



EFFECT OF THREE ANIONIC SURFACTANTS UPON THE SOLUBILIZATION OF DECANE

Rahal S.*, Khalladi R., Moulai-Mostefa N

¹ Materials and Environmental Laboratory
University of Medea, Ain D'Heb, 26001 Medea, Algeria

Abstract

Surfactants are amphiphilic molecules that reduce aqueous surface tension and increase the solubility of hydrocarbon. Surfactant remediation of soil and water polluted by organic compounds is a widespread environmental problem and has received increasing attention, (because the water immiscibility of these compounds severely limits the effectiveness of conventional remediation approaches). The objective of this study is to examine the solubilization of decane oil in the presence of three different anionic surfactants. These surfactants are extended surfactant (X-AES), sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS). The ability of these surfactants to solubilize the decane was characterized by the measurement of the micelle–water partition coefficient (K_m) and the masse solubilization ratio (WSR). The obtained results showed that the critical micelle concentration (CMC) of X-AES determined experimentally is lower than that of SDS and SDBS. The order of increasing solubility enhancement of decane was $SDBS < SDS < X-AES$, and The extent of solubility enhancement is linearly proportional to the surfactant concentration.

Keywords: Anionic surfactant; Decane; Solubilization, Surface tension, CMC.

Introduction

The contamination of soils and groundwater by petroleum hydrocarbons may be due to industrial accidents (spills, leaks, and leaking underground storage tanks and pipelines...). This contamination is a widespread environmental problem, and the removal of hydrophobic organic compound from them is becoming a major concern, and presents a challenge to scientists and engineers, Their removal from contaminated soils and aquifers is difficult because they possess low solubilities, high interfacial tensions and low vapor pressure due to their hydrophobicity [1-6]. On the contrary, hydrocarbons often show strong tendency to be sorbed onto soil and in incorporation into soil micropores [7]. Surfactants can increase the solubility of hydrocarbons by partitioning them into the hydrophobic cores of surfactant micelles.

It has been known that surfactants are able to improve the mass transfer of hydrophobic pollutants from solid or nonaqueous liquid phase into aqueous phase by decreasing the interfacial tension and by accumulating the hydrophobic compounds in the micelles [8]. In general, surfactants are amphiphilic molecules with a hydrophilic head and one or two hydrophobic tails. The tail, usually a long hydrocarbon chain, acts to reduce solubility in water while the polar head, often ionizable, has the opposite effect [9]. Many works on surfactant micellar solubilization of Hydrocarbons have focused on the conventional surfactants that contain single monomer with a single hydrophobic tail and a single hydrophilic head group. Recently, there has been interest in a new kind of surfactant that has both lipophilic and hydrophilic linkers [10].

The objective of this work was to compare the effect and efficiency of an extended surfactant (X-AES) with that of common surfactants (sodium dodecyl sulfate and sodium dodecylbenzene sulfonate) for

the solubilization of decane, and to quantify the extent of hydrocarbon solubilization in the presence of surfactants and develop an understanding of solubilization process.

Materials And Methods

1.Materials

Decane was selected as representative organic pollutant model; it is obtained from Sigma- Aldrich Chemical Company, with a purity $\geq 99\%$. The water solubility of decane is $S_w = 0,052 \text{ mg}\cdot\text{l}^{-1}$ at 25°C . Surfactants were obtained either directly from the manufacturer or through a distributor and were used without further purification. The structure and properties of surfactants are listed in Table 1. Surfactant solutions were prepared by dissolving the relevant surfactant in deionized water.

2.Methods

2.1.Measurement of surface tension and CMC

Surface tension of surfactant solution was measured by using a DuNouy tensiometer model 70545 manufactured by CSC Scientific Company, INC. The critical micelle concentration (CMC) was determined by measuring the surface tension versus surfactant concentration; the plotted surface tension value was taken when stable reading was obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value . The CMC values were obtained through a conventional plot of the surface tension versus the logarithm value of the surfactant concentration, over a wide concentration range shown in Fig. 1.

