Adsorption of Some Alkyloxyethylene Pyridinium Chlorides at Solid-Water Interface

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The adsorption of cetylalkyl pyridinium and alkyloxyethylene pyridinium chlorides at the silica-alumina water interface at ph =7 and 25 ^{0}C was analyzed to determine the type of interaction between surfactant molecules and solid substrat between adsorbed adiacent molecules and with the surfactant molecules in the equilibrium water solution. The experimental adsorption isotherm for the entire concentration range consists of four regions with the maximum adsorption attained at the critical micelle concentration of each surfactant in aqueous solutions. Different models and equations of adsorption suitable to describe different types of forces implicated in adsorption of cationic surfactant at the opposite charged solid surfaces were applied. The free energy of adsorption, free energy of hydrophobic interaction and mean surface aggregation number were calculated. Insertion of oxyethylene groups leads to the increase of the hydrophobicity of these cationic surfactants. From the calculated free energy of adsorption through electrostatic and van der Waals interactions different surface structures were attributed to each region: neutralization of electrical charges, formation of hemimicelles, admicelles and bilayers.

Keyword: adsorption; alkyloxyethylene pyridinium chlorides, silica-alumina, hemimicelles, admicelles

Adsorption of surfactants on the solid materials has been the object of many researches due to its implication in industrial processes, waste-water treatment and other important areas. The oxide-solution interfacial phenomena are of great significance in many fields such as geochemical processes, flotation, water pollution, agriculture, paint industry, and control stability of colloid particles.

The aim of the present study is to quantitatively analyze the adsorption process of a series of cationic surfactants of different chain lengths and hydrophobically modified by the presence of one or two oxyethylene groups between alkyl chain and the polar group from water solution to silica-alumina interface.

This analysis is necessary because the adsorption isotherms experimentally obtained [1] are complex, and there is no complete theoretical model for all the experimental information available. Different modeles for adsorption are compared in order to explain the hemimicelle or admicelle formation, the bilayer presence at CMC, etc. In previous studies of the adsorption of new class of cationic surfactant the influence of *p*H, electrolyte (KNO_3) and temperature was investigated [2]. The adsorption of cetylpyridinium surfactants especially cethylpyridinium bromide has been the subject of general adsorption studies [3]. The many aspects of the adsorption process remain unknown concerning the precise structures of the surface aggregation: hemimicelles, admicelles, incomplete or complete bilayers , surface – adsorbed micelles and adsorption kinetics. The silica-alumina was selected as the solid substrates for the adsorption of some cationic surfactants due to the possibilities of detailed characterization, purity and possibility to compare the results with by far more studied silica surfaces [4].

Experimental part

The particular class of cationic surfactants, namely alkyl oxyethylene pyridinium chloride: C_mE_nPC where m=12 and 16 and n=0, 1, and 2 were obtained by Williamson Synthesis [5]. The CMC values were determined [6].

The silica-alumina (SA) cracking catalyst was a sample from Hydrocarbons Co. with 24% Al_2O_3 and a point of zero charge (P.Z.C.) of *p*H= 6±0,2 surface area of 268 m^2/g

Table1
ADSORPTION CHARACTERISTICS OF CATIONIC SURFACTANTS AT LIQUID/SOLID INTERFACES

Surfactant	Cmcx10^3 mole/L	HMCx10^4 mole/L	CSACx10^3 mole/L	Effective Alkyl chain
$C_{12}PC$	14.80	17.00	9.50	12.0
$C_{12}E_1PC$	5.80	11.30	4.55	12.8
$C_{12}E_2PC$	4.00	8.00	2.48	13.2
$C_{16}PC$	0.90	1.00	6.80	16.0
$C_{16}E_1PC$	0.28	0.32	1.90	17.4
$C_{16}E_2PC$	0.18	0.20	0.60	18.4

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and isoelectric point at *p*H = 5, determined by microelectrophoretic method [2].

The adsorption of cationic surfactants at silica-alumina/ water interface was described in details in [1].

Results and discussions

The adsorption isotherms of alkylpyridinium and alkyloxyethylene pyridinium chlorides on silica-alumina at 25 ^{0}C and *p*H=7 are shown in F. 1. At pH =7, the silica-alumina is negatively charged because of hydroxylation of the surface and acidic dissociation of the surface hydroxyl groups [value of 1.17x10^{-10} mole/cm^2].

