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PREPARATION OF SOME CATIONIC BIPHENYL SURFACTANTS. SURFACE AND BIOLOGICAL ACTIVITIES

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ABSTRACT

A series of cationic surfactants was prepared by chloromethylation of some alkyl biphenyls and using the produced compounds as quaternizing agent for methyl diethanolamine. The products obtained were characterized by FTIR and elemental analysis. The physicochemical properties of these compounds were studied at room temperature in their aqueous solutions by measuring the critical micelle concentration (CMC) as function of their molecular structures, where the conventional surface tension vs. –log concentration curve showed the classical sharp break which coincided with CMC point. Also, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}), minimum surface area (A_{min}) and free energies of micellization and adsorption were investigated. Their antimicrobial effects were also determined.

Key words

Alkyl biphenyl, quaternary cationic surfactants, critical micelle concentration, effectiveness, efficiency, maximum surface excess, minimum surface area, micellization, adsorption free energy, antibacterial activity, antifungal activity.

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INTRODUCTION

Conventional surfactant molecules consist of hydrophobic and hydrophilic parts. With increasing concentrations, they form micelles and then lyotropic mesophases. These organized microstructures are considerably dependent on their own structure [1]. The discrete positive charge on the quaternary ammonium ion promotes strong adsorption on negatively charged substrates, such as fabrics and it is the basis for the wide spread use of these surfactants in domestic fabric softening compositions. Many quaternized compounds are used as textile auxiliary agents for finishing textiles [2, 3], for processing fibers and fabrics [4] and for dyeing paper or textile [5, 6] to give them a soft hand. Some quaternaries are antibacterial agents [7], where several studies indicate that some quaternary ammonium compounds act as corrosion inhibitor and decreased sulfide production by sulphate reducing bacteria SRB at low concentration than some biocides of a commercial sources [8]. This meant that quaternary ammonium compounds have double purpose. Moreover, it was found that quaternary compounds are safe to handle [9].

In this study, a new series of cationic compounds was synthesized and evaluated as surface active agents. Their surface and thermodynamic properties in aqueous solutions were evaluated. Also, their applicability as antibacterial and antifungal agents was realized.

EXPERIMENTAL PROCEDURES

Preparation of alkyl biphenyl ketones

Alkyl biphenyl ketones, namely pentyl, heptyl, nonyl and unidecyl biphenyl ketones were prepared by the reaction of biphenyl with

stoichiometric amounts of the corresponding acid chlorides (hexanoyl, octanoyl, decanoyl and dodecanoyl chloride) [10]

Reduction of the alkyl biphenyl ketones

The prepared four ketones were reduced to the corresponding alkyl biphenyls using the methodology of Clemmensen's reduction [11].

Chloromethylation of alkyl biphenyls

0.224moles of the alkyl biphenyl, (9gm) of paraformaldehyde, (25gm) of glacial acetic acid, (28cc) of concentrated hydrochloric acid and (13.5cc) of 85% phosphoric acid were all placed in three necked flask, fitted with a reflux condenser and a mechanical stirrer. The reaction mixture was agitated at 100°C in a steam bath for four and a half hours. On cooling, the organic layer was separated, washed three times with cold water, dissolved in ethanol, and then evaporated under vacuum [12].

Synthesis of the quaternary derivatives

Each of the prepared chloromethylated (hexyl, octyl, decyl and dodecyl) biphenyl used respectively as quaternizing agent for N,N-methyl diethanolamine, in benzene at 40°C overnight [13] to produce compounds (I-IV). Elemental analyses were made to ensure the purity of the prepared surfactants, (Table 1). While, FTIR spectroscopic analyses were performed to determine the functional groups within their chemical structures, (Table 2)

Surface tension measurements

Surface tension measurements were performed for freshly prepared solutions of the quaternary compounds in a concentration range of 0.1 – 0.0001M/L at room temperature using Du-Nouy tensiometer [14]

Antimicrobial activity

The antimicrobial measurements were done in Fermentation Biotechnology and Applied Microbiology Center (FBAM) Al-Azhar University.

