpler AAAs like MEA.

TABLE 6—INTERFACIAL TENSIONS @ 20°C CALCULATED BY DROP WEIGHT (CAPILLARY ORIFICE DIAMETER = 0.96 MM) ALONG WITH MEASUREMENTS MADE BY EITHER MAXIMUM BUBBLE PRESSURE OR CAPILLARY CONTACT ANGLE

Phase 1	Phase 2	Drop Weight (g)	Interfacial Tension (drop weight, Eq. [10])	Interfacial Tension (bubble pressure)
DI Water	Air	0.0224	72.8	72.8
5% BAE	Air	0.0118	38.4	37.9
5% BDEA	Air	0.0127	41.3	41.0
5% AMP	Air	0.0191	62.1	60.6
5% MAE	Air	0.0190	61.8	68.0
5% DGA	Air	0.0220	71.5	64.6
5% MEA	Air	0.0216	70.2	70.6
5% TEA	Air	0.0202	65.7	66.6
Dodecane	Air	0.0088	28.6	39.3
Methyl oleate	Air	0.0101	32.8	34.6
Soybean oil	Air	0.0124	40.3	54.8

Phase 1	Phase 2	Drop Weight (g)	Interfacial Tension (drop weight, Eq. [10])	Interfacial Tension (contact angle, Table 5)
DI Water	Dodecane	0.072	59.0	65.1
5% BAE	Dodecane	0.022	17.8	3.6
5% BDEA	Dodecane	0.024	19.6	4.4
5% AMP	Dodecane	0.054	43.8	24.4
5% MAE	Dodecane	0.058	47.1	22.5
5% DGA	Dodecane	0.059	48.6	34.2
5% MEA	Dodecane	0.068	55.6	37.2
5% TEA	Dodecane	0.056	46.6	40.5

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

BDEA = N-butyl-diethanolamine (available as Synergex<sup>®</sup> T from Taminco, Allentown, PA).

AMP = 95% (aq) solution of 2-amino-2-methyl-1-propanol (available from Dow Chemicals, Midland, MI).

MAE = Methylaminoethanol (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

DGA = Diglycolamine (product of Huntsman Corporation, Salt Lake City, UT).

MEA = Monoethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

TEA = Triethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

In general, the same trend was seen in all the data we collected. Higher molecular weight alkylalkanolamines like BAE allowed for the greatest decrease in liquid/liquid interfacial tension between aqueous solutions and nonpolar liquids.

### Measurement Corroboration by Drop Weight

An alternative method for determining the interfacial tension between two immiscible phases is by measuring the weight at drop formation of the less dense phase in the more dense phase. This method was first published by Thomas Tate in 1864, and the relationship between drop weight and interfacial tension is generally known as Tate's law (15). One assumes that a drop will start to

TABLE 7—EMULSION STABILITY DATA COLLECTED FOR DISPERSIONS OF DODECANE IN AQUEOUS ALKANOLAMINE SOLUTIONS

Organic Liquid	Aqueous Phase	Time (s)
Dodecane	Water	8
Dodecane	5% BAE	480
Dodecane	5% BDEA	900
Dodecane	5% AMP	20
Dodecane	5% MAE	60
Dodecane	5% DGA	20
Dodecane	5% MEA	60
Dodecane	5% TEA	120

BAE = 2-Butylaminoethanol (available as Synergex<sup>®</sup> from Taminco, Allentown, PA).

BDEA = N-butyl-diethanolamine (available as Synergex<sup>®</sup> T from Taminco, Allentown, PA).

AMP = 95% (aq) solution of 2-amino-2-methyl-1-propanol (available from Dow Chemicals, Midland, MI).

MAE = Methylaminoethanol (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

DGA = Diglycolamine (product of Huntsman Corporation, Salt Lake City, UT).

MEA = Monoethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

TEA = Triethanolamine (purchased from Sigma-Aldrich Chemical Company, Milwaukee, WI).

break from the orifice in which it is forming at the point where the effective weight of the drop is equal to the circumference of the orifice times the interfacial tension between the two phases. The effective drop weight can be set equal to the volume of the drop multiplied by the difference in density between the two phases involved. This relationship is shown in Eq. [10] (orifice radius measured in cm, interfacial tension in dynes/cm):

$$\begin{aligned}
 (\text{drop volume in mL}) \times (\Delta \text{ density in g/mL}) \times (980 \text{ cm/s}^2) \\
 = 2\pi r \gamma_{\text{interfacial}} \quad [10]
 \end{aligned}$$

Interfacial tensions (dynes/cm) determined by drop weight are compared to values determined by either maximum bubble pressure or contact angle in Table 6 with the results plotted in Fig. 4.

