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EFFECT OF CAFFEINE AND CHLOROGENIC ACID AS FOOD ADDITIVES ON THE PROPERTIES OF SODIUM DODECYL SULFATE FOR PROSPECTIVE REDUCING THE AMOUNT OF FOOD EMULSIFIERS USED

– Research paper –

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Abstract: Over recent years, there has been an increase in the consumption of processed food, and its spread has made it the subject of numerous studies aimed at determining its impact on human health. The latest literature reports indicate the need to limit the use of food additives, including the most frequently used emulsifiers. The study attempted to determine the effect of caffeine and chlorogenic acid on the properties of sodium dodecyl sulfate in order to potentially reduce the amount of emulsifiers in food. In this work, research was carried out to determine the surface, antioxidant and thermal stability properties of SDS-caffeine/chlorogenic acid systems. Spectroscopic analyzes were also performed. The thermal stability of O/W emulsions with addition of caffeine or chlorogenic acid were the higher than the ones with no additives. These values were respectively, 75.56% and 71,11%. The effect of both additives on the CMC values of binary model systems was also observed, which were 4.53 mmol/dm^3 for SDS-caffeine system and 4.59 mmol/dm^3 for SDS-chlorogenic acid system. Moreover, for SDS-chlorogenic acid system at SDS concentration of $4 \cdot 10^{-1}$ mmol/dm^3 the higher increase in FRAP value (7.12 mmol Fe^{2+}/g) compared to pure chlorogenic acid was observed. The obtained results allow us to conclude that the addition of caffeine or chlorogenic acid to food emulsion systems, due to positive effect on their stability, may enable an attempt to modify the recipes to reduce the concentration of the emulsifiers used.

Keywords: caffeine, chlorogenic acid, emulsifier, surface properties, antioxidant properties, spectral analysis

INTRODUCTION

Emulsions are heterogeneous systems composed of at least two immiscible phases in such a way that one of them is dispersed as droplets in the other called the continuous phase. Emulsion systems are used in food industry as popular individual foods like mayonnaise or cream as well as delivery systems which may improve stability and availability of bioactive ingredients (Ai, 2023). As thermodynamically unstable systems, emulsions may undergo the breakdown over the time due to physicochemical mechanisms such as coalescence, flocculation, Ostwald ripening, or combination of all these processes (McClements and Jafari, 2018, Tadros, 2013). Therefore, for the long-term stability achieving emulsifiers are used in emulsion formulations. These type of stabilizers are crucial components in the formation of emulsion system and determine the functional attributes of final products. Among most commonly used food emulsifiers are small molecule surfactants, natural amphiphilic macromolecules, solid particles, and auxiliary emulsifiers (Ai, 2023). Literature data suggest that currently permitted food emulsifiers may adversely affect the functioning of the digestive system by impairing intestinal barrier function and modulation the biology of the gut microbiota which may contribute to increase the risk of inflammatory bowel disease or metabolic syndrome (Halmos et al 2019). For this reason any options to reduce the intake of these additives while ensuring the stability of products should be considered.

In addition to emulsifiers, other types of additives, like e.g. β-glucans or proteins, are also used to obtain stable dispersion systems (Kaur et al. 2020; Liu et al 2024). It has been proven that interactions between proteins and emulsifiers at the interface are correlated with emulsion stability (Liu et al., 2024). Moreover, addition of selected bioactive compounds may influence the surface activity of

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ionic surfactants, which affects their emulsifying ability (Kwaśniewska and Kiewlicz, 2022a, 2022b). In line with prevailing trends, consumers are paying more attention to the origin of additives used and increasingly prefer natural ingredients, especially those that have health-promoting properties. Caffeine (CA) and chlorogenic acid (CGA) are described in literature as valuable components in coffee beans with widely documented health-promoting properties (Awwad, 2021). Literature data suggest that the preventive effect from the intake of CGA and CA is partly correlated with their ability to scavenge radicals, which in turn limits the formation of oxidative stress considered to be the etiological factor of some degenerative diseases Vieira et al. 2020). The dietary sources of CA and CGA may be lightly processed products such as coffee and tea, but also ultra-processed foods, e.g. energy drinks and cola-type soft drinks and many others (Thomson et al., 2014, Tajik et al., 2017).

Although the benefits of limiting the use of emulsifiers are known, it seems that the literature data on the possibility of replacing them with health-promoting ingredients is very limited.

All data above made the authors attempt to determine the effect of CA and CGA on the surface properties of SDS and the stability of a model emulsion containing SDS as an emulsifier. Confirmation of the positive effect of the additives used on emulsion stability could constitute a basis for further research that would allow on a larger scale for limiting the use of food emulsifiers by adding bioactive ingredients. Moreover, an attempt was made to determine the antioxidant properties of model SDS-CA and SDS-CGA systems.

MATERIALS AND METHODS

Materials

The following reagents were used for the research: caffeine (Thermo Fisher Scientific), chlorogenic acid (Angene), sodium dodecylsulfate (SDS) (Alfa Aesar), 2,4,6-tris-(2-pyridyl)-s-triazyne (TPTZ) (Sigma-Aldrich), acetic acid, hydrochloric acid (0.1 mol/dm3, 0.1 N), sodium acetate trihydrate, iron (II) sulfate heptahydrate, and ferric chloride (III) anhydrous (all from Chempur).

Surface tension measurements

Tensiometric measurements were performed using a Kruss K100 tensiometer using the Wilhelmy method. The platinum plate was burned in a flame after each measurement. The tests were carried out at a temperature of 298 K for aqueous solutions with SDS concentration ranging from 0.0078 mmol/dm^3 to 16 mmol/dm^3 and a constant content of CA or CGA of 40 mg/100 cm^3.

Tensiometric techniques provide information about the orientation of molecules at the interface and also enables the estimation of adsorption parameters. Based on the Gibbs adsorption equation, the excess surface concentration (Γ_{max}) was determined according to the equation below (Zhou and Rosen, 2003):

$$\Gamma_{max} = -\frac{1}{2nRT}\left(\frac{\partial\gamma}{\partial logC}\right)_{T,P} \quad (1)$$

According to available literature data (Chauhan et al., 2013) the value of n was set to 2, while the value $\left(\frac{\partial\gamma}{\partial logC}\right)_{T,P}$ corresponds to the slope of the surface tension isotherm graph at a concentration lower than the CMC value. R represents the value of the gas constant (8.314 J mol^{-1} K^{-1}), γ expresses the surface tension and C is the value of the surfactant concentration. The obtained surface excess value made it possible to estimate the value of the Gibbs energy of adsorption $\left(\Delta G^0_{ads}\right)$ in accordance with the relationship presented below (Alfakeer et al., 2024):

$$\Delta G^0_{ads} = \Delta G^0_m - \frac{\Pi_{cmc}}{\Gamma_{max}} \quad (2)$$

where the Gibbs free energy of micellization (ΔG^0_m) can be expressed by the equation (Kiewlicz and Kwaśniewska, 2023):

$$\Delta G^0_m = RTlnX_{cmc} \quad (3)$$

However, surface pressure at CMC (Π_{cmc}) states a simple relationship between the surface tension of the solvent (γ_0) and the surface tension of the surfactant solution at its concentration corresponding to CMC (γ_{cmc}) (Alfakeer et al., 2024):

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad (4)$$

In addition to the value of surface excess, the parameter indicating packing in the surface layer is the minimum area per molecule (A_{min}) at air–water interface (Kiewlicz and Kwaśniewska, 2023):

$$A_{min} = \frac{1}{N_A\,\Gamma_{max}} \quad (5)$$

were N_A is Avogadro's number.

