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A Normalized HLD (HLD_N) Tool for Optimal Salt-Concentration Prediction of Microemulsions

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Abstract: Optimal condition-based microemulsion is key to achieving great efficiency in oil removal. One useful empirical equation to predict an optimal condition is a hydrophilic–lipophilic deviation (HLD). However, the K constants of each surfactant should be the same to combine the HLD equations for the mixed surfactant. Recently, a normalized hydrophilic–lipophilic deviation (HLD_N) was presented to avoid this limitation. This work sought to determine the phase behaviors and predict the optimal salt concentrations, using HLD_N for the mixed surfactant. Sodium dihexyl sulfosuccinate (SDHS) as an anionic surfactant, and alcohol alkyl polyglycol ether (AAE(6EO4PO)) as a nonionic surfactant, were both investigated. Alkanes and diesel were used as a model oil. The results showed that AAE(6EO4PO) enforced both the hydrophilic and the hydrophobic characteristics. The Winsor Type I–III transition was influenced by the ethylene oxide, while the propylene oxide presence affected the Winsor Type III–II inversion. For the HLD_N equation, the average interaction term was 1.82 ± 0.86 , which markedly showed a strong correlation with the fraction of nonionic surfactant in the mixed systems. The predicted optimal salt concentrations using HLD_N of SDHS–AAE(6EO4PO) in the diesel systems were close to the experimental results, with an error of <10% that is significantly beneficial due to the shorter time required for optimal determination.

Keywords: microemulsions; anionic–nonionic mixed surfactant; extended surfactant; hydrophilic–lipophilic deviation



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1. Introduction

The rapid growth of both industries and population leads to environmental concerns. Oil cleaning and decontamination applications have been receiving increased attention due to enhancing resource recovery potentials, such as oil-contaminated materials and waste. For many years, microemulsion formulation has been an attractive method and is applied not only for cleaning products but also for other applications, e.g., enhanced oil recovery (EOR) and soil remediation [1,2]. With this technology, the surfactant–oil–water (SOW) system was formed by detaching and trapping organic/oil molecules in the surfactant micelles. Surfactants, an emulsifier to solubilize water and organic/oil molecules, have been formulated to attain a microemulsion system with low interfacial tension (IFT) and high oil solubilization.

Among surfactant-based microemulsion systems, the binary surfactant mixtures mostly reduce interfacial tension or enhance certain properties (e.g., more oil/water solubilization, less critical micelle concentration), which is better than using a single surfactant [3–10]. Extended surfactants are a novel classification that has been widely used to formulate microemulsions. They contain intermediate polarity groups between a head and a tail part of the surfactant structure [11–15]. Intermediate polarity molecules, for

example, contain polyethylene oxide (EO), polypropylene oxide (PO), or polyethylene-polypropylene oxide (EO-PO) [11,15]. The EO (C_2H_4O) group can enhance the interactions between the water and the surfactant. Influenced by oxygen molecules, the EO group acts as the hydrophilic part, while the PO (C_3H_6O) acts as the lipophilic part by extending further into the oil phase [11,13]. Regarding the intermediate structure, extended surfactants can expand the thickness of the interfacial region, which helps to reach ultralow interfacial tension (< 0.01 mN/m) and increase surfactant-oil or surfactant-water interactions [13,14,16–18]. Relative to conventional surfactants, extended surfactants also show a good solubility of oil and water. Miñana-Pérez et al. (1995) first introduced extended surfactants, the alkyl polypropylene oxide ether sulfates [12]. The addition of PO resulted in a reduction in the optimal salt concentration level for all the SOW systems. Moreover, extended surfactants could form the middle-phase microemulsion, reduce the interfacial tension to ultralow, and increase the oil solubilization for various oils [15].

Microemulsions are isotropic, transparent and thermodynamically stable liquid systems of water, oil, and amphiphile (i.e., SOW system) [1,19]. Hence, microemulsions have been used in many industries or products, especially for cleaning processes, due to the assembled capability of immiscible liquids [20]. The dispersed size and zeta potential of the emulsion depend on the conditions of the SOW, such as pH, temperature, and salinity [21–23]. In the SOW system, the middle phase (Winsor Type III) at an equal volume of oil and water phases shows a low interfacial tension (IFT) and high solubilization among four types of microemulsions (i.e., Winsor Type I oil in water, Winsor Type II water in oil, Winsor Type III bi-continuous phase, and Winsor Type IV single-phase microemulsion with high surfactant concentration [24–26]. The optimal condition is defined as the lowest IFT in the middle phase region [1]. The SOW system transforms the Winsor Type I-III-II by increasing the salinity or the temperature for the ionic or the nonionic surfactants (i.e., ethylene oxide-based surfactants), respectively. Therefore, when optimizing the performance, the characteristics of the surfactants are key to designing the phase behaviors and, as a result, determining the appropriate condition of any SOW system.

The determination of optimal conditions in the SOW system is a time-consuming process, achieved through a conventional phase scan experiment [27]. Many empirical equations have been proposed to describe a surfactant characteristic and predict a microemulsion formation, which can save time in an experiment [26,28–32]. The hydrophilic-lipophilic deviation (HLD), a pioneer work introduced by Salager et al. (1979), is one of the empirical equations [28]. The HLD is normalized from the change of the chemical potential for the surfactant transfer that is derived from the surfactant affinity difference (SAD) [28,32]. The value of the HLD can be used to identify the type of microemulsions [1,28,32]. The positive value is Winsor Type II. The zero HLD is an optimal condition in Winsor Type III. The negative value is Winsor Type I. The HLD equation is divided into two equations for the ionic and the nonionic surfactants, as follows [28,33–40]:

$$HLD_{ionic} = \ln(S) - K_i(EACN) - f(A) - \alpha_T(T - T_{ref}) + \sigma \quad (1)$$

$$HLD_{nonionic} = bS - K_n(EACN) - \varnothing(A) + c_T(T - T_{ref}) + \beta \quad (2)$$

where S is the salinity (g/100 mL), b is a co-efficiency constant of salinity (g/100 mL) $^{-1}$, K_i and K_n are the constants for the ionic and nonionic surfactant, respectively, $EACN$ is an equivalent alkane carbon number, $f(A)$ and $\varnothing(A)$ are the functions of the alcohol or the cosurfactant, α_T and c_T are the temperature constants ($^{\circ}C^{-1}$), $T - T_{ref}$ is the difference between the experiment temperature and the reference temperature ($25^{\circ}C$), and σ and β are the surfactant characteristic parameter of the ionic and nonionic surfactants, respectively.

