Effect of chemical structure on the cloud point of some new non-ionic surfactants based on bisphenol in relation to their surface active properties

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Abstract A series of non-ionic surfactants were prepared from bisphenol derived from acetone (A), acetophenone (AC) and cyclohexanone (CH). The prepared bisphenols were ethoxylated at different degrees of ethylene oxide (27, 35, 43). The ethoxylated bisphenols were non-esterified by fatty acids; decanoic, lauric, myristic, palmitic, stearic, oleic, linoloic and linolinic. Some surface active properties for these surfactants were measured and calculated such as, surface tension [γ], critical micelle concentration [CMC], minimum area per molecule [A_{min}], surface excess [Γ_{max}], free energy of micellization and adsorption [ΔG_{mic}] and [ΔG_{ads}]. At a certain temperature, the cloud point was measured for these surfactants. From the obtained data it was found that; the cloud point is very sensitive to the increase of the alkyl chain length, content of ethylene oxide and degree of unsaturation. The core of bisphenol affected the cloud point sharply and they are ranked regarding bisphenol structure as BA > BCH > BAC. By inspection of the surface active properties of these surfactants, a good relation was obtained with their cloud points. The data were discussed on the light of their chemical structures.

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1. Introduction

Non-ionic surfactants become water soluble by the hydration of ether oxygen of the polyoxyethylene group. The longer chain of ethylene oxides containing ether oxygen is more hydrated and consequently, more solubility. An increase in temperature causes the cleavage of the hydrogen bond between the ether oxygen of the ethylene oxide group and the hydrated hydrogen to the ether oxygen. As a result, the aggregation number of micelles increases and the micelles of polyoxyethylene non-ionic surfactant become larger and larger until they are so large that the solution becomes visibly turbid [1].

The depletion of water from non-ionics decreases their solubility in water [2]. The water depleted non-ionic surfactants solution, therefore, becomes turbid and separates into two immiscible phases a surfactant rich phase and a surfactant lean phase. The phase separation occurs as a result of the density difference between the micelle-rich and micelle poor phases [3]. This sudden onset of turbidity of a non-ionic surfactant solution when the temperature rises is called the "cloud point". This turbidity is a reversible process, so that the solution clears again on cooling. In general, non-ionics having a longer polyoxyethylene chain consequently have a higher cloud point, meaning a greater capacity to hydrate. The cloud point of a non-ionic surfactant or glycol solution is the temperature at which the dissolution of solids is no longer complete, and the mixture starts to phase separate and two phases appear, thus becoming cloudy [4]. This behavior is characteristic of non-ionic surfactants containing polyoxyethylene chains, which exhibit reverse solubility versus temperature behavior in water and, therefore, cloud out at some point as the temperature is raised. The cloud point is effected by salinity, being generally lower in more saline fluids [5]. This term is relevant to several applications with different consequences, knowing the cloud point is important for determining storage stability [6]. Storing formulations at temperatures significantly higher than that of the cloud point may result in phase separation and instability [7]. Wetting, cleaning and foaming characteristics can be different above and below the cloud point. Generally, non-ionic surfactants show optimal effectiveness when used near or below their cloud point [8]. Low-foam surfactants should be used at temperatures slightly above their cloud point [9].Cloud point is typically measured using 1% aqueous surfactant solutions. Cloud points range from 0° to 100 °C (32–212 °F), limited by the freezing and boiling points of water. Cloud point is characteristic of non-ionic surfactants. Anionic surfactants are more water-soluble than non-ionic surfactants and will typically have much higher cloud points (above 100 °C). The presence of other components in a formulation can depress or increase the cloud point of a solution. For example, the addition of a coupler or hydrotrope can increase the cloud point of a solution, whereas builders or other salts will depress the cloud point temperature. For standard and low-foam applications [10,11], the cloud point of the product should be just below the used temperature. The cloud point of TRITON CF-32 defoamer is 23 °C (73.4 °F), which should be used around 25–28 °C (77–82 °F) for maximum efficiency. The first object of this work is to prepare some bisphenols such as; bisphenol based on acetone (BA), bisphenol of acetophenone (BAC) and bisphenol of cyclohexanone (BCH). These bisphenols were ethoxylated at different ethylene oxide contents. The ethoxylated products were monoesterified by long chain fatty acids. The second object is to measure surface tension and calculate their surface active properties and then measure their cloud points. The third object of this investigation is to try to find a relation between the surface properties and the cloud point of these surfactants.

2. Experimental

2.1. Preparation of surfactants

Three bisphenols based on acetone (diphenylol propane, bisphenol A), acetophenon and cyclohexanone were prepared and named as; BA, BAC and BCH, respectively. These bisphenols were ethoxylated at different ethylene oxides (27, 35 and 43). The ethoxylated bisphenols were monoesterified by fatty acids, decanoic, lauric, myristic, palmitic, stearic, oleic, linoloic and linolinic. The method of preparation was described clearly in a previous work [12]. Fig. 1 shows the generalized formula and designation of the prepared surfactants.