Estimating the value of the minimum area per molecule (A_{min}) at air–water interface is helpful in determining the molar Gibbs energy at CMC at maximum adsorption (G_{min}) (Sheng et al., 2021):

$$G_{min} = \gamma_{cmc}A_{min}N_A \quad (6)$$

Determination of total antioxidant capacity (TAC) as the FRAP value

In order to determine the effect of SDS concentration on the total antioxidant capacity of the SDS-CA and SDS-CGA binary systems, FRAP assay were performed. For both investigated systems, sets of six solutions with different SDS concentrations were prepared, which in final samples were as follows: 0 mmol/dm^3, $4 \cdot 10^{-3}$ mmol/dm^3, $8 \cdot 10^{-3}$ mmol/dm^3, $4 \cdot 10^{-2}$ mmol/dm^3, $8 \cdot 10^{-2}$ mmol/dm^3, and $4 \cdot 10^{-1}$ mmol/dm^3. The concentrations of caffeine and chlorogenic acid were constant in each set of solutions and were respectively, 15 µmol/dm^3 of chlorogenic acid in SDS-CGA system and 2 mmol/dm^3 of caffeine in SDS-CA system. These values were determined experimentally, having into regard the literature data and methodological limitations.

FRAP assay was performed according to the method proposed by Benzie and Strain (1996) with further modifications (Kwaśniewska and Kiewlicz, 2022 b). Before the measurements the FRAP reagent was prepared. Its composition included: acetic buffer solution (pH 3.6; C_m=300 mmol/dm^3), TPTZ solution (C_m=10 mmol/dm^3) in 40 mmol/dm^3 hydrochloric acid solution and ferric chloride solution (C_m=20 mmol/dm^3), mixed in 10:1:1 ratio, respectively. Subsequently, 30 µL of the sample was added to 2970 µL of FRAP reagent, mixed, left for 4 min and the absorbance was measured at 593 nm against blank with UV–Vis spectrometer (Metertech SP-8001, Taiwan). The standard curve was prepared using $FeSO_4 \cdot 7H_2O$. The results were expressed as mmol Fe^{2+}/g of the antioxidant.

UV-vis analysis

Before the measurements, the aqueous solutions of pure CA and CGA at the concentration of 0.11 mmol/dm^3 were prepared. This concentration was set based on the literature data (Navarra et al., 2017; Belay et al., 2008). Then, using constant concentrations of CA and CGA, sets of binary solutions as SDS-CA and SDS-CGA systems were prepared. SDS concentrations used in the research were 0.0, 0.2, 0.4, 2.0, 4.0 and 8.0 mmol/dm^3, respectively. The solutions were analyzed in spectral range from 200 to 400 nm using UV–vis spectrometer (Metertech SP-8001, Taiwan). The baseline correction was performed using distilled water.

FTIR analysis

Infrared spectra were collected for solutions with a concentration of 6 mmol/dm^3 and 0.25 mmol/dm^3 SDS which contained CA or CGA in an amount of 40 mg/100 cm^3 of solution, as well as for an SDS solution with a concentration of 32 mmol/dm^3. IR spectra for pure CA and CGA were also collected. Measurements were made on a Jasco (Japan) FT-IR 4700 device.

Determination of the emulsion thermal stability

In order to obtain an O/W emulsion, the water and oil phases in a ratio of 40:60 (%), previously heated to 70°C, were combined using a magnetic stirrer. SDS was added to the oil phase as an emulsifier, its content in the total emulsion was 5%. CA and CGA acid were added to the aqueous phase at a concentration of 40 mg/100 g of the emulsion. Three types of emulsions were obtained, i.e. with the addition of CA, CGA and without additives.

The emulsions thus obtained were assessed for thermal stability. The emulsion samples were incubated for 30 min at 80°C and then placed in an ice bath for 15 min. The final step was centrifugation at 1300g for 5 min. The test was repeated three times and emulsion thermal stability (EST) was calculated using the formula (Kasiri and Fathi, 2018):

$$EST = \frac{Remaining\ emulsion\ volume}{Initial\ emulsion\ volume} \cdot 100\% \quad (7)$$

Statistical analysis

The statistical analysis was conducted using Statistica 12.0 software (StatSoft, Inc. 2013). It included calculation of mean values and standard deviations from three determinations, one-way ANOVA and Fisher's Least Significant Differences (LSD) test.

RESULTS AND DISCUSSION

Determination of surface tension and adsorption parameters

In the conducted analyzes of model binary systems (SDS-CA and SDS-CGA), tensiometric analysis was used. All parameters evaluated based on tensiometric measurements are presented in Table 1. These measurements also made it possible to plot surface tension isotherms (Figure 1) and, on their basis, determine the value of the critical micelle concentration, these values are similar for both analyzed systems.

Table 1 Adsorption parameters for SDS-CA and SDS-CGA binary systems

	CMC [mmol/dm^3]	ΔG_m [kJ/mol]	ΔG_{ads} [kJ/mol]	G_{min} [kJ/mol]	$\Gamma_{max} \cdot 10^6$ [mol/m^2]	A_{min} [nm^2]
SDS-CA	4.53	-13.37	-27.45	16.06	2.38	0.70
SDS-CGA	4.59	-13.34	-33.06	20.72	1.78	0.94