The slope of the regression line for the bubble pressure versus the drop weight was 0.8098 with a y intercept of 12.42 dynes/cm and a statistical  $r^2$  value of 0.8802 (11 data points). The slope of the regression line for the capillary contact angle versus the bubble pressure of 1.1704 with a y intercept of -20.47 dynes/cm and a statistical  $r^2$  value of 0.7971 (8 data points). The correlation between the maximum bubble pressure method and the drop weight method is comparable to the correlation between the capillary contact angle method and the drop weight method, thus establishing the validity of the capillary contact angle approach.

### The Role of Low $\gamma_{\text{Oil/Solution}}$ in Emulsion Stability

One of the most significant consequences of the liquid/liquid interfacial tension between an oil and aqueous phase is the influence on the stability of the emulsions produced from them. A picture of an oil/water emulsion is given in Fig. 5.

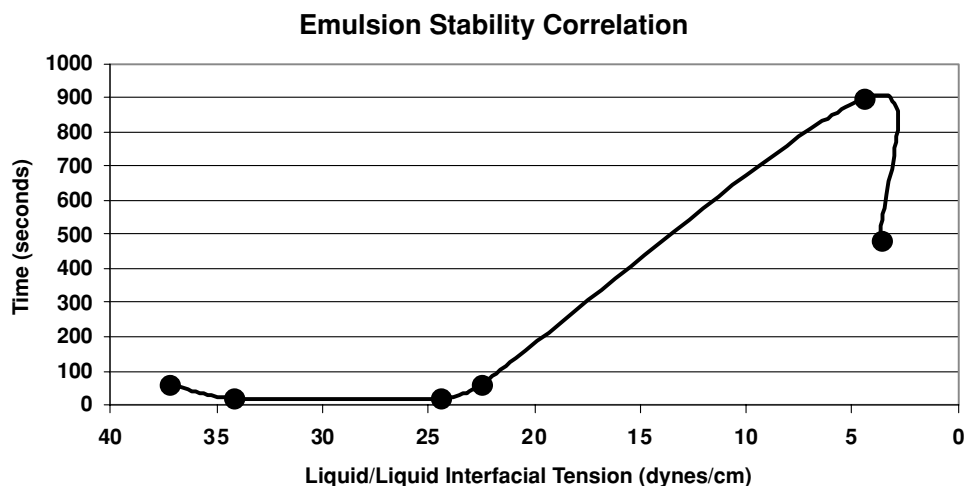


Fig. 6—Plot of the time (y axis) required for an emulsion of the two immiscible liquids to separate as a function of the liquid/liquid interfacial tension (x axis) between the two immiscible liquids (in this case, dodecane and 5% aqueous alkanolamine solutions).

The energy change upon forming an emulsion from separate oil and water phases is given by Eq. [11].

$$\begin{aligned} \Delta E = & \Delta G_{\text{water}} + \Delta G_{\text{oil}} + \gamma_{\text{water/glass}} \Delta A_{\text{water/glass}} \\ & + \gamma_{\text{oil/glass}} \Delta A_{\text{oil/glass}} + \gamma_{\text{water/air}} \Delta A_{\text{water/air}} + \gamma_{\text{oil/air}} \Delta A_{\text{oil/air}} \\ & + \gamma_{\text{water/oil}} \Delta A_{\text{water/oil}} \end{aligned} \quad [11]$$

Upon examination of the seven terms in Eq. [11], it is apparent that only the last term changes significantly upon mixing. There is also a small increase in the entropy of the system upon the formation of the emulsion. The energy of emulsification is thus given by Eq. [12]:

$$\Delta E = (\gamma_{\text{water/oil}}) \Delta A_{\text{water/oil}} - T \Delta S_{\text{mixing}} \quad [12]$$

The  $\Delta A_{\text{water/oil}}$  term represents the change in the interfacial area between the oil and water phases upon mixing. An idea of the magnitude of the interfacial area change that accompanies emulsification can be obtained with a quick calculation. The surface area of a sphere is  $4\pi r^2$  and the volume of a sphere is  $(4/3)\pi r^3$ . Take a drop of oil with radius 1 cm and mix it into an aqueous phase until it is dispersed into drops of radius  $1 \mu\text{m}$ .