2.2.Decane solubilization

The solubility of decane in different surfactant solutions was measured between 0.1 CMC and 10 CMC. Such concentration range was taken to study the effect of micellar concentration on solubilization. An individual 250 ml glass vial sample consisted of 20 ml surfactant solution containing 0.2 ml of decane. The sample vials were sealed with a screw cap to prevent any loss from solution. These samples were then agitated at 200 rpm for a period of 24, 48, 72 and 96 hours on a magnetic stirrer at room temperature ($20\text{--}25^\circ\text{C}$) to ensure maximum solubility. The solutions were subjected to centrifugation at 4000 rpm for 1 hour to remove the undissolved decane. The concentration of solubilized decane was determined spectrophotometrically with a GBC Cintra spectrophotometer (ModelUV–303) following appropriate dilution of an aliquot of the supernatant with the corresponding surfactant concentration. The surfactant concentration was kept the same in both the reference and the measurement cells to eliminate the effect of surfactant on UV–absorbance. The absorbance of decane was determined at the wavelength of 200 nm; and its solubility was deduced from the standard curve of decane established in methanol solution.

RESULTS AND DISCUSSION

1.CMC of Surfactants

Above a certain concentration of surfactant in an aqueous medium, the surfactant monomers start assembling together to form aggregates known as micelles and the concentration above which this occurs is known as critical micelle concentration (CMC). According to Fig.1, the CMC values were determined by the intersection of two linear segments on a plot of the surface tension versus surfactant concentration. CMC values of three surfactants are presented in Table 1. The experimental CMC value close to the reported values by Baowei, Z. et al. [11]. In this case, the CMC of X-AES is lower than that of the SDS and SDBS. This may be due to the the surfactant chain length, because the surfactant chain length is a major driving factor for micellization and hydrophobic interactions.

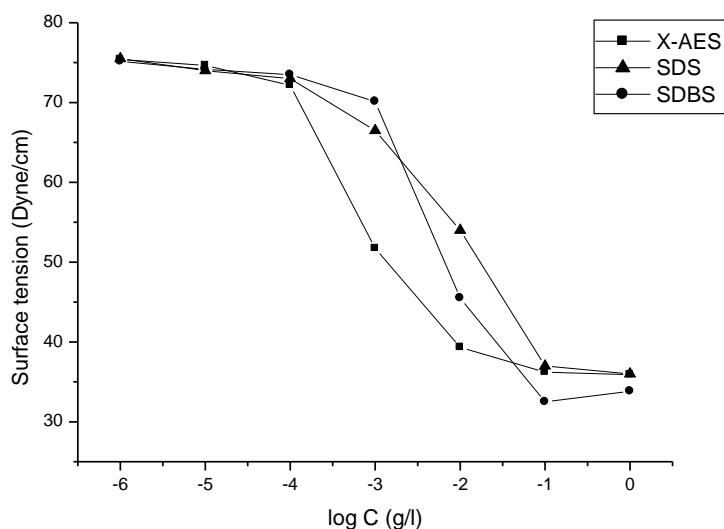
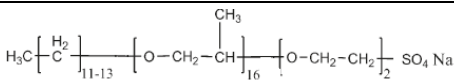
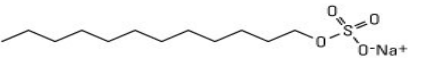
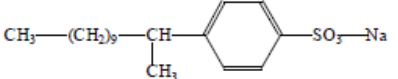


Fig.1: Plots of the surface tension (γ) vs the total surfactant concentration (C)

Entropy increases when water molecules around the hydrophobic parts of surfactant tails are released in the process of micelle formation [9]. The length of hydrophobic chain decides micellization concentration. So, larger the chain length lower is the CMC.

Table 1: Characteristic of the selected surfactants.

Surfactant	Molecular formula	Structure	MW	CMC _{exp} (mg/l)	CMC* (mg/l)
X-AES	C ₁₂₋₁₄ -PO ₁₆ -EO ₂ -SO ₄ Na		–	46.7	–
SDS	C ₁₂ H ₂₅ SO ₄ Na		288.38	1620	1586
SDBS	C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ Na		348.5	794.3	963.2

CMC*: The critical micelle concentration reported by Baowei, Z. et al.[11]

2.Solubization of Decane

Quantitative studies on solubilization capacities of surfactants could be found elsewhere in the literature [11-13]. There are few common expressions to quantify the solubilization capacity of the surfactant. One of these expressions is the micelle–water partition coefficient K_m [11]. Two others are the mass solubilization ratio (WSR) and the molar solubilization ratio (MSR). WSR is defined as the weight of the pollutant solubilized by the unit mass of surfactant above its CMC. Similarly, the MSR is described as the moles of pollutant solubilized by moles of surfactant above its CMC.

