Journal of Basic and Environmental Sciences 4 (2017) 94-106

ISSN
Online: 2356-6388
Print: 2536-9202

Research Article Open Access

Synthesis of nonionic polymeric surfactants with amide oxime terminal groups

A. M. F. Eissa[a], M. A. Radwan[b], M. M. Azab[a], M. El Hefnawy[b], M. M. Deef Allah[b].

Chemistry department, Faculty of Science, Faculty of engineering, Benha University, Benha, Egypt

Abstract

Nonionic polymeric surfactants were prepared by formation of polymer from reaction of allyl alcohol with acrylonitrile. Then product reacted with different fatty acids (Capric, myrestic and stearic) inorder to obtain half ester polymer. Then propylene oxide was added directly to polymer (5, 10, 15 and 20 mole), in the presence of KOH as catalyst, then nitrile group in polymer react with hydroxyl amine in the presence of NaOH to obtain amide oxime nonionic surfactants. The unique structural features of these compounds were confirmed by IR and ^{1}HNMR spectra. Molecular weights of polymers were determined and physical properties of polymers were evaluated. The surface properties of these compounds such as surface tension, interfacial tension, cloud point, wetting power, foam power, emulsification stability, critical micelle concentration, effectiveness, minimum surface area maximum surface excess and hydrophile-lipophile balance were evaluated. Stability to hydrolysis in acidic and alkaline medium was determined. Thermodynaomic parameters were evaluated at different temperature. The biodegradability in aqueous medium was evaluated.

Keywords: Surfactant, surface tension, CMC, thermodynamic parameters biodegradability.
Received; 15 Jul. 2014, In Revised form; 2 May.2014, Accepted; 2 Aug.2016, Available online 1 Jan., 2017

1. Introduction.

Surfactants or surface active agents are molecules that possess at least two parts in their chemical structure, i.e. hydrophobic and hydrophilic groups, and are sometimes called amphiphiles [1, 2].

In recent years, polymeric surfactants containing both hydrophilic segments have attracted considerable interest because of their amphiphilic molecular structure. They are very versatile products and have found applications in emulsion polymerization [3], enhanced oil recovery [4], lubricating oil additives [5], biomedical materials [6], Langmuir-Blodgett films, biomimetism [7], etc. Thus, extensive studies in academic and industrial laboratories have focused on the development of functional polymeric surfactants, especially those containing unsaturated bonds. Such functional surfactants can be used as emulsifiers in emulsion polymerization and can copolymerize with latex, thus providing it with excellent stability against high electrolyte concentrations, freeze-thaw cycling, and high shear rates.

Environmental considerations are a major driving force in the development of new surfactants. As a result of increasing legislative pressure, more environmentally benign products are continually replacing conventional surfactants. The most important property of these surfactants is that they break down rapidly in the environment, i.e., has a good biodegradability profile [8].

In this study nonionic polymeric surface active agents containing long chain fatty acids of low coast, economically and environmentally friendly were prepared. The surface activity, foaming ability and thermodynamic properties of the produced surfactants were determined. In addition, the biodegradability of the synthesized nonionic surfactants was tested.

2. Experimental

2.1. Materials and medium

Acrylo nitrile and allyl alcohol (Alpha), fatty acids (Capric, myrestic and stearic acids)[Fluka Chemika],propylene oxide(Aldrich),p-toluene sulphonic acid, hydroxylamine hydrochloride and potassium hydroxide (Winlab,98%), Benzoyl peroxide(BDH Co.) was used and repreciptating by addition of excess methyl alcohol, filtered and dried, m.p. 102-105°C.

All solvents (dimethylformamide, methylene chloride, methanol and xylene) were dried and supplied by (Al-Gomhuria Co.,Egypt). Paraffin oil (Aldrich,dynamic viscosity; 110-230 mPa s,density;0.827-0.890 g/ml at

20ºC). The water used for measuring surface properties was distilled twice.

Methods

2.2.1 Copolymerization reaction

The copolymers were obtained by the solution polymerization techniques shown in scheme1. The monomers were placed in polymerization tubes and diluted with methylene chloride (acrylo nitrile placed with allyl alcohol). The polymerization was initiated by adding 1 mol % benzoyl peroxide as a free radical initiator. The tubes were flushed with nitrogen gas for about 20 min then sealed and thermostated at 65ºC for about 17-30 hr depending on monomer pairs and composition.

The copolymers were obtained by reprecipitation from petroleum ether (40-60) and finally vaccum at 60ºC. Then the product polymer was cooled and neutralized with sodium hydroxide solution [9].

2.2.2 Preparation of half ester polymer

Polymer prepared was esterified by different molar amounts of fatty acid (decanoic,myrectic and stearic acids) individually and respectively with polymer in a molar ratio 2:1 in a sufficient amount of xylene and 0.1% by weight of p-toluene sulphonic acid under condition until the theoretical amount of water was obtained. The product was washed with a hot supersaturated sodium chloride solution. Then, the organic layer which contains the products was separated and the solvent was distilled off under vaccum [10].

