VOL. 8, NO. 2, FEBRUARY 2013 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

CALCULATION OF INTERFACIAL TENSIONS BETWEEN MACROMOLECULAR SOLUTIONS AND SOLTROL-130 FROM CONTACT ANGLES MEASUREMENTS

Sinayobye E.[1], Mensah-Brown H.[1], Yaya A.[2], Kakane V. C. K.[3] and Baryeh E. A.[4]
[1]Department of Food Process Engineering, Faculty of Engineering Sciences, University of Ghana, Legon, Ghana
[2]Department of Materials Science and Engineering, University of Ghana, Legon, Ghana
[3]Physics Department, Faculty of Science, University of Ghana, Legon, Ghana
[4]Department of Agricultural Engineering, Faculty of Engineering Sciences, University of Ghana, Legon, Ghana
E-Mail: emsinay@gmail.com

ABSTRACT

The determination of the surface tension of some liquids or solutions has been carried out using a tensiometer. The determination of the contact angle between the liquids and a planar surface has also been carried out using photography. Polar and dispersive contributions of the surface tension were obtained by calculation while the polarities of the liquids and solutions were determined applying Wu equations. This method gave the different results for solutions prepared from macromolecular compounds (acroleine - ethanolamine macromolecular solution 1g/l, acroleine - diethanolamine macromolecular solution 1g/l, polyglutaraldehyde-ethanolamine macromolecular solution 0.7 g/l and polyglutaraldehyde - diethanolamine macromolecular solution 1 g/l) synthesized by Malonda from glutaraldehyde and acroleine. The dispersive and polar contributions of the surface tension were computed and used to calculate the interfacial tensions of solutions by the simple measurement of the contact angle. The results have revealed that the computed interfacial tensions were comparable to the values measured directly by the tensiometer for polyglutaraldehyde-ethanolamine macromolecular solution 0.7 g/l and polyglutaraldehyde - diethanolamine macromolecular solution 1 g/l) making an interface with Soltrol-130 of 17.1 and 16.9 dynes/cm compared to direct measured values of 17.2 and 17.7 dynes/cm respectively representing 1% and 5% error, respectively.

Keywords: surface tension, interfacial tension, contact angle, polarity, dispersive, polar contributions.

1. INTRODUCTION

The extraction of oil from a well can be done in three stages: primary, secondary and tertiary recuperations (Sinayobye, 1980). The first two are the most used whereas the third is under development. The primary recuperation is done by internal pressure of the oil that is high enough to make the oil gush out of the well. The oil thus recuperated is 10-15% of the initial total oil in the well.

The secondary recuperation, where the pressure has been decreased, is done by injecting water or gas into the well. The volume of oil recuperated by this method is 30-40% of the total volume (Bradley, 2005). The quantity recovered is low compared to the total initial volume because the water pushing the oil out of the well will take the path of least resistance and will not get into contact with the oil that is trapped in the porous rocks and sediments whose pores range from 0.1 to 100 microns. The capillarity effects are predominant and the oil is trapped in the form of micro globules. The oil is attached more or less rigidly to the surface of the sediment, generally by physisorption. Chemical bonds and the dipole-dipole interactions are also present.

In order to improve the efficiency of the water in the tertiary phase additives are used. The additives decrease the mobility of the water thus increasing the volume of the well treated. The method consists of using hydro-soluble macromolecules in the recuperation water (whose mass is generally higher than 10^6); polyacrylamides and the polysaccharides eg. xanthate have been used with success (Kaelbel and Cirha, 2003). Electrical charges can be introduced in the polyacrylamides' chains in order to decrease the viscosity and the dimensions of the dissolved particles leading to the efficiency of the polymer which is linked to the molecular expansion. The use of micellar solutions of tensioactive macromolecules (surfactants) helps in reaching a large number of pores of the sediment. The use of this method at the laboratory level has led to 100% recuperation (Sinayobye, 1980).