#### Initial Oil Drop

$$\begin{aligned} 1 \text{ cm radius} &= 1 \times 10^4 \mu \text{ radius, surface area} = 1.26 \times 10^9 \mu^2, \\ \text{volume} &= 4.19 \times 10^{12} \mu^3 \end{aligned}$$

#### Final Oil Drops

$$\begin{aligned} 1 \mu \text{ radius drop has volume} &= 4.19 \mu^3 @ \text{ total volume of oil} \\ &= 4.19 \times 10^{12} \mu^3 = 10^{12} \text{ drops with surface area of } 12.6 \mu^2 \\ &= \text{total surface area of } 12.6 \times 10^{12} \mu^2 \end{aligned}$$

Thus, the increase in the interfacial area upon dispersing oil into drops of radius  $1 \mu\text{m}$  is approximately 10,000-fold. The surface area increase for the dispersion of oil into drops of 1 nm radius is 10,000,000-fold. If a 12.6 mL of oil (drop of 1 cm radius) is dispersed into drops of 1 nm radius in 12 mL of water wherein the interfacial tension between the oil and water is 30 dynes/cm, then the total enthalpy of the interfacial area change will be  $30 \text{ dynes/cm} \times 12.6 \text{ cm}^2 \times 10,000,000 = 1.26 \times 10^8 \text{ dynes/cm} = 12.6 \text{ joules}$ . This is enough energy to heat the water by  $1^\circ\text{C}$  upon coalescence. Remember that emulsion formation is endothermic, while coalescence is exothermic.

The entropy of mixing term  $-T \Delta S_{\text{mixing}}$  will be negative and will thus contribute to emulsion stability. The enthalpy change caused by the increase in the interfacial area between immiscible phases will be positive, and the term  $\gamma_{\text{water/oil}} \Delta A_{\text{water/oil}}$  will contribute to emulsion instability.

#### Emulsion Stability Correlation

The liquid/liquid interfacial tension between an organic liquid and an aqueous solution will be inversely proportional to the inherent thermodynamic stability of an emulsion of the organic liquid (dispersed phase) in the aqueous solution (continuous phase). As an experimental verification of this, the time it took to break a dispersion of dodecane in an aqueous continuous phase was measured. Our data are collated in Table 7.

Figure 6 presents a plot of the liquid/liquid interfacial tensions measured between dodecane and some 5% aqueous alkanolamine solutions versus the emulsion-breaking time as described in Table 7.

It can be seen that there is a fairly good correlation between the lower aqueous/oil interfacial tension and the emulsion stability.

The interfacial tension between two liquid phases is generally found to increase as the phases become less miscible in each other. For example, the interfacial tension between water and partially comiscible amyl alcohol is far less (approximately 4 dynes/cm) than the interfacial tension measured between water and virtually completely immiscible hexane (approximately 50 dynes/cm;

Donahue and Bartell (6)). The origin of the interfacial tension is the attraction of the molecules within a given phase for themselves as compared to their attraction for the molecules of another phase, and the magnitude of this tension will manifest itself in many ways including cosolubility. Thus, the liquid/liquid interfacial tension measurements can be used to quantitatively rank liquids in terms of their like/dislike for each other. As a corollary to this, negative interfacial tensions should be difficult to measure. A negative interfacial tension implies that the surface area of contact between two phases should spontaneously increase to infinity, a result that is tantamount to the two phases dissolving together. Thus, negative interfacial tensions will at the least be very difficult to measure in static systems, as the two phases within such a system will be continuously merging into one.

## SUMMARY

Capillary contact angle data can be used to calculate aqueous/oil interfacial tensions. The approach presented herein involved a consideration of the interfacial area changes that occur when a meniscus forms inside a capillary tube. An energy balance was set up as follows ( $\gamma \equiv$  interfacial tension, G = gas, L = liquid, S = solid,  $\Delta A_{G/S}$  = surface area change of gas/solid interface,  $\Delta A_{L/S}$  = surface area change of liquid/solid interface,  $\Delta A_{G/L}$  = surface area change of gas/liquid interface):

$$\gamma_{G/S}(\Delta A_{G/S}) = \gamma_{L/S}(\Delta A_{L/S}) + \gamma_{G/L}(\Delta A_{G/L})$$

After plugging in values for the interfacial area changes and considering three distinct capillary tube equilibria (aqueous solution under air, oil under air, aqueous solution under oil), the following equation for the desired aqueous/oil interfacial tension was derived:

$$\gamma_{\text{Oil/Solution}} = 1/h(\theta)\{f(\theta)\gamma_{\text{Air/Solution}} - g(\theta)\gamma_{\text{Air/Oil}}\} \quad [13]$$

$$f(\theta), g(\theta), h(\theta) = \frac{1}{\cos\theta} - \frac{1}{2} \left\{ \frac{\cos\theta}{1 - \sin\theta} \right\}$$

