IJO - International Journal of Applied Science

(ISSN: 2992-247X)
https://ijojournals.com/

Shirley Marfisi Valladares[3*]
Volume 07 || Issue 09|| September, 2024 ||

ORIGINAL RESEARCH

IMPACT OF ALCOHOL CONCENTRATION AND TYPE ON OPTIMAL SALINITY IN SURFACTANT-OIL-WATER MICROEMULSION SYSTEMS

Rayda Patino-Camino[1], Alexis Cova-Bonillo[1,2], Shirley Marfisi Valladares[3*], Michael Kluchuikon[3]

[1] Universidad de Castilla-La Mancha, Escuela Técnica Superior de Ingenieros Industriales, Edificio Politécnico, Avda. Camilo José Cela s/n, 13071, Ciudad Real, Spain.

[2] Department of Mechanical Engineering, University of Birmingham. Edgbaston, Birmingham, B15 2TT, United Kingdom.

[3] Universidad de Oriente, Departamento de Ingeniería Química, Laboratorio de Sistemas Dispersos y Ambiente, Grupo Sistemas Dispersos y Electroquímica, Barcelona, Venezuela.

*Corresponding Author: ***Shirley Marfisi Valladares[3*]***

HIGHLIGHTS

- Alcohol type and concentration significantly influence optimal salinity in SOW/A systems.
- Intermediate-chain alcohols act as co-surfactants, enhancing microemulsion formation.
- Optimal salinity decreases with increasing alcohol concentration for most alcohols.
- Iso-pentanol deviates from linear S*-alcohol concentration relationship, impacting microemulsion design.
- Laser light scattering and interfacial tension measurements yield consistent results for optimal salinity.
- Correlations developed for alcohol function *f(A)*enable *HLD* estimation and interpretation.

ABSTRACT

In this study, the influence of cosurfactants (n-butanol, sec-butanol, iso-butanol, n-pentanol, iso-pentanol) on the formulation of sodium dodecyl sulfate-oil-water systems was investigated. Salinity sweep, stability and interfacial tension measurements were used to determine the optimum salinity and function alcohol, f(A). The results showed that systems without alcohol form gelled structures requiring longer equilibration times than systems with alcohols, where an increase in concentration significantly modifies the value of the optimal formulation, especially for primary alcohols in the range of 3 to 5 % v/v alcohol. With n-

pentanol, the optimal salinity was shifted from 12 g/dL (1 % v/v n-pentanol) to 5.5 g/dL (3 % v/v n-pentanol), maintaining the same WI-WIII-WII phase behavior contributed by the salinity variation in the formulation sweep. Also, salinity adjustment models were developed as a function of alcohol concentration and function f(A) for each alcohol, which allow numerically estimating the HLD correlation parameter for the studied system and its interpretation out of equilibrium to form or break emulsions; as well as in detergent formulations and microemulsions for cleaning or transport of substances in controlled release of ingredients.

Keywords: *formulation, cosurfactant, interfacial tension, stability, stability*

INTRODUCTION

Surfactants and cosurfactants are crucial across a wide range of applications. Their use has significantly grown in sectors as varied as food processing [1], cosmetics [2], pharmaceuticals [3], and anticorrosion [4], particularly in the gas-oil-petrochemical industry for tasks like asphaltene inhibition and enhanced oil recovery [5, 6, 7, 8]. Their effectiveness relies heavily on the optimal formulation of the surfactant-oil-water (SOW) system. At this point a substantial reduction in interfacial tension(*IFT*), related tothe balance between hydrophilic and lipophilic interactions dictates phase separation and stability. While previous studies have been conducted to explore the use of alcohols as cosurfactants, their quantitative influence on optimal formulation remains unclear [9, 10, 11, 12].Theoretical models, like molecular thermodynamic and phenomenological approaches, have tried to describe microemulsion behavior. However, these models often rely on many parameters and assumptions, limiting their practical use and predictive accuracy[13].

Alany et al. [14] conducted a study on the effect of different alcohols as cosurfactants on the phase behavior of the pseudoternary systems water/ethyl oleate/non-ionic surfactant. They found that the alcohol increased the percentages of water and oil in the microemulsions. Alvarez et al. [15] determined that a small amount of sec-butanol in the aqueous phase decreases the time required for the emulsification system to produce an emulsion of normal morphology at equilibrium (time of apparent equilibrium, t_{APE}) of an unequilibrated SOW system. Studies by Marfisi [16] suggest that alcohols like sec-butanol facilitate the de-emulsifying surfactant move to the oil-water interface faster. This improves separation by lowering the *IFT* and speeding up the adsorption process. However, the effectiveness of the alcohol depends on its properties very lipophilic (lipophilic liker), or highly hydrophilic (hydrotropic and hydrophilic linker) alcohols hinder the transfer of the separating agent [15]. Intermediate hydrophilicity alcohol(butanol and pentanol) is added to SOW systems to prevent the formation of gels and to accelerate the process of reaching equilibrium of the SOW/A systems, where alcohol is incorporated. For example, secondary butanol (sec-butanol) and tert-pentanol are commonly used because they interact well with both the aqueous and the oil phase [17]. However, alcohols with longer hydrocarbon chains tend to accumulate more in the oil phase, which further increases the stability of the mixture [18, 19].

The different formulation parameters are empirically correlated. The correlation for optimal formulation Hydrophilic Lipophilic Difference (*HLD*), quantifies the overall effect of the variables involved on formulation of the SOW systems [20]. The correlation for anionic surfactantsis useful to determine the location of the optimal formulation in a salinity formulation scan, which occurs when the *HLD* equals zero, i.e., when there is an exact balance between hydrophilic and lipophilic interactions of the surfactant on both phases of the SOW system. Salager et al. [21] recently introduced the normalized version of this concept, the normalized *HLD* (HLD_N), to enable a fairer comparison between different surfactant systems, irrespective of their alkyl chain lengths.

A quantitative understanding of how different alcohols affect optimal formulation, is lacking. The present study investigates the influence of various alcohols on the optimal formulation of anionic surfactant-oil-water systems. By incorporating the effects of these alcohols into *HLD*, expressed through the function alcohol, *f(A)*, the research aims to establish both qualitative and quantitative trends. This approach offers a framework to elucidate how the addition of alcohols alters the optimal formulation, ultimately facilitating more efficient engineering of SOW systems. Interfacial tension (*IFT*) serves as a key response variable to identify the optimal formulation for each alcohol-containing system. Furthermore, analysis of *IFT* evolution over time provides insights into the stability of the resulting emulsions. This comprehensive investigation seeks to deliver valuable knowledge for optimizing SOW formulations that incorporate alcohol cosurfactants.

MATERIALS AND METHODS

Salinity scanning phase behavior experiment

The following two concentrated solutions were prepared: a) Sodium dodecyl sulfate surfactant (SDS) solution at 10 g/dL in water, from Scharlaü Chemie S.A. (95% purity for synthesis); b) Sodium chloride (NaCl) solution at 20 g/dL in water, manufactured by Sigma-Aldrich (99% purity). All components were weighed on an analytical balance (Cole-Palmer Instruments, with a capacity of 120 g and a precision of ±0.0001 g), and dissolved in distilled water to a total volume of 1 L in a volumetric flask.