These micellar solutions must be:

- Stable at high temperatures up to 120°C.
- Stable in the presence of ionized water of injection and/or of the liquids in the well (i.e., 3 to 200 g/l of NaCl and 30 g/l $CaCl_2$).
- Chemically stable (pH between 3 and 9).
- Less adsorbed on the surface of the pores.
- Non biodegradable by bacteria from injection waters.

The mechanism of oil recuperation will depend on what happens at the interface of the fluid being recuperated and the fluid being used for recuperation. The physicochemical properties of interfaces, such as capillary forces, contact angles, wettability, interfacial tension and viscosity forces are fundamental in the understanding of the retention of the oil in the sediment (Treiber *et al*., 1972; McGuire, 1990).

Their alteration is thus the key to enhancing the oil recuperation from the sediment.

1.1. Theoretical background

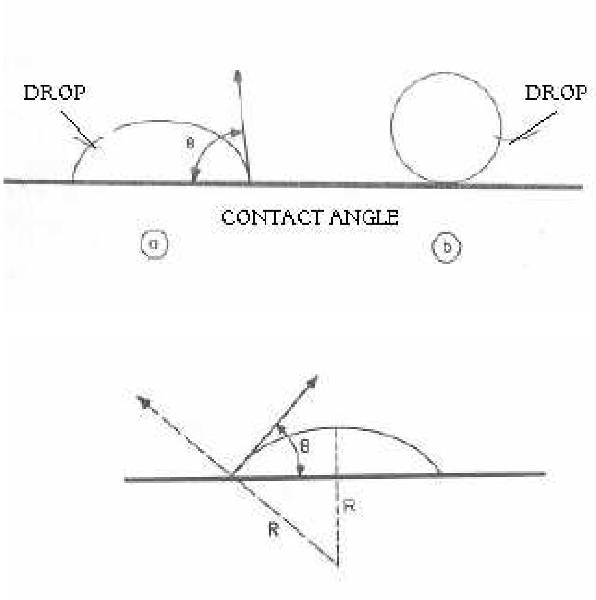
Wu (1971) has postulated that the surface tension of polymers is given by

$$\gamma_i = \gamma_i^d + \gamma_i^p \tag{1}$$

γ_i is the surface tension of the substance, i; (γ_L and γ_S are used for liquid and solid respectively). γ_S is also the free energy at the surface of the solid considered. The first term of the surface tension γ_i^d on the right hand side of equation (1) corresponds to the dispersive forces of London resulting from the interaction of instantaneous dipoles of Van der Waals forces (Li and Lu, 2001).

The second term γ_i^p corresponds to polar forces resulting from the interactions such as dipole-dipole, dipole-induced dipoles, hydrogen bonding, π bonding, and charge-transfer interactions. According to Wu (1975), γ_i^d can be calculated by using the theory of London which makes use of the electronic frequency of vibration, the polarisability and Planck's constant.

Sinayobye (1980) and Wu (1969, 1975) noted Young's work establishing that when a drop of liquid is deposited on a solid surface the equation linking the characteristics of the solid and the interfacial fluids and the contact angle θ is given by (Figure-1):



(c)

Figure-1. (a) Contact angle θ of a drop that wets the solid surface. (b) Contact angle (180°) of a drop that does not wet the solid surface. (c) Determination of contact angle of a drop of radius R on a solid surface.

$$\gamma_S = \gamma_{SL} + \gamma_L Cos\theta \tag{2}$$

or $\gamma_L Cos\theta = \gamma_S - \gamma_{SL}$ (3)

Where γ_{SL} is the interfacial tension between the solid and the liquid deposited.

In order to determine γ_i^d and γ_i^p, Fowkes (1965) has proposed an equation also called Fowkes' equation as follows:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \tag{4}$$

Where 1 and 2 refer to two different matters respectively of the same or different phases: solid-liquid or liquid-liquid.

