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# INTERFACIAL ENERGY AND MICELLE CONDITIONS OF TERNARY MIXTURES FOR IMPROVED HEAT TRANSFER

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### ABSTRACT

The search for suitable mixtures as boiling fluids leads to the development of ternary liquid mixtures that could handle even higher heat fluxes than binary mixtures through the formation of stable bubble-micelles departing from the heater's surface. The amount of experimental work for testing the combinations is reduced using the interfacial tension prediction capabilities of simulation software, although it is not possible to predict singularities in the interfacial tension behavior of the mixtures. The ethanol aqueous mixture shows a singularity in its interfacial tension value at 16% ethanol by weight. In this work was combined with glycols for enhancing boiling heat transfer by decreasing the mixture interfacial tension. Also, the effect of the surfactants Dodecyl Benzene Sodium Sulfonate (DBSS) and Sodium Lauryl Sulfonate (SLS) in the mixture interfacial tension was studied. The measurements of sessile drop contact angles of mixtures with added surfactant allowed finding the singularities in the surface tension values that are related to critical micelle concentrations and the increment in boiling heat transfer. The propilenglycol-ethanol-water mixture produced the lowest values of contact angles, while for the etilenglycol-ethanol-water mixtures no such reduction was obtained with the same amount of the glycol. The use of DBSS and SLS at their critical micelle concentration decreased further the interfacial tension of the propilenglycol ternary mixture to generate a mixture that could improve the convective heat transfer coefficient.

**Keywords:** Interfacial tension, boiling heat transfer, critical micelle concentration

### INTRODUCTION

There is a considerable amount of research on the influence of interfacial properties on boiling heat transfer because the interfacial properties of liquid mixtures and solids are relevant to the enhancing of heat transfer.

The description of the interfacial properties on a molecular scale has been a major goal of some research groups. In situ measurement of the interfacial properties at the evaporating meniscus has been extensively studied and the contribution of the meniscus to evaporation is now well established.

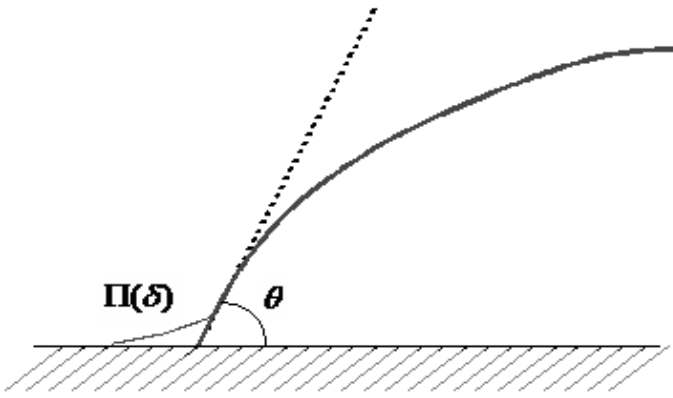
For calculating the interfacial forces present in boiling, the expression of intermolecular forces through a very thin adsorbed liquid layer at the contact line region is considered (Reyes and Wayner, 1995; 1997). The Hamaker constant describes the intermolecular interactions between the solid surface, the adsorbed liquid layer, and the vapor phase at the contact line region of rewetting phenomena (Reyes and Wayner, 1996) and at a nucleation site cavity under critical heat flux conditions (Reyes and Wayner, 1997). The Hamaker constant is used for the calculation of the disjoining pressure of the adsorbed liquid film breaking apart the gas and the solid. The evaluation of the Hamaker constant for very thin liquid films has had a considerable experimental development (Derjaguin and Churaev, 1989; Derjaguin et al., 1988; Derjaguin and Landau, 1941).

Derjaguin and Churaev (1987) experimentally demonstrated the relationship between an isotherm of the disjoining pressure of wetting films,  $\Pi(h)$ , and the equilibrium contact angle,  $\theta_o$ :

$$\cos \theta_o = 1 + \left( \frac{1}{\sigma} \right) \left[ \int_{h_o}^{\infty} \Pi(h) dh + \Pi_o h_o \right] \quad \text{Eq. (1)}$$

where  $\sigma$  is the surface tension of liquids,  $h_o$  is the thickness of a wetting film in equilibrium with the bulk liquid, and  $\Pi_o$  is the disjoining pressure corresponding to that thickness. The measurement of contact angles with conventional optical equipment relates the macroscopic view of the meniscus region

to the microscopic that is available only to more sophisticated techniques like ellipsometry and image processing interferometry (DasGupta et al., 1993).



