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Surface and Thermodynamic Studies of N-((Octyl, Dodecyl, and Cetyl) Oxycarbonylmethyl) Pyridinium Bromide

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Summary. N-Octyloxycarbonylmethyl pyridinium bromide (C_8), N-dodecyloxycarbonylmethyl pyridinium bromide (C_{12}) and N-cetyloxycarbonylmethyl pyridinium bromide (C_{16}) were prepared. Several studies were carried out with their aqueous solutions. Surface tensions, electrical conductivities, and biodegradabilities were evaluated. The antibacterial and antifungal activities of the cationic surfactants were studied. Surface properties, particularly critical micelle concentration (*CMC*), effectiveness (Π_{CMC}), efficiency (P_{c20}), maximum surface excess ($\Gamma_{\max}$), and minimum surface area ($A_{\min}$) were investigated at different concentrations at 20, 35, and 50°C respectively. Free energies, enthalpies, entropies of micellization, and adsorption of the surfactants in the aqueous solution were studied.

Keywords. *Gibb*'s equation; Alkyl bromoacetate; Critical micelle concentration; Micellization; Adsorption; Thermodynamic parameters.

Untersuchung der Thermodynamik und der Oberflächeneigenschaften von N-((Octyl-, Dodecyl- und Cetyl)oxycarbonylmethyl)-pyridiniumbromid

Zusammenfassung. Verschiedene Untersuchungen an wäßrigen Lösungen von N-Octyloxycarbonylmethyl-pyridiniumbromid (C_8), N-Dodecyloxycarbonylmethyl-pyridiniumbromid (C_{12}) und N-Cetyloxycarbonylmethyl-pyridiniumbromid (C_{16}) wurden durchgeführt. Oberflächenspannungen, elektrische Leitfähigkeiten und biologische Abbaubarkeit wurden bestimmt. Die bakterizide und fungizide Aktivität der kationischen Tenside wurde untersucht. Oberflächenparameter, insbesondere kritische Micellenkonzentration (*CMC*), Effektivität (Π_{CMC}), Effizienz $P_{c_{20}}$), maximaler Oberflächenüberschuß ($\Gamma_{\max}$) und minimale Oberfläche ($A_{\min}$) wurden bei verschiedenen Konzentrationen und bei Temperaturen von 20, 35 und 50°C untersucht. Die freien Energien, Enthalpien, Entropien und die Asorption der Tenside in wäßriger Lösung wurden bestimmt.

Introduction

Cationic surface active agents, characterized by the fact that the hydrophobic group forms part of a cation when the compound is dissolved in water, are used almost exclusively for producing water-repellent finishes on fabrics. Commonly, they are prepared by esterification of chloroacetic acid with a fatty alcohol [1–5]. The chlorine atom of the resultant chloroacetic ester is then replaced by reaction with an amine. Correlation between the chemical structure of the surface acitive agents and their surface and thermodynamic properties has been the subject of many publications [6–9]. In this study, the structural effects of Na-(N-alkyloxycarbonylmethyl) pyridinium bromide on the surface and thermodynamic properties of their solutions is investigated using the methodology of *Rosen et al.* [8, 9].

Results and Discussion

Critical micelle concentration (CMC)

Figure 1 represents the changes in surface tension (γ) with the concentrations of aqueous solutions of N-octyl-, dodecyl-, and cetyloxycarbonylmethyl pyridinium bromide at 20, 35, and 50°C. The critical micelle concentration (*CMC*) was determined at each temperature from the intersection points in the γ *vs.* log$c$ curves. It demonstrates that the surface tension of the surfactants is greatly affected by temperature and concentration changes. Raising the temperature from 35 to 50°C causes a large decrease in surface tension for C_8 and C_{12}. However, C_{16} is only slightly affected by thermal changes befor *CMC*. The *CMC* values given in Table 1 show a decreasing trend with increasing temperature. The same trend has been obtained for sarcosinate surfactants [10]. On the contrary, anionic surfactants with the same hydrophobic moiety show an increase of *CMC* with increasing temperature. Micelle formation is apparently controlled by two opposing factors: a temperature increase causes hydration of the hydrophilic group which favours micellization, but at the same time temperature induces disruption of the structured water surrounding the hydrophobic group. The relative magnitude of these two opposing effects determines whether *CMC* increases or decreases over a particular temperature range.