The HLD for the mixture of the same type of surfactants, such as anionic-anionic, cationic-cationic, or nonionic-nonionic, is assumed as the ideal case. The mixed HLD is a sum of each HLD equation multiplied by the mole fraction of each surfactant. In the case of

different type mixtures (e.g., anionic-nonionic, or cationic-nonionic), the excess free energy will be included in the HLD as a non-ideal case, as follows [41,42]:

$$\text{HLD}_{\text{mixed ionic-nonionic surfactant}} = X_i \text{HLD}_i + X_n \text{HLD}_n + \frac{G_{\text{EX}}}{RT} \quad (3)$$

where X_i and X_n are the mole fractions of ionic surfactant and nonionic surfactant, respectively (in this case: $X_n = 1 - X_i$), HLD_i and HLD_n are the HLD equations of ionic and nonionic surfactant, respectively, $\frac{G_{\text{EX}}}{RT}$ is the term of the excess free energy, G_{EX} is the excess free energy of the surfactant transference, R is the gas constant (8.31 J/mol·K), and T is the experiment temperature (Kelvin). Positive values of $\frac{G_{\text{EX}}}{RT}$ indicate the hydrophobicity of the actual mixture relative to the ideal mixture, whereas negative values indicate the hydrophilicity of the actual mixture relative to the ideal mixture. The zero $\frac{G_{\text{EX}}}{RT}$ is the ideal mixture, which is assumed for the same-types-of-surfactant mixture. The $\frac{G_{\text{EX}}}{RT}$ value of the binary mixture can be determined by the thermodynamic method [42,43]. The Margules expression, which assumes that no entropic parameter is involved in excess free energy, is the simplest one and is shown in Equation (4) [42,43]:

$$\frac{G_{\text{EX}}}{RT} = A_1 X_i X_n^2 + A_2 X_i^2 X_n \quad (4)$$

where A_1 and A_2 are the constants, X_i is the mole fraction of the ionic surfactant, and X_n is the mole fraction of the nonionic surfactant.

The HLD equation has been applied in a large number of studies [27,42,44–50]. The HLD equation is not only used to reduce the time-consuming of the experiment but also to characterize the hydrophobicity of the oil and phase behavior of microemulsions [27]. Poprawski et al. (2003) applied the nonionic HLD equation to determine the EACN value of pine oil, which was found to be -12.1 [50]. Withayapanyanon et al. (2008) used the HLD equation as a method to determine the σ values of anionic surfactants (e.g., sodium dioctyl sulfosuccinate (AOT), sodium dihexyl sulfosuccinate (SDHS or AMA), $\text{C}_{12,13}\text{-(PO)}_8\text{-SO}_4\text{Na}$, $\text{C}_{12}\text{-SO}_4\text{Na}$, $\text{C}_{12,15}\text{-(EO)}_2\text{-SO}_4\text{Na}$), [27]. The results showed that the anionic surfactants had a wide range of σ values from positive to negative values. For example, the σ of AOT was positive, and the σ of the SDHS was negative. In the case of an ionic-nonionic mixture, to our knowledge, there are only a few pieces of research [42,51].

However, there is one critical point of view on the HLD equation. In the case of a mixture of surfactants with different K coefficients, Equation (3) might not always be true. Therefore, Salager et al. (2020) suggested that the HLD should be divided by the K value to avoid this issue. The new formation of HLD is called the normalized hydrophilic-lipophilic deviation (HLD_N), as presented in Equation (5) [52]. For the ionic-nonionic mixture, the excess free energy term would be replaced by the interaction term, as shown in Equation (6).

$$\text{HLD}_N = \frac{\text{HLD}}{K} \quad (5)$$

$$\text{HLD}_{N,\text{mixed ionic-nonionic surfactant}} = X_i \text{HLD}_{N,i} + X_n \text{HLD}_{N,n} + \text{interaction term} \quad (6)$$

In this work, we investigated the characteristics of the mixed anionic-nonionic system by a phase behavior study, determined the HLD_N equations for both single and mixed systems, and predicted the optimal condition in the diesel system via the HLD_N equations. SDHS was selected as an anionic surfactant. The extended nonionic surfactant for this work was alkyl polyglycol ether ($\text{C}_{16-18}\text{-(PO)}_4\text{-(EO)}_6\text{-OH}$), abbreviated as AAE(6EO4PO). This commercial nonionic surfactant is a low-foaming emulsifier. According to the testing guidelines of the Organization for Economic Cooperation and Development (OECD), AAE(6EO4PO) is identified as a substance harmful to aquatic life in the long term, but it is readily biodegradable [53]. With these intermediate structures, AAE(6EO4PO) was expected to improve the solubilization of both the water and the oil phases in the mixed system. The SDHS-AAE(6EO4PO) ratios were varied to determine the effect of the extended

nonionic surfactant on the optimal condition for these factors, such as the phase transition, interfacial tension, and optimal salinity. These systems were combined with the model n-alkane oils, including n-pentane, n-heptane, n-octane, and n-decane. In this study, diesel was employed as the model oil. The HLD_N with diesel oil from the experiment and prediction were compared and discussed. Moreover, as the available literature regarding the HLD and HLD_N equations of the anionic-extended nonionic mixture is still limited, this work can contribute to a better understanding and growing knowledge of this field.

2. Materials and Methods

2.1. Materials

Sodium dihexyl sulfosuccinate (SDHS) (80% active) was purchased from Sigma-Aldrich (Bangkok, Thailand). Alcohol alkyl polyglycol ether, with an average of six EO and four PO (AAE(6EO4PO)), was obtained from Sasol (Sasol Germany GmbH). AAE(6EO4PO) had a >99% purity solution. Table 1 shows the properties and the structures of SDHS and AAE(6EO4PO). All the model oils with different carbon chains were purchased from Acrös Organics (Italmar, Bangkok, Thailand). The n-pentane, n-heptane, n-octane, n-decane, and n-hexadecane all had >95% purity. The commercial diesel was purchased from a local market (Shell, Bangkok, Thailand). The salt for the salinity scan was sodium chloride (>99%), which was purchased from Sigma-Aldrich (Bangkok, Thailand). For all the experiments in this study, deionized water with an 18-M Ω -cm resistivity (PURELAB Ultra and ELGA LabWater) was used.

Table 1. Properties of surfactants.

Surfactant Name	Formula	MW (g/mol)	L (Å)	CMC (%wt/v)	HLB
Sodium dihexyl sulfosuccinate (SDHS)	$C_{16}H_{29}NaO_7S$	388 ¹	10 ³	0.25	-
Alcohol, C16-18, 6-ethoxylated 4-propoxylated Alkyl polyglycol ether (AAE(6EO4PO))	$C_{17}H_{35}(PO)_4(EO)_6OH$	784 ²	35.7 ⁴	0.08	10 ²

¹ obtained from Acosta and Bhakta, 2009 [42]. ² obtained from Sasol Performance Chemicals, 2019 [54]. ³ obtained from Acosta et al., 2008 [41]. ⁴ calculated from $L_{nonionic} = 1.4 \times \text{linear carbon tail} \times 1.5 \text{ Å}$ [55].