**Figure (1) Graphic explanation of the connection between the disjoining pressure in the extended meniscus and the equilibrium contact angle,  $\theta$ .**

The structural forces of repulsion for water wetting films in  $\Pi(h)$  explained the colloid stability, wetting phenomena, and liquid flow in thin pores as functions of concentrations, pH values and temperature of aqueous solutions. The description of these phenomena was developed from the observation of polymolecular solvate (adsorbed) films as applied to the development of a mathematical theory of the stability of colloids (Derjaguin and Kussakov, 1939). The experimental determination and modeling of the extended meniscus related to heat transfer problems has been the subject of several publications (Renk and Wayner, 1979 (a); Potash and Wayner, 1972; Wayner et al., 1976; Renk and Wayner, 1979 (b)).

McNutt and Andes (1959) analytically reviewed the validity of the relationship of the contact angle to interfacial energies called the Young equation.

$$\sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos \theta + p \quad \text{Eq. (2)}$$

where  $\sigma_{sv}$  and  $\sigma_{sl}$  are the interfacial surface tensions of the solid/vapor and solid/liquid interfaces, respectively;  $\sigma_{lv}$  is the interfacial tension of the liquid/vapor interface;  $\theta$  is the measured sessile drop contact angle; and  $p$  is the spreading pressure, a term normally negligible for low energy surfaces. Eq. (2) also relates the contact angle to the wettability of the liquid on a solid surface, as lower values of  $\theta$  describe higher values of the solid surface energy or lower interfacial energy liquids. The discussion of the contact angle as a thermodynamic property confirmed a range of conditions for which it is a valid affirmation (Adamson and Ling, 1963).

Sullivan (1981) treated the contact angle between a liquid film and a solid substrate in the van der Waals model to account for the occurrence of the three types of wetting behavior and its temperature dependence. For high energy surfaces, the contact angle decreases on increasing temperature; the opposite behavior is predicted to occur on sufficiently low-

energy surfaces. Adam (1963) deduced from contact angles the relation between adhesion forces and the chemical nature of the groups exposed at the surface. It has been established that for a series of liquids a linear correlation exists between  $\sigma_{lv}$  and  $\cos \theta$  (measured on low energy solids) (Kinloch, 1982). The critical  $\sigma_{lv}$ , or the maximum wettability, appears when  $\theta = 0^\circ$ .

The lack of direct methods for evaluation of the real magnitudes of the surface free energy promotes the use of relative values, which at present can be evaluated experimentally (Chibowski and Perea-Carpio, 2002, Lyklema, J., 1999). Despite the conceptual limitations for the use of the geometric mean for the polar, P (non dispersion), components of the surface tension, the expression proposed by Fowkes (1964, 1964b, 1967) is sufficient for analysis of wetting phenomena:

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^D \sigma_2^D} - 2\sqrt{\sigma_1^P \sigma_2^P} \quad \text{Eq. (3)}$$

For the calculation of the dispersion and polar components of the solid's surface energy Eq. (2), and Eq. (3), applied to the solid/liquid interface, are arranged in a linear relationship:

$$\frac{\sigma_{lv}(1 + \cos \theta)}{2\sqrt{\sigma_l^D}} = \sqrt{\frac{\sigma_l^P \sigma_s^P}{\sigma_l^D}} + \sqrt{\sigma_s^D} \quad \text{Eq. (4)}$$

Eq. (4) can be used to calculate  $\sigma_s^P$  and  $\sigma_s^D$  ( $\sigma_{ss} = \sigma_s^P + \sigma_s^D$ ) from a linear regression analysis using a set of probe liquids of known  $\sigma_{lv}$ ,  $\sigma_l^D$  and  $\sigma_l^P$ . The experimental error associated with the evaluation of  $\sigma_{ss}$  depends on the reliability of the interfacial tension data of the probe liquids and the measurement of the equilibrium contact angles. Conversely, it is possible to use Eq. (4) for the calculation of  $\sigma_l^D$  and  $\sigma_l^P$ . Thus, in-situ measurement of surface and interfacial tensions is possible through the sessile drop contact angle technique and the analysis associated with Eq. (4) (Mantel and Wightman, 1994).