For a homologous series of surfactants, the *CMC* value may also be expressed by the empirical equation given by *Klevens* and *Corrin* [11] (log$CMC = A - BN$; N: number of carbon atoms in the hydrocarbon, A and B: constants representing temperature and homologous series). The non-linearity between logCMC and N (Fig. 2) indicates that the equation is not applicable for N-(alkyloxy-carbonylmethyl) pyridinium bromides.

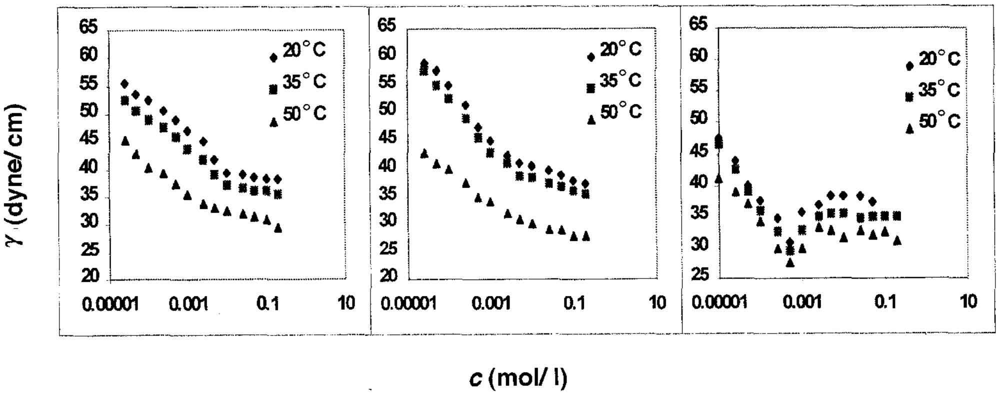

Fig. 1. Variation of surface tension (γ) with concentration of N-((octyl, dodecyl, and cetyl)oxycarbonylmethyl) pridinium bromide solution at 20, 35, 50°C

Table 1. Critical micelle concentration (*CMC*), effectiveness (Π_{CMC}), efficiency (c_{20}), maximum surface excess ($\Gamma_{\max}$), and minimum area ($A_{\min}$) of the cationic surfactants

	T (°C)	CMC (mol · l^{-1})	Π_{CMC} (dyne·cm^{-1})	$^{P}c_{20}$ (−log(mol/l))	$\Gamma_{\max} \times 10^{10}$ (mol · cm^{-2})	$A_{\min}$ (nm^2)
N-(Octyloxycarbonyl-	20	7×10^{-3}	30.50	4.00	4.67	0.353
methyl) pyridinium	35	6.5×10^{-3}	33.00	4.69	3.67	0.448
chloride (C_8)	50	6×10^{-3}	39.50	5.6	2.99	0.562
N-(Dodecyloxycarbonyl-	20	1×10^{-3}	26.50	3.80	8.05	0.204
methyl) pyridinium	35	1×10^{-3}	28.00	4.00	7.28	0.226
chloride (C_{12})	50	1×10^{-3}	38.00	5.4	5.08	0.324
N-(Cetyloxycarbonyl-	20	5×10^{-4}	40.75	5.45	8.02	0.205
methyl) pyridinium	35	5×10^{-4}	42.00	5.6	7.23	0.228
chloride (C_{16})	50	5×10^{-4}	43.25	5.7	6.32	0.260