By using the single scan technique[22], a series of 30 mL calibrated tubes were used for the formulation scans of the SOW systems. Each tube was filled sequentially with distilled water, brine, the SDS solution at 1 g/dL concentration, heptane (Sigma Aldrich, ≥ 96 % purity), and a variable quantity of alcohol affecting the total system volume. A consistent water-oil ratio (WOR) of unity was maintained throughout, with varying concentrations of NaCl as the salinity formulation variable. Alcohol content was varied from 0 to 5% vol. (in increments of 1%), with additional variables including the chain length of the alcohol and the position of the OH functional group. Five alcohols were assessed: n-butanol, sec-butanol, iso-butanol, n-pentanol and iso-pentanol (Sigma Aldrich, 99 % purity for synthesis). Reference scans without alcohol were also prepared.

The phase behavior at equilibrium was determined placing the SOW/A systems in a water bath maintained at 25 °C for a period ranging from 48 to 72 h. After equilibration, the phase volumes were measured, and the systems were characterized using laser light scattering to identify the dominant phase behavior by Winsor's theory (1954): Winsor I indicated by transmission in the aqueous phase, Winsor II by transmission in the oleic phase, and Winsor III by transmission in the bicontinuous middle phase, as shown in Figure 1a. Some of these systems at low alcohol concentration of 1 to 3 % v/v required equilibration times greater than 48 h and formed gelled structures in one of the phases, as shown in Figure 1b.

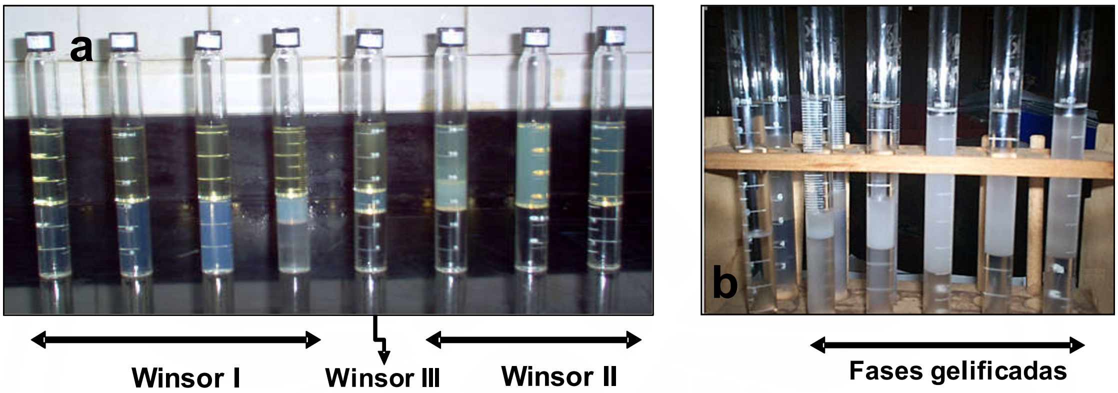

Figure 1. Phase behavior in salinity scans (WOR = 1) for SOW/A systems: a) 1 g/dL SDS in NaCl water, heptane, 3 % n-pentanol; b) 1 g/dL DSS in NaCl water, heptane, 3 % n-butanol

Stability of emulsified SOW system

Stability was measured as a function of the coalesced volume of aqueous phase (Vc) for a predetermined time, after each of the SOW systems of the formulation scan was agitated with a blender mixer at 600 rpm for 1 min up to emulsification. $V\infty$ was set as the total volume of aqueous phase in the tube and equal to 15 mL. Vc was recorded at coalescence time(tc). Then, $Vc/V\infty$ was plotted with respect to tc, obtaining a sigmoidal curve, typical of these processes. The time required to separate 50% of the initial aqueous phase, which was called the meantime ($tc_{1/2}$) was estimated.

Stability measurements in systems prepared with 1 and 2 % v/v alcohol were performed only at the optimum formulation. At these concentrations very stable O/W and W/O emulsions were formed due to the high stability of the resulting WI and WII type systems. Stability diagrams of $tc_{1/2} versus HLD$ were constructed by estimating the $f(A)$ term for each alcohol. This was achieved by setting HLD = 0 in Eq. 1 (where σ = -2,8; κ = 0,10; T = 25 °C, a_T = -0,01ºC^{-1}) and solving for $f(A)$ as follows: $f(A) = \ln(S*) + K$, where K represents the combined contribution of other formulation variables (salinity, oil, and temperature). Thus, $f(A)$ is solely determined by the optimal salinity ($S*$) for each formulation sweep.

$$HLD = \frac{SAD}{RT} = \ln S^{*} - k(EACN) - f(A) + \sigma - a_T \Delta T = 0 \qquad (1)$$

In this equation, *SAD* is the Surfactant Affinity Difference, *R* is the universal gas constant, *T* the temperature of the system, *S** is the optimum salinity of the aqueous phase expressed as g NaCl/dL aqueous phase, *EACN* is the carbon atoms number equivalent of the oil phase represented by a linear alkane, *f(A)* is a function depending of the type and alcohol concentration, σ and k are characteristic parameters depending on the structure of surfactant; ΔT is a deviation of the set temperature from room temperature (25°C) and subscript*T* is the numerical coefficient which expresses the deviation of the formulation with respect to room temperature (25°C)[23].

Interfacial tension measurement

Interfacial tension was measured using the automated TGG110-M3 Rotating Drop Tensiometer[24] [25]. For each case stabilized in the optimum formulation sample of the aqueous phase was drawn using a graduated syringe and introduced into a capillary tube (0.245 mm diameter) to avoid air entrapment. Similarly, a sample of the oil phase was taken, and a drop placed centrally in the capillary, which was then sealed and inserted into the sample holder of the tensiometer. The equipment, pre-calibrated with the tensiometer software for capillary size, spun the capillary at a predetermined speed to elongate the oil drop until its diameter was approximately four times its original size. An image of the elongated drop was captured and analyzed using Aldo's Visual Capture application, as shown in Figure 2. The interfacial tension was calculated using equation 2, proposed by Cayias [26], considering the measured drop diameter (*d*), the density difference between the water and oil phases ($\Delta\rho$), the period of revolution (*p*), and a magnification adjustment factor provided by the camera setup and unit correction factor.

