Adsorption of *N*-decanoyl-*N*-methylglucamine at the Interface Electrode–NaClO$_4$ Solution. Comparison of Adsorption Properties of Different Surfactants

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Abstract: The electrosorption behaviour of non-ionic surfactant: *N*-decanoyl-*N*-methylglucamine on mercury electrode in 1 mol dm^{-3} NaClO$_4$ solution was determined. The values of the relative surface excess were determined on the basis of double layer differential capacity. A set of parameters of maximal adsorption and the constants of Frumkin, modified Flory-Huggins and virial adsorption isotherms were obtained. It was stated that the adsorption of this surfactant is determined by the adsorption energy, however here is no simple relation between a surface excess and the values of repulsive interactions parameter *A*. Adsorption properties of three surfactants: cationic, anionic and non-ionic were compared.

Keywords: electrochemistry, differential capacity, surface, adsorption isotherm, electrosorption, non-ionic surfactant.

INTRODUCTION

THIS work is part of a project devoted to the study of adsorption properties of surfactants with different functional groups.[1–4] The adsorption of surfactants on charged surfaces is a topic of both practical and academic interest. The surfactants, both ionic and non-ionic have been reported as corrosion inhibitors for various metals.[5–9] Inhibitors adsorb on the metal surface, thus resulting in an adsorption-film acting as a barrier between the metal surface and the corrosive medium, and blocking the active sites.[10] The study of adsorption of organic substances at electrodes attracts wide interest as it relates to understanding the electrical double layer structure,[11,12] the kinetics of electron transfer[13,14] and the mechanism of electrode processes.[15–21] The thermodynamic analysis of surface concentrations is still the most frequently used route to gain an insight into the mode of organic compounds adsorption.[22] This

entails the description of experimental data by means of an adsorption isotherm, and the construction of an adsorption model based on the derived adsorption parameters.

The aim of this work was to analyze the adsorption properties of *N*-decanoyl-*N*-methylglucamine (MEGA-10, C$_{17}$H$_{35}$NO$_6$) at the mercury electrode from the 1 mol dm^{-3} NaClO$_4$ solution. In addition, the adsorption properties of cationic, anionic and non-ionic surfactants were compared. The choice of NaClO$_4$ solution resulted from the fact that ClO$_4^-$ ions cause the strongest disruption in water structure.[23] In our studies on adsorption from solutions, the double-layer capacitance was usually chosen as the primary experimental quantity. Such a measurement is far more accurate when performed on liquid rather than solid metal surfaces, which is why mercury played a dominant role as an electrode material in our studies. This is due to the highly reproducible, readily renewable and smooth surface of mercury drops.

EXPERIMENTAL

Analytical grade $C_{17}H_{35}NO_6$ and $NaClO_4$ (Fluka, Switzerland) were used without further purification. Water and mercury were double distilled before use. The $C_{17}H_{35}NO_6$ solution of concentrations ranging from 1×10^{-6} mol dm^{-3} to 7.5×10^{-4} mol dm^{-3} were prepared. The chosen surfactant concentrations were lower than the surfactant critical micelle concentration (CMC). The solutions were deaerated by passing high purity nitrogen over the solution during the measurements at 298 ± 0.1 K. The three-electrode system was used, with a dropping mercury electrode as a working electrode, and Ag|AgCl as a reference electrode, to which all potentials in this paper are referred. A controlled growth mercury drop electrode (CGMDE M165, MTM ANKO, Poland) was used. The differential capacity, *C*, of the double layer was measured with an Autolab frequency response analyzer (µAutolabIII/FRA2, Metrohm Autolab B. V., The Netherlands) using the AC impedance technique. The measurements were carried out at several frequencies in the range from 400 to 2000 Hz, with an amplitude of 5 mV. The equilibrium capacities were obtained by extrapolation of the dependence of the measured capacity versus square root of frequency to zero frequency.

