



## Determination of polar and dispersive contributions of surface tensions of some macromolecular solutions

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### 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 1 g/l, acroleine-diethanolamine macromolecular solution 1 g/l, acroleine-urea macromolecular solution 0.7 g/l and polyglutaraldehyde-ethanolamine 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 surface tensions of solutions by the simple measurement of the contact angle. The results have revealed that the polarities were weak: 2% for all solutions except for the acroleine-diethanolamine macromolecular whose polarity was 6%. The surface tensions for all solutions varied from 67 to 59 dynes/cm.

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**Keywords:** Surface tension, interfacial tension, contact angle, polarity, dispersive and polar contributions.

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### 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 less 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 big 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<sub>2</sub>).
- 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.

*Theoretical background:* Wu (1971) has postulated that the surface tension of polymers is given by

$\gamma_i = \gamma_i^d + \gamma_i^p \dots\dots[1]$ ;  $\gamma_i$  is the surface tension of the substance, i ( $\gamma_L$  and  $\gamma_S$  are used for liquid and solid respectively).  $\gamma_S$  is also the free energy at the surface of the solid considered. The first term of the surface tension  $\gamma_i^d$  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  $\gamma_i^p$  corresponds to polar forces resulting from the interactions such as dipole-dipole, dipole-induced dipoles, hydrogen bonding,  $\pi$  bonding, and charge-transfer interactions. According to Wu (1975),  $\gamma_i^d$  can be calculated by using the theory of London which makes use of the electronic frequency of vibration, the polarisability and Planck's constant.

According to Sinayobye (1980) and Wu (1969, 1975), Young has established 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  $\theta$  is given by (Figure 1):

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \dots\dots\dots[2]$$

or  $\gamma_L \cos\theta = \gamma_S - \gamma_{SL} \dots\dots\dots[3]$

Where  $\gamma_{SL}$  is the interfacial tension between the solid and the liquid deposited.

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

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

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

Equation [3] contains a term with a geometric mean stressing the importance of dispersive contributions to the interfacial tension. This equation [3] could not be applied to all systems because polar contributions were ignored. As a result, Tamai (1967) introduced a correction term,  $I_{12}$  relating to the polar forces contributing to the interfacial tensions:

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

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:

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

where i, j can be solid, liquid, or gas or combinations of these.

For a solid-liquid system Eq. (4) becomes:

$$\gamma_{SL} = \gamma_S + \gamma_L - 4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} - 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \dots[7]$$

When Eq. (4) is introduced in Eq. (2) the result is:

$$\gamma_L(1 + \cos\theta) = + 4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \dots[8]$$

The unknown terms in equation (8) are  $\gamma_L^d$  and  $\gamma_L^p$  because  $\gamma_L$  can be measured directly using a tensiometer. The terms  $\gamma_S^d$  and  $\gamma_S^p$  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):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} - 4 \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \dots\dots[9]$$

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.

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

Equation (5) then becomes:

$$\gamma_L(1 + \cos\theta) = 4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} \dots\dots\dots[10]$$

This gives:

$$\gamma_L^d = \frac{\gamma_S^d \gamma_L(1 + \cos\theta)}{4\gamma_S^d - \gamma_L(1 + \cos\theta)} \dots\dots\dots[11]$$

$\gamma_L^d$  can be determined after measuring  $\theta$  and  $\gamma_L$  and  $\gamma_L^p$  can then be deduced from  $\gamma_L^p = \gamma_L - \gamma_L^d$ .

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  $\gamma_L^p$  and  $\gamma_L^d$  will be established. The solution of the system of equations will give  $\gamma_L^p$  and  $\gamma_L^d$  whose sum will give the surface tension of the liquid. The value obtained from the calculations above will then be compared to the measured  $\gamma_L$ .

Thus the system will be:

$$\gamma_L(1 + \cos\theta) = +4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \dots\dots[12]$$

$$\gamma_L(1 + \cos\theta) = +4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \dots\dots[13]$$

$\gamma_L$ ,  $\theta$  and  $\theta'$  are measured, while for solids 1 and 2,  $\gamma_S^d$ ,  $\gamma_S^p$  and  $\gamma_S^d$ ,  $\gamma_S^p$  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 polarity 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.

**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).

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 °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.

**Method used for the 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,  $(\gamma_S^d, \gamma_S^p)$  are known.

**Method of one plane surface**

Since solids polyethylene and paraffin are non-polar they have been used. 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. Therefore, the method with two planar surfaces was used.