2.2.3 Oxypropylation of half ester polymer

0.5 wt% KOH solutions containing 0.01 mol of the prepared half ester polymer was stirred and heated to 70ºC while passing a slow stream to nitrogen through the system to flush out oxygen. The nitrogen stream was stopped and propylene oxide was added drop-wise with continuous stirring and heating under an efficient reflux system to retain the propylene oxide. The reaction was conducted for different intervals of time ranging from 1-10hr.the apparatus was then filled with nitrogen and cooled. The reaction vessel was weighed. The amount of reacted propylene oxide and the average degree of propoxylation were determined from the increment in the mass of the reaction mixture [11,12]. The selected average numbers of moles n, 5, 10, 15 and 20.

2.2.4 Preparation of nonionic oxypropylated amide oxime surfactants

Hydroxylamine hydrochloride (3.5 g, 51 mmole) in methanol (30 ml) was added to sodium hydroxide (2.11 g, 50 mmole) in methanol (30 ml) at ºC, and insoluble solids were separated off by filtration. To this filtrate (20 mmole) of polymer containing nitrile in methanol (40 ml) was dropped and the mixture was stirred at room temperature for 24 h. (The pH of this mixture was ranged from 5-7 under these conditions). After filtration and subsequent evaporation of the filtrate, methylene chloride (50 ml) was added to the residue. Insoluble solids were filtered off again, and the crude product was obtained by the evaporation of filtrate [13].

3. Analysis

IR spectra were obtained with a Shimadzu (Kyoto, Japan) IR 470, and 'H-NMR spectra were obtained with a Varian USA EM 390 spectrometer at 90 MHz with dimethylsulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as a zero reference.

4. Measurements

4.1 surface tension and interfacial tension measurements

Surface tension measurements were obtained using a De-Noüy Tensiometer (Kruss-K6 type; Germany) with a platinum ring device. A freshly prepared aqueous solution of the synthesized surfactants.

In deionized water was prepared with a concentration range of 0.01-0.00001 M at 30 ºC. The ring was washed twice after each reading, first by ethanol then by distilled water. The apparent surface tension was measured 5 times for each sample within a 2-min interval between each reading. Interfacial tension was measured between two layers of surfactant solution and light paraffin oil at 25.0 ± 0.5 ºC .The surfactant solution (15 ml of 0.1% wt) was added firstly into the Teflon holder and the platinum ring was adjusted to touch the solution surface. Light paraffin (15 ml) oil was then added smoothly onto the surface and the system was left to equilibrate for 2 h. The readings were recorded at the point which the ring detached itself from the aqueous to the organic layer (paraffin oil). The ring was removed and washed with acetone followed by distilled water and the measurements repeated three times for each surfactant. The interfacial tension values were taken as the mean values of three readings [14,15].

4.2 Critical Micelle Concentration (CMC) Measurements

The critical micelle concentration (CMC) is minimum concentration at which surfactants molecules begin to form micelles [16]. CMC values were obtained through a conventional plot of the surface tension versus the -logarithm of concentration of surfactant at temperatures 303,313 and 333K. The CMC concentration corresponds to the point where the surfactant first shows the lowest surface tension, and after which the surface tension remains nearly constant.

4.3 Foamability

The foaming property of surfactants was measured using a Ross-Miles apparatus [17]. In this method, 200 ml of the surfactant solution (0.1 wt %) was taken in a foam pipet. The solution in it was allowed to drop from a height of 90 cm on 50 ml of the same solution already present in a cylindrical vessel. A constant temperature 303 ± 1 K was maintained with the help of a water jacket. The foam height in the receiver is measured immediately after the last drop of the solution fell from the foam pipet and is reported as the foamability of the solution.

4.4 Emulsification power

A 20-ml amount of a different surfactant solution (1.0 wt %) was individually placed in a 100-ml cylinder and then 20 ml of the paraffin oil was added. The cylinder was shaken vigorously for 10 min and then allowed to settle. The time required to separate 18 ml of pure surfactant (aqueous solution) was recorded and the experiment was repeated three times for each surfactant. The average separation time of the three experiments was taken as an indication of the emulsification power of each surfactant [18].

4.5 Cloud point

The cloud point, measure as inverse solubility characteristic of nonionic surface actives agents, was determined by gradual heating 1.0 wt % solution in a controlled temperature bath and recording the temperature at which the clear or nearly clear solutions become definitely turbid. Cooling the solutions until they become clear again checked the reproducibility of this temperature. Cloud point was determined visually by nothing the temperature at which turbidity is observed or disappeared. The average of the temperature of appearance and disappearance of turbidity was taken as a cloud point [19].

4.6 Stability to Hydrolysis

A mixture of 10 ml of surfactant and 10 ml of 2 N sulfuric acid or 0.05 N NaOH were placed in a thermostat at 40 ºC. The time required for a sample solution to be clouded as the result of hydrolysis represents the stability of the surfactant to hydrolysis [20].

4.7 wetting time

Wetting power of the tested surfactants were determined by immersing a sample of cotton fabric in 1.0 wt% aqueous solution of the surfactants and measuring the sinking time in second [21].

4.8 biodegradability

Samples taken daily or more frequently using die-away test were filter through filter paper before measuring the surface tension. Surface tension measurements were made periodically (each day) on each sample during the degradation test [22].

Biodegradation percent (D) for each sample was calculated using the following relation.

$$D= [(\gamma_t-\gamma_0)]/ [(\gamma_{bt}-\gamma_0)] \text{ x } 100$$

Where:

γ_t =Surface tension at time t.