The use of the contact angle for the measurement of industrial surfaces has been studied for assessing the cleanliness of solid surfaces (Stepanov et al., 1972; Yang et al., 1991; Schreiber, 1992).

A critical micelle concentration (CMC) is the concentration of a dissolved surfactant that first reaches the lowest value of the contact angle of the mixture. Concentrations of the additive greater than the CMC generate a value of the contact angle equal to the lowest. The CMC concentration also represents the value that produces a stable micelle state that is related to an increase in the wettability of the system. If the concentration of the surfactant is higher than the CMC, the wettability and the micelle stability is reduced. In the same way, the addition of a poly-ionic salt (high ionic strength) causes an increase on the contact angle (that represents a reduction in the wettability and micelle stability) of the solid surface by the solution (Israelachvili, 1985).

Gurkov et al. (1998) investigated the influence of surfactants on heat exchange systems. The rupture of an extremely thin layer of the surfactant on the solid initiates the evaporation. The changes of interfacial tension on the solid cause a Marangoni effect that produces an oscillatory disturbance on supposed spherical bubbles of the boiling liquid. Wasekar (2001) offered a completed evaluation of the effect of anionic and cationic surfactants on  $h$ , and reached the conclusion that the highest value of  $h$  is obtained close to the CMC. Zhang and Manglik (2003) observed that the CMC of cetyl-trimethylammonium-bromide (CTAB) occurred at 400 ppm, and that the increase of  $h$  depends on the molecular weight of the surfactant and its ionic charge. Tzan and Yang (1990) performed a series of experiments with SLS in the range of 0 to 1500 ppm. For concentrations between 100 and 700 ppm there was an increase in the value of  $h$  because the surfactant reduced the tendency of the bubbles to coalesce, and increased their number. Yang and Maa (2001) demonstrated that the addition of surfactants SLS and SLBS (sodium-lauryl benzyl-sulfate) caused an increase of 100 to 200% in  $h$  because the surfactants reduced the interfacial tension and promoted the heater's wetting.

The experimental description of the effect of mixture composition and the use of surfactants at its critical micelle concentration on the contact angle is intended to find increased wetting conditions that enhance boiling heat transfer.

## NOMENCLATURE

$h$	absorbed liquid thickness
$p$	spreading pressure, mPa/m
$\Pi$	disjoining pressure, Pa
$\sigma$	interfacial or surface tension or free energy; mJ/m <sup>2</sup>
$\theta$	equilibrium contact angle, degrees

### Sub-fixes and super-fixes

D	dispersion forces
l	liquid
P	non-dispersion or polar forces
s	solid
v	vapor
1,2	two phases

## METHODOLOGY

To assess the wettability of a system it is necessary to guarantee the quality, in terms of repeatability and low experimental error, of the measurements of contact angles. Several improvements were introduced in the experimental set up to reduce the experimental error associated to the measurement of the sessile drop contact angle (Melendez and Reyes, 2004).

The solid surfaces used in the contact angle measurements were aluminum and copper. The surfaces of the metallic blocks supporting the liquid drops were polished using the recommended polishing to achieve a mirror plate finishing: a rotating wetted-pad at 3000 rpm with alumina of 0.05  $\mu\text{m}$  in distilled water. Before each sessile drop measurement the cleaning procedure of the metal consisted on mild soap cleaning, rinsing with deionized water, and evaporating the water with acetone.

A Sony DSC-F717 (10x) with 2 cm macro was used for grabbing the sessile drop images. The angle was measured on the printed photographs. The proper illumination of the volume close to the solid-liquid-vapor interface ensures that the images produce a reliable measurement of the contact angle. Figure (2) is an example of a photograph of the contact angle of a solution measured on the copper surface.

