Calculation of interfacial tensions between macromolecular solutions and Soltrol-130 from contact angles measurements

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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 (Treibert et al., 1972; McGuire, 1990).

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 CaCl₂).
- Chemically stable (pH between 3 and 9).
- Less adsorbed on the surface of the pores.
- Non biodegradable by bacteria from injection waters.
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

$$\gamma_i = \gamma_i^d + \gamma_i^p$$  \hspace{1cm} (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.

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 $$\theta$$ is given by (Figure-1):

$$\gamma_{SL} = \gamma_S + \gamma_L - 4 \frac{\gamma_S \gamma_L}{\gamma_S^d + \gamma_L^d} - 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}$$  \hspace{1cm} (6)

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

$$\gamma_{SL} = \gamma_S + \gamma_L - 4 \frac{\gamma_S \gamma_L}{\gamma_S^d + \gamma_L^d} - 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}$$  \hspace{1cm} (7)

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

$$\gamma_L (1 + \cos \theta) = 4 \frac{\gamma_S \gamma_L}{\gamma_S^d + \gamma_L^d} + 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}$$  \hspace{1cm} (8)

The unknown terms in equation (8) are $$\gamma_L^d$$ and $$\gamma_L^p$$ because $$\gamma_L$$ can be measured directly using
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 between the solution and a planar surface whose properties are known. 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:

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

This gives

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

\( \gamma_L^d \) 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:

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

\[ \gamma_L(1 + \cos \theta') = 4\frac{\gamma_S^d \gamma_L^{dp}}{\gamma_S^d + \gamma_L^{dp}} + 4\frac{\gamma_S^p \gamma_L^{pp}}{\gamma_S^p + \gamma_L^{pp}} \]

$\gamma_L$, $\theta$ and $\theta'$ are measured, whilst for solids 1 and 2, $\gamma_S^d$, $\gamma_S^p$ and $\gamma_L^{dp}$, $\gamma_L^{pp}$ 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).

Figure-2. Experimental apparatus.

a) Thermostatic chamber
b) Water at constant temperature: 20°C
Experimental solution in bubble chamber and thermostatic chamber

Horizontal blade

Drop of oil

Nitrogen flow

Syringe needle

Bubble chamber

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°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, \((\gamma'_{S}, \gamma'_{P})\) 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 \(\gamma'_{S}=17.3\) dynes/cm and \(\gamma'_{P}=1.7\) dynes/cm; and polymethylmethacrylate (PMMA) with \(\gamma'_{S}=33\) dynes/cm and \(\gamma'_{P}=12.4\) 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:

\[
\frac{1}{4} \gamma_{L} (1 + \cos \theta) = \frac{17.3 \gamma'_{L} + 1.7 \gamma'_{P}}{17.3 + 1.7} \quad (14)
\]

\[
\frac{1}{4} \gamma_{L} (1 + \cos \theta') = \frac{33 \gamma'_{L} + 12.4 \gamma'_{P}}{33 + 12.4} \quad (15)
\]

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

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

\[
P = \frac{\gamma'_{P}}{\gamma'_{L}}
\]

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.
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 $90^\circ$ 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.

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

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

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REFERENCES