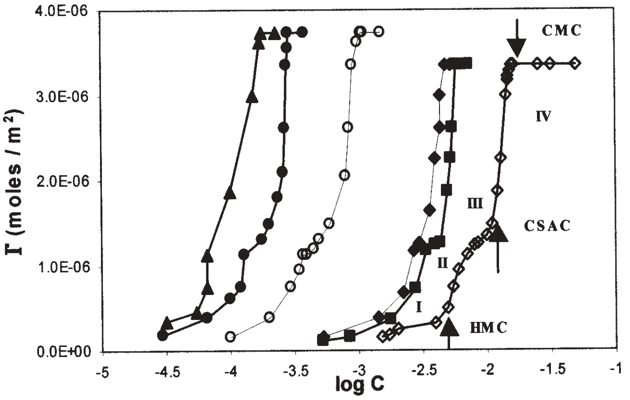

Fig. 1. Adsorption isotherm of cationic surfactants:
(◊) C_{12}PC; (■) $C_{12}E_1$PC; (♦) $C_{12}E_2$PC; (o) C_{16}PC; (•) $C_{16}E_1$PC;
(▲) $C_{16}E_2$PC on silica-alumina at 25^{0}C, *p*H 7

The adsorption isotherm for the entire concentration range of surfactant concentration shows four distinct regions: region I characterized by a low increase in adsorption but with the tipical Langmuir isotherm shape at the surfactant aqueous solution/air, region II by an abrupt increase in the slope with a S shape characteristic to cooperative isotherm type [7], region III, by a lower dependence of adsorption of surfactant concentration and region IV, by a new increase. For all alkylpyridinium chlorides the saturation values of adsorption were reached to an equilibrium concentration in solution corresponding to the CMC value for each surfactant.

The general shape of the isotherm is similar for all cationic surfactants studied. The four region isotherms were formed also in the case of adsorption of anionic surfactant on positively charged metal oxide surfaces [8].

Corroboration of adsorption data with electrophoretic mobility obtained from the same surfactant concentration range allow us to presume that the end of the region I before the high rise of region II corresponds with the hemimicelle concentration and the end of region II to the equilibrium concentration of the surfactant needed to reach zero charge density (p.c.z.) of solid surface (table 1).

In the literature can be found two concepts for organization type of surfactant in the region II, hemimicelles and admicelles [9,10]. We prefer to consider hemimicelles as local aggregates of surfactants adsorbed with their head groups in contact with the solid surface and their tails clustered together, protruding into the solution and admicelles as local bilayer structures. We presume that the admicelles begin to form in the region IV and at CMC the bilayer formation may be complete, such that the solid surface change the electrical sign. In the region III, after the neutralization of the electrical charges of the SA and formation of hemimicelles, characterized by a very little slope, more concentration of the surfactant in the solution is necessary to determine the reorganization of the surface to permit the increase of the surfactant adsorption steeply in the region IV, by hydrophobic interaction between surfactant molecules oriented "head-on" and the new one oriented "head-off" the solid surface.

Adsorption coefficient Γ value at the CMC is about two times Γ value at p.c.z. as it can be seen from figure 1 (not exactly a symmetrical bilayer).

In the region I at low concentration the surfactant ions are adsorbed individually and adsorption results primarily from electrostatic interactions between surfactant cation and negatively charged solid surface. The complete screening of the solid charged surface take place only after addition of van der Waals interactions between hydrophobic parts of the surfactants (hemimicelles).

Some general adsorption isotherm equations have been derived for systems in which adsorption of the solute take place through electrostatic and van der Waals interactions [7, 11,12].

In order to demonstrate the model of adsorption of cationic surfactants presented in table 1. on SA from aqueous solution different models and equations from the literature developed for the adsorption for the ionic surfactants on electrical charged solid surfaces were used. Some of these equations tried to describe the different stages of adsorption in accordance with different interaction between surfactant-surface and surfactant adsorbed molecules.

