

1 **SOLUBILIZATION OF HERBICIDES BY SINGLE AND MIXED**
2 **COMMERCIAL SURFACTANTS**

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1 **ABSTRACT**

2 Solubilization capabilities of the micellar solutions of three single surfactants, the two
3 alcohol alkoxyates B048 and B266, and the tallow alkyl ethoxylated amine ET15, as
4 well as their equimolar mixed solutions towards the herbicides flurtamone (FL),
5 metribuzin (MTZ) and mesotrione (MST) was investigated. Solubilization capacity was
6 quantified in terms of molar solubilization ratio (*MSR*), critical micellar concentration
7 (CMC), micelle water partition coefficient (K_{mc}), the binding constant (K_1), the number
8 of aggregation (N_{agg}) and the Stern-Volmer constant (K_{sv}). The herbicides were
9 greatly solubilized into different loci of the micelles: FL within the inner hydrophobic
10 core, MST at the micelle/water interface and MTZ in the palisade region. Equimolar
11 binary surfactant mixtures did not improve the solubilization of herbicides over those of
12 the single ones, with the exception of MTZ by the B266/ET15 system which accounted
13 for enhanced solubilization by 10-20%. This enhanced solubilization of MTZ was due
14 to the increasing number of micelles both arising from the intermediate N_{agg} relative to
15 those of the single surfactants and, the lowering of the CMC. The use of K_{sv} values was
16 found to be a better predictor for the solubilization of polar molecules within binary
17 mixtures of these surfactants than the interaction parameter β^M from Regular Solution
18 Theory (RST). The results suggest herein that the use of mixed surfactant systems for
19 solubilization of polar molecules in environmental remediation technologies may be
20 very limited in scope, without clear advantages over the use of single surfactant
21 systems.

22

23 **Key words:** solubilization, ethoxylated surfactants, polar solutes, mixed surfactants.

24

1. INTRODUCTION

Environmental applications of surfactants have been increasing during the late decades due to their unique properties as solubilizing agents (Deshpande et al., 2000; Zhou & Zhu, 2004; Mishael & Dubin, 2005; Mohamed & Mahfoodh, 2006). Surfactants are amphiphile molecules which aggregate in solution beyond certain concentration called the critical micellar concentration (CMC), forming usually spherical structures of several nm with large hydrophobic domains in their core whereas hydrophilic surface groups are located in the outer surface. Non-aqueous phase liquids (NAPLs) such as polycyclic aromatic hydrocarbons (PAHs) and in general, hydrophobic organic chemicals (HOCs) tend to be strongly incorporated within the micellar core because the hydrocarbon region forms a liquid-like region having a viscosity approximately an order of magnitude greater than that of liquid hydrocarbons of similar chain length (Zana, 2003). Surfactant-enhanced remediation (SER) technologies take the benefit of this property. Desorption of contaminants from soils is improved by surfactant addition in “pump and treat” technologies (Childs et al., 2004; Rosas et al., 2011). Field-scale experiments have shown the success of this approach (McCray et al., 2011). In addition, surfactants can also improve microbial degradation of HOCs by increasing their desorption from soil, therefore facilitating their assimilation by bacteria (Guha et al., 1998; Bueno-Montes et al., 2011; Lu et al., 2011). The performance of permeable reactive barriers based on different materials used in aquifer remediation is enhanced by the presence of surfactants (Wang et al., 2010; Shin et al., 2011).

Surfactants are also used in membrane separation processes in the treatment of wastewater and groundwater, such as micellar-enhanced ultrafiltration (MEUF), that are based on the addition of surfactants above the CMC that would trap solutes in solution in the form of micelles which would not pass through polymeric ultrafiltration

1 membranes because the hydrodynamic size of the micelles is larger than that of the
2 pores of the membrane, provoking its rejection (Van der Bruggen et al., 2003; Alka et
3 al., 2011; Li et al., 2011). Another water treatment process employing surfactants is the
4 adsorptive micellar flocculation. This technique consists of the adsorption of an organic
5 pollutant on an amorphous substrate formed by the flocculation of micelles of
6 surfactants like laurylsulphate and α -olefinsulphonate by trivalent cations as Al^{3+} and
7 Fe^{3+} (Paton-Morales et al., 2002; Talens-Alession et al. 2004).

8 The solubilization capabilities of the surfactants are dependent on the solution pH, ionic
9 strength, surfactant concentration and strongly on the chemical nature of the surfactant
10 (Kim et al., 2005; Zhou et al., 2011). The surfactants used in MEUF mainly comprise
11 ionic surfactants such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium
12 bromide (CTMA), cetyltriethylammonium bromide (CTAB), cetylpyridinium chloride
13 (CyPCl), dichloroacetic acid, trichloroacetic acid, etc. (Huang et al., 2010). For
14 instance, the cationic surfactants CTMA and CyPCl removed efficiently dyes (Khosa &
15 Shah, 2011). The anionic surfactant sodium dodecyl sulfate is the most widely used for
16 the removal of heavy metals (Alka et al., 2011). However, nonionic surfactants are
17 preferred in SER technologies because of their higher efficiency in solubilizing HOCs
18 due to their lower CMC compared to cationic and anionic surfactants (Zhu & Rhue,
19 2000).

20 Surfactant application can be broadened by the use of surfactant mixtures. They can
21 pose higher cloud points than those of the single surfactant and be employed under a
22 wider range of temperature, salinity and hardness conditions than the individual
23 surfactants (Zhou & Zhu, 2004). In addition, surfactants' CMC can be lowered by the
24 use of mixtures. The use of surfactant mixtures will result in mixed micelles with lower
25 CMC than those of the single components at comparable surfactant concentrations,

1 resulting in enhanced solubilization of the target molecules. For instance, in the case of
2 mixture of nonionic surfactants, higher micellar partition coefficients for HOCs were
3 reported because of the lower polarity of the mixed micelles (Mohamed & Mahfoodh,
4 2006). Attractive interactions (synergism) between surfactant molecules in mixtures
5 have been observed which are dependent on the nature of the surfactants. Several
6 nonionic-anionic surfactant mixtures have been reported to show synergism and
7 enhanced solubilization of hexachlorobenzene (Yuan et al., 2007), dense NAPLs (Zhao
8 et al., 2006), and PAHs (Zhu & Feng, 2003). Synergism has been also noticed in
9 nonionic-cationic (Bérlabi et al., 2010) and cationic-cationic surfactant mixtures (Al-
10 Wardian et al., 2004; Wei et al., 2011).