The solubilization of decane as a function of time in aqueous solution containing the anionic surfactants at 3 CMC and 10 CMC is shown in Fig.2 and Fig.3. The experimental results showed 48 h to be sufficient for reaching solubilization equilibrium. For this reason all experimental results are taken after 48h for the calculation of WSR and K_m .

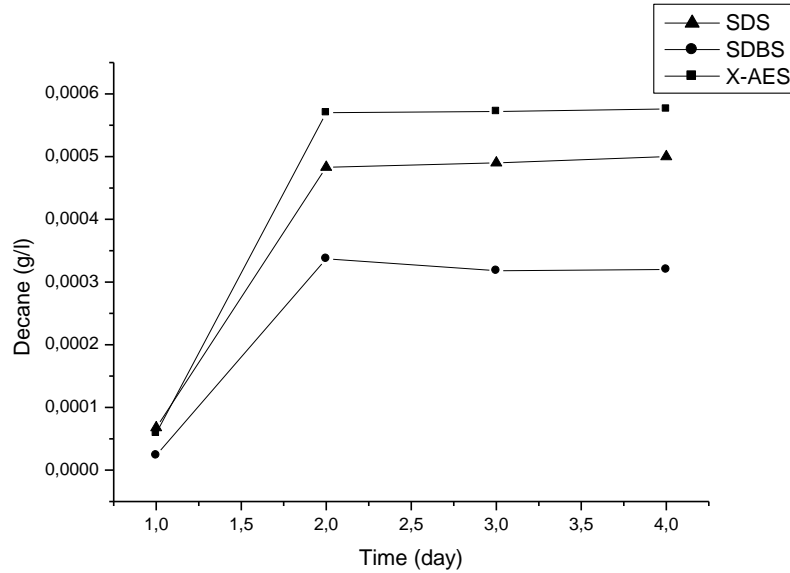


Fig.2. Solubilization of decane by surfactant for 3 CMC

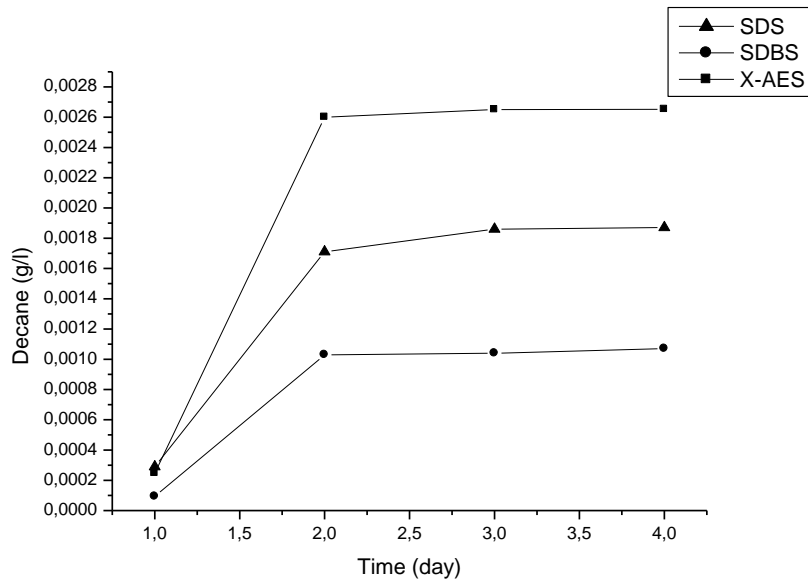


Fig.3. Solubilization of decane by surfactant for 10CMC

Decane solubilization ratio (S_D/S_w) was plotted as a function of surfactant solution concentrations for each data as shown in Fig.4. Obviously, the aqueous solubilities of decane increased linearly over the range of surfactant concentrations.