The method 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.

**Method of two plane surfaces**

The previous method requires sophisticated apparatus especially for the

spreading of the paraffin layer on the solid surface. The following were used (Figures 3 and 4):

The tetrafluoroethylene (Teflon) whose  $\gamma_S^d = 17.3$  dynes/cm and  $\gamma_S^p = 1.7$  dynes/cm. The polymethylmethacrylate (PMMA) whose  $\gamma_S^d = 33$  dynes/cm and  $\gamma_S^p = 12.4$  dynes/cm.

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:

$$\frac{1}{4} \gamma_L (1 + \cos \theta) = 17.3 \frac{\gamma_L^d}{17.3 + \gamma_L^d} + 1.7 \frac{\gamma_L^p}{1.7 + \gamma_L^p} \dots [12.1]$$

$$\frac{1}{4} \gamma_L (1 + \cos \theta) = 33 \frac{\gamma_L^d}{33 + \gamma_L^d} + 12.4 \frac{\gamma_L^p}{12.4 + \gamma_L^p} \dots [12.2]$$

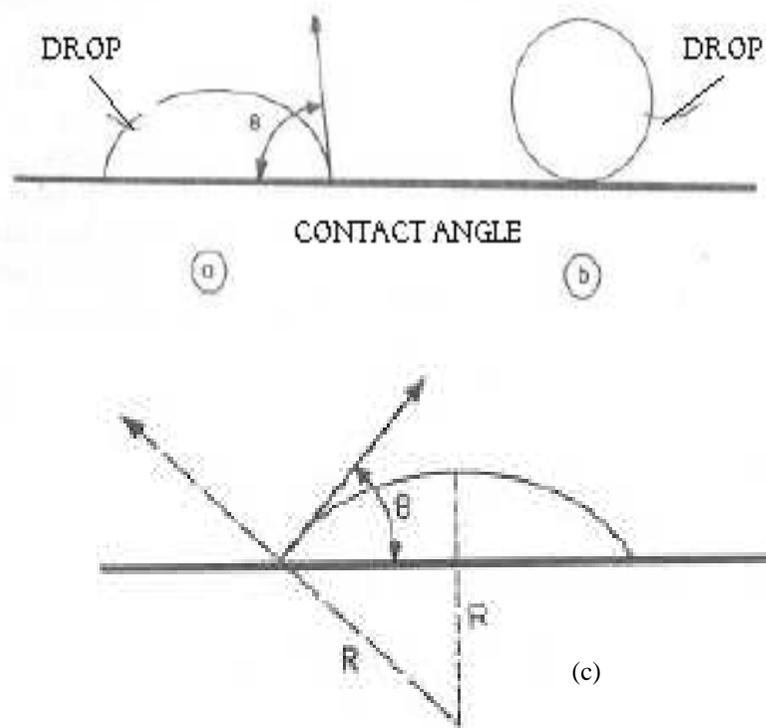
The system was solved by iteration after measuring the contact angles  $\theta$  and  $\theta'$  (Table 1). The polarity can be determined from the polar contributions of the surface tension by:

$$p = \frac{\gamma_i^p}{\gamma_i} \dots \dots \dots [14]$$

And for a liquid or a solution L:

$$p = \frac{\gamma_L^p}{\gamma_L} \dots \dots \dots [15]$$

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



**Figure 1:** (a) Contact angle  $\theta$  of a drop that wets the solid surface. (b) Contact angle ( $180^\circ$ ) 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.