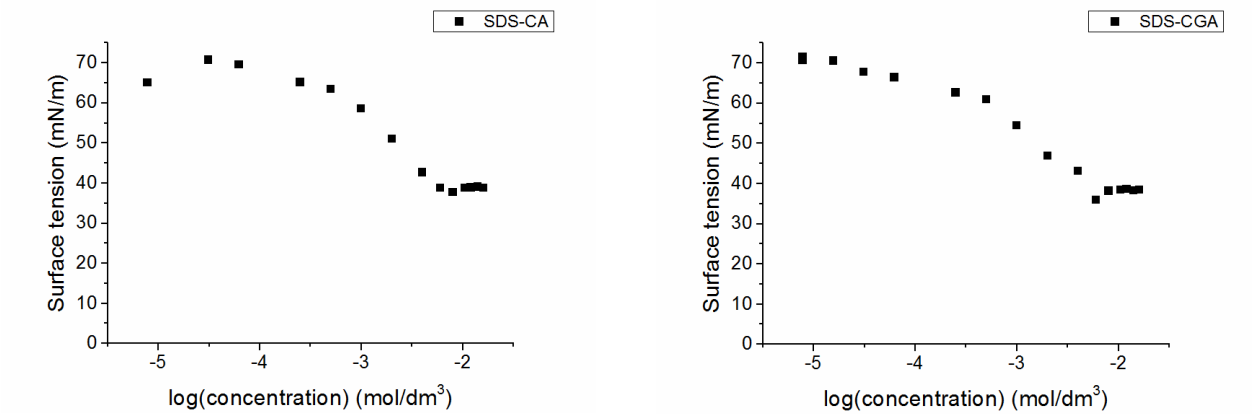

Figure 1. Surface tension isotherms of SDS-CA and SDS-CGA binary systems

The addition of CA or CGA resulted in the equilibrium between aggregates and monomers being achieved at a concentration of approximately 4.5 mmol/dm^3 for the binary systems, which is almost half the CMC value of the SDS solution without additives. For mixed micelles containing ionic surfactants, non-ideal behavior is usually observed as a result of synergistic or antagonistic phenomena (Naqvi and Panda, 2021). It is believed that achieving balance between the various forces allows the formation of mixed micelles, but the electrostatic forces between the heads are the most important in this process (Kabir-ud-Din et al., 2011). Similarly, in the analyzed case, the addition of both CA and CGA prevents the negatively charged SDS heads from mutual repulsion. The spontaneous nature of the micellization process is evidenced by negative values of the Gibbs free energy of micellization. Comparing the ΔG_m^0 values for both analyzed systems does not make it possible to conclude that the micellization process is more spontaneous and thermodynamically more favorable for either of them. Above insights regarding SDS-CA system are consistent with reports of Malik and Farooq (Malik and Farooq, 2022). Analysis values of the Gibbs free energy of micellization (ΔG_m^0) and the Gibbs energy of adsorption (ΔG_{ads}^0) allows to conclude that adsorption processes are preferred and micellization is certainly a secondary process to adsorption for the analyzed binary systems. Adsorption processes may occur with different dynamics within a few seconds or hours (Li et al., 2011). Estimated values of the Gibbs energy of adsorption of the analyzed systems, expose that for the SDS-CGA system the adsorption process at the interface occurs slightly easier. At the interface between the adsorbing SDS molecules, repulsive interactions generated by the anionic heads arise. CA and CGA molecules partially eliminate this phenomenon. It appears that the imidazolopyrimidine stem derived from CA causes less steric hindrance compared to the CGA molecule, and therefore shields the repulsive effect of the heads less effectively. The intercalation of molecules between the anionic heads of the surfactant also increases the surface area occupied by the head; the greater steric hindrance of CGA results in a higher A_{min} value compared to the system containing CA. In light of this, Γ_{max} adopts the opposite behavior.

Phenomenon consisting in eliminating the repulsive action of the heads is known and more often described for binary systems of two anionic and non-ionic surfactants (Kabir-ud-Din et al., 2011). There are also reports on mixed systems with high application potential, such as surfactant-drug systems. The obtained results for SDS-CA and SDS-CGA systems show similar trends with data known for surfactant-drug systems (Kumar et al., 2018; Nabi et al., 2018; Saha et al. 2023).

A parameter that correlates with the phenomena of surface activity, and in particular with the stability of the formed surface at the interface, is molar free energy at the maximum adsorption attained at CMC (G_{min}). It is assumed that the decrease in the value of G_{min} indicates an increase in the stability of the formed surface (Kabir-ud-Din et al., 2011). Comparison of the data obtained for both analyzed

systems indicates that a slightly more stable structure on the adsorbed surface is created by the SDS-CA binary system.

Determination of total antioxidant capacity (TAC) via FRAP assay

The effect of SDS concentration on the total antioxidant capacity of SDS-CA and SDS-CGA binary systems was determined spectrophotometrically using FRAP assay. It should be noted that the investigated solutions prepared within SDS-CA and SDS-CGA binary systems had a constant antioxidant (CA or CGA) concentrations, but differed in SDS concentrations which were in the range from 0 to 0.4 mmol/dm^3. The obtained results were shown in Table 2.

Table 2 Changes in FRAP values of tested binary systems depending on SDS concentration

C_{SDS} [mmol/dm^3]	FRAP value [mmol Fe^{2+}/g]	
	SDS-CA	SDS-CGA
0	not detected	5.53±0.02^a
$4\cdot10^{-3}$		5.50±0.05^a
$8\cdot10^{-3}$		5.58±0.11^a
$4\cdot10^{-2}$		5.66±0.02^{ab}
$8\cdot10^{-2}$		5.80±0.03^b
$4\cdot10^{-1}$		7.12±0.18^c

Mean values marked with different letters in the column were significantly different at α = 0.05

According to some authors (Vieira et al., 2020; León-Carmona and Galano, 2012) CA and its selected metabolites may be considered as effective antioxidants. Literature data confirm protective effect of CA against oxidative degradation of adenine and rat liver microsomes induced by hydroxyl radical (HO$^\bullet$) (Vieira et al., 2020). The available results of theoretical research confirmed a strong scavenging activity of CA towards hydroxyl radical (HO$^\bullet$), but indicated also weak or no activity toward alkoxylradical, hydroperoxyl radical (HOO$^\bullet$), and superoxide anion ($O_2^{\bullet-}$). Similarly, caffeine turned out to be inactive towards DPPH$^\bullet$ and $ABTS^{\bullet+}$ which are described in the literature as moderate hydrogen/electron scavengers (Petrucci et al., 2018). Nevertheless, there was lack of objective studies regarding the activity of CA or SDS-CA binary systems toward reduction of Fe^{3+} -TPTZ complex, that prompted the authors to conduct such research. The results of FRAP assay did not show the reducing activity of CA, and the addition of SDS did not change this property.

CGA is described in the literature as an phenolic antioxidant (Tošovic et al., 2017). Its radical scavenging activity towards DPPH$^\bullet$ radical, hydroxyl radical (HO$^\bullet$), superoxide anion ($O_2^{\bullet-}$), and peroxide nitride ($ONOO^-$) was emphasized in several studies and considered as comparable to those of ascorbic acid (Rojas-Gonzalez et al., 2022). On the other hand, so far, no studies have been conducted on the effect of surfactants concentration on the TAC of their binary systems with CGA.