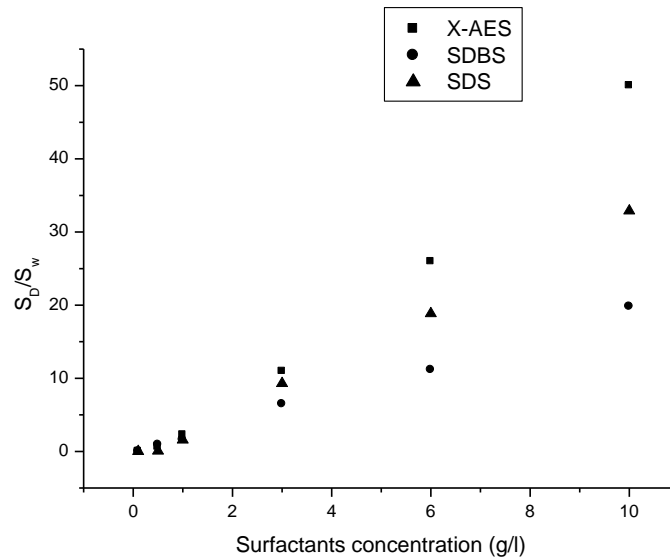


Fig.4. Solubilization of decane by surfactant

Solubilization of Decane by X-AES, SDS and SDBS is characterized by the WSR for the slope of the apparent solubility curve that correlates with surfactant concentrations [11-12]. To compare the partitioning and the solubilization efficiency, the mass solubilization ratio (WSR) and the micelle-phase/aqueous-phase partition coefficient (K_m) are introduced, which are the measures of the effectiveness of a particular surfactant in solubilizing of a given solute.

The WSR is defined as:

$$WSR = \frac{S - S_{cmc}}{c_{surf} - CMC} \quad (1)$$

where S is the total apparent solubility of hydrocarbon in g/L in the micellar solution at the particular surfactant concentration equal to c_{surf} in g/L; and S_{cmc} is the saturation concentration of hydrocarbon in g/L at the CMC in g/L. The WSR can be obtained from the slope of solubilization curve [12].

The micelle–water partition coefficient K_m is a parameter that indicates the distribution of organic molecules between the micellar phase and the aqueous phase and can be calculated from experimental measurements by using the following formula .

$$K_m = \frac{X_m}{X_a} \quad (2)$$

where X_m is the mass fraction of hydrocarbon in the micellar pseudophase and X_a is the mass fraction of hydrocarbon in the micelle-free aqueous phase. The mass fraction of decane in the micellar pseudophase, X_m , can be calculated in terms of WSR [12]:

$$X_m = \frac{WSR}{(1 + WSR)} \quad (3)$$

The mass fraction of decane in an aqueous phase is approximated for dilute solutions by:

$$X_a = S_{cmc} * V_m \quad (4)$$

where V_m is the specific volume of water equal to $V_m = \frac{1}{\rho_w}$.

The relationship of K_m can be expressed by:

$$K_m = \frac{WSR}{(1 + WSR) \cdot S_{cmc} / \rho_w} \quad (5)$$

where ρ_w is the density of water.

The measured values of WSR and K_m are summarized in Table 2.

Table 2: Mass solubilization ratios and partitioning coefficients of Decane in solubilization tests

Surfactant	WSR	R ²	LogK _m
X-AES	2,63611 × 10 ⁻⁴	0,99628	3.390
SDBS	1,02798 × 10 ⁻⁴	0,99848	3.096
SDS	1,76409 × 10 ⁻⁴	0,99911	3.334

In all experiments, the decane dissolution level was increased in the presence of surfactant. And this increase depended on the type of surfactant. The solubilization capacity of the surfactants for decane was quantified by the WSR. In this research, the solubilization powers of extended surfactants (X-AES) was compared with that of two anionic surfactants possessing different hydrophobic chain lengths (Table 1). From WSR values, it was noted that the solubilization power of X-AES is approximately higher than that of SDS and SDBS. Solubilization power increased with increasing hydrocarbon chain length [11]. However, it is about the double of that of SDBS.

Conclusion

The work presented here focused on the comparison of the enhanced solubility of decane among three anionic surfactants with different structures. These properties affect the ability of surfactants to remove contaminant by interfacial tension reduction. The order of solubility enhancement of decane was X-AES > SDS > SDBS. The difference in solubilization power among the three anionic surfactants can be attributed to the structure of surfactants, the shape and size of micelles especially the hydrophobic tail length, and their CMC values. According to the results we can suggest that the extended surfactant X-AES could find suitable application in soil and aquifer remediation processes.