All the prepared surfactants were tested for their antimicrobial activities. The test was done using the diffusion agar technique. Chloromphenicol was used as a standard antibacterial agent, while Grisofluvine was used as a standard antifungal agent.

RESULTS AND DISCUSSION

Surface properties

The surface tension vs. –log molar concentration (-log C) curves for the prepared compounds are shown in Figure (1). These curves showed two characteristic regions. At lower concentration, the variation of the surface tension against concentration variation is very fast. At higher concentrations, that variation is relatively low. The intercept of these two regions indicate a certain point of concentration which is an intermediate between two phases. That point is called the critical micelle concentration (CMC). From the curves, several surface parameters and energetic factors could be extracted including; CMC, Pc_{20}, π_{cmc}, Γ_{max}, A_{min}, ΔG_{mic} and ΔG_{ads} [15] values are listed in Table (3).

Critical micelle concentration (CMC)

It is indicated clearly from Figure (1) that the surface tension decreases as the concentration increases. Where, the surfactant molecules adsorbed on the liquid/air interface of the solution until the surface of the solution is completely occupied, and then the excess molecules tend to self aggregate in the bulk forming micelles. There are two antagonistic effects

controlling the micellization. The hydrophobic group which is an important driving force in micellization and the hydrophilic group which opposes micellization. In this investigation, where the hydrophilic group is constant, we observe that the CMC values of the prepared compounds decrease as the length of the alkyl chains increase. Plots of log CMC vs. number of carbon atoms (n), for the prepared compounds are shown in Figure (2). It has been established that the CMC decrease with the increasing of chain length according to the expression:

$$log\ CMC = A - Bn$$

where, A, B are the intercept and the slope of the log CMC vs. n curve [16].

That could be explained through the following fact: increasing the hydrophobic chain length increase the repulsion forces between the nonpolar phase (alkyl chains) and the polar phase (water). That repulsion increases the kinetic energy of surfactant molecules, which encourage their aggregation into other phase (micelle). That phase capable to locate in the bulk of the solution with lower kinetic energy

The surface tension values at the respective CMCs (γ_{cmc}) were given in Table (3). The results indicate that an increase from hexyl- to dodecyl- in the hydrophobic chain length renders the surfactants more surface active [17].

Efficiency (Pc_{20})

Away of measuring the relative effects of some structural factors on micellization and on adsorption is to determine its Pc_{20} values [18], where Pc_{20} is the concentration of the surfactant in the bulk phase that produces a reduction of 20 dyne/cm in the surface tension of the solvent. The Pc_{20} value measures the efficiency of adsorption of surfactant molecules at the interface.

Table (3) shows that Pc_{20} values of the synthesized surfactant solutions increase with increasing number of carbon atoms in the hydrophobic chain (n). The longer the chain length of the surfactant, the larger the Pc_{20} value and the smaller the bulk liquid phase concentration required to attain either saturation adsorption or surface tension reduction of 20 dyne/cm.

Results also indicate that micellization process of surfactant molecules in the bulk of their solutions is inhibited more than their adsorption at the air/water interface, i.e., adsorption is facilitated more than micellization.

Figure (3) shows the linear relation between Pc_{20} (-log Pc_{20}) and number of carbon atoms in the hydrophobic chains (n). That linearity showed the ideal behaviour of the surface properties of these surfactants as their alkyl chain length changed in regular order .

Effectiveness (π_{cmc})

The surface tension (γ) values at CMC were used to calculate values of the surface pressure (effectiveness) from:

$$\Pi_{cmc} = \gamma_o - \gamma$$

where γ_o is the surface tension measured for pure water at room temperature and γ is the surface tension at critical micelle concentration (CMC). Values of π_{cmc} were represented in Table (3). The most efficient surfactant is that one gives the greater lowering in surface tension at CMC.

Compound IV found to achieve the maximum reduction of the surface tension at its critical micelle concentration value.