$f(\theta)$  employs the contact angle between the aqueous solution and air

$g(\theta)$  employs the contact angle between the oil and air

$h(\theta)$  employs the contact angle between the aqueous solution and the oil

The measurement method is summarized as follows:

- Measure air/liquid interfacial tension for aqueous solution
- Measure air/liquid interfacial tension for oil
- Take picture of aqueous solution in capillary tube
- Take picture of oil in capillary tube
- Layer oil on top of aqueous solution—take picture
- Expand pictures and print—calculate contact angles
- Calculate liquid/liquid interfacial tension with Eq. [9]

Digital photography was employed as a means of getting an expanded image of the capillary meniscus, and the application of constructive geometry to the expanded meniscus image was used for the determination of accurate and reproducible contact angles. A spherical approximation of the meniscus shape was employed in order to calculate the change in the air/liquid interfacial area.

In practice, the interfacial tension values measured for biphasic oil/aqueous systems were found to correlate inversely with the stability of emulsions prepared from the said oil and the aqueous solution. Furthermore, the liquid/liquid interfacial tension of aqueous N-alkylalkanolamine (AAA) solutions with various oils was lower for AAAs that incorporated higher molecular weight alkyl groups. In general, the measurement of liquid/liquid interfacial tension was found to be an important adjunct to the complete study of emulsion structure and energetics.

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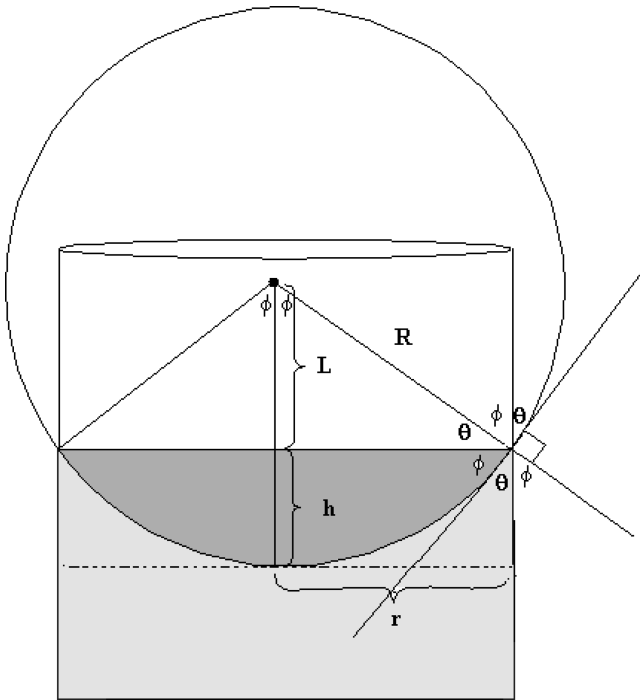
## APPENDIX (SPHERICAL APPROXIMATION OF MENISCUS SHAPE)

In this work, a spherical approximation of meniscus shape was employed. Referring to Fig. A1 with the liquid in the capillary tube designated by a light grey color, the surface area of the spherical cap (SASC, dark grey color) created by the meniscus can be calculated from the known quantities  $r$  (radius of capillary tube),  $h$  (meniscus height), and contact angle ( $\theta$ ).

$$\text{Surface area of the spherical cap (SASC)} = 2\pi Rh$$

$$\tan\theta = L/r \quad L = r\tan\theta \quad R = L + h \quad R = r\tan\theta + h$$

$$\text{SASC} = 2\pi hr\tan\theta + 2\pi h^2$$



**Fig. A1**—The spherical assumption for a meniscus within a capillary tube. The light grey area represents liquid within the capillary tube. The dark grey area represents the spherical cap used to calculate surface area change that occurs upon formation of the meniscus. The angle  $\theta$  is the measured contact angle.

The difference in gas/liquid surface area caused by formation of the meniscus is designated as  $\Delta SAS$  (surface area change with spherical assumption). The value of  $\Delta SAS$  is given by the surface area of the actual meniscus minus the surface area that would be present with the liquid laying flat ( $\pi r^2$ ).

$$\Delta SAS = SAS - \pi r^2 = 2\pi hr \tan \theta + 2\pi h^2 - \pi r^2$$

The three variables  $h$ ,  $\theta$ , and  $r$  are related by the following:

$$R = r / \cos \theta \quad L = r \tan \theta \quad h = R - L = r \left\{ \frac{1}{\cos \theta} - \tan \theta \right\}$$