

Analysis of Three Detergent Products and Identification of Surface Active Agents by Infrared Absorption Spectra and a Reflectance Graph

Chryssou K*, Stassinopoulou M and Lampi E

General Chemical State Laboratory, B' Chemical Division of Athens, Department A'Tsocha
16, 11521 Athens, Greece

Research Article

Received date: 06/04/2020;

Accepted date: 11/04/2020;

Published date: 16/04/2020;

*For Correspondence:

General Chemical State Laboratory, B'
Chemical Division of Athens, Department
A'Tsocha 16, 11521 Athens, Greece, Tel :
+306972192070

E-mail: katerinachrysou1967@gmail.com;
katerinachrysou@outlook.com

Keywords: Detergent, Surface active agent,
FT IR spectra, Kubelka-Munk expression,
Diffuse reflectance spectra.

ABSTRACT

Three types of commonly used detergents (i.e. detergent for all surfaces Ajax Fkte des Fleurs by Colgate Palmolive, dishwashing detergent maki by AlindaVelco, limescale remover spray Nuevo Kirikoantical made by Casa Kiriko S.L. Spain) have been analyzed with the mixed indicator titration method which makes use of the mixed indicator dimidium bromide/disulphine blue. Also the use of infrared spectroscopy for qualitative identification of the anionic and non-ionic surfactants present in them is reported. Diffuse reflectance spectra (DRS) analysis is applied for the third detergent product. From the diffuse reflectance spectra the band gap energy (Eg) of the material has been estimated. This method has been investigated with a single integrating sphere system over the visible wavelength range.

INTRODUCTION

Surfactants are amphiphilic compounds which have very wide application due to their ability to reduce surface tension, increase the solubility of many substances connected with micelle formation and detergency power^[1]. Two fundamental properties of surfactants their tendency to adsorb at the interfaces, and to form micellar aggregates are connected with changes in water structure when an aqueous solution is applied.

The Kubelka-Munk theory is an analytical solution of a radiative transfer equation. The simplicity of the Kubelka-Munk method has been the reason for its widespread uses. This model has been studied and tested by several research groups on chemical substances as well as biological tissues. Thus, high color strengths are observed in a C14 glucose-based surfactant^[2]. The 14-G surfactant produced the strongest color (K/S) indicating the optimal dyeing effect. Glucose is widely available in nature and is one of the constituent units in starch, cellulose and glycogen. Glucose is used as a raw material to synthesize non-ionic surfactants. The properties of these surfactants are modified using fatty alcohols with varying carbon chain lengths to produce a series of biodegradable surfactants. The color difference test showed that the 08-G surfactant exhibited the least difference in color, indicating more even dye coverage. When arranged according to fluorescence intensity, the surfactants were in the descending order of 16G>14G>08G>10G>12G matching the results of the surface tension analysis^[2].

Surfactants are compounds which have ionic centres of different charge in their molecules. Most often a cationic part is a quaternary ammonium group. On the other hand the anionic group is typically a carboxylic acid, sulfonic acid, sulfuric acid

ester and phosphoric acid ester. The adsorption properties and micelle lifetime of a surfactant compound significantly depend on the length of its alkyl chain^[3].

In this work three detergent products were analyzed and identified with their infrared absorption spectra. The detergents analyzed were a mixture of anionic surfactants and non-ionic surfactants. The first detergent sample consists of a mixture of C10-13 alkyl benzene sodium sulfonate, decan-1-ol ethoxylated, and sodium laureth sulfate, and glutaral. The second detergent sample consists of a mixture of alcohols C12-14 ethoxylated sulfates sodium salts, and benzene sulfonic acid C10-13 alkyl derivatives sodium salts. The third detergent sample consists of a mixture of alcohols C12-13 branched and linear ethoxylated C>5-10 (E.O. moles), trisodiumdicarboxymethylalaninate and citric acid.

The multi-spanning membrane proteins usually require solubilization to allow proper purification and characterization, which generally impairs their structural and functional integrity^[4]. We know also that the selection of a proper biomimetic system is crucial for the structural and functional studies of membrane proteins. Here in this work in order to select a suitable surfactant to properly solubilize and stabilize particular membrane proteins we here have tested various detergents to assess their spectral properties, and structural state. These surfactant mixtures could potentially be used for solubilization of multi-spanning membrane proteins.

EXPERIMENTAL CRITERIA

Reagents

- All compounds were AR quality and they were used without further purification. All solutions were prepared using deionized water of conductivity <1 μ S/cm.
- Hyamine 1622 0,004M solution (Benzethonium chloride standard volumetric solution c (CHCINO)=0,004mol/l, Merck 1.15480.1000 HC892461 Barcode4022536160498
- Ethanol absolute anhydrous (1L) Carlo Erba UN1170 Gradient grade
- Ethanol 95% v/v solution, neutralized to the phenolphthalein solution
- Sulphuric acid RPE 0,5M (1N) For analysis Carlo Erba UN 2796
- Sulfuric acid standard solution 2,5M Fluka Analytical 1L Sigma-Aldrich UN 2796 M.W.: 98,08 g/mol
- Sodium hydroxide 0.1N (N/10) RPE UN 1824 For analysis Carlo Erba
- Potassium hydroxide approximately 0,5N standard volumetric solution in ethanol
- KOH (Potassium hydroxide) 1Kg ERFAR, MW: 56,11, DAB 6, B.P. 1968
- Phenolphthalein 1% w/v in ethanol 95 °
- Water solution 0,1%v/v of 2,7-dichlorofluorescein indicator
- Chloroform AG PENTA 1000 ml Batch No. 2110271016, Product code 17130-11000
- PAN indicator 0.1% w/w solution of 1- (2-pyridylazo)-2-naphthol in ethanol
- Copper (II) sulfate standard volumetric solution c (CuSO) 0,0100mol/l
- PotassioPermanganato N/10 Carlo ErbaNormex Cod. 473591 PP900101

