

Study of Physicochemical Properties of Sodium Dodecyl Sulphate Surfactant: its Micellization, Oil in Water Emulsification and Industrial Applications

Dina Murshed^{1,*}

Niyazi A. S. Al-Areqi¹

¹Department of Chemistry, Faculty of Applied Sciences, Taiz University, Taiz, Yemen

Fuad Saleh²

²Department of Chemistry, Faculty of Sciences, Chulalongkorn University, Thailand

Nermeen Al-Absi³

³Department of Industrial Chemistry, Faculty of Applied Sciences, Taiz University, Taiz, Yemen

Corresponding Author:- Dina Murshed^{1,*}

Abstract:- Surfactants play an important role in many industries such as cosmetics, perfumes, medicines, and foods, as they are widely recognized due to the diversity of their structures and their analysis, and are responsible for the formation of O/W or W/O emulsions as reported in the literature. The current work presented an investigation on the physicochemical properties of sodium dodecyl sulfate (SDS) and its effect on the formation of sesame oil/ water microemulsion in the presence of lauryl alcohol (LA) as a cosurfactant using electrical conductivity and hydrodynamic viscosity measurements. It has been found that the critical micelle concentration (CMC) of SDS in the aqueous environment is 10.75×10^{-3} M, which is consistent with its literature value reported. It was observed that the CMC gradually decreases with increasing temperature. However, the variation in the degree of micelle ionization with temperature showed a maximum and minimum at 35 °C and 45 °C, respectively. The variation of Gibbs free energy of SDS micellization as a function of temperature. Indicated that the SDS micellization in aqueous media is a spontaneous process and is thermodynamically favorable. It was clearly noticed that the CMC of SDS goes on increasing with the addition of sesame oil. which was also reflected by a gradual drop in the relative viscosity as the oil % increases. This may be attributed to the fact that oil droplets undergo fractioning and then get emulsified in the hydrophobic cores of SDS micelles. Because of such emulsification, the size of SDS micelle increased, and consequently higher concentrations of SDS would be required to reach an equilibrium micellization with the further addition of oil as a disperse phase. The effectiveness of SDS on emulsification demonstrated the ability of SDS surface hypotension in the formation of Microemulsions. Accordingly, SDS can be used as a powerful emulsifying agent to minimize the surface tension in the water medium and produce

Microemulsions that would have many promising future applications.

Keywords:- Surfactants; Microemulsions; Sodium Dodecyl Sulfate; Sesame Oil; Lauryl Alcohol; CMC; Electrical Conductivity.

I. INTRODUCTION

The surfactant is known as the surface anti-stress or active surface factors, which are Surfactants play an important role in many industries such as cosmetics, perfumes, medicines and foods as they are widely recognized due to the diversity of their structures and their analysis are responsible for the formation of O/W or W/O emulsions containing at least one group of lyophilic of freeze-loving aggregates. (Solvent-loving) And lyophobic group of solvents in the molecule in case the solvent is water where appears in two phenomena: adsorption and aggregation. Adsorption migrates surfactant particles out in the water medium and in the region, its molecules migrate out in the fixed solution with a head group lyophilic of cylindrical shape called 'micelles' and start with a low concentration known as critical micelle concentration. In recent studies, CMC has been defined as the concentration of the solution surfactant in which the molecules self-assemble to form spherical-shaped solvents. The CMC refers to the usually narrow range of concentrations that prefer boundaries and which are limited by most of the surface hypotensive material in the mono state and almost above. [1-4]

The physical methods of CMC assessment are conductivity, solubility, viscosity, dispersion of light and measurement of surface tension by wilhelmy slide method or by the method of maximum bubble pressure, measurement of ion activity, dye incorporation of method, gel filtration spectrum and anti-magnetic resonance [5-6]

