THE LINE/PSEUDO-LINE TENSION IN THREE-PHASE SYSTEMS

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ABSTRACT

The effect of drop (bubble) size on contact angle was examined over a wide range of drop (bubble) sizes for the CCl₄-toluene solution/NaClaqueous solution/quartz, ethylene glycol/CCl₄-toluene solution/quartz, bitumen/Na₂P₂O₇ aqueous solution/quartz, water/kerosene/quartz, heptane/water/quartz, and air bubble/water/polyethylene systems. For most systems, a nonlinear relationship between cosine of the contact angle and reciprocal of drop (bubble) base radius was obtained. All known factors affecting the contact angle/drop size relationship are discussed. It was found that the effect of gravitational forces as well as solid strain in the vicinity of the three-phase contact line are not responsible for the contact angle/drop size relationship for the systems examined. It appears that surface heterogeneities (contaminants) have the greatest effect on the contact angle/drop size relationship as is evident for these results from our laboratory. Also, surface roughness can contribute to the effect of drop size on contact angle. A theoretical background is presented and modifications of both the Cassie Equation and Wenzel Equation are derived.

A linear correlation of cosine of the contact angle vs. reciprocal of drop base radius was obtained for the heptane/water/quartz systems, when high purity single-component liquids and a smooth, chemically cleaned, quartz plate were used. The line tension was determined for this system to be $(5.1 \pm 4.3) \times 10^{-9}$ N.

1. INTRODUCTION

Wetting phenomena at a solid surface play a very important part in many phase separation processes, for example; bitumen separation from tar sands, remediation of contaminated soil, wetting and flotation of particles, tertiary oil recovery, separation/removal of dispersed oil from waste water, agglomeration of solid particles by dispersed liquids, and in many other areas of technology. Although significant developments in the theory of wetting processes have occurred in recent years, the understanding of these phenomena is not complete.

It is generally known that the drop shape can be deformed by the effect of gravity but for a long time there has been a controversy regarding the effect of drop size, for a small volume of liquid, on the contact angle. Only a short note regarding the influence of line tension (the definition of line tension is given later) on contact angle can be found in the 3rd edition of Physical Chemistry of Surfaces by A. W. Adamson. More information about the line tension term can be found in the book of J. S. Rowlinson and B. Widom, Molecular Theory of Capillarity. Most other texts ignore the fact that observed changes in contact angle occur with changes in drop size. On the other hand the technical literature, especially during recent years, provides more information on the effect of drop size on contact angle. The systematic study of this phenomenon has been performed by two research teams directed by Neumann (Gaydos and Neumann, 1987; Boruvka et al., 1990; Li and Neumann, 1990; Li et al., 1991) and by Ponter (Ponter and Boyes, 1972; Boyes and Ponter, 1974; Ponter and Yekta-Fard, 1985; Yekta-Fard and Ponter, 1988), respectively, as well as other scientists (Vesselowsky and Pertzow, 1936; Leja and Poling, 1950; Herzberg and Marlan, 1970; Good and Koo, 1979; Wallace and Schurch, 1990). Studies on the influence of line tension on heterogeneous nucleation (Gretz, 1966; Scheludko, 1980; Scheludko et al., 1981), on liquid lens shape at fluid-fluid interfaces (Langmuir, 1933; Gershfeld and Good, 1967; Torza
and Mason, 1971; Wallace and Schurch, 1988), and on the structure of foams (De Feijter and Vrij, 1972; Kolarov and Zorin, 1979, 1980; Platikanov et al., 1980) have also been published but these cases will not be taken into consideration in this paper. Also, the variation of contact angle with fiber diameter has been considered and is reported in the literature (Carroll, 1976, 1986; Brochard, 1986).

Experimental evidence for the effect of drop size on contact angle has already been published (Vesselovsky and Pertzow, 1936; Ponter and Boyes, 1972; Boyes and Ponter, 1974; Good and Koo, 1979; Ponter and Yekta-Fard, 1985; Gaydos and Neumann, 1987; Yekta-Fard and Ponter, 1988; Li and Neumann, 1990; Wallace and Schurch, 1990) but only a limited range of drop volumes was investigated for a few systems. In most of these experiments the drop-solid contact diameter was larger than 1 mm. Only Wallace and Schurch (1990) studied much smaller droplets ranging in diameter from 2 to 50 μm. Our own results (Drellich et al., 1992) proved that this phenomenon should be examined over a wide range of drop size. Notwithstanding, the recently published correlations between contact angle and drop size the relationship is still not satisfactorily explained. Further analysis of new experimental data is required to elucidate the significance of the line tension term at the three-phase contact line. Also, the practical significance of the drop size effect on contact angle has not been considered sufficiently.

In this paper, new experimental contact angle/drop size data for several systems; air bubble/water/polyethylene, heptane/water/quartz, ethylene glycol/CCl₄-toluene solution/quartz, CCl₄-toluene solution/NaCl aqueous solution/quartz, bitumens/Na₂P₂O₇ aqueous solution/quartz, and water/kerosene/quartz, are presented. The drop (bubble) size was changed over a wide range of drop-solid contact diameter from 0.02 mm to 7.1 mm. These new results support our previous postulate (Drellich et al., 1992) that the common interpretation of the effect of drop size on contact angle is incorrect and that observed changes in the contact angle often cannot be interpreted as a simple contribution from the line tension. A theoretical explanation for the observed effect of drop size on contact angle is offered and modified equations of Young, Cassie and Wenzel have accordingly been prepared. Most of the line tension theory included in this paper is presented for the first time in an extended form (however, still simplified!) and is indispensable for a complete understanding of the effect of drop size on contact angle.

2. YOUNG EQUATION AND LINE TENSION

The Young Equation describes a force balance in the plane of the solid surface for three-phase systems in which the equilibrium contact angle is established in order to resolve the interfacial tensions. There can be no doubt, however, that the contact angle is also affected by the nature of the molecules near the contact line; the line common for the three phases (Gibbs, 1957). In this regard modification of the Young equation is required to account for the drop size effect, and derivation of this modification based on thermodynamic considerations is presented below.

Only the simplest three-phase system being in thermodynamic equilibrium is considered with the following assumptions:

— the surface free energy as well as the line free energy are constant and independent of drop size,
— the three-phase system is simplified to a spherical liquid drop resting on a homogeneous, horizontal, isotropic, and flat solid surface,
— the temperature (T), pressure (P), volume (V), chemical potential (μ), and composition are constant.