11 Most of the studies on solubilization by surfactants have focused on non-polar solutes
12 such as PAHs, NAPLs. In the current work, the solubilization of three herbicides (two
13 nonionic and one acidic) by single and binary combinations of several commercial
14 surfactants was examined. The results will help to understand the processes involved in
15 the solubilization of molecules with different polar functional moieties in their structure,
16 and to predict the solubilization properties of mixed surfactant solutions based on that of
17 single surfactant. This will provide valuable information for the selection of different
18 surfactant systems on their employment in environmental remediation technologies.

19

20 **2. MATERIALS AND METHODS**

21 **2.1. Materials.**

22 The analytical herbicides flurtamone (FL), mesotrione (MST) and metribuzin (MTZ)
23 were purchased from Sigma-Aldrich Co. (Sigma Chemical Co., St Louis, MO). Their
24 water solubilities at 25°C were 0.06 mM for FL, 0.62 mM for MST and 5.84 mM for
25 MTZ. The surfactants used were two alcohol alkoxylates (B048, B266) and a tallow

1 alkyl ethoxylated amine (ET15). They were kindly provided by AKZONobel
2 (Amsterdam, The Netherlands). Figure 1 shows the molecular structure of the
3 herbicides and the surfactants. Physical and chemical properties of the surfactants are
4 described in Table 1. Pyrene, CyPCI and H₃PO₄ were also provided by Sigma-Aldrich
5 Co. HPLC-acetonitrile was purchased from Teknokroma S.A. (Barcelona, Spain).

6

7 2.2. Measurements of surface tension.

8 The surface tension (γ) measurements were performed with a LAUDA TD 3
9 tensiometer using Du Nuoy ring detachment method. The ring was cleaned with ethanol
10 and flamed after every measurement. For each measurement at least five readings were
11 taken and the mean γ value was recorded. Before each experiment the instrument was
12 calibrated and checked by measuring the surface tension of distilled water. Surface
13 tension measurements of ET15 solutions were performed in the presence of 0.01 M
14 NaCl as a background electrolyte.

15

16 2.3. Solubility studies.

17 10 mL of surfactant solutions ranging up to 20 g/L were added in duplicate to a solid
18 excess of each herbicide and the suspensions shaken for 1 week at 25°C. Then the
19 suspensions were let to settle down; the supernatant was removed and filtered through
20 0.20 μ m PTFE membranes, and the herbicide analyzed. The solubility curves were built
21 by plotting the amount of herbicide solubilized versus the amount of surfactant
22 employed.

23 The solubility enhancement factor of the herbicides by the use of surfactants was
24 determined from S_w^*/S_w , where S_w^* is the apparent solubility at a surfactant
25 concentration and S_w is the intrinsic herbicide solubility in water. The effectiveness of

1 the micelles of a surfactant in the solubilization of a solute can be estimated from the
 2 molar solubilization ratio (*MSR*) and the micelle-water partition coefficient (K_{mc}). The
 3 *MSR* which is the ratio of the mol of solute solubilized to the mol of surfactant present
 4 as micelles, was obtained from the slope of the solubility curve above the critical
 5 micelle concentration (CMC). The K_{mc} which represents the distribution of solute
 6 between surfactant micelles and the aqueous phase is given by

$$7 \quad K_{mc} = \frac{X_m}{X_a} \quad \text{Eq. (1)}$$

8 where X_m is the mol fraction of the solute in the micellar phase and X_a is the mol
 9 fraction of the solute in the micelle-free aqueous phase. The value of X_m was calculated
 10 from the *MSR* :

$$11 \quad X_m = \frac{MSR}{MSR+1} \quad \text{Eq. (2)}$$

12 and X_a from the expression $X_a = S_{CMC} V_w$ where S_{CMC} is the solute concentration at the
 13 CMC, and V_w is the molar volume of water.

14

15 2.4. Steady-state fluorescence measurements.

16 The aggregation number (*N_{agg}*) was determined by the quenching of the luminescent
 17 probe (pyrene) by CyPCl on a Hitachi F-2500 spectrofluorometer provided with a
 18 thermostatically controlled cell holder equipped with a magnetic stirring device. The
 19 excitation wavelength for pyrene was 335 nm and emission spectra were recorded
 20 between 350 and 550 nm. The quenching experiments were analyzed by using the
 21 Tachiya equation:

$$22 \quad \ln\left(\frac{I_0}{I_1}\right) = \frac{N_{agg} [C_Q]}{C_s - cmc} \quad \text{Eq. (3)}$$

23 where I_0 , I_1 , C_Q and C_s represents the fluorescent intensity of the first vibronic peak of
 24 pyrene (374 nm) in the absence of quencher, in the presence of quencher, total quencher

1 concentration [Q], and total surfactant concentration, respectively. Surfactant
2 concentrations were fixed to 3 mM; pyrene was used at a concentration of 1 μM, and
3 CyPCL concentration was varied between 10-100 μM.

4 From the fluorescence quenching experiments, the Stern-Volmer constant (K_{sv}) was
5 calculated for each single/binary surfactant system from the expression:

$$6 \frac{I_0}{I_1} = 1 + K_{sv} [Q] \quad \text{Eq. (4)}$$

7 The greater is the hydrophobic environment, the larger is the solubilization and
8 quenching of CyPCL and pyrene in the inner core, and the larger the K_{sv} value.

10 2.5. Herbicide analysis.

11 Herbicides were analyzed by HPLC (Shimadzu Model 10A) equipped with a PDA
12 detector. The reverse phase column was a 15 cm Kromasil 100 C18. The flow rate was
13 1.0 mL min⁻¹. The mobile phase was 40% acetonitrile and 60% water containing 0.1%
14 H₃PO₄. The wavelengths were set at 220 nm for FL, 254 nm for MST and 230 nm for
15 MTZ. The retention times were 15.19, 3.05 and 2.86 min for FL, MST and MTZ,
16 respectively.

18 2.6. Data analysis

19 2.6.1. Interfacial properties of single surfactant solutions.