The potential of zero charge, E_z, was measured using a streaming electrode. The interfacial tension, γ_z, at E_z was measured by the maximum bubble pressure method according to Schiffrin. The charge density and surface tension were obtained by the back integration of differential capacity-potential dependences. No corrections were made for the effect of the medium on the activity of the supporting electrolyte and the activity coefficient of the adsorbate.[24–26]

RESULTS AND DISCUSSION

Analysis of Experimental Data

Figure 1 presents the selected differential capacity-potential curves extrapolated to zero frequency. This procedure assumes that the impedance of the double layer is equivalent to the combination of a capacity-resistance series and that the rate of adsorption is diffusion-controlled.

By introducing $C_{17}H_{35}NO_6$ to the 1 mol dm^{-3} $NaClO_4$ solution a decrease of differential capacity occurred in a wide range of potential from $E = -150$ mV to $E = -1100$ mV. This decrease is also detected even at lower surfactant concentrations. For the highest surfactant concentrations the desorption peaks developed whose potentials shifted with the increase of the $C_{17}H_{35}NO_6$ concentration towards negative values.

The addition of $C_{17}H_{35}NO_6$ to the solution shifts the potential of zero charge from $E_z = -461$ mV for 1 mol dm^{-3} $NaClO_4$ to $E_z = -459$ mV for the solution containing 7.5×10^{-4}
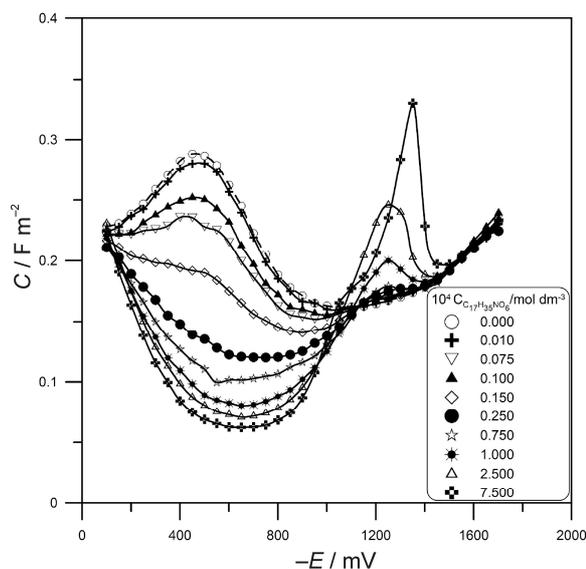
Figure 1. Differential capacity-potential curves at Hg/1 mol dm^{-3} $NaClO_4$ for various $C_{17}H_{35}NO_6$ concentrations as in figure legend.

mol dm^{-3} $C_{17}H_{35}NO_6$. The obtained results show the mechanism of surfactant adsorption; the positive pole, that is the radical $-C_{10}H_{21}$ is directed to the mercury, while the hydrophilic atoms of oxygen and nitrogen are directed towards the solution. The value of surface tension γ_z at E_z decreases from 421 mN m^{-1} to 391 mN m^{-1} with the increase of concentration of $C_{17}H_{35}NO_6$ (Table 1).

The capacity versus potential data were numerically integrated from the point of E_z to obtain the values of electrode charge, σ.

Figure 2 presents the dependences of electrode charge on electrode potential. The common intersection point marks the maximum adsorption parameters: $E_{max} = -466$ mV and $\sigma_{max} = 0$. It also confirms that the equilibrium for the measured capacities is reached.[27]

Table 1. The value of zero charge potential, E_z, and of surface tension measurements at this potential, γ_z