In our research, the FRAP value of pure CGA was 5.53 mmol Fe^{2+}/g that is in line with the existing data (Hajimehdipoor et al., 2014). Analyzing SDS-CGA binary system no significant changes in FRAP value compared to pure CGA were observed at SDS concentrations ranging from $4\cdot10^{-3}$ mmol/dm^3 to $8\cdot10^{-3}$ mmol/dm^3, but at SDS concentrations above $4\cdot10^{-2}$ mmol/dm^3 the successively increase of FRAP values was found, i.e., with the increase in the SDS concentration in the system, the total antioxidant capacity also increased.

$$CGA \rightleftarrows CGA^- + H^+ \quad (8)$$

$$CGA^- + R^\cdot \rightarrow CGA^\cdot + R^- \quad (9)$$

$$CGA + R^- \rightarrow CGA^- + RH \quad (10)$$

The antioxidant activity of surfactant-antioxidant binary systems and its correlation with surfactant concentration has been already described in the literature and concerned binary systems such as ascorbic acid–CTAB, ascorbic acid–SDS, niacinamide-CTAB as well as catechin-SDS (Kwaśniewska and Kiewlicz, 2022a; Kwaśniewska and Kiewlicz, 2022b; Kiewlicz and Kwaśniewska, 2023; Laguerre et al., 2014). For all examples mentioned, an increase in total antioxidant capacity was associated with the increase in surfactant concentration in the system that is consistent with our results The explanation is related to antioxidative mechanism of CGA based on electron transfer, which is dominant in the case of FRAP method (Irshad et al., 2012). Literature data suggested that according to thermodynamic approach the sequential proton loss electron transfer (SPLET) mechanism (Equations 8-10) is more favorable than single electron transfer-proton transfer (SET-PT) mechanism (Marković and Tosović, 2016). The first step of SPLET mechanism is deprotonation (Eq. 8). In base environment CGA can form three types of monoanion: carboxylate anion and two phenolate anions. The first of them does not show the ability to spontaneously react with radicals by electron transfer while the phenolate anions may donate electrons to radicals turning them into the form R^- which may then act as base (Eq. 9-10) (Tosović et al., 2017). According to Tosović and Marković (2019), based on standard analytical approach, CGA in aqueous solution at pH of 7.4 exists primarily in the form of carboxylate monoanion and at lower concentration as dianion, that follows from experimental pK_a values. Due to the fact that the FRAP assay was conducted at pH

of 3.6, most likely the concentration of phenolate anions (pK_a= 8.21 and 12.5) in the rection mixture was minor while the dominant ionic form was carboxylate anion (pK_a= 3.35). It is assumed that the observed increase in the FRAP value at SDS concentrations above $4 \cdot 10^{-2}$ mmol/dm^3 may be a consequence of electrostatic interactions between CGA and surfactant molecules. Literature data show that negatively charged head groups of SDS repels anions while attracting H^+ ions and probably hereby may promote the first step of SPLET mechanism (Jaiswal et al., 2005; Kwaśniewska and Kiewlicz, 2022b). It should be noted that some authors (Jaiswal et al., 2005) described the possibility of shifting (increasing or decreasing) pK_a values of different compounds by anionic micelles, but these observations concerned surfactant concentrations much above the CMC value. In the studies conducted by Jaiswal et al. (2005) using the pH-metric and spectrophotometric techniques it was found that even at SDS concentrations of 10 mmol/dm^3, the effect of SDS micelles on the pK_a value of ascorbic and maleic acids was minor and suggested a slight decrease in the pK_a value. In our study, the SDS concentrations used were well below the CMC, therefore, only interactions between the antioxidant and monomeric surfactant molecules were considered.

IR analysis

In binary systems, various types of molecular interactions can be generated, including electrostatic, ion-dipole, steric, van der Waals and hydrogen interactions. Analysis of the infrared spectra of binary systems was used to assess the interaction between the head, tail of SDS and CA or CGA molecules. For the neat SDS solution spectrum, the antisymmetric stretching vibrations originating from the sulfate head group (ν_{as} S-O) are assigned a band at 1238 cm^{-1} and the band at 1087 cm^{-1} to the symmetric vibrations (ν_s S-O), what is consistent whit literature data (Weers et al., 1990). In turn, information about the conformation of alkyl chains can be obtained from the analysis of CH_2 scissoring region and C-H stretching region. In the case of the analyzed spectrum of the aqueous SDS solution, there is a band at 1635 cm^{-1} indicating the trans conformation observed for methylene chains. This band is not wide, which may be correlated with side-by-side interactions of the chains (Viana et al., 2012). The all-trans conformation of the hydrocarbon chain is also indicated by the bands: at 2916 cm^{-1} and 2977 cm^{-1} correlated with symmetric and asymmetric stretching vibrations. A low-intensity band is also visible at approximately 1467 cm^{-1}, its presence can be attributed to the end-gauche conformation of the CH_3 and CH_2 groups of the alkyl chain.

FTIR analysis of binary systems was used to confirm the existence of mutual interactions between individual components of the analyzed systems. Binary solutions intended for analysis were prepared assuming the use of SDS at two concentration variants, below and above CMC, and at the constant concentration of CA or CGA. Generally, it is believed that micellar processes, structural rearrangements of micelles and an increase in the ordering of surfactant alkyl chains will be accompanied by shifts in the wave number of the bands.

It is considered that interactions with the heads will cause disturbances in the local environment, resulting in a shift of the bands generated by the sulfate group. The shifts of the ν_{as} S-O bands probably result from a decrease in the symmetry of the sulfate group, which is the result of side interactions with additives (CGA) (Khodaparast et al., 2021). Spectra taken for SDS-CGA binary systems (Figure 2.), regardless of the SDS concentration, indicate large shifts of the bands originating from asymmetric and symmetric stretching vibrations characteristic of the sulfate head. This indicates the occurrence of lateral electrostatic interactions of the surfactant heads with CGA molecules. These interactions eliminate the repulsion of the anionic heads, influencing the change in the size of the surface occupied by the hydrophobic heads, but at the same time, the change in the symmetry of the heads results in the spatial reorganization of the tails. The increase in organization and probably the appearance of a larger number of trans conformers is visible in the infrared spectra with significant shifts in the bands assigned to asymmetric and symmetric stretching vibrations of methylene groups.

Surprisingly, no significant shifts of the ν_{as} S-O bands were found in the IR spectra (Figure 3.) of SDS-CA systems, which would indicate interactions of anionic heads with caffeine molecules, however, the A_{mni} value obtained on the basis of tensiometric measurements suggests the existence of this type of interaction. Less significant shifts of the discussed bands for SDS-CA systems compared to the SDS-CGA system may indicate that the steric hindrance generated by CA is smaller or that CA molecules interact with long SDS chains, as previously suggested (Tasneem et al., 2020). However, the presence of CA in the SDS solution probably did not change the conformation of the long chains, as evidenced by the presence of bands in an almost unchanged range (2917-2920, 2975-2977 cm^{-1}) compared to the SDS spectra.