2.2. Surface tension measurement and calculations of surface active properties

The values of surface tension (γ) were measured at 303 °K for various concentrations of the surfactant. The measured values of (γ) were plotted against the surfactant concentration, ln C. The intercept of the two straight lines designates the critical micelle concentration (CMC), where saturation in the surface adsorbed layer takes place. The main importance of the CMC consists of the fact that, at this concentration, most of the physical and chemical properties of the surfactant solutions present an abrupt variation. The surface active properties of the surfactant, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) were calculated using the following equations [13]:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \tag{1}$$

$$\Gamma_{max} = -10^{-7}[1/RT][d\gamma/d\ln C]_T \tag{2}$$

$$A_{min} = 10^{16}/[\Gamma_{max} \cdot N_A] \tag{3}$$

$$\Delta G_{mic} = RT \ln CMC \tag{4}$$

$$\Delta G_{ads} = \Delta G_{mic} - [0.6022 \times \pi_{cmc} \times A_{min}] \tag{5}$$

where γ_o is the surface tension measured for pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC, Γ is the surface excess concentration in mol/dm^2, R is the molar gas constant ($R = 8.314$ J/(mol K)), T is the
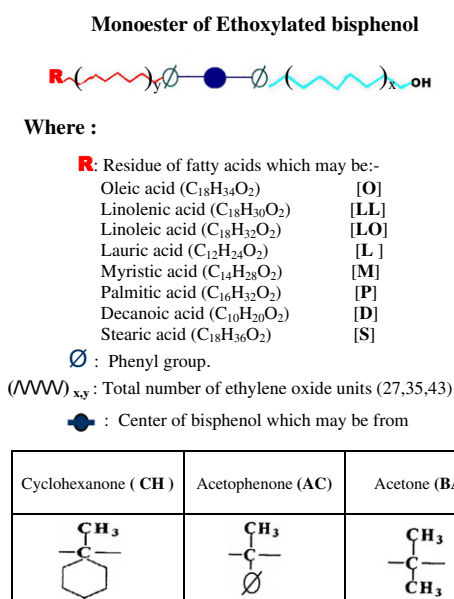

Monoester of Ethoxylated bisphenol

Where :

R: Residue of fatty acids which may be:-

Oleic acid (C$_{18}$H$_{34}$O$_2$)	[O]
Linolenic acid (C$_{18}$H$_{30}$O$_2$)	[LL]
Linoleic acid (C$_{18}$H$_{32}$O$_2$)	[LO]
Lauric acid (C$_{12}$H$_{24}$O$_2$)	[L]
Myristic acid (C$_{14}$H$_{28}$O$_2$)	[M]
Palmitic acid (C$_{16}$H$_{32}$O$_2$)	[P]
Decanoic acid (C$_{10}$H$_{20}$O$_2$)	[D]
Stearic acid (C$_{18}$H$_{36}$O$_2$)	[S]

$\emptyset$: Phenyl group.

(ΛΛΛ)$_{x,y}$: Total number of ethylene oxide units (27,35,43)

: Center of bisphenol which may be from

Cyclohexanone (CH)	Acetophenone (AC)	Acetone (BA)

Figure 1 Generalized formula and structure designation.

absolute temperature = $(t \,^\circ C + 273)\,^\circ K$, γ is the surface or interfacial tension mN/m and C is the concentration of surfactant mol/l), A_{min} is the surface area per molecule of solute in square nanometers (nm²/molecule), NA is the Avogadro's number (6.023×10^{23} molecules/mol) ΔG_{mic} is the Gibbs free energy of micellization and ΔG_{ads} is the Gibbs free energy of adsorption.

2.3. Cloud point measurements (Cp)

The cloud points of the prepared surfactant solutions were determined visually by observing the temperature at which the continuously heated solution (1% surfactant solution) until suddenly becomes cloudy. The reproducibilityof this temperature was checked by cooling the solution until it becomes clear again. In all measurement cases, the surfactant solutions were heated starting at room temperature [3,14]. The cloud point was recorded between the start cloud temperature and 2°C above, at which completely cloudy was obtained.