2.2. Microemulsion Phase Behaviors

The microemulsion phase behavior of SDHS was discussed thoroughly in our previous study [51]. In this part of the current work, we investigated the microemulsion formation of AAE(6EO4PO) and the SDHS-AAE(6EO4PO) mixed system. For AAE(6EO4PO), the concentration was fixed at 1% wt/v with various model oils (i.e., n-heptane, n-decane, and n-hexadecane) and temperatures (i.e., 25, 30, 35 and 40 °C). The 2.5-mL surfactant solutions were prepared by varying the salinity in flattened tubes with Teflon screw caps. After being well mixed, an equal volume of oil was added to each tube. The samples were shaken each day for the first three days and were kept in an oven to maintain the required temperatures. They were then left in order to reach equilibrium and observed for the Winsor Type by visual observation. For the mixed system, the total concentration of the surfactant was fixed at 2% wt/v because the preliminary data showed that this concentration of SDHS could first form the middle phase (Winsor Type III). The anionic–nonionic ratio was varied from the anionic side to achieve the following by weight ratios: 10:0, 9:1, 8:2, 7:3, 6:4, and 5:5. Additionally, the 2.5-mL samples were prepared with different salinities. After that, they were mixed with 2.5 mL of oil (i.e., n-pentane, n-heptane, n-octane, n-decane, and diesel oil). All the samples were shaken once a day for three days and left to achieve equilibrium in the same way as in the phase behavior study of AAE(6EO4PO). However, the mixed system was controlled at a temperature of 25 ± 2 °C.

2.3. Interfacial Tension (IFT) Measurement

The equilibrium microemulsion samples were selected to measure the IFTs by a spinning drop tensiometer (SVT20, Dataphysics, Germany) at 2% wt/v of the total surfactant concentration. The excess of the aqueous phase was collected into a spinning drop capillary tube, and the excess oil from the equilibrium sample was collected and then injected into the tube. Then, the tube was rotated at 6000 rpm for 20 min. The IFT result of each sample was determined in triplicate to find the average value. The optimal salt concentration was examined by the minimum IFT at Winsor Type III.

2.4. Empirical Models (HLD and HLD_N)

The HLD of SDHS was determined with Equation (1) using constants, including $K_i = 0.13$ and $\sigma = -1.13$, that were supported by our previous work [51]. The $f(A)$ and the $\alpha_T(T - T_{ref})$ values were zero because this study did not add a cosurfactant, and the temperature was controlled at 25 ± 2 °C. The constants for the $HLD_{nonionic}$ of AAE(6EO4PO) were investigated by the optimal salt concentration and Excel Solver as mentioned in the study by Muñoz et al. (2016) [56]. At the optimal condition with no cosurfactant addition, the values of b , K_n , c_T and β were the remaining constants. The assumption for Excel Solver to solve these constants was the minimum of the squared difference between the predicted optimal salt concentration and the optimal salt concentration obtained from the experiment. The values of b , K_n , c_T and β were proposed as the average of all the model oils and all the temperatures. For the mixed system, $\frac{G_{EX}}{RT}$ was examined by Equations (3) and (4). The constants (A_1 and A_2) in the Margules expression were also specified as the average of all the mixing ratios.

The HLD_N of SDHS used the same constants as mentioned previously, while the HLD_N of AAE(6EO4PO) employed the results of $HLD_{AAE(6EO4PO)}$. The HLD equation is divided by the K coefficient to determine the HLD_N equations (Equation (5)). Regarding the mixed systems, the interaction terms were examined for each anionic–nonionic ratio and each model oil. The HLD_N is zero at the optimal condition, and hence the interaction terms in Equation (6) were determined by:

$$\text{Interaction term} = X_i HLD_{N,i} + X_n HLD_{N,n} \quad (7)$$

To formulate these empirical equations, the model oils included n-pentane, n-heptane, n-octane, and n-decane. The commercial diesel oil was applied to predict the optimal salt concentrations compared to the results from HLD and HLD_N .

3. Results and Discussion

3.1. Phase Behavior of AAE(6EO4PO)

In all the model oils and all the temperature systems, we observed Winsor Type III, which appeared in a wide range of salt concentrations. Winsor Type III seemed mostly cloudy in the middle phase. Figure 1 shows some results of the salinity scans of the n-decane systems at 25 °C and 40 °C. At reference temperature (25 ± 2 °C), Winsor Type III was observed at 1–18% wt/v of NaCl for the n-decane system. When the temperature increased to 40 ± 2 °C, Winsor Type III was observed at 6–18% wt/v of NaCl. The different temperatures and NaCl concentrations affected the zeta potential of the micelles that resulted in the different salt concentrations forming Winsor Type III [57–59].

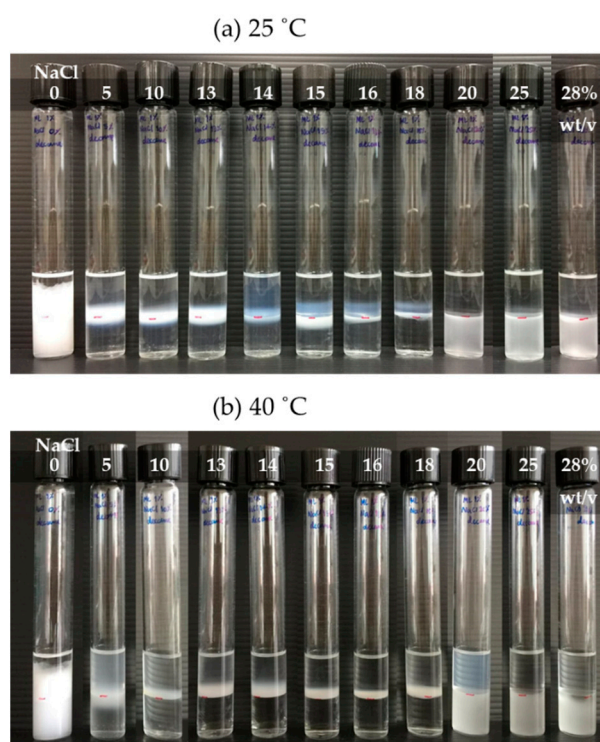


Figure 1. Salinity scans of 1% wt/v AAE(6EO4PO) in the n-decane systems at temperature (a) 25 °C and (b) 40 °C.

The IFT of each sample was measured to identify the optimal salt concentration for each temperature and oil. It was found that the optimal salinity tended to decrease when the temperature increased, as shown in Figure 2. At high temperatures, the interactions between the head of the nonionic surfactant and the water molecules are lower because of weaker hydrogen bonds [1,56]. This resulted in fewer interactions with the head of the surfactants. If this was not the case, the head–head interactions of the surfactants would be more repulsive forces. Therefore, the optimal salt concentration was reduced to obtain the optimal condition. The effect of the model oils is presented in Figure 2. The optimal salinities increased with increases in EACN, which is in line with the study by Muñoz et al. (2016) [56]. Because higher EACNs exhibited stronger interactions between the oil molecules, therefore, stronger interactions of the surfactant heads were required to solubilize the oils [27,60,61]. The addition of salt reduced the repulsive force of the surfactants, which resulted in stronger head–head interactions of the surfactants. Thus, the six-molecule ethylene oxide in the AAE(6EO4PO) structure played an important role in achieving optimal salinity.