Equation (4) contains a term with a geometric mean stressing the importance of dispersive contributions to the interfacial tension. Unfortunately however, equation (4) could not be applied to all systems because polar contributions were ignored. As a result, Tamai (1967) introduced a correction term, I_{12} to account for the polar forces contributing to the interfacial tensions:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} - I_{12} \tag{5}$$

Equation (5) cannot be applied to polar-polar systems, polymers, and organic solids because it does not give a good correlation of the interfacial tension between products 1 and 2. As the products used were organic macromolecules it is necessary to look for another general equation established by Wu (1975) which makes use of the reciprocal mean value term:

$$\gamma_{ij} = \gamma_i + \gamma_j - 4\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - 4\frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \tag{6}$$

where i, j can be solid, liquid, or gas or combinations of these.
For a solid-liquid system equation (6) becomes:

$$\gamma_{SL} = \gamma_S + \gamma_L - 4\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_j^d} - 4\frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \tag{7}$$

Substituting equation (2) into equation (7), we have

$$\gamma_L(1 + Cos\theta) = +4\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4\frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \tag{8}$$

The unknown terms in equation (8) are γ_L^d and γ_L^p because γ_L can be measured directly using a tensiometer. The terms γ_S^d and γ_S^p are dispersive and polar contributions respectively of the surface tension of the solid and they are supposed to be known because a known solid with known characteristics is chosen for the investigation.

Equation (8) helps to determine the surface tension between polymers, or between a polymer and an ordinary liquid, making it possible to calculate the surface tension and the polarity of polymers and organic solids after measuring the contact angle (Shibata *et al*., 1993).

The smaller the interfacial tension is, the more similar the polarities of the two phases involved.

Equation (8) is general for it can be applied to polar systems as well as non polar systems.

In Equation (6), the polar term represented in the reciprocal mean value is based on the empirical reasoning whereas the non polar term is based on the fact that the polarisabilities of element interacting with either of the two phases are not very different.

This is especially true for systems involving liquid and organic polymers and water.

It is not evident that equations (6) to (8) apply to a system whose polarisabilities are very different, such as water and mercury. For such a system the relationship including the geometric and the reciprocal means is rather used, Wu (1968, 1971):

$$\gamma_L^p \quad \gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \text{-} 4\frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{9}$$

This equation is called geometric and harmonic means equation. It is applicable to systems with high energy such as mercury, glass, graphite and metallic oxides (Nguyen and Johns, 1978). It covers a large domain of polymers and organic compounds as well as situations in which water is present.

The laboratory work can be simplified by eliminating the polar term i.e., by using a solid without any polar contribution $\gamma_S^p = 0$ and equation (8) then becomes:

$$\gamma_L(1 + Cos\theta) = 4\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} \tag{10}$$

This gives

$$\gamma_L^d = \frac{\gamma_S^d \gamma_L (1 + Cos\theta)}{4\gamma_S^d - \gamma_L(1 + Cos\theta)} \tag{11}$$

γ_L^d can be determined after measuring θ and γ_L and γ_L^p can then be deduced from $\gamma_L^p = \gamma_L \text{-} \gamma_L^d$.

Otherwise by using two solid planes a combination of two solid surfaces with different but known characteristics will have to be used to determine the contact angles in each case; thus a system of two equations and two variables γ_L^p and γ_L^d will be established. The solution of the system of equations will give γ_L^p and γ_L^d whose sum will give the surface tension of the liquid. The value obtained from the calculations above will then be compared to the measured γ_L.

Thus the system will be:

$$\gamma_L(1 + Cos\theta) = +4\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4\frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \tag{12}$$

$$\gamma_L(1 + Cos\theta') = +4\frac{\gamma'^d_S \gamma_L^d}{\gamma'^d_S + \gamma_L^d} + 4\frac{\gamma'^p_S \gamma_L^p}{\gamma'^p_S + \gamma_L^p} \tag{13}$$

γ_L, θ and θ' are measured, whilst for solids 1 and 2, γ_S^d, γ_S^p and γ'^d_S, γ'^p_S are found from reference books.