$10^4 \cdot c$/mol dm^{-3}	$-E_z$ / mV	γ_z / mN m^{-1}
0.010	462	421
0.075	461	420
0.100	461	420
0.150	461	419
0.250	461	419
0.750	461	416
1.000	461	415
2.500	460	406
7.500	459	391
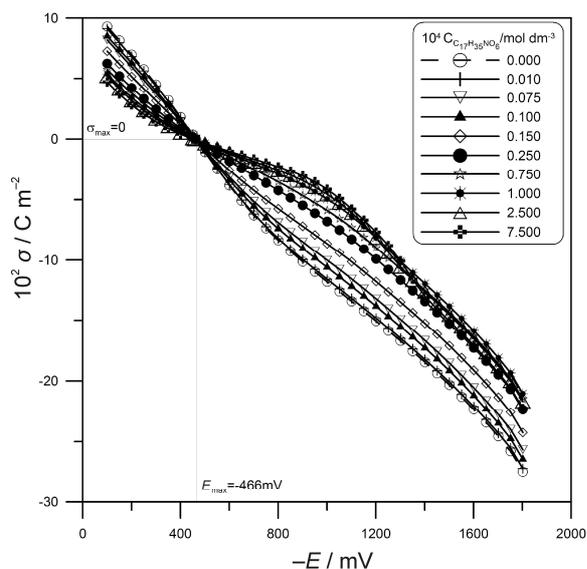
Figure 2. Dependences of electrode charge *vs.* the electrode potential for the studied $C_{17}H_{35}NO_6$ concentrations.

Figure 3. Relative surface excess of $C_{17}H_{35}NO_6$ as a function of the electrode potential and $C_{17}H_{35}NO_6$ concentration in the bulk.

Adsorption Isotherms

Knowing the change in surface tension for the base electrolyte solution, γ_0, as well as the corresponding changes in the presence of $C_{17}H_{35}NO_6$, γ, the surface pressure, Φ, can be calculated for given values of electrode potential and surfactant concentration: $\Phi = (\gamma_0 - \gamma)_E$. According to the Gibbs adsorption isotherm, the relative surface excess, Γ', of $C_{17}H_{35}NO_6$ is given by equation:

$$\Gamma' = \frac{1}{RT}\left(\frac{\partial \Phi}{\partial \ln c}\right)_E \qquad (1)$$

where c is the bulk concentration of $C_{17}H_{35}NO_6$.

Positive values of surface pressure, Φ, were obtained in the potential range from $E = -300$ mV to $E = -800$ mV subsequently for the above potential range, the values of Γ' were calculated.

Figure 3 presents the dependence of Γ' values obtained for the studied concentrations of surfactant in the bulk as a function of electrode potential. The maximum Γ' corresponds to the electrode potential $E = -400$ mV, that is potentials close to E_{max} (Table 2). The shape of curves in Figure 3 shows competitive electrostatic interactions: organic molecules-water dipoles.

Using the obtained Γ' values for the determined electrode potentials and $C_{17}H_{35}NO_6$ concentrations, the linear Frumkin isothermal test was determined based on the equation:

$$\beta x = \left[\theta / (1 - \theta)\right]\exp(-2A\theta) \qquad (2)$$

where x is the mole fraction of $C_{17}H_{35}NO_6$ in solution, β is the adsorption coefficient, which is defined as $\beta = \exp(-\Delta G° / RT)$ and θ is the surface coverage, $\theta = \Gamma' / \Gamma_s$.[4]

The surface excess at saturation, Γ_s, was estimated by extrapolation of the $1/\Gamma'$ vs. $1/c(C_{17}H_{35}NO_6)$ lines at different electrode potential to $1/c(C_{17}H_{35}NO_6) = 0$. The surface occupied by one $C_{17}H_{35}NO_6$ molecule, S, ($S = 1/\Gamma_s$) was 0.249 nm². Such a small S value indicates the perpendicular orientation of the adsorbed molecule. The values of interaction parameter, A_F, were calculated from the standard Gibbs energy of adsorption, $\Delta G_F°$ values were determined by extrapolation of linear dependences $\ln(1 - \theta) / \theta$ *vs.* θ to the value $\theta = 0$. Table 3 presents the values of the Frumkin isotherm constants. $\Delta G°$ values are strongly dependent on the Γ' values (Figure 3): the highest Γ' value with the potential of electrode $E = -400$ mV corresponds to the highest adsorption energy. At the same time, with this potential the