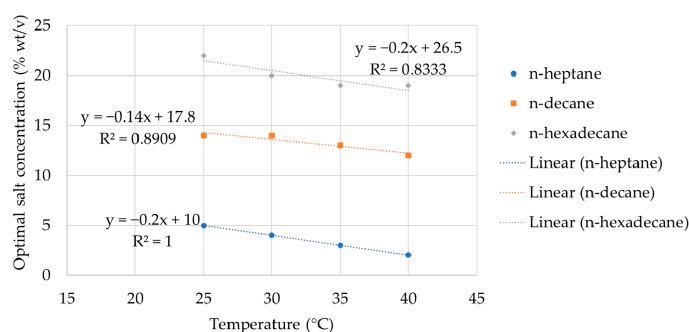


Figure 2. Optimal salt concentrations (S^*) of 1% wt/v AAE(6EO4PO).

Regarding the minimum interfacial tensions (IFT*) in optimal conditions, the results could not reach the level of ultralow IFT (<0.01 mN/m) [17,18]. However, the IFT* tended to decrease when the EACN value of the oil increased. From the research by Barakat et al. (1989) [62], it is known that each nonionic surfactant is suitable for a different EACN. The IFT* trend steadily declined, and then increased again when the hydrophobicity of the oil increased [62]. Therefore, the IFT* results of our study are likely within the first part of this trend.

3.2. Phase Behavior of the SDHS-AAE(6EO4PO) Mixed System

The phase transitions of all the oils are shown in Figure 3. In the SDHS-AAE(6EO4PO) mixed system, the same trends as those of the anionic–nonionic ratios were observed. The salt concentration of the Winsor Type I–III transition tended to remain the same or increase slightly when AAE(6EO4PO) was added, changing from the anionic–nonionic ratio of 9:1 to 5:5. The six-ethylene oxide (EO) of AAE(6EO4PO) played a key role in the Winsor Type I–III inversion. The EO in the extended surfactant exhibited hydrophilic characteristics and could increase the AAE(6EO4PO)–water interactions, while the salt concentration for the Winsor Type III–II transition of all the oils was reduced. When AAE(6EO4PO) increased, propylene oxide (PO) played a key role relative to the effect of the EO. The PO enhanced the AAE(6EO4PO)–oil interactions because of the hydrophobic characteristics of the PO. Therefore, the phase behavior of anionic–nonionic surfactant was influenced by both the EO and the PO. For this reason, the range of the salt concentration for Winsor Type III (middle phase) tended to decrease. Figure 3d presents SDHS-AAE(6EO4PO) with *n*-decane. The salt concentration for the Winsor Type I–III transformation increased from 6.5 (9:1 ratio) to 7.5 (5:5 ratio) % wt/v. The salt concentration for the Winsor Type III–II transition decreased from 19 (9:1 ratio) to 15 (5:5 ratio) % wt/v. The salt concentration range for the middle phase decreased from a ratio of 9:1 to 5:5, which was around 40% in the *n*-decane system.

The results of the phase behavior of the single SDHS (10:0 ratio) are shown in Figure 3. The phase behavior of the mixed system and the SDHS-only system were divided into two cases, which included the short-chain oils (*n*-pentane, *n*-heptane, and *n*-octane) and the long-chain oil (*n*-decane). In the short-chain oil system, the range of salinity to form Winsor Type III tended to decrease, compared to the single SDHS system when the AAE(6EO4PO) ratio increased. Even with a small amount of AAE(6EO4PO) (0.2 %wt/v from 2% wt/v total surfactant concentration, 9:1 anionic–nonionic ratio), the salt concentration range for the middle phase formation was reduced (see Figure 3b). Due to the lipophilicity of the PO in the AAE(6EO4PO) molecules, the oil–surfactant interactions tended to increase. Hence, Winsor Type III would transform to Winsor Type II in the mixed system more easily than in the single SDHS system. However, the salt concentration required for the Winsor Type I–III transformation of the mixed system was still the same and close to that of the single SDHS system because the EO in AAE(6EO4PO) helped to maintain the water–surfactant interactions. For the long-chain oil system (i.e., EACN > 8), the salt concentration required for the Winsor Type I–III and III–II inversions decreased, relative to the single SDHS system. In this case, the PO was the predominant factor leading to the mixed system being more hydrophobic than the single SDHS system. Moreover, the salt concentration range of the middle phase expanded relative to the single SDHS system. Therefore, the conclusion is that the intermediate molecules in AAE(6EO4PO) strongly affected the *n*-alkane oil. Both the EO and the PO were involved in the phase behavior of the mixed system for the short-chain oils, whereas for the long-chain oil, the role of the PO was mainly related to the phase inversions of the mixed system.

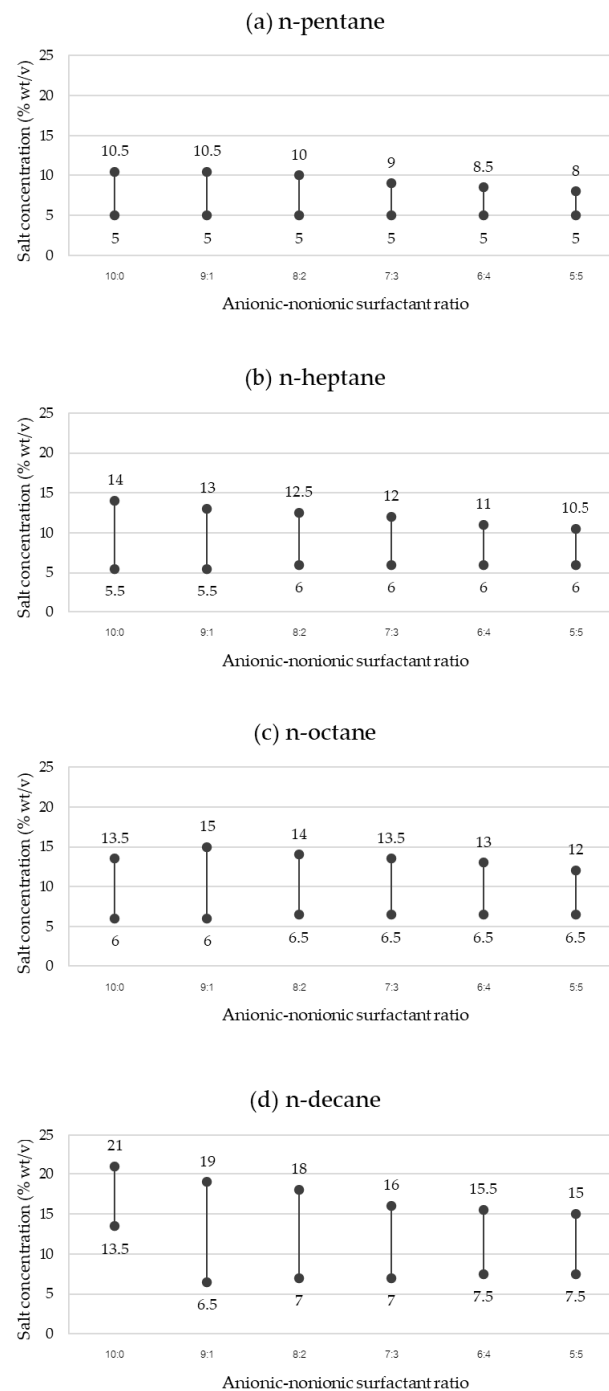


Figure 3. Phase transitions of SDHS-AAE(6EO4PO) systems with (a) n-pentane, (b) n-heptane, (c) n-octane, and (d) n-decane.