$$IFT(mN/m) = 5{,}33x10^{5}\,\frac{d^{3}\Delta\rho}{p^{2}} \qquad (2)$$

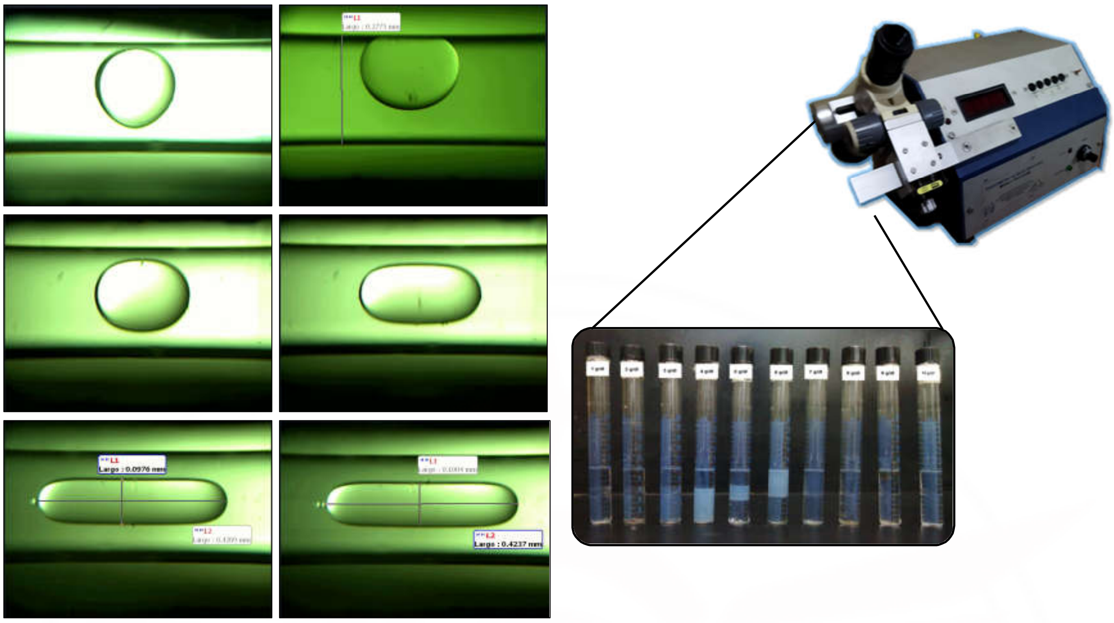

Figure 2. Deformation of the oil drop by the adsorption of the anionic surfactant at the water/oil interface of the SOW/A systems during the measurement of the interfacial tension by the drop deformation method (Spinning Drop Tensiometer, model TGG110-M3, CITEC-FIRP-ULA, capillary 0.245 mm diameter, "Aldo's Visual Capture" and "Tensgg" programs)

RESULTS AND DISCUSSION

Optimal phase behavior and formulation

As illustrated in the micrographs in Figure 3, the expected phase transition for surfactant-oil-water type WI-WIII-WII, occurred for salinity sweeping with water-to-oil ratio WOR 50/50, heptane as the oil phase, 1 g/dL of sodium dodecyl sulfate and 3% v/v n-pentanol. The micrographs captured the variations of phase behavior in the salinity range. In these systems, the WIII microemulsion was observed between 6 and 7 g/dL, where bicontinuous micellar structureis present, as can be seen in the image at salinity of 6 g/dL, and it was necessary to change the microscope objective (10/0.25) compared to the other systems (objective 40/0.65). At salinities less than 6.0, WI type aqueous microemulsions are observed and WII type oil microemulsions above 7.0, with notable visual differences when the association of the molecules is modified according to their affinity with the medium to subtract the lipophilic group from the surfactant, forming normal micelles (type S1), characteristic of Winsor WI systems; or the hydrophilic group forming inverse micelles (type S2) generated by Winsor WII systems.

The optimal salinity (S^*) for these systems containing each of the five alcohols studied was determined by identifying the salinity at which a Winsor III microemulsion formed. This characteristic Winsor III phase, marked by approximately equal volumes of excess aqueous and oil phases, indicates that the microemulsion itself also contains equal volumes of solubilized water and oil [27]. This surfactant-rich middle phase consists of colloidal aggregates of swollen normal and inverse micelles, effectively solubilizing both water and oil. In this state, surfactant interactions with both phases of the emulsion are balanced, indicating that the system is at the optimal formulation.

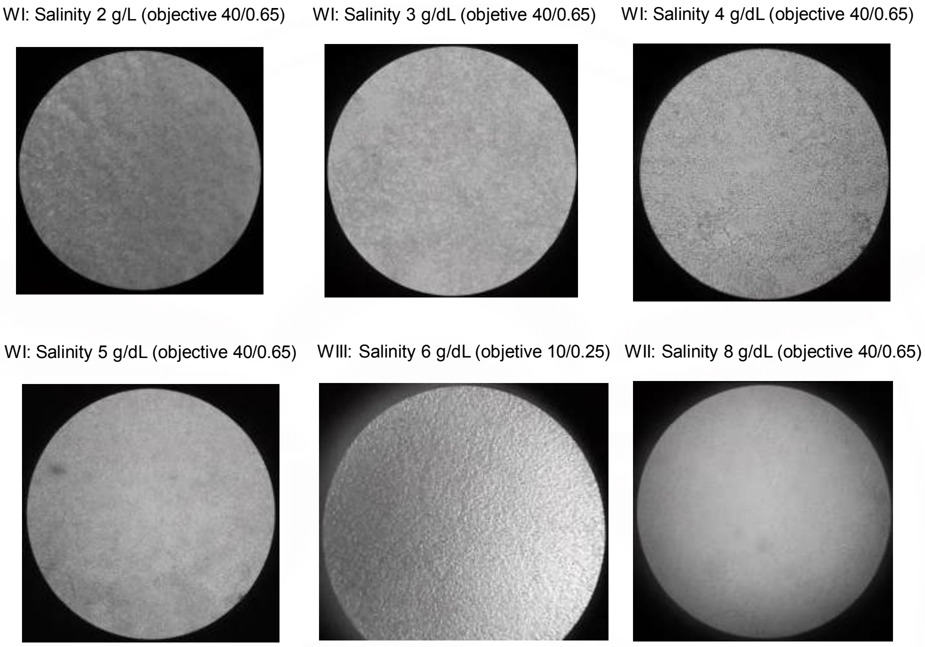
WI: Salinity 2 g/L (objective 40/0.65)
WI: Salinity 3 g/dL (objetive 40/0.65)
WI: Salinity 4 g/dL (objetive 40/0.65)
WI: Salinity 5 g/dL (objetive 40/0.65)
WIII: Salinity 6 g/dL (objetive 10/0.25)
WII: Salinity 8 g/dL (objetive 40/0.65)

Figure 3. Phase behavior variation in salinity scan for SWO/A surfactant system (1 g/dL DSS in water with NaCl, heptane, WOR 50/50, 3 % n-pentanol)

Figure4a illustrates the variation of the clarified aqueous phase fraction as a function of time for various salinity levels (1 g/dL to 16 g/dL) in systems with 3% v/v n-pentanol, revealing the characteristic sigmoidal behavior of phase separation. The mean coalescence time ($tc_{½}$) identified for each salinity level allows the construction of a salinity scan (Figure4b), which exhibits a U-shaped curve with a minimum $tc_{½}$ of approximately 156 seconds at the optimal salinity (S^*) of 6.4 g/dL. This optimal salinity, corresponding to the Winsor III region, represents the point of optimal balance between the surfactant's affinity for oil and water, leading to the formation of a highly interconnected bicontinuous microemulsion phase with maximum stability.