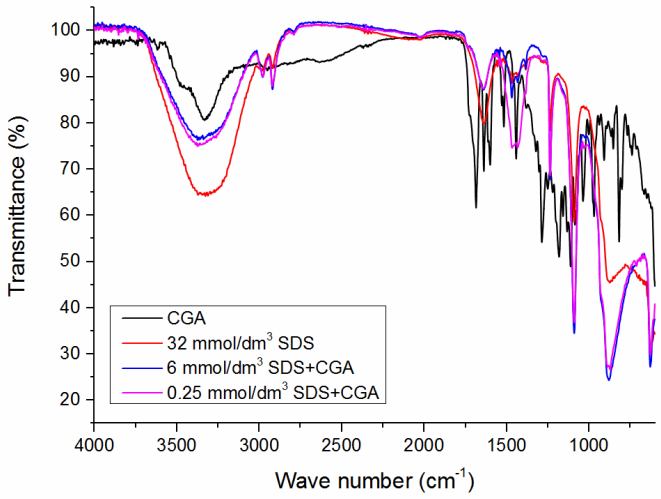

Figure 2. IR spectrum of the analyzed systems containing SDS and CA

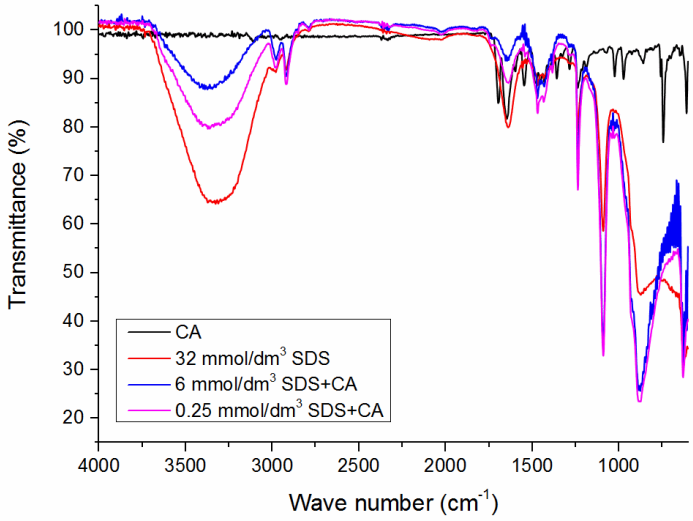

Figure 3. IR spectrum of the analyzed systems containing SDS and CA

UV-vis analysis

The UV-vis absorption spectra of investigated aqueous solutions were collected at spectral range 200 – 400 nm. The analyzed systems included pure CA solution, pure CGA solution, binary solutions of CA and SDS, and binary solutions of CGA and SDS. In binary solutions, a constant concentration of CA or CGA was used, while the SDS concentrations were respectively, 0.0, 0.2, 0.4, 2.0, 4.0 and 8.0 mmol/dm^3. The results of UV-vis analysis confirms the findings above. UV-vis absorption spectrum of pure caffeine, shown in Figure 4. (A), displays two absorption bands at λ_{max}=205 nm and λ_{max}=273 nm that is consistent with literature data (Gayathri et al., 2023). The first peak, at λ_{max}=205 nm, resulted from $\pi \rightarrow \pi^*$ transition related to the conjugation present in the ring and carbonyl groups, while the second one, at λ_{max}=273 nm, resulted from $n \rightarrow \pi^*$ transition associated with presence of carbonyl groups (Gayathri et al., 2023). As can be seen in Figure 4 (A), the successively increase in SDS concentration in the SDS-CA system caused changes in UV-vis spectra such as splitting of the absorption band at the wavelengths ranging from 200 to 245 nm. Moreover, at SDS concentration of 4 and 8 mmol/dm^3 a slight hyperchromic effect for both absorption bands was identified. Literature data suggested that increase in the intensity of absorption bands as we observed may be related with chromophore association (Sigurdson et al., 2016). The SDS concentrations at which the hyperchromic effect was observed correspond to the region at which micelle formation can be expected and the observed effects may be due to the interactions between CA and surfactant head groups.

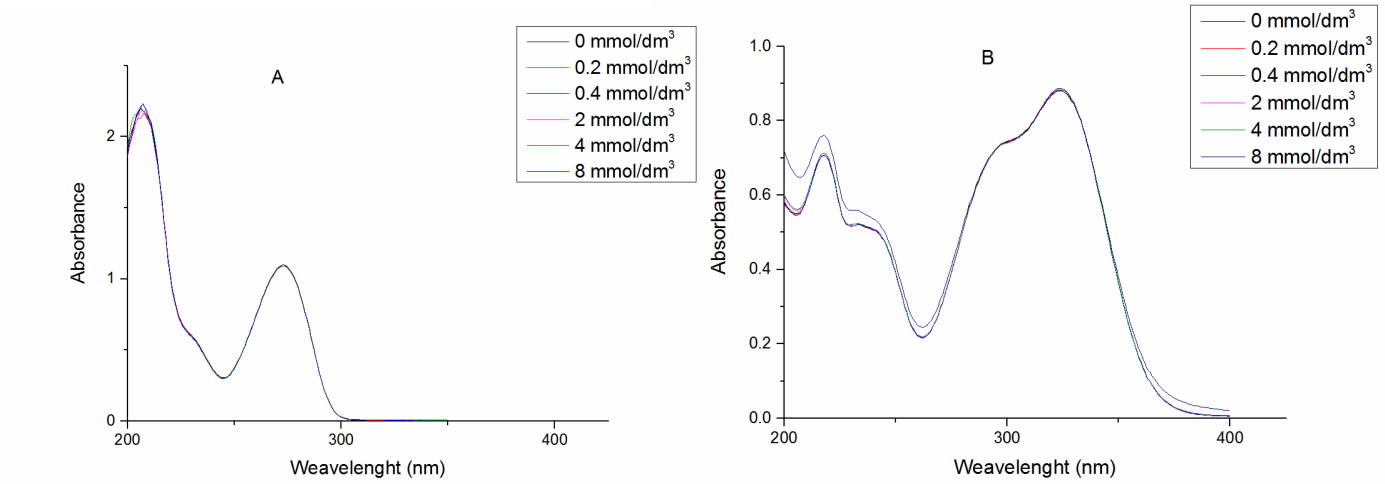

Figure 4. The UV–vis absorption spectra of SDS-CA (A) and SDS-CGA (B) systems at various SDS concentrations (marked with different colors)

According to Tasneem et al. (2020) CA is incorporated into the micelle structure due to strong ion-dipolar attraction, with the most favorable interactions between the polar N atoms of caffeine ring attached with -CH_3 group with the anionic head groups (SO_4^-) of SDS. Presumably, this kind of interaction is also responsible for the changes within the absorption band at the wavelengths ranging from 200 to 245 nm.

UV-vis absorption spectrum of CGA (Figure 4. (B)) was characterized by two main absorption bands with the maxima at λ_{max}=218 nm and λ_{max}=324 nm. These results are comparable to those obtained by other authors (Belay and Gholap, 2009, Tosović and Marković, 2016). According to literature data (Tosović and Marković, 2016), the most intensive absorption band with maximum at λ_{max}=324 nm corresponds to $\pi \rightarrow \pi^*$ transition from orbitals delocalized over the caffeic moiety. Whereas, the band at λ_{max}=218 nm may be attributed to $\pi \rightarrow \pi^*$ electronic transition within carbonyl groups. Figure 4. (B) shows that for SDS-CGA binary systems, as SDS concentration increased the absorption value at λ_{max}=218 nm also increased. The most pronounced changes in absorbance values at this point concerned SDS concentration of 8 mmol/dm^3 and similarly to the case of CA may indicate the incorporation of CGA molecules into the micelle structures. An analogous phenomenon of increasing absorbance values with increasing SDS concentration, caused by the penetration of solute molecules into the micelles, has been described in the literature for binary systems containing SDS and flavonoids, e.g. kaempferol. The authors pointed out that after incorporation of molecule into the micelle structure the chromophores still oriented at the surface of the micelles absorb light more favorably than that of the molecules dispersed in bulk aqueous phase which is reflected in hyperchromic effect. (Naseem et al., 2004). It might be expected that analogous effect resulting from the location of chlorogenic acid chromophores oriented at the surface of the micelles would concern also investigated SDS-CGA system.

