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Research Article

Synthesis and Characterization of a Novel Nonionic Glucosamine-Based Surfactant and its Comparison with *N*-Methylglucamine Surfactant

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ABSTRACT

In this study, the synthesis, surface evaluation, and thermodynamics properties a novel non-ionic glucosamine-based surfactant (2-(dodecyloxy)-*N*-((2*R*,3*R*,4*R*,5*S*,6*R*)-2,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3-yl)acetamide (NGAS) is carried out and the comparison of the results with *N*-methylglucamine surfactant is reported. NGAS was synthesized via the facile and straightforward reaction of glucosamine with 2-(dodecyloxy) acetyl chloride in the presence of triethylamine. The surface tension of NGAS was determined by tensiometric methods. The surface properties including Critical Micelle Concentration (CMC), the efficiency of adsorption (pC20), the surface excess (Γ_{max}) and the area occupied by each of the surfactant molecules (A_{min}) were investigated at 298.15 K in deionized water. The surface tension of water was reduced to about 41 $mN.m^{-1}$ by using the surfactant at the concentration level of 2.06×10^{-3} $molL^{-1}$. The thermodynamic parameters of micellization ($\Delta G°_{mic}$) and surface adsorption ($\Delta G°_{ads}$) were calculated from CMC data. The hydrophilicity and lipophilicity balance parameter (HLB) were obtained from the Griffin equation. According to the results, micellization and surface adsorption of this surfactant is a spontaneous process in aqueous solution. In addition, these results show that NGAS can be used as an emulsifier in oil-in-water emulsions.

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1. Introduction

Surfactants are considered as essential materials in numerous industries, including personal care formulations and cleaning products, since they are able to reduce the surface tension between different phases [1, 2]. The four main types of surfactants are categorized in anionic, cationic, non-ionic, and amphoteric [3-8] subgroups. Among these categories, non-ionic surfactants are widely used in personal care formulations, due to their compatibility with various ionic strengths and pH levels. Recently, non-ionic sugar-based surfactants have gained significant attention, owing to their unique properties, including remarkable mildness, biodegradability, and excellent cleaning ability [9-12]. Moreover, they exhibit low toxicity and are gentle on sensitive skins, being ideal for personal care products such as body washes, hand soaps, facial cleaners, and shampoos [13-18]. Based on these features, non-ionic sugar-based surfactants are considered as a sustainable alternative to traditional surfactants. In this context, glucosamine-based surfactants have especially gained popularity, due to their superior surface activity, low toxicity, and emulsification properties, making them suitable for various applications in the industry [19-29]. Comprehensive evaluation and discussion in this context are presented in three recent reviews, compiling and describing related useful synthetic methods for the production of sugar-based surfactants [30-32].

In this study, the synthesis and evaluation of a sugar-based surfactant derived from glucosamine was carried out for the first time in both computational and experimental levels. In the computational phase, all geometrical optimizations and energy calculations were performed using the M06-2X function and the 6-31 G (d, p)-basis, being set on the structure of the new sugar-based surfactant derived from glucosamine (NGAS). The results showed that NGAS has high solvation energy and excellent solubility in water [33], and is synthesized based on this procedure. Next, we conducted the experimental phase by evaluating the properties and structure of NGAS. Characterization of NGAS was performed using FTIR and mass analyses. In addition, the critical micelle concentration (CMC) value was obtained using surface tension measurement at 298.15 K. The parameters affecting the micellization and interfacial behaviors such as Γ_{max} (maximum surface excess concentration), CMC, the surface tension at the CMC (γ_{CMC}), free energies of micellization ($\Delta G°_{m}$), and free energies of adsorption ($\Delta G°_{ads}$) were also surveyed. Due to similarity of the chemical structure of NGAS and the non-ionic surfactant *N*-methylglucamine (C12GA), the surface properties of the two surfactants were compared. Both surfactants differ in the type and the size of their hydrophilic head groups, but have exactly the same side alkyl chain (12 carbon atoms tail). Structures of the two surfactants are shown in Fig. 1.