20 The surface tension (γ) measurements allow the determination of the surface area per
21 surfactant molecule at the interface, which can be calculated by using the Gibb's
22 adsorption equation

$$23 \Gamma_{\max} = \frac{-1}{2.303 n R T} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad \text{Eq. (5)}$$

1 where Γ_{\max} is the maximum surface excess concentration, n represents the number of
 2 species at the interface whose concentration changes with surfactant concentration, R is
 3 the gas constant, T is the temperature and C is the surfactant concentration.

4 The minimum area occupied by a surfactant molecule at the air/solution interface, a_{\min} ,
 5 can be estimated from the relation

$$6 \quad a_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \quad \text{Eq. (6)}$$

7 where N_A is Avogadro's number.

8 The molecular packing parameter g is defined as

$$9 \quad g = v/a_{\min}l \quad \text{Eq. (7)}$$

10 v is the surfactant tail volume (nm^3) and l is the tail length (nm). Values of the volume
 11 and the length of the hydrocarbon tail were calculated according to Tanford's formula
 12 (Tanford, 1972).

13 2.6.2. Solubilization of herbicides into single surfactant micelles.

14 The binding constant K_1 of a solubilize (S) incorporated into micelles is interrelated to
 15 the total surfactant concentration (C_t), the critical micellar concentration (CMC) and
 16 N_{agg} through the equation (Ud-Din et al., 2009; Mehta & Chaudhary, 2011):

$$17 \quad \frac{S_t - S_{CMC}}{S_{CMC}} = \frac{K_1}{N_{agg}(C_t - CMC)} \quad \text{Eq. (8)}$$

18 in which S_t and S_{CMC} are the total solubilize concentration and that solubilized at the
 19 CMC, respectively. From the slope of $(S_t - S_{CMC})$ vs. $(C_t - CMC)$, K_1/N_{agg} can be
 20 determined, that serves as a parameter to characterize the solubilization powers of
 21 different surfactants; and K_1 evaluated if knowing N_{agg} and further used to calculate the
 22 average number of solubilize molecules per micelle, S^M , according to

$$23 \quad S^M = K_1 S_{CMC} \quad \text{Eq. (9)}$$

24 2.6.3. Interfacial properties of mixed surfactant solutions.

1 Clint's equation (Clint, 1974) can be used to predict the CMC of the mixtures for ideal
 2 mixing and is given for binary systems by

$$3 \frac{1}{CMC_{12,theor}} = \frac{\alpha}{CMC_1} + \frac{1-\alpha}{CMC_2} \quad \text{Eq. (10)}$$

4 where α is the mole fraction of surfactant 1 in the total surfactant in the solution phase;
 5 CMC_1 , CMC_2 and $CMC_{12,theor}$ are respectively the critical micelle concentrations of
 6 surfactants 1, 2 and that of their ideal mixture at a given value of α .

7 An analysis of the molecular interactions between two different surfactants in the
 8 micelles is measured by the β^M parameter from Regular Solution Theory (RST) by
 9 using Rubingh's approach (Rubingh, 1979) which is calculated by an iterative method
 10 based on Eqs. (11) and (12)

$$11 \left(\frac{(X_1^M)^2 \ln(\alpha CMC_{12}/X_1^M CMC_1)}{(1-X_1^M)^2 \ln[(1-\alpha) CMC_{12}]^2 / (1-X_1^M) CMC_2} \right) = 1 \quad \text{Eq. (11)}$$

$$12 \beta^M = \frac{\ln\left(\frac{\alpha CMC_{12}}{X_1^M CMC_1}\right)}{(1-X_1^M)^2} \quad \text{Eq. (12)}$$

13 where X_1^M is the mole fraction of surfactant 1 in the total surfactant in the mixed
 14 micelle. Positive values of β^M indicate that the interaction between both surfactants for
 15 mixed monolayer formation is repulsive (antagonism); negative values point to
 16 attractive interactions (synergism) while zero values state no interaction, hence ideal
 17 mixing.

18

19 **3. RESULTS AND DISCUSSION**

20 **3.1. Interfacial properties of single surfactant solutions.**

21 The plots of γ vs. $\log C$ for the aqueous solutions of the surfactants are shown in Figure
 22 2. The Γ_{max} and a_{min} values of the surfactant obtained from the plot of surface tension
 23 measurements vs. the logarithmic concentration of the surfactants are listed in Table 1.

1 The self-assembly of the surfactants in solution is highly dependent on their structure
2 which on turn, would determine the solubility enhancement of chemicals in their core.
3 The bulk self-assembly is usually described by the packing parameter g that was
4 calculated to find out the aggregation behavior of the surfactants in solution. g -values
5 less than $1/3$ yields globular aggregates, between $1/3$ and $1/2$ rodlike micelles and
6 vesicles for values larger than $1/2$.

7 The calculated g parameter in Table 1 indicates the formation of globular aggregates in
8 solution for the surfactants B048 and ET15, and cylinders for B266. Because the ratio v
9 $/l$ is a constant independent of tail length and equal to 0.21 nm^2 for single tail
10 surfactants, the packing parameter is highly determined by the area a_{min} , which is
11 influenced by the headgroup interactions. ET15 molecules become protonated in
12 solution on the amine moiety $[\text{R-NH}^+(\text{EO})_5\text{H}_2]$ which will increase the headgroup
13 repulsion in the micelles explaining the large a_{min} value observed, and therefore, the
14 formation of globular micelles because of the corresponding small g -value. In the case
15 of non-ionic ethoxylated surfactants, the steric repulsion between headgroups is large
16 when the number of ethylene oxide (EO) units of the surfactant is also large, therefore
17 a_{min} is large, g becomes small enough and globular micelles will form as observed with
18 B048 (10 EO units). For a smaller number of ethylene oxide units (5.5) as in B266, the
19 headgroup repulsion decreases with a concomitant decrease in a_{min} and increase in g
20 values, so that cylindrical or rod-like micelles are formed. However, Nagarajan (2002)
21 demonstrated that the surfactant tail has also influence in determining the size and shape
22 of equilibrium aggregates. This author showed that for a g -value of 0.42 as that
23 observed with B266, only tail lengths larger than 10 carbon atoms will form cylindrical
24 micelles where shorter tails as in B266 will yield globular micelles.

