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SYNTHESIS AND SOME STUDIES ON QUATERNIZED COMPOUNDS: SURFACE AND BIOCIDAL ACTIVITIES

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Abstract

A homologous series of cationic surfactants namely: Hexamine, N-(carboxy methyl) alkylchloride, (alkyl=octyl, dodecyl, hexadecyl and octadecyl) were synthesized.

Surface properties of their solutions including surface tension, critical micelle concentration (CMC), effectiveness (Π_{cmc}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) were investigated with respect to different concentrations at 25°C. Standard free energies of micellization and adsorption of the prepared surfactants in the aqueous solution were studied. Minimal inhibitory concentrations of the synthesized compounds and of cetyltriammonium bromide (CTAB) were determined for the stabilized mixed culture containing sulfate reducing bacteria, (SMC-SRB). Sulfide production using different concentrations of the biocides ranging from 10 to 250ppm was determined.

Key words

Critical micelle concentrations, Quaternary ammonium compounds, Biocides, Stabilized mixed culture-sulphate reducing bacteria.

Introduction

A clear understanding of the process of micellizations is necessary for rational interpretation of the effect of structural and environmental factors on the value of the critical micelle concentration.

Quaternary ammonium compounds have scores of uses because of their affinity for negatively charged surfaces. Their single largest market is as fabric softeners. A quaternary formulation is added with the wet clothes when they are loaded into dryer. A large market for quaternary compounds is in manufacture of organo modified clay, coatings, cosmetics and printing inks. Their surface active properties also help in removing oil from the sand stone formation. They also exhibit excellent germicidal activity in the bactericidal market[1]. These compounds are most effective against anaerobic bacteria (e.g. those that occur in oil wells). These bacteria are mainly sulfate reducers, and their growth frequently causes severe corrosion problems in oil wells pipes.

Due to the economic losses as well as environmental health and safety hazards caused by the activity of SMC-SRB in many industrial sectors such as the oil and gas industry, it was important to minimize the risks resulting from SRB activity. Chemical control by the use of the biocides was probably the most common method of controlling of biocorrosion(2). Quaternary ammonium compounds are frequently used. However, it ought to be emphasized that SRB varied in their susceptibility to biocides(3).

Several studies indicated that some quaternary ammonium compounds act as corrosion inhibitors and decrease sulfide production by SRB at low concentration than some biocides of commercial source(4). This meant that quaternary ammonium compounds had double purposes. Further more, it was found that quaternary compounds were safe to handle(5).

Experimental

Synthesis of Quaternary Ammonium Surfactants

Synthesis of quaternary ammonium surfactants was performed on two steps;

a- Synthesis of Alkyl Chloroacetate Ester

Fatty alcohol namely: octyl-, dodecyl, Hexadecyl, and octadecyl alcohol (0.1 mole) was esterified by chloro acetic acid in toulene as a solvent in presence of concentrated hydrochloric acid as a catalyst till the desired amount of water (0.1 mole, 1.8ml) was removed. The removal of excess solvent and unreacted materials was performed in rotary evaporator under reduced pressure(6).

b- Preparation of Quaternary Ammonium Surfactant

A mixture of equimolecular amounts of Hexamine (0.1 mole) and each of octyl-, dodecyl, Hexadecyl, and octadecyl chloroacetate (0.1 mole) was stirred without solvent (fusion) respectively for 5 hours,(7,8,9) the following quaternary ammonium salts were produced:

I_a : Hexamine, N- (carboxymethyl) octyl chloride
I_b : Hexamine, N- (carboxymethyl) dodecyl chloride
I_c : Hexamine, N- (carboxymethyl) hexadecyl chloride
I_d : Hexamine, N- (carboxymethyl) octadecyl chloride

The product was poured on ether, recrystalized from ethanol, and eventually dried at room temperature. Elemental analysis were carried out (Table 1). The analysis showed good compatibility with the calculated values.

The IR-spectra of these compounds show definite band frequencies corresponding to the presence of the functional groups, Table(2).

Surface Tension Measurements

Surface tension measured using a Du Nouy ring tensiometer (Kruss type 8451) with a platinum ring for various concentrations of the synthesized surfactants I_{a-d} (from $2.5x10^{-7}$ to $5x10^{-2}$ mol/l) at 25°C. Doubly distilled water having a surface tension of 72.8 dyne cm^{-1} at 25°C was used to prepare all solutions.