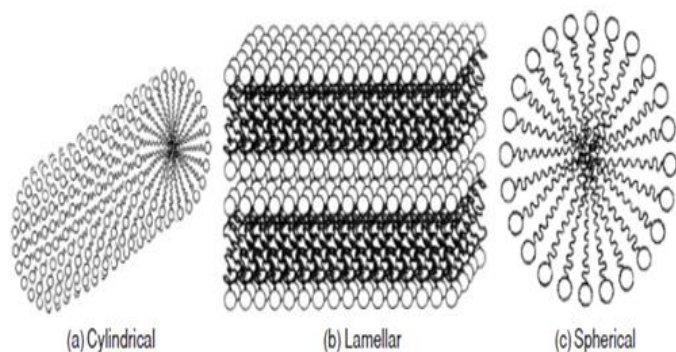


Fig 1 Typical Micelle Configurations

The CMC decreases sharply with the increase of the water hydrophobic part of the surface tension and is faster in the case of non-ion substances than in the ion surface [7] tension lowering substances and by one methylene group The length of the hydrocarbon chain is increased and another group also reduces the CMC to one third of its original value clearly so that the CMCs various surface tension congeners are tracked with alkyl chain follow the equation:

$$\log CMC = A + Bn$$

Where, n is the alkyl chain and A and B are constants.[8] Hydrodynamic viscosity measurements Using Ostwald's viscometer, determine the flow time of solution to flow time of water by the following equation:

$$\eta = ts / t^{\circ} \quad \text{Eq. (2.1)}$$

where η is the relative viscosity. ts is the flow time of solution, t° is the flow time of water

Calculation of thermodynamic parameters of micellization Gibb's free energy of micellization is computed by:

$$\Delta GM = RT \ln CMC \quad \text{Eq. (2.2)}$$

$\Delta^{\circ}S_m$ is equal to the slope obtained from the plot of $\Delta^{\circ}GM$ VS T. $\Delta^{\circ}H_m$ is calculated using the relation: cation

$$\Delta^{\circ}GM = \Delta^{\circ}HM - T \Delta^{\circ}SM$$

Properties affecting surfactant are Moisturizing, dissolving, dispersing the aggregation of solids, and rolling reactions with lowering agents,, foam/foam removal and emulsification/emulsification and adsorption It is classified surfactant to anionic, citeons and cationic surfactants such as alkyl sulfate, ammonium lauryl sulfate, sodium laurel sulfate are the most common surface stress-lowering substances.

It is known as sodium ether laurel sulfate (SLS), consisting of alkyl carboxylate such as sodium nitrate beneficial in emulsion polymerization. Non-ionic surfactant where some long, smooth alcohols show some properties of a surface reactor [9, 10]

The cations surfactant which contain a positive charge head is used as an antimicrobial, antifungal and so on HI & I (Benzalconium Chloride (BAC), Cinyl Peridenium Chloride (CPC) and Benzethonium Chloride (BZT) Studies have shown that can procedure changes in the structure of surfactant by addition a number of methylation aggregates that change its shape as it was observed that the ion was not sensitive to the high concentrations of salt solutions where it was thought that non-ion ones absorbed more than the ion and dissolved more. It was found that greater molecular weight leads to greater melting and that surface tension is lower and the resolution of melting by increasing the partial weight of the surface reactor while maintaining balance fitting Hydrophilic Lipophilic Balance. HLB [11, 12]

In a previous study, the non-ionized type of surfactant was influenced and concentration on the motility of Ostwald oleo-dynamics, where the drops of the oil and water emulsion (hydrocarbon suspended in aqueous solutions) were measured by a 5% change in the distribution the diameter. Ostwald Ripening (OR) Large droplet growth process on small droplets solubility (OR) The material is larger inside the drop with increased intercommon bending in matching oil with water.[4]

Large emulsions with diameter greater than 400 nm, 5-50 nm precision emulsions and medium size miniature emulsions in the case of unmixed emulsions, surface tension reducers are added to increase the stability of large emulsions and their surface tension reduces free energy between two non-mixable phases, increasing electrostatic dissonance between them. At low temperatures a fine emulsion is formed balanced with excess oil At high temperature the head group requires less space so it produces a negative curvature, either system Termed Winsor The phase turns and forms a W/O microemulsion (W/O) It is a state of equilibrium in the phase of excess water. At medium temperature three stages consist of the water phase, micro emulsifier and oil phase in a state of equilibrium called (Termed Winsor System) [13, 14]

So according to the size of emulsion droplets, micro-emulsifiers are thermodynamically stable systems with low viscosity. Large emulsions are dynamically stable systems with high viscosity. The entropy system is increased by having more dispersed droplets where surface areas and corresponding surface energies increase as droplets increase. Oil, water and surface-neutral substances are mixed in the most basic forms. Studies have shown that microemulsion remains constant in terms of the size of its drops and does not grow over time [15]