1 Globular micelles comprise both spherical and ellipsoid micelles with either prolate or
2 oblate form. The aggregation number (*N_{agg}*) was experimentally determined to be 62 ± 1
3 for B048 and 58 ± 2 for B266 (Table 2), which are in good agreement to the theoretical
4 values of 65 for spherical micelles and 60 for prolate micelles with an axial ratio of 1.5
5 (Tanford, 1972). Spherical micelles would have largely underestimated the
6 experimental *N_{agg}* of B266 by yielding a theoretical value of 40.

7

8 **3.2.Solubilization of herbicides by single surfactants.**

9 Enhanced solubility of the herbicides was greatly influenced by the molecular properties
10 of the surfactants and the herbicides (Fig. 3; Table 3). In Fig. 3, mesotrione solubility
11 was enhanced from 0.6 to 37 mM when rising ET15 concentration from 0 to 50 mM;
12 however, the nonionic surfactants slightly enhanced MST solubility, up to 0.8 and 1.1
13 mM for B266 and B048, respectively. The greater solubility by ET15 was due to
14 electrostatic interactions because MST is a weak acid ($pK_a=3.12$) remaining as anionic
15 species at the equilibrium pH (5.4) whereas ET15 molecules were protonated
16 ($pK_a=8.5$). Flurtamone was greatly solubilized by the three surfactants (Fig. 4, Table 3),
17 with increments of two orders of magnitude. Metribuzin solubility was enhanced up to
18 15, 12 and 10 mM with 50 mM surfactant solutions of B048, B266 and ET15 (Figure
19 5), accounting respectively for solubility enhancement factors of 2.6, 2.0 and 1.8. These
20 low solubility enhancement values despite the high concentrations of MTZ in solution
21 obtained in the presence of the surfactants, were due to the high intrinsic water
22 solubility of MTZ (5.85 mM).

23 The effectiveness of a particular surfactant in solubilizing a given solute through
24 micelle- formation in solution can be estimated from the *MSR* values. In Table 3, FL
25 exhibited in general the lowest *MSR* values despite of the large increases in solubility

1 factors. Because the solubility of this herbicide in water is very low (10.7 mg L^{-1}), the
2 total amount of herbicide solubilized with the surfactants is several-fold smaller when
3 compared to the other herbicides for a fixed surfactant concentration. Thus, the amount
4 of FL solubilized per mol of surfactant will be smaller.

5 The *MSR* values obtained for FL with the surfactants ET15 and berols paralleled those
6 of MTZ. The largest *MSRs* were for Berol 048, followed by B266 and by last ET15.

7 Due to the hydrophobic character of the herbicides FL and MTZ, their interaction
8 mechanism within the micelles may be by a partition mechanism which can be
9 estimated by comparing the solvency of both molecules in the micelles in relation to
10 that of an organic phase as 1-octanol, because of its partial resemblance to the structure
11 of nonionic surfactants (Kile & Chiou, 1989). The $\log K_{mc}$ value for FL was slightly
12 higher but quite close to its $\log K_{ow}$ value (3.22). This indicated that (i) hydrophobic
13 interactions are responsible for the large solubilization of FL into the micelles; and (ii)
14 the efficiency of the organic phase for a partition mechanism within the micelle is
15 superior to that of 1-octanol. However, the $\log K_{mc}$ value of MTZ was about 90%
16 higher than its $\log K_{ow}$ value (1.65) suggesting a different source in its solubilization
17 other than hydrophobic interactions.

18 An indirect method to determine the loci of solubilization within the micelles may be
19 provided by estimating the increase in the micellar core volume after the incorporation
20 of the solute.

21 The S^M values for MTZ were 12 and 8 for B048 and B266 systems, respectively;
22 whereas smaller values of 2.5 for B048 and 1.3 for B266 were obtained for the higher
23 hydrophobic FL (Table 4). This pattern suggests different solubilization loci within the
24 micelles for both herbicides. The micellar core volume (V_C^M) of the micelles was
25 calculated to be 21.7 nm^3 for B048 and 15.6 nm^3 for B266 by using Tanford's equation.

1 From their relative densities, the molecular volume of the herbicides FL and MTZ was
2 determined to be respectively 0.40 and 0.29 nm³. This means that incorporation of FL
3 S^M into the micelles will account for volume increments of 4.5 and 3.3% for B048 and
4 B266 micelles, respectively; however, the increments for MTZ are of 16% for B048 and
5 13% for B266. The significantly estimated higher micellar core volume increments with
6 MTZ despite its lower hydrophobicity corroborated that MTZ was not allocated into the
7 micellar core, but most probably into the palisade region. Molecules with intermediate
8 polar character are reported to be solubilized between the hydrophilic head groups of
9 polyoxyethylene micelles and in the palisade layer between the hydrophilic groups and
10 the first few carbon atoms of the hydrophobic core (Bhat et al., 2008). The herbicide
11 alachlor was solubilized in the outer layer of the micelles with its polar groups oriented
12 toward the polar ethyleneoxide chains and its hydrocarbon portion toward the interior of
13 the micelle (Xiarchos & Doulia, 2006). A similar mechanism was proposed for MTZ
14 encapsulation into liposomes (Undabeytia et al., 2011). These authors indicated that
15 MTZ was solubilized through hydrophobic interactions with the lipid chains in addition
16 to water bridges between the herbicide and the lipid headgroups.

17 The $K_1/Nagg$ values serve as indicative of the solubilization powers of surfactants (Ud-
18 Din et al., 2009). These values were extremely high for FL; they were two orders of
19 magnitude larger than with MTZ (Table 4). Solubilization of chemicals occurring into
20 the palisade layer of non-ionic micelles presented $K_1/Nagg$ values that were between
21 one and four orders of magnitude lower than that of FL (Bhat et al., 2008; Mehta &
22 Chaudhary, 2011). These data pointed out that FL was mainly allocated into the
23 micellar core in agreement with its high hydrophobicity.