Apparatus

- pH-meter Metrohm 716 DMS Titrino, Swiss made
- Analytical balance Mettler Toledo AB 204-S/FACT accurate to 0,1mg, maximum capacity 220g
- Oven Memmertdirekt, capable of being controlled at 103 °C \pm 2 °C
- Water bath FALC, 220/240V, 50Hz
- FT-IR Spectrometer Perkin Elmer Inc Spectrum 2000 Version 5.0.2 Copyright 2004
- Spectrophotometer CM-3630 BCMTS M Type 40605, S.N. 43029, TouchScreen-M V 2.0, Frank-PTI

Ordinary laboratory apparatus

- Beakers of capacity 250 ml, 500 ml volumetric flasks, burette capacity 50ml.

Sample preparation

The samples of the detergent samples were analyzed directly and no sample preparation was required on the finished detergent products.

Analysis of detergent products

Preparation of the mixed acid indicator stock solution: We weighed 0,5g of dimidium bromide into a 100 ml beaker and we added 20 ml of hot 10%v/v ethanol to the beaker. We weighed 0,25g of Disulfine Blue VN 150 into a second beaker and we added to it 30 ml of hot 10%v/v ethanol. We stirred the two solutions until dissolved and we transferred the two

solutions to a 250 ml one-mark volumetric flask. We rinsed the beakers into the volumetric flask with the hot 10%v/v ethanol and we diluted to the mark with the ethanol.

Preparation of the acid solution of the mixed indicator solution: We added 100 ml of water to 10 ml of the stock solution (2.5.1.1.) in a 250 ml one-mark volumetric flask. We added 10 ml of 2.5M (5N) sulfuric acid solution, we mixed and we diluted to the mark with water. We stored it in the dark.

Preparation of water solution 0,1%v/v of 2,7-dichlorofluorescein indicator: We weighed 0.1g of 2,7-dichlorofluorescein into a 100 ml one-mark volumetric flask and we diluted to the mark with the water.

Determination of soluble-insoluble matter ethanolic 95% w/v: We weighed 18,2381 g of the detergent sample 1, or 15,1808 g of the detergent sample 2, or 15,7813 g of the detergent sample 3, in a 250 ml beaker. We added 75 ml ethanol 95% w/v and we heated on a water bath for 2 hours while stirring often with a glass rod. The glass beaker was covered with a watch glass all time. We then dried a filter paper to be used for the filtration of the insoluble matter, in the oven controlled at $103^{\circ} \pm 2^{\circ}\text{C}$ for 1hour. We allowed it to cool to ambient temperature in a desiccator for 20min and we weighed it to be about 0,9990 g. We placed it in a funnel mounted on a glass container on the water bath. When the dissolution of the detergent appeared to be complete, we decanted the supernatant liquid, on to the filter paper. After decantation we added 25 ml of ethanol 95% w/v to the 250 ml glass beaker and after heating it to near its boiling point, we transferred the insoluble matter to the filter paper with the aid of small quantities of the warm ethanol. The filter paper and the residue were washed with the warm ethanol until entirely free from detergent. We then dried the filter paper in air and we placed it in the oven at $103^{\circ} \pm 2^{\circ}\text{C}$. After 1hour we removed the filter paper and we left it in the desiccator for 20min for it to cool, and we weighed it. Yield: 0,0044 g, 0,024% w/w for detergent sample1; Yield: 0,0135 g, 0,09% w/w for detergent sample 2; Yield: 0,0085 g, 0,05% w/w for detergent sample 3. The ethanolic solution of the filtrate in the glass container on the water bath was then heated. We evaporated off all of the ethanolic solution. We then heated the glass container with the soluble matter to constant mass in the oven controlled at $103^{\circ} \pm 2^{\circ}\text{C}$. We finally cooled it in a desiccator and we weighed its contents. Yield: 0,3043g, 1,67% w/w for detergent sample 1; Yield: 1,2429 g, 8,19% w/w for detergent sample 2; Yield: 0,3733 g, 2,37% w/w for detergent sample 3.