Before each measurement, the glass plate was thoroughly washed by immersion in hot chromic acid followed by washing with doubly distilled water. It was then gently wiped with filter paper. Care was always taken that the glass plate was wetted with the solution. The surfactant solution was placed in a double walled vessel through which water was circulated from a thermostat bath. The establishment of equilibrium was checked by repeated measurements at 5 minute intervals until the surface tension readings stablized.(10) This generally required 30-45min.

Determination of Critical Micelle Concentration (CMC)

Surface tension (γ)-log c (where C is the concentrations of surfactant) plots (Fig.1) were established. CMC values of the aqueous solutions of the prepared compounds I_{a-d} were determined at 25°C from the intersection points of the two straight lines in the γ log c plots(11).

Determination of Surface Parameters, Standard Free Energies of Micellization and Adsorption

Maximum surface excess concentration Γ_{max}, minimum surface area A_{min}, effectiveness "Π_{cmc}", the standard free energies of micellization (ΔG^0_{mic}), the standard free energies for adsorption (ΔG^0_{ads}) for the synthesized surfactants I_{a-d} were calculated as will be shown later. Results are listed in Table (3).

Biocidal Activity of Quaternary Compounds

Materials and Methods

Micro organisms

The stabilized mixed culture sulphate reducing Bacteria (SMC-SRB) was isolated from the National Research Center (NRC) garden soil.

Media:

Postage medium B(3) was expressed in gram/liter (g/l). This medium contained a precipitate. It was used for enrichment of SRB.

Biocides:

Cetyltriammonium bromide (CTAB); Hexatrimethyl ammonium bromide ($C_{16}H_{33}NC_3H_9Br$) is the biocidal reference (from Sigma-chemical company).

Samples:

The synthesized surfactants from I_{a-d} are the biocidal compounds under test

Collection of SMC-SRB:

A garden soil (G.S.) sample was collected at a depth of 20-25 cm and stored in sterial container. The soil sample was shaken in steril distilled water to loosen the soil particles and the soil suspension allowed to settle for 30min. An appropriate volume was taken form the supernatant and inoculated into steril bottles contained 35ml of Postgate medium B each. The vials were incubated at 30°C for 3-4 days. Blackening meant the presence of SMC-SRB.

Isolation and Enrichment of the SMC-SRB

Prerequisted for reproducibility of the experimental results(3), the method described by Postgate (1984) was used with some modifications by using the deep agar method(12).

Determination of the Minimal Inhibitory Concentrations (mic) of (CTAB) Pure Biocide as a Reference Biocide and Quaternary Ammonium Compounds

CTAB and prepared quaternary ammonium compounds I_{a-d} were used as biocide. The (mic) of these compounds on sulfide production by SMC-SRB were determined by preparing Postgade medium B containing the following biocides concentrations 10,90,120,150,200, 250, 300ppm. The inoculation was done by adding 1ml of a four days enriched old culture of SMC-SRB into the sterile capped bottles containing each biocide amended media. Incubation was done at 30°C for seven days. The sulfide concentration, were determined iodometrically(13) and the results are shown in Table (4).

The biocidal efficiency of quaternary compounds I_{a-d} against SMC-SRB were calculated as shown in Table (5), from the following equation:

$$E = \frac{A-A'}{A} \times 100$$

Where E is the efficiency of biocide, A,A' are uninhibited and inhibited sulphide concen-tration in mg/l respectively.

Results and Discussion

Surface properties

Micellization is an important phenomenon, in detergency and solubilization, micelles have become a subject of a great interest to the organic chemist and the biochemist, to the former because of the utilization in catalyzed organic reactions, to the later because of their similarity to biological membranes and globular proteins.

A clear understanding of the process of micellization is necessary for rational interpretation of the effect of structure and environmental factors on the values of the critical micelle concentration (CMC). So, the determination of the parameters of micellization and adsorption has played an important role in developing, such an understanding about the behaviour of surfactants in their media.

The surface activities of I_{a-d}, stem from the hydrophobic character of long chain alkyl moiety (octyl, dodecyl, hexadecyl, and octadecyl) and the cationic group.

The hexamethylene tetramonium salts containing large hydrocarbon radicals were found to be only sparingly soluble in cold water and the water solutions were not stable over long periods of time, but the dry compounds have been kept several months at room temperature.