Determination of the emulsion thermal stability

Stability is an important parameter that determines the quality of the product. Typically, emulsion destabilization may occur by creaming, sedimentation, flocculation, and coalescing, and the factors limiting emulsion stability are temperature, centrifugation, stirring, and shaking.

SDS, in accordance with the guidelines of U. S. Food and Drug Administration, is defined as “the food multipurpose additive permitted for direct addition to food for human consumption” as an emulsifier, a whipping agent, surfactant or wetting agent, and besides that is also a popular emulsifier used in non-food formulations (FDA, 2024; Banipal et al., 2016). SDS as an emulsifier exhibits typical properties attributed to a single ionic emulsifier. Too low a concentration that does not ensure electrostatic stabilization leads to coalescence. A concentration close to CMC allows obtaining an emulsion resistant to coalescence and creaming. Higher concentrations associated with excess surfactant lead to destabilization of the emulsion (Dickinson and Ritzoulis, 2000). In this study, an emulsion characterized by a significant excess of emulsifier was prepared, assuming that it would be a system with less stability, and then an attempt was made to determine the impact of the addition of CA and CGA on this quality parameter.

In the discussed O/W emulsion, SDS particles are adsorbed on the rapeseed oil droplets, which acts as an emulsifier, reducing the surface tension at the oil-

water interface. The anionic SDS heads orient towards the water phase, giving the oil droplets a negative charge. The repulsion of negatively charged droplets prevents the flocculation of particles and thus prolongs the stability of the emulsion. As can be seen in Figure 6., the addition of CA and CGA improved the stability of the emulsion. This suggests that the presence of CA or CGA induces greater migration of surfactant molecules to the phase barrier. Additionally, the obtained results (Figure 5) indicate that even a small addition (0.04%) of CA/CGA improves the stability of the emulsion.

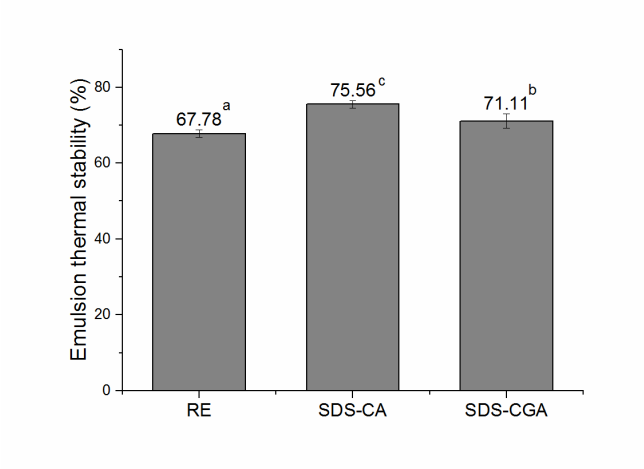

Figure 5. The thermal stability of emulsions with the addition of caffeine (SDS-CA), chlorogenic acid (SDS-CGA) and reference emulsion (RE). Mean values marked with different letters were significantly different at $\alpha = 0.05$

CONCLUSIONS

Achieving food quality that is satisfactory for the consumer is currently associated with meeting a number of requirements regarding: taste, smell, appearance, form, texture and durability. This result can be obtained by using food additives, the most frequently used are emulsifiers. Although the conditions for safe use and, consequently, the standards of acceptable daily intake for emulsifiers are known, literature reports indicate a negative impact of the consumption of emulsifiers on the intestinal microbiota, the occurrence of inflammation and the possibility of cancer (Sellem et all 2024).

The disturbing data should encourage consideration of the possibility of limiting the use of food additives. The expected effect would be to modify the recipe in such a way that the useful effect of the emulsifier is maintained while limiting its concentration in the product. In their model studies, the authors attempted to assess the influence of caffeine and chlorogenic acid on the functional activity of SDS as an emulsifier. The decision to choose caffeine and chlorogenic acid was determined by reports of their health-promoting activity. Which is also in line with observable market trends related to functional food.

The conducted studies indicated that in the model system, the addition of caffeine and chlorogenic acid influenced the reduction of the surface tension of the system containing SDS. Surface activity correlates with the emulsifying potential, which suggests that in appropriately selected concentrations, SDS-caffeine/chlorogenic acid systems will exhibit comparable emulsifying properties to SDS used alone in a higher concentration. Analysis of thermal stability indicated a slightly higher stability of emulsions containing SDS and the addition of caffeine/chlorogenic acid than the emulsion in which only SDS was used as an emulsifier.

The enrichment of food with antioxidants is important for two reasons: their health-promoting effect and the ability to extend the oxidative stability of product. The antiradical activity of chlorogenic acid and caffeine is widely known, but our studies have shown that the addition of SDS at concentrations above 4 10^{-2} mmol/dm^3 improves the antioxidant effectiveness of chlorogenic acid.

REFERENCES

1. Ai, C. (2023). Recent advances on the emulsifying properties of dietary polysaccharides. *eFood*, 4(4), e106. DOI: 10.1002/efd2.106
2. Alfakeer, M., Rub, M. A., Azum, N., Marwani, H. M., Alamry, K. A., Hoque, M. A., Asiri, A. M. (2024). Interaction of antidepressant drug with surfactant mixture in various compositions: effect of electrolyte and urea. *Chem. Pap.* 78(1), 23-34.