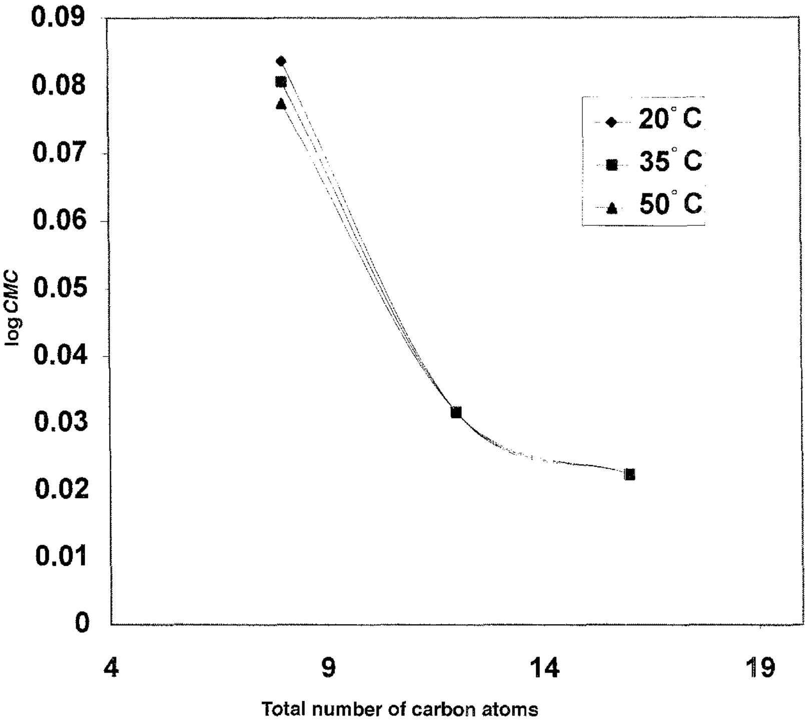

Fig. 2. Variation of log*CMC* with number of carbon atoms

Electrical conductivity

When the equivalent conductance values of the cationic surfactants are plotted against the square root of the concentration (Fig. 3), the curves slope sharply downward in diluted solution. A break in the slope of the curves apparently

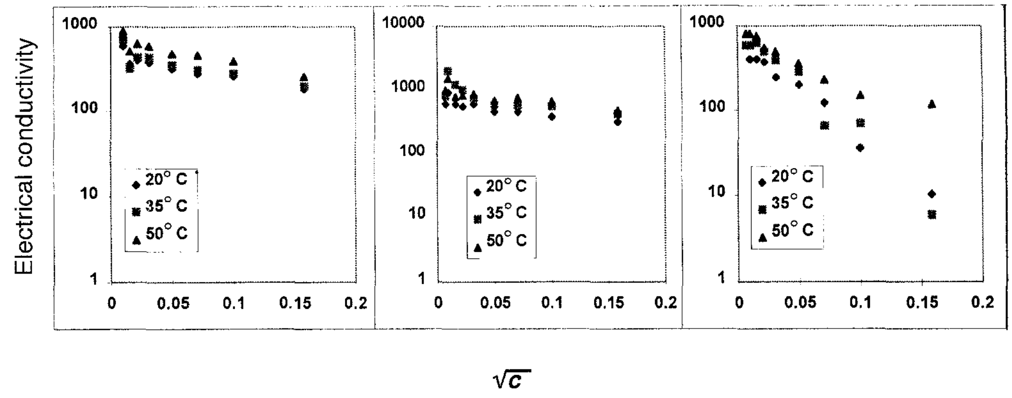

Fig. 3. Variation of electrical conductivity with the square root of the concentration of anionic surfactants at different temperatures

coincide with the point at which ionic micelles begin to form rapidly. In this series, it could be observed that raising the temperature causes the slope in the pre-critical range to become steeper; the critical point itself, however, occurs at almost the same concentration. It should be noted that the plots of γ *vs.* log$c$ (Fig. 1) for these compounds show that the critical micelle concentration decreases with increasing temperature. It is evident that the temperature obviously is not an important factor in determining the critical micelle concentration.

Effectiveness (Π_{CMC})

The surface tension values at *CMC* were used to calculate the surface pressure (effectiveness) from $\Pi_{CMC} = \gamma_0 - \gamma$, where γ_0 is the surface tension measured for pure water at the appropriate temperature and γ is the surface tension at the critical micelle concentration. Values of Π_{CMC} at 20, 35, and 50°C are represented in Table 1. The most efficient surfactant is that which causes the greatest lowering in surface tension at the critical micelle concentration. Obviously, this is the case for C_{16}.