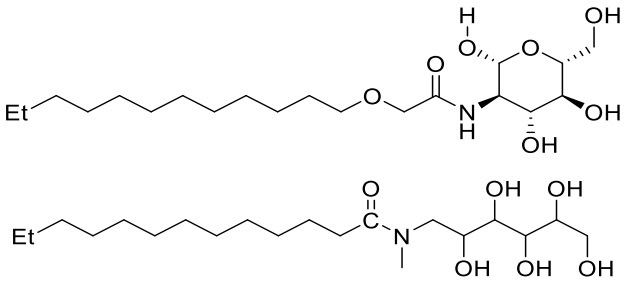


Fig. 1. NGAS (top) and C12GA (bottom) with 12-carbon aliphatic chain

1. Experimental

2.1. Materials and instrumentation

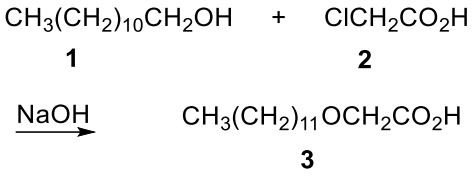
1-Dodecanol (≥98.0%), sodium chloroacetate (98%), thionyl chloride (97%), and glucosamine

hydrochloride (≥99%) were purchased from Sigma-Aldrich Company and used as received. Triethylamine (≥99.5%), sodium hydroxi de (≥ 97.0 %), hydrochloric acid (37%) were purchased from Merck Company and used as received. Fourier Transform Infrared (FT-IR) spectra were recorded on an ABB Bomem MB-100 spectrometer, using KBr pellet for sample preparation. Mass spectra were carried out on an Agilent 5975C instrument at 70 eV. The surface tensions of the surfactant were measured at 298.15 K, using a Krüss K12 tensiometer and du Nouy ring, calibrated with deionized water and thermostated to within ±0.05 °C. All glassware were rinsed with acetone and then with double distilled water, prior to be used. Prior to each measurement, the platinum ring was cleaned by using acetone followed by rinsing with double-distilled water and then it being heated briefly by being hold above a Bunsen burner until glowing. The value of the critical micelle concentration was obtained from the intersection of the two lines in low and high concentrations areas of the surface tension curves. Surfactant solutions were prepared with double-distilled water. A stock solution (2000 ppm) was prepared in double-distilled water and it was used for the preparation of more dilute solutions (10-1500 ppm). The surface tension of the deionized water was measured prior to the measurement of the stock solutions, starting from the most dilute solution. This value was 72.1±0.2 mNm^{-1}. All reported experimental values are the average of three measurements.

2.2. Synthesis of NGAS

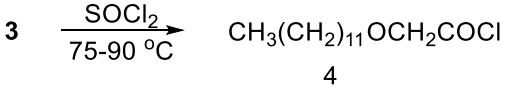
The synthesis of the glucosamine-based surfactants involves three steps, including the preparation of the required fatty acid from the corresponding fatty alcohol, conversion of the fatty acid to the corresponding fatty acyl chloride, and synthesis of the glucosamine-based surfactant, NGAS. For the first two steps, a known procedure was used [34, 35]. Detailed procedures for each step are provided in the following.

2.2.1. Preparation of 2-dodecoxyacetic acid from 1-dodecanol



In order to synthesize 2-dodecoxyacetic acid, a reaction was carried out using 1-dodecanol (9.3 g, 50 mmol) in a 250 mL round bottom flask. The reaction was conducted at 70 °C with the aid of a magnetic heater stirrer. To the flask, were added NaOH (2.2 g, 55 mmol) and sodium monochloroacetate (6.4 g, 55 mmol) and the mixture was continued to stir for another 5 hours at 70 °C. The completion of the reaction was monitored by thin layer chromatography (TLC), using ethyl acetate/petroleum ether (4:1) as the eluent. The resulting precipitate was filtered by a Buchner funnel and washed with 10 mL of 32% HCl. The alkyl ether carboxylic acid (2-dodecoxyacetic acid) was obtained as the product 3 (10.9 g, 90%).