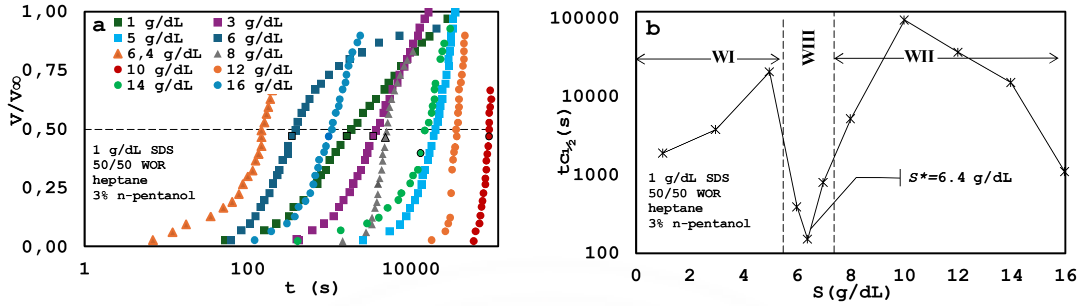

Figure 4. (a) Kinetics of aqueous phase clarification (Vc/V∞ *versus* time) in 1 g/dL SDS systems with 50/50 WOR, heptane, 3% v/v n-pentanol. (b) Impact of salinity on mean clarification time ($tc_{½}$) for the same system

The increased $tc_{½}$ values observed on either side of the *S**are a consequence of the growth and subsequent coalescence of emulsion droplets as the system transitions between Winsor I (at low salinities) and Winsor II (at high salinities) behaviors. In the Winsor I region, the emulsion is primarily composed of O/W droplets and increasing salinity up to *S** reduces interfacial tension, leading to larger, more stable droplets and longer coalescence times, reaching a maximum at 4 g/dL. Conversely, beyond *S**, the system transitions to Winsor II, where the emulsion consists of W/O droplets. The $tc_{½}$ decreases from the local maximum at 10 g/dL as the salinity increases, likely due to the formation of larger, less stable W/O droplets that coalesce more readily at higher salinities.

Figures 5a to 5e show a U-shaped relationship between $tc_{½}$ and salinity for various alcohols at 3-5 % v/v concentrations. The minimum $tc_{½}$ indicates optimal salinity for reduced emulsion stability due to increased droplet coalescence [28]. As alcohol concentration rises, the optimal salinity sh*ift*s lower, and $tc_{½}$ decreases. This is attributed to alcohol acting as a cosurfactant, reducing interfacial tension, and promoting smaller, more stable droplets and microemulsion formation at lower salinity. Alcohol also disrupts water's hydrogen bond network, reducing salt solubility and further lowering the optimal salinity [29]. Figure 5f illustrates this linear decrease in optimal salinity with increasing alcohol concentration.

Notably, iso-pentanol deviates from the linear behavior in Figure 5f, showing a marked decrease in optimal salinity starting at 3 % concentration, converging towards n-pentanol. This may be a result of the increased steric hindrance from iso-pentanol's branched structure, disrupting surfactant packing at the interface and leading to a more pronounced reduction in interfacial tension. Stronger hydrophobic interactions between iso-pentanol's branched chains and the oil phase may further contribute to the lower salinity required for microemulsion formation. These findings align with Monje-Galvan and Klauda[30], who demonstrated that the chemical structure of butanol isomers significantly affects their interfacial behavior. Isomers with similar spatial arrangements around the hydroxyl group exhibited comparable effects on interfacial tension, while those with different structures displayed distinct interfacial dynamics. Finally, it is important to reiterate that the optimal salinity for sec-butanol at 1%, 2 % and 3 % could not be determined using this method.

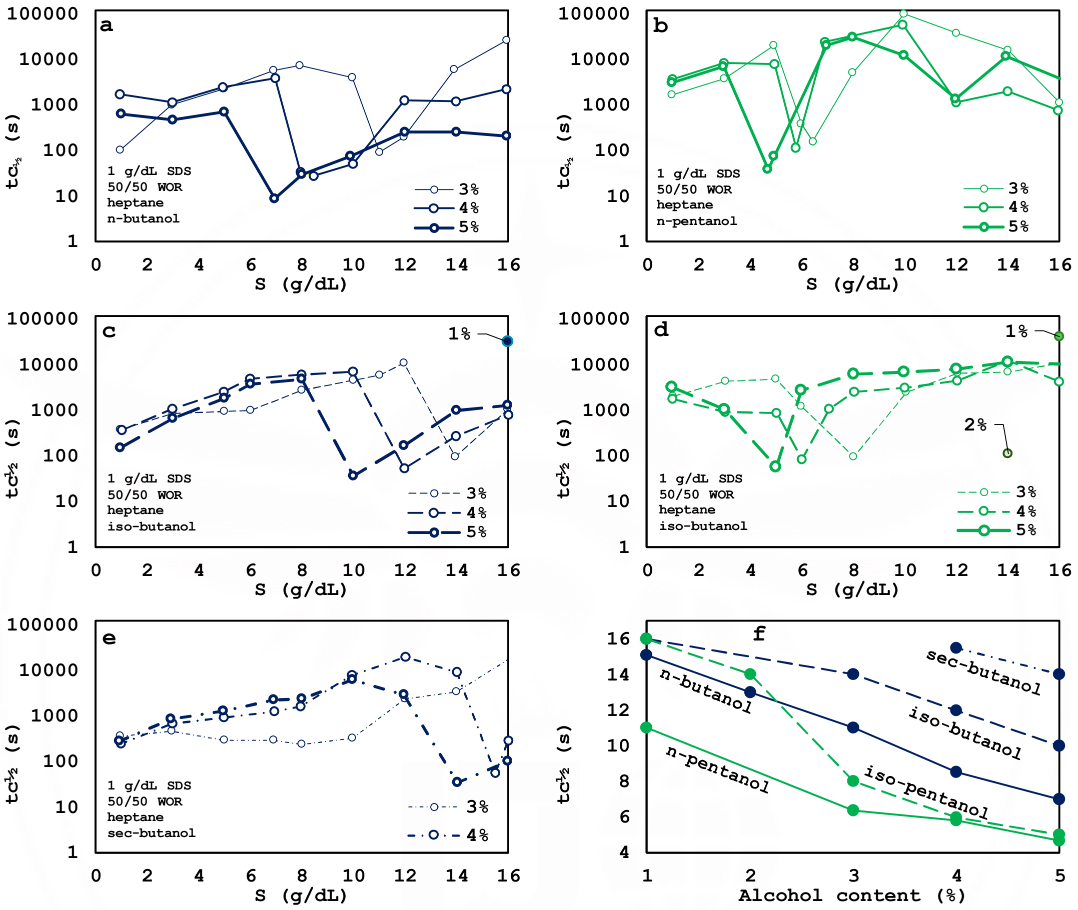

Figure 5. Effect of alcohol type and concentration on emulsion stability in surfactant-oil-water (SOW) systems. (a-e) Mean coalescence time (*tc½*) vs. salinity for various alcohols and concentrations. (f) Optimal salinity (*S**) as a function of alcohol concentration