References

- [1] Jia, W. et al: EFFICIENCY OF SINGLE AND MIXED GEMINI/CONVENTIONAL MICELLES ON SOLUBILIZATION OF PHENANTHRENE, *CHEMICAL ENGINEERING JOURNAL*, **168** (2011) 201–207.
- [2] Lizhong, Z., Shaoliang, F.: SYNERGISTIC SOLUBILIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY MIXED ANIONIC–NONIONIC SURFACTANTS, *CHEMOSPHERE*, **53** (2003) 459–467.
- [3] Sudipta, C. et al: ENHANCED SOLUBILIZATION OF PHENANTHRENE IN TRITON X-100 SOLUTIONS BY THE ADDITION OF SMALL AMOUNTS OF CHITOSAN, *CHEMICAL ENGINEERING JOURNAL*, **163** (2010) 450–453.
- [4] Kabir-ud-Din et al: SOLUBILIZATION CAPABILITIES OF MIXTURES OF CATIONIC GEMINI SURFACTANT WITH CONVENTIONAL CATIONIC, NONIONIC AND ANIONIC SURFACTANTS TOWARDS POLYCYCLIC AROMATIC HYDROCARBONS, *JOURNAL OF HAZARDOUS MATERIALS*, **167** (2009) 575–581.

- [5] Sung-Kil, P. Angela, R.B.: EQUILIBRIUM PARTITIONING OF A NON-IONIC SURFACTANT AND PENTACHLOROPHENOL BETWEEN WATER AND A NON-AQUEOUS PHASE LIQUID, *WATER RESEARCH*, **37** (2003) 3412–3420.
- [6] Wenjun, Z., Lizhong, Z.: ENHANCED SOIL FLUSHING OF PHENANTHRENE BY ANIONIC–NONIONIC MIXED SURFACTANT, *WATER RESEARCH*, **42** (2008) 101–108.
- [7] Li, J.L., Chen, B.H.: SOLUBILIZATION OF MODEL POLYCYCLIC AROMATIC HYDROCARBONS BY NONIONIC SURFACTANTS, *CHEMICAL ENGINEERING SCIENCE*, **57** (2002) 2825 – 2835.
- [8] Deshpande, S. et al.: DOWFAX SURFACTANT COMPONENTS FOR ENHANCING CONTAMINANT SOLUBILIZATION, *WATER RESEARCH*, **34** (2000) 1030–1036.
- [9] Chi, K.A. et al.: SELECTIVE ADSORPTION OF PHENANTHRENE DISSOLVED IN SURFACTANT SOLUTION USING ACTIVATED CARBON, *CHEMOSPHERE*, **69** (2007) 1681–1688.
- [10] Matilde, M. et al: SOLUBILIZATION OF POLAR OILS WITH EXTENDED SURFACTANTS, *COLLOIDS AND SURFACES A: PHYSICOCHEMICAL AND ENGINEERING ASPECTS*, **100** (1995) 217-224.
- [11] Baowei, Z. et al : A NOVEL SOLUBILIZATION OF PHENANTHRENE USING WINSOR I MICROEMULSION-BASED SODIUM CASTOR OIL SULFATE, *JOURNAL OF HAZARDOUS MATERIALS*, **119** (2005) 205–211.
- [12] Edwards, D.A. et al: SOLUBILIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MICELLAR NONIONIC SURFACTANT SOLUTIONS, *ENVIRONMENTAL SCIENCE AND TECHNOLOGY*, **25** (1991) 127–133.
- [13] Chan, L.C. et al : SOLUBILIZATION OF PAH MIXTURES BY THREE DIFFERENT ANIONIC SURFACTANTS, *ENVIRONMENTAL POLLUTION*, **118** (2002) 307–313.

Corresponding author

Soufiane RAHAL

Materials and Environmental Laboratory, Faculty of Science and Technology

University of Medea, Ain D'Heb, 26001 Medea, Algeria

Phone/Fax: 00 (213) 25594540 E-mail: rahalsoufiane@yahoo.f