3. Results and discussion

3.1. Effect of unsaturation in the alkyl chain on the (A_{min}) and (ΔG_{ads})

This factor is cleared in Table 1 and illustrated in Fig. 2. From this Table and Figure, it can be noted that, the A_{min} values of E(27) BACO, E(27) BACLO and E(27) BACLL were 338, 440 and 453 nm², respectively, as representative samples. While, the A_{min} value of the E(27) BAC (ethoxylated bisphenol only) is 644 nm², it is nearly equal to twice the A_{min} value of E(27) BACO (338 nm²). On the other hand, the A_{min} values of E(27) BACLO and E(27) BACLL are greater than half A_{min} of E(27) BAC. This may be due to the increase of the unsaturated and number of double bonds in the alkyl chain which increases the A_{min}, as a result of P_Z orbital effect. This behavior is generally found for all the undertaken surfactants. The large difference in the A_{min} values between the ethoxylated bisphenols (uncomplete surfactant model) and the esterified ethoxylated bisphenols (completely surfactant model) can be explained by the sketch in Fig. 3. The sketch shows that, in case of E(x)B(y) [general formula of the ethoxylated bisphenols only], the adsorption of molecules on the interface may be done by the two terminal –OH group of ethylene oxide chains. But in the case of E(x)B(y)M(R) [general formula of the monoesterified ethoxylated bisphenol derivatives], the molecules are completely surfactant model. So that the molecules have self direction to adsorb on the interface by one terminal –OH as shown in the sketch until formation of complete monolayer adsorption. This interpretation answers the question, why the E(x)B(y) has A_{min}/molecule equal to nearly twice than A_{min} which was obtained with E(x)B(y)M(R). It is also clear from Fig. 2, that, the increasing degree of unsaturation decreases the negative value of ΔG_{ads}. The ΔG_{ads} of E(43) BACO, E(43) BACLO and E(43) BACMLL were -17.2, -14.48 and -12.51 kJ mol⁻¹, respectively, as representative samples (Table 1). The difference in these values may be due to the unsaturated double bonds effect on the configuration of the alkyl chain in the solution. The configuration may be a hindrance to the adsorption of surfactant molecules on the liquid/air interface.

3.2. Effect of ethylene oxide content on A_{min} and ΔG_{ads}

General behavior has been seen from the values of A_{min} in Table 1 and Fig. 2. The A_{min}/molecule decreases with increasing the total number of ethylene oxide units. This may be due to coiling that could be formed as a result of increasing the ethylene oxide chain, which decreases the area covered per molecule [15]. From Table 1 and Fig. 2b, the ΔG_{ads} values are all negative. The negative values of ΔG_{ads} are greater than the values of ΔG_{mic}, this shows that the adsorption at the interface is associated with a decrease in the free energy of the system. This observation indicates that the surfactant molecules prefer adsorption on the surface than micellization. It is also clear from Fig. 2b, that the increasing of ethylene oxide units is accompanied with decreasing of ΔG_{ads}. This may be due to the coiling of ethylene oxide chain which inhibited the adsorption process.

3.3. Effect of alkyl chain length on A_{min}/molecules and ΔG_{ads}

The results are shown in Table 1 and Fig. 4a. The data reveal that, as the alkyl chain length increases, the value of A_{min}/molecule increases. This is due to increase in the distortion motion of molecules in the solution, which is directly effected by increasing the alkyl chain length. This motion acts to push the surfactant molecule to the interface to occupy the largest area/molecule [16]. As shown in Fig. 4a, the maximum value of A_{min} (410 nm²) was exhibited by E(43) BACMS, but the minimum area/molecule (280 nm²) was obtained by E(43) BACMD. The effect of alkyl chain length on the ΔG_{ads} is shown in Fig. 4b. It is clear that, by increasing the alkyl chain length (C_{10}–C_{18}), the corresponding negative values of ΔG_{ads} should be increased. This may be due to the fact that the longest alkyl chain length does a high motion in the solvent, which increases the free energy of the system. So that, the energy of the longest alkyl chain regarding E(43) BACMS was -9.44 kJ mol⁻¹ this helps the surfactant molecules to adsorb on the interface stronger than the $-\Delta G$ of the shortest alkyl chain of E(43) BACMD ($\Delta G = -8.53$ kJ mol⁻¹).

3.4. Effect of bisphenol skeleton on ΔG_{ads}

The bisphenol skeleton effect on ΔG_{ads} is clearly shown in Fig. 5. The negative values of ΔG_{ads} were -8.54, -12.51 and -9.18 kJ mol⁻¹ for E(43) BAMLL, E(43) BACMLL and E(43) BCHMLL, respectively (Table 1). This may be due to the surfactant which based on BAC has the greatest adsorption capability on the interface than the surfactants based on BA or BCH.

3.5. Effect of bisphenol skeleton on cloud point

Effect of bisphenol skeleton on CP is clear from the data in (Table 1). It was noticed that the monooleate derivatives of ethoxylated BA give a higher CP among the BCH or BAC. Also the CP of E(43) BA, E(43) BAC and E(43) BCH at 5% NaCl were 94°, 92° and 90 °C, respectively. These compounds are only ethoxylated bisphenols, but they gave a higher CP than the corresponding monooleate esters. This behavior can be explained by the sketch in Fig. 3. From the sketch it can be noted that the ethoxylated bisphenols are disordered because they have two free chains of ethylene oxide which build

Table 1 Cloud point and surface properties of the ethoxylated and monoesterified ethoxylate of bisphenol.