Formulations containing 1-3% v/v of all alcohols, particularly at low salinities formed gelled liquid crystal-like structures (see Figure 1b). This gelation is likely due to the absence orlow alcohol concentration, as alcohol typically disrupts gel formation and favors the formation of three-phase systems. In contrast, formulations with 4-5% v/v alcohol exhibited the expected phase behavior, except for n-butanol at 5% v/v and salinities between 10 and 16 g/dL, where the oil phase gelled. Liquid crystals are partially ordered fluids exhibiting both solid-like (e.g., anisotropy) and liquid-like (e.g., fluidity) properties. The lamellar liquid crystal consists of alternating bilayers of surfactant molecules with their hydrophobic tails facing inward and hydrophilic heads facing outward, separated by solvent layers [31].

At certain salinities, tetraphasic states were observed, comprising: an aqueous phase, an intermediate phase, a gel phase, and an oil phase. In some instances, the gelled phase significantly reduced the volume of the oil phase. This type of system is rare and is attributed to the branched nature of the alcohol. Unlike other alcohols, sec-butanol acts as an independent component (A) rather than a pseudo-component (S+A = Surfactant + Alcohol), (as shown in Figure 1b). The behavior of branched alcohols in the formation of gelled microemulsions has been observed in similar systems [32] [33]. In this case, the ternary phase diagram is not applicable, and a quaternary representation (e.g., a tetrahedron) is required to depict the four components of the SOW/A.

The formation of four phases was evident with sec-butanol but not with n-butanol or iso-butanol at the same concentration (3% v/v). This confirms that the position of the polar OH group in the alcohol's molecular structure influences the formulation of SOW systems. The sec-butanol molecule possesses two lipophilic carbon tails of different lengths: an ethyl radical (CH_3-CH_2) on one side of the OH group and a methyl radical (CH_3-) on the other. This asymmetry leads to strong interactions with both water and oil, competing with the surfactant's interactions between its lipophilic chains. This competition results in the formation of both normal and inverse micellar structures, as well as two middle phases (microemulsions) with distinct densities. As emulsions typically do not encounter high salinities in practical applications, the study did not extend beyond 16 g/dL NaCl, as higher salinities would force the surfactant out of the aqueous phase. In sweeps where the optimal salinity could not be achieved, it is necessary to modify another formulation variable to attain the optimal salinity and subsequently investigate the electrolyte's behavior.

Optimal salinity by the interfacial tension method

While previous studies report similar trends in *IFT* reduction with alcohols [34], discrepancies at the optimum formulation highlight the need for further research into alcohol-surfactant-water interactions. The progressive decrease in optimal salinity with higher alcohol concentration underscores alcohol's role in disrupting water structure and impacting surfactant adsorption at the interface [35].

Figure6 shows the impact of alcohol type and concentration on interfacial tension as a function of salinity in the studied SOW systems, using the same nomenclature as Figure5. The optimal salinity, defined as the point where the lowest *IFT* is achieved, generally decreases with increasing alcohol concentration.

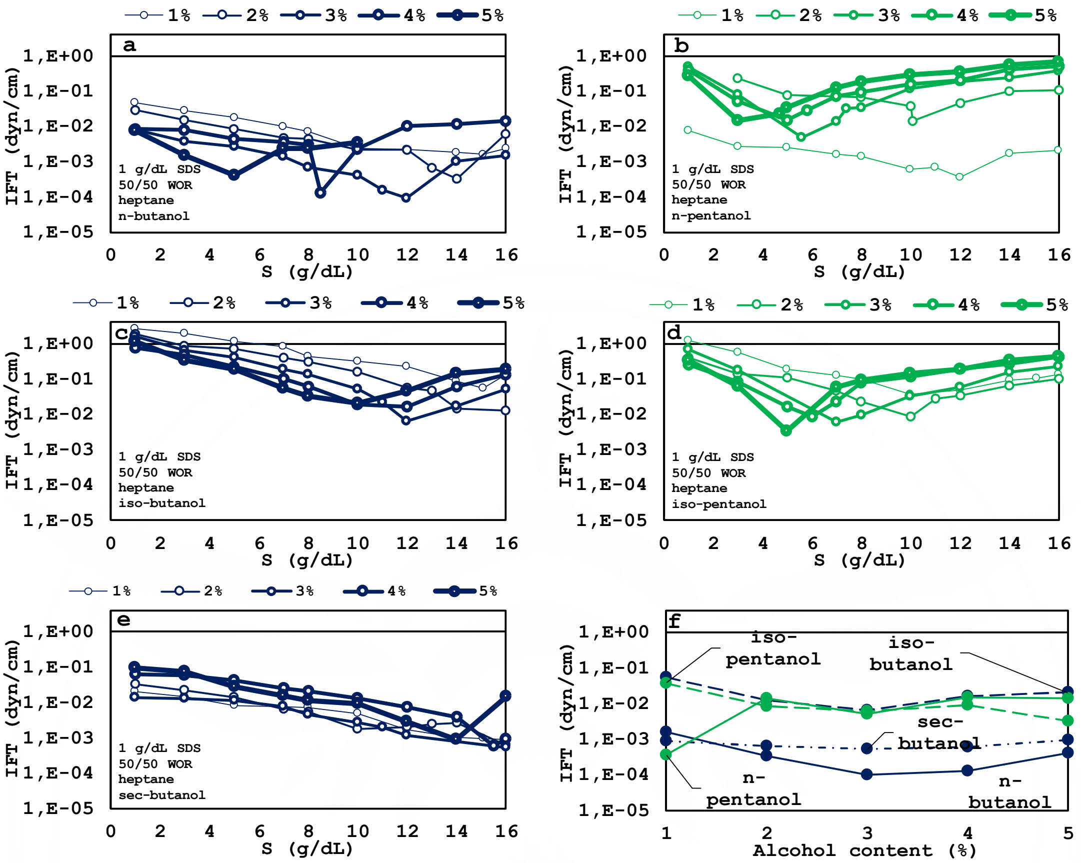

Figure 6. Effect of alcohol on interfacial tension varying the salinity of the SOW/A systems (a-e) and alcohol concentration (f)

This behavior, shown in Figure 6, can be attributed tomolecular interactions and thermodynamic properties inherent to alcohol-water-surfactant systems. At higher alcohol concentrations, competition between alcohol molecules and salt ions for hydrogen bonding with water intensifies. This competition reduces the solvation of ions, thereby decreasing salt solubility and shifting the optimal salinity to lower values. Furthermore, as noted by Gaiduk and Galli [36], alcohol reduces the dielectric constant of the solution, further diminishing salt solubility and reinforcing this shift. Additionally, He et al. [35] explain that this alteration in the solvation dynamics, caused by changes in the hydrogen bonding network, affects the adsorption behavior of the surfactant molecules at the interface, resulting in a lower *IFT* at reduced optimum salinity. Another approach to the same phenomenon explained by Geethu et al. [37], show that alcohols influence the interfacial film's elastic bending rigidity, with short-chain alcohols decreasing the optimal salinity. This behavior impacts the curvature of the interface, and the salinity needed for optimal microemulsion formation, further explaining the trends in Figure 6.