Thus, the general equation for the free energy relationships can be simply expressed as follows:

$$
\frac{dF}{dA} = \left( \frac{\delta F}{\delta A_{SL}} \right) dA_{SL} + \left( \frac{\delta F}{\delta A_{SV}} \right) dA_{SV} + \left( \frac{\delta F}{\delta A_{LV}} \right) dA_{LV} + \left( \frac{\delta F}{\delta L_{SV}} \right) dL_{SV} \tag{1}
$$

or

$$
\frac{dF}{dA_{SL}} = 0 = \left( \frac{\delta F}{\delta A_{SL}} \right) dA_{SL} + \left( \frac{\delta F}{\delta A_{SV}} \right) dA_{SV} + \left( \frac{\delta F}{\delta A_{LV}} \right) dA_{LV} + \left( \frac{\delta F}{\delta L_{SL}} \right) dL_{SL} \tag{2}
$$

where F is the free energy; A is the area of interface; L is the length of the three-phase contact line; and subscripts S, L, V correspond to solid, liquid, and vapour phase, respectively.
A change in the free energy with a change in the interfacial area leads to the surface free energy, whereas a change in the length of the three-phase contact line leads to the line free energy as shown below:

\[
\frac{\delta F_{SV}}{\delta A_{SV}} = \gamma_{SV} \\
\frac{\delta F_{LV}}{\delta A_{LV}} = \gamma_{LV} \\
\frac{\delta F_{LV}}{\delta L_{SLV}} = \gamma_{SLV}
\]

For the model under consideration the following substitutions are valid:

\[ dA_{SV} = -dA_{SL} \]
\[ dA_{LV} = dA_{SL} \cos \theta \]
\[ \frac{dL_{SLV}}{dA_{SL}} = \frac{1}{r} \]

where \( \theta \) is the contact angle, and \( r \) is the drop base radius.

Thus, Equation (2) leads to modification of the Young Equation (3) for a spherical drop resting on a homogeneous and smooth solid surface (Vesselovskiy and Pertzow, 1936; Pethica, 1977):

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta + \frac{\gamma_{SLV}}{r} \]  

(3)

The generalized Young Equation was derived by Boruvka and Neumann (1977) to be:

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta + \gamma_{SLV} \kappa_{p} \]  

(4)

where \( \kappa_{p} \) is the geodesic curvature of the three-phase contact line, which is equal to the reciprocal radius of the three-phase contact line (\( \kappa_{p} = 1/r \)) for an axisymmetric drop on a smooth, homogeneous, isotropic, and horizontal solid surface.

The line tension \( \gamma_{SLV} \) is associated with the three-phase contact line and for this region the analog of the Laplace Equation was postulated (Gershfeld and Good, 1967):

\[ \pi_{SLV} = \frac{\gamma_{SLV}}{r} \]  

(5)

The line tension was predicted by Gibbs (1957) to be a one-dimensional analog of the surface tension. The experimental procedure, based on contact angle and drop base radius measurements, which leads to the calculation of the line tension from Equation (3), often expressed as Equation (6), is not complicated.

\[ \cos \theta = \cos \theta_{\infty} - \frac{\gamma_{SLV}}{r \gamma_{LV}} \]  

(6)

where \( \theta = \theta_{\infty} \) for \( r \to \infty \).

Results from contact angle measurements for drops of different dimension are used to establish a straight line relationship between \( \cos \theta \) and \( 1/r \) as required by Equation (3) and (6), and examples of this procedure are presented in the literature (Gaydos and Neumann, 1987; Li and Neumann, 1990; Wallace and Schurch, 1990).
Unfortunately, the experimentally determined line tension values, ranging from $10^{-4}$ N to $10^{-4}$ N, are much greater than those values predicted from theoretical calculations ($10^{-11}$ N to $10^{-10}$ N) (Harkins, 1937; Rowlinson and Widom, 1984), and greater than those values obtained using other experimental techniques ($10^{-10}$ N to $10^{-8}$ N) (Mingins and Scheludko, 1979; Schultze, 1984). The reason why the experimental line tension values calculated from contact angle/drop size data are inconsistent with theoretical values is that solid surface imperfections, heterogeneities and/or roughness are believed to be significant factors which cannot be ignored. The commonly used Cassie Equation — a modification of the Young Equation for heterogeneous surfaces — and the Wenzel Equation — a modification of the Young Equation for rough surfaces — do not take the line-tension term into consideration and furthermore do not consider the effect of surface imperfections on the contact angle/drop size relationship. In both cases, the equations are incomplete and the line-tension term must be taken into consideration as presented in the following sections.

3. MODIFICATION OF THE CASSIE EQUATION

Cassie derived an equation describing contact-angle changes for composite smooth solid surfaces with varying degrees of heterogeneity, which for two-component surfaces is expressed as follows (Cassie and Baxter, 1944; Cassie, 1948):

$$\cos \theta = f \cos \theta_1 + (1-f) \cos \theta_2$$

(7)

where $f$ is the fractional area of the surface with contact angle of $\theta_1$ and $(1-f)$ is the fractional area of the surface with contact angle of $\theta_2$.

When Cassie considered the equilibrium, the three-phase contact angle, the concept and significance of the line-tension term was not appreciated. It should be noted that Cassie only predicted the effect of surface heterogeneity on the interfacial free energy of a system, but he did not predict the effect of surface heterogeneity on the line free energy, nor did he predict the effect on the corrugation of the three-phase contact line. A portion of a hypothetical three-phase contact line is shown in Figure 1, and it is known that the excess energy associated with the triple junction has, in some cases, made a significant contribution to the total energy of the three-phase system. In this regard, a modified Cassie Equation is derived, based on the same model as used in the previous section, except that now the solid surface is heterogeneous. A two-component solid surface is shown in Figure 1, and the three-phase contact line is contorted in this system (Figure 1), as reported in the literature (Boruvka et al., 1990; Li et al., 1991). The general equation for the free-energy change in the three-phase system can be expressed by Equation (1) or (2) with the following substitutions:

$$\left( \frac{\delta F_{SL}}{\delta A_{SL}} \right) dA_{SL} = \left( \frac{\delta F_{SL1}}{\delta A_{SL1}} \right) dA_{SL1} + \left( \frac{\delta F_{SL2}}{\delta A_{SL2}} \right) dA_{SL2}$$