24 In Table 3, the MSR and $\log K_{mc}$ values of FL and MTZ were always higher with B048
25 than with B266. The solubilization of MTZ and FL should increase with an increase in

1 the number of EO units and the micellar core volume, respectively. Because the
2 aggregation numbers of B048 and B266 in micelles were pretty similar (Table 2), the
3 larger micellar volume for B048 micelles in addition to the largest content of EO units
4 in B048 resulted in an enhanced solubilization of both herbicides. Unlike B048 and
5 B266, the lowest *MSR* and $\log K_{mc}$ values obtained for FL and MTZ with ET15 was
6 due to the fact that the micellar volume was not large enough for enhanced
7 solubilization despite of the largest tail in ET15 molecules. The reason was its low
8 aggregation number (40) in solution together with its low EO number. Thus, ET15
9 micelles showed poorer solubilization efficiency for these hydrophobic herbicides.
10 On the contrary, this surfactant yielded the largest *MSR* with the herbicide MST because
11 of the larger magnitude of electrostatic forces. In the calculation of this *MSR* value, all
12 the MST solubilization values with the surfactant added in Figure 3 were used for lineal
13 fitting yielding a *MSR* value of $7.18 \cdot 10^{-1}$ and $R^2=0.968$. However, the slope of MST vs.
14 surfactant concentration plot was changed after 40 mM of ET15 indicating that
15 additional solubilization of the solute may either change the CMC, the shape/size or
16 charge density of the micelles. Most probably, the increase in MST concentration in the
17 micelles greatly decreases the positive charge density of the micelles resulting in lower
18 affinity of MST to the micelles. The calculation of *MSR* by taking only the
19 solubilization points before the change of slope yielded a value of $9.27 \cdot 10^{-1}$ and
20 $R^2=0.999$; that is, about one mol of MST solubilized per mol of ET15 surfactant in the
21 micelles.

22

23 **3.3.Mixed micellization.**

24 The mixing behavior of the surfactants will depend on the differences in the headgroups
25 and tail lengths, and the mixing ratio. Clint's equation [Eq. 10] was used to predict the

1 CMC of the mixtures for ideal mixing. As seen in Table 5, the experimental values of
2 the CMCs of the mixtures (CMC_{12}) are in general lower than the corresponding
3 theoretical values with the exception of the B048/B266 system at the highest fraction of
4 B048, and the B048/ET15 at concentrations other than the equimolar one. This
5 indicated the existence of interactions that resulted in nonideality of the binary systems
6 between the constituent surfactants in the mixed aggregates. Lower CMC_{12} values
7 arises from attractive interactions (synergism) between the surfactants in the mixed
8 micelles; they are stronger for the B048/B266 and B048/ET15 systems at the lowest and
9 highest B048 ratio, respectively, as reflected in a one-order-of magnitude decrease
10 relative to its theoretical value.

11 The β^M parameters for mixed micelle formation were negative for most of the
12 surfactant systems and molar fractions used (Table 5). In the system B048/ET15 for non
13 equimolar ratios, the β^M values were not obtained due to the lack of self-consistency
14 in solving Equations [11] and [12], which can be due to the concurrence of very
15 asymmetric micellar mixing ratios, the large difference between the CMC values of the
16 used components and strong antagonistic interactions (Hoffman and Pössnecker, 1994;
17 Dubey et al., 2014). The B048/B266 system had the greatest negative β^M value for the
18 smallest B048 molar ratio used, in accord to the larger reduction in CMC_{12} . The balance
19 between the molecular interactions of two surfactants in mixed micelles can be
20 considered as the result of two contributions: one related to hydrophobic interactions
21 between the hydrophobic domains of the aggregates (micellar core); and another related
22 to hydrophilic interactions between the headgroups. In the B048/B266 system, the
23 incorporation of B266 molecules into B048 micelles yielded lower hydrophobic
24 interactions as a result of their shorter tails. These interactions were overbalanced by the
25 reduction in the steric repulsions between the EO chains when intercalated the shorter

1 polyethylene chains of B266. When the molar fraction of B048 molecules was
2 increased, the enhanced hydrophobic interactions were of smaller magnitude compared
3 to the reduction in the repulsions between the headgroups; thus, β^M values were
4 significantly increased from -6.8 to even positive values.

5 The balance between these two factors was clearly visualized by studying mixed
6 aggregates formed by ET15. For $\alpha=0.5$, β^M values increased from -4.1 to -1.7 when
7 B266 was replaced by B048. The interaction between surfactants for the formation of
8 mixed aggregates was favoured with B266 despite containing 7 less methylene units in
9 its hydrophobic tail. The electrostatic self-repulsion between the ET15 monomers in the
10 micelles is partly replaced by electrostatic attractive ion-dipole interactions between the
11 charged ET15 headgroups and the negatively polarized EO chains. An analysis of the
12 nonionic composition into the mixed aggregates indicated that X_1^M was similar with both
13 surfactants (B048 and B266). Therefore, the larger steric repulsion contribution when
14 intercalating B048 toward inter-headgroup interactions resulted as overall in lower
15 synergistic interactions. According to Rubing's theory, in addition to negative β^M
16 values, the existence of synergism also require that $|\beta^M| > |\ln(CMC_1 / CMC_2)|$. This
17 condition was only satisfied simultaneously in the three surfactant systems for the same
18 molar ratio when α was 0.5. Consequently, for the sake of comparison in the studies of
19 solubilization of the herbicides by binary surfactant mixtures, only equimolar ratios
20 were chosen. It is also expected that the greater is the synergistic interaction, the more
21 hydrophobic the micellar core is and the larger the partition of solutes.

22

23 **3.4.Solubilization by binary surfactant systems.**

24 As noticed in the solubility enhancement factors in Table 3 (see also Figs. S1-S3 in
25 Supplementary Information), solubilization of herbicides by binary surfactant systems

1 showed lower solubilization over that of the single surfactant in the mixture with the
2 highest solubilization power of the herbicide. The only exceptions were solubilization
3 of metribuzin by the equimolar mixture of ET15/B266 which was higher than that by
4 both surfactants, and also by B048/B266 whose solubilization power was lower than
5 those of the single surfactants.

6 The effect of mixed surfactant systems on solubilization of herbicides can be estimated
7 from the deviation ratio (R) between the MSR_{exp} and the MSR_{ideal} which can be
8 evaluated from $R=MSR_{exp}/MSR_{ideal}$. Here $MSR_{ideal}=\sum_i MSR_i X_i+MSR_{water}$, where MSR_i is
9 the experimental MSR value of solubilize in pure i th surfactant whose bulk mole
10 fraction in the mixture is X_i , and MSR_{water} is the molar solubilization ratio of the
11 solubilize in pure water. Values of R larger than 1 indicate a positive effect of
12 surfactant mixing on the solubilization whereas on the contrary, values lower than unity
13 showed a poor efficiency relative to the single surfactant systems. In Table 6, R values
14 were mostly close to the unity indicating no effect of the use of surfactant binary
15 mixtures on herbicides solubilization. Only significant positive deviation values were
16 recorded for MTZ in the system B266/ET15 and in all the ET15 surfactant mixtures
17 used with MST.