IJO - International Journal of Applied Science

(ISSN: 2992-247X)
https://ijojournals.com/

Shirley Marfisi Valladares[3]*

Volume 07 || Issue 09|| September, 2024 ||

Table 1 shows a comparison of the optimal salinities obtained by the two methods used in this document. In most cases, the two methods yield comparable results, but notable differences emerge, especially with certain alcohols and concentrations.For example, at 1% v/v n-pentanol, the optimal salinities differ by 1 g/dL (SI = 11.0, SII = 12.0). This discrepancy likely reflects the sensitivity of each method to different aspects of phase behavior, such as dynamic versus static interfacial properties. Another significant observation is sec-butanol at 4% v/v, where both methods yield the same optimal salinity (15.5 g/dL), indicating a stable microemulsion phase that aligns well between the two measurement approaches.Such variations emphasize the complexity of alcohol-surfactant interactions and highlight the need for multi-method evaluations to fully capture the behavior of these systems. The stability of sec-butanol across all concentrations is particularly noteworthy.

Table 1. Comparison of optimal salinities obtained by the laser method, the mean coalescence time method, and the t100 automated spinning drop tensiometer

Alcohol content	1 %		2%		3%		4%		5%	
Optimal salinity	$S*^{I}$	$S*^{II}$	$S*^{I}$	$S*^{II}$	$S*^{I}$	$S*^{II}$	$S*^{I}$	$S*^{II}$	$S*^{I}$	$S*^{II}$
n-butanol	15.1	15.1	13.0	15.1	11.0	12.0	8.5	8.5	7.0	5.0
sec-butanol	-	16.0	-	16.0	-	16.0	15.5	15.5	14.0	14.0
iso-butanol	16.0	15.1	-	16.0	14.0	12.0	12.0	12.0	10.0	10.0
n-pentanol	11.0	12.0	-	10.1	6.4	5.6	5.8	5.0	4.7	3.0
iso-pentanol	16.0	10.0	14.0	10.0	8.0	7.0	6.0	6.0	5.0	5.0

$S*^{I}$: Optimum salinity (g/dL NaCl) by the mean coalescence time method.
$S*^{II}$: Optimum salinity (g/dL NaCl) by interfacial tension method.

Correlation of optimum salinity with alcohol content

The optimum salinityobtained by the interfacial tension method was correlated with the alcohol contentfor each alcohol, using second-order polynomial regressions. All adjustments were performed using a nonlinear solving method, i.e., Generalized Reduced Gradient (GRG), available in the Solver tool of MS Excel. The correlations obtained and coefficients of determination are shown in Table 2.

The Pearson correlation coefficient (R^2) values indicate an acceptable adjustment for the data, with a minimum of 0.847. This suggests that the second-order polynomial model adequately captures the relationship between optimal salinity and alcohol content for the studied systems. The negative quadratic term in the correlations indicates that the optimal salinity initially decreases rapidly with increasing alcohol content, and then the rate of decrease slows down. This trend is consistent with the observation that alcohols act as co-surfactants [38], lowering the interfacial tension and shifting the optimal salinity towards lower values. Furthermore, this observation aligns with the findings of He et al. [35], who reported a decrease in optimal salinity with increasing alkyl chain length in extended surfactants. This agreement suggests that the underlying mechanism might involve the enhanced lipophilicity of longer chains, necessitating lower salinity to achieve an optimal balance between hydrophilic and lipophilic interactions. However, as the alcohol concentration increases further, its effect on interfacial tension becomes less pronounced, leading to a less steep decrease in optimal salinity. This behavior is in agreement with previous studies on the effect of alcohol on surfactant systems, where a similar trend was observed [39] [40].

Table 2. Correlations between optimal salinity (S^*) and alcohol content

Alcohol	Correlations	R^2
n-butanol	$S^* = -0.577(\%A)^2+0.813(\%A)+15.03$	0.995
sec-butanol	$S^* = -0.257(\%A)^2+1.099(\%A)+15.03$	0.972
iso-butanol	$S^* = -0.275(\%A)^2+0.318(\%A)+15.03$	0.847
n-pentanol	$S^* = -0.201(\%A)^2-3.429(\%A)+15.03$	0.962
iso-pentanol	$S^* = -0.351(\%A)^2-3.719(\%A)+15.03$	0.943

As described, the systems under study exhibit a water-to-oil ratio of 1:1 (R = 1), utilize heptane as the oil phase, sodium dodecyl sulfate as the surfactant, and scan temperature of 25°C, Equation 1 can be simplified to estimate the alcohol function f(A). At the optimal formulation, where *HLD*and the deviation in temperature are zero. Given that heptane has a carbon atom number of 7 and using the previously reported characteristic parameters of the surfactantSDS (k = 0.10 and σ = -2.8)[20], these values are substituted into Equation 1. Consequently, the simplified form of the equation becomes Equation 3.

$$f(A) = ln\, S^* - 3.5 \tag{3}$$

By integrating the experimental data correlating the optimal salinity (S^*) with the alcohol content from Table 2, the alcohol function for each alcohol used is presented in Table 3. These results are graphically represented in Figure 7. The consistency in the trends found for optimal salinity through the different techniques (laser, coalescence time, interfacial tension) reinforce the validity of the results. This agreement provides researchers and formulators with a robust set of tools to assess and optimize microemulsion behavior, facilitating the development of innovative products and processes based on these versatile systems.