With regards to the effect of the n-alkane oils, the salt concentration required for phase inversion (both Winsor Type I-III and Winsor Type III-II) tended to increase when the EACN of the oil increased at the same anionic–nonionic ratio. As the hydrophobicity of the oil increased, the interactions between the oil molecules increased as well. To solubilize the oil molecules with long chains into micelles (Winsor Type I), the surfactant head interactions should be increased by increasing the salt concentration in the system [1]. Moreover, the increase of EACN extended the salt concentration range for the Winsor Type III formation. This is beneficial for the removal of oil with a higher EACN (i.e., long-chain hydrocarbons).

3.3. Interfacial Tension (IFT) and Optimal Salt Concentration of the SDHS-AAE(6EO4PO) Mixed System

The IFT of microemulsion samples from the phase behavior studies were measured to determine the optimal salt concentration for each model oil, as presented in Figure 4. The IFT at the optimal condition is well known as an optimal IFT (IFT*) [1]. Regarding the effect of the SDHS-AAE(6EO4PO) mixing ratio, the IFT* tended to decrease with the increase of AAE(6EO4PO). The nonionic surfactants could reduce the repulsive forces of the head groups of the anionic surfactant in the mixed system, which resulted in closer surfactant packing [63,64]. Thus, the 5:5 ratio could solubilize both water and oil molecules better than the other ratios. Regarding the effect of the oil's EACN at the same surfactant ratio, the IFT* was not observed in any trends of these systems. In the mixed surfactant with 9:1 ratio, the IFT* tended to decrease. For the other ratios (i.e., 8:2, 7:3, 6:4, 5:5 ratio), the IFT* was not observed, as shown in Table 2.

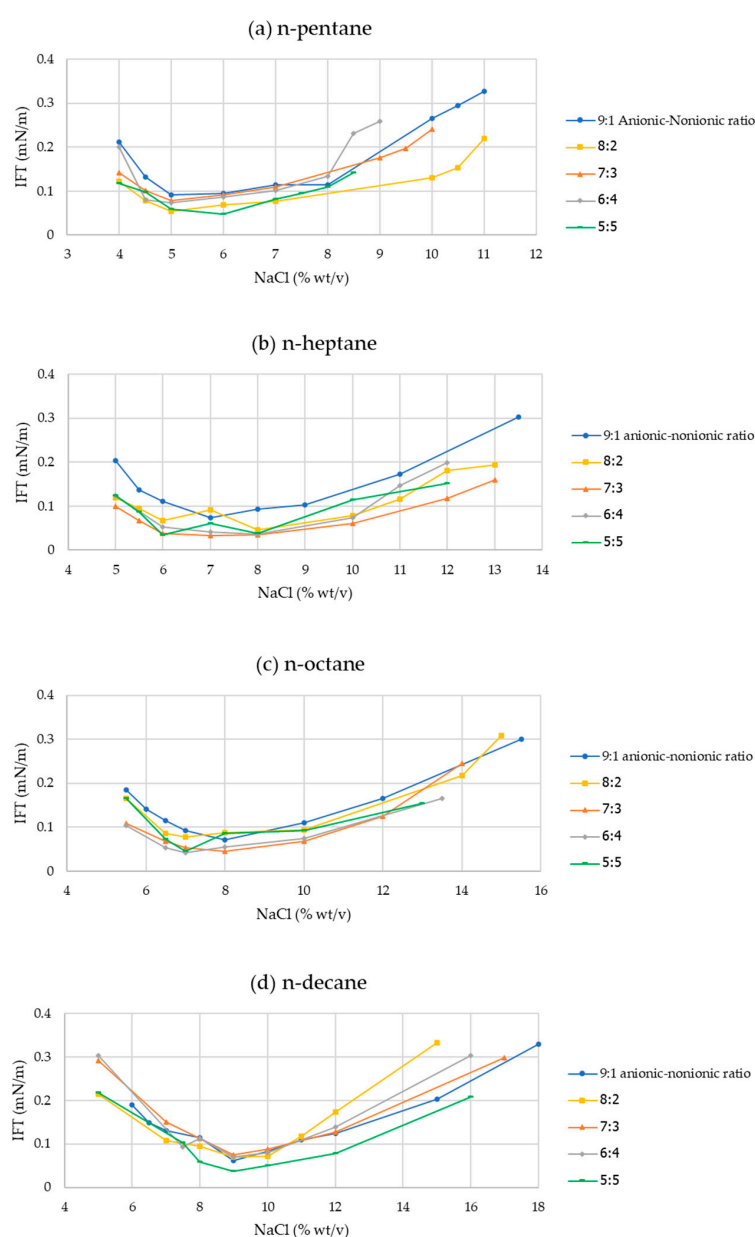


Figure 4. Interfacial tensions (IFTs) of SDHS-AAE(6EO4PO) systems with (a) n-pentane, (b) n-heptane, (c) n-octane, and (d) n-decane.

Table 2. Optimal salt concentrations (S^*) and optimal interfacial tensions (IFT*) of SDHS-AAE(6EO4PO) systems.

Anionic–Nonionic Ratio	Oil	EACN	Optimal NaCl concentration (S^*) (% wt/v)	IFT* (mN/m)
10:0	n-pentane	5	6 ¹	0.091 ± 0.009 ¹
9:1	n-pentane	5	5	0.091 ± 0.006
8:2	n-pentane	5	5	0.054 ± 0.001
7:3	n-pentane	5	5	0.078 ± 0.005
6:4	n-pentane	5	5	0.074 ± 0.005
5:5	n-pentane	5	6	0.047 ± 0.004
10:0	n-heptane	7	7 ¹	0.089 ± 0.000 ¹
9:1	n-heptane	7	7	0.073 ± 0.000
8:2	n-heptane	7	8	0.046 ± 0.004
7:3	n-heptane	7	7	0.033 ± 0.002
6:4	n-heptane	7	8	0.036 ± 0.003
5:5	n-heptane	7	6	0.034 ± 0.003
10:0	n-octane	8	8 ¹	0.138 ± 0.000 ¹
9:1	n-octane	8	8	0.071 ± 0.004
8:2	n-octane	8	7	0.077 ± 0.000
7:3	n-octane	8	8	0.046 ± 0.003
6:4	n-octane	8	7	0.042 ± 0.000
5:5	n-octane	8	7	0.046 ± 0.005
10:0	n-decane	10	14 ¹	0.274 ± 0.000 ¹
9:1	n-decane	10	9	0.063 ± 0.004
8:2	n-decane	10	9	0.070 ± 0.004
7:3	n-decane	10	9	0.075 ± 0.004
6:4	n-decane	10	9	0.071 ± 0.004
5:5	n-decane	10	9	0.037 ± 0.002
9:1	diesel	9.10 ¹	9	0.074 ± 0.000
8:2	diesel	9.10	9	0.077 ± 0.005
7:3	diesel	9.10	9	0.050 ± 0.000
6:4	diesel	9.10	9	0.029 ± 0.002
5:5	diesel	9.10	9	0.020 ± 0.000

¹ Obtained from our previous study [51].