Microemulsions have many applications including drug delivery and pharmaceutical industry for its characteristic antibacterial, fungal, viral, anti-cancer and sperm freezing where it acts as an anti-adhesive that makes it suitable for its vital and therapeutic role produced by microbial cell surfaces and can be excreted outside the cell [10], cosmetics, food, fuel, lubricants, Coating, detergents, agrochemicals, analytical chemistry, Nanoscale synthesis that lowers interpersonal tension between droplets to prevent

the integration of droplets is transparent 50-100 sized systems applied in the field of personal care, health care and beauty [10], Biotechnology and chemical reactors because of their distinctive high dissolution of water-loving substances in oil and hydrophobic systems in water systems, very low surface tension is heard for micro-droplets in the dispersed phase and the protection of coated substances and the ability to penetrate biological membranes [16]

Sodium dodecyl sulphate (SDS) with a formula $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4 \text{Na}$ It is an anionic surfactant used in cleaning and hygiene products. It consists of a tail consisting of 12 carbon atoms associated with a sulfate group so that the carbon tail with the polar head group gives the properties of the amphibious compound and derives from inexpensive coconut and palm oils where it produces the treatment of pure, hard-fought laurel alcohol from coconut and palm with sulfur trioxide gas, Oleum or Chloroacetic acid to produce hydrogen lauryl sulfate Inside in all household, personal and industrial cleaning products [17, 18].

The presence research work aims to investigate the physicochemical properties and micellization of SDS surfactant in aqueous media and to study influence of sesame oil on the emulsifying efficiency of SDS in the presence of lauryl alcohol (LA) as a non-ionic cosurfactant.

II. METHODS

Sodium dodecyl sulphate (SDS) was purchased from Aldrich with a purity of 99.5 w/w%. Lauryl alcohol (LA) was obtained by Desulphonating of SDS. Sesame oil was obtained from local market with a high purity.

A series of aqueous SDS surfactant solutions (series A) in concentration range of 1×10^{-3} - 2×10^{-2} M was prepared by diluting 0.1 M SDS stock solution with accurate portion of distilled water. A 0.2 - ml cosurfactant (LA) was added into each as-prepared SDS surfactant solution of series A. The resulting mixtures were subjected to instant shaking for 15 minutes to attain equilibrium stabilization, followed by addition of different amounts of sesame oil (oil) at a varying weight percent ranging from 0.1672 - 1.672 %, with a instant shaking for 15 minutes, constituting a series B. The specific conductivity (K) of each solution of series A and B was measured using conductivity bridge (METRIC model) in temperature range of 25 – 55 °C. Values of CMC was obtained by plotting of K vs. surfactant concentration, where CMC corresponds to the point at which two lines intersect. However, the estimated value of degree of the micelle ionization (α) is obtained from the absolute ratio of two-line slopes and thermodynamic parameters of the micellization was calculated using equations (3) and (4). The relative viscosities (η_r) at CMC of all solutions were measured using Ostwald viscometer. Origin Pro. version 6.1 was used for data presentation and line- regression fitting.

III. RESULTS AND DISCUSSION

A typical plot of specific conductivity vs. surfactant concentration at 25 °C without addition of LA and oil is presented in Figure 2. Two regions of different line slopes can be recognized well. This can be attributed to the difference in the trend of measured values of conductivity before and after the critical micelle concentration (CMC). The two red-colored lines depicted represent the best straight lines exhibiting the linear relationships between the specific conductivity and concentration before and after the micellization of SDS at a given temperature. These straight lines were obtained by applying the line regression fitting to the experimental data.