18 In the calculation of MSR_{ideal} for MST in Table 6, the MSR_{ET15} value used was $7.18 \cdot 10^{-1}$
19 (Table 3); however, the use of the MSR value calculated in the MST solubilization for
20 low ET15 concentrations of $9.27 \cdot 10^{-1}$ lowered R . The new R values were close to unity,
21 specifically 1.08 and 1.07 for MST solubilization in the B048/ET15 and B266/ET15
22 systems, respectively. These values are in agreement with the trend in Table 3 and
23 Figure S1 where no enhanced MST solubilization was noticed for the mixed surfactant
24 systems relative to the use of only ET/15.

1 No improvement was noticed in the solubilization of FL by the use of mixtures of
2 surfactants over those of the single surfactant in the mixture with the highest
3 solubilization (Table 3, Fig. S2). However, the binding affinity of FL increased greatly
4 for the B048/B266 system as reflected in its larger K_1 value (Table 4). An increase in
5 the herbicide solubilization is not only related to its affinity to the surfactant system but
6 also to the number of micelles that, on its turn, is dependent on the critical micellar
7 concentration and the average number of aggregation of monomers for the formation of
8 a micelle. Therefore, when the K_1 values are normalized to N_{agg} , the K_1/N_{agg} ratio
9 followed the same trend as those specifying the distribution of the herbicide in the
10 surfactant/water system ($\log K_{mc}$, Table 3). The increase in the affinity (K_1) of FL to
11 B048/B266 system relative to B048, the surfactant with the highest affinity for FL and
12 accounting for the largest micellar mole fraction in the mixed micelles (0.64, Table 5),
13 is approximately of the same magnitude as the increase in N_{agg} (about 23%). As a
14 general trend for FL, no enhanced solubility is obtained for mixed surfactant systems
15 because of the balance between (i) the increase in the effective solubilization area in the
16 mixed micelles when increasing the radius of the mixed micelle; and (ii) the reduction
17 in the number of micelles because of the formation of larger aggregates.

18 The FL solubilization in the mixed surfactant systems was larger for B048/B266
19 followed by B048/ET15 and the last one, B266/ET15 (Table 3). Solubilization of
20 hydrophobic molecules into the micellar core was related to a looser packing of
21 surfactant molecules that facilitated the penetration and interaction of the solute with the
22 hydrophobic core (Wei et al., 2011.). The interaction parameter β^M was larger for the
23 equimolar system B266/ET15 (Table 5) indicating the formation of more closely packed
24 micelles and hindering the passage of FL. However, the micelles are in an exchange
25 dynamic equilibrium with a small concentration of monomers, yielding a continuous

1 destruction and reformation of the micelles (Mishael et al., 2002; Viseu et al., 2014);
2 thus, the inner core of the micelle becomes lately accessible in the equilibrium. In this
3 context, the short-range interactions occurring between the hydrophobic chains and
4 those with the hydrophobic solute are the driving force.

5 An indirect factor to measure the degree of this interaction is the Stern-Volmer constant
6 (K_{sv}), which provides a measure of the hydrophobicity of the micellar core (Table 2).
7 The K_{sv} values decreases greatly from $3.720 \cdot 10^{-4}$ for the B048/B266 system to 0.342
8 10^{-4} for B048/ET15 and $0.292 \cdot 10^{-4}$ for B266/ET15. These values paralleled those of the
9 ability of the mixed micellar systems for FL solubilization (S_w^*/S_w , Table 3),
10 indicating that the microenvironment of mixed micelle is becoming less hydrophobic
11 and thus disfavoring the interaction of the herbicide with the mixed surfactants and its
12 partition into the micelle. This pattern is relevant for FL, whose locus of solubilization
13 occurred mainly into the micellar core; but not for MST or MTZ.

14 MTZ is solubilized into the palisade layer of the micelles as previously deduced and in
15 that case, a lesser hydrophobic microenvironment as reflected in a decrease in K_{sv} will
16 favor its incorporation into the micelles (Table 3). Thus, the enhanced solubilization of
17 MTZ by the mixed surfactant systems followed the inverse order of K_{sv} (Table 2).
18 However, this rule cannot be generally extended when also including single surfactant
19 systems. Whereas in the particular case of FL, its solubilization followed exactly the
20 increasing order of K_{sv} , this was not the case for MTZ whose solubilization was largest
21 for B048 despite of its highest K_{sv} value. These results point out the use of K_{sv} values
22 for prediction of the solubilizing power of a surfactant system when the solute is
23 incorporated mainly into the hydrophobic micellar core.

24 The MTZ solubility was enhanced in the B266/ET15 over those of the single surfactant
25 systems (Table 3, Fig. S3). In this case, the affinity of the herbicide did not increase as

1 revealed by K_1 values (Table 4), but as was discussed earlier, this was overbalanced by
2 the increase in the number of micelles both arising from the intermediate N_{agg} relative
3 to those of the single surfactants (Table 2), and specially, the lowering of the CMC
4 relative to the predicted values (Table 5). This reduction in the experimental CMCs over
5 the theoretical ones was of 46% for the B266/ET15 vs. lower values of 16 and 33% for
6 the B048/ET15 and B048/B266 systems, respectively.

7 The use of binary surfactant systems did not improve MST solubilization with respect to
8 the surfactant in the mixture which provided the highest solubility (Table 3). As
9 occurred with FL, the affinity of this herbicide (K_1 , Table 4) increased for the
10 B048/B266 system over that of the single surfactants but once this value was
11 normalized to N_{agg} , there was no improvement in the partition of MST over that of the
12 surfactant with the largest solubilizing power in the mixture (B048). The use of
13 mixtures based on ET15 reduced the overall positive charge relative to the use of only
14 ET15 with the subsequent decrease in K_1 values which paralleled those of K_1/N_{agg} and
15 $\log K_{mc}$.