Maximum surface excess (Γ_{max})

The surface excess Γ at the air/water interface can be calculated by applying the Gibb's adsorption equation:

$$\Gamma = 1 / RT\,(d\gamma / d\ln C)$$

γ is the surface tension and C is the surfactant concentration below CMC, T is absolute temperature, R is the gas constant.

A substance that lowers the surface energy is thus present in excess at or near the surface, i.e., when the surface tension decreases with increasing activity of surfactant, Γ is positive.

The maximum surface excess of the surfactant solution showed the number of surfactant molecules located in unit area at the air/water interface. That ability is increased by increasing the hydrophobic characters of these molecules.

Values of Γ_{max} represented in Table (3) indicate that increasing the hydrophobic character of the prepared compounds causes a corresponding increase in Γ_{max} values. This indicates that the molecules are more tightly packed in the water/air interface for longer alkyl surfactants [19].

Minimum surface area (A_{min})

The average area occupied by each surfactant molecule at the air/water interface is given by:

$$A_{min} = 1 / N_{av}\,\Gamma_{max}$$

where Γ_{max} is the maximum surface excess and N_{av} is Avogadro's number.

Increase Γ_{max} of the surfactant solutions indicates the increasing number of their molecules at the air/water interface. Hence, the area available for each molecule at the interface will be decreased. It is obvious form the data of A_{min} in Table (3) that increasing the alkyl chain length decreases the area occupied by each molecule. From Table (3), it can be concluded that compound (IV) has the lowest area at the air/water interface.

Standard free energies of micellization and adsorption (ΔG_{mic}, ΔG_{ads})

The energetic parameters of micellization and adsorption of the prepared surfactants were calculated using Gibb's equation of thermodynamics. From Table (3), it is obvious that the standard free energies of micellization for the synthesized surfactants are always negative values indicating that the micellization process is a spontaneous one. Increasing the chain length of the hydrophobic moiety causes a decrease in ΔG_{mic} values, which indicate that micellization is more spontaneous.

On the other hand, from Table (3), it was observed that the standard free energies of adsorption (ΔG_{ads}) of the synthesized surfactants were found to be in higher negative values rather than those of micellization process. This leads to the fact that adsorption process of the surfactant molecules was more preferable than the micellization process.

From the energetic data of adsorption and micellization processes, one could conclude that the synthesized biphenyl cationic surfactants have high tendency towards adsorption at the interfaces than micellization in the bulk of the solution. So that, these surfactants will be highly efficient in the surface applications.

Antimicrobial Activity

One of the most important applications of surfactant series which have high tendency towards adsorption is their use as antibacterial and antifungal agents to prevent their growth and spreading, i.e., antimicrobial agents. The role of these compounds can be summarized in increasing the permeability of the cell membranes of these microorganisms. That effect damages the biological balance in their cytoplasm leading to their death [20].

Hence, the synthesized cationic surfactants were evaluated as antibacterial and antifungal agents for the growth of different types of bacteria and fungi.

Antibacterial activity

The antibacterial activity of the products was tested against four test organisms namely: E. coli, Salmonella typhi., Staphylococcus aureus and Bacillus subtillus. From the results listed in Table (4), it was found that compound III has the greatest activity towards all the test organisms.

On the other hand, Bacillus subtillus growth inhibition has been occurred by all compounds at their lowest concentrations. Staphylococcus aureus found to be affected by the prepared compounds only at higher concentration.

Antifungal activity

The antifungal activity of the prepared compounds was tested against Aspergillus niger and Aspergillus flavus. From Table (5), it was observed that only compound IV has a considerable activity towards both Aspergillus niger and Aspergillus flavus. The other three compounds (I – III) showed a moderate activity towards Aspergillus niger rather than Aspergillus flavus.

CONCLUSIONS:

A new set of cationic surfactants were synthesized. Some of their surface properties were characterized. It was found that their CMC values decrease as the length of the alkyl chains increase. Values of the surface tension of the respective CMCs (γ_{CMC}) found to be increase as the hydrophobicity of the compounds increase. The synthesized surfactants were evaluated as antibacterial and antfungal agents. Compound III found to has the greatest antibacterial activity and compound IV has considerable activity towards both fungi types.