The variables considered in the experimental design were the concentration of a glycol and a surfactant over a base mixture of 16% weight ethanol in water. The mixtures were prepared following recommended practices for volumetric chemical analysis and are expressed in percent weight. The surfactants Dodecyl Benzene Sodium Sulfonate (DBSS) and Sodium Lauryl Sulfonate (SLS) were added to the tested mixtures in increasing concentrations to find the critical micelle concentration in the base ethanol-water mixture.

Each experiment was repeated four times for evaluating the standard deviation of the measurements and a unique value of the variance was presented in all the sets of experiments. The standard deviation (SD) of all sets of experiments had a maximum value of 0.4508, minimum of 0.3987 and mean of 0.424642 for all the experiments performed. To reduce the experimental error associated to higher SD values, the experimental results were filtered by  $\bar{x} \pm sd$ , where  $\bar{x}$  is the sample average.

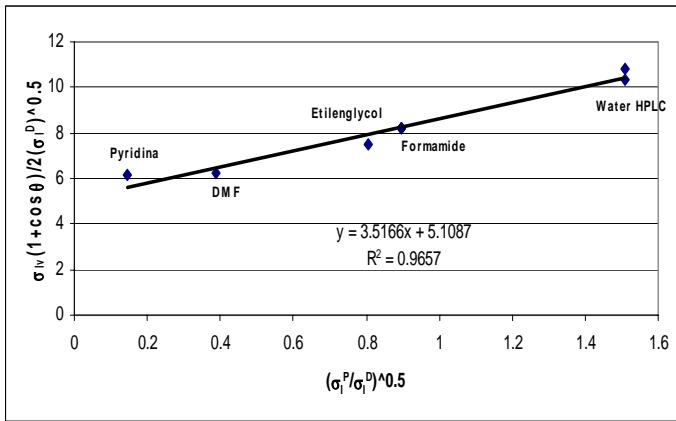
The experiments were grouped in sets. Although the contact angle is not a thermodynamic property, it follows the behavior of the liquid interfacial tension when the solid surface is kept at constant conditions. For some sets of experiments there is a comparison of the trend in contact angle values, directly linked to the interfacial tension through the Young equation with the values predicted from a simulation package (HYSYS v 3.2). The HYSYS predictions were based on the Wilson model for interfacial tension.



**Figure (2) The contact angle of a solution of water-ethanol-propilenglycol.**

## RESULTS

### Set 0. Characterization of the solid surface



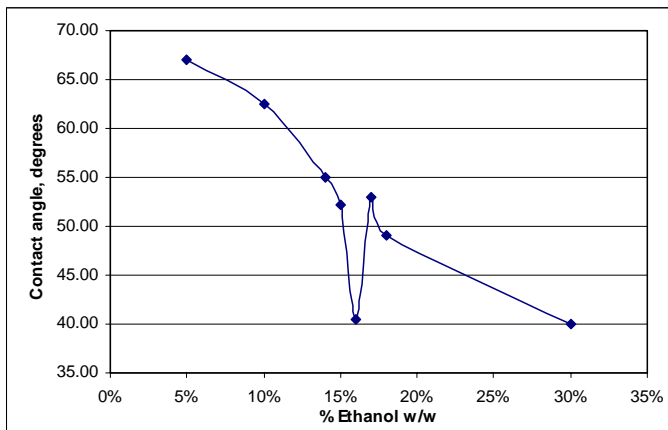
**Figure (3) Calibration curve to determine solid surface energy parameters according to Equation (4).**

Equation 4 relates the contact angle ( $\theta$ ) with the surface tension components ( $\sigma_s^P$ ,  $\sigma_s^D$ ). Using Fig (3),  $\sigma_{ss}$  for the polished copper block was measured and produced a value of  $38.5 \text{ mJ/m}^2$ . The compounds used for the evaluation of  $\sigma_{ss}$  in Figure (3) were previously reported (Kinloch, 1987). DMF is dimethyl formamide, and water of HPLC (high performance liquid chromatography) grade.