Efficiency $(^{P}c_{20})$

Efficiency is determined by the concentration of surfactant capable to supress the surface tension by 20 dyne/cm. The values of efficiency of the synthesized surfactants are shown in Table 1. As the temperature increases, the values of $^{P}c_{20}$ for C_8, C_{12}, and C_{16} increases. For the given series of homologues, C_{16} has the highest efficiency.

Surface excess (Γ_{max})

According to $\Gamma = \frac{1}{RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c}\right)_T$ (*Gibb*'s equation; Γ: surface excess, dγ: surface pressure, c: concentration of the surfactant), a substance which lowers the surface

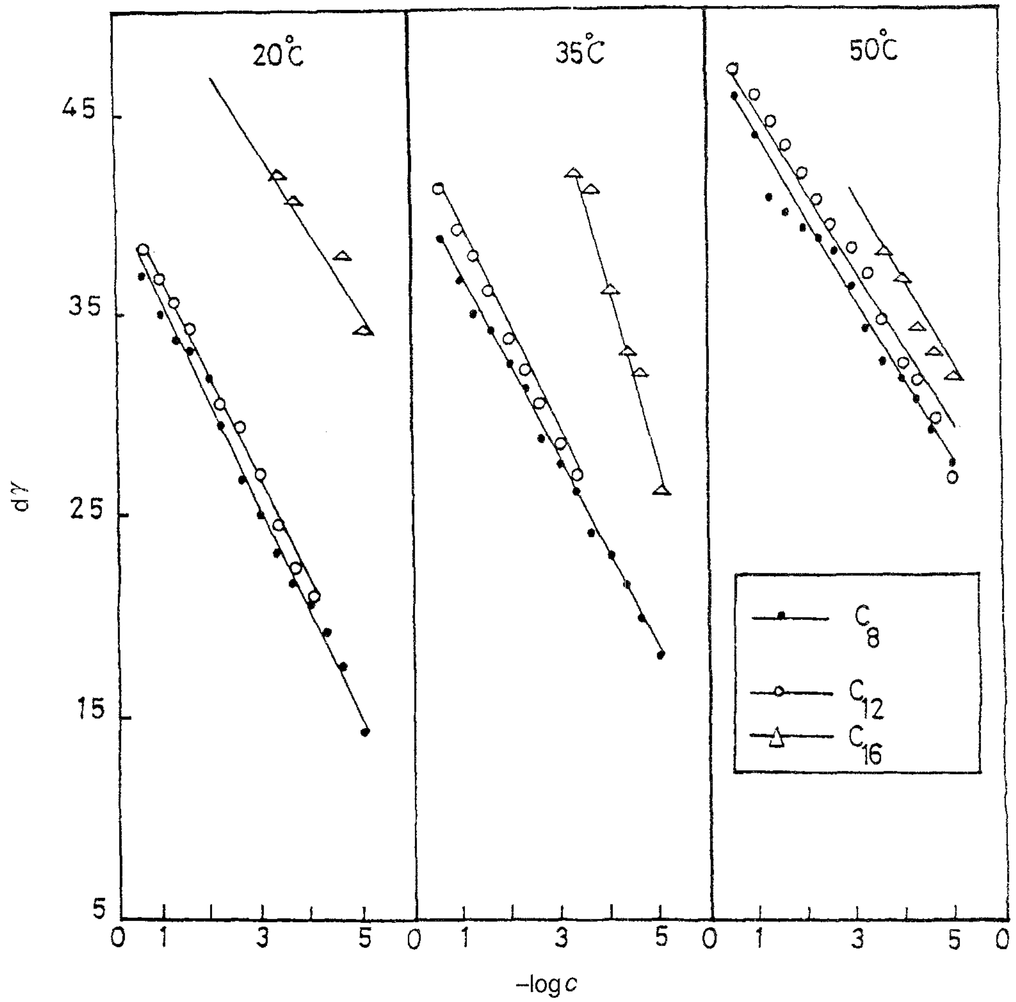

Fig. 4. Variation of surface pressure (dγ) with log*c* at 20, 35, and 50°C

energy is present in excess at or near the surface, *i.e.* when the surface tension decreases with increasing activity of surfactant, Γ is positive. Fig. 4 represents the variation of the surface pressure with the logarithm of the concentration) of C_8, C_{12} and C_{16} at different temperatures.