In contrast to the single SDHS system, the presence of AAE(6EO4PO) in the mixture could reduce the IFT*, especially in the n-decane system (see Table 2). The IFT* of the single anionic system tended to increase when the hydrophobicity of the oil increased (i.e., when the EACN increased). In the mixed system, the nonionic surfactant helps the anionic surfactant in solubilizing the oil molecules in the middle phase by reducing the electrostatic repulsive forces between the anionic heads [1,15,27]. In addition, the EO and PO, as an intermediate polarity group, facilitate the nonionic surfactant molecules to balance the solubilization of the long-chain alkane oils (i.e., high EACN). Thus, the presence of the nonionic extended surfactant in the mixed system showed the synergism of the microemulsions that affected the long-chain alkane oil system by making them stronger than the short-chain alkane oil system. It is interesting to note that the mixed system of nonionic extended surfactant decreased the IFT*, ranging about 0.25–48%, 18–63%, 44–70%, and 73–86% for the n-pentane, the n-heptane, the n-octane, and the n-decane, respectively, compared with the single SDHS system. However, the IFT* of SDHS-AAE(6EO4PO) could not reach ultralow interfacial tension (<0.01 mN/m) [17,18].

The optimal salt concentrations of the microemulsion system are shown in Table 2. No trends were observed for the effect of the mixing ratios in the mixed system. Comparing the mixed system and the single SDHS system, the optimal salt concentration for the n-pentane, the n-heptane, and the n-octane were not significantly different. For the n-decane, the optimal salt concentration was reduced from 14% wt/v NaCl (for the single SDHS) to 9% wt/v NaCl (for the mixed system). At the same anionic–nonionic ratio, the optimal salt

concentration tended to increase when additional nonionic surfactant was presented. This is likely due to the stronger interactions between anionic head moieties and the EO and PO group in the nonionic extended surfactant, which were needed to solubilize the long-chain oil molecules by increasing the salinity in the mixed system.

3.4. HLD Equation of AAE(6EO4PO)

Concerning Figure 2, the slopes ($-c_T/b$) and the intercepts ($(K_n/b)\text{EACN} - (\beta/b)$) of the graph plotted between the optimal salt concentration and the temperature were used to determine the constants (i.e., b , K_n , c_T , and β) of each model oil and each temperature with Excel Solver. According to the solver assumption, Figure 5 shows the optimal salt concentrations from the HLD prediction and the actual experiment. Linear regression was fitted with $R^2 = 0.99$, meaning that the HLD equation with the constants resulting from the solver process could effectively predict the optimal salinity of the single AAE(6EO4PO) system.

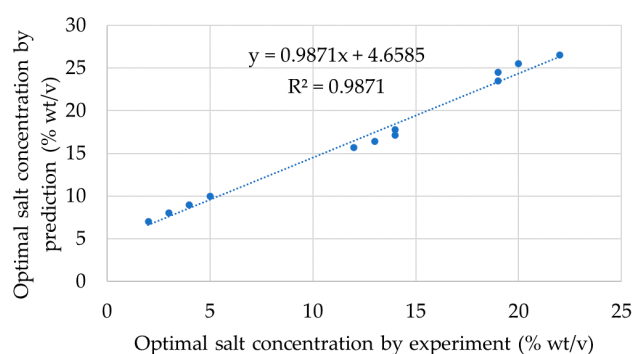


Figure 5. Optimal salt concentrations (S^*) from the HLD prediction and the experiment of AAE(6EO4PO) through Excel Solver.

The average values of the results obtained from all the model oils and all the conducted temperatures showed that $b = 0.12 \pm 0.00$ (g/100 mL) $^{-1}$, $K_n = 0.15 \pm 0.01$, $c_T = 0.02 \pm 0.00$ °C $^{-1}$, and $\beta = -0.46 \pm 0.18$. The electrolyte co-efficiency constant (b) was close to the typical value, which is 0.13 for NaCl [27,29,30,65,66]. Moreover, this finding is also supported by the work of Muñoz et al. (2016), who found that the b value for NaCl of the nonionic surfactant system was $0.10\text{--}0.12 \pm 0.01$ (g/100 mL) $^{-1}$ [56]. The hydrophilicity of the surfactant (K_n) depended on the hydrophilic part (the head) of the surfactant structure. The K_n of this study showed the same result as the K_n value for the alkyl ethoxylated alcohol, which was 0.15 [29]. The similarity could be due to the six-ethylene oxides in the AAE(6EO4PO) molecule, which affected the K_n value. For the temperature factor (c_T), this work showed a lower value than the previous report value of c_T (~ 0.06 °C $^{-1}$ for the nonionic surfactants) [42]. From the controlled condition in this work, the β value of AAE(6EO4PO) was negative, which indicated that AAE(6EO4PO) was a hydrophilic surfactant. The HLD of AAE(6EO4PO) is presented in Equation (8):

$$\text{HLD}_{\text{AAE(6EO4PO)}} = (0.12)S - (0.15)(\text{EACN}) + (0.02)(T - T_{\text{ref}}) - 0.46 \quad (8)$$

3.5. HLD Equation of the SDHS-AAE(6EO4PO) Systems

The HLD equation of the binary anionic–nonionic mixture can be completed by the HLD equations of SDHS and AAE(6EO4PO). As noted, the mixed system of this study was conducted at reference temperature (25 ± 2 °C) ($T - T_{\text{ref}} = 0$) with no cosurfactant addition ($f(A) = \phi(A) = 0$). The constants of the HLD_{SDHS} were already known, as mentioned in the method part of this study ($K_i = 0.13$ and $\sigma = -1.13$). The constants of the $\text{HLD}_{\text{AAE(6EO4PO)}}$ were also determined and are shown in Equation (8). The $\frac{G_{\text{EX}}}{RT}$ values at the optimal condition were calculated by Equation (3) and Table 2. The $\frac{G_{\text{EX}}}{RT}$ results were fitted with the polynomial trendlines (2nd order) with $R^2 = 0.71\text{--}0.92$ as presented in Figure 6. All

the $\frac{G_{EX}}{RT}$ values were in the positive region. Thus, the actual SDHS-AAE(6EO4PO) mixed system was more hydrophobic than the ideal mixture. The $\frac{G_{EX}}{RT}$ values of all the model oils, except for the n-pentane, tended to increase when the mole fractions of the nonionic surfactant increased. At the same anionic-nonionic mixing ratio, the $\frac{G_{EX}}{RT}$ value tended to increase with an increase in the hydrophobicity of the oil. However, for the n-pentane, the $\frac{G_{EX}}{RT}$ value initially increased along with an increase of AAE(6EO4PO), and then suddenly decreased at the 5:5 ratio.