3. Awwad, S., Issa, R., Alnsour, L., Albals, D., Al-Momani, I. (2021). Quantification of caffeine and chlorogenic acid in green and roasted coffee samples using HPLC-DAD and evaluation of the effect of degree of roasting on their levels. *Molecules*, 26(24), 7502. DOI: 10.3390/molecules26247502
4. Banipal, T., Kaur, H., Kaur, A. and Banipal, P.K. (2016). Effect of tartarate and citrate based food additives on the micellar properties of sodium dodecylsulfate for prospective use as food emulsifier. *Food Chem.* 190, 599-606. DOI: 10.1016/j.foodchem.2015.05.130.
5. Belay, A., Gholap, A.V. (2009). Characterization and determination of chlorogenic acids (CGA) in coffee beans by UV-Vis spectroscopy. *Afr. J. Pure Appl. Chem.* 3, 234–40. DOI: 10.5897/AJPAC.
6. Belay, A., Ture, K., Redi, M., Asfaw, A. (2008). Measurement of caffeine in coffee beans with UV/vis spectrometer. *Food Chem.* 108, 310–315. DOI: 10.1016/j.foodchem.2007.10.024.
7. Benzie, I.F.F., Strain, J.J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. *Anal. Biochem.* 239, 70-76.
8. Chauhan, S., Chauhan, M. S., Sharma, P., Rana, D. S. (2013). Thermodynamics and micellization of cetyltrimethyl ammonium bromide in the presence of lysozyme. *J. Mol. Liq.* 187, 1-6. DOI: 10.1016/j.molliq.2013.06.001
9. Dickinson, E., Ritzoulis, C. (2000). Creaming and rheology of oil-in-water emulsions containing sodium dodecyl sulfate and sodium caseinate. *J. Colloid Interface Sci.* 224(1), 148-154. DOI: 10.1006/jcis.1999.6682
10. Food and Drug Administration, (2024). Code of Federal Regulations Title 21 —Food and Drugs. Chapter I —Food and Drug Administration Department of Health and Human Services. Subchapter B —Food for Human Consumption. Part 172 —Food Additives Permitted for Direct Addition to Food for Human Consumption. Subpart I —Multipurpose Additives. Sec. 172.822. Sodium lauryl sulfate (up to date as of 2/29/2024). https://www.ecfr.gov/current/title-21/chapter-I/subchapter-B/part-172/subpart-I/section-172.822.
11. Gayathri, G., D'Souza, J.Q., Sundaram, N.G. (2023). UV induced photocatalytic degradation of caffeine using TiO_2–H-beta zeolite composite. *Minerals*, 13, 465. DOI: 10.3390/min13040465.
12. Hafizah, M. A. E., Riyadi, A. F., Manaf, A. (2019, April). Particle size reduction of polyaniline assisted by anionic emulsifier of sodium dodecyl sulphate (SDS) through emulsion polymerization. In IOP Conference Series: Materials Science and Engineering (Vol. 515, No. 1, p. 012080). IOP Publishing. DOI: 10.1088/1757-899X/515/1/012080
13. Hajimehdipoor, H., Shahrestani, R., Shekarchi, M. (2014). Investigating the synergistic antioxidant effects of some flavonoid and phenolic compounds. *Res. J. Pharmacogn (RJP)*, 1, 35-40.
14. Halmos, E.P., Mack, A., Gibson, P.R. (2019). Review article: emulsifiers in the food supply and implications for gastrointestinal disease, *Aliment Pharmacol Ther.* 49, 41–50, DOI: 10.1111/apt.15045
15. Irshad, M., Zafaryab, M., Singh, M., Rizvi, M.M. (2012). Comparative analysis of the antioxidant activity of Cassia fistula extracts. *Int. J. Med. Chem.* 2012, 157125. DOI: 10.1155/2012/157125.
16. Jaiswal, P.V, Ijeri, V.S., Srivastava, A.K. (2005). Effect of surfactants on the dissociation constants of ascorbic and maleic acids. *Colloids Surf. B: Biointerfaces.* 46, 45-51. DOI: 10.1016/j.colsurfb.2005.09.001.
17. Kabir-ud-Din, Sharma, G., Naqvi, A. Z. (2011). Micellization and interfacial behavior of binary surfactant mixtures based on cationic geminis and nonionic Tweens. *Colloids Surf. A: Physicochem. Eng.* 385(1-3), 63-71. DOI: 10.1016/j.colsurfa.2011.05.053
18. Kasiri, N., Fathi, M. (2018). Production of cellulose nanocrystals from pistachio shells and their application for stabilizing Pickering emulsions. *Int. J. Biol. Macromol.* 106, 1023-1031. DOI: 10.1016/j.ijbiomac.2017.08.112
19. Kaur, R., Sharma, M., Ji D., Xu M, Agyei D. (2020). Structural features, modification, and functionalities of beta-glucan. *Fibers*, 8(1), 1. DOI: 10.3390/fib8010001
20. Khodaparast, S., Sharratt, W. N., Tyagi, G., Dalgliesh, R. M., Robles, E. S., Cabral, J. T. (2021). Pure and mixed aqueous micellar solutions of Sodium Dodecyl sulfate (SDS) and Dimethyldodecyl Amine Oxide (DDAO): Role of temperature and composition. *J. Colloid Interface Sci.* 582, 1116-1127. DOI: 10.1016/j.jcis.2020.08.002
21. Kiewlicz, J., Kwaśniewska, D. (2023). Study of the properties of binary systems: Selected derivatives of B-vitamins-cationic surfactant. *J. Mol. Liq.* 374, Article 121237. DOI: 10.1016/j.molliq.2023.121237.
22. Kumar, D., Rub, M. A., Azum, N., Asiri, A. M. (2018). Mixed micellization study of ibuprofen (sodium salt) and cationic surfactant (conventional as well as gemini). *J. Phys. Org. Chem.*, 31(1), e3730. DOI: 10.1002/poc.3730