Surfactant	CP (°C)	$[\gamma_{cmc}]$ (m Nm^{-1})	CMC (mol dm^{-3})	A_{min} (nm$^2 \times$ 100)	ΔG_{mic} (kJ mol^{-1})	G_{ads} (kJ mol^{-1})
BCH						
E(27) BCH	86–88[a]	43.50	1.20×10^{-3}	6.59	8.37	−9.51
E(35) BCH	87–89[a]	42.10	3.00×10^{-2}	5.89	−4.30	−5.37
E(43) BCH	88–90[a]	41.53	7.00×10^{-2}	4.39	−3.21	−4.03
E(27) BCHO	67–69	37.12	1.23×10^{-4}	3.55	−13.50	−14.28
E(35) BCHO	71–73	35.51	6.30×10^{-4}	3.18	−13.20	−13.92
E(43) BCHO	74–76	33.02	3.89×10^{-3}	2.98	−12.17	−12.89
E(27) BCHLO	71–73	27.20	7.76×10^{-5}	3.83	−11.79	−12.17
E(35) BCHLO	74–76	28.40	3.98×10^{-4}	3.75	−9.78	−10.12
E(43) BCHLO	75–77	29.36	2.63×10^{-3}	3.34	−7.40	−7.712
E(27) BCHLL	72–74	36.90	1.58×10^{-4}	4.46	−10.90	−11.85
E(35) BCHLL	75–77	35.50	7.94×10^{-4}	4.31	−8.89	−9.84
E(43) BCHLL	75–77	33.80	1.58×10^{-3}	4.06	−8.03	−9.18
E(43) BACD	53–55	30.4	1.90×10^{-3}	2.80	−7.80	−8.53
E(43) BACL	54–56	27.6	1.70×10^{-3}	3.40	−7.95	−8.89
E(43) BACM	55–57	30.0	1.40×10^{-3}	3.60	−8.18	−9.13
E(43) BACP	59–61	38.5	1.30×10^{-3}	3.70	−8.29	−9.20
E(43) BACS	65–67	40.7	1.18×10^{-3}	3.80	−8.41	−9.44
E(27) BA	84–86[a]	38.8	3.0×10^{-24}	7.94	−4.30	−5.90
E(35) BA	88–90[a]	37.2	6.3×10^{-2}	6.60	−3.44	−5.12
E(43) BA	92–94[a]	36.0	1.0×10^{-2}	5.44	−2.87	−4.30
E(27) BAO	79–81	32.1	2.5×10^{-4}	3.02	−10.33	−13.48
E(35) BAO	81–83	31.4	7.9×10^{-4}	2.54	−8.89	−9.50
E(43) BAO	83–85	30.0	2.5×10^{-3}	2.20	−7.458	−8.01
E(27) BALO	80–82	33.7	1.4×10^{-4}	3.57	−10.90	−11.73
(35) BALO	83–85	32.5	4.0×10^{-4}	2.91	−9.75	−10.41
E(43) BALO	84–86	31.2	7.9×10^{-4}	2.31	−8.89	−9.46
E(27) BALL	81–83	34.2	5.0×10^{-4}	4.50	−9.57	−10.41
E(35) BALL	84–86	33.4	6.1×10^{-4}	3.62	−9.04	−9.74
E(43) BALL	81–83	32.4	7.9×10	2.70	−7.95	−8.54
BAC						
E(27) BAC	84–86[a]	41.1	9.00×10^{-2}	6.44	−5.45	−6.65
E(35) BAC	86–88[a]	40.1	3.00×10^{-2}	5.92	−4.3	−5.45
E(43) BAC	90–92[a]	39.8	1.90×10^{-2}	5.61	−3.41	−4.51
E(27) BACMO	63–65	34.8	1.58×10^{-4}	3.38	-11.15	−17.81
E(35) BACMO	65–67	33.4	3.16×10^{-4}	3.23	−10.29	−17.53
E(43) BACMO	68–70	32.5	7.94×10^{-3}	3.04	−9.15	−17.02
E(27) BACMLO	65–67	34.2	1.58×10^{-4}	4.4	−11.15	−16.38
E(35) BACMLO	68–70	33.5	1.00×10^{-4}	4.05	−9.72	−15.49
E(43) BACMLO	70–72	33.1	1.41×10^{-4}	3.74	−8.17	−14.48
E(27) BACMLL	67–69	37.2	8.00×10^{-4}	4.53	−9.81	−15.35
E(35) BACMLL	70–72	36.8	1.17×10^{-4}	4.2	−8.4	−13.51
E(43) BACMLL	74–76	36.2	2.04×10^{-4}	3.81	−7.72	−12.51

[a] Cloud point was measured at 5% NaCl solution.