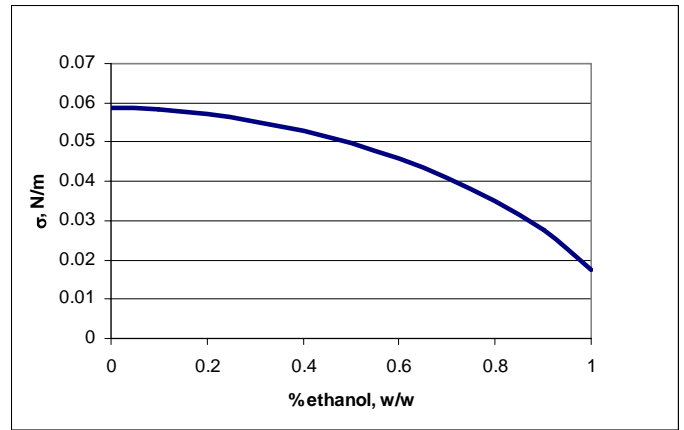
To solve Eq. (4) for the liquid-vapor interfacial tension, there are three independent variables, and an additional equation is needed. This equation is the composition of the liquid-vapor interfacial tension data reported or calculated from another method like the pendant drop technique

$$\sigma_{lv} = \sigma_l^P + \sigma_l^D \quad \text{Eq. (5)}$$

### Set 1. Contact angles measured on a metallic polished surface.



**Figure (4) Experimental measurements of the contact angle of ethanol-water mixtures.**

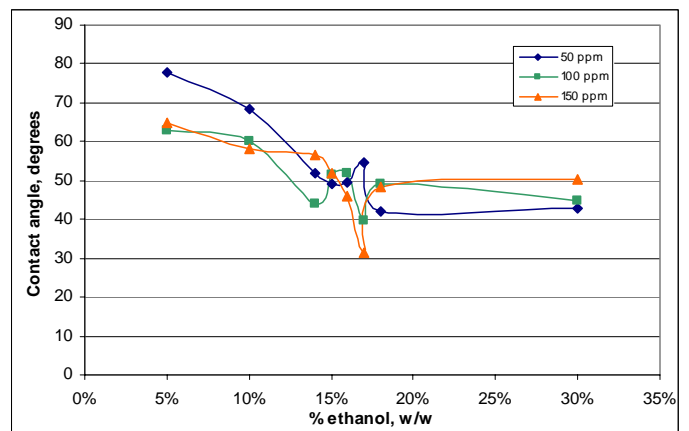


**Figure (5) Predicted values of the interfacial tension of ethanol-water mixtures.**

Fig (4) shows the measured values of equilibrium contact angles of ethanol-water mixtures. It is important to notice a sharp decline of the value of the contact angle at 16% ethanol by weight. This behavior is similar to that found with surfactants at their CMC. It has also been described a substantial improvement of the convective heat transfer coefficient at this composition. The mechanism for the enhanced heat transfer was the release of smaller bubbles (similar to stable micelles) from the heater (Meléndez and Reyes, 2004).

Fig (5) shows the  $\sigma_{lv}$  values calculated from HYSYS v 3.2 for the ethanol-water mixtures. The global trend in the values of  $\sigma_{lv}$  as a function of the increasing contribution of ethanol is similar to the description obtained from contact angles in Fig. (4), as expected. However, the prediction of  $\sigma_{lv}$  from the correlations summarized in HYSYS v 3.2, are not capable of detecting the singularity at 16% ethanol by weight.

### Set 2. Influence of the surfactant DBSS on the contact angle of the ethanol-water mixtures

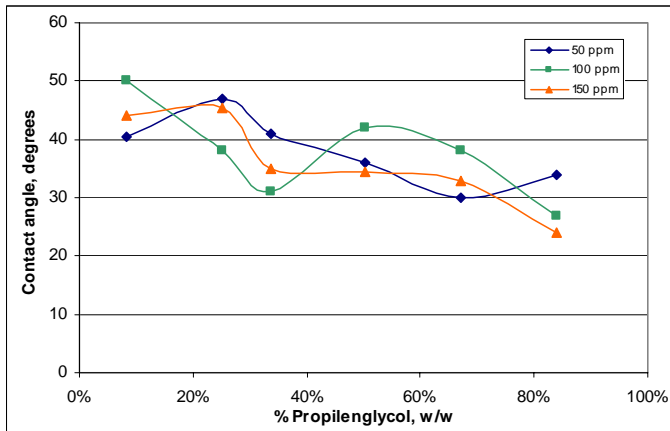


**Figure (6) Experimental measurements of the contact angle of ethanol-water mixtures with 50, 100, and 150 ppm DBSS.**

Due to the lack accurate prediction models for the interfacial tension properties, and their singularities in multi-component mixtures, it is necessary to continue the search of lower interfacial tension fluids with experimental measurements.