γ_0 = Surface tension at time zero (initial S.T.).

γ_{bt} = Surface tension of the blank experiment at time t (without sample).

Results and Discussion

Scheme 1 describes the preparation of nonionic polymeric surfactant. The analytical data, physical properties and calculated molecular weight of prepared surfactants are shown in table (1).

The IR spectra of compounds I_a shows the following peaks (^{3}) in cm^{-1} at 3449, 3255, 2924, 1732, 1650 and 1085 corresponding to NH, OH, CH aliphatic, C=O of ester, C=N and C-O-C respectively.

The IR spectra of compounds II_b shows the following peaks (^{3}) in cm^{-1} at 3355, 3223, 2978, 1739, 1635 and 1068 corresponding to NH, OH, CH aliphatic, C=O of ester, C=N and C-O-C respectively.

The IR spectra of compounds III_d shows the following peaks (^{3}) in cm^{-1} at 3455, 3233, 2938, 1735, 1655 and 1088 corresponding to NH, OH, CH aliphatic, C=O of ester, C=N and C-O-C respectively.

The 'H-NMR spectra of compounds I_a gives the following signals (¢ in ppm) at 0.980 ppm (t,3H of terminal CH_3-), 1.078 (m,14H of CH_2), 1.232 (m,1H of CH_2-$\underline{CH}$-(CH_2-O-C=O), 2.492(t,2H of $\underline{CH_2}$-O-C=O), 3.518-3.702 (m,6H of repeated oxypropylene oxide units), 4.118-4.548 (singlet,1H of C=N-OH), and 7.950 (broad s,1H of OH).

The 'H-NMR spectra of compounds II_b gives the following signals (¢ in ppm) at 0.981 ppm (t,3H of terminal CH_3-), 1.067 (m,22H of CH_2), 1.35 (m,1H of CH_2-$\underline{CH}$-(CH_2-O-C=O), 2.507(t,2H of $\underline{CH_2}$-O-C=O), 3.363-3.481 (m,6H of repeated oxypropylene oxide units), 4.629(singlet,1H of C=N-OH), and 7.950 (broad s,1H of OH).

The 'H-NMR spectra of compounds III_d gives the following signals (¢ in ppm) at 0.988 ppm (t,3H of terminal CH_3-), 1.205 (m,30H of CH_2), 2.503(t,2H of $\underline{CH_2}$-O-C=O), 3.251-3.525 (m,6H of repeated oxypropylene oxide units), 4.213 (singlet,1H of C=N-OH), and 7.950 (broad s,1H of OH).

5.1 Surface tension and interfacial tension

Surfactants are used in large number of applications due to their ability to alter the energy relationships at interfaces and to lower surface tension and interfacial tension [23].

As surfactant molecules dissolve in water, they orientate themselves in-between the water molecules and weaken hydrogen bond between them. This in turn decreases the holding forces and lowers the surface and interfacial tension.

The extent by which surfactant decreases the surface tension depend on two competing forces. These are repulsion forces between water molecule and hydrophobic part of surfactant; and attraction forces between water molecules and hydrophilic part of the surfactant molecules. The values of surface tension and interfacial tension were listed in Table 3. The surface tension and interfacial tension of the prepared nonionic surfactant increases by increasing the number of propylene oxide units included in the molecule [24].

5.2 Critical micelle concentration (CMC)

The relation between the surface tension and concentration of the synthesized surfactants at 30ºC is represented in Fig.1. The concentration ranges were chosen to cover wide range to describe all the expected changes in the behaviors of the surface tension of the surfactant solutions. It is clear that the surface tension – concentration relations are characterized by distinguishable two regions, one at lower concentration range and characterized by a fast decrease in the surface tension value, the other at higher concentrations at which the surface tension value remain almost constant. The concentration at the intercept of these two regions produces which called critical micelle concentration. From the values of CMC are listed in Table 2 it is clear that the CMC values increases as the propylene oxide units and length of alkyl chain increase[25].

The effectiveness of a certain surfactant πCMC is expressed in terms of the decrease in the surface tension that is induced by this surfactant at the critical micelle concentration [26]. It is calculated from the difference between the surface tension of pure water (γ_0) and the surface tension of the surfactant solution at the critical micelle concentration (πCMC).Eq(1).

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad \text{……………..} \quad \text{Eq.(1)}$$

The effectiveness of a surfactant (π) is measured by its ability to induce the maximum reduction in the surface tension. Since the CMC point presents the minimum surfactant concentration needed to produce the maximum reduction in surface tension; consequently, the effectiveness of a surfactant (π_{CMC}) can be measured from the decrease in the surface tension of pure water (γ_0) that is induced by this surfactant at the CMC [27]. Logically, effectiveness of the prepared surfactants decreases as (γ_{CMC}) increase, Table 2.

Table (1): Physical properties of nonionic polymeric surfactants at 30ºC.