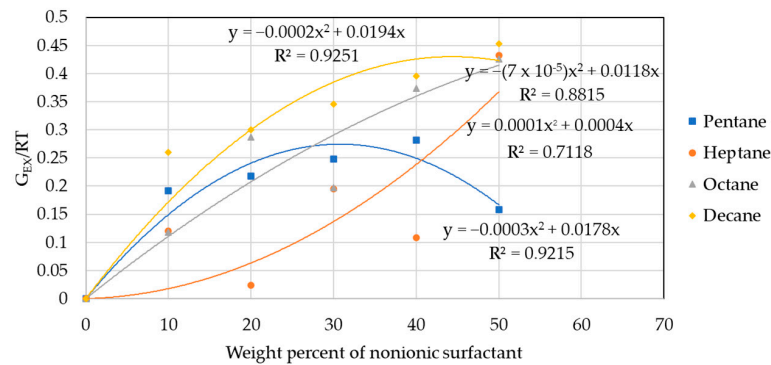


Figure 6. The $\frac{G_{EX}}{RT}$ values of SDHS-AAE(6EO4PO) systems.

According to the Margules equation (Equation (4)), the thermodynamic constants (A_1 and A_2) could be determined. Acosta and Bhakta (2009) mentioned that the A_1 value is zero for systems that have a controlled temperature of 25 °C [42]. Thus, the A_2 values could be calculated by $\frac{G_{EX}}{RT}$ and the molar fraction ($A_2 = \frac{G_{EX}}{X_1^2 X_n}$). The average A_2 value of all the model oils and all the anionic-nonionic ratios was 2.53 ± 1.17 . The HLD equation of SDHS-AAE(6EO4PO) at 25 ± 2 °C, which, to our knowledge, is being proposed for the first time, would be as follows:

$$\begin{aligned} \text{HLD}_{\text{SDHS-AAE(6EO4PO)}} &= X_{\text{SDHS}} \{ \ln(S) - 0.13(\text{EACN}) - 1.13 \} + X_{\text{AAE(6EO4PO)}} \{ (0.12)S - (0.15)(\text{EACN}) - 0.46 \} \\ &+ 2.53 X_{\text{SDHS}}^2 X_{\text{AAE(6EO4PO)}} \end{aligned} \quad (9)$$

3.6. HLD_N Equation of SDHS-AAE(6EO4PO) Systems

After dividing by the K coefficient, the HLD_N equations of SDHS and AAE(6EO4PO) are presented in Equations (10) and (11), respectively. The $k_{\ln(S)}$ coefficient of SDHS was 7.75 and the ionic surfactant contributing parameter ($\text{SCP}_i : \frac{\sigma}{K_i}$) was -8.77 . The salinity coefficient (k_s) of AAE(6EO4PO) was 0.78, temperature constant (k_T) was 0.13, and the nonionic surfactant contributing parameter ($\text{SCP}_n : \frac{\beta}{K_n}$) was -2.99 .

$$\text{HLD}_{N, \text{SDHS}} = 7.75 \ln(S) - \text{EACN} - 8.77 \quad (10)$$

$$\text{HLD}_{N, \text{AAE(6EO4PO)}} = 0.78S - \text{EACN} + 0.13(T - T_{\text{ref}}) - 2.99 \quad (11)$$

At the optimal condition, the HLD_N of the SDHS-AAE(6EO4PO) mixture was assumed to be zero. The interaction terms were determined by Equation (7), with the result shown in Figure 7. The interaction-term results were fitted with the polynomial trendlines (2nd order) with $R^2 = 0.67$ – 0.91 . Surprisingly, it shows that the interaction terms had a trend close to the $\frac{G_{EX}}{RT}$ results of HLD in Figure 6. The average interaction term was 1.82 ± 0.86 . The HLD_N equation of SDHS-AAE(6EO4PO) would be as follows:

$$\text{HLD}_{N, \text{SDHS-AAE(6EO4PO)}} = X_{\text{SDHS}} \{ 7.75 \ln(S) - \text{EACN} - 8.77 \} + X_{\text{AAE(6EO4PO)}} \{ 0.78S - \text{EACN} + 0.13(T - T_{\text{ref}}) - 2.99 \} + 1.82 \quad (12)$$

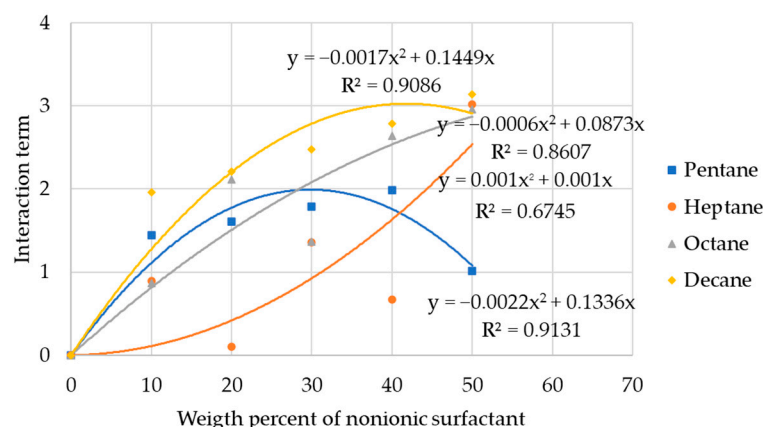


Figure 7. The interaction terms of SDHS-AAE(6EO4PO) systems.

The interaction terms of each anionic–nonionic mixing ratio showed a strong linear relationship with $R^2 = 0.98$, as presented in Figure 8. An increase of AAE(6EO4PO) in anionic-rich conditions resulted in an increase of the term of interaction. Therefore, it should be remarked that the interaction terms of the SDHS-AAE(6EO4PO) system could be represented in the function of the mole fraction of nonionic surfactant. The HLD_N equation of SDHS-AAE(6EO4PO) in another form is shown in Equation (13).

$$HLD_{N, \text{SDHS-AAE(6EO4PO)}} = X_{\text{SDHS}} \{7.75 \ln(S) - EACN - 8.77\} + X_{\text{AAE(6EO4PO)}} 0.78S - EACN + 0.13(T - T_{\text{ref}}) - 2.99 \} + \{4.33X_{\text{AAE(6EO4PO)}} + 1.02\} \quad (13)$$

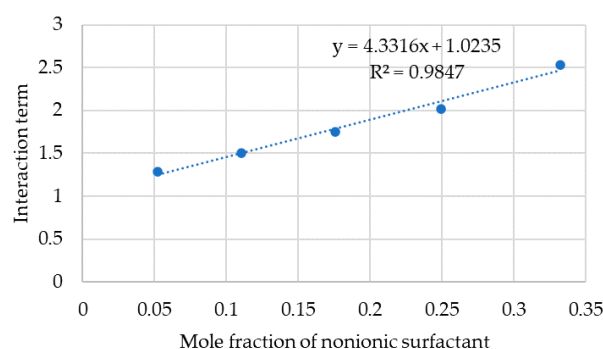


Figure 8. The average interaction terms of each anionic–nonionic ratio of SDHS-AAE(6EO4PO) systems.