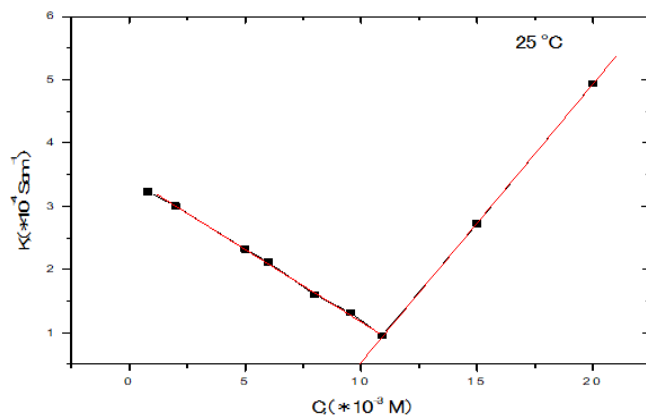


Fig 2 K Vs. Surfactant Concentration at 25°C Without Addition of LA and Oil

Table 1 summarizes the estimate values of CMC and α of SDS measured at different temperatures (25 to 55 °C) along with the corresponding statistical parameters (where R^2 = the squared correlation coefficient or variance, and SD = the standard deviation). It can be noticed that the CMC of SDS gradually drops with increasing temperature. This indicates that the aggregation number (i.e., number of surfactant molecules per a micelle) of SDS micelles decreases as the temperature rises. However, the variation in the degree of micelle ionization with temperature shows a maximum and minimum at 35 °C and 45 °C, respectively.

Table 1 Estimate Values of CMC and Degree of Micelle Ionization for SDS as A Function of Temperature.

| T (°C) | CMC(M) | α | SD | R^2 |
|--------|--------|-----------|---------|----------|
| 25 | 10.75 | -0.44157 | 0.63299 | 0.784021 |
| 35 | 9.32 | 10.44886 | 0.44667 | 0.722891 |
| 40 | 8.133 | 2.627982 | 0.44497 | 0.836127 |
| 45 | 7.35 | 0.1211828 | 0.07276 | 0.903735 |
| 50 | 6.48 | 2.826185 | 0.37801 | 0.852796 |
| 55 | 5.06 | 4.6542575 | 0.28282 | 0.570886 |

Table (2) and Figure (3) show the variation of Gibbs free energy of SDS micellization as a function of temperature. The standard entropy of micellization (ΔS°_M) was obtained from the slope of ΔG°_M vs. T, plot shown in Figure (3). The negative sign of ΔG°_M and positive one of ΔS°_M (Table 2) indicate that the SDS micellization in aqueous media is an spontaneous process and is thermodynamically favorable.

Table 2 Thermodynamic Parameters of SDS Micellization in the Absence of LA and Sesame Oil.

| T(K) | Ln CMC | $\Delta G^{\circ} m$ | $\Delta S^{\circ} m$ | $\Delta H^{\circ} m$ | R ² | SD |
|------|--------|----------------------|----------------------|----------------------|----------------|----------|
| 298 | 2.37 | -5871.84 | 45.7856 | 45.7856 | 0.879018 | 205.1236 |
| 308 | 2.23 | -5710.38 | | | | |
| 313 | 2.095 | -5451.78 | | | | |
| 318 | 2.018 | -5335.29 | | | | |
| 323 | 1.86 | -4999.88 | | | | |
| 328 | 1.62 | -4417.72 | | | | |

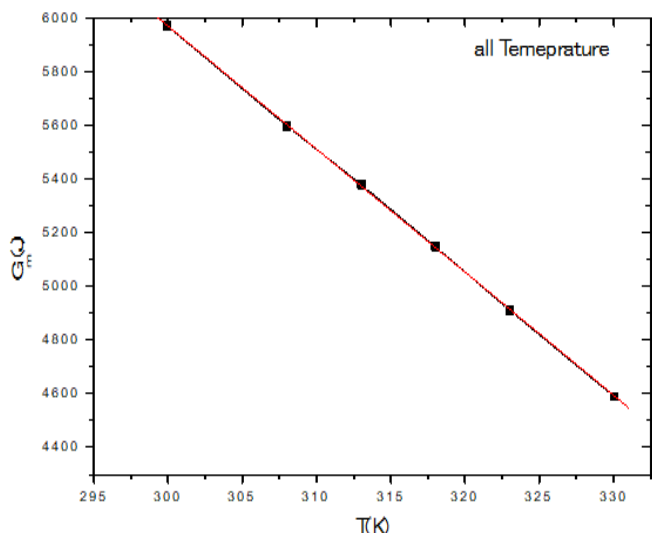


Fig 3 $\Delta G^{\circ}m$ vs. T Plot of SDS Micellization.