Determination of the anionic-active matter content by manual direct two-phase titration procedure : We weighed 30,1480g of the detergent sample 1 product, or 8,1621g of the detergent sample 2 product, or 15,0589g of the detergent sample 3 product, into a 250 ml beaker, an amount of laboratory sample which contained about 0,004mol of the anionic-active matter. We transferred quantitatively to a 500 ml one-mark volumetric flask with ground glass stopper and we diluted to the mark with water. We mixed thoroughly and by means of a pipette we transferred 20 ml of this solution to a measuring cylinder. We then added a few drops of the phenolphthalein solution, and we neutralized it to a faint pink colour with the sodium hydroxide solution 0,1M as required. We then added to the measuring cylinder solution 10 ml of water, 15 ml of chloroform and finally 10 ml of the mixed indicator solution. We then titrated against the benzethonium chloride solution. We stoppered the measuring cylinder after each addition of the Hyamine 1622, 0,004M, and we shook it well. Then the lower chloroform layer was coloured pink. We continued the titration with repeated vigorous shaking. As the end point approached, the emulsion formed during shaking, tended to break easily. We continued the titration drop by drop shaking after each addition of titrant until the end point was reached. The end point was reached at the moment when the pink colour was completely discharged from the chloroform layer, which became a faint greyish blue color. Volume of benzethonium chloride solution used: 8,8 ml for detergent sample 1; Volume of benzethonium chloride solution used: 14,0 ml for detergent sample 2; Volume of benzethonium chloride solution used: 0,0 ml for detergent sample 3.

Yield: 1,02% w/w from 60,296g of detergent sample 1 in 1Lt water deionized solution; Yield: 5,98% w/w from 16,3242g of detergent sample 2 in 1Lt water deionized solution; Yield: 0,00% w/w from 30,1178g of detergent sample 3 in 1Lt water deionized solution

Determination of soap by manual direct two phase titration procedure in detergent: We weighed 30,1480g into a 250 ml beaker of the detergent sample 1 product, or 8,1621g of the detergent sample 2 product, or 15,0589g of the detergent sample 3 product, which contained about 0,004mol of soap. We transferred quantitatively to a 500 ml one-mark volumetric flask with ground glass stopper and we diluted to the mark with water. We mixed thoroughly and by means of a pipette we transferred 20 ml of this solution to a marked measuring cylinder. We then added to the measuring cylinder solution 10 ml of water and 5 drops of the indicator solution 2,7-dichlorofluorescein 0,1%v/v. We then added 15 ml of chloroform and finally 2 ml ethanolic solution KOH 0,5M. We then titrated against the benzethonium chloride solution. We stoppered the measuring cylinder after each addition of the Hyamine 1622 0,004M, and we shook it well. Then the lower chloroform layer was coloured yellow. We continued the titration with repeated vigorous shaking. As the end point approached the emulsion formed during shaking tended to break and coloured faintly pink. We continued the titration drop by drop, shaking after each addition of titrant, until the end point was reached. This was at the moment when the faintly pink colour from the chloroform layer became a strong pink. Volume of benzethonium chloride solution for detergent sample 1 product : (9,3ml-8,8ml): 0,5 ml, Yield: 0,05% w/w soap in the detergent sample 1 product; Volume of benzethonium chloride solution for detergent sample 2 product : (14,4ml-14,0ml): 0,4 ml, Yield: 0,16% w/w soap in the detergent sample 2 product; Volume of

benzethonium chloride solution for detergent sample 3 product : 0,0 ml, Yield: 0,00% w/w soap for the detergent sample 3 product.

Determination of chelating agent content with titration: We weighed 10,0338g of the detergent sample 1, or 10,2209g of the detergent sample 2, into a conical flask. We added 100 ml of warm water to the test portion and stirred vigorously to dissolve. After the operation of dissolution we introduced the electrodes, connected to previously calibrated pH-meter and added hydrochloric acid solution until the pH was $4,6 \pm 0,5$ (i.e., pH 4,98 for detergent sample 1; pH 4,27 for detergent sample 2). We raised, rinsed and removed the electrodes. We added 0,4 ml of the PAN indicator solution. We heated to about 60 °C and we titrated with the copper (II) sulfate solution until the indicator changed from yellow to wine-red (i.e. 0,1 ml of CuSO₄ for detergent sample 1; 0,2 ml of CuSO₄ for detergent sample 2). The wine-red colour persisted for at least 1min. Yield: 0,003% w/w EDTA for the detergent sample 1 product; Yield: 0,006% w/w EDTA for the detergent sample 2 product.

RESULTS AND DISCUSSION

Determination of pH

We measured the pH of the detergent sample 1 solution as it is to be pH 7,0 at 25,3 °C in the Metrohm 716 DMS Titrimo pH-meter. We prepared a 1% w/w solution of the detergent sample 1 solution in deionized water and we measured pH=8,0 at a temperature of 25,4 °C in the Metrohm 716 DMS Titrimo pH-meter. We then prepared a 10% w/w solution of the detergent sample 1 solution and we measured pH=7,6 at a temperature of 25,3 °C in the Metrohm 716 DMS Titrimo pH-meter.

We measured the pH of the detergent sample 2 solution as it is to be pH 7,1 at 25,4 °C in the Metrohm 716 DMS Titrimo pH-meter. We prepared a 1%w/w solution of the detergent sample 2 solution in deionized water and we measured pH=7,8 at a temperature of 25,3 °C in the Metrohm 716 DMS Titrimo pH-meter. We then prepared a 10% w/w solution of the detergent sample 2 solution and we measured pH=7,4 at a temperature of 25,4 °C in the Metrohm 716 DMS Titrimo pH-meter.