3.7. Prediction of Optimal Salt Concentration for Diesel

The phase behavior of the SDHS-AAE(6EO4PO) system with commercial diesel was investigated with different anionic–nonionic mixing ratios at reference temperature ($25 \pm 2^\circ\text{C}$). It was found that the middle phase appeared as a thin layer between the water and the oil phases. Table 2 shows the optimal salt concentration (S^*) and the minimum IFT (IFT^*) of the diesel system. The anionic–nonionic mixing ratio did not affect optimal salt concentration. All the ratios showed the same result for S^* , which was 9% wt/v NaCl. However, the anionic–nonionic ratio affected the IFT^* value. The IFT^* tended to decrease when AAE(6EO4PO) increased. For example, the IFT^* of 0.07 mN/m for the 9:1 ratio was reduced to 0.02 for the 5:5 ratio. The IFT^* results did not reach ultralow interfacial tension [17,18].

The EACN of the commercial diesel in this study was 9.10 ± 0.51 , which was determined from our previous studies [51]. Due to our knowledge of the value of EACN, the optimal salt concentration could be predicted via the HLD and HLD_N equations. The three

scenarios were conducted, including HLD (Equation (9)), HLD_N with average interaction term (Equation (12)), and HLD_N based on nonionic mole fraction (Equation (13)). Figure 9 presents the optimal salt concentrations from the experiment, with three case predictions. It was found that the optimal salt concentration by HLD prediction did not fit with linear regression, while the other two predictions by HLD_N (i.e., $HLD_{N,average}$, $HLD_{N,based\ X_n}$) could fit with the linear trends ($R^2 > 0.99$). The HLD equation predicted optimal salt concentrations lower than in the actual experiment, in contrast to the HLD_N based on mole fraction. Equations (9) and (13) were more precise when estimating the optimal salt concentrations at the low AAE(6EO4PO) fraction than regarding the high weight of AAE(6EO4PO). In the case of HLD_N with an average interaction term, the results showed that it was close to the experimental value when AAE(6EO4PO) in the mixed system increased. The errors between experimental results and the predictions of salt concentrations were 1.89–7.44, 1.11–9.62, and 0.28–9.54% for HLD/ HLD_N with the average interaction term, and HLD_N based on mole fraction, respectively. The precision in all cases was more than 90%. Thus, both $HLD_{SDHS-AAE(6EO4PO)}$ and $HLD_{N,SDHS-AAE(6EO4PO)}$ equations had high efficiency. As noted, the precisions of the optimal salt-concentration prediction between $HLD_{SDHS-AAE(6EO4PO)}$ and $HLD_{N,SDHS-AAE(6EO4PO)}$ differences cannot be compared because the K values (K_i and K_n) of SDHS and AAE(6EO4PO) are too close [29,52]. Moreover, the effect of polydispersity of the EO and PO groups in the extended surfactant (i.e., industrial grade) on the prediction was not considered in this study.

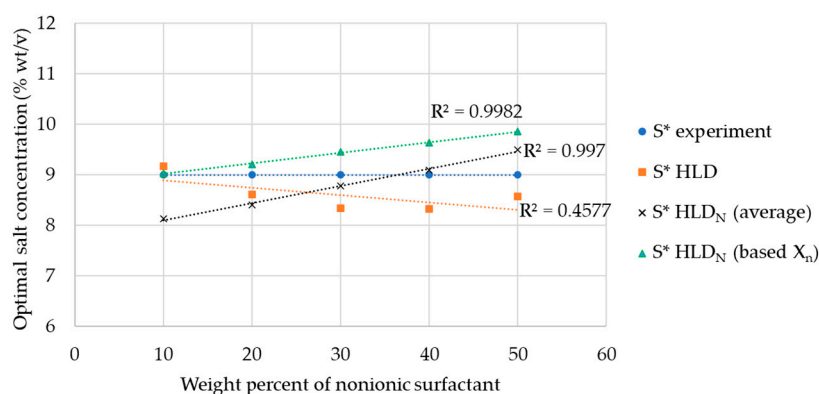


Figure 9. Optimal salt concentrations (S^*) from the HLD, and HLD_N prediction of SDHS-AAE(6EO4PO) systems for commercial diesel (EACN = 9.10).

In this case, the HLD and HLD_N equations are useful prediction tools to reduce the time-consuming nature and cost of the experimental process. They can be applied to many applications, especially petroleum oil-based cleaning/decontamination and soil remediation. Optimal conditions are crucial for environmental and economic considerations in large-scale clean-up—however, there is one important point to consider before applying the HLD equation. In the case of the mixed surfactant, the K values of each surfactant need to be determined. If the K values are close, both HLD and HLD_N equations can be applied. When the K values are different, the HLD_N equation might be better to use for more precision. For optimal prediction, the EACN of the targeted oil should be determined. Therefore, the time period was required when investigating the EACN of the targeted oil. In addition, the HLD and HLD_N equations should be formulated from the oils, with EACNs covering the targeted oil. For example, the HLD and HLD_N equations in this study were determined from the C5–C10 alkanes; the model oil (diesel: EACN 9.10) for the prediction should have an EACN that does not exceed 10.

4. Conclusions

In this study, the mixed surfactant systems of anionic and extended nonionic surfactants containing EO and PO groups were analyzed to enhance the solubilization of the

n-alkane oils with different EACNs. The optimal salt concentrations were determined from the microemulsion phase scan and predicted from the HLD/HLD_N equation; the findings from the study can be summarized as follows.

In the SDHS-AAE(6EO4PO) systems, the intermediated polar molecules (i.e., EO and PO) of AAE(6EO4PO) were key to the formation of microemulsions. The ethylene oxide (EO) affected the phase inversion by increasing the salt concentration for the Winsor Type I-III transition when the mole fraction of AAE(6EO4PO) in the mixed system increased. Concurrently, the presence of the PO group in the extended nonionic surfactant resulted in salt concentration reduction. Thus, the salt concentration range for Winsor Type III was narrower with the addition of AAE(6EO4PO). When the EACN increased, the PO became the dominant factor that could reduce the salt concentration required for phase transitions (Winsor Type I-III and III-II) compared with the single SDHS system. For optimal salt concentration (S^*) and the minimum interfacial tension (IFT^*), the SDHS-AAE(6EO4PO) mixed system showed strong synergism relative to the single SDHS system. Especially in the case of long-chain carbons (i.e., n-decane), SDHS-AAE(6EO4PO) definitely reduced the optimal salinity ($\sim 36\%$) and the IFT^* (up to 86%). Moreover, the salt concentration range forming Winsor Type III for the n-decane was expanded. Remarkably, the SDHS-AAE(6EO4PO) system was suitable for high-hydrophobic oil starting at $EACN = 10$.

At the reference temperature ($25 \pm 2^\circ C$), the HLD_N equation of the SDHS-AAE(6EO4PO) mixture was proposed as a tool for determining a suitable surfactant formulation in cleaning applications, including oil decontamination. The accuracy was investigated to determine the optimal salt concentrations and compared to those obtained from the experiment. The results were remarkable and showed that the error difference was less than 10%. This result demonstrated that even when many steps (e.g., the phase behavior experiment, the optimal condition, the interaction term) were required to determine the HLD_N , SDHS-AAE(6EO4PO), the HLD_N equation could be applied as a guideline for establishing the formulators. The preparation of optimal conditions is a goal to reduce the length of time and cost required for conducting experiments.

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