

A NEW SIGHT ON HYDROPHOBIC BEHAVIOUR OF OXYETHYLENE GROUPS LOCATED BETWEEN ALKYL CHAIN AND IONIC GROUP IN CATIONIC SURFACTANTS

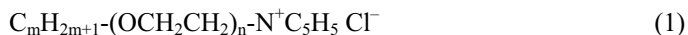
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abstract: The behaviour of amphiphilic molecules having oxyethylene groups EO located between alkylchain and ionic group of the type $C_mH_{2m+1}-(OCH_2CH_2)_n-N^+C_5H_5 Cl^-$ in micellization, reduction of surface tension and adsorption at solid/liquid interface have been investigated. Insertion of oxyethylene groups leads to the increase of hydrophobicity of these molecules in all process studied. For this reason, a certain hydrophobic value HV for oxyethylene groups was attributed. The hydrophobic values for the processes of micellization and adsorption at liquid/air interface are similar but higher than for adsorption at solid/liquid interface where hemimicelle are formed.

Introduction

The amphiphilic molecules characterized by existence of two parts, one nonpolar as a rule a hydrocarbon tail of at least eight methylenic groups and a hydrophilic one (ionic or nonionic) have a specific behaviour determined by the tendency of the two parts to accommodate with the most favourable medium. In order to decrease the unfavourable interactions with the environment, the surfactants tend to accumulate to liquid/gas or liquid/liquid as well as liquid/solid interfaces and to form association micelles in aqueous medium. In these processes, the tendencies of hydrocarbon parts to reduce the contact with aqueous environment is known as hydrophobic bonding characterized by a certain free energy of transfer. Even so, the nature of interactions involved is the same, the free energy of transfer in adsorption and micellization is different because the final state of amphiphilic molecules is different.

In the present study, the behaviour of particular class of cationic surfactants, namely alkyloxyethylene pyridinium chloride:



where $m=12$ and 16 and $n=0, 1$ and 2 , is investigated by micellization, determination of efficiency in reduction of surface tension of aqueous solution in comparison with the capacity to adsorb at solid/liquid interfaces characterized by hemimicelle formation.

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The capacity of these compounds to form micelles in aqueous solution has been investigated [1]. The insertion of oxyethylene groups EO between hydrophobic part and ionic groups as a spacer leads to the increase of solubility that should have as effect an increase of CMC of compound. These facts do not happen, the CMC of compounds containing oxyethylene groups is lower than of parent compounds. Due to this behaviour, a certain hydrophobic value HV for oxyethylene groups can be attributed. The HV value can be looked as a contribution of oxyethylene groups to extension of alkylic chain of amphiphilic molecules in micellization, surface tension reduction and adsorption at solid/liquid interface.

The same behaviour has been found for the adsorption of these compounds at solid/water interface [2], phenomenon accompanied by hemimicelle formation [3]. The addition of oxyethylene groups in amphiphilic molecules leads to the increase of hydrophilic character of whole molecules due to capacity of ether groups to form hydrogen bonds. This general behaviour is not confirmed when oxyethylene groups is a spacer between alkyl chain and ionic groups.

Materials and Methods

The cationic surfactants studied were unitary compounds as length of hydrophobic parts as well as oxyethylene groups obtained by Williamson Synthesis [4, 5].

The CMC were determined from surface tension measurements using du Nouy ring method.

The adsorption determinations at silica-alumina/water interface were conducted by reduction of surfactant concentration in contact with the solid for 48 hours, using interferometric measurements.

Results and Discussions

The surface tension measurements are presented in Figs. 1 and 2. Adsorption of cationic surfactants on silica-alumina from water is presented in Figs. 3 and 4.

From surface tension measurements, the CMC of these compounds were determined as the concentration of surfactants where surface tensions remain unchanged (Table 1). The values of CMC obtained from surface tension measurements are in good agreement with those obtained from adsorption on silica –alumina (Figs. 3 and 4).

The critical hemimicelle concentration (CHC) obtained from adsorption measurements at silica-alumina interface are much lower than CMC of corresponding compounds (Table 1) showing that adsorption is more favourable energetically than micellization.

The adsorption at liquid/gas interface is governed by Gibbs equation:

$$\Gamma_2 = -\frac{c}{RT} \left(\frac{d\gamma}{dc_2} \right)_T = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln c_2} \right) \quad (2)$$

where γ is the surface tension and Γ_2 the surface excess expressed in moles/m².