IJO - International Journal of Applied Science
(ISSN: 2992-247X)
https://ijojournals.com/

Shirley Marfisi Valladares[3]*

Volume 07 || Issue 09|| September, 2024 ||

Table 3. Correlations for function alcohol

Alcohol	Correlations	R^2
n-butanol	$f(A) = -0.0699(\%A)^2+0.1325(\%A)-0.790$	0.996
sec-butanol	$f(A) = -0.0170(\%A)^2+0.0721(\%A)-0.790$	0.965
iso-butanol	$f(A) = -0.0224(\%A)^2+0.0282(\%A)-0.790$	0.873
n-pentanol	$f(A) = -0.0165(\%A)^2+0.2377(\%A)-0.790$	0.953
iso-pentanol	$f(A) = 0.0136(\%A)^2-0.22863(\%A)-0.790$	0.963

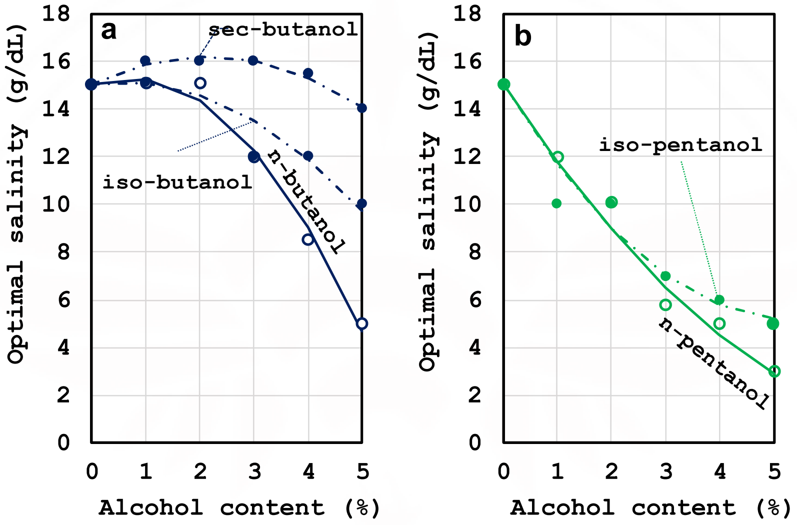

Figure 7. Effect of alcohol type and concentration on optimal formulation as *f(A)*. The lines represent the second-order polynomial correlations

CONCLUSIONS

The experimental investigation of surfactant-oil-water-alcohol (SOW/A) systems, detailed above, reveals a complex interplay between alcohol type, concentration, and the resulting optimal salinity for microemulsion formation. Several key conclusions emerge, each with significant implications for the design and optimization of microemulsion-based formulations:

The type and concentration of alcohol significantly influence the optimal salinity in surfactant-oil-water-alcohol systems. This finding provides formulators with a powerful tool to tailor microemulsions for specific applications by adjusting these parameters, potentially leading to more efficient and cost-effective formulations in fields such as enhanced oil recovery and drug delivery.

IJO - International Journal of Applied Science

(ISSN: 2992-247X) **Shirley Marfisi Valladares[3]***

https://ijojournals.com/ *Volume 07 || Issue 09|| September, 2024 ||*

Intermediate-chain alcohols act as co-surfactants in SOW/A systems, enhancing the surfactant's ability to reduce interfacial tension and form microemulsions. This co-surfactant behavior can be exploited to reduce the amount of primary surfactant required, offering economic benefits, and minimizing the environmental impact of formulations.For most of the alcohols studied, the optimal salinity decreases with increasing alcohol concentration. This relationship allows the development of S^* prediction models based on alcohol content, streamlining formulation optimization processes, and accelerating the development of new microemulsion-based products.

A notable deviation from the linear relationship between optimal salinity and alcohol concentration was observed with iso-pentanol. This finding emphasizes the importance of considering the specific molecular structure of alcohols in microemulsion design, as subtle differences can lead to significant variations in behavior. Further research into iso-pentanol's unique properties may uncover novel formulation strategies.The formation of gels at low alcohol concentrations highlights the importance of careful alcohol selection and concentration control in SOW/A systems. Understanding the conditions that promote this behavior is crucial to avoiding undesirable gelation in industrial applications, while also suggesting potential uses for these systems in materials science.

REFERENCES

[1] Elaine E, Bhandari B, Tan CP, Nyam KL. Recent advances in the formation, stability, and emerging food application of water-in-oil-in-water double emulsion carriers. Food and Bioprocess Technology. 2024. . https://doi.org/10.1007/s11947-024-03350-y.

[2] Benhur AM, Pingali S, Amin S. Application of biosurfactants and biopolymers in sustainable cosmetic formulation design. Journal of Cosmetic Science. 2020;71(6):455–480.

[3] Das S, Rao KVB. A comprehensive review of biosurfactant production and its uses in the pharmaceutical industry. Archives of Microbiology. 2024;206(60).https://doi.org/10.1007/s00203-023-03786-4.

[4] Aslam R, Mobin M, Aslam J, Aslam A, Zehra S, Masroor S. Application of surfactants as anticorrosive materials: A comprehensive review. Advances in Colloid and Interface Science. 2021;295:102481.https://doi.org/10.1016/j.cis.2021.102481.

[5] Chegenizadeh N, Saeedi A, Quan X. Most common surfactants employed in chemical enhanced oil recovery. Petroleum. 2017;3(2):197–211.https://doi.org/10.1016/j.petlm.2016.11.007.

[6] Achinta B, Hadi B. Ionic liquids as alternatives of surfactants in enhanced oil recovery—A state-of-the-art review. Journal of Molecular Liquids. 2016;224(A):177–188.https://doi.org/10.1016/j.molliq.2016.09.105.

[7] Park S, Lee E, Sulaiman W. Adsorption behaviors of surfactants for chemical flooding in enhanced oil recovery. Journal of Industrial and Engineering Chemistry. 2015;21:1239–1245.https://doi.org/10.1016/j.jiec.2014.05.040.

[8] Massarweh O, Abushaikha AS. The use of surfactants in enhanced oil recovery: A review of recent advances. Energy Reports. 2020;6:3150–3178.https://doi.org/10.1016/j.egyr.2020.11.009.

[9] Safinya CR, Sirota E, Roux D, Smith G. Universality in interacting membranes: The effect of cosurfactants on the interfacial rigidity. Physical Review Letters. 1989;62(10):1134–1137.https://doi.org/10.1103/PhysRevLett.62.1134.

[10] Zhou J, Dupeyrat M. Alcohol effect on interfacial tension in oil-water-sodium dodecyl sulphate systems. Journal of Colloid and Interface Science. 1990;134(2):320–335.https://doi.org/10.1016/0021-9797(90)90142-B.

[11] Farago B, Richter D. Shape and size fluctuations of microemulsion droplets: The role of cosurfactant. Physical Review Letters. 1990;65(26):3348–3351.https://doi.org/10.1103/PhysRevLett.65.3348.

[12] Sun M, Wang Y, Firoozabadi A. Effectiveness of alcohol cosurfactants in hydrate antiagglomeration. Energy and Fuels. 2012;26:5626–5632.https://doi.org/10.1021/ef300922h.

[13] Saboorian-Jooybari H, Chen Z. Critical review of microemulsion phase behavior models: Benefits, research gaps, industrial challenges, and roadmap. Journal of Industrial and Engineering Chemistry. 2024;129:1–23.https://doi.org/10.1016/j.jiec.2023.07.051.

[14] Alany R, Rades T, Agatonovic-Kustrin S, Davies N, Tucker I. Effects of alcohols and diols on the phase behaviour of quaternary systems. International Journal of Pharmaceutics. 2000;196(2):141–145.https://doi.org/10.1016/S0378-5173(99)00408-1.

[15] Alvarez G, Antón R, Marfisi S, Márquez L, Salager JL. Apparent equilibration time required for surfactant−oil−water systems to emulsify into the morphology imposed by the formulation. Part 2: Effect of sec-butanol concentration and initial location. Langmuir. 2004;20:5179–5181.https://doi.org/10.1021/la049727h.