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Table 1. Elemental analysis of the prepared compounds (I – IV)

Compound	Carbon		Hydrogen		Nitrogen		Chlorine	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
I	73.75	73.81	9.47	9.63	3.59	3.37	9.09	9.16
II	74.55	74.33	9.80	9.49	3.35	3.41	8.48	8.53
III	75.25	75.18	10.08	10.26	3.14	3.22	7.95	8.13
IV	75.87	75.57	10.33	10.18	2.95	3.13	7.48	7.29

Table 2. FTIR spectroscopy of the prepared compounds (I – IV)

Compound	$CH_{arom.}$	CH_{aliph}	$-CH_3$	C-N	-OH
I	3130	2890	1380	3350	3650
II	3100	2870	1375	3300	3630
III	3030	2870	1390	3310	3650
IV	3050	2860	1380	3340	3600

Table 3. Surface properties of the prepared compounds (I – IV)

Compound	-log CMC	γ_{cmc}	π_{cmc}	Pc_{20}	$\Gamma_{max} \times 10^{-9}$ (mol/cm^2)	A_{min} (nm^2)	ΔG_{mic} (kJ/mol)	ΔG_{ads} (kJ/mol)
I	1.66	41	30.8	2.51	1.387	1.179	-22.64	-44.80
II	1.83	40	31.8	2.60	1.452	1.143	-24.95	-46.85
III	1.96	37	34.8	2.66	1.502	1.105	-26.73	-49.89
IV	2.00	33	38.8	2.84	1.973	0.841	-27.27	-51.48

Table 4. Antibacterial activity of the prepared compounds (I – IV)

Compound	Bacteria											
	Salmonella typhi			E. coli			Bacillus subtillus			Staphy. coccus		
Dose, mg/ml	1	2.5	5.0	1	2.5	5.0	1	2.5	5.0	1	2.5	5.0
I	-	-	-	-	-	-	+	+	+	-	-	+
II	-	-	-	-	-	-	+	+	+	-	-	+
III	-	+	+	-	-	+	+	+	+	-	+	+
IV	-	-	-	-	-	-	+	+	+	-	-	+

Table 5. Antifungal activity of the prepared compounds (I – IV)

Compound	Fungi					
	Aspergillus niger			Aspergillus flav.		
Dose, mg/ml	1	2.5	5.0	1	2.5	5.0
I	-	-	+	-	-	-
II	-	-	+	-	-	+
III	-	-	+	-	-	-
IV	-	+	+	-	+	+

++ = Strong inhibition zone = 1.0 – 0.6 cm.

+ = Moderate inhibition zone = 0.5 – 0.1cm.

- = No inhibition, well diameter = 1 cm.