The Fowler-Guggenheim model: adsorbed film with lateral interaction

In this model the equation of adsorption is:

$$-\log\left(c\cdot\frac{\Gamma_m}{\Gamma}-1\right)=\log K-\frac{2\cdot\omega}{2.303}\cdot\frac{\Gamma}{\Gamma_m} \qquad (1)$$

where Γ- the adsorption coefficient at the equilibrium concentration of the surfactant in solution c; Γ_m - the maximum adsorption coefficient; K - the characteristic constant of the interaction between the adsorbed molecules and the solid surface sites, ω a parameter owed to interaction between two neighboring adsorbed molecules. From the Fowler-Guggenheim equation it can be obtained the free energy of adsorption ΔG_{ads} and the free energy of interaction ΔG_{int} from the following relations:

$$\Delta G_{ads} = -RT\ln K \quad \text{and} \quad \Delta G_{int} = RT\omega \qquad (2)$$

In the table 2 the results obtained from the equations (1) and (2) for the whole adsorption isotherm (regions I-IV) and particularly for each region are presented. The model was not able to verify the data for region I and III.

The model shows us the existence of strong interactions of van der Waals type, the value ΔG_{ads} is large but closer to ΔG_{int} value. For the I – IV, this model gives medium values for adsorption parameters but no information on the structure of surface aggregates. The ΔG_{ads} and ΔG_{int} increases with alkyl chain-length and with the presence of one or two -CH_2CH_2O- groups between the alkyl chain and the ionic head group of the cationic surfactants studied. Thus it can be concluded that oxyethylene groups occurring between an alkyl chain and ionic group produce an increase in the number of the CH_2- groups involved in the formation of hydrophobic bonds.

The modeling process applied on each region shows clearly that in region III of the isotherm the Fowler-Guggenheim equation does not verify the data, possibly because in this region the reorientation of the adsorbed molecules occurred, which subsequently favours the formation of the bilayer ($\Delta G_1 \approx \Delta G_h$ where ΔG_h is the energy

Table 2
DATA FOR ADSORPTION OF CATIONIC SURFACTANTS C_XE_YPC ON SILICA-ALUMINA AT 25^{0}C AND pH=7
(THE FOWLER –GUGGENHEIM MODEL)

Surfactant	Region	K	ΔG_{ads} Kcal/mole	ΔG_{int} Kcal/mole
C_{12}PC	I-IV	25.2	-1.930	-1.096
	II	41.7	-2.238	-1.013
	IV	7.10	-1.165	-0.909
$C_{12}E_1$ PC	I-IV	40.0	-2.208	-1.131
	II	51.9	-2.350	-1.330
	IV	31.6	-2.056	-1.126
$C_{12}E_2$ PC	I-IV	50.2	-2.346	-1.200
	II	52.3	-2.486	-1.490
	IV	28.4	-1.948	-1.353
C_{16} PC	I-IV	332.0	-3.477	-1.281
	II	813.4	-3.993	-0.920
	IV	170.3	-3.061	-1.267
$C_{16}E_1$ PC	I-IV	915.0	-4.084	-1.449
	II	1807.6	-4.460	-1.070
	IV	296.4	-3.390	-1.580
$C_{16}E_2$ PC	I-IV	1045.6	-4.305	-1.648
	II	1953.8	-4.512	-0.980
	IV	355.4	-3.720	-1.176

of hydrophobic interaction, who favorises the formation of the bilayer, due to hydrophobic effect which can determine the formation of admicelles and with the possibility to bilayer complete surface aggregation. In the region of III, further increase in bulk concentration has little influence on the surface excess until a critical surface aggregation concentration (CSAC) is reached (between one- and two-thirds of solution critical micelles concentration). At the CSAC, the surface excess increases sharply and admicelles are formed.

In the region I, equation (1) cannot be valid because the adsorption takes place only through electrostatic forces in the electrical double layer (oppositely charges in the case of silica-alumina solid surface). The experimental charge density for SA at pH=7, at 25^{0}C, show a sensible number of negative charges, but it is no relevant data to appreciate that their distribution is uniform.

It is sure that in region I adsorption coefficient increase only through ion-ion attraction and the Langmuir model of adsorption is the best one.

The S-shape segment of the surfactant adsorption isotherm is very well described by the Fowler-Guggenheim equation in the region II because hemimicelles formation is involved also in the region IV, where the bilayer formation depends on the hydrocarbon chain interaction and electrostatic repulsion between polar cationic groups. Sometimes this repulsion is diminished by counterion adsorption (in this case the chloride ion).

In general, ΔG_{ads} in region II is greater than ΔG_{ads} in region IV for all cationic surfactants and shows a preponderant influence of the neutralization process at the solid surface until the z.p.c. is reached.

In the region IV, where the electrostatic interactions between similar polar groups are unfavorable and that determines that hydrophobic ΔG_{intt} to be greater in the IV than in the II region.