up a great number of hydrogen bonds with water molecules. This means that they have complete hydrophilic moiety and complete solvation in water. So that, the EB phenols need higher energy to breakdown the hydrogen bonds than the corresponding esterified EB phenols. The sketch also explains why the CP of the esterified EB phenols is lesser than the corresponding ethoxylated bisphenols before esterification. The sketch clears that the EB phenol ester derivative is a complete surfactant model. The surfactant model has a tail (hydrophobic) and head (hydrophilic). This model structure named amphipathic character, at which the surfactant molecule has self-orientation toward the bulk of solution. Therefore, the CP was measured at 1% conc., at this concentration the surfactant molecules are forming micelles. As shown in the sketch, it can be exaggerated that, the specimens of bisphenols (BA, BAC and BCH) are articling on the surface of the micelle. The free ethylene oxide chains are situated on the outer surface of the micelle in the bulk of the solvent (water). On the other hand, the esterified ethylene oxide chains are toward the inner core of the micelle. This configuration decreases the chances to build up new hydrogen bonds in the inner core of the micelle with the esterified chain. So the self-orientation of the surfactant molecules in the micelle helps the bisphenol skeleton to play a role in the variations of CP from structure to other. By an inspection of CP values in (Table 1), a comparison can be held between E(43) BAMO, E(43) BCHMO and E(43) BACMO on the light of bisphenol skeleton variations. The CP was 85, 76 and 70 °C, respectively. It is remarked that the discrepancy of CP corresponding to bisphenol skeleton may be due to the following reasons:
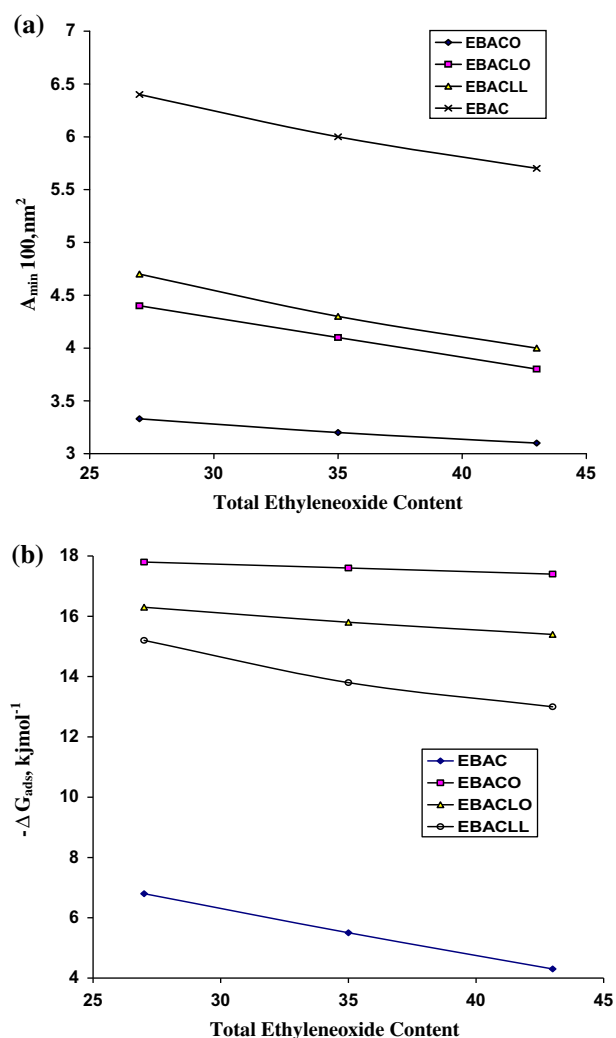
Figure 2 Effect of unsaturation in the alkyl chain on (a) A_{min} and (b) ΔG_{ads} of EBAC monoester derivatives.

1. The maximum CP was obtained with BA, its skeleton is completely aliphatic moiety (based on acetone). So that, it may be allowed to penetrate great water molecules via the surface of the micelle to build up hydrogen bonds with the esterified ethylene oxide chain. This needs high energy (85 °C) to breakdown the hydrogen bonds.

2. The minimum CP was obtained against BAC, its skeleton is mixed aliphatic/aromatic based on (acetophenon) moiety [17]. The aromatic ring in this configuration may cause strain and hindrance to penetrate a large quantity of water molecules via the surface to the inner core of the micelle. So that it needs low energy (70 °C) to breakdown these hydrogen bonds.