$$\left( \frac{\delta F_{SV}}{\delta A_{SV}} \right) dA_{SV} = \left( \frac{\delta F_{SV1}}{\delta A_{SV1}} \right) dA_{SV1} + \left( \frac{\delta F_{SV2}}{\delta A_{SV2}} \right) dA_{SV2}$$

$$\left( \frac{\delta F_{LV}}{\delta L_{SLV}} \right) dL_{SLV} = \left( \frac{\delta F_{SLV1}}{\delta L_{SLV1}} \right) dL_{SLV1} + \left( \frac{\delta F_{SLV2}}{\delta L_{SLV2}} \right) dL_{SLV2}$$

$$\left( \frac{\delta F_{SL1}}{\delta A_{SL1}} \right) = \gamma_{SL1} \quad \left( \frac{\delta F_{SL2}}{\delta A_{SL2}} \right) = \gamma_{SL2}$$

$$\left( \frac{\delta F_{SV1}}{\delta A_{SV1}} \right) = \gamma_{SV1} \quad \left( \frac{\delta F_{SV2}}{\delta A_{SV2}} \right) = \gamma_{SV2}$$

$$\left( \frac{\delta F_{SLV1}}{\delta L_{SLV1}} \right) = \gamma_{SLV1} \quad \left( \frac{\delta F_{SLV2}}{\delta L_{SLV2}} \right) = \gamma_{SLV2}$$
FIGURE 1. A liquid drop in equilibrium at a heterogeneous solid surface showing corrugation of the three-phase contact line.

\[
\frac{dA_{SL1}}{dA_{SL}} = -\frac{dA_{SV1}}{dA_{SL}} = f \quad \frac{dA_{SL2}}{dA_{SL}} = -\frac{dA_{SV2}}{dA_{SL}} = (1-f)
\]

\[
\frac{dA_{LV}}{dA_{SL}} = \cos \theta
\]

\[
\frac{dL_{SL1V1}}{dA_{SL}} = \frac{dL_{SL1V1}}{dA_{SL1}} \frac{dA_{SL1}}{dA_{SL}} = f \frac{dL_{SL1V1}}{dA_{SL1}}
\]

\[
\frac{dL_{SL2V2}}{dA_{SL}} = \frac{dL_{SL2V2}}{dA_{SL2}} \frac{dA_{SL2}}{dA_{SL}} = (1-f) \frac{dL_{SL2V2}}{dA_{SL2}}
\]

Now, Equation (2) for the heterogeneous system being considered can be reduced to the dependence given by Equation (8):

\[
\frac{dF}{dA_{SL}} = 0 = f(\gamma_{SL1} - \gamma_{SV1}) + (1 - f)(\gamma_{SL2} - \gamma_{SV2}) + \gamma_{LV} \cos \theta
\]

\[
+ f \gamma_{SL1V1} \frac{dL_{SL1V1}}{dA_{SL1}} + (1-f) \gamma_{SL2V2} \frac{dL_{SL2V2}}{dA_{SL2}}
\]

Equation (8)

Two types of heterogeneous patches can be simply described by the Young Equation as follows:

\[
\gamma_{SV1} - \gamma_{SL1} = \gamma_{LV} \cos \theta_1
\]
and the general equation describing the model system can now be written as,

$$\cos \theta = f \cos \theta_1 + (1 - f) \cos \theta_2 = \frac{f \gamma_{SLV}}{\gamma_{LV}} \frac{dL_{SLV}}{dA_{SL}} - \frac{(1 - f) \gamma_{SLV}}{\gamma_{LV}} \frac{dL_{SLV}}{dA_{SL}}$$

(9)

In the case of the system presented in Figure 1, when the corrugation of the three-phase contact line is symmetrical and the local deformations are all of circular shape, the following dependences can be used:

$$\frac{dL_{SLV}}{dA_{SL}} = \frac{1}{r_1} \quad \frac{dL_{SLV}}{dA_{SL}} = \frac{1}{r_2}$$

Thus, the final form of the modified Cassie Equation for the simplified case is as follows:

$$\cos \theta = f \cos \theta_1 + (1 - f) \cos \theta_2 = \frac{f \gamma_{SLV}}{r_1 \gamma_{LV}} + \frac{(1 - f) \gamma_{SLV}}{r_2 \gamma_{LV}}$$

(10)

The general formula for the modified Cassie Equation for a multicomponent heterogeneous solid surface (n-components), where the shape of the three-phase contact line does not need to be circular in selected regions of solid surface, can be derived based on the generalized Young Equation (4), and is expressed by Equation (11) (Drellich and Miller, 1992a):

$$\cos \theta = \sum \left( f_n \cos \theta_n - \frac{1}{\gamma_{LV}} f_n \gamma_{SLV} \kappa_{nm} \right)$$

(11)

It follows from this modified Cassie Equation that a corrugation of the three-phase contact line affects the contact angle due to the line-tension term, the value of which, depends on the size and distribution of heterogeneous patches.

The modified Cassie Equation would seem to have particular significance in the analysis of the effect of drop size on contact angle and in the analysis of contact-angle hysteresis (Drellich and Miller, 1992a).

4. MODIFIED WENZEL EQUATION FOR ROUGH SURFACES

For rough solid surfaces, Wenzel proposed the following modification of the Young Equation (Wenzel, 1936):

$$x (\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \theta$$

(12)

$$x = \frac{a}{A} = \frac{da}{dA} \geq 1$$

with $a$ as the actual interfacial area, and $A$ as the “apparent” area of the “geometrical” interface.

Of course, similar to the case of Cassie, Wenzel did not predict a contribution of the three-phase contact line in the contact-angle analysis. Continuing our thermodynamic consideration of three-phase systems the Wenzel Equation can also be modified with respect to the line tension term. A simple model can be used, as in the previous discussion of the modified Young Equation. When the solid surface is homogeneous but rough (Figure 2) the general equation expressing the free energy relations of the three-phase system at equilibrium is as follows:

$$\frac{dF}{dA_{SL}} = 0 = \left( \frac{\delta F}{\delta a_{SL}} \right) \left( \frac{da_{SL}}{dA_{SL}} \right) + \left( \frac{\delta F}{\delta a_{LV}} \right) \left( \frac{da_{LV}}{dA_{LV}} \right) + \left( \frac{\delta F}{\delta a_{SV}} \right) \left( \frac{da_{SV}}{dA_{SV}} \right)$$

$$+ \left( \frac{\delta F}{\delta L_{LV}} \right) \left( \frac{dL_{LV}}{dA_{LV}} \right) + \left( \frac{\delta F}{\delta L_{SL}} \right) \left( \frac{dL_{SL}}{dA_{SL}} \right)$$

(13)
\[ \Theta < 90^\circ \]

Two possible cases for the three-phase contact line:

- no corrugation of the three-phase contact line in plan view
- corrugation of the three-phase contact line in plan view

FIGURE 2. A liquid drop resting on a rough solid surface.