Polymer	**Number of moles of propylene oxide**	**Color**	**Form**	**yield %**	**M.wt**
I_a	5	Yellow	Viscous	66.37	3240
I_b	10	Yellow	Viscous	65.34	4960
I_c	15	Brown	Viscous	65.9	5740
I_d	20	Brown	Viscous	67.54	6590
II_a	5	Golden yellow	Viscous	72.54	3720
II_b	10	Yellow	Viscous	77.12	5270
II_c	15	Brown	Viscous	74.87	6210
II_d	20	Brown	Viscous	76.45	7870
III_a	5	Yellow	Semi- solid	83.51	4153
III_b	10	Brown	Semi- solid	85.34	5780
III_c	15	Brown	Semi- solid	86.45	6907
III_d	20	Brown	Semi- solid	85.8	9780

5.3 Effectiveness (π_{CMC})

5.4 Maximum Surface Excess Γ_{max} and Minimum Surface Area (A_{min})

The values of the maximum surface excess Γmax expressed in mol/cm2 were calculated from surface or interfacial data by the use of Gibbs equation [28], Eq. (2):

$$\Gamma_{max} = \frac{-1}{RT}\left(\frac{\delta\gamma}{\delta \ln C}\right)_T \quad \text{……………..} \quad \text{Eq.(2)}$$

Where $\delta\gamma$ surface pressure in mN/m. C surfactant concentration. ($\delta\gamma / \delta$ ln C)T is the slope of a plot of surface tension versus concentration curves below CMC at constant temperature.

The extent of surfactant adsorption at a liquid surface is expressed in terms of its surface excess concentration Γ. This is defined as the excess of surfactant present per unit area of surface over what would be present if uniform surfactant concentration exists right up to the surface. The maximum surface excess concentration (Γmax) in mol/cm2 was calculated from Eq.(2). The Γmax values in Table (2) were increased by increasing the number of polyoxypropylene groups and ranged between 1.27 and 2.97 mol/cm2.

Knowing Γmax, it is easy to calculate the effective area occupied by each surfactant molecule adsorbed at the air/water interface at surface saturation [29,30]. The average area Amin (in nm2/molecule) is given by Eq. (3):

Amin $=$1016/ ΓmaxN …………….. Eq.(3)

Where N Avogadro's number $6.023x10^{23}$.

Values of A_{min} are listed in Table (2). It is evident that A_{min} decreases with increase in the number of propylene oxide in polymer for nonionic surfactants [31]. The A_{min} also increase with increase in temperature, as would be expected from the increased in thermal agitation of the molecules in the surface film [32].

5.5 Wetting time

The degree of wetting is the resultant of two competing forces. These are adhesive force between a liquid and solid cause a liquid drop to spread across the surface and cohesive forces within the liquid which causes the drop to addition of surfactants to water lower the surface tension and interfacial tension, this in turn lower contact angle between the liquid – vapor interface and solid – liquid interface; resulting in more surface wetting. The efficiency of the prepared nonionic surfactants as wetting agents was measured in terms of wetting time according to Draves method (21), which measures the ability of a surfactant solution to displace air from a weighted skein of cotton by spreading wetting. From Table (3) surfactant (Id) exhibited the shortest sinking time due to increase in the adhesive forces [33].

5.6 Foaming power

In general the nonionic surfactants form unstable foams. The nonionic surfactants show foam stability smaller than the ionic and cationic surfactants in aqueous medium, due to large surface area per molecule and absence of highly charged films in these foam. The data of foaming power listed in Table(3).In polyoxypropylated nonionic surfactants both foam stability and foam volume reach a maximum at a particular propylene oxide units [34,35]. This is due to maximum intermolecular cohesive forces in the adsorbed film as polyoxypropylene group increases.

5.7 Emulsification power

The emulsion formation of paraffin oil in water using the prepared surfactant solutions was measured as an indication for the emulsifying tendency of these surfactants. The synthesized nonionic surfactants showed moderated emulsification power for paraffin oil ranged between 477 sec. for (Id) in case of capric acid and 1903 sec. for (IIIa) using stearic acid at room temperature Table(3).

As a general observation, increasing the number of the hydrophobic chains in the molecules increases the stability of the formed oil-in-water emulsion. The moderate emulsifying power is attributed to the polar nature of the nonionic surfactants with low hydrophobic chain contents [36]. On the other hand, increasing the hydrophobic chains increases the hydrophobicity of the molecules, which increases their tendency for migration from the aqueous medium to the oil medium and consequently increases their emulsifying power.

5.8 Cloud point

The cloud point is a measure of the inverse solubility characteristic of nonionic surfactant. The energy of the hydrogen bond is insufficient to retain the surfactant molecules and the dehydration takes place when the surfactant solution is heated at elevated temperature, and the most of surfactants molecules separate out with little amount of water. The surfactant solubility in water at certain temperature shows turbidity by heating. This turbidity is reversible, so that the solution clears again on cooling [37,39]. The data presented in Table 3 reveal that, the cloud point increases with increasing polyoxypropylene groups [40].

5.9 Stability to Hydrolysis

All the prepared nonionic polymeric surfactants exhibited good stability as listed in Tables 3, especially in an acidic medium but have lightly lower stability in a basic medium. The increase in lengths of both the saturated fatty alkyl chain and the polyoxyenthylene chain lead to an increase in stability in both acidic and basic media [41].

5.10 Hydrophilic –Lipophilic Balance

The HLB values were calculated using the general formula of nonionic surfactants [42].