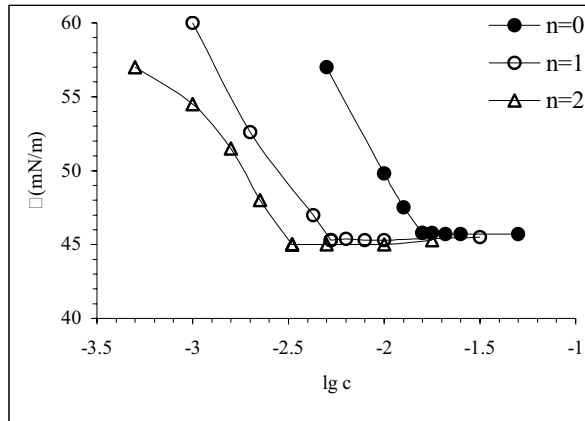


Fig. 1: Dependence of surface tension on $\lg c$ for $C_{12}EO_nPy Cl$

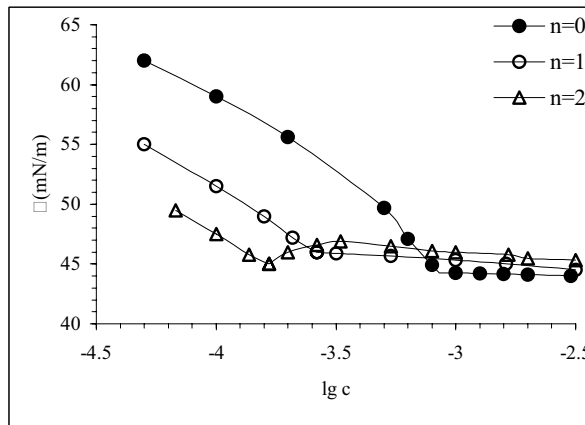


Fig. 2: Dependence of surface tension on $\lg c$ for $C_{16}EO_nPy Cl$

Using Gibbs equation (2), one can obtain the minimum surface occupied by a molecule of surfactant in adsorption layer A in the vicinity of CMC from:

$$A = \frac{1}{N_A \Gamma_{2,\max}} \quad (3)$$

where $\Gamma_{2,\max}$ is the surface excess near CMC and N_A , Avogadro's number. The surface occupied by molecules is given in Table 1. One can point out the constancy for C_{12} series and an increase of surface for C_{16} series in the presence of EO as spacer.

The efficiency of amphiphilic molecules to reduce surface tension is expressed generally by Traube rule [6]. A new way of expressing the efficiency in lowering the surface tension that can accommodate other structural effects than number of methylenic groups contained in Traube rule was proposed by Rosen [7] as the concentration of surfactants that produces a reduction of surface tension with 20mN/m:

$$-\lg(C)_{20} = pC_{20} \quad (4)$$

The values of pC_{20} of cationic surfactants studied are given in Table 1. At this value of surface tension about 80% of adsorption layer is occupied.

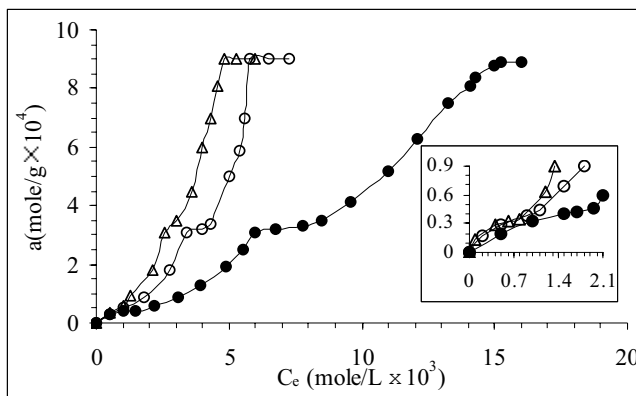


Fig. 3: Adsorption isotherms of $C_{12}EO_nPy Cl$ on silica-alumina at pH 7 and $25^\circ C$: (\bullet) $n=0$, (\circ) $n=1$, (Δ) $n=2$. The data for very diluted range are presented in small box.