Critical micell concentration

From Fig. (1), it is indicated clearly that the surface tension decreases, as the activity (concentration) increases. Definitely, first, the surfactant molecules are adsorbed on the liquid/air interface of the solution until the surface of the solution is completely occupied. Second, the excess molecules tend to self aggregate in the bulk forming micelles.

From, the intersection points of the two straight lines in the γ-log plots, the critical micelle concentration, CMC, was determined. There are two antagonistic effects controlling the micellization. The hydrophobic group is an important driving force in micellization. In contrast, the hydrophilic group opposes micellization. The number of carbon atoms in the hydrophobic moiety was found to be a determining factor in the values of CMC. For the prepared surfactant series I_{a-d}, the values of log CMC decreases as the chain length increases.

Effectiveness Π_{cmc}

Above the CMC the surface tension γ didn't change with concentration. Accordingly γ at CMC were used to calculate values of the surface pressure (effectiveness) $\Pi_{cmc} = \gamma_o - \gamma$, where γ_o is the surface tension measured for pure water at the appropriate temperature and γ is the surface tension at critical micelle concentration (CMC).

The most efficient is the one that gives the greatest lowering in surface tension for a critical micelle concentration (CMC). According to the result of effectiveness shown in table (3), I_a is found to be the most efficient, it achieves the maximum reduction of the surface tension at CMC Fig. (1).

Maximum surface excess concentration Γ_{max}

The values of the maximum surface excess concentration Γ_{max} were calculated according to Gibb's equation[14];

$$\Gamma_{max} = \frac{-1}{RT}\left(\frac{d\gamma}{d\ln c}\right)$$

where dγ: is the change in surface tension C: the concentration of the surfactant below CMC, T: absoulte temperature, R: gas constant. The values of Γ_{max} are shown in table (3). As the surface tension decreases with increasing concentration of surfactant, Γ_{max} is positive. Increasing the hydrophobic character in the prepared surfactants shifts Γ_{max} to lower concentrations. It was clear that change in length of the hydrophobic group beyond (12) carbon atoms appears to have very little effect on Γ_{max}.

Minimum Surface area A_{min}

The average area occupied by each adsorbed molecule is given by

$$A = \frac{1}{\Gamma_{max} N}$$

where, Γ_{max} maximum surface excess, N Avogadros's number = 6.062×10^{23}.

The minimum area per molecule at the aqueous solution / air interface increases with increasing the length of the hydrophobic part.

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule. According to the cross sectional area of an aliphatic chain oriented perpendicular(15) to the interface is about $0.2 nm^2$. Table (3) showed greater values than $0.2 nm^2$, this indicates that the surfactant molecules seems to be not located in perpendicular position but tilled with respect to interface. The greater average area occupied by surfactant molecules on the interface can be refered to water / hydrophobes interaction.

Standard free energies of micellization and adsorption

These parameters were calculated at 25°C using Gibb's equations (16,17):

$$\Delta G^{o}_{mic} = RT \ln CMC$$

$$\Delta G^{o}_{ads} = \Delta G^{o}_{mic} - \Pi_{CMC} A_{min}$$

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 is a spontaneous process. At a constant temperature ΔG^{o}_{mic} decreased as the chain length of the hydrophobic moiety increased indicating that the micellization is more spontaneous i.e. introduction of additional methylene group into the hydrophobnic part favors the micellization, which accounts for the fact that CMC decreases with increase in the length of the hydrophobic group.

The standard free energies of adsorption (ΔG^{o}_{ads}) of the synthesized surfactants were found to be in higher negative values than those of micellization process, this means that the adsorption process of the surfactant molecules was more preferable than the micellization due to the fewer interactions by water molecules in the former one.

Biocidal activity of quaternary compounds

The reproducible stabilized mixed culture was called SMC-SRB indicating that it contained the sulfate reducing bacteria, in addition to the most biolfilm aerobic coexisting bacteria which caused pitting corrosion of mild steel. However there was no evidence that any of SRB was more destructive than another.

The synthesized quaternary ammonium compounds and CTAB were tested to evaluate their effect on SMC-SRB. Since, sulphide was the final product of sulphate reduction by SMC-SRB, the sulphide prouced was taken as an indicator for the inhibition activity of compounds I_{a-d} towards SMC-SRB. Obviously, the synthesized quaternaries I_{a-d} showed a relatively higher inhibiting efficiency towards SMC-SRB than the reference (CTAB). This higher boicidal activity could be explained due to electrostatic attraction of positively charged (N^+) of the quaternaries and negatively charged of phospholipids present in the cell wall.