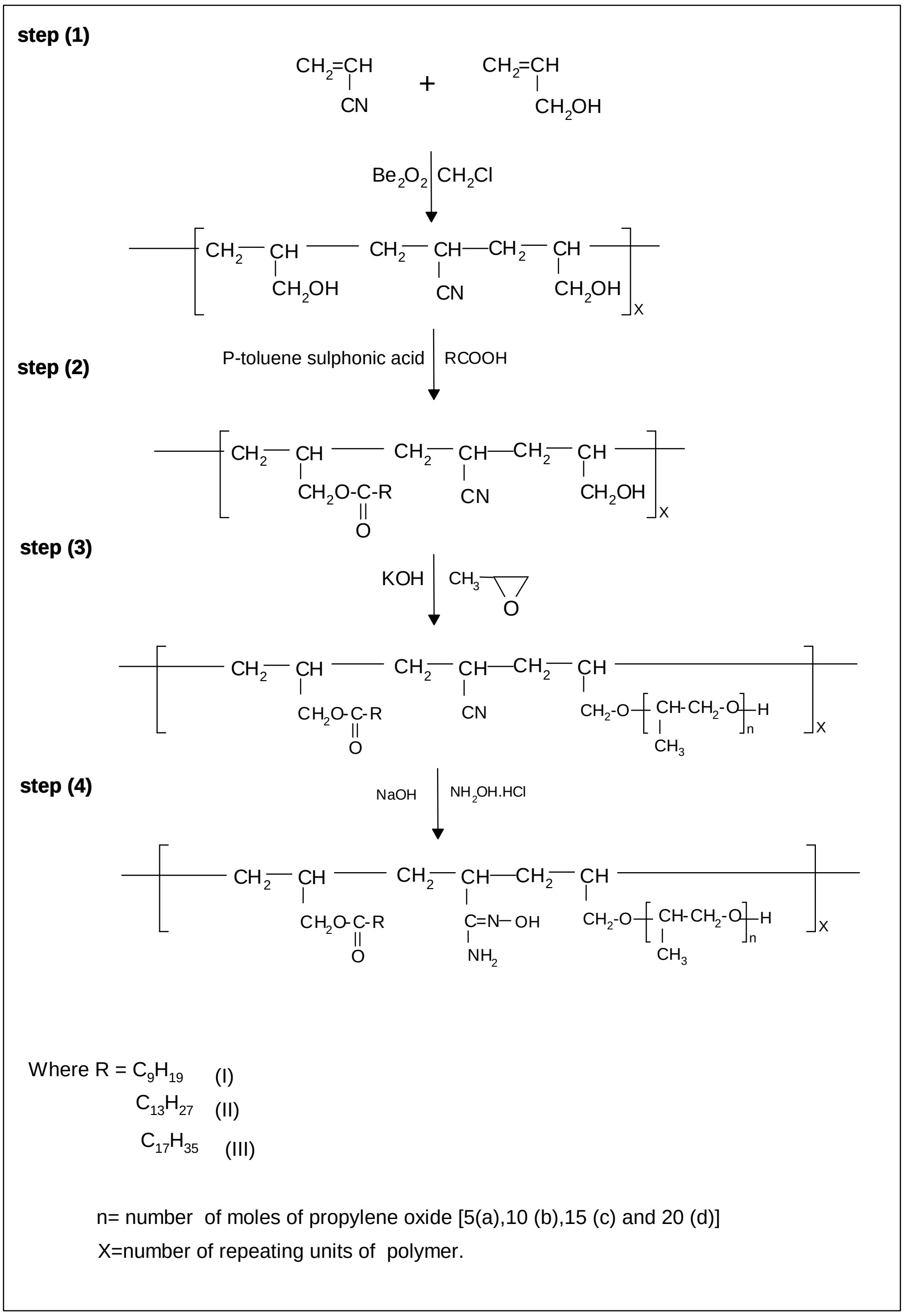
$$HLB = \frac{M_H}{M_H + M_L} \times 20 \quad \cdots\cdots\cdots\cdots \quad Eq(4)$$

Where:

M_H: formula weight of the hydrophilic portion of the surfactant molecule, ML: formula weight of the hydrophobic portion of the surfactant molecule.

The hydrophilic-lipophilic balance (HLB) of a surfactant is a measure of degree to which it is hydrophilic or lipophilic. Griffin's method (42) for nonionic surfactants was used. The HLB value can be used to predict the surfactant properties of molecule as follow: a value $<$ 10: lipid soluble (water insoluble); and a value $>$ 10: water soluble.

HLB values of the synthesized surfactants using Eq. 4 range between 7 and 16 which describe these compounds as water in oil emulsifiers.



Where R = C_9H_{19} (I)
$C_{13}H_{27}$ (II)
$C_{17}H_{35}$ (III)

n= number of moles of propylene oxide [5(a),10 (b),15 (c) and 20 (d)]
X=number of repeating units of polymer.

Scheme (1): Preparation of nonionic polymeric surfactants.