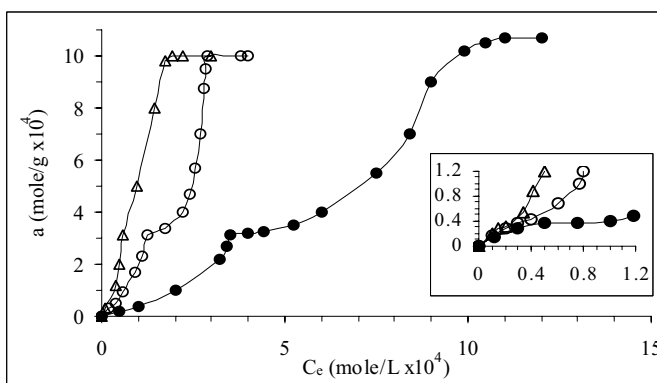


Fig. 4: Adsorption isotherms of $C_{16}EO_nPy Cl$ on silica-alumina at pH 7 and $25^\circ C$: (\bullet) $n=0$, (\circ) $n=1$, (Δ) $n=2$. The data for very diluted range are presented in small box.

Table 1. Adsorption characteristics of cationic surfactants at liquid/water and liquid/solid interfaces.

Compound	Abreviation	CMC $\times 10^3$ mole/L	CHC $\times 10^4$ mole/L	A at CMC, \AA^2	pC_{20}
$C_{12}H_{25}NC_5H_5Cl$	$C_{12}PyCl$	14.80	17.00	48	2.10
$C_{12}H_{25}(OCH_2CH_2)_1NC_5H_5Cl$	$C_{12}EO_1PyCl$	5.80	11.30	52	2.57
$C_{12}H_{25}(OCH_2CH_2)_2NC_5H_5Cl$	$C_{12}EO_2PyCl$	4.00	8.00	45	2.76
$C_{16}H_{33}NC_5H_5Cl$	$C_{16}PyCl$	0.90	1.00	45	3.38
$C_{16}H_{33}(OCH_2CH_2)_1NC_5H_5Cl$	$C_{16}EO_1PyCl$	0.28	0.32	63	3.90
$C_{16}H_{33}(OCH_2CH_2)_2NC_5H_5Cl$	$C_{16}EO_2PyCl$	0.18	0.20	92	4.25

The oxyethylene groups located between alkyl chain and ionic groups have different effects on micellization and adsorption as can be seen from Table 2.

Table 2. Hydrophobic values of oxyethylene groups located between hydrophobic and hydrophilic parts of cationic surfactants.

Parent Compound	Hydrophobic values		
	from CMC	from L/S adsorption	from L/G adsorption
C ₁₂ PyCl			
-First EO group	1.50	0.80	1.47
-Second EO group	0.35	0.40	0.50
C ₁₆ PyCl			
-First EO group	1.75	1.40	1.63
-Second EO group	0.75	1.00	1.09

The effect of oxyethylene groups or hydrophobic values is higher at micellization comparative to formation of hemimicelles (Table 2) very likely due to different degree of packing at the interface.

For the case of adsorption at water/air interface, expressed as pC_{20} vs. m , the following relation applies:

$$pC_{20} = -1.74 + 0.32(m + HV) \quad (5)$$

The hydrophobic value of oxyethylene groups in this case is comparable with the process of micellization but higher than for adsorption at liquid/solid interface.

It is well known that behaviour of amphiphilic compounds is dominated by the nature of hydrophobic group. The alteration of hydrophobic part by introduction of ethylenic unsaturation, ether, ester or amide linkage, or hydroxyl located away from the head groups, will result in a significant lowering of both micellization capacity as well as efficiency in reduction of surface tension comparative to materials without these polar groups [8]. These effects are usually attributed to changes in orientation of the adsorbed molecules, the effect being less dramatic if the polar group is located near ionic part.

In the case of oxyethylenic groups located between alkyl chain and ionic group as a spacer, the effect is an increase of surface activity expressed by pC_{20} . That's why one can speak of a "lengthening" of alkyl chains or of a hydrophobic value of oxyethylenic groups, the specific values depending on the process involved.

Conclusions

The introduction of oxyethylene groups in the nonionic surfactants are known as having a hydrophilic effect. The data presented in this study demonstrate an opposite effect when the oxyethylene groups are located between alkylic chain and ionic groups in alkyl pyridinium chloride compounds. The increase of hydrophobic character of these molecules has been proved by the decrease of CMC, CHC and pC_{20} .

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