The results in Table (4), (5) showed that the tested compounds showed biocidal activities and efficiencies against the SMC-SRB. The CTAB was the reference pure biocide recorded its (MIC) at 30ppm. On the other hand compound I_c was more effective than CTAB itself at the same concentration while the two other compounds (I_a, I_b) recorded a lower activity against the SMC-SRB at 87 and 85 mg S/L respectively. This may be due to that the biocidal activity of quaternary ammonium compounds depend on the length of alkyl chain, the optimum activity lied between C_{12} and C_{16} which agree with the result given in ref.$^{(18)}$. Compound I_a recorded the best biocidal efficiency at 60ppm (96%) in comparison with CTAB. However, it ought to be emphasized that SRB varied in their susceptibility to biocide$^{(3)}$. But I_c recorded the lowest biocidal activity against SMS-SRB at 150ppm, this is may be due to as the molecular weight of quaternary increases by increasing the length of alkyl chains attached to the nitrogen atom, water solubility decreases. This trend may continue until the heavy quaternaries exhibit dispersability and not true solubility in aqueous systems$^{(19)}$. This is very clear in its fluctuation results against SMC-SRB.

Conclusion

A homologous series of cationic surfactants namely; Hexamine, N. (carboxy methyl) alkyl chloride, where alkyl: octyl, dodecyl, hexadecyl and octadecyl were synthesized. It was found that Hexamine, N (carboxy methyl) octyl chloride is the most efficient one.

The standard free energies of adsorption of the synthesized surfactants were found to be in higher negative values rather than those of micellization process.

The synthesized quaternary ammonium compounds and CTAB were tested to evaluate their effect on SMC-SRB. They showed a relatively higher inhibiting efficiency towards SMC-SRB rather than the reference CTAB.

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Table (1) : Elemental Analysis of the prepared compounds I_{a-d}

compound	Carbon		Hydrogen		Nitrogen		Chlorine	
	Calc.	found	Calc.	found	Calc.	found	Calc.	found
I_a	55.35	55.85	8.94	9.71	16.14	16.46	10.20	10.75
I_b	59.55	59.25	9.67	10.34	13.89	13.56	8.81	8.32
I_c	62.75	62.97	10.24	10.80	12.20	11.73	7.70	7.35
I_d	64.07	65.57	10.47	11.22	11.49	11.34	7.29	6.70

Table (2): IR-Spectral band of the prepared compounds I_{a-d}

Compound	$_{C=O}$ cm^{-1}	$_{C-N}$ cm^{-1}	$_{CH_3}$ cm^{-1}	$_{CH_2}$cm^{-1}
I_a	1742	716	2880	2862
I_b	1740	709	2917	2883
I_c	1745	702	2970	2921
I_d	1750	709	2970	2921

Table (3): The critical micell concentration (CMC), surface parameters, free energies of micellization and adsorption of compounds I_{a-d} at room temperature

compound	CMC (M/L)	Π_{cmc} (dyne/cm)	Γ_{max} (mole/cm^2)	A_{min} (nm^2)	ΔG^0_{mic} KJ/mol	ΔG^0_{ads} KJ/mol
I_a	0.07943	41.5	4.8×10^{-11}	3.43	-12.54	- 98.27
I_b	0.03160	38.0	3.8×10^{-11}	4.26	- 17.095	- 113.22
I_c	0.00052	29.0	0.11×10^{-11}	1.44	- 37.38	- 74.74
I_d	0.00018	37.0	0.10×10^{-11}	1.56	- 42.62	- 64.71

Table (4): The effect of different concentrations CTAB, Quaternary compounds Ia-d on the sulphide production as an indicator for SMC-SRB activity.

Biocide concentration ppm	Concentration of sulphide produced mg/L				
	CTAB	I_a	I_b	I_c	I_d
0	114	114	114	114	114
10	111	109	108	113	106
30	87	85	54	114	91
60	49	4.0	56	94	40
90	5.0	3.0	44	108	40
120	2.0	1.0	N.D.	110	N.D
150	2.0	1.0	35	48	N.D
200	1.0	1.0	57	4.0	N.D
250	1.0	1.0	4.0	4.0	N.D.