The aim of this study is to assess the interfacial behaviour of new macromolecular solutions with moderate molecular mass (acroleine, glutaraldehyde) in contact with the oil. The interfacial tension of the macromolecular solutions used will be determined by simply measuring the surface tension of the solution and the contact angle between the solution and a planar surface whose properties are known.

2. MATERIALS AND METHODS

The apparatus used, which is shown in Figure-2 consists of a thermostatic chamber (1) inside which a horizontal blade (4) is installed, a nitrogen bubble chamber (8), and a goniometer (9).

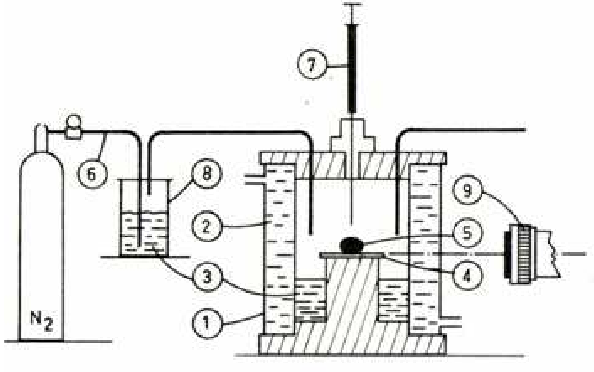


FIG. 1B

Figure-2. Experimental apparatus.

a) Thermostatic chamber
b) Water at constant temperature: 20°C

c) Experimental solution in bubble chamber and thermostatic chamber
d) Horizontal blade
e) Drop of oil
f) Nitrogen flow
g) Syringe needle
h) Bubble chamber
i) Ocular goniometer

The solution used produces an inversion of wettability on rock because the macromolecule is adsorbed on the solid thus changed the interfacial tension between the solid and the oil leading to an increase in the contact angle (Treiber *et al*., 1972). The thermostatic chamber is surrounded by a jacket at a constant temperature of 20^{o}C. It is in this chamber that a drop of oil is deposited on a horizontal blade using a graduated syringe with a long needle. The nitrogen gas is blown on the solution from the bubble chamber and carries the drop towards the thermostatic chamber (1) where the drop is deposited making the atmosphere around the drop saturate with the vapour of the solution under investigation. In case the solution is denser than the oil the thermostatic chamber will be held upside down and the chamber will be full. That was the case in most of the experiments.

2.1. Calculation of polarities of liquids and solutions

Wu's method (1975) for the determination of polarities of liquids was used in this study and it was extended to the determination of polar and dispersive contributions of macromolecular solutions. For the determination of the surface tension the Dognon Abribat tensiometer commercialized by Prolabo was used (Kaelble and Cirhn, 2003; Bradley, 2005).

The measurement of the contact angle was made by depositing a drop of the solution to be studied on a plane surface saturated with the liquid vapour whose characteristics, (γ_S^d , γ_S^p) are known.

2.2. Method of one plane surface

Solid polyethylene and paraffin are non-polar and they were used in this study.

Paraffin was deposited on a solid surface but the method seemed irreproducible: the state of the surface varied with working conditions despite all the precautions taken, for the liquid paraffin could not be homogeneously distributed on the solid before its solidification. As a result the contact angle could not be reproducible for all the experiments.

As a result, the method with two planar surfaces was used.

The method was used and extrapolated to all components for equation (6) is applicable to all components whether polar or not. But the method with one planar surface will always be best for it implies less measurements thus less errors and less laboratory work if only the problem of homogeneity of the solid surface is solved.