23. Kwaśniewska, D., Kiewlicz, J. (2022a). Spectroscopic and tensiometric considerations on anionic surfactants (SDS) and ascorbic acid/ascorbates interactions. *J. Saudi Chem. Soc.* 26, 101532. DOI: 10.1016/j.jscs.2022.101532.
24. Kwaśniewska, D., Kiewlicz, J. (2022b). Study of interaction between cationic surfactant (CTAB) and ascorbic acid/ascorbic acids derivatives by tensiometric and spectroscopic methods. *J. Mol. Liq.* 354, 118917. DOI: 10.1016/j.molliq.2022.118917118917.
25. Laguerre, M., Hugouvieux, V., Cavusoglu, N., Aubert, F., Lafuma, A., Fulcrand, H., Poncet-Legrand, C. (2014). Probing the micellar solubilisation and inter-micellar exchange of polyphenols using the DPPH free radical. *Food Chem.* 149, 114-120. DOI: 10.1016/j.foodchem.2013.10.034.
26. León-Carmona, J.R., Galano, A. (2012). Free radical scavenging activity of caffeine's metabolites. *Int. J. Quantum Chem.* 112, 3472-3478. DOI: 10.1002/qua.24084.
27. Li, N., Zhang, G., Ge, J., Luchao, J., Jianqiang, Z., Baodong, D., Pei, H. (2011). Adsorption behavior of betaine-type surfactant on quartz sand. *Energy Fuels.* 25 4430–4437. DOI: 10.1021/ef200616b.
28. Liu, Y., Wu, Q., Zhang, J., Yan, W., Mao, X. (2024). Food emulsions stabilized by proteins and emulsifiers: A review of the mechanistic explorations, *Int. J. Biol. Macromol.* 261, 129795. DOI: 10.1016/j.ijbiomac.2024.129795
29. Malik, N. A., Farooq, U. (2022). Effect of caffeine on the micellization and related thermodynamic parameters of sodium dodecyl sulphate, hexadecyltrimethylammonium bromide and triton x-100: a physicochemical study. *Phys. Chem. Liq.* 60(2), 265-274. DOI: 10.1080/00319104.2021.1949594
30. Marković, S., Tošović, J. (2016). Comparative study of the antioxidative activities of caffeoylquinic and caffeic acids, *Food Chem.* 210, 585-592. DOI: 10.1016/j.foodchem.2016.05.019.
31. McClements, D.J., Jafari, S.M. (2018). Improving emulsion formation, stability and performance using mixed emulsifiers: A review, *Adv. Colloid Interface Sci.* , 251, 55-79, DOI: 10.1016/j.cis.2017.12.001.
32. Nabi, A., Tasneem, S., Jesudason, C. G., Lee, V. S., Zain, S. B. M. (2018). Study of interaction between cationic surfactant (CTAB) and paracetamol by electrical conductivity, tensiometric and spectroscopic methods. *J. Mol. Liq.* 256, 100-107. DOI: 10.1016/j.molliq.2018.01.185
33. Naqvi, A. Z., Panda, M. (2021). Mixed micellization: Improved physicochemical behavior of different amphiphiles in presence of gemini surfactants. *J. Mol. Liq.* 343, 116876. DOI: 10.1016/j.molliq.2021.116876
34. Naseem, B., Sabri, A., Hasan, A., Sakhawat Shah, S. (2004). Interaction of flavonoids within organized molecular assemblies of anionic surfactant. *Colloids Surf. B: Biointerfaces.* 35, 7–13. DOI: 10.1016/j.colsurfb.2004.01.012.
35. Navarra, G., Moschetti, M., Guarrasi,V., Mangione, M.R., Militello, V., Leone, M. (2017). Simultaneous determination of caffeine and chlorogenic acids in green coffee by UV/Vis spectroscopy. *J. Chem.* 6435086. DOI: 10.1155/2017/6435086.
36. Petrucci, R., Zollo, G., Curulli, A., Marrosu, G. (2018). A new insight into the oxidative mechanism of caffeine and related methylxanthines in aprotic medium: May caffeine be really considered as an antioxidant? *Biochim. Biophys. Acta - Gen. Subj.* 1862, 1781-1789. DOI: 10.1016/j.bbagen.2018.05.011.
37. Rojas-González, A., Figueroa-Hernández, C. Y., González-Rios, O., Suárez-Quiroz, M. L., González-Amaro, R. M., Hernández-Estrada, Z. J., Rayas-Duarte, P. (2022). Coffee chlorogenic acids incorporation for bioactivity enhancement of foods: A review. *Molecules*, 27(11), 3400. DOI: 10.3390/molecules27113400
38. Saha, U., De, R., Das, B. (2023). Interactions between Loaded Drugs and Surfactant Molecules in Micellar Drug Delivery Systems: A Critical Review. *J. Mol. Liq.*, 382, 121906. DOI: 10.1016/j.molliq.2023.121906
39. Sellem, L., Srour, B., Javaux, G., Chazelas, E., Chassaing, B., Viennois, E., Debras, C., Druesne-Pecollo, N., Esseddik, Y., Szabo de Edelenyi,F., Arnault, N, Agaësse, C., De Sa, A., Lutchia, R., Huybrechts, I., Scalbert, A., Pierre, F., Coumoul, X., Julia, C., Kesse-Guyot, E., Allès, B., Galan, P., Hercberg, S., Deschasaux-Tanguy, D., Touvier, M. (2024). Food additive emulsifiers and cancer risk: Results from the French prospective NutriNet-Santé cohort. *Plos Med.* 21(2), e1004338
40. Sheng, R., Ding, Q. Y., Ren, Z. H., Li, D. N., Fan, S. C., Quan, X. F., Wang, Y., Yi. M. T., Zhang, Y. X., Cao, Y. X. Wang, H., Wang, J. R., Zhang, Q. H., Qian, Z. B. (2021). Interfacial and micellization behavior of binary mixture of amino sulfonate amphoteric surfactant and octadecyltrimethyl ammonium bromide: Effect of short chain alcohol and its chain length. *J. Mol. Liq.* 334, 116064. DOI: 10.1016/j.molliq.2021.116064

41. Sigurdson, G.T., Robbins, R.J., Collins, T.M, Giusti, M.M. (2016). Evaluating the role of metal ions in the bathochromic and hyperchromic responses of cyanidin derivatives in acidic and alkaline pH, *Food Chem.* 208, 26–34. DOI: 10.1016/j.foodchem.2016.03.109
42. Tadros, TF, (2013) Emulsion Formation, Stability, and Rheology. In: Tadros, TF (ed.) *Emulsion Formation and Stability* (pp. 1– 75). Wiley-VCH Verlag GmbH & Co. KGaA., Weinheim DOI: 10.1002/9783527647941.ch1
43. Tajik, N., Tajik, M., Mack, I., Enck, P. (2017). The potential effects of chlorogenic acid, the main phenolic components in coffee, on health: a comprehensive review of the literature. *Eur. J. Nutr.* 56, 2215-2244. DOI: 10.1007/s00394-017-1379-1
44. Tasneem, S., Nabi, A., Hasan, N., Malik, M. A., Khedher, K. M. (2020). Thermodynamic insights into molecular interactions of sodium lauryl sulfate (SLS) with caffeine and theophylline in aqueous media at different temperatures. *J. Mol. Liq.*, 305, 112776. DOI: 10.1016/j.molliq.2020.112776.
45. Thomson, B. M., Campbell, D. M., Cressey, P., Egan, U., Horn, B. (2014). Energy drink consumption and impact on caffeine risk. *Food Addit. Contam. Part A.* 31(9), 1476-1488. DOI: 10.1080/19440049.2014.940608.
46. Tošović, J., Marković, S. (2016). Structural and antioxidative features of chlorogenic acid. *Croat. Chem. Acta.* 89, 535–541. DOI: 10.5562/cca3026.
47. Tošović, J., Marković, S. (2019). Antioxidative activity of chlorogenic acid relative to trolox in aqueous solution – DFT study. *Food Chem.*, 278, 469-475. DOI: 10.1016/j.foodchem.2018.11.070.
48. Tošović, J., Marković, S., Dimitrić Marković, J.M., Mojović, M., Milenković, D. (2017). Antioxidative mechanisms in chlorogenic acid. *Food Chem.* 237, 390-398. DOI: 10.1016/j.foodchem.2017.05.080.
49. Viana, R. B., da Silva, A. B., Pimentel, A. S. (2012). Infrared spectroscopy of anionic, cationic, and zwitterionic surfactants. *Adv. Phys. Chem.* 2012. DOI: 10.1155/2012/903272.
50. Vieira, A.J.S.C., Gaspar, A.M., Santos, P.M.P. (2020). Mechanisms of potential antioxidant activity of caffeine. *Radiat Phys Chem.* 174, 108968. DOI: 10.1016/j.radphyschem.2020.108968.
51. Weers, J. G., Rathman, J. F., Scheuing, D. R. (1990). Structure/performance relationships in long chain dimethylamine oxide/sodium dodecylsulfate surfactant mixtures. *Colloid Polym. Sci.*, 268, 832-846. DOI: 10.1007/BF0141096.1
52. Zhou, Q., Rosen, M. J. (2003). Molecular interactions of surfactants in mixed monolayers at the air/aqueous solution interface and in mixed micelles in aqueous media: the regular solution approach. *Langmuir* 19(11), 4555-4562. DOI: 10.1021/la020789m.