In these experiments was confirmed a combined effect of the binary mixture composition at 16% ethanol by weight with the effect of the surfactant close to its CMC of 150 ppm. At these conditions, in Fig (6), the contact angle was reduced (increased wettability) from 40 degrees for the binary mixture (Fig (4)) to 30 degrees adding the surfactant.

**Set 3. Combined effect of a third component and the use of a surfactant close to its critical micelle concentration.**



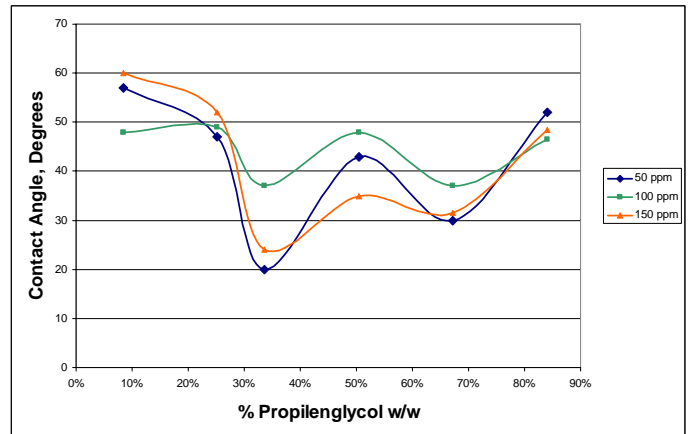
**Figure (7) Experimental measurements of the contact angle of ethanol-propilenglycol-water mixtures with 50, 100, and 150 ppm DBSS.**

In this set of experiments, the concentration of ethanol was maintained at 16% by weight and the contribution of water reduced to introduced propilenglycol or etilenglycol instead. The surfactant was added in 50, 100, and 150 ppm.

A reduction of the measured values of the contact angle in these mixtures is observed. The mixture with 84 % propilenglycol, 16% ethanol, and 150 ppm of DBSS had the lowest contact angle,  $\theta = 23^\circ$ . The experimental exploration of additional combinations of these components is necessary. The prediction capabilities of software like HYSYS v 3.2 are even more limited for studying the influence of the surfactants that are made of complex molecules not available in the prediction packages.

The best combinations for the mixtures of propilenglycol with a surfactant are presented in Fig (8). The trend in values of the contact angle decreases while increasing the propilenglycol content. Combinations of propilenglycol-ethanol-water with DBSS could get very low values of the contact angle. The mixture with 50% water, 34% propilenglycol, 16% ethanol and 50 ppm of DBSS produced the lowest contact angle measured of 20 degrees.

**Set 4. Mixtures of ethanol-water-propilenglycol with the surfactant DBSS.**



**Figure (8) Experimental measurements of the contact angle of propilenglycol-water mixtures with 50, 100, and 150 ppm DBSS.**

The search for the influence of the chemical structure of the boiling mixture components and the enhanced boiling heat transfer can be continued with the measured equilibrium contact angles. In the search of increased wettability, the liquid mixtures with ethanol-water and propilenglycol with the surfactant DBSS produced the best results.

**CONCLUSIONS**

The experimental search of increased wettability of solutions is the first step in defining boiling fluids. The predictive capabilities of interfacial tensions are still limited.

Increased boiling heat transfer is achieved with higher wettability fluids. The wettability of the fluids is correlated to lower sessile drop contact angle.

The search for the influence of the chemical structure of the boiling mixture components and the enhanced boiling heat transfer can be continued measuring equilibrium contact angles and liquid-vapor interfacial tensions.

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