2.3. Method of two plane surfaces

Tetrafluoroethylene (Teflon) with γ_S^d =17.3 dynes/cm and γ_S^p =1.7 dynes/cm; and polymethylmethacrylate (PMMA) with γ_S^d =33 dynes/cm and γ_S^p =12.4 dynes/cm were used for this investigation. The measurements of the contact angle between each solid and the macromolecular solution were done after saturated nitrogen current with the macromolecular vapour was passed on the drop deposited on the solid material (either Teflon or PMMA). The use of the two plane surfaces made of Teflon and PMMA gives the following system of simultaneous equations respectively:

$$\frac{1}{4}\gamma_L(1+Cos\theta) = 17.3\frac{\gamma_L^d}{17.3+\gamma_L^d}+1.7\frac{\gamma_L^p}{1.7+\gamma_L^p} \quad (14)$$

$$\frac{1}{4}\gamma_L(1+Cos\theta') = 33\frac{\gamma_L^d}{33+\gamma_L^d}+12.4\frac{\gamma_L^p}{12.4+\gamma_L^p} \quad (15)$$

The system of simultaneous equations was solved by iteration according to Sinayobye *et al*. (2012) after measuring the contact angles θ and θ'.

The polarity is determined from the polar contributions of the surface tension by:

$$P = \frac{\gamma_i^p}{\gamma_i}$$

The polarity is an important parameter which is constant and independent of the temperature at which the experiment is done (Wu, 1971).

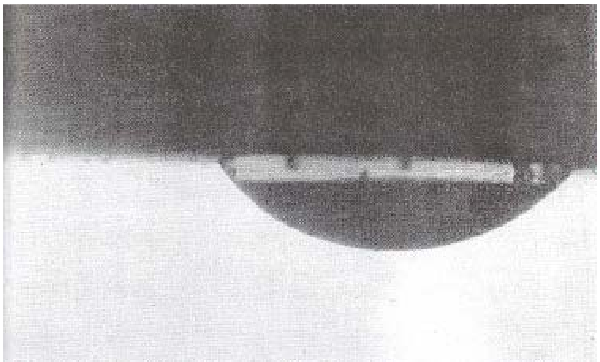


Figure-3. Drop Soltrol-130 on Teflon in water.

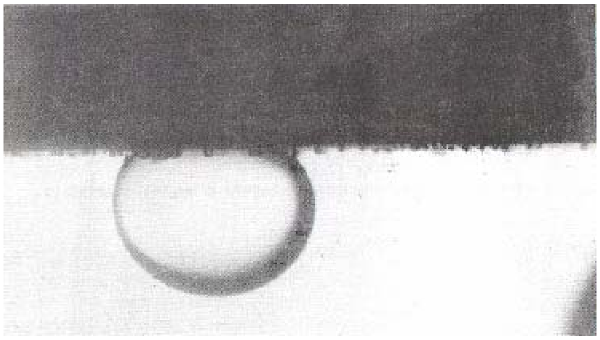


Figure-4. Drop Soltrol-130 on Teflon in a macromolecular solution.

3. RESULTS AND DISCUSSIONS

The results are compiled in the Table-1 below. The interfacial tensions of macromolecular aqueous solutions agree quite well with the measured values using conventional tensiometers. The interfacial tension of polyglutaraldehyde-ethanolamine and polyglutaraldehyde-diethanolamine in interface with Soltrol-130 calculated is almost the same as the measured value (making a physical interface) with an error less than 5% (Table-1).

As the angle of contact increases more fluid can be extracted. Therefore in the oil industry it is necessary to have the angle of contact close to 90° to have maximum extraction. When the angle of contact is 90° total extraction is obtained. Also waterproof surfaces tend to have the angle of contact close to 90° making the wettability approach zero. Wetting a surface reduces the angle of contact by using tensioactive products.

Table-1. Interfacial tension between the solution and Soltrol-130.

Compound/solution	**Experimental value** $\gamma_{i(1,2)}$ **dynes/cm**	**Calculated value** $\gamma_{i(1,2)}$ **dynes/cm**
Acroleine-ethanolamine. $\gamma_L^d = 65.8$, $\gamma_L^p = 1.3$ dynes/cm	26.5	22.3
Acroleine-diethanolamine. $\gamma_L^d = 56.5$, $\gamma_L^p = 5.1$ dynes/cm	19.1	16.8
Polyglutaraldehyde-ethanolamine $\gamma_L^d =$ 58.7, $\gamma_L^p = 1.5$ dynes/cm	17.2	17.1
Polyglutaraldehyde-diethanolamine $\gamma_L^d = 58.1$, $\gamma_L^p = 1.1$ dynes/cm	17.7	16.9

The concentration of all solutions was 1g/l except for polyglutaraldehyde-ethanolamine which had a concentration of 0.7g/l.