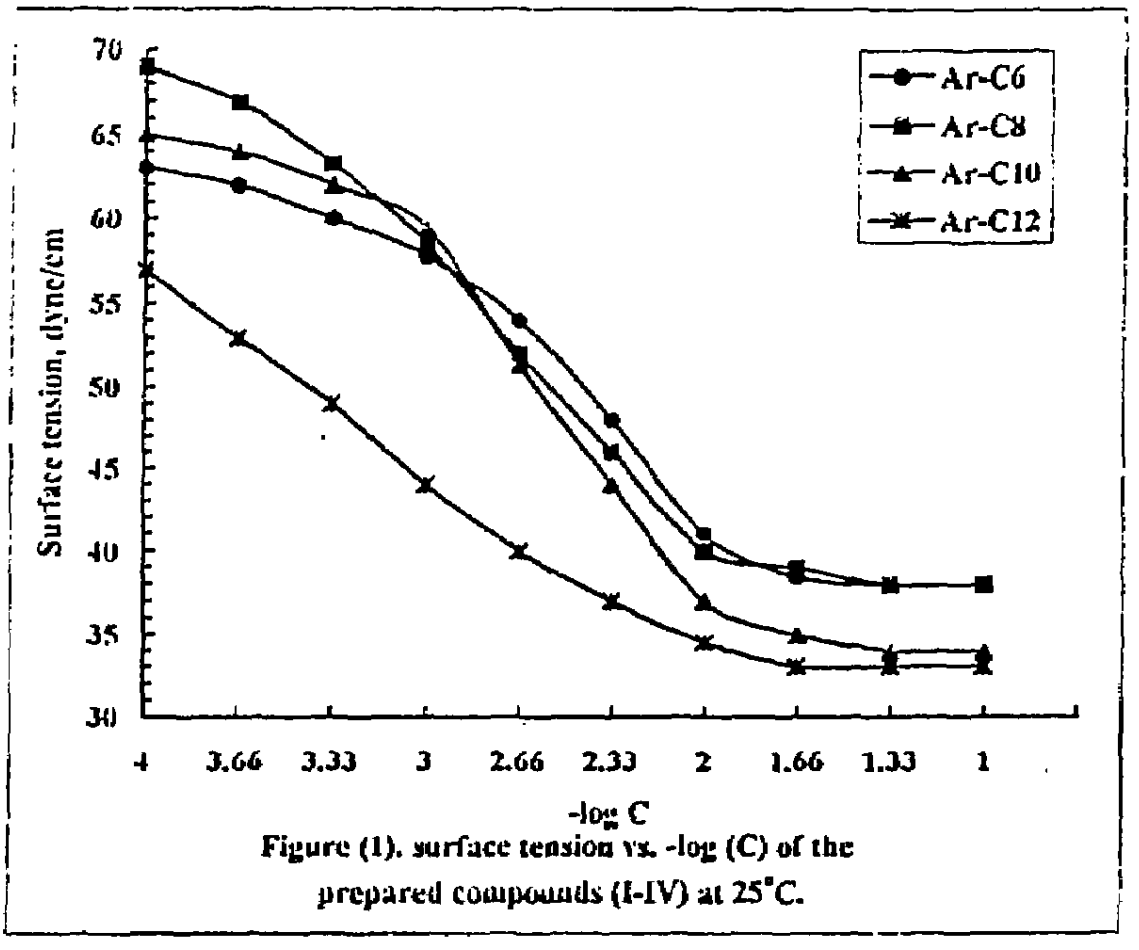

Figure (1). surface tension vs. -log (C) of the prepared compounds (I-IV) at 25°C.