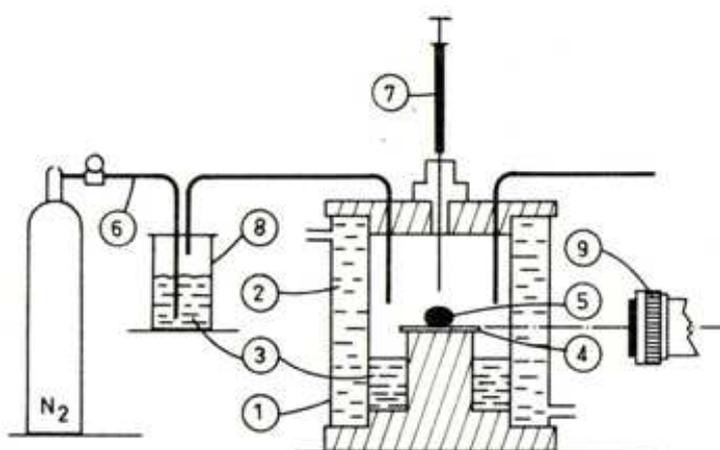
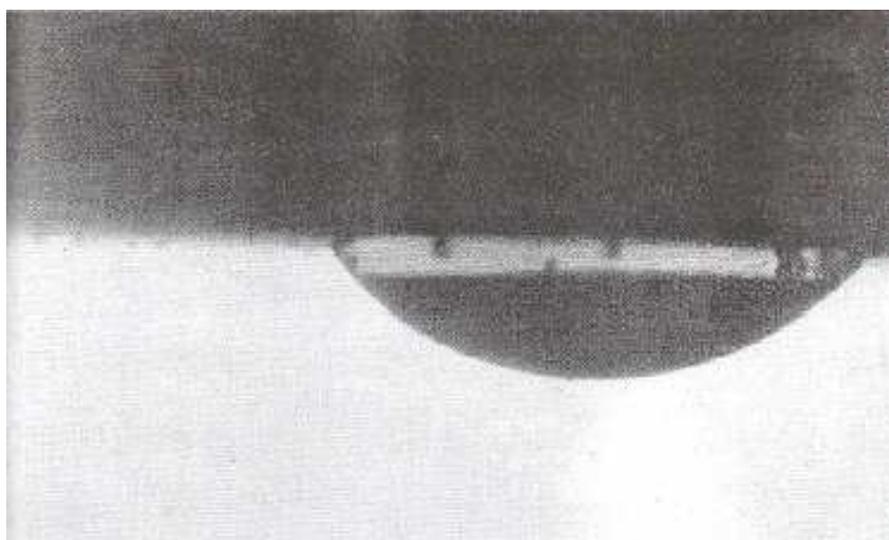


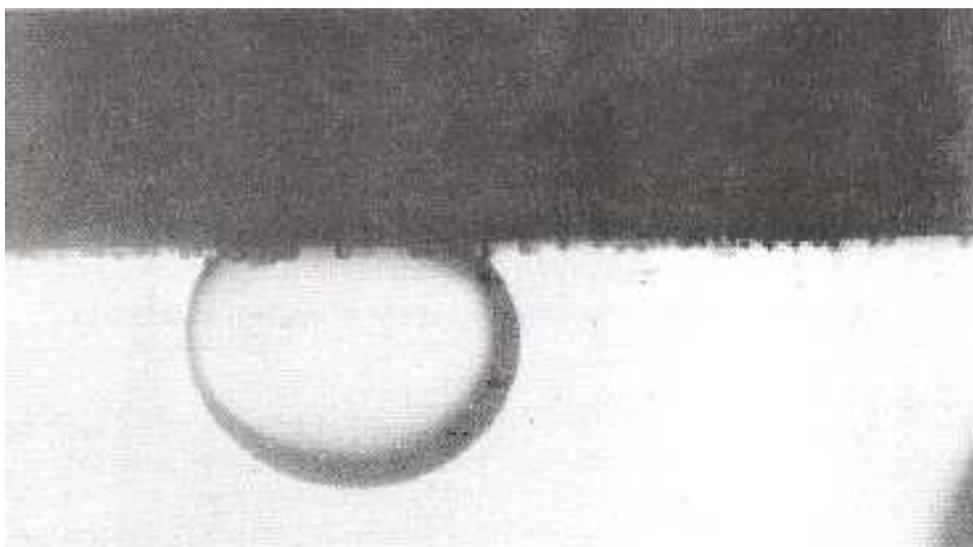
FIG 1B

**Figure 2:** Experimental apparatus.

1. Thermostatic chamber
2. Water at constant temperature: 20 °C
3. Experimental solution in bubble chamber and thermostatic chamber
4. Horizontal blade
5. Drop of oil
6. Nitrogen flow
7. Syringe needle
8. Bubble chamber
9. Ocular goniometer



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



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

## RESULTS AND DISCUSSION

The results are compiled in the Table 1 below. According to these results the polarity of macromolecular aqueous solutions is small or weak. This is due to the fact that the polar contribution is small compared to the surface tension. The result seems surprising knowing that the polarity of the water molecule is about 70%. There is no theoretical explanation is available. But when this method is used with pure substances for the determination of interfacial tensions as well as the macromolecular solutions, the values found agree well with the calculated ones ( Table 2).