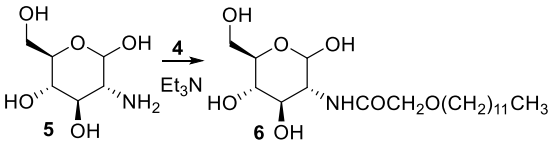
2.2.2. Conversion of 2-dodecoxyacetic acid to fatty acyl ether chloride



For the synthesis of the fatty acyl chloride, a 250 mL three-necked flask was equipped with a dropping funnel, a reflux condenser, a mechanical stirrer, and a thermometer. 2-Dodecoxyacetic acid **3** (4.88 g, 20 mmol) was introduced to the flask, followed by gradual addition of thionyl chloride (3 mL, 40 mmol) within 2.5 hours, maintaining vigorous stirring throughout the mixing. Then, the reaction mixture was heated at 90 °C for 4 hours. The completion of the reaction was monitored by TLC, using ethyl acetate/petroleum ether (4:1) as the eluent. The excess thionyl chloride was removed

under vacuum. The fatty acyl ether chloride 4 was obtained in 85% yield (4.5 g).

2.2.3. Conversion of the fatty acyl ether chloride to NGAS



In a round bottom flask, glucosamine hydrochloride (4.3 g, 20 mmol) was added to 4. Next, triethylamine (5.5 mL, 40 mmol) was added to the reaction content and the resulting mixture was stirred for 4-5 hours at ambient temperature. The completion of the reaction was monitored by TLC, using ethyl acetate/petroleum ether (1:1) as the eluent. NGAS **6** (mp 200-202 °C) was obtained in 75% yield (5.2 g).

2.3. Surface properties calculations

The surface parameters, Γ_{max} (the maximum surface excess concentration), A_{min} (minimum surface area per surfactant molecule), pC20 (adsorption efficiency),P (packing parameter), $\Delta G°_{mic}$ (free energy of micellization), $\Delta G°_{ads}$ (free energy of adsorption), and HLB (hydrophilic-lipophilic balance) were calculated using the equations 1-7 , respectively [6, 27].

$$\Gamma_{max} = -\frac{1}{2.303RTn}\left(\frac{\partial\gamma}{\partial log C}\right) \quad (1)$$

$$A_{min} = 10^{20}/N_A.\Gamma \quad (2)$$

$$pC20 = -\log C20 \quad (3)$$

$$P = (V_H/I_c a_0) \quad (4)$$

$$\Delta G°_{mic} = RT\ln X_{cmc} \quad (5)$$

$$\Delta G°_{ads} = \Delta G°_{mic} - \left(\frac{\pi cmc}{\Gamma max}\right) \quad (6)$$

$$HLB = \frac{20G}{G+A} \quad (7)$$

3. Results and Discussion

3.1. Characterization of NGAS

The product was characterized using various analytical techniques including MS spectroscopy and FT-IR. The mass spectrum of NGAS showed a molecular ion peak (M^+) at m/z 405, corresponding to the molecular weight of the surfactant (Fig. 2, top). Major fragmentation peaks observed in the mass spectrum are summarized in Table 1. The FTIR spectrum of NGAS showed characteristic peaks corresponding to the functional groups present in the molecule (Fig. 2, middle). The broad peak at 3460 cm^{-1} was attributed to O-H stretching vibrations, while the peak at 3295 cm^{-1} was attributed to the N-H stretching vibrations of the amide group. In addition, the peak at 1600 cm^{-1} was assigned to the C=O stretching vibrations of the amide group. Additionally, the peaks at 1105 cm^{-1} was assigned to C-O-C stretching vibrations, indicating the presence of ether linkages in the molecule. To further support the structural elucidation, superimposition of the IR spectra of NGAS and its precursor is presented in Fig. 2, bottom.

Table 1. Major mass spectrum fragmentation peaks of NGAS

m/z	Relative intensity %	*m/z*	Relative intensity %
404	0.1	142	2.0
368	3.0	111	22.0
242	0.5	96	42.0
220	1.0	83	56.0
202	32	52	100

3.2. Surface tension measurements

The surface tension measurements for dilute aqueous solutions of NGAS, performed at 298.15 K, are provided in Table 2. The surface tension data of C12GA were collected from the literature [36]. The corresponding surface tension curve of aqueous solutions of NGAS has been shown in Fig. 3. At first, the surface tension decreases with increasing the concentration of the component, indicating that the surfactant molecule is adsorbed in the interface. Then, a plateau region with an almost constant slope appears in the (γ -log[C]) plot, indicating that a stable micelle has been created. The minimum surface tension (γ_{CMC}) value is obtained by the analysis of the plateau region of the plots. The critical micelle concentration (CMC) is determined at the intersection of the two fitting straight lines

above and below the breaking point of the tension vs (log) concentration plot using a linear regression analysis method. A summary of the data is compiled in Table 3.