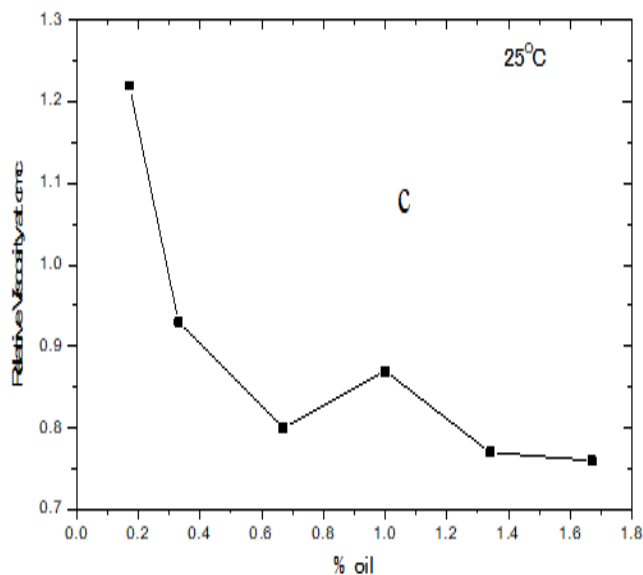
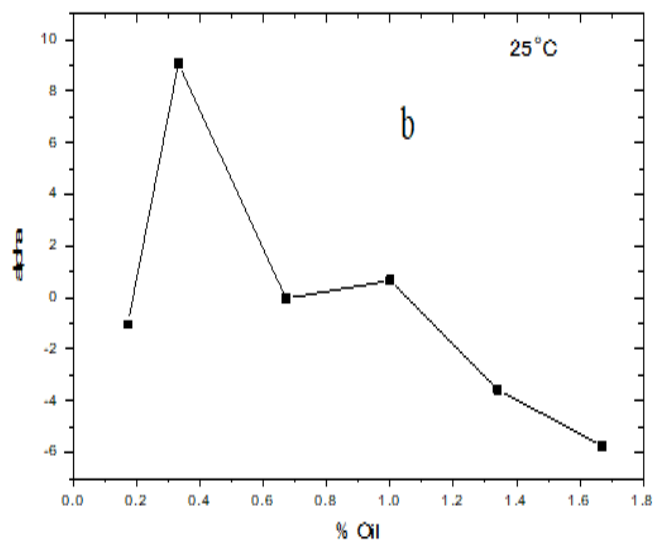
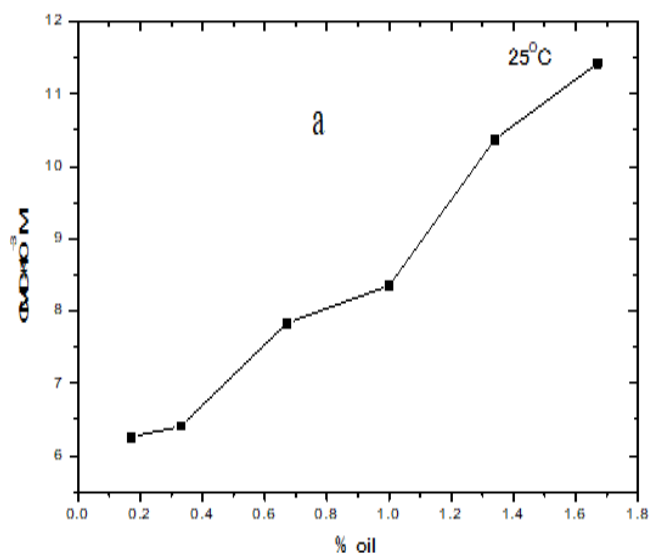


Fig 3 (A) Variation of CMC as A Function of Wt% Oil added. (B) Variation of Degree Micelle Ionization as A Function of Wt% Oil Added (C) Variation of η_r at CMC as A Function of Wt% Oil Added.