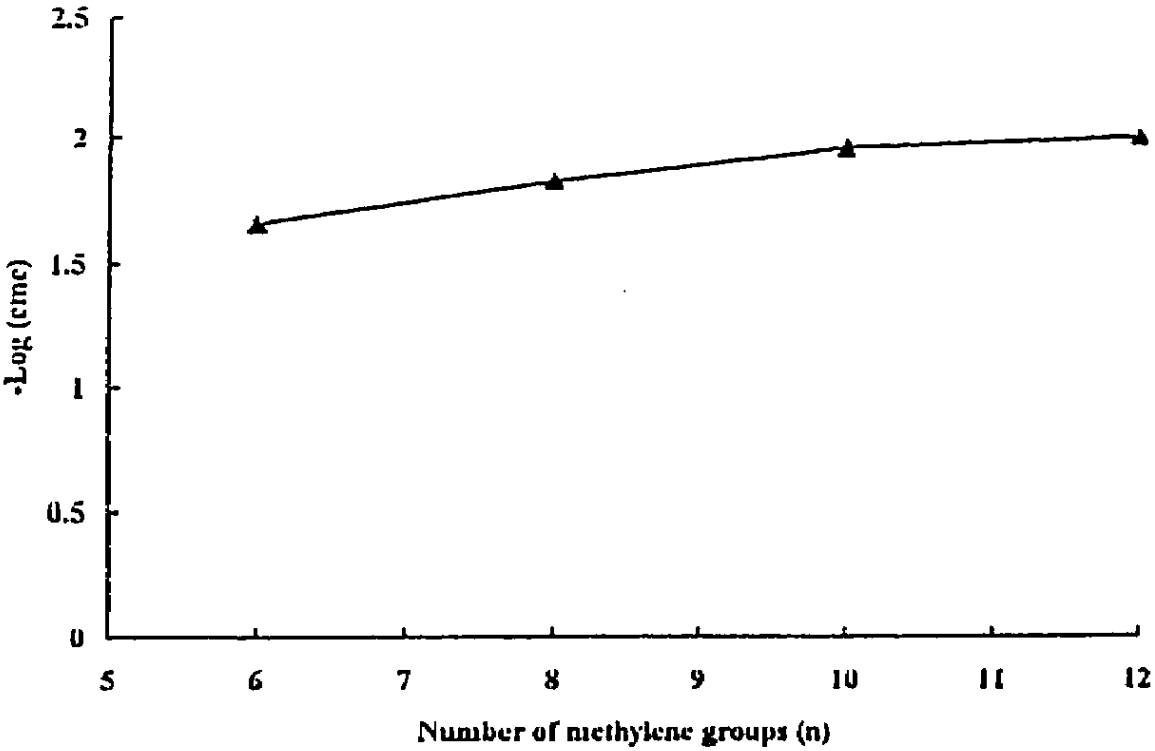

Figure (2). relation between -log (cmc) and number of methylene groups (n) of the prepared compounds (I-IV) at 25°C.

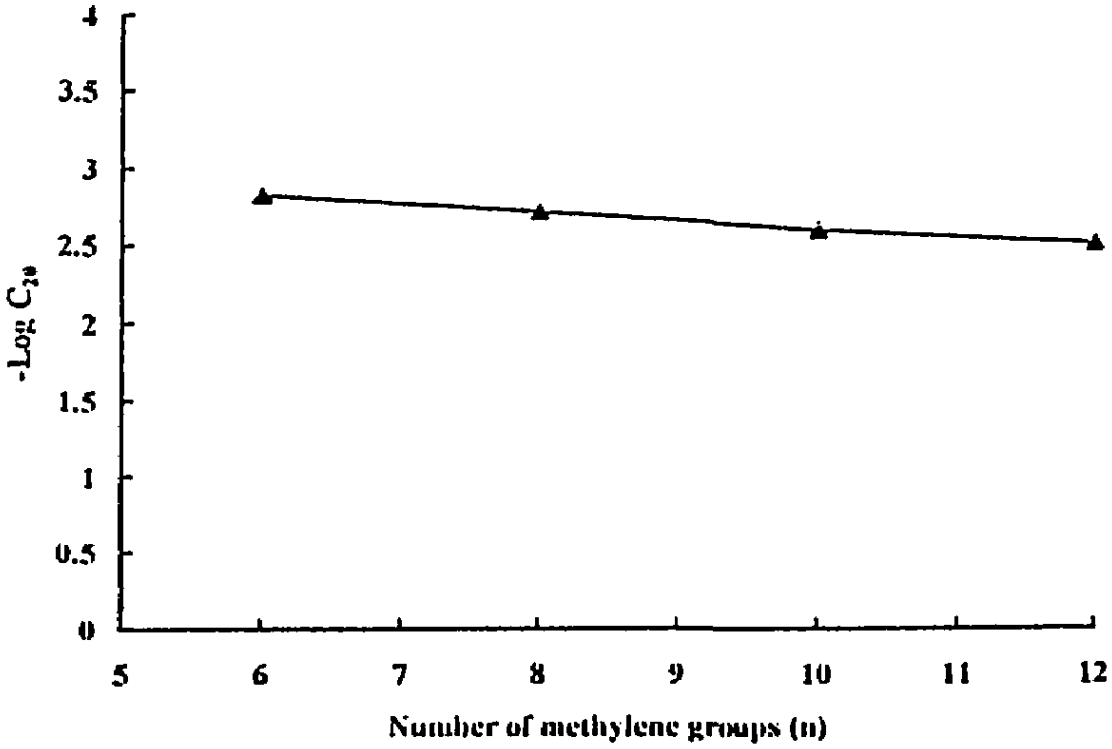

Figure (3). relation between -log C_{20} and number of methylene groups (n) of the prepared compounds (I-IV) at 25°C.