The dependencies describing the surface free energy or the line free energy used for Equation (2) are still valid for Equation (13). Also, for the system with a spherical drop, the following substitutions can be used:

\[
\frac{d\alpha_{LV}}{dA_{LV}} = 1
\]

\[
\frac{dl_{LV}}{dA_{LV}} = \frac{1}{r}
\]

Next, the following parameters can be introduced:

\[
\frac{d\alpha_{SL}}{dA_{SL}} = \frac{d\alpha_{SV}}{dA_{SV}} = x
\]

and

\[
\frac{dl_{LV}}{dl_{SV}} = y
\]

Thus, the modified Wenzel Equation is as follows:

\[
x (\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \Theta + \frac{y \gamma_{SLV}}{r}
\]

or

\[
x (\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \Theta + \frac{y}{r}
\]
\[ \cos \theta_r = x \cos \theta_s - \frac{y \gamma_{SV}}{r \gamma_{LV}} \]  

(15)

where subscripts \( r \) and \( s \) correspond to rough and smooth surface, respectively.

In the first approximation it can be shown that a ratio between actual and apparent length of the three-phase contact line is the same as the ratio for actual and apparent areas, \( y = x \).

The modified Wenzel Equation is significant when \( y >> 1 \) and for small drops where the modification seems to be important for the interpretation of the contact angle/drop size data. The surface roughness affects the length of the three-phase contact line and can also affect its horizontal corrugation (Hu and Mason, 1977) (Figure 2), and thus the modified Wenzel Equation should be expressed as follows:

\[ x(\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \theta + \gamma_{SL} \phi_{DS} \]  

(16)

Also, a heterogeneous rough surface makes the system even more complex, and the modified Cassie-Wenzel Equation should be derived to describe these systems. This case will be considered in a separate contribution (Drellich, 1993).

5. EXPERIMENTAL PROCEDURE

5.1. Reagents and Materials

The basic chemicals in our experiments were as follows: distilled water with specific conductivity < 10^{-4} S; spectrograde heptane (Mallinckrodt, Inc., U.S.A.); ethylene glycol AR (Mallinckrodt, Inc., U.S.A.); toluene GR (EM Science, U.S.A.); carbon tetrachloride GR (EM Science, U.S.A.); kerosene — commercial product; bitumen extracted from Whiterocks tar sand; sodium chloride AR (Mallinckrodt, Inc., U.S.A.); sodium carbonate AR (Mallinckrodt, Inc., U.S.A.); sodium tripolyphosphate — technical (GFS Chemicals, U.S.A.).

Two different solids were used in the experiments: a polyethylene plate obtained by melting granulated polyethylene at 130°C (originating from Chemical Works “Blachownia,” Poland), and optical-grade quartz plates originating from Wilmad Glass Company, Inc., U.S.A. (quartz A, stored several years) and purchased from Minarad Scientific Inc., U.S.A. (quartz B, recent acquisition).

The systems examined in our experiments are briefly characterized in Table 1. The Wilhelmy plate technique was applied for surface/interface tension measurements using Digital-Tensiometer K10T (KRUSS, GmbH; Germany) with an accuracy of 0.2 mN/m. Some systems were examined by the pendant drop technique using a Hamilton standard needle SK-1, and it was found that the accuracy of these measurements was 0.2–0.3 mN/m.

The calibrated volumes of liquids were weighed in a pycnometer and the densities were determined with an accuracy of 1–2 kg m^-3.

5.2. Solid Surface Preparation

The quartz plates were cleaned with toluene, distilled water, acetone, chroronic acid, distilled water and methanol, and next heated in a clean oven for 0.5–1 hour at 110°C. The contact angle for water drops placed on the first quartz plate (A) was close to zero, <5–7 degrees, but never reached zero even after several cleaning operations. Water drops placed on the second quartz plate (B) spread over the quartz surface and exhibited a zero contact angle. The quartz plates were kept immersed in distilled water before use in order to eliminate the accumulation of dust particles on the surface.

Polyethylene plates were prepared using two different procedures:

- plate A — granulated polyethylene was pre-washed with distilled water for dust removal before melting (130°C), (also the same distilled water washing was used after casting the plate);
- plate B — as before, granulated polyethylene was washed with distilled water, prior to casting; after casting the plate was rinsed in distilled water and then immersed in concentrated (70%) nitric acid (30 min.), and washed with distilled water again.
5.3. Contact Angle Measurements

A Zeiss stereo microscope coupled with a camera was used to examine the shape of drops and bubbles. The contact angle was measured from photographs with an accuracy ±2 degrees for large drops (bubbles) and ±3 degrees for small droplets (bubbles). The plates were kept in a closed cell with glass windows. The commonly used captive-bubble (drop) technique, for the placement of the drop (bubble) at the solid surface, was adopted in these experiments. It was discussed in our previous paper (Drellich et al., 1992) that the sessile-drop technique has a limited application in the examination of the contact angle/drop (bubble) size relationship and only large drops (bubbles) with a base diameter larger than about 0.6 mm can be examined. Nevertheless, this technique offers better reproducibility. The captive-bubble technique permits examination of the entire bubble (drop) range and is limited only by the optical equipment. However, a larger hysteresis in contact angle data was observed (Drellich et al., 1992). Poorer reproducibility of results with this technique is due to the variation of contaminants over the entire solid surface examined, as discussed previously (Drellich et al., 1992).

The receding contact angle was measured for the bitumen/aqueous phase/quartz system. The following experimental procedure was used: a dried plate of quartz was covered by a thin layer of bitumen, and next immersed into the aqueous phase. The receding contact angle was measured through the bitumen phase after rupture of the film and formation of bitumen lenses. The measurements were performed after the system had reached an equilibrium state.