Table 3 Variation of CMC, α and η_r at CMC for SDS as a function of weight % of sesame oil added.

| Sesame oil % | CMC $\times 10^{-3} m$ | αJ | $\eta_r @ CMC$ Jk-1 |
|--------------|------------------------|------------|---------------------|
| 0.1672 | 6.26 | -1.043976 | 1.22 |
| 0.3344 | 6.41 | 9.07971 | 0.93 |
| 0.6688 | 7.83 | -0.03358 | 0.80 |
| 1.0032 | 8.35 | 0.6667 | 0.587 |
| 1.3376 | 10.37 | -3.56089 | 0.77 |
| 1.672 | 11.42 | -5.74712 | 0.76 |



The variation of CMC, degree of micelle ionization, and relative viscosity of SDS corresponding to the CMC are listed in Table 4 and presented as well in Figure 4(a,b and c), respectively. It is clearly noticed that the CMC of SDS goes on increasing with the addition of sesame oil as shown in Figure 4(a), which is also reflected by a gradual drop in the relative viscosity as the oil % increases. This may be due to the fact that oil droplets undergo fractioning and then get emulsified in the hydrophobic cores of SDS micelles.

Because of such emulsification, the size of SDS micelle tends to increase, and consequently higher concentrations of SDS would be required to reach an equilibrium micellization with the further addition of oil as a disperse phase.

IV. CONCLUSION

Surfactants play very important roles in many industries, such as cosmetics, perfumes, drugs, foods, etc. Because of their diverse structures (i.e., polar head groups and hydrophobic long chains), the micellization of surfactant molecules constitutes a necessary requirement for the formation of either O/W or W/O emulsions. In this research work, an attempt had been made to investigate the physicochemical properties of SDS surfactant and its O/W emulsion formed from sesame oil, water in the presence of LA as a non-ionic cosurfactant. Electrical conductivity and hydrodynamic viscosity measurements were performed at different temperatures and varying oil additions. The value of CMC of SDS in aqueous media was found to be 10.75×10^{-3} M at room temperature, which is well agreed with its literature value. It has also been found that the CMC of SDS gradually decreases with the rise of temperature from 25 to 45 °C. the emulsifying efficiency of SDS has also been investigated using sesame oil in the presence of LA. Microscopic images revealed the ability of SDS surfactant in the formation of Microemulsions.