Taking Γ as the slope of the plots in Fig. 4, it can be seen that it is approximately the same for each surfactant as various temperatures except for C_{16}, at 35°C. As we go up the homologous series of the surfactants, this value is reached at a progressively lower concentration.

The maximum surface excess of the surfactants was calculated from *Gibb*'s adsorption equation at *CMC*. The values of Γ_{max} are represented in Table 1. Increasing the hydrophobic character of the cationic surfactants shifts Γ_{max} to lower concentrations. For all instances, Γ_{max} decreases as the temperature increases.

Minimum surface area $(A_{\min})$

The average area occupied by each adsorbed molecule is given by

$$A_{\min} = \frac{1}{\Gamma_{\max} \cdot N}$$

$\Gamma_{\max}$: maximum surface excess; N: *Avogadro*'s number. Table 1 indicates that the minimum area per molecule at the aqueous solution/air interface for cationic surfactants increases with increasing temperature, as would be expected from the increased thermal agitation of the molecules in the interface film. The values of $A_{\min}$ indicate that the cationic surfactants, particularly C_{12} and C_{16}, seem to be oriented vertically at the aqueous solution/air interface [12].

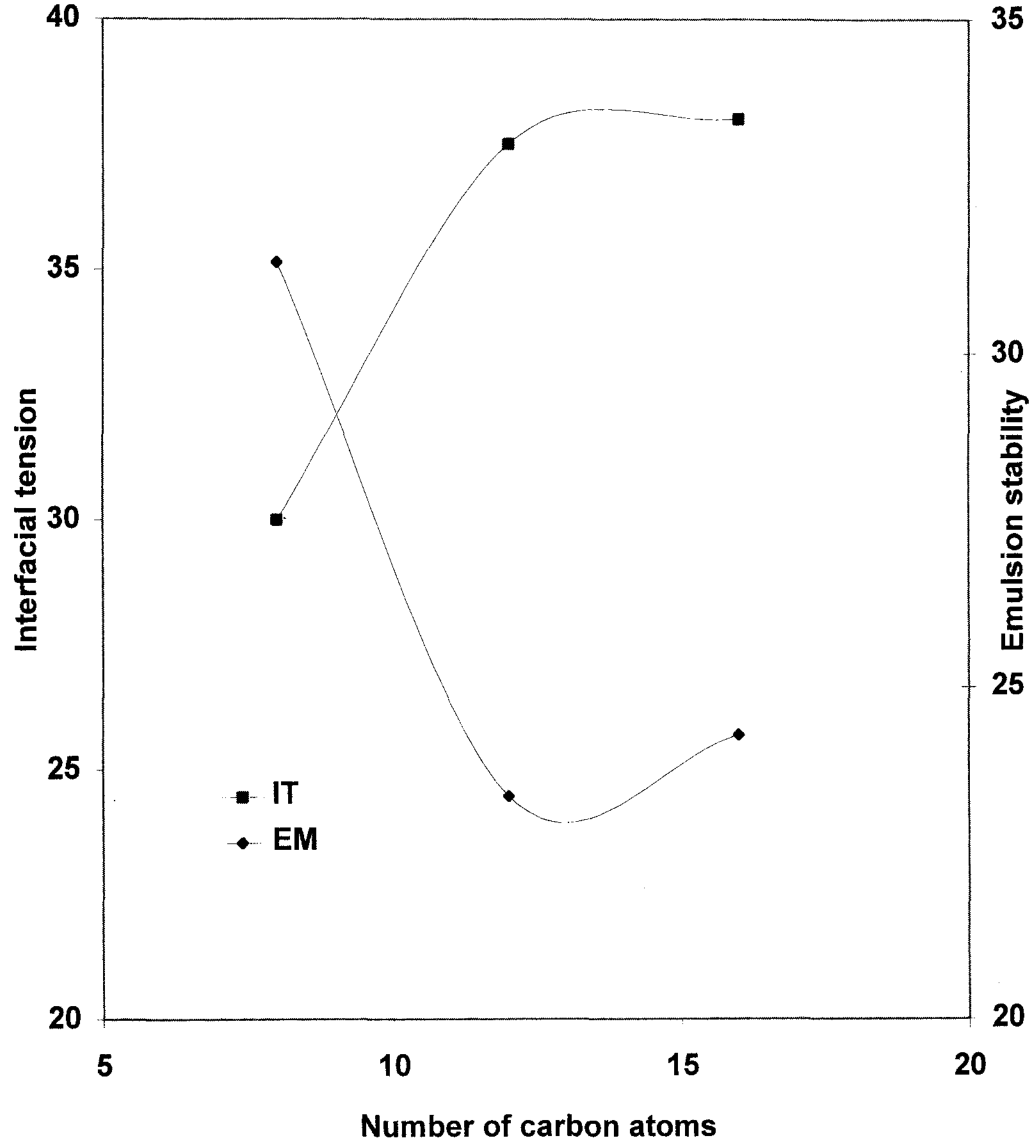

Fig. 5. Variation of interfacial tension and emulsion stability with number of carbon atoms

Interfacial tension and emulsion stability

The data of interfacial tension and emulsion stability (Fig. 5) indicate that the variation of both interfacial tension and emulsion stability are independent on the change of the number of carbon atoms in the alkyl chain of the surfactants. C_8 was found to be more effective in depressing the interfacial tension than C_{12} and C_{16}, resulting in the formation of more stable emulsions.

Biodegradability and antimicrobial and antifungal activity

A biodegradation die-away test in ordinary river water gave satisfactory results (Table 3). It could also be shown that the biodegradation of the surfactants decreased with increasing number of carbon atoms of the alkyl chain. Moreover, the results of antimicrobial and antifungal activity evaluation indicated that C_{16} is less biodegradable with respect to C_8 and C_{12}.

