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Effect of surfactant on single drop mass transfer for extraction of aromatics from lubricating oils

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Abstract. Solvent extraction is an effective method for the reduction of the content of aromatic of lubricating oil. Frequently, with phenol, furfural, the NMP (out of N-methyl pyrrolidone). The power solvent and the selectivity can be still to increase while using surfactant as additive which facilitates the separation of phase and increases the yeild in raffinat. Liquid-liquid mass transfer coefficients for single freely rising drops in the presence of surfactant in an extraction column have been investigated. The surfactant used in this study was sodium lauryl ether sulfate (SLES). The experiments were performed by bubbling a solvent as a series of individual drops from the top of the column containing furfural-SLES solution. The column used in this experiment was made from glass with 17 mm inner diameter and a capacity of 125ml. The effects of the concentration of surfactant on the overall coefficient of mass transfer was investigated.

1. Introduction
The process of manufacturing lubricating oil base stocks requires the removal of aromatic hydrocarbons from vacuum distillates [1,2]. Under atmospheric conditions, the crude oil Residue is transferred firstly to a vacuum distillation column, and then separated into different lube oil cuts which are characterized by their boiling range and viscosity.

N – methyl –2 – pyrrolidone, furfural, phenol and liquid sulfur dioxide are the largest used solvents [3-5].

Liquid- liquid extraction is an important separation process. It is a widely used separation process in industry.

Some studies on the use of surfactants as additives in liquid-liquid extraction have been mentioned in literature [6-9]. A surfactant is a substance that significantly decreases the surface tension of a liquid when added in small quantities. If a small amount of surfactant is added during the extraction process, both masses of the transfer coefficient and the interfacial area may be affected.

Several investigators [10-12] suggest that the effects of surfactants cause a decrease in mass transfer rate. The results indicate that surfactants often reduce the mass transfer coefficient but increase the mass transfer area per unit volume.
Abolghasemi and al [13] in their studies performed on extraction, the decrease in the mass transfer coefficient by surfactant was attributed either to the decrease in interfacial mobility and internal circulation or to the blocking action of surfactant molecules at the interface it has been generally assumed that such activity should facilitate mass transfer across the interface.

Audeh and al [14], discovered an improved furfural extraction process for lube oil base stock containing aromatic type material by the addition of demulsifiers to furfural to facilitate phase separation, selectivity, and increase the raffinate yield while maintaining the same raffinate measured by raffinate refractive index.

They suggested a wide variety of surfactant. Among these are included those of the type having the formula R-CONH-CH$_2$CH$_2$SO$_3$Na.

For a class of the sulfonic acid salt surfactant, the metal may be taken from Groups IA, HA and HE of the Periodic table, as, for example, sodium, calcium, barium and zinc, wherein the alkyl contains 1 to 30 carbon atoms, preferably 10 to 20 carbon atoms.

We present in this paper our investigations regarding the use of sodium lauryl ether sulfate (SLES) as surfactant.

Our choice for this particular class of surfactants (ethoxylated anionic surfactants) was also motivated by the fact that in spite of their wide range of applications, their self-aggregation in aqueous solutions is not clearly understood. For instance, it may be anticipated that the addition of hydrophilic oxyethylene (OE) groups adjacent to the anionic sulfate moiety would increase the overall hydrophilic character of the molecule and increase the CMC accordingly [15].

2. Experimental procedures

2.1. Chemicals

The SPD (spindle distillat) and furfural were provided by a refinery of Arzew (Algeria). The feedstock for vacuum distillation unit was atmospheric residue produced from light Hassi Messaoud crude oil. Their physical properties are listed in table 1.

Anhydrous calcium chloride and Cyclohexane were purchased from Fluka. (SLES) C$_{12}$H$_{25}$(OC$_2$H$_4$)$_2$SO$_3$Na with trade name Galaxy LES 70 with 70 % active matter was provided by Galaxy Surfactants Ltd. Surfactant solutions were prepared with furfural solvent.

2.2. Experimental section

The SPD and furfural were provided from Arzew refinery (Oran-Algeria). The SPD sample was collected from the light crude oil of Hassi Messaoud.

The extraction is carried out in a column of extraction out of glass, of a capacity of 125ml with a diameter of 17mm, the temperature is regulated, by the circulation of oil and the solvent (furfural) in a bath thermostat, the thermostat will have to keep the temperature of constant measurement to 95°C.

The counter-current is carried out by gravity, it is to say by difference in density between the phases. The phase continues is pumped in bottom of the column, and the dispersed phase is pumped at the top of the column, the time of flow of the droplet which represents the dispersed phase is measured by chronometer.

The decantation is carried out during one hour of time in order to reach balance. After that one separates the sub-base (phase of extract) in Matras and the road base (phase D in the column from extraction.

The raffinate obtained is washed with distilled water heated at a temperature of 90°C in order to remove from furfural. The operation is repeated six times. The washed product is dehydrated by the calcium dichloride.