6. RESULTS AND DISCUSSION

6.1. Contact Angle/Drop Size Data

A number of systems, differing in physico-chemical properties as shown in Table 1, were examined with respect to the correlation between contact angle and drop size. Results are presented in Figures 3–8 as plots of \( \cos \theta \) vs. \( 1/r \) for CCl₄-toluene solution/NaCl aqueous solution/quartz A system (Figure 3), ethylene glycol/CCl₄-toluene solution/quartz A system (Figure 4), bitumen/Na₃P₂O₁₀ aqueous solution/quartz A systems (Figure 5), kerosene/water/quartz A and water/kerosene/quartz A systems (Figure 6), air bubble/water/polyethylene systems (Figure 7), and heptane/water/quartz B system (Figure 8). The equilibrated contact angle after attachment of the drop (bubble) to the solid surface was measured for most systems. The receding contact angle was measured for bitumen/aqueous phase/quartz A systems.

The polyethylene plates were either washed by water or treated by nitric acid, and each polyethylene surface appears to be in a different state with different contact angle values as shown in Figure 7.

In the case of the kerosene/water/quartz A and water/kerosene/quartz A systems the physico-chemical properties were the same but a different liquid was used as the dispersed phase (Figure 6). The contact angle measured through the dispersed phase increases with the drop size for both systems.

A linear correlation between \( \cos \theta \) and \( 1/r \) has been obtained only for the heptane/water/quartz B system (Figure 8), where the quartz plate was high purity after several cleaning operations. There is no significant change in contact angle, and the value calculated from a slope of a straight line of \( \cos \theta \) vs. \( 1/r \), as required by Equation (6), is a reasonable estimation of the line tension value for this system, \( (5.1 \pm 4.3) \times 10^{-4} \) N. The experimental technique used did not allow for a more precise determination of contact angle values, and thus the experimental error in these contact angle measurements was ±2–3 degrees. Consequently, the estimated value for the line tension is reasonable but still must be regarded with some uncertainty.

None of the other systems examined (Figures 3–7) gave a linear correlation between \( \cos \theta \) and \( 1/r \). Of course, this nonlinearity is in disagreement with the expected dependence according to Equation (6), often used for the interpretation of the contact angle/drop size data by some authors (Gaydos and Neumann, 1987; Li and Neumann, 1990), and the data are not suitable for the calculation of a true line tension value. Obviously, the traditional interpretation of these results can not be used. The line tension being a thermodynamic property can not change over an entire drop size range. We can expect that the line tension will be dependent on the triple junction length when it reaches molecular dimensions as is the case for the surface tension. It is clear that a system in thermodynamic equilibrium can be characterized by only one value for the line tension. Thus, the observed nonlinear correlation between contact angle and drop size can only be explained based on the deviation of the system from the theoretically ideal case. In the available literature five different factors, which
FIGURE 3. The effect of drop size on contact angle in the CCl₄-toluene solution/NaCl aqueous solution/quartz A system.

FIGURE 4. The effect of drop size on contact angle in the ethylene glycol/CCl₄-Toluene solution/quartz A system.
FIGURE 5. The effect of drop size on contact angle in the bitumen/Na₂P₂O₇ aqueous solution/quartz A system.

FIGURE 6. The effect of drop size on contact angle in the kerosene/water/quartz A system.
FIGURE 7. The effect of bubble size on contact angle in the air bubble/water/polyethylene system.

FIGURE 8. The effect of drop size on contact angle in the heptane/water/quartz B system.
<table>
<thead>
<tr>
<th>System</th>
<th>Difference in Fluid Density [kg/m³]</th>
<th>Interfacial Tension [mN/m]</th>
<th>Drop Base Diameter [mm]</th>
<th>Pseudo-Line Tension [N]</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>air bubble/water/polyethylene</td>
<td>1000</td>
<td>72.8</td>
<td>0.32-8.00</td>
<td>(1.7±0.3)×10⁴</td>
<td>Drelich et al. 1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.10-0.32</td>
<td>(0.2±0.7)×10⁻⁷</td>
<td>Drelich et al. 1992</td>
</tr>
<tr>
<td>air bubble/water/polyethylene²</td>
<td>1000</td>
<td>72.8</td>
<td>0.34-4.44</td>
<td>(2.2±0.5)×10⁴</td>
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<td></td>
<td></td>
<td></td>
<td>0.08-0.30</td>
<td>(3.3±1.3)×10⁻⁷</td>
<td>This work</td>
</tr>
<tr>
<td>CCl₄-toluene/NaCl solution/quartz A</td>
<td>30</td>
<td>30.7</td>
<td>0.32-0.72</td>
<td>(3.0±1.8)×10⁷</td>
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<td>0.02-0.08</td>
<td>(2.5±0.7)×10⁻⁸</td>
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</tr>
<tr>
<td>ethylene glycol/CCl₄-toluene/quartz A</td>
<td>5</td>
<td>9.0</td>
<td>0.50-7.10</td>
<td>(5.3±0.9)×10⁷</td>
<td>This work</td>
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<td></td>
<td></td>
<td>0.18-0.38</td>
<td>(1.9±7.3)×10⁻⁸</td>
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<tr>
<td>bitumen/10⁻⁴M Na₃P₂O₁₀/quartz A³</td>
<td>24</td>
<td>17.3</td>
<td>0.20-1.20</td>
<td>(4.8±1.1)×10⁷</td>
<td>This work</td>
</tr>
<tr>
<td>pH = 8.2; T = 50°C</td>
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<td></td>
<td>0.04-0.10</td>
<td>(2.6±0.7)×10⁻⁸</td>
<td>This work</td>
</tr>
<tr>
<td>bitumen/0.05M Na₃P₂O₁₀/quartz A³</td>
<td>24</td>
<td>0.8</td>
<td>0.20-0.40</td>
<td>(1.2±0.3)×10⁻⁸</td>
<td>This work</td>
</tr>
<tr>
<td>pH = 9.2; T = 45°C</td>
<td></td>
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<td>0.04-0.10</td>
<td>(1.7±0.5)×10⁻⁸</td>
<td>This work</td>
</tr>
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<td>bitumen-kerosene/water/quartz A</td>
<td>122</td>
<td>21.1</td>
<td>0.30-2.00</td>
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<td>Drelich et al. 1992</td>
</tr>
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<td></td>
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<td></td>
<td>0.05-0.30</td>
<td>(1.2±7.0)×10⁻⁸</td>
<td>Drelich et al. 1992</td>
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<tr>
<td>kerosene/water/quartz A</td>
<td>212</td>
<td>33.2</td>
<td>0.40-1.40</td>
<td>(1.4±0.1)×10⁻⁶</td>
<td>Drelich et al. 1992</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>0.04-0.40</td>
<td>(4.3±1.0)×10⁻⁸</td>
<td>Drelich et al. 1992</td>
</tr>
<tr>
<td>water/kerosene/quartz A</td>
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<td>0.40-1.90</td>
<td>(2.4±0.3)×10⁻⁶</td>
<td>This work</td>
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<td></td>
<td></td>
<td></td>
<td>0.09-0.40</td>
<td>(1.9±1.0)×10⁻⁷</td>
<td>This work</td>
</tr>
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<td>heptane/water/quartz B</td>
<td>316</td>
<td>51.1</td>
<td>0.03-0.5</td>
<td>(5.1±4.3)×10⁻⁶</td>
<td>This work</td>
</tr>
</tbody>
</table>