16

17 **4. CONCLUSIONS**

18 The present study investigated the solubilization of three herbicides (FL, MTZ, MST)
19 with different functional moieties and degree of hydrophobicity by the nonionic (B048,
20 B266) and cationic (ET15) surfactants and their binary mixture through the CMC and
21 solubilization approaches. The solubilization of MTZ was mainly occurring into the
22 palisade region of the micelles, FL in the inner hydrophobic core and MST at the
23 micelle/water interface.

24 The use of three herbicides with different preferential loci of solubilization into the
25 micelles provided insight into the mechanisms operating for binary equimolar surfactant

1 mixtures. The use of binary mixtures did not improve the solubilization of herbicides
2 over those of the single ones, with the exception of MTZ by the B266/ET15 mixture.
3 Enhanced solubilization of organics by mixed surfactant systems was in previous
4 studies related to the degree of attractive interactions between the surfactants; however,
5 this was not noticed in the current study, since a an analysis of these interactions
6 showed attractive interactions (synergism) in all the binary mixtures.
7 The results of this study illustrated the importance of not only of the intrinsic nature of
8 the surfactants but specially, the polarity of the solutes in their enhanced solubilization
9 by binary combinations of surfactants when applied in environmental remediation
10 technologies. There is a need to find new descriptors that correlate the surfactants in the
11 mixture and solutes properties with solubility enhancement of polar molecules. The
12 advantage of the use of mixtures of surfactants in SER technologies for polar solutes
13 can arise mainly from the improvement in the physical properties of the mixture than on
14 its solubilization power. For example, the lowering of CMC in the mixtures will permit
15 to use lower surfactant concentrations for solute solubilization reaching a compromise
16 between the surfactant concentrations to be used, the amount of pollutant to be
17 solubilized and the economic costs.

18

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25

1 **Supplementary material**

2 Solubilization in single and equimolar mixed surfactants of MST (Fig. S1), FL (Fig. S2)

3 and MTZ (Fig. S3).

4

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- 18

1 **Figure captions**

2 Figure 1. Molecular structure of the herbicides and the surfactants used.

3 Figure 2. Variation of surface tension (γ) with concentration of aqueous solutions of the

4 single surfactants.

5 Figure 3. Solubilization of the herbicides in single solutions of surfactants.

6

Table 1. Surface and chemical properties of the surfactants.

	B048	B266	ET15
MW (g mol ⁻¹)	640	400	480
R	C ₁₃	C ₁₀	C ₁₇
N. Ethoxyl (EO) units	10	5.5	5
CMC (M) ^a	1.26 10 ⁻⁴	3.74 10 ⁻⁴	2.74 10 ⁻⁵
Γ _{max} x10 ⁶ (mol m ⁻²)	2.57	3.41	1.60
<i>a</i> _{min} (nm ²)	0.65	0.49	1.04
<i>g</i>	0.32	0.43	0.20

1

2 a. From this study, experimentally determined. Error limits of CMC are ±2%.

3

Table 2. N_{agg} and K_{sv} for single and binary equimolar surfactant systems.¹

System	N_{agg}	K_{sv} (10^{-4}) (M^{-1})
B048	62	4.756
B266	58	0.304
ET15	40	0.120
B048/B266	80	3.720
B048/ET15	56	0.342
B266/ET15	46	0.292

1. Error limits in the measurements of N_{agg} y K_{sv} are ± 4 and $\pm 2\%$, respectively.

2

Table 3. Solubility enhancement factors (S_{w}^*/S_w), molar solubilization ratios (MSRs) and micelle-water partition coefficients (K_{mc}) of herbicides for single and mixed surfactant systems.^{1,2}

Surfactant	MST			FL			MTZ		
	S_{w}^*/S_w	<i>MSR</i>	log K_{mc}	S_{w}^*/S_w	<i>MSR</i>	log K_{mc}	S_{w}^*/S_w	<i>MSR</i>	log K_{mc}
B048	1.9	$1.05 \cdot 10^{-2}$	2.95	33.8	$3.96 \cdot 10^{-2}$	5.08	2.6	$1.88 \cdot 10^{-1}$	3.18
B266	1.3	$3.8 \cdot 10^{-3}$	2.60	19.5	$2.24 \cdot 10^{-2}$	4.81	2.0	$1.21 \cdot 10^{-1}$	3.02
ET15	61.7	$7.18 \cdot 10^{-1}$	4.69	13.3	$1.44 \cdot 10^{-2}$	4.35	1.8	$8.4 \cdot 10^{-2}$	2.84
B048/B266	1.6	$7.98 \cdot 10^{-3}$	2.83	26.5	$3.08 \cdot 10^{-2}$	5.06	1.8	$1.11 \cdot 10^{-1}$	2.91
B048/ET15	43.0	$5.06 \cdot 10^{-1}$	4.50	22.3	$2.83 \cdot 10^{-2}$	5.02	2.0	$1.24 \cdot 10^{-1}$	2.99
B266/ET15	37.8	$4.37 \cdot 10^{-1}$	4.47	17.0	$1.96 \cdot 10^{-2}$	4.87	2.2	$1.48 \cdot 10^{-1}$	3.08

1. The molar ratio between the single surfactants in the mixed systems was 0.5:0.5.

2. Error limits of the parameters S_{w}^*/S_w , *MSR* and log K_{mc} are ± 4 , $\pm 5\%$ and $\pm 1.5\%$, respectively.

Table 4. $(K_1/Nagg)$, K_1 and S^M in single and equimolar mixed micellar systems at 298 K.¹

System	MST			FL			MTZ		
	$(K_1/Nagg)$	K_1	S^M	$(K_1/Nagg)$	K_1	S^M	$(K_1/Nagg)$	K_1	S^M
	(mol ⁻¹ L)	(mol ⁻¹ L)		(mol ⁻¹ L)	(mol ⁻¹ L)		(mol ⁻¹ L)	(mol ⁻¹ L)	
B048	18.7	1160	0.65	2266	140368	2.45	32.47	2013	11.7
B266	7.1	414	0.20	1199	69517	1.30	21.27	1233	7.0
ET15	1450	58000	28.71	416	16628	0.58	13.32	532	3.3
B048/B266	15.7	1256	0.64	2149	171912	2.47	17.72	1417	8.6
B048/ET15	993	55615	28.36	1973	110516	1.58	21.05	1178	6.9
B266/ET15	851	39145	19.18	1367	62889	0.90	26.43	1215	6.8