The chemical system used in these experiments is lubricating oil/aromatics/furfural/SLES, where the lubricating oil is considered as the continuous phase (feed phase), furfural as the dispersed phase, aromatics as a solute and SLES as a surface active agent (surfactant). At the beginning of the operation, lubricating oil and furfural are brought to saturation. SLES with known and different concentrations
are added to the furfural phase (solvent phase). The mass transfer direction in this system is from raffinate phase to extract phase, the Schematic diagram of experimental setup is shown in figure 1.

The Experimental conditions are:
Solvent ratio relative to oil equal to 1
Extraction temperature: 95 °C
Surfactant concentration in the solution of furfural: 0; 0.01%; 0.05%; 0.1%

![Schematic diagram of experimental setup.](image1)

The column is provided with a device of dispersion to improve contacts it with diameter of 3mm as shown in figure 2.

![Dispersing device.](image2)

2.3. Determination of the composition according to the cycle number of aromatic
To determine, the selectivity, the oil composition in aromatic hydrocarbons (mono, di, poly), we used the method of Burdett [16]. This method takes into account the fact that among the hydrocarbons, only aromatics give an absorption in ultraviolet, with a maximum ratio, which shifts to longer wavelengths when the condensed nucleus number increases:

- Mono aromatic: 197 nm
- Diaromatic: 230 nm
- Tri et polyaromatic: 260 nm

The compositions of aromatic (mono, di, Poly) were measured by absorption spectroscopy with ultraviolet using ASTM D 2008 standard test method [17].

The absorption coefficients $a_1$, $a_2$ and $a_3$ were measured at three wavelengths with the following characteristics (concentration of 1 g/l for a cell thickness of 1 cm). The raffinate and extract phases were diluted with cyclohesane. In current study Spectrophotometer (spectroScan 80DV-UV/Vis) was used.

The mass percentages of aromatics (Mono, Di, Poly) are determined according to the following equation:

$$X_d = 10^{-4}(20.17a_1 - 2.59a_2 - 5.47a_3)$$  \(1\)
\[ X_{A2} = 10^{-4} \left( -0.68a_1 + 12.83a_2 - 3.00a_3 \right) \]  
\[ X_{A3} = 10^{-4} \left( -0.05a_1 - 0.45a_2 + 17.98a_3 \right) \]

The saturated compound was calculated using following equation:
\[ X_b = 100 - X_r \]

2.4. Mass transfert calculation model
In this process, the surfactant is transfered from drop to the solvent as dispersed phase. From the mass balance of SLES in single drop, the following equation is obtained:
\[ K_{d}a_{d} \left(C_{d} - C^*_{d}\right) = -a_{d}C_{d} \]

were \( k_{d} \) is the overal mass transfer coefficient for the dispersed phase (fufural), and \( a_{d} \) and \( V_{d} \) are surface area and volume of a drop, \( C_{d} \) is the solute concentration in the dispersed phase and \( C^*_{d} \) is the solute concentration in the dispersed phase in equilibrium with its concentration in the continuous phase. If the solute concentration in the continuous phase is symbolized by \( C_{c} \), then \( C^*_{d} \) and \( C_{c} \) can be correlated by the following expression:
\[ C^*_{d} = mC_{c} \]

where \( m \) is the equilibrium distribution coefficient.
\[ K_{d} = \frac{V_{d} \ln \left( \frac{C_{d1}}{C_{d2}} \right)}{a_{d} \ln \left( \frac{C_{d1}}{C_{d2}} \right)} \]

with the assumption that the drop is spherical, its surface area and volume are
\[ a_{d} = \pi d_{d}^2 \]
\[ V_{d} = \left( \frac{\pi}{6} \right) d_{d}^3 \]

Substituting Eqs. (8) and (9) into Eq. (7) gives:
\[ k_{d} = \left( \frac{d_{d}}{\xi_{d}} \right) \ln \left( \frac{C_{d1}}{C_{d2}} \right) \]

In this study, the drop diameter (\( d_{d} \)) was calculated from the following equation (McCab, Smith, and Harriot 1993):
\[ d_{d} = \left( \frac{\varepsilon_{d0} \varepsilon_{d} \varepsilon_{g} \varepsilon_{d} \varepsilon_{g} \varepsilon_{d}}{\varepsilon_{d0} \varepsilon_{d} \varepsilon_{g} \varepsilon_{d} \varepsilon_{g} \varepsilon_{d}} \right)^{\frac{1}{3}} \]

The drop rise time (\( \xi_{d} \)) in Eq. (6) was experimentally measured by using a stopwatch. \( C_{d1} \) and \( C_{d2} \) are the measured solute concentrations in the feed and raffinate solutions, respectively.