¹ calculated for dispersed phase; ² treated with nitric acid; ³ for receding contact angle; ⁴ line tension
can affect the contact angle/drop size relationship, have been postulated and/or discussed; the solid surface heterogeneity (Good and Koo, 1979; Li et al., 1991; Drellich and Miller, 1992b), the solid surface roughness (Good, 1979), the effect of gravitational forces (Leja and Poling, 1960), the effect of solid strain in the vicinity of the triple line (Shahanahan, 1987, 1989), and the effect of a thin liquid film covering solid surface (Li and Neumann, 1991). These factors are discussed with respect to the experimental data and the theoretical modifications presented herein.

6.2. Factors Affecting the Contact Angle/Drop Size Relationship

Gravitational Forces. The effect of gravitational forces on contact angle/drop size data was considered and discussed by Leja and Poling (1960). Unfortunately, their theoretical analysis was incorrect (Good, 1979). Lucassen-Reyniers and Lucassen (1984) wrote: "Gravitational effects play no part in the Young Equation. They can alter the shape of bubbles and drops but not their contact angle." Our results for several systems differing in density support the position that the effect of gravitational forces is negligible. Two systems particularly important in reaching this conclusion are the ethylene glycol/CCl₄-toluene solution/quartz system (Figure 4) and the CCl₄-toluene solution/NaCl aqueous solution/quartz system (Figure 3). The results from these two cases show that even though the density difference between the liquids is very small, 5 kg/m³ and 30 kg/m³, there is still a significant change in contact angle with drop size.

Solid Surface Deformation. It is generally known that the solid surface in the vicinity of the triple junction can be deformed due to the effect of solid strain. However, it is also true that the effect of solid strain should be important only for elastic solid surfaces as rubber, thin membranes, or gels. A simple theoretical background for a deformable solid surface was presented by Lester (1961). He derived a modification of the Young Equation for deformable solids as follows:

\[
\gamma_{LV} \cos \theta = (\gamma_{SV} - \gamma_{SL}) \cos \alpha \tag{17}
\]

where \( \alpha \) is the angle, invisible even with a microscope, which appears for the deformable solid surface, and which can be predicted by the following dependence (Lester, 1961):

\[
\alpha = \tan^{-1} \left( \frac{4\gamma_{LV} (1 - \nu)}{\pi \xi \bar{R}} \right)
\]

here \( E \) and \( \nu \) are the Young's modulus and Poisson's ratio for the solid; \( \bar{R} \) is the radius of curvature of the drop surface; \( \xi = \bar{L} / a \) (\( a = r \)), \( t \) is the dimension of solid deformation (for more details see Lester, 1961).

For most common solids the Young's modulus is high, \( E = 10^9 \) dynes/cm (Lester, 1961), and the effect of solid strain on the contact angle for these solids should be negligibly small. A proof of the negligible significance of surface deformation for a rigid solid with respect to the contact angle/drop size correlation is as follows. From Equation (17) it is evident that the additional parameter introduced into the Young Equation (cos \( \alpha \)) should change when there is a change in the interfacial tension between liquids, for the same system with constant parameters of \( \nu, \bar{R}, E, R \). This case is presented in Figure 4, where the interfacial tension between the bitumen and aqueous phases was changed using different concentrations of sodium tripolyphosphate. For a Na₅P₃O₁₀ concentration of 10⁻⁴ M, the interfacial tension was about 17.3 mN/m, and this dropped more than 20 times to a value of 0.8 mN/m for a Na₅P₃O₁₀ concentration of 0.05 M. Thus as is shown in Figure 4, there is a significant effect of drop size on contact angle for systems with quite different interfacial tension. The shapes of the cos \( \theta \) vs. \( 1/r \) plots are similar. This means that other factors are of much greater significance for the contact angle/drop size relationship observed in our experiments.

Nevertheless, it should be emphasized that deformation of an elastic solid surface can be an important factor in the analysis of the contact angle/drop size data as the theoretical background indicates (Shahanahan, 1987, 1989), however, there is still no experimental proof for the validity of Equation (17).

Surface Heterogeneity. It was shown, using a theoretical approach (Li et al., 1991), that corrugations of the three-phase contact line with local contact angles, caused by the heterogeneity of the solid surface, play an important role in the effect of drop size on contact angle. Our experimental results for the water/methylated quartz surface have supported the importance of surface heterogeneity in the contact angle/bubble size relationship (Drellich and Miller, 1992b). Also, results presented in Figure 7 for the air bubble/water/polyethylene systems where the solid surface was prepared by different procedures confirm this effect. It is shown in Figure 7 that different treatments of the solid surface can cause varying degree of surface
heterogeneity and thus can affect both the contact angle and the relationship between contact angle and bubble base diameter.

Even carefully washed quartz surfaces must possess some degree of heterogeneity due to results of \( \cos \theta \) vs. \( 1/r \) for systems presented in Figures 3-6. An examination of the surface of quartz A using electron scanning microscope showed the presence of attached fine particles with a size of 1 \( \mu m \) and less (Drellich, 1993). Also, in most cases, our experiments involved multicomponent liquids. Some adsorption of selected organic species at the quartz surface could create additional heterogeneous patches. Further, of course, it can be supposed that our solid surfaces do not need to be isotropic over the entire surface area.