1. Error limits in the parameters are $\pm 6\%$.

Table 5. Values of C_{12} , X_1 and β of binary surfactant mixtures using Rubingh's method at 25°C.^{1,2}

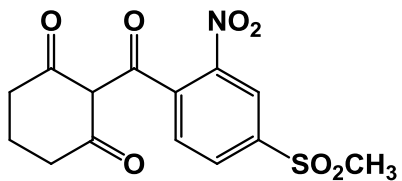
System	Molar ratio	X_1	β	$C_{12, \text{theor}}(\text{M})$	$C_{12}(\text{M})$
B048/B266	0.3:0.7	0.51	-6.8	$2.35 \cdot 10^{-4}$	$4.29 \cdot 10^{-5}$
	0.5:0.5	0.64	-1.9	$1.88 \cdot 10^{-4}$	$1.26 \cdot 10^{-4}$
	0.7:0.3	0.61	2.8	$1.57 \cdot 10^{-4}$	$1.68 \cdot 10^{-4}$
B048/ET15	0.3:0.7	n.d. ³	n.d. ³	$3.58 \cdot 10^{-5}$	$4.60 \cdot 10^{-5}$
	0.5:0.5	0.30	-1.7	$4.50 \cdot 10^{-5}$	$3.30 \cdot 10^{-5}$
	0.7:0.3	n.d. ³	n.d. ³	$6.06 \cdot 10^{-5}$	$1.15 \cdot 10^{-4}$
B266/ET15	0.3:0.7	0.13	-2.1	$3.79 \cdot 10^{-5}$	$3.30 \cdot 10^{-5}$
	0.5:0.5	0.29	-4.1	$5.11 \cdot 10^{-5}$	$2.77 \cdot 10^{-5}$
	0.7:0.3	0.21	-0.8	$7.80 \cdot 10^{-5}$	$6.97 \cdot 10^{-5}$

1. Subscript 1 represents the first surfactant in each combination.
2. Error limits of parameters are $\pm 4\%$.
3. n.d., not determined because of lack of self-consistency in the calculations.

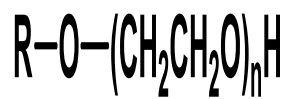
Table 6. Experimental (MSR_{exp}) and ideal (MSR_{ideal}) molar solubilization ratios for herbicides by equimolar binary surfactant mixtures, as well as their deviation ratio (R).¹

Surfactant system	Herbicide	MSR_{exp}	MSR_{ideal}	R
B048/B266	FL	$3.08 \cdot 10^{-2}$	$3.11 \cdot 10^{-2}$	0.99
	MST	$7.88 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$	1.09
	MTZ	$1.11 \cdot 10^{-1}$	$1.55 \cdot 10^{-1}$	0.71
B048/ET15	FL	$2.83 \cdot 10^{-2}$	$2.71 \cdot 10^{-2}$	1.04
	MST	$5.06 \cdot 10^{-1}$	$3.64 \cdot 10^{-1}$	1.39
	MTZ	$1.24 \cdot 10^{-1}$	$1.36 \cdot 10^{-1}$	0.91
B266/ET15	FL	$1.96 \cdot 10^{-2}$	$1.84 \cdot 10^{-2}$	1.06
	MST	$4.37 \cdot 10^{-1}$	$3.61 \cdot 10^{-1}$	1.21
	MTZ	$1.48 \cdot 10^{-1}$	$1.02 \cdot 10^{-1}$	1.45

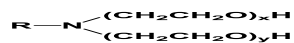
1. Error limits in the parameters are $\pm 5\%$.



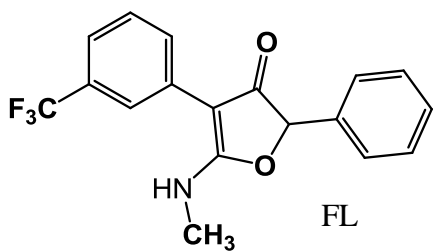
MST



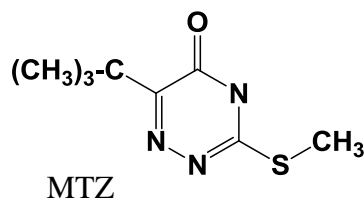
ET15



Berols (B266, B048)



FL



MTZ

Figure 1

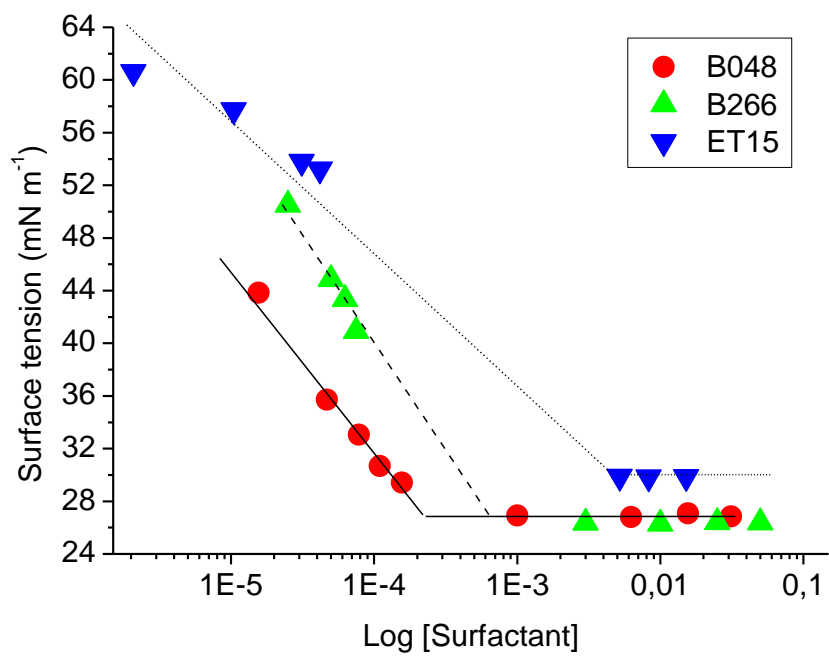


Figure 2