REFERENCES

- [1]. J. Weiss and D. J. McClements, "Mass Transport Phenomena in Oil-in-Water Emulsions Containing Surfactant Micelles: Solubilization," *Langmuir*, vol. 16, no. 14, pp. 5879-5883, 2000/07/01 2000, doi: 10.1021/la9914763.
- [2]. J. A. Lucey, C. Gorry, B. O'Kennedy, M. Kalab, R. Tan-Kinita, and P. F. Fox, "Effect of acidification and neutralization of milk on some physico-chemical properties of casein micelles," *International Dairy Journal*, vol. 6, no. 3, pp. 257-272, 1996/03/01/ 1996, doi: [https://doi.org/10.1016/0958-6946\(95\)00014-3](https://doi.org/10.1016/0958-6946(95)00014-3).
- [3]. M. A. Desando and L. W. Reeves, "The effects of high temperatures (29–123 °C) on critical micelle concentrations in solutions of potassium n-octanoate in deuterium oxide: A nuclear magnetic resonance study," *Canadian Journal of Chemistry*, vol. 64, pp. 1823-1828, 1986.
- [4]. H. Matsumoto, C. Kaneko, K. Yamada, T. Takeuchi, T. Mori, and Y. Mizuno, "A convenient synthesis of 9-(2-hydroxyethoxymethyl)guanine (acyclovir) and related compounds," (in eng), *Chem Pharm Bull (Tokyo)*, vol. 36, no. 3, pp. 1153-7, Mar 1988, doi: 10.1248/cpb.36.1153.
- [5]. D. Q. M. Craig, S. A. Barker, D. Banning, and S. W. Booth, "An investigation into the mechanisms of self-emulsification using particle size analysis and low frequency dielectric spectroscopy," *International Journal of Pharmaceutics*, vol. 114, no. 1, pp. 103-110, 1995/01/31/ 1995, doi: [https://doi.org/10.1016/0378-5173\(94\)00222-Q](https://doi.org/10.1016/0378-5173(94)00222-Q).
- [6]. G. F. Koser, P. B. Kokil, and M. Shah, "Direct functionalization of sulfides with hypervalent iodine reagents: Methoxysulfonium and amidosulfonium tosylates," *Tetrahedron Letters*, vol. 28, no. 45, pp. 5431-5434, 1987/01/01/ 1987, doi: [https://doi.org/10.1016/S0040-4039\(00\)96746-7](https://doi.org/10.1016/S0040-4039(00)96746-7).
- [7]. "Subject Index," in *Applied Surfactants*, 2005, pp. 631-634.
- [8]. D. Attwood, P. H. Elworthy, and S. B. Kayne, "Micellar polydispersity of the non-ionic detergent cetomacrogol," *Journal of Pharmacy and Pharmacology*, vol. 21, no. 9, pp. 619-620, 1969, doi: 10.1111/j.2042-7158.1969.tb08331.x.
- [9]. H. Wiese, "A. W. Adamson: "Physical Chemistry of Surfaces", 5. Auflage, John Wiley & Sons Inc., New York, Chichester, Brisbane, Toronto, Singapore 1990. 777 Seiten, Preis: £ 47.50," *Berichte der Bunsengesellschaft für physikalische Chemie*, <https://doi.org/10.1002/bbpc.19910950629> vol. 95, no. 6, pp. 758-758, 1991/06/01 1991, doi: <https://doi.org/10.1002/bbpc.19910950629>.
- [10]. S. M. Shaban, J. Kang, and D.-H. Kim, "Surfactants: Recent advances and their applications," *Composites Communications*, vol. 22, p. 100537, 2020/12/01/ 2020, doi: <https://doi.org/10.1016/j.coco.2020.100537>.
- [11]. Y. Barakat, L. N. Fortney, R. S. Schechter, W. H. Wade, S. H. Yiv, and A. Graciaa, "Criteria for structuring surfactants to maximize solubilization of oil and water: II. Alkyl benzene sodium sulfonates," *Journal of Colloid and Interface Science*, vol. 92, no. 2, pp. 561-574, 1983/04/01/ 1983, doi: [https://doi.org/10.1016/0021-9797\(83\)90177-7](https://doi.org/10.1016/0021-9797(83)90177-7).
- [12]. J. Kroll, "Microemulsions and Emulsions in Foods (ACS Symposium Series 448). Herausgegeben von M. El-Nokaly und D. Cornell. 268 Seiten, zahlr. Abb. und Tab. American Chemical Society, Washington, DC, 1991. Preis: 54,95 \$," *Food / Nahrung*, vol. 35, no. 8, pp. 899-899, 1991, doi: <https://doi.org/10.1002/food.19910350832>.
- [13]. M. Antonietti and K. Landfester, "Single molecule chemistry with polymers and colloids: a way to handle complex reactions and physical processes?," *Chemphyschem : a European journal of chemical physics and physical chemistry*, vol. 2 4, pp. 207-10, 2001.
- [14]. K. Landfester, N. D. Bechthold, F. Tiarks, and M. Antonietti, "Miniemulsion Polymerization with Cationic and Nonionic Surfactants: A Very Efficient Use of Surfactants for Heterophase Polymerization," *Macromolecules*, vol. 32, pp. 2679-2683, 1999
- [15]. Y.-Y. Luk and N. L. Abbott, "Applications of functional surfactants," *Current Opinion in Colloid & Interface Science*, vol. 7, no. 5, pp. 267-275, 2002/11/01/ 2002, doi: [https://doi.org/10.1016/S1359-0294\(02\)00067-5](https://doi.org/10.1016/S1359-0294(02)00067-5).
- [16]. B. K. Paul and S. P. Moulik, "Uses and applications of microemulsions," *Current Science*, vol. 80, no. 8, pp. 990-1001, 2001. [Online]. Available: <http://www.jstor.org/stable/24105809>.

- [17]. L. Salvo, G. Martin, M. Suard, A. Marmottant, R. Dendievel, and J.-J. Blandin, "Processing and structures of solids foams," *Comptes Rendus Physique*, vol. 15, no. 8, pp. 662-673, 2014/10/01/2014, doi: <https://doi.org/10.1016/j.crhy.2014.10.006>.
- [18]. C. Gloxhuber and K. Klunster, *Anionic Surfactants: Biochemistry, Toxicology, Dermatology*, Second Edition. Taylor & Francis, 1992.