The effect of solid surface heterogeneity can be better understood when the modified Cassie Equation (10) or (11) is taken into consideration. The contact angle is affected by the fractional area of surface contaminants \( f \) as well as by the shape of the contorted three-phase contact line \( r \) and \( r_1 \) or \( r_2 \) and \( r_3 \). The shape of a contorted triple line changes with drop size (Li et al., 1991), but at the present time, a change in corrugation of the triple-phase contact line with a change in drop size is unpredictable, and the literature does not provide any satisfactory analysis of this problem. It is assumed that the radii of a corrugated three-phase contact line in different regions of drop-solid contact can increase as well as decrease with decreasing drop size, depending on the system (Li et al., 1991). In this regard, we can not even qualitatively predict the change in a contorted triple junction with drop size.

**Surface Roughness.** The next factor, which can affect the contact angle/drop size correlation is roughness of the solid surface. The experimental data of contact angle vs. drop size for systems with a rough surface are still not available. In our experiments, the polyethylene plates were prepared by melting granulated material and cooling on a glass surface, which is assumed to be smooth. Thus, the polyethylene surface had a configuration similar to that of the glass. Only after polyethylene surface treatment by nitric acid is an additional degree of nonuniformity produced. In the case of quartz, the surface roughness did not exceed 10-30 nm as was observed through a scanning electron microscope. The effect of surface roughness on contact angle can be explained based on the modified Wenzel Equation (14) or (16). Surface roughness can significantly contribute to the line tension term \( (\gamma g_{lv} l) \) when \( \gamma > 1 \) and for small drops. In this regard, the "line tension" values calculated from contact angle data can be larger than the true value depending on the value of \( \gamma \). Of course, systems with rough surfaces can be much more complex. A layer of air or an other fluid, depending on the system, is sometimes entrapped inside pores, when the contact angle is close to or larger than 90 degrees. For such cases a system with surface roughness as well as surface heterogeneities must be considered. More discussion of the modified Wenzel Equation will be presented in a separate publication.

**Thin Liquid Film.** Li and Neumann (1991) considered a thermodynamic model for a liquid drop setting on a solid surface covered by a thin film and they concluded that the effect of the thin film on the contact angle/drop size dependence is negligibly small, four to five orders of magnitude smaller than the line-tension term observed in our experiments. However, a change in film thickness with drop size for liquid/gas/solid system is rather hard to believe, but if the phenomenon does exist, it is expected that this factor does not affect our experimental data, and is negligibly small compared to the effect of solid surface imperfections, heterogeneities and/or roughness.

### 6.3. Line/Pseudo-Line Tension

A linear relationship of \( \cos \theta \) vs. \( 1/r \) was obtained for the heptane/water/quartz B system (Figure 8). Other examples will be presented in another contribution (Drellich, 1993). The line tension, \( (5.1 \pm 4.3) \times 10^9 \) N, calculated from a slope of \( \cos \theta \) vs. \( 1/r \) relationship is close to that obtained for other systems using different techniques, \( 10^{-6} \) to \( 10^{-9} \) N (Mingins and Scheludko, 1979; Schultz, 1984).

In other systems, nonlinear relationships between the cosine of the contact angle (\( \cos \theta \)) and the reciprocal radius of the drop base (\( 1/r \)) were obtained over a wide range of drop (bubble) sizes, confirming our previous results (Drellich et al., 1992). From first principles, the lack of linearity for this range of drop sizes cannot be attributed to a variation in the line tension which should be constant. In fact it is expected for these nonideal systems that the slope of a plot of \( \cos \theta \) vs. \( 1/r \) should not allow for the calculation of the line tension value but rather a pseudo-line tension value. The concept of the pseudo-line tension was suggested by Good and Koo (1979) for the interpretation of the observed changes in contact angle with drop (bubble) size, and next discussed in our first paper (Drellich et al., 1992). The calculated line tension values for all three-phase systems examined in our laboratory or by other research teams are far from theoretical expectations. It appears that surface contamination and/or the surface roughness affect the contact angle data as discussed in
the previous section. For all these systems we can simply postulate that $\kappa \neq 1/r$. The values calculated from a slope of a plot of $\cos \theta$ vs. $1/r$ are the values of the pseudo-line tension ($\gamma_{L}^{V}$), which is different from the line tension due to imperfections of the experimental surface; noncircularity of the drop base ($\kappa \neq 1/r$), heterogeneity of surface ($\Sigma \kappa_{i} \gamma_{i}^{L} \neq \gamma_{L}^{V}/r$), and/or roughness of solid surface ($\gamma_{S}^{L} \kappa \neq \gamma_{L}^{V}/r$). The pseudo-line tension, $\gamma_{L}^{\ast}$, must be determined experimentally for each system individually, since the geodesic curvature ($\kappa_{i}$) as well as the line tension ($\gamma_{L}^{V}$) itself are still difficult to determine for real systems. The pseudo-line tension, $\gamma_{L}^{\ast}$, is equivalent to $\gamma_{L}^{V}$ for a smooth, flat, homogeneous, and isotropic solid surface, and can change with drop size (Drellich et al., 1992). This new term, $\gamma_{L}^{\ast}$, is equivalent to the hypothetical force which should be applied to the system to cause the observed changes in the contact angle, and allows for the comparison of experimental results. Thus, the pseudo-line tension accommodates all the additional imperfection factors and is significantly greater in magnitude than the theoretically expected line tension.

Of course, the pseudo-line tension can be calculated from a plot of $\cos \theta$ vs. $1/r$ but it changes for the entire range of drop (bubble) sizes. Two ranges of drop (bubble) size were selected from Figures 3 through 7 for further discussion; those with $r > 0.10-0.25$ mm and those with $r < 0.10-0.05$ mm, depending on the system, as shown in Table 1. In each range the $\cos \theta$ vs. $1/r$ relationship can be approximated as a linear one. On this basis, the pseudo-line tensions were calculated and are presented in Table 1. The pseudo-line tensions for most systems are positive when the contact angle measured through the drop (bubble) is considered. Only in one case, the polyethylene plate treated with a nitric acid, is the pseudo-line tension negative. This result supports the concept of Li and others (1991) that a change in the contour of a three-phase contact line can affect not only the value of the pseudo-line tension but also its sign.

The magnitude of the pseudo-line tension varies in a wide range from $1.2 \cdot 10^{8}$ N to $2.4 \cdot 10^{4}$ N for large drops (bubbles) ($r > 0.10-0.25$ mm), depending on the system. For small drops (bubbles) ($r < 0.05-0.10$), there are observed changes from $1.7 \cdot 10^{8}$ N to $3.3 \cdot 10^{2}$ N. Again, these changes can be attributed to a difference in the corrugation of the triple junction which obviously should be dependent on the size and distribution of contaminants, the interfacial tension between liquids, and the contact angle. At the present time, neither theory nor experiment permit any estimation of the shape of the contorted three-phase contact line with respect to variation in drop size, contact angle, degree of heterogeneity, size of heterogeneous patches or interfacial tension.