We also measured the pH of the detergent sample 3 solution as it is to be pH 2,4 at 23,5 °C in the Metrohm 716 DMS Titrimo pH-meter. We prepared a 1% w/w solution of the detergent sample 3 solution in deionized water and we measured pH=3,29 at a temperature of 23,5 °C in the Metrohm 716 DMS Titrimo pH-meter. We then prepared a 10% w/w solution of the detergent sample 3 solution and we measured pH=2,75 at a temperature of 23,4 °C in the Metrohm 716 DMS Titrimo pH-meter. All measurements were done in duplicate and the average values are reported. The measurement uncertainty in the analysis of pH was $\pm 4\%$ (Uexpanded).

Acidity of the hydrocarbon in the detergent sample three product

In the discussion of the relative acidity of the carboxylic acid citric acid present in the detergent sample 3 product, the thermodynamic acidity, expressed as the acid dissociation constant, is taken as the measure of acidity. We measure the dissociation constant of this acid present in the detergent sample three product mixture in aqueous media by measurement of the titration curve with a pH-sensitive electrode (pH meter). The determination of the relative acidity of most carbon acids is difficult. Because they are weak acids strong bases such as NaOH are required to cause their deprotonation. The acidity of an acid solvent system may be specified by the Hammet acidity function H_0 : $RH + B \rightarrow R^- + BH$. The $pK_{RH}^{[5]}$ is determined by the titration curve with a pH-sensitive electrode by measurement of the ratio (RH): (R-) at the known H_0 . $pK_{RH} = H_0 + \log(RH)/(R^-)$ (1).

$pK_{RH} = -\log(2,74) + \log(0,06/3,94) = -2,2550$. The acid dissociation constant K_{RH} is calculated as $1,7992 \times 10^2$ at 29,3 °C and is taken as the measure of acidity. Any reaction will have associated with it a change in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) which are independent of the reaction path. The value of free energy (ΔG) is related to the equilibrium constant K for the reaction by the equation $\Delta G = -RT \ln K_{RH} = -(8,314 \text{ JK}^{-1} \text{ mol}^{-1}) \cdot (302,47 \text{ K mol}) \cdot (\ln 179,924) = -13,057 \text{ KJ} < 0$ (2), where R is the gas constant, and K is the temperature in Kelvin. The above reaction is thermodynamically favorable since $\Delta G < 0$ is a negative number. The above measurements and calculations provide a useful measure of the relative hydrogen ion activity of concentrated acid solutions that are used in the study of reactions that proceed only at high acid concentration.

Acquisition of IR-spectra

Infrared transmittance data: The infrared spectra were recorded in the solid state. The material of the ATR crystal was diamond.

For compounds containing sulfur-oxygen bonds (FT-IR spectrum, **Figure 1**) the absorption of the organic sulfates is at the 1408 cm^{-1} peak and at the 1377 cm^{-1} peak. The asymmetric (higher frequency, shorter wavelength) and symmetric S=O

stretching frequency for the compounds sulfonates is at 1204cm^{-1} . For sulfonate salts is at 1048cm^{-1} . Various strong S-O-C stretching absorptions appear between 1013cm^{-1} and 833cm^{-1} .

The α,β -unsaturated and aryl conjugated acids show absorption of the dimer at the 1734cm^{-1} peak.

At 1112cm^{-1} there is the alcoholic C-O absorption for the saturated tertiary and secondary high symmetrical alcohols. The C-O stretching vibrations in alcohols and phenols generally produce a strong band in the $1260\text{-}1000\text{cm}^{-1}$ region of the spectrum. The C-O stretching mode is coupled with the adjacent C-C stretching vibration, thus in primary alcohols the vibration might better be described as an asymmetric C-C-O stretching vibration. Thus the C-C ring stretch appears here at 1462cm^{-1} . This long wavelength band is the stronger of the two.

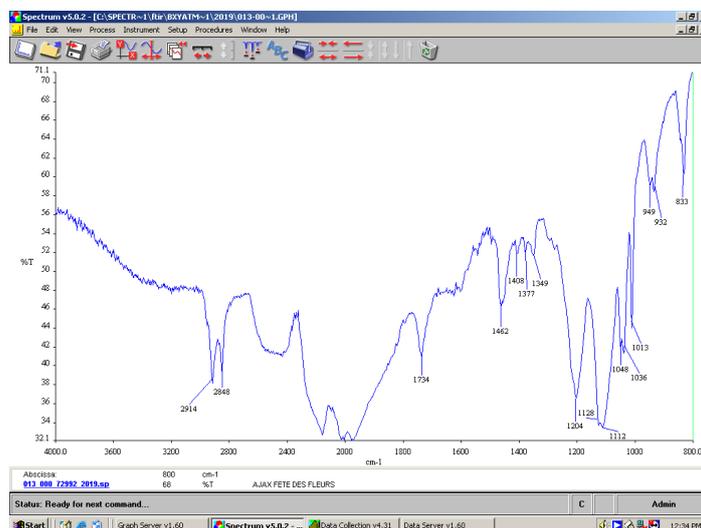


Figure 1. FT-IR spectrum of the detergent sample 1 product as it is showing the absorptions of the anionic and the non-ionic surfactant.