Probably one of the difficult problem is the influence of the counterions which determines directly the electrostatic

Table 3

ADSORPTION DATA OF CATIONIC SURFACTANTS C_XE_YPC ON SILICA-ALUMINA AT 25°C AND pH=7 (THE GU-ZHU MODEL APPLIED IN REGION I-II)

Surfactant	K_1 x10^7	N	K_2
$C_{12}PC$	333.38	6.50	1.84 E+ 29
$C_{12}E_1PC$	519.21	6.39	5.82 E +30
$C_{12}E_2PC$	981.62	6.58	2.35 E+32
$C_{16}PC$	2.24	3.98	5.00E+19
$C_{16}E_1PC$	5.37	4.55	9.90E+24
$C_{16}E_2PC$	10.53	*	*

* The region II was difficult to be delimitated and no values for the adsorption parameters were obtained.

repulsion forces by charge compensation. Their effectiveness correlates with their hydration and other properties.

The Tamamushi model: adsorbed film with multiplayer formation

The Tamamushi model has been applied for the whole isotherm data in order to evidence the formation of surfactant multilayer on the solid surface.

The equation derived by Tamamushi and Tamaki [13] is:

$$\frac{a}{a_m}=\frac{k\cdot x}{1-x}\cdot\frac{1-(n+1)\cdot x^n+n\cdot x^{n+1}}{1+(k-1)\cdot x-k\cdot x^{n+1}} \qquad (3)$$

where:

$x=\frac{c}{c_m}$, a - adsorption coefficient at the equilibrium concentration c of the surfactant in solution;

a_m - maximum adsorption coefficient;

K - general constant of the adsorption;

n - number of formed layers.

The Tamamushi equation allows obtaining the values of general adsorption constant in the same range for all surfactants studied and does not evidence the existence of different interactions involved in the case of these complex systems.

The Zhu – Gu model: adsorbed film with surface aggregate formation.

The initial part of the isotherms (region I + II) was modeled based on the new theory of adsorption, applied especially to surfactant adsorption [12]. The general isotherm equation is:

$$\Gamma=\frac{\Gamma_m\cdot K_1\cdot c\cdot\left(\frac{1}{n}+K_2\cdot c^{n-1}\right)}{1+K_1\cdot c\cdot\left(1+K_2\cdot c^{n-1}\right)} \qquad (4)$$

where:

Γ - amount of surfactant adsorbed at concentration c;

Γ_m - limited adsorption at high concentration (both of them measured from adsorption experiments);

K_1 - equilibrium constants of adsorbed monomer surfactant at solid surface sites, the same with the *K* constant (the Langmuir equilibrium constant) from the region I;

K_2 - equilibrium constant between surface aggregate and monomer surfactant in solution;

n - the aggregation number of the surface aggregate.

Equation (4) was used in this work to obtain information about the aggregation number of hemimicelles and the influence of surfactant molecule structure. The calculated adsorption parameters are presented in table 3.

The equilibrium constants k_1 and k_2 values increase with the chain length and the number of oxyethylenic groups due to increased hydrophobicity of the molecule. It is possible to assign an effective number of $-CH_2-$ groups to each surfactant, or an effective alkyl chain length (table 1).

The aggregation number *n* does not increase with the hydrophobicity of the surfactant probably because the equilibrium concentration in solution corresponding to region II for C_{16} compound is substantially lower than for C_{12} compound and the counterions concentration also decreases. An increase in concentration of the surfactant counterion causes a decrease in electrostatic repulsion between charged headgroups, thus favouring the formation of aggregates.

Conclusions

In this paper, we present experimental data, some of them previously obtained [1,2], on the adsorption of some new cationic surfactants with one and two oxyethylene groups between alkyl chain and cationic groups [5,6] on the silica-alumina cracking catalysts at 25°C. At *p*H 7 the SA has an electrical double layer of opposite charges.

The adsorption of cationic surfactants, especially for the pyridinium compounds, rises some difficulties in interpreting the surface film structure dependence on the surfactant concentration in aqueous solution.

The aim of this study is to fit the different model and equations proposed in the literature in order to understand the type of surface aggregation in different stages of adsorption.

The Fowler-Guggenheim, Tamamushi and Zhu-Gu equations were analysed being obtained some interesting information.

No studied model was able to describe the whole range of concentration. To know exactly the kind of surface type of aggregation new experimental methods are needed such as AFM (atomic force microscopy) and optical reflectometry [3,4].

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