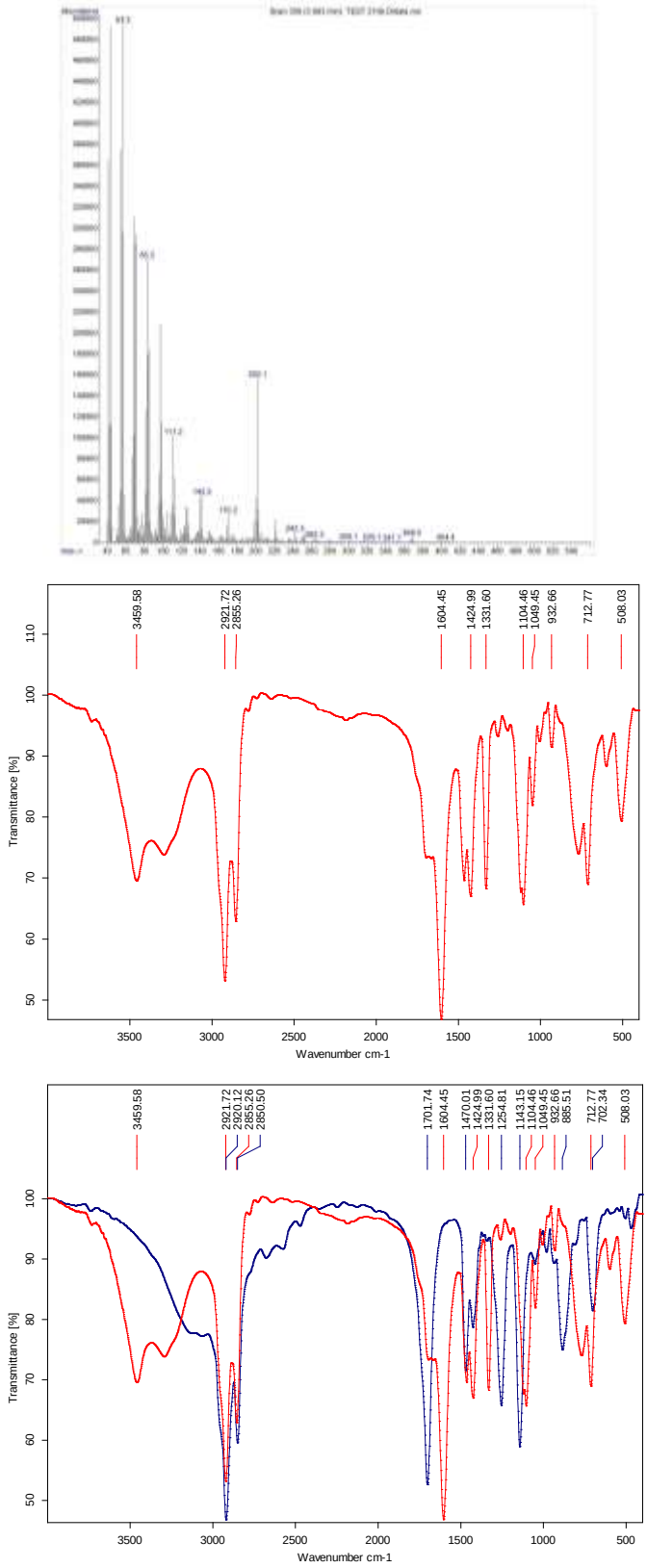


Fig. 2. (top) MS spectrum, (middle) FT-IR spectrum, and superimposition of the IR spectra of NGAS (red) and its precursor (blue) (bottom).