N.D. Not determined

Table (5) : Biocidal efficiency of quaternary compounds I_{a-d} against SMC-SRB

Biocide concentration ppm	CTAB control	I_a	I_b	I_c	I_d
0	0%	0%	0%	0%	0%
10	3%	4%	5%	1%	7%
30	24%	25%	53%	0%	20%
60	57%	96%	51%	18%	65%
90	96%	97%	61%	5%	65%
120	98%	99%	---	4%	---
150	98%	99%	69%	58%	---
200	99%	99%	50%	97%	---
250	99%	99%	97%	97%	---

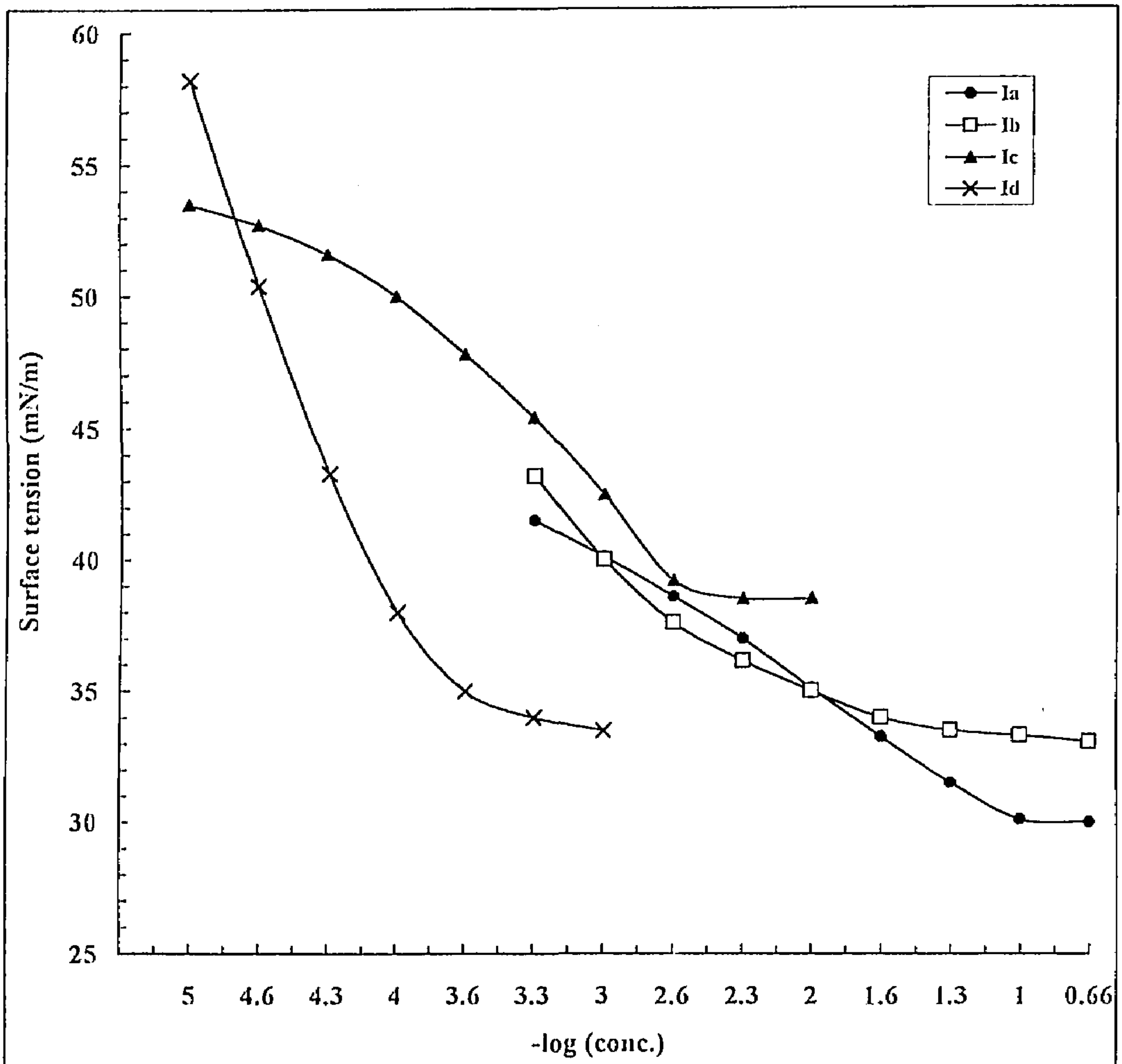

Figure (1): Variation of surface tension of compounds (I_{a-d}) vs. different concentrations at 25°C.