6.4. Practical Aspects of the Effect of Drop Size on Contact Angle

The line/pseudo-line tension is an important factor in many areas of technology: nucleation, organic phase separation from solids, froth flotation, particle agglomeration, and emulsion stabilization by fine particles. A discussion of all processes exceed the limit of this paper, and thus the practical aspect of contact angle dependence on drop size is restricted to two examples directly related to other research activities in our laboratories.

**Oil Separation from Solid Surfaces.** The separation of an organic phase from a solid surface using hot water with the assistance of chemicals is a common phenomenon in detergency, bitumen separation from tar sands, remediation of soil after an oil spill, etc. Our experimental data for the kerosene/water/quartz (Figure 6) and bitumen/water/quartz (Figure 5) systems indicate that the effect of drop size on contact angle is significantly large, much larger than could be expected from consideration of the theoretical line tension value. The contact angle determined for large drops is always greater than for tiny droplets. This means that the analysis of small drops, which are dominant in most systems, e.g., bitumen separation from tar sands (Drellich, 1993), will be necessary to predict the effective experimental conditions (concentration of chemicals and temperature), for which separation is possible. Common measurements of contact angle for drops of 2-5 mm in diameter in these systems can lead to incorrect conclusions, and in this way the optimal conditions (temperature, concentration of reagents) may be in error.

**The Flotation Limit of Fine Particles.** The theoretical particle size limit for the flotation of fine particles was considered by Scheludko et al. (1976), and the minimum particle diameter which can be floated was found to be:

$$D_{min} = \frac{3}{4} \sqrt{\frac{\gamma_{L}^{\ast}}{\Delta \rho \gamma_{LV} (1 - \cos \theta)}}$$

(18)

where $V$ is the bubble ascent velocity and $\Delta \rho$ is the density difference between the particle and the liquid.
It has been shown that the experimental data for the flotation limit of fine hydrophobized quartz particles do not correspond to the theoretical values calculated using Equation (18), when the theoretical line tension is taken into account (Blake and Ralston, 1985; Crawford and Ralston, 1988). As has been discussed previously, factors other than the line tension, i.e., surface heterogeneity and/or roughness, are even more important in the analysis of the variation in contact angle with bubble size. Automatically in these cases, the pseudo-line tension should replace the line tension in Equation (18). Unfortunately, the pseudo-line tension changes with bubble size and the calculation of $D_{min}$ based on Equation (18), with the replaced pseudo-line tension instead of the line tension, can be complicated. In this regard it has been shown that Equation (18) can be expressed in another form (Drellich and Miller, 1992b):

$$D_{min} = 2 \left[ \frac{3}{2} \frac{\gamma_{lv} (1 - \cos \theta)}{\Delta \rho \gamma^2} \right]^{1/3} \ldots (19)$$

where $r_c$ is the critical bubble base radius for which there is no effective attachment between solid surface and dispersed phase (bubble), $\theta = 0$. This critical value, $r_c$, can be estimated from the effect of bubble size on contact angle which is discussed in another publication (Drellich and Miller, 1992b). The limit of fine particle flotation as determined by this theoretical approach (Drellich and Miller, 1992b) agrees exceedingly well with the experimental data reported in the literature (Blake and Ralston, 1985; Crawford and Ralston, 1988) as shown in Figure 9.

7. SUMMARY AND CONCLUSIONS

The effect of drop (bubble) size on contact angle has been presented for several systems; CCl₄-toluene solution/NaCl aqueous solution/quartz, ethylene glycol/CCl₄-toluene solution/quartz, bitumen/Na₂P₂O₇ aqueous solution/quartz, kerosene/water/quartz, water/kerosene/quartz, heptane/water/quartz, and the air bubble/water/polyethylene system, differing in physico-chemical properties of interfacial tension and density. A linear correlation of the cosine of the contact angle versus reciprocal of the drop base radius was obtained for only one system, heptane/water/quartz, when pure single-component liquids were used and freshly prepared quartz surface was chemically cleaned several times. For other systems, no linear correlation between cos $\theta$ and $1/r$ was observed for a wide range of drop (bubble) size, which supports our previous discovery that the changes

![Graph](image_url)

**FIGURE 9.** The flotation limit of methylated quartz particles (Drellich and Miller, 1992b):
- experimental flotation data: (•) Blake and Ralston, 1985; (○) Crawford and Ralston, 1988;
- calculated from Equation (19): (△) V = 0.3 m/s; (□) V = 0.2 m/s.
in contact angle cannot be simply explained by the effect of the thermodynamic line tension. It has been found experimentally and discussed theoretically based on the derivation of a modified Cassie Equation that the surface heterogeneity is mainly responsible for the nonlinear contact angle/drop size relationship. Also, surface roughness can contribute to a change in contact angle with drop (bubble) size as has been shown by the derivation of a modified Wenzel Equation. Experimental data for the CCl₄-toluene solution/NaCl aqueous solution/quartz and ethylene glycol/CCl₄-toluene solution/quartz systems suggest that the correlation between contact angle and drop size cannot be explained by the effect of gravitational forces. Also, the contact angle/drop size relationship for rigid material cannot be interpreted as the effect of solid strain in the vicinity of the triple junction, as the experimental results for the bitumen/aqueous phase/quartz system indicate.

It was calculated for large drops (bubbles) with a drop base radius larger than 0.19–0.25 mm that the pseudo-line tension value varies from 1.2 - 10⁴ N to 2.4 - 10⁴ N, depending on the system. For small drops (bubbles) with the drop base radius smaller than 0.05–0.10 mm but larger than 0.02 mm, the pseudo-line tension is smaller and changes from 1.7 - 10⁴ N to 3.3 - 10³ N. These smaller values of the pseudo-line tension approach the expected thermodynamic line tension value.

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REFERENCES


Drelich, J., Miller, J. D., and Hupka, J., 1992, The Effect of Drop Size on Contact Angle over a Wide Range of Drop Volumes, J. Colloid Interface Sci., accepted for publication.
Line/Pseudo-line Tension in Three-Phase Systems