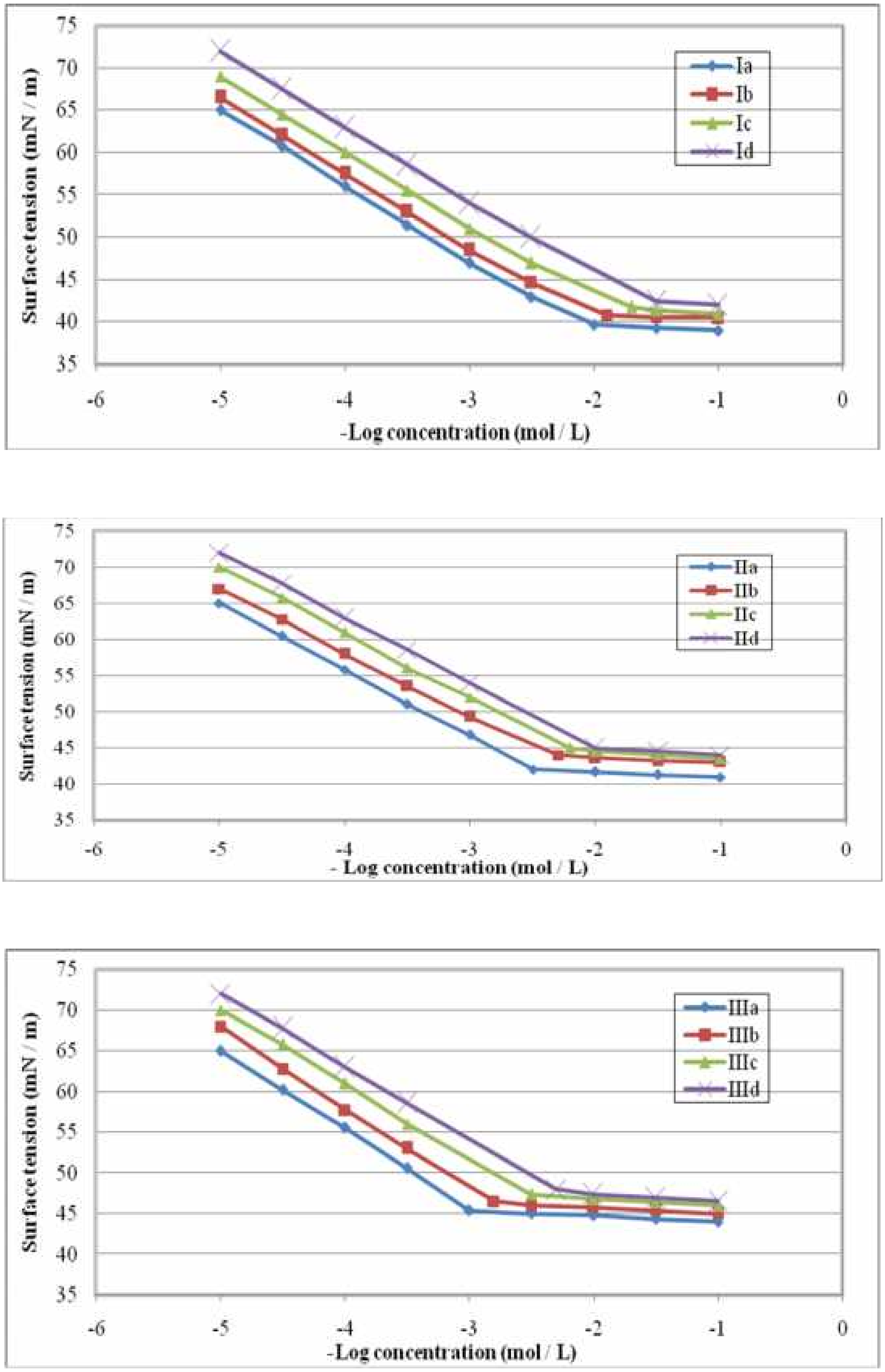


Fig (1): Relation between surface tension and -log concentration of nonionic polymeric surfactants at 30ºC;(1) polymer I_a-I_d, (2) polymer II_a-II_d and (3) polymer III_a-III_d.

Table (2): Surface active parameters of nonionic polymeric surfactants at 30,40 and 60ºC.

Polymer	Number of moles of propylene oxide	T(K)	γCMC (mN/m)	CMC (mol/L)	πCMC (mN/m)	Γmax (mol/cm2) 10-10	Amin (nm2 /mol)
Ia	5	303	40	0.05	32	1.27	1.25
		313	39.5	0.034	32.5	1.15	1.39
		333	38	0.025	34	1.03	1.55
Ib	10	303	42	0.0316	30	1.5	1.066
		313	40	0.0199	32	1.438	1.112
		333	39	0.016	33	1.39	1.15
Ic	15	303	42.5	0.0158	29.5	1.748	0.915
		313	41	0.0125	31	1.63	0.98
		333	40.5	0.0079	31.5	1.6	1.00
Id	20	303	43	0.01	29	1.92	0.83
		313	42.5	0.0063	29.5	1.86	0.86
		333	41	0.005	31	1.7	0.94
IIa	5	303	42	0.01	30	1.88	0.85
		313	40	0.006	32	1.75	0.91
		333	39.5	0.005	32.5	1.64	0.97
IIb	10	303	44	0.006	28	2.23	0.71
		313	42.5	0.005	29.5	2.04	0.78
		333	42	0.003	30	1.93	0.83
IIc	15	303	45	0.005	27	2.36	0.67
		313	44	0.0034	28	2.18	0.73
		333	43.5	0.0025	28.5	2.00	0.8
IId	20	303	46	0.00316	26	2.43	0.65
		313	45	0.0025	27	2.39	0.67
		333	43.5	0.00158	28.5	2.19	0.73
IIIa	5	303	45	0.005	27	2.35	0.68
		313	44.5	0.003	27.5	2.27	0.7
		333	43	0.0025	29	2.05	0.78
IIIb	10	303	46.5	0.00316	25.5	2.51	0.63
		313	45	0.0025	27	2.46	0.65
		333	42.5	0.0016	29.5	2.34	0.68
IIIc	15	303	47	0.0019	25	2.81	0.56
		313	46	0.0016	26	2.72	0.58
		333	44	0.001	28	2.6	0.615
IIId	20	303	48	0.001	24	2.97	0.54
		313	46.5	0.0008	25.5	2.87	0.56
		333	45	0.0005	27	2.68	0.59