The symmetric S=O stretching frequency of sulfonic acids (FT- IR spectrum **Figure 2**) appears at 1150cm^{-1} . There is also the C-O stretching mode which is coupled with the adjacent C-C stretching vibration in alcohols and phenols. Thus for the alcohols C12-14-ethoxylated sulfates sodium salts the vibration might better be described as an asymmetric C-C-O stretching vibration at 1101cm^{-1} . The C-O stretching vibration in alcohols and phenols produce in general a strong band in the region $1260\text{-}1000\text{cm}^{-1}$. We also have the C-H bend for linear alcohols. There is a pair of bands for the gem di-methyl groups at 1377cm^{-1} and at 1351cm^{-1} . Also for the alcohol saturated secondary or α -unsaturated or cyclic tert there is the absorption at 1126cm^{-1} .

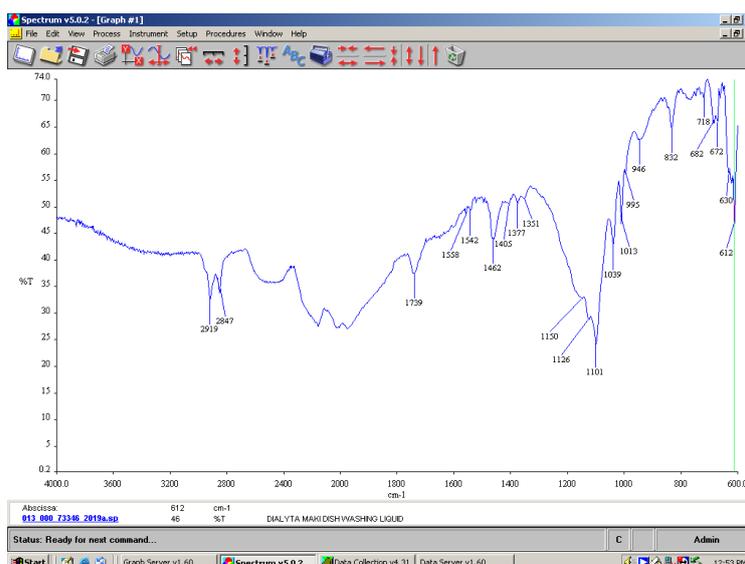


Figure 2. FT-IR spectrum of the detergent sample 2 product as it is showing the absorptions of the anionic and the non-ionic surfactant.

In **Figures 1 and 2** there are the spectrums of the finished products of anionic surfactants containing both C10-13 Alkyl Benzene sodium sulfonate. We note that even though the peak of interest is due to SO₃ in each case, there is some shifting of the position of that peak as evidenced by the wavenumbers listed 1204cm⁻¹ against 1150cm⁻¹.

In the below spectrum (FT-IR spectrum, **Figure 3**) there appears the C-O stretching vibration at 1099cm⁻¹, which is for the alcohols present and is a strong band. There is also the C=O stretch at 1732cm⁻¹ because of the trisodiumdicarboxymethylalaninate [6-8] present in the sample, and is the frequency of the carbonyl absorption. This absorption is lower frequency than that due to normal ester C=O stretch at 1740cm⁻¹. This phenomenon is due to unsaturation with the carbonyl group which causes this C=O stretch to be lower than normal frequency.

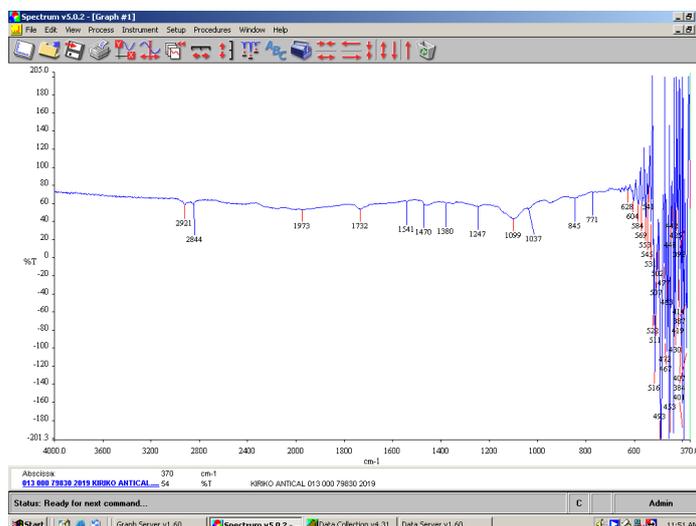


Figure 3. FT-IR spectrum of the detergent sample 3 product as it is showing the absorption of the non-ionic surfactant.

The assayed sample standard raw materials were carefully assayed by the determination of soluble-insoluble matter ethanolic 95% w/v method and the results are summarized in the **Table 1** below. The percentage of yield in **Table 1** is calculated as [(mass of soluble matter ethanolic in g)/(mass of detergent sample in g)]*100. Also the percentage of yield in **Table 1** is calculated as [(mass of insoluble matter ethanolic in g)/(mass of detergent sample in g)]*100.