3. The medium CP was obtained with BCH (76 °C). This is related to the skeleton of bisphenol based on (cyclohexanone), which has aliphatic/alicyclic system. It is neither pure aliphatic such as BA nor aliphatic/aromatic such as BAC. So that the bisphenol specimen on the surface of micelle does not allow to penetrate a large quantity of water molecules to the inner core of the micelle such as BA. But it allows penetrating a greater quantity of water molecules than in the case of BAC.
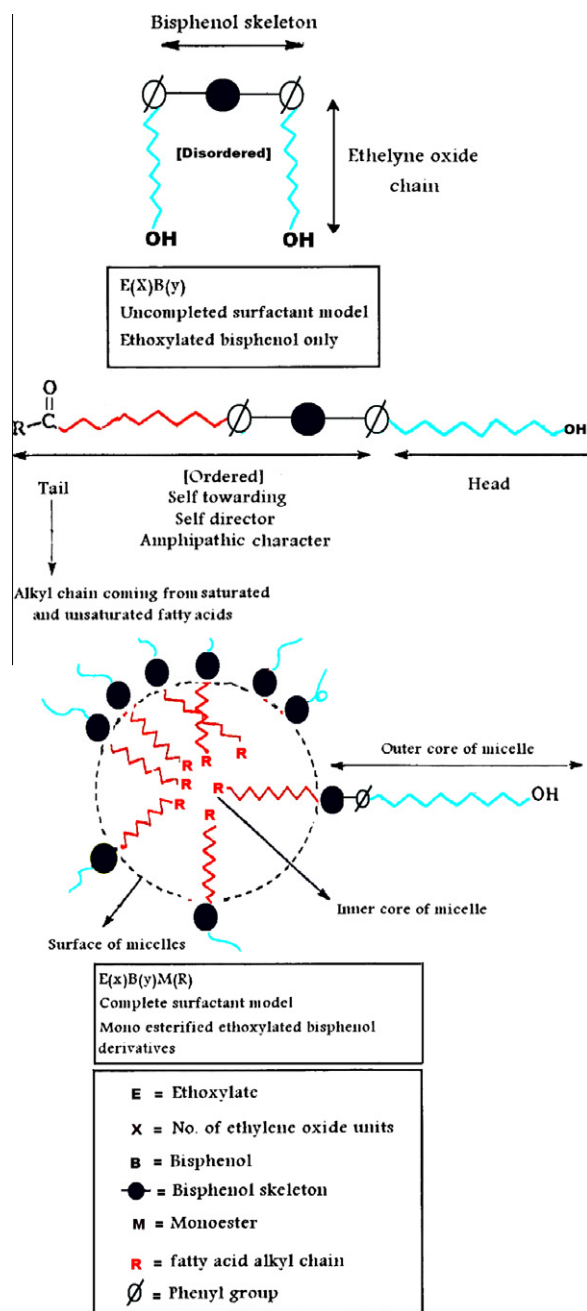

Figure 3 Sketch diagram shows configuration model of ethoxylated and monoesterified ethoxylated bisphenols.

3.6. Effect of total ethylene oxide content on cloud point

The listed data in (Table 1) for the undertaken surfactants clear the effect of ethylene oxide content on the CP. The CP of monooleate esters of ethoxylated bisphenol of acetone E(27) BAO, E(35) BAO and E(43) BAO is 79, 81 and 83 °C, respectively, were taken as representative samples. Fig. 6 shows that the increasing of ethylene oxide content increases the CP. This behavior was noticed for all ethoxylated bisphenol ester derivatives. The increasing of ethylene oxide (units) increases the number of ethereal bonds (–O–), which play a central role to build up great numbers of hydrogen bonds
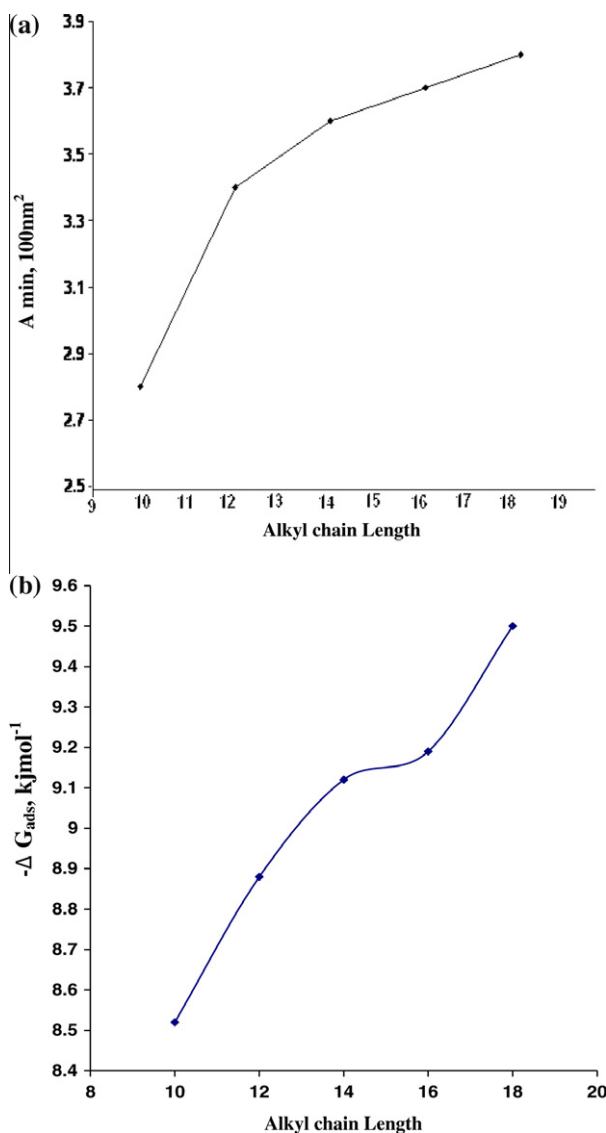
Figure 4 Effect of alkyl chain length of E (43) BAC monoester derivatives on (a) A_{min} and (b) ΔG_{ads}.