Table (3): Surface active parameters of nonionic polymeric surfactants at 30ºC

Polymer	Number of moles of propylene oxide	Surface tension (mN/m) 0.1 wt% at 30oC	Interfacial tension (mN/m) 0.1 wt % at 30oC	cloud point (oC) 1.0 wt%	Wetting time (Sec.) 0.1 wt%	Foam height (mm) 1.0 wt%	Emulsion stability (min: sec) 1.0 wt%	Stability to hydrolysis min: sec		HLB
								Acidic (2.0 N)	Alkaline (0.05 N)	
Ia	5	39	9	72	39	73	14:23	15:27	01:16	9.02
Ib	10	40.5	11	78	36	82	12:08	17:22	01:47	12.32
Ic	15	41	11.5	85	32	88	09:38	18:12	02:13	13.04
Id	20	42	13	100>	32	107	07:57	20:35	03:38	16.12
IIa	5	41	12	56	53	94	27:13	27:32	05:23	8.36
IIb	10	43	13.5	63	51	110	26:45	28:16	08:12	10.43
IIc	15	43.5	14	72	45	117	22:32	32:45	11:52	11.32
IId	20	44	15	73	40	125	19:42	37:30	14:36	15.18
IIIa	5	44	14.5	43	58	113	31:43	35:16	13:22	7.3
IIIb	10	45	15	59	56	129	28:57	42:35	17:50	8.8
IIIc	15	46	16	64	55	135	28:08	48:19	21:18	10.19
IIId	20	46.5	16.5	69	50	141	23:42	54:52	26:49	13.2

5.11 Micellization and adsorption thermodynamics

According to the gibb's equation of thermodynamics, the thermodynamic functions of micellization including, standard free energy, entropy and enthalpy change (ΔG,ΔS and ΔH) respectively were calculated from the surface parameter data ,according to the following equations$^{(34)}$:

$$\Delta G_{mic} = RT \ln CMC \text{ …………………Eq.(5)}$$

Where R is the gas constant in J mol^{-1}K^{-1} (R= 8.314)

The value of ΔS_{mic} was obtained from Eq.(6)using the value of ΔG_{mic} at 303,313 and 333 k.

$$\Delta S_{mic} = -\frac{\delta \Delta G_{mic}}{\delta T} \text{ ……..………. Eq.(6)}$$

In addition, ΔH_{mic} was calculated from ΔG_{mic} and ΔS_{mic} by applying Eq.(7)

$$\Delta H_{mic} = \Delta G_{mic} + T\, \Delta S_{mic} \text{ ……..…… Eq.(7)}$$

The thermodynamic parameter values of adsorption ΔG_{ads}, ΔS_{ads} and ΔH_{ads} were calculated via the following equations (8-10), respectively $^{(34)}$:

$$\Delta G_{ads} = RT \ln CMC - 0.6023\, \gamma_{CMC}\, A_{min} \text{ …. Eq. (8)}$$

$$\Delta S_{ads} = -\frac{\delta \Delta G_{ads}}{\delta T} \text{ ………………………… Eq.(9)}$$

$$\Delta H_{ads} = \Delta G_{ads} + T\, \Delta S_{ads} \text{ ……………………… Eq.(10)}$$

The thermodynamics parameters of adsorption and micellization of the synthesized copolymer nonionic surfactants are listed Table (4). Analyzing the data of each process (micellization and adsorption) showed the following:

The standard free energy of both adsorption and micellization processes is always negative, which indicates the spontaneous occurrence of the two processes and that reveals the equilibrium between the adsorbed and micellized surfactant molecules in both phases[43-45].Furthermore, ΔG_{ads} is more negative than ΔG_{mic} which indicates the predominance of the adsorption process at the air-solution interface than the micellization in the bulk of the aqueous solution.

1. Increasing the temperature of measurements increases the negativity of ΔG_{ads} and ΔG_{mic}, which indicates that the agitation of the solutions increases the surfactant adsorption and micellization. It shows also that the adsorption is more favored in case of higher temperatures than micellization. That refers to the repulsion occurred between the surfactant molecules at high temperatures and the aqueous medium due to the rupture of the water of hydration of the hydrophobic chains.
2. It is observed that the enthalpy for adsorption (ΔH_{ads}) and micellization processes (ΔH_{mic}) are positive in sign. Furthermore, the enthalpy of adsorption is more positive than of the micellization process. This indicates that fewer bonds between oxypropylated groups and water molecules are broken in the process of adsorption at the air/aqueous solution interface than in micellization, the number of bond broken increases with an increase in the number of polyoxypropylene groups in the molecules.
3. The entropy for adsorption (ΔS_{ads}) values are all positive and slightly greater than the entropy for micellization (ΔS_{mic}) values. This may reflect the greater freedom of motions of the hydrocarbon chains at the planar air/aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle. On other hand, the change in ΔS_{ads} with an increase in the polyoxypropylene units in the molecule, approximates that observed in ΔS_{mic}[46].