The assayed sample standard raw materials were carefully assayed using the mixed indicator titration method and the results are summarized in the **Table 2** below. The anionic active matter in **Table 2** is calculated as [(volume V in ml of Hyamine 1622 used)*0,004 M* (348,49 g/mol)*5]/(mass of detergent in 1L solution)}. Also the soap present in the detergent samples in **Table 2** is calculated as [(volume (V'-V) in ml of Hyamine 1622 used)*0,004* (326 g/mol)*5]/(mass of detergent in 1L solution)}. The samples analyzed and their wavenumbers of maximum absorbance are summarized in the **Tables 3 and 4** below:

Table 1. The assayed sample standard raw materials which were assayed by the determination of soluble-insoluble matter ethanolic 95%w/v method in gr.

Detergent sample	Soluble matter ethanolic 95% w/w	Insoluble matter ethanolic 95% w/v	Non-ionic surfactant
(1)18,2381g	0,3043g Yield: 1,67% w/w	0,0044g, Yield: 0,024% w/	0,60% w/w
(2)15,1808g	1,2429g Yield: 8,19% w/w	0,0135g, Yield: 0,09% w/w	2,05% w/w
(3)15,7813g	0,3733g Yield: 2,37% w/w	0,0085g, Yield: 0,05% w/w	2,37% w/w

Table 2. The assayed sample standard raw materials which were assayed using the mixed indicator titration method in gr, and the relevant results as % anionic-active matter and % soap are presented.

Detergent sample	Anionic –active matter	Soap
(1) 60,296g in 1Lt	1,02% w/w	0,05%w/w
(2) 16,3242g in 1Lt	5,98% w/w	0,16%w/w
(3) 30,1178g in 1Lt	0,0% w/w	0,0%w/w

Table 3. The maximums of the S=O stretching vibrations of the two different anionic surfactants are listed.

Sample	Wavenumber of max S=O stretching Abs (cm ⁻¹)
Anionic surfactant names:	
C10-13 AlkylBenzene Sodium Sulfonate (Figure 1)	1204
Benzenesulfonic acid, C10-13-alkyl derivs., sodium salts (Figure 2)	1150

The shifting of these absorbance bands is due to changes in the structural features of each anionic surfactant molecule present into its detergent mixture.

Table 4. The C-O stretching vibrations of the three different alcohols present in the three detergent products are listed. Sample analyzed and its wavenumber of maximum C-O stretch vibration in alcohols absorbance.

Sample	Wavenumber of max C-O stretching Abs (cm ⁻¹)
Non-ionic surfactant names	
Decan-1-ol, ethoxylated (Figure 1)	1112
Alcohols, C12-14, ethoxylated sulfates, sodium salts (Figure 2)	1101
Alcohols C12-13-branched and linear, ethoxylated (>5-10E.O.moles) (Figure 3)	1099

Alcohols produce in general a strong band in the region 1260-1000cm⁻¹. The differences in the maximum of absorbances are due to coupling of the C-O vibration with the adjacent C-C stretching vibrations of the molecules of the three different detergent sample mixtures.

Calculation of Kubelka-Munk K/S values for the third detergent product (absorption coefficient/scattering coefficient ratio)

The K/S ratio for the third detergent product was found K/S=2,69 which contains only a nonionic surfactant [2,6,9]. The reflectance ISO brightness used was measured 7,25%. The ISO brightness measured is the numerical value of the reflectance of the detergent sample 3 product at 457nm, blue light reflectance.

In this work the Kubelka-Munk theory is used for predicting optical properties for the third detergent product. The appearance of this detergent is the result of its optical properties. As known the Kubelka-Munk theory is based on the assumption that the interaction between the diffuse light and the liquid detergent material can be described in terms of two fundamental optical constants. The specific scattering coefficient (S) and the specific absorption coefficient (K). Although the Kubelka-Munk theory holds strictly for homogeneous materials only, it works also for detergent solutions containing more than one substances. The equation of Kubelka-Munk used above is: $K/S = (1-R)^2/2R$ (3) where K is the absorption or coefficient of reflectivity and S is the coefficient of light scattering; R is the observed reflectivity for monochromatic light. The Kubelka-Munk expression is for reflectance R, of a partly absorbing, partly reflecting, light scattering surface which is depended on the reflectivity R_s of the observed surface. In this work the simplified equation $F(R_s) = (1-R_s)^2/2R_s = K/S$ (4) is used in order to relate the chromophore concentration present to the intensity of the sample diffuse reflection (Tables 5 and 6).

Table 5. The properties of the third detergent product are presented i.e. its ISO Brightness value, its Opacity value, and its pH value.

Property	Detergent sample 3	
ISO Brightness (ISO 2470-1):	7,25%	
Opacity (ISO 2471):	73,69%	
pH (1% w/w solution) (EN ISO 1262/1996)	3,29	T=23,5°C+273,16°C=296,7K
pH (10% w/w solution) (EN ISO 1262/1996)	2,75	T=23,4°C+273,16°C=296,6K

pH (as it is solution) (EN ISO 1262/1996)	2,42	T=23,5°C+273,16°C=296,7K
---	------	--------------------------

Table 6. In the table CIE L*, a*, b* values for the detergent sample three product are presented, as well as of the calibration standard used, and the ΔE^* = $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ value is calculated L*(C/2) a*(C/2) b*(C/2) ΔE^* .