4. CONCLUSIONS

Wu's method applied to liquids and macromolecular solutions leads to the determination of polar and dispersive contributions of the surface tension of such liquids and solutions.

The interfacial tension between two solutions *i* and *j* is determined by Wu's equation using the polar and dispersive contributions of the surface tension of each solution:

$$\gamma_{ij} = \gamma_i + \gamma_j - 4\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - 4\frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}$$

This method has been used to determine the interfacial tension between two components (solid or liquid) without making a physical contact between the concerned components. The measured interfacial tensions were comparable to the computed values.

Solutions leading to low interfacial tension with oils or other solutions will be used to recuperate those oils.

ACKNOWLEDGEMENTS

The raw oil sample was given generously by Elf SNEA Boussens France whereas the soltrol-130 was given by Institut Français du pétrole (IFP) Malmaison, France and we are grateful. Most of the laboratory work was done at INSA Toulouse France.

REFERENCES

Bradley J.M. 2005. Determining the polar and dispersive contributions to the surface tension of water-based printing ink as a function of surfactant surface excess. Journal of Physics: Applied Physics. 38(12): 271-280.

Fowkes F. M. 1965. In Chemistry and Physics of Interfaces. Amer. Chem. Soc. 1: 1-12.

Kaelble D.H. 2003. Dispersion and polar contributions to ST of poly (methylene oxide) and Na-treated polytetrafluoroethylene. Polymer Physics. 9(12): 363-368.

Li Z and Lu B.C.Y. 2001. A molecular model for representing surface tension for polar liquids. Chemical Engineering Science. 56: 6977-6987.

McGuire J. 1990. On evaluation of the polar contribution to contact material surface energy. Journal of Food Engineering. 12(3): 239-247.

Nguyen T. and Johns W.E. 1978. Polar and dispersion force contributions to the total surface free energy of wood. Wood Science and Technology. 12(1): 63-74.

Shibata A., Tsukamoto R., Ueoka T., Ueno S. and Yamashika T. 1993. Dispersion-polar surface free energies of polypeptide films. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 78: 189-192.

Sinayobye E. 1980. Contribution à l'étude de l'Influence de Nouveaux Composés Macromoléculaires sur la Mouillabilité des Surfaces par les Hydrocarbures. These INSA Toulouse. pp. 77-78.

Sinayobye E., Kakane V.C.K. and Baryeh E.A. April 2012. Determination of polar and dispersive contributions of surface tensions of some macromolecular solutions. Int. J. Biol..Chem. Sci. 6(2): 887-896.

Tamai Y., Makuuchi K. and Suzuki M. 1967. Experimental Analysis of Interfacial Forces at the plane Surface of Solids. J. Phys. Chem. 13(71): 41176.

Treiber L.E., Archer D.L. and Owens W.W. 1972. A laboratory evaluation of the wettability of fifty oil-producing Reservoirs. Soc. Petr. Eng. J. 12: 531.

Wu S. 1968. Estimation of the critical surface tension for polymers from molecular constitution by a modified Hildebrand-Scott Equation. J. Phys. Chem. 72: 3332.

Wu S. 1969. Surface and Interfacial Tensions of Polymers Melts. I-Polyethylene, Polyisobutylene, and polyvinyl Acetate. J. colloid Interface Sci. 31: 153.

Wu S. 1971. Calculation of interfacial tensions in polymer systems. J. Polymers Sci. part C. 34: 19.

Wu S. 1975. Polar and non polar interactions in adhesion. J. Adhes. 5: 39.

Young T. 1805. Phil. Trans. Roy. Sco. (London). 95: 65.