Figure 5 Effect of bisphenol skeletons on the ΔG_{ads} via E (43) monoester LL.
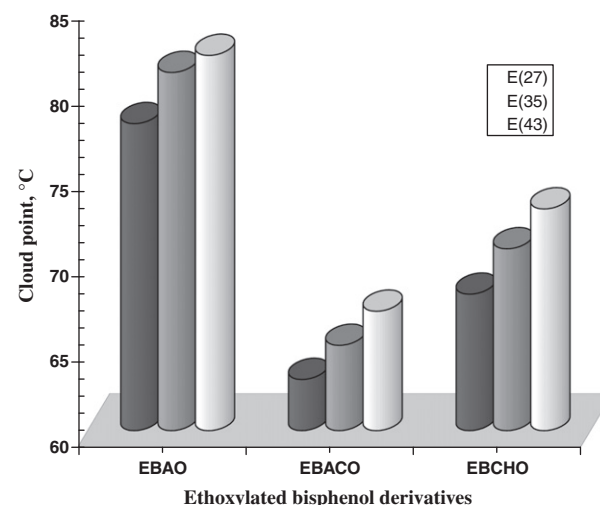
Figure 6 Effect of ethylene oxide content on the cloud point of ethoxylated bisphenol monoester.

between water molecules and the lone pairs of electron of the ethereal oxygen atoms, [18,19]. So that the surfactant which contains 43-ethylene oxide unit needs a higher energy to breakdown the hydrogen bonds among other surfactants, which contain 35 and 27-ethylene oxide units.

3.7. Effect of alkyl chain length on cloud point

This factor can be shown in Fig. 8. The ester of decanoic, lauric, myrestic, palmetic and stearic acids at ethoxylated (43) bisphenol AC were selected as representative samples. Generally, the increasing of alkyl chain length increases the cloud point. By inspection of the data of cp in (Table 1), it was found that the CP is 55 °C of the E(43) BACMD (the shortest chain length) but of E(43) BACMS is 67 °C. This is may be due to the distortion motion of the alkyl chain which increases the free energy of the solvent [16]. As a result of the low distortion motion formed by short chain length as in E(43) BACMD has no effect on the coiling of ethylene oxide chain [17]. So that,
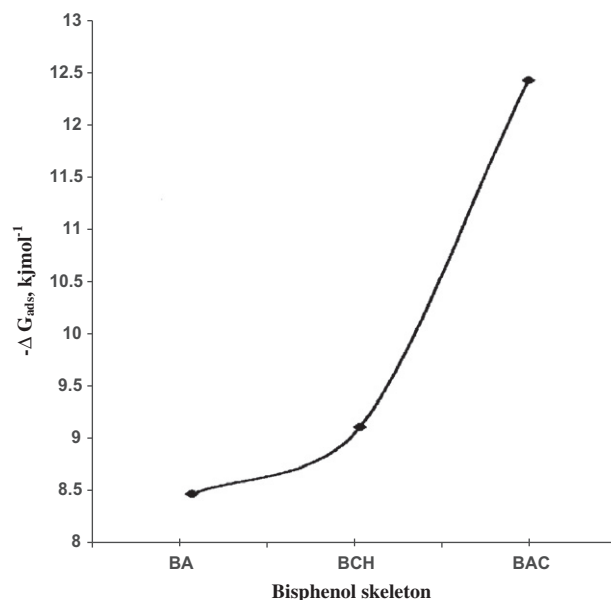
the small number of hydrogen bonds could be formed as a result of coiling, which need less energy (55 °C) to breakdown. But, the long alkyl chain length as in E(43) BACMS increases the distortion motion of the molecule in the solvent (water). This increasing of motion could be exposed to the ethylene oxide chain to decoil and solvated by a larger number of water molecules to form a larger number of hydrogen bonds than those formed with E(43) BACMD. As a result, the E(43) BACMS needs greater energy (67 °C) to breakdown these hydrogen bonds than in the E(43) BACD (55 °C).

3.8. Effect of unsaturation of alkyl chain on cloud point

The data of CP are listed in (Table 1). The effect of unsaturation degree on the CP is shown in Fig. 7. This figure shows the
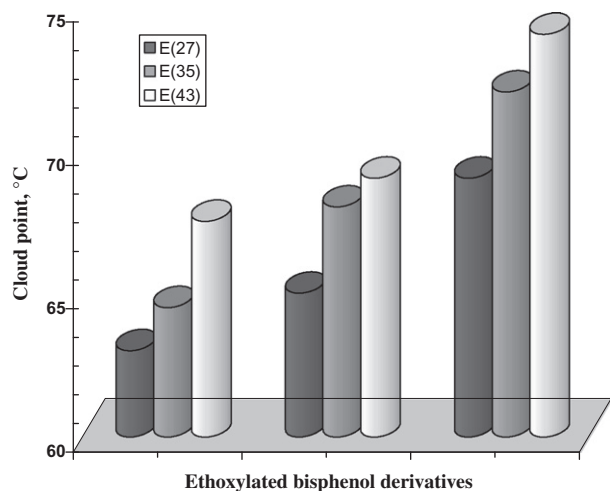
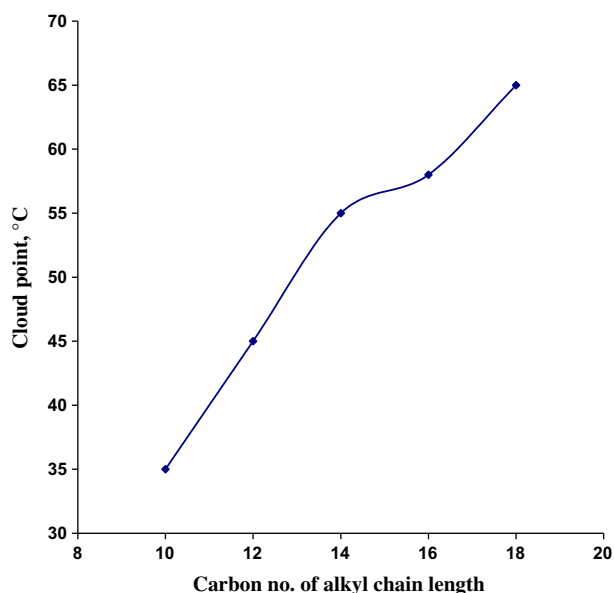**Figure 7** Effect of unsaturation on the cloud point of E (43) BAC monounsaturated esters.