Variables	L* (C/2)	a* (C/2)	b* (C/2)	ΔE^*
standard	96,66	-0,134	-0,296	
Detergent sample 3	31,26	-0,86	-1,96	65,45

Temperature has an effect of both pH buffers and solutions, as the hydrogen ion activity increases with increasing pH. From the two K/S ratio calculated above we can assume that light absorption is high in the third surfactant indicating the presence of more colored matter other than anionic matter which is converted to heat thereby reducing the brightness of the detergent product sample 3.

CIE L*a*b* values for the third detergent analyzed

The color of the third detergent in the CIE L*a*b* system for illuminant C/2 is L*=31,26, a*=-0,86 and b*=-1,96. L is the measure of lightness and varies from 100 for a perfect white to 0 for the absolute black. Here -a indicates the greenness of the detergent and -b indicates its blueness. Here the color measured indicates the presence of a green blue detergent. The CIE whiteness D65/10° measured is 27% while the function $W=L+3a-3b$, gives $W=31,26+3*(-0,86)-3*(-1,96)=28\%$ which is the CIE whiteness C/2°. The CIE D65/10° whiteness -UV is 18% which indicates fluorescent whitening agents present. Theoretically the maximum reflectance that can be obtained by removal of light absorbing bodies is 100% (measured against MgO) at all wavelengths between 400 nm and 700 nm. Whites are normally preferred with a higher radiance in the 420 nm to 450 nm region than in other ranges of the visible spectrum; this is the region in which naturally yellowed substrates show a deficiency in reflectance T. The FWA's that exhibit their strongest emission in the 420 nm to 450 nm region are able to compensate for the deficiency in blue reflectance of the detergent substrate and to contribute additional radiance to produce the appearance of preferred whites. This is why whiteners are used in detergents and other laundry products. The opacity calculated for the third detergent is 73,69% and the transparency is 51,20% (Figures 4 and 5).

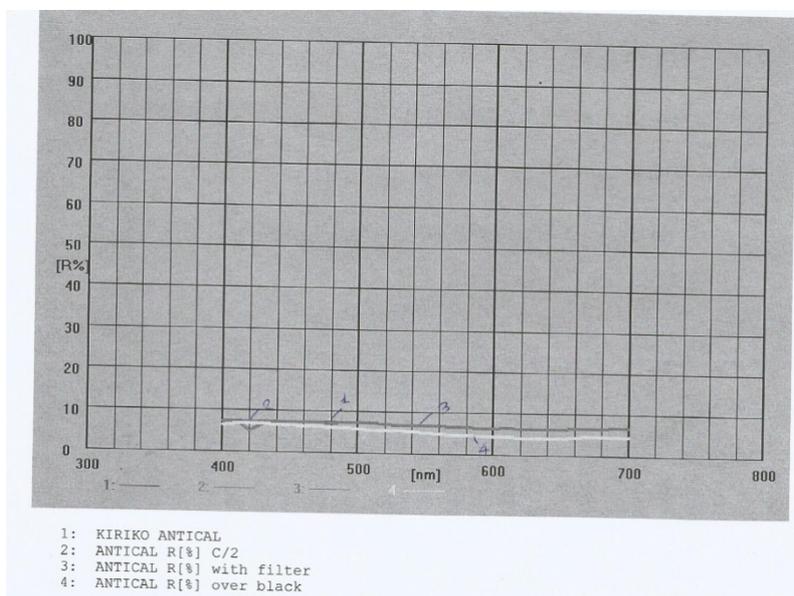


Figure 4. Reflectance graph for the third detergent product in an aqueous solution.

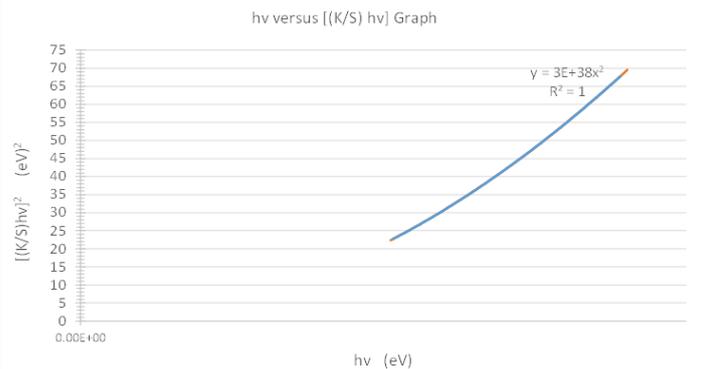


Figure 5. $h\nu$ versus $[(K/S) h\nu]^2$ of the chromophore in third detergent product in an aqueous solution.

Estimation of band gap energy (E_g) from DRS studies for the third detergent product

The reflectance graph of the molecules of detergent sample 3 may be discussed also in terms of the chromophore it contains. In the detergent product three there is trisodiumdicarboxymethyl al