Thermodynamic parameters

Standard free energies, ethalpies, and entropies of micellization and adsorption of the surfactants were calculated at each of the three temperatures 20, 35, and 50°C according to Rosen *et al.* [8, 9]. Obviously, the standard free energies of micellization for C_8, C_{12}, and C_{16} are always negative indicating that micellization is a spontaneous process. The free energy change $\Delta G(\mathrm{CH_2})$ involved in the transfer of a methylene group from an aqueous environment to the interior of the micelle is negative, thus favouring micellization and accounting for the fact that *CMC* decreases with increasing length of the hydrophobic chain. As the temperature increases, $\Delta G^0_{\mathrm{mic}}$ for C_8, C_{12}, and C_{16} becomes more negative.

$\Delta H^0_{\mathrm{mic}}$ and ΔH^0_{ad} are sometimes negative and sometimes positive. Therefore, the micellization and adsorption process is governed primarily by the entropy gain associated with it, and the driving force for the process is the tendency of the hydrophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle or to the liquid/air interface. The positive values of $\Delta S^0_{\mathrm{mic}}$ due to the increased freedom of the hydrophobic chain in the nonpolar interior of the micelles compared to the aqueous environment. ΔS^0_{ad} values of C_8, C_{12}, and C_{16} are all positive and slightly greater than $\Delta S^0_{\mathrm{mic}}$. This may reflect the greater freedom of motion of the hydrocarbon chain at the planar aqueous solution/air interface compared to that in the relatively cramped interior beneath the convex surface of the micelles.

Experimental

Synthesis

Alkyl bromoacetates were prepared from 0.3 mol of bromoacetic and 0.3 mol of octyl, dodecyl, and cetyl alcohol, respectively. 3 ml of concentrated hydrochloric acid in 200 ml of toluene were added, and the reaction mixture was heated and stirred at reflux temperature for 4 h with azeotropic removal of water.