Table 2. Surface tension of NGAS in aqueous media at different concentrations at 298.15 K

Entry	g/l	ppm	C(M)	log (c/mol.dm^{-3})	γ mN.m^{-1}
1	0	0	0		72.1
2	0.01	10	2.47E-05	-4.6	66.1
3	0.025	25	6.17E-05	-4.2	63.69
4	0.05	50	1.23E-04	-3.9	59.47
5	0.1	100	2.47E-04	-3.6	55.25
6	0.15	150	3.70E-04	-3.43	52.86
7	0.2	200	4.94E-04	-3.3	50.8
8	0.25	250	6.17E-04	-3.2	48.9
9	0.35	350	8.64E-04	-3.06	46.3
10	0.4	400	9.88E-04	-3.005	45.12
11	0.55	550	1.36E-03	-2.9	43.9
12	0.6	600	1.48E-03	-2.83	43.15
13	0.8	800	1.98E-03	-2.7	42.1
14	1	1000	2.47E-03	-2.6	41.15
15	1.5	1500	3.70E-03	-2.43	41.1
16	2	2000	4.94E-03	-2.3	41.1

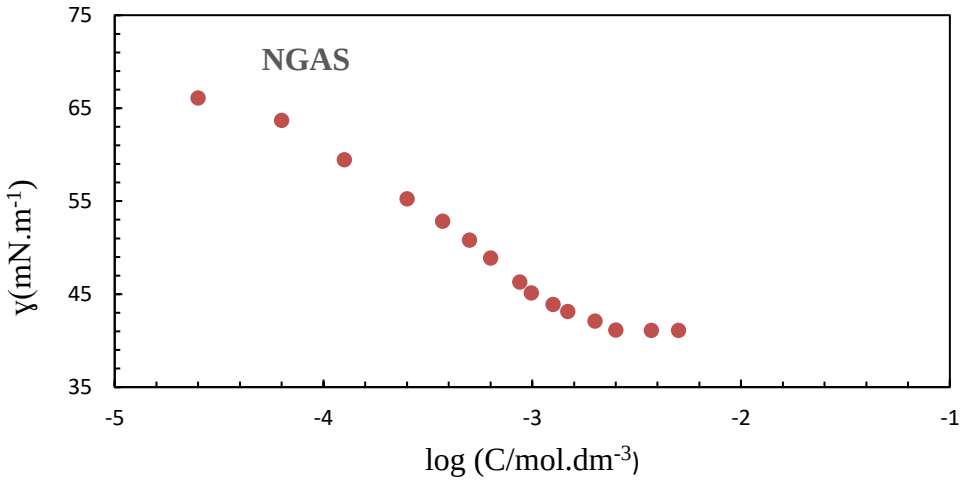


Fig. 3. Plot of equilibrium surface tension of aqueous solutions of NGAS versus log C.

Table 3. Micellar and surface properties of NGAS & C12GA

Compound	NGAS	G_{12}GA [36]
CMC (mol.L^{-1})	2.06×10^{-3}	7.76×10^{-5}
γ_{CMC}(mN.m^{-1})	41.90	28.4
Γmax (mol. m^{-2})	2.65	4.60
pC_{20}	3.43	5.02
A_{min} (Å^2/molecule)	62.55	36.1
$\Delta G°_{ads}$ (kJ/mol)	-36.68	-42.8
$\Delta G°_{mic}$ (kJ/mol)	-25.29	-33.6

Comparison of CMC values of NGAS with those of C12GA suggests that NGAS has a larger CMC than C12GA does. This could be due to having additional ether and NH functional groups residing in the NGAS structure, making NGAS more polar than C12GA. This may result in lower tendency in migration of molecules from the bulk solution to the interface and higher concentrations formation of micelles.

The surface excess concentrations (Γ_{max}) in mol/m^2, and minimal area/molecule (A_{min}) in Å^2, at the interface of water and air were calculated from Eq. (1) and Eq. (2) [37-39], where$(\frac{\partial \gamma}{\partial log C})$ is the slope below the CMC in the surface tension plot, T is the temperature (K), R = 8.314 (J/mol K), *n* is 1 for

nonionic surfactants, and N_A = Avogadro constant. Another important parameter is pC20, which is calculated as shown in Eq. (3) [40], Where pC_{20} is the efficiency of surface adsorption, and the negative log of the bulk surfactant concentration, C_{20}, required to reduce the surface tension of the solvent by 20 mN/m.