Figure 8 Effect of alkyl chain length on the cloud point of E(43) BAC monoester derivatives (alkyl chain; C10, C12, C16, C18 coming from fatty acids.

CP of E(43) BAC ester with oleic, linoleic and linolinic acids as representative samples. It can be noted that the increasing number of double bond increases the cloud point. This is related to the presence of P_Z orbital [20], which builds up a partial negative charge on the double bond. This negative charge plays a role to build up hydrogen bonds between the water molecules and the double bond. From (Table 1) the CP. values were; 67, 70, 72 and 76 °C corresponding to E(43) BACMS; E(43) BACMO; E(43) BACMLO and E(43) BACMLL respectively. The higher CP was exhibited with the linoleneate ester E(43) BACMLL (3-double bonds), but the minimum CP was obtained with stearate ester E(43) BACMS (Zero-double bond). This means that the linoleneate ester needs more energy to breakdown the hydrogen bonds. So that the higher CP among others was obtained (76 °C).

3.9. Relation between cloud point and surface active properties

The relation between CP and both of A_{min}/mol and ΔG_{ads} is shown in Table 1. From the obtained data it was found that the CP depends on the break down of hydrogen bonds on the surfactant molecule, which depends on the degree of ethoxylation. At the same time, the increase of ethylene oxide contents increases both of A_{min} and CP. It was seen also from Table 1 the highest CP and A_{min} were obtained by diethoxylated BA at different ethylene oxide contents before esterification. At the same time, the lowest CP was obtained against the monoesterified bisphenol derivatives (EBAMLL, EBAMLO, EBAMO). This note proves that the good relation may be existing between the CP and A_{min}/molecule. By inspection Table 1, it was found that, the controversy results were obtained between CP and $-\Delta G_{ads}$ in comparison to A_{min}. The ethoxylated bisphenol (EBA) exhibited less values of $-\Delta G_{ads}$ but the mono ester of ethoxylated derivatives considered a typical surfactant form (i.e. Fig. 3), at which the alkyl group makes distortion motion in the solution to rise the free energy of the system to push the molecule into the surface. The decreasing of $-\Delta G_{ads}$ of the diethoxylated bisphenol may be due to its incomplete surfactant form. This form is mainly non-ionic ethoxylated form without alkyl chain that exhibited the minimum value of $-\Delta G_{ads}$ at all ethylene oxide contents. At the same time, the increase in values of $-\Delta G_{ads}$ is accompanied by decreasing of the CP of surfactant. The same behavior of these relationships has been seen for the bisphenol (EBAC). but from the plotted data of CP versus $-\Delta G_{ads}$ it was found that the values of $-\Delta G_{ads}$ for (EBAC) and their derivatives are greater than those obtained by (EBA) and their derivatives. This result may be due to the core skeleton of bisphenol that plays a role to increase the free energy of the solution system.

The plotted data in Table 1 show the relation between A_{min} and $-\Delta G_{ads}$ against of CP of bisphenol (ECH) and their derivatives. The same behavior also was remarked regarding the relation between CP and both of A_{min} and $-\Delta G_{ads}$. From the data obtained it was found that, the increase of alkyl length increases both of A_{min} and CP; which is remarkable for [E(43) BACMS, E(43) BACMP, E(43) BACMM, E(43) BACML and E(43) BACMD]. At the same time, the increase of alkyl chain length leads to increase of $-\Delta G_{ads}$ values and CP. From the obtained observations one can conclude that a strong relation should exist between surface active properties of surfactants and their cloud points.

4. Conclusion

A series of non-ionic surfactants were prepared based on three bisphenols derived from acetone, acetophenon and cyclohexanon. The conclusion of this work can be drawn in the following points:

- The cloud point of the non-ionic surfactants effects by the alkyl chain length, number of ethylene oxide units, structure of bisphenol skeleton and the degree of unsaturation in the alkyl chains.
- By studying the surface active properties of the investigated non-ionic surfactants, a good relationship between cloud point and surface active properties was found.

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