0.3 mol of alkyl bromoacetate and 0.5 mol of pyridine in benzene were stirred and refluxed for 1 h. The crude product was purified by triple recrystallization from petroleum ether and dried at room

Table 2. Thermodynamic parameters of micellization and adsorption

	T (°C)	ΔG^0_{mic} (kJ · mol^{-1})	ΔS^0_{mic} (kJ · mol^{-1} · K^{-1})	ΔH^0_{mic} (kJ · mol^{-1})	ΔG^0_{ad} (kJ · mol^{-1})	ΔS^0_{a} (kJ · mol^{-1} · K^{-1})	ΔH^0_{a} (kJ · mol^{-1})
N-(Octyloxycarbonylmethyl) pyridinium chloride (C_8)	20	−24.09	–	–	−30.58	–	–
	35	−25.76	0.111	8.428	−34.66	0.136	7.228
	50	−34.66	0.112	8.736	−40.82	0.205	25.395
N-(Dodecyloxycarbonylmethyl) pyridinium chloride (C_{12})	20	−33.61	–	–	−36.86	–	–
	35	−34.57	0.064	−14.85	−38.38	0.101	−7.27
	50	−37.05	0.114	−0.228	−44.46	0.253	37.25
N-(Cetyloxycarbonylmethyl) pyridinium chloride (C_{16})	20	−36.99	–	–	−42.02	–	–
	35	−38.87	0.125	−0.370	−44.63	0.173	8.65
	50	−40.76	0.125	−0.385	−47.53	0.183	11.57

Table 3. Biodegradability and antimicrobial and antifungal activity

	D (%)				*Bacillus subtilis*	*Escherichia coli*	*Asperigllus niger*	*Candida albicans*
	2 days	4 days	6 days	8 days				
N-(Octyloxycarbonylmethyl) pridinium bromide (C_8)	50	55	60	65	–	–	+	+
N(Dodecyloxycarbonylmethyl) pridinium bromide (C_{12})	48	52	58	62	–	+	++	+
N-(Cetyloxycarbonylmethyl) pridinium bromide (C_{16})	45	50	55	60	+	++	++	+++

temperature under reduced pressure. The purity of the compounds (white-yellowish powder) was confirmed by elementary analysis, IR, and ^{1}H NMR spectroscopy.

Surface and interfacial tension measurements

These measurements were performed using a DU Nouy Tensiometer (Kruss Type 8451) for various concentrations of the surfactants (from 1×10^{-5} to 2×10^{-5} mol/l) and at different temperatures (20, 35, and 50°C). Doubly distilled water from an all-glass apparatus with a surface tension of 72.8 dyne/cm at 25°C was used to prepare all solutions.

Electric conductivity

An electrical conductimeter (Type 522, Crison instruments S.A.) was used to measure the conductivity of the various surfactant solutions. Their concentrations were similar to those used for the surface tension measurements.

Emulsion stability

Test samples were prepared as 20 m*M* solutions in liquid paraffin (10 ml). The samples were shaken 15 times (5 s each) at 40°C. The time for the recovery of 9 ml of the aqueous phase was recorded [13].

Biodegradability

Die-away tests in river water were performed employing the surface tension method [14] using a Du Noüy Tensiometer (Kruss Type 8451). Samples taken daily were filtered through No. 1 Whatman filter paper before measuring the surface tension. Biodegradation was calculated by the following equation:

$$D = \frac{\gamma_t - \gamma_0}{\gamma_{bt} - \gamma_0} \cdot 100$$

(γ_t: surface tension at time t; γ_0: surface tension at time zero (initial surface tension); γ_{bt}: surface tension of the control sample at time *t*).

Antibacterial and antifungal activity

The cup-plate method [15] was adopted for this test. The activity of each of the substances against four microorganisms representing gram-positive and gram-negative bacteria, fungus, and yeast (*Bacillus subtilis*, *Escherichia coli*, *Aspergillus niger*, and *Condida albicans*) was investigated. The activity of the test substances at different concentrations towards any test organism was expressed as follows: + + +: at concentrations of 50 µg/ml; ++: at concentrations of 100—500 µg/ml; +: at concentrations of 1000—2000 µg/ml. If no activity could be noticed with solutions containing 2000 µg/ml of surfactant, the substance was considered to be inactive (−).

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