3. Results and discussions

Table 1. Values of yield; compositions in mono-aromatics (\( X_{A1} \)), di-aromatic (\( X_{A2} \)), poly-aromatics (\( X_{A3} \)) and saturates (\( X_{BR} \)) in the raffinate phase.

| Fraction | \( X_{A1} \) (wt.%) | \( X_{A2} \) (wt.%) | \( X_{A3} \) (wt.%) | \( X_{AT} \) (wt.%) | \( X_{BR} \) (wt.%) |
|----------|----------------------|---------------------|---------------------|---------------------|---------------------|
| SPD      | 14.60                | 5.16                | 3.48                | 23.24               | 76.77               |
| R1       | 9.68                 | 2.62                | 1.73                | 14.03               | 85.98               |
| R2       | 10.04                | 3.18                | 1.95                | 15.17               | 84.84               |
| R3       | 9.032                | 2.23                | 1.38                | 12.65               | 87.36               |
| R4       | 9.54                 | 2.43                | 1.47                | 13.43               | 86.57               |
In view of the results obtained, it is noted that:

A different surfactant concentration, polyaromatic and diaromatic extracts are better than monoaromatic. It was found that the maximum polyaromatic extraction was carried out using SLES concentration at 0.05%wt.

The diaromatic extraction was for a SLES concentration of 0.05% better quality in raffinate was obtained with the SLES of 0.05%, whose total aromatic is of 12.64%. From which it is deduced, the decrease in the aromatic content that is due to the increase in the selectivity of furfural for SLES concentration of 0.05%.

![Surface Tension vs Surfactant Concentration](image1.png)

**Figure 3.** Variation of the surface tension as a function of the surfactant concentration.

From figure 3, it can be seen that the surface tension decreases with increasing surfactant concentration. This decrease is slower in the area of high concentrations.

The surfactant is capable of decreasing the surface tension due to adsorption and orientation of the molecules on the phase separation surface.

![Diffusion Coefficient vs SLES Concentration](image2.png)

**Figure 4.** Variation of the diffusion coefficient as a function of the concentration of SLES.

From figure 4, the addition of surfactant in the dispersed phase lowers the overall mass transfer coefficient (the diffusion coefficient).

Increasing the surfactant concentration decreases the diffusion coefficient value.

![Diffusion Coefficient vs Surface Tension](image3.png)

**Figure 5.** Correlation between diffusion coefficient and surface tension.

Figure 5 shows the correlation between the diffusion coefficient and the surface tension. The $K_d$ value increases with increasing the surface tension value of the dispersed phase. The increase in the surface tension of the dispersed phase caused a high gradient of the surface tension between the continuous phase and the dispersed phase. This difference increases the interfacial turbulence between the continuous and dispersed phase, which increasing the value of the mass transfer coefficient.
4. Conclusion

The aim of the work presented is to extract the aromatic compounds from a petroleum cut with and without the presence of the surfactant.

The extraction of the aromatics is carried out in an apparatus making it possible to carry out the following two operations:

- An intimate contact between the two liquids: the solvent and the oily charge.
- A separation of the two phases obtained: the extract and the raffinate.

This differential contact between a dispersed phase and a continuous phase, which takes place by countercurrent flow with external energy supply, establishes a concentration gradient giving rise to a transfer of material, by continuous and progressive diffusion, over the whole Length of countercurrent.

The experiments carried out clearly show that, with the addition of different concentrations of surfactant in the dispersed phase, it is possible to:

- Ensure good phase separation.
- Reduction of the overall mass transfer coefficient (the diffusion coefficient), and consequently an improvement in raffinate quality.

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Nomenclature
Mw Mean molecular weight
SG Density (20°C/20°C)
RI Refractive index (20°C)
mA Distribution coefficient of aromatic
mB Distribution coefficient of saturated
a1 Absorption coefficient at longer wavelengths of 197nm
a2 Absorption coefficient coefficient at longer wavelengths of 230nm
a3 Absorption coefficient coefficient at longer wavelengths of 260nm
A1 Monoaromatic hydrocarbon
A2 Diaromatic hydrocarbon
A3 Polyaromatic hydrocarbon
AT Total aromatic hydrocarbon
B Saturated hydrocarbon
XA1 Monoaromatic concentration (%mas.)
XA2 Diaromatic concentration (%mas.)
XA3 Polyaromatic concentration (%mas.)
XAR Aromatic concentration in raffinat phase (%mas.)
XBR Saturated concentration in extract phase (%mas.)
XER Saturated concentration in raffinat phase (%mas.)
a d Specific surface area of a drop
V d Volume of a drop
C d The solute concentration in the dispersed phase.
C*d The solute concentration in the dispersed phase at equilibrium with its
circumference in the continuous phase.
m Coefficient of equilibrium distribution.
\(d_0\) Diameter of the orifice for the dispersed phase
\(\rho_c\) Continuous phase density (kg/m³)
\(\rho_d\) Dispersed phase density (kg/m³)
\(\sigma\) Surface tension (mN/m)
g Constant of gravity (m/s²)
\(d_d\) Drop diameter of the dispersed phase (mm)
C1 Initial aromatic charge concentration (spindle) (mol/m³)
C2 Concentration of aromatics after extraction (mol/m³)
td Droplet flow time of the dispersed phase (s)

Subscripts
SPD Spindle (light lubricating oil)
SLES Sodium lauryl ether sulfate
R Raffinate phase
E Extract phase

Greek letters
B Selectivity
\(\gamma\) Activity coefficient