aninate which has the common chromophore carbonyl group. The $\pi^* \leftarrow n$ transition in the carbonyl group which normally occurs in the vicinity of 290 nm involves a removal of the electron density on the oxygen to the carbon to a slight extent, because the non-bonding orbital is confined to the oxygen whereas the π^* -orbital extends over both atoms. The shift of $\pi^* \leftarrow n$ transition to higher transition energies occurs in the mixture of the third detergent product because the chromophore i.e. the carbonyl group, is immersed in water which is a polar solvent and which is also a hydrogen-bonding solvent; the ground state favours a particular conformation of the surrounding solvent but the transition occurs in a time too short for complete reorientation of the solvent, and so while the lower state is stabilized by an interacting solvent the upper state is stabilized to only a lesser extent and consequently the transition moves to higher energies. Of course the $\pi^* \leftarrow n$ transition is forbidden, but partially allowed. But intensity may be acquired by the transition by virtue of the fact that the non-bonding orbital is not strictly localized and is not pure p_x but also a major source of intensity is the coupling of the electronic and vibrational modes of the molecule to give rise to vibronic transition. The $\pi^* \leftarrow \pi$ transition on the other hand is allowed and the transition dipole moment is directed along the direction of the bond. This transition reduces the strength of the bond because a bonding electron is transferred to an antibonding orbital. This reduction may be important that the bonded $-ONa$ groups of the trisodiumdicarboxymethylalaninate molecule may twist about the bond direction in order to reduce the antibonding effect. Finally the carbonyl intensity stems from an out-of-plane bending vibration.

Diffuse Reflectance Spectroscopy (DRS) is a simple but powerful spectroscopic tool to estimate the band gap energy (E_g) of samples unambiguously. The band gap energy (E_g) is a characteristic feature of all materials which determines their application potential. It depends not only on the material but on its characteristics like crystallinity and stoichiometry. The band gap is obtained from optical absorption edge energy, which is the minimum photon energy required to excite an electron from the highest occupied molecular orbital to the lowest occupied molecular orbital. These are electronic transitions of the direct type. The direct transitions require only that photons excite electrons. When the sample in solution is radiated with light a portion is reflected at its surface and the remaining enters the solution and diffuses. As the light of particular length is absorbed by the sample the measurement of the diffuse reflected light at different wavelengths yields the diffuse reflectance spectrum (DRS). We determine here the band gap of small amount of sample. The intensity of diffused reflectance spectrum in the limiting case of infinitely thick sample is expressed by the Kubelka-Munk equation $F(R_\infty) = (1-R_\infty)/2R_\infty = K/S$ (4), where K is the absorption coefficient and S is the scattering coefficient which varies with the size of the molecule present in the detergent sample and density. A graph is plotted between $(K/S h\nu)^2$ as ordinate and $h\nu$ as abscissa [9,10]. The extrapolation of straight line to $(K/S h\nu)^2 = 0$ axis (Tauc Plot) gives the value of the band gap energy. In this work estimation of the band gap energy from DRS studies is performed for the third detergent product.

From the plot of $h\nu$ versus $[(K/S) h\nu]^2$ (Figure 5) the band gap energy (E_g) of the material in the third detergent product in aqueous solution is estimated as $1.86217E-19$ eV. The band gap energy was calculated from the function trend in the excel spreadsheet with data calculated for the whole range 400-700 nm. The range of wavelength used was 400-700 nm. The electronic spectra of polyatomic molecules have complexity. Their absorption depends on their structure caused by blurred vibrational and rotational transitions. Also their absorption may be due to a transition involving a particular group of atoms in their molecule. Such a group the chromophore occurs in different types of molecules and gives rise to an absorption band at about the same wavenumber. Thus the absorption spectrum of the molecule may be based on the chromophores present and the perturbations caused by the presence of other groups also present in the detergent sample.

CONCLUSION

In conclusion, the FTIR method and the Reflectance graph, are simple, accurate and easily applicable methods to the identification of finished products of surfactant samples. Presently, we are investigating the use of FTIR for a more wide variety of detergent products.

REFERENCES

1. Manko D, et al. Adsorption and aggregation activity of sodium dodecyl sulfate and rhamnolipid mixture. *J SurfactDeterg* 2017;20: 411-423.
2. Lin LH, et al. Surface Properties of glucose-based surfactants and their application in textile dyeing with natural dyes. *J SurfactDeterg* 2019;22: 73-83.
3. KwasniewskaD,et al . Synthesis and interfacial activity of novel heterogeminisulfobetaines in Aqueous solution. *J SurfactDeterg* 2015;18: 477-486.
4. Ganapathy S, et al. Membrane matters: The impact of a nanodisc-bilayer or a detergent microenvironment on the properties of two eubacterialrhodopsins. *Biochimica et BiophysicaActa (BBA)-Biomembranes* 1862;2: 1-36.
5. Steward R, et al. A Comparison of the acidity and basicity of aromatic amines *Canadian. J Chem* 1967;45: 925-928.
6. Kairaliyeva T, et al. Surface tension and adsorption studies by drop profile analysis tensiometry. *J SurfactDeterg* 2017;20: 1225-1241.
7. Grzadka E. The Adsorption layer in the system: Carboxymethylcellulose/Surfactants/NaCl/MnO₂. *J SurfactDeterg* 2012;15: 513-521.
8. Greber KE. Synthesis and surface activity of cationic amino acid-based surfactants in aqueous solution. *J SurfactDeterg* 2017;20: 1189-1196.
9. Shahin A. et al. Polystyrene microsphere optical properties by Kubelka-Munk and diffusion approximation with a single integrating sphere system: A comparative study. *J Spectrosc*2019.
10. Aneesh PM, et al. Hydrothermal synthesis and characterization of undoped and Eu-Doped ZnGa₂O₄ Nanoparticles. *J Electrochem* 2009;156: 33-36.