### Determination of polarity of raw oil and soltrol-130

The application of Wu's method to the calculation of  $\gamma_L^d$  and  $\gamma_L^p$  of raw oil and the soltrol-130 gave the following results:

$\gamma_{rawoil}^d = 21.65$  dynes/cm;  $\gamma_{rawoil}^p = 6.45$  dynes/cm. The polarity of that raw oil is 23%.

$\gamma_{soltrol-130}^d = 21.8$  dynes/cm;  $\gamma_{soltrol-130}^p = 2.2$  dynes/cm

The polarity of soltrol-130 is found to be 9%. The polarity of the raw oil is higher than that of the soltrol-130 and that explains why the interfacial tension between the oil and macromolecular solutions is higher than that between soltrol-130 and the same macromolecular solutions.

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  $90^\circ$  to have maximum extraction. When the angle of contact is  $90^\circ$ , total extraction is obtained. Also waterproof surfaces tend to have the angle of contact close to  $90^\circ$  making the wettability approach zero. Wetting a surface reduces the angle of contact by using tensioactive products.

### Conclusion

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 polarity of each solution is determined by dividing the polar contribution of the surface tension and the surface tension itself:  $P = \frac{\gamma_i^p}{\gamma_i}$

Solutions with low polarity will be used to recuperate oils of low polarity as it was the case for soltrol-130 and vice versa. Soltrol-

130 whose polarity was 9% was recuperated best with the macromolecular solutions of polarities varying between 2 and 6%.

The interfacial tension between two liquids with similar and low polarities will be lower than the interfacial tension between two liquids with higher values of polarities.

**Table 1:** Determination of polar and dispersive contributions to surface tensions of macromolecular solutions.

Compound	Concentration g/l	Solid used	$\theta^\circ$ Contact angle	$\gamma_L$ solution Dynes/cm	$\gamma_L^p, \gamma_L^d$ Dynes/cm	P %
acroleine- ethanolamine	1.0	Teflon	95	67.1	$\gamma_L^d = 65.8$ $\gamma_L^p = 1.3$	2
		PMMA	42			
acroleine- diethanolamine	1.0	Teflon	91	61.6	$\gamma_L^d = 58.0$ $\gamma_L^p = 3.6$	6
		PMMA	42			
acroleine-urea	0.7	Teflon	91	60.2	$\gamma_L^d = 58.7$ $\gamma_L^p = 1.5$	2
		PMMA	41			
polyglutaraldehyde- ethanolamine	1	Teflon	80.5	59.2	$\gamma_L^d = 58.1$ $\gamma_L^p = 1.1$	2
		PMMA	27			

**Table 2:** 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-urea. $\gamma_L^d = 58.7, \gamma_L^p = 1.5$ dynes/cm	17.2	17.7
polyglutaraldehyde-ethanolamine $\gamma_L^d = 58.1, \gamma_L^p = 1.1$ dynes/cm	17.1	16.9

## 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 JM. 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 FM. 1965. Chemistry and physics of interfaces. *Amer. Chem. Soc.*, **1**: 1-12.
- Kaelble DH. 2003. Dispersion and polar contributions to ST of poly (methylene oxide) and Na-treated polytetrafluoroethylene. *Polymer Physics*, **9**(12): 363-368.
- Li Z, Lu BCY. 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, Johns WE. 1978. Polar and dispersion force contributions to the total surface free energy of wood. *Wood Science and Technology*, **12**(1): 63-74.
- Sinayobye E. 1980. Contribution à l'étude de l'influence de nouveaux composés macromoléculaires sur la mouillabilité des Surfaces par les hydrocarbures. Thèse INSA, Toulouse, p. 77-78.
- Shibata A, Tsukamoto R, Ueoka T, Ueno S, Yamashika T. 1993. Dispersion-polar surface free energies of polypeptide films. *Colloids and Surfaces A: Physico-chemical and Engineering Aspects*, **78**: 189-192.
- Tamai Y, Makuuchi K, Suzuki M. 1967. Experimental analysis of interfacial forces at the plane surface of solids. *J. Phys. Chem.*, **13**(71): 41176.
- Treiber LE, Archer DL, Owens WW. 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.*, **34**: 19.
- Wu S. 1975. Polar and non polar interactions in adhesion. *J. Adhes.*, **5**: 39.