[16] Mafisi S. Estabilidad de emulsiones relacionada con el proceso de deshidratación de crudos. Ph.D. Thesis, Universidad de Los Andes, Mérida, 2005.

[17] Salager JL. Microemulsions. In: Broze G, editor. Handbook of Detergents Part A: Properties. CRC Press; 1999. p. 253–302.

[18] Sabatinia D, Acosta E, Harwell J. Linker molecules in surfactant mixtures. Current Opinion in Colloid & Interface Science. 2003;8(4–5):316–326.https://doi.org/10.1016/S1359-0294(03)00082-7.

[19] Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL. Improving solubilization in microemulsions with additives. 1. The lipophilic linker role. Langmuir. 1993;9:669–672.https://doi.org/10.1021/la00027a010.

[20] Salager JL, Anton R, Anderéz J, Aubry JM. Formulation des microémulsionspar la méthode du HLD. Techniques de l'ingénieur. 2001;2(157):1–20.https://doi.org/10.51257/a-v1-j2157.

[21] *Aubry JM, Ontiveros JF, Salager JL, Nardello-Rataj V. Use of the normalized hydrophilic-lipophilic-deviation (HLDN) equation for determining the equivalent alkane carbon number (EACN) of oils and the preferred alkane carbon number (PACN) of nonionic surfactants by the fish-tail method (FTM). Advances in Colloid and Interface Science. 2020;276.https://doi.org/10.1016/j.cis.2019.102099.*

[22] *Salager JL, Bullon RMJ, Forgiarini A. Formulation in surfactant systems: From Winsor to HLDN. Encyclopedia. 2022;2(2):778–839.https://doi.org/10.3390/encyclopedia2020054.*

[23] *Salager JL. Formulation concepts for the emulsion maker. In: Pharmaceutical Emulsions and Suspensions. New York: Marcel Dekker, Inc.; 2000. p. 19–72.*

[24] *Zamora JM, Marquez R, Forgiarini AM, Langevin D, Salager JL. Interfacial rheology of low interfacial tension systems using a new oscillating spinning drop method. Journal of Colloid and Interface Science. 2018;519:27–37.https://doi.org/10.1016/j.jcis.2018.02.015.*

[25] *Marquez R, Bullon J, Forgiarini A, Salager JL. The oscillatory spinning drop technique: An innovative method to measure dilational interfacial rheological properties of brine-crude oil systems in the presence of asphaltenes. Colloids and Interfaces. 2021;5(3).https://doi.org/10.3390/colloids5030042.*

[26] *Cayias J, Schechter R, Wade W. The measurement of low interfacial tension via the spinning drop technique. In: Adsorption at Interfaces, ACS Symposium Series. 1975;8(17):234–247.https://doi.org/10.1021/bk-1975-0008.ch017.*

[27] *Salager JL. Microemulsions. In: Handbook of Detergents, Part A. CRC Press; 1999. p. 50.*

[28] *Marquez R, Ontiveros J, Barrios N, Tolosa L, Palazzo G, Nardello-Rataj V, Salager JL. Advantages and limitations of different methods to determine the optimum formulation in surfactant–oil–water systems: A review. Journal of Surfactants and Detergents. 2024;27(1):5–36.https://doi.org/10.1002/jsde.12703.*

[29] *Rafique AS, Khodaparast S, Poulos AS, Sharratt WN, Robles ESJ, Cabral JT. Micellar structure and transformations in sodium alkylbenzenesulfonate (NaLAS) aqueous solutions: Effects of concentration, temperature, and salt. Soft Matter. 2020;16:7835–7844.https://doi.org/10.1039/D0SM00982B.*

[30] *Monje-Galvan V, Klauda JB. Interfacial properties of aqueous solutions of butanol isomers and cyclohexane. Fluid Phase Equilibria. 2020;513:112551.https://doi.org/10.1016/j.fluid.2020.112551.*

[31] *Winsor PA. Solvent properties of amphiphilic compounds. Butterworths Scientific Publications; 1954.https://api.semanticscholar.org/CorpusID:92766345.*

[32] *Thampi N, Ojha K, Nair U. Effect of branched alcohols on phase behavior and physicochemical properties of Winsor IV microemulsions. Journal of Surfactants and Detergents. 2014;17:371–381.https://doi.org/10.1007/s11743-013-1482-0.*

[33] *Ezrahi S, Tuval E, Aserin A, Garti N. The effect of structural variation of alcohols on water solubilization in nonionic microemulsions: 2. Branched alcohols as solubilization modifiers: Results and interpretation. Journal of Colloid and Interface Science. 2005;291(1):273–281.https://doi.org/10.1016/j.jcis.2005.04.098.*

[34] *Marquez R, Alvarado J, Meza L, Bullón J, Langevin D, Forgiarini A, Salager JL. Interfacial rheology measured with a spinning drop interfacial rheometer: Particularities in more realistic surfactant–oil–water systems close to optimum formulation at HLDN = 0. Journal of Surfactants and Detergents. 2021;24(4):587–601.https://doi.org/10.1002/jsde.12502.*

[35] *He W, Ge J, Zhang G, Jiang P, Jin L. Effects of Extended Surfactant Structure on the Interfacial Tension and Optimal Salinity of Dilute Solutions. ACS Omega 2019;4:12410–17. https://doi.org/10.1021/acsomega.9b00495.*

[36] *Gaiduk AP, Galli G. Local and Global Effects of Dissolved Sodium Chloride on the Structure of Water. The Journal of Physical Chemistry Letters 2017;8:1496–1502. https://doi.org/10.1021/acs.jpclett.7b00239.*

[37] *Geethu PM, Aswal VK, Satapathy DK. Interfacial rigidity and topology of reverse microemulsions: Influence of alcohol molecules. Journal of Applied Physics 2020;127:1–12. https://doi.org/10.1063/1.5140729.*

[38] *Lu J, de Castilla AG, Müller S, Xi S, Chapman WG. Dualistic Role of Alcohol in Micelle Formation and Structure from iSAFT Based Density Functional Theory and COSMOplex. Industrial & Engineering Chemistry Research 2023;62:1968–83. https://doi.org/10.1021/acs.iecr.2c04983.https://doi.org/10.1021/acs.iecr.2c03507.*

[39] *Xia Y, Li HL, Chai J, Yu XY, Liu J, Qin C, Chen JF. Effects of Short-chain Alcohols on the Phase Behavior, Solubilities and Solubilization Ability in Microemulsion Systems. Polish Journal of Chemistry 2009;83:315–24. https://api.semanticscholar.org/CorpusID:94290458.*

[40] *Zdziennicka A, Jańczuk B. Modification of adsorption, aggregation and wetting properties of surfactants by short chain alcohols. Advances in Colloid and Interface Science 2020;284:102249. https://doi.org/10.1016/j.cis.2020.102249.*