Table (4): Thermodynamic parameters of micellization and adsorption of nonionic surfactants.

Polymer	Number of moles of propylene oxide	T(K)	ΔGmic (KJ mol-1)	ΔSmic (KJ mol-1K-1)	ΔHmic (KJ mol-1)	ΔGads (KJ mol-1)	ΔSads (KJ mol-1 K-1)	ΔHads (KJ mol-1)
Ia	5	303	-7.5	0.0919	20.37	-24.1	0.246	50.44
		313	-8.79		19.97	-26.16		50.84
		333	-10.21		20.39	-29.9		52.02
Ib	10	303	-8.7	0.095	20.08	-24.2	0.248	50.94
		313	-10.19		19.54	-26.8		50.82
		333	-11.45		20.18	-29.49		53.09
Ic	15	303	-10.45	0.121	25.19	-24.3	0.249	51.14
		313	-11.40		26.16	-26.7		51.23
		333	-13.4		26.56	-30.2		52.71
Id	20	303	-11.6	0.124	25.97	-25.2	0.252	51.15
		313	-13.18		25.63	-27.15		51.73
		333	-14.67		26.62	-30.6		53.32
IIa	5	303	-11.6	0.126	26.58	-24.23	0.273	58.94
		313	-13.31		26.13	-27.1		58.35
		333	-14.67		27.28	-30.3		60.61
IIb	10	303	-12.88	0.144	30.75	-24.6	0.275	58.72
		313	-13.78		31.29	-26.48		59.59
		333	-16.08		31.87	-30.39		61.18
IIc	15	303	-13.34	0.149	31.9	-24.8	0.28	60.04
		313	-14.79		31.8	-27.6		60.04
		333	-16.58		33.03	-31.07		62.17
IId	20	303	-14.5	0.151	31.25	-26.9	0.302	64.6
		313	-15.59		31.67	-30.8		63.7
		333	-17.86		32.42	-33.6		66.96
IIIa	5	303	-13.3	0.142	29.7	-26.09	0.29	58.78
		313	-15.11		29.3	-28.46		62.31
		333	-16.58		30.7	-32.22		64.35
IIIb	10	303	-14.5	0.151	31.25	-26.7	0.295	62.68
		313	-15.59		31.67	-29.69		62.96
		333	-17.82		32.46	-32.37		65.86
IIIc	15	303	-15.78	0.163	33.61	-27.9	0.31	66.03
		313	-16.75		34.26	-31.6		65.43
		333	-19.12		35.16	-34.3		68.93
IIId	20	303	-17.4	0.179	36.8	-31.5	0.38	83.64
		313	-18.55		37.4	-35.99		82.95
		333	-21.04		38.56	-41.95		84.59

5.12 Biodegradability

Biodegradation is the destruction of a chemical by the metabolic activity of microorganisms. Since surfactants are susceptible to biodegradation and in order to examine their effect on water pollution, the biodegradation of the synthesized copolymer nonionic surfactant was evaluated by the conventional river die-away test employing surface tension technique as an analytical tool [47].

The biodegradability data are listed in Table (5). Within experimental accuracy, all the prepared copolymer nonionic surfactants seem to degrade easily. The results showed that, 45-50% of the surfactants were biodegradable within the first day, further degradation occurred on the next days until it almost died away on the 7th day. Consequently, these compounds are safe for human beings and the environment. It should be noted that, the biodegradability of a certain surfactant decrease by increasing length of alkyl chain and number of propylene oxide units [48].

Table (5): Biodegradability of nonionic surfactants.

Polymer	Number of moles of propylene oxide	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
I_a	5	65	72	78	83	90	-	-
I_b	10	62	69	75	81	87	92	-
I_c	15	57	64	71	78	85	90	-
I_d	20	51	58	63	69	78	85	89
II_a	5	59	63	71	77	83	92	-
II_b	10	56	61	68	73	80	89	-
II_c	15	50	56	63	70	78	85	91
II_d	20	48	53	61	67	73	80	89
III_a	5	53	56	61	69	75	82	90
III_b	10	49	53	59	67	73	80	89
III_c	15	48	50	56	64	72	79	92
III_d	20	46	49	53	62	70	82	90

6. CONCLUSION

- Increasing concentration of the synthesized surfactants in solution decreases their surface tension gradually. The surface activity of the synthesized polymeric surfactant depends on both lengths of fatty chain and oxypropylene chains.
- The CMC decreases as the propylene oxide number increases, as expected from the fact that the propylene oxide chain is globally lipophilic.
- The cloud temperature increases with large polyoxypropylene chains and decreases with large alkyl tails.
- The nonionic surfactants with lower polypropylene oxide content have a better wetting property.
- The emulsifying properties increased with decreasing the number of propylene oxide units and with increasing the alkyl chain length of fatty acids.
- Low foam tendency of nonionic surfactants increases with increasing length of poly oxypropylene chains as well as alkyl chain length of fatty acids.
- Thermodynamic data of adsorption and micellization showed great tendency of these compounds toward adsorption at the interfaces rather than micellization in the bulk of their solutions.

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