Comparison of Γ_{max} and A_{min} values of NGAS with those of C12GA (shown in Table 3) suggests that NGAS has lower Γ_{max} and larger A_{min} than C12GA does. This is due to the special structure of the ring head of NGAS. Increased charge repulsion in the ring structure of NGAS compared to the linear structure of C12GA (with similar alkyl chain lengths, ($C_{12}H_{25}$), leads to a lower packing density at the air-water interface and subsequently to an increase in the A_{min} value of the NGAS molecule. Moreover, the value of pC20 for NGAS is lower than that of C12GA, which indicates the low tendency of NGAS to be absorbed at the interface compared to the tendency to enter the bulk. Also, the results of Table 3 show that the values of γ_{CMC} for NGAS is greater than those of C12GA and this surface activity is due to the decreased solubility of NGAS in the oil phase and low tendency to migrate from the bulk to the interface.

The packing parameter (P) is calculated as shown in Eq. (4), where P determines the shape of the micelle, (V_H) is the volume occupied by the hydrophobic groups in the micellar core, I_c is the length of the hydrophobic group in the core, and a_0 is the cross-sectional area occupied by the hydrophilic group at the micelle–solution interface. According to the packing parameter value of NGAS (P<1/3), the structure of its micelle is spheroidal in aqueous media.

The standard free energy of micellization per mole of the monomer unit ($\Delta G°_{mic}$) of the surfactant is related to the CMC, as shown by Eq. (5) [41], where X_{CMC} is the CMC as a molar fraction (CMC/55.5). The free energy of adsorption $\Delta G°_{ad}$ at the air/water interface is calculated from the Eq. (6) [42], where (Π_{cmc}) is the surface pressure at CMC. The free energy of micellization ($\Delta G°_{mic}$) (Eq. 5) and adsorption ($\Delta G°_{ads}$) (Eq. 6) of the glucosamide surfactants (NGAS and C12GA) are a negative value, indicating that the processes are desired thermodynamically. The magnitude of $\Delta G°_{ads}$ is more negative than that of $\Delta G°_{mic}$, signifying that the adsorption process is more favorable than micellization. The values of $\Delta G°_{mic}$ and $\Delta G°_{ads}$ are collected in Table 3.

3.3. Hydrophilic and hydrophobic balance parameter (HLB)

HLB criterion helps to choose the suitable surfactant so that surfactants with low HLB of 2-3 are suitable as antifoam, while those with HLB of 3-6 can be used as emulsifier for water-in-oil (W/O) emulsion systems. In addition, surfactants with HLB 0f 7-9 are useful as wetting agents, and those with HLB of 8-16 are suitable for oil-in-water (O/W) emulsions. Finally, surfactants with HLB above 13 can be used as cleaners and resolving agents [43]. The HLB values of the two non-ionic surfactants NGAS and C12GA were determined according to Griffin's Eq. (7) [44], where A is the molecular mass of the whole molecule, and G is the molecular mass of the hydrophilic part of the molecule.

The value of the HLB for NGAS with a molecular weight of 405 $gmol^{-1}$ determined to be equal to 11.65, while it was found to be equal to 11.35 for C12GA with a molecular weight of 391 $gmol^{-1}$. According to these HLB values, both surfactants can be used as emulsifiers in the oil-water system.

4. Conclusions

In summary, surface behaviours and micellization of the two nonionic surfactants, NGAS and C12GA, with similar alkyl chain lengths, were investigated for the first time by the tensiometric method, and the following results were concluded:

1. comparison of CMC between the two surfactants shows that the CMC value is higher for NGAS, due to more excellent solubility in the aqueous phase,

2. the obtained results indicate that Γ_{max} decreased and A_{min} increased with increasing hydrophilicity,

3. surfactant adsorption efficiency in water-air interface (pC20) decreases with increasing hydrophilicity,

4. the negative values of $\Delta G°_{mic}$ and $\Delta G°_{ads}$ in both of the surfactants show that surfactant adsorption and micelle formation at the interface are spontaneous processes,

5- moreover, it was found that the adsorption of the surfactant at the air-water interface is more favourable than the micelle formation (or $|\Delta G^{\circ}_{mic}| < |\Delta G^{\circ}_{ads}|$), and

6. HLB measurements show that both NGAS and C12GA with HLB values equal to 11.65 and 11.35 can be used as emulsifiers for the O/W systems.

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Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript.

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