Table 2. Relative surface excess, Γ', of $C_{17}H_{35}NO_6$ for electrode potential $E = -400$ mV

$10^4\ c$/mol dm^{-3}	$10^6\ \Gamma'$/mol m^{-2}
0.010	0.19
0.075	0.82
0.100	0.98
0.150	1.12
0.250	1.53
0.750	2.41
1.000	2.65
2.500	3.47
7.500	4.57

Table 3. The constants of Frumkin (*F*), corrected Flory-Huggins (*H*) and virial (*V*) isotherms for the system: 1 mol dm⁻³ NaClO₄ + C₁₇H₃₅NO₆

−*E*/mV	ΔG_F^o/kJ mol⁻¹	−A_F	ΔG_H^o/kJ mol⁻¹	−A_H	ΔG_V^o/kJ mol⁻¹	*B*
300	33.9	1.5	35.6	0.9	113.1	0.5
400	35.4	1.8	37.1	1.2	114.7	0.6
500	34.8	1.7	36.5	1.2	113.5	0.5
600	34.2	1.8	35.8	1.2	113.2	0.5
700	33.3	1.5	35.1	1.0	112.5	0.5
800	32.5	1.6	34.2	1.0	111.6	0.5

most important finding is the repulsive interaction between the adsorbed molecules. Thus, the size of adsorption is determined by the changes of adsorption energy, Δ*G°*.

The adsorption of C₁₇H₃₅NO₆ was further analyzed on the basis of constants obtained from the modified Flory-Huggins isotherm for long-range particle-particle interactions:[28,29]

$$\beta x = \left[\theta / \left(1 - \theta \right)^n \right] \exp\left(-2A\theta \right) \qquad (3)$$

where *n* = 2.02 is the number of water molecules replaced by one C₁₇H₃₅NO₆ molecule.

In the presented studies the projected area for water molecule is 0.123 nm².[30] As the ClO₄⁻ ions cause the strongest disruption in water structure,[23] the surface of one water molecule was used in calculations instead of water clusters.

Figure 4 shows the test of the modified Flory-Huggins isotherm for electrode potential from *E* = −300 mV to
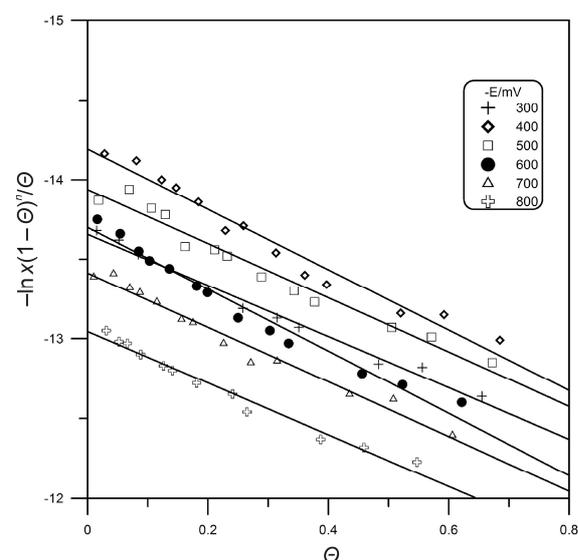
Figure 4. A linear test of the modified Flory-Huggins isotherm in the system 1 mol dm⁻³ NaClO₄ + C₁₇H₃₅NO₆ for different electrode potentials.

E = −800 mV. The values of ΔG_H^o and A_H were calculated in the same way as presented previously. The trends of constant changes in the modified Flory-Huggins isotherm are similar to constant changes of the Frumkin isotherm. However, the values of adsorption energy are slightly higher and are accompanied by weaker repulsive interactions. Because the above isotherms are burdened with some inaccuracy connected with the determination of *Γ*ₛ for their verification the virial isotherm was applied, the use of which does not require the knowledge of *Γ*ₛ. The virial isotherm equation is:

$$\ln \beta c = \ln \Gamma + 2B\Gamma \qquad (4)$$

where *B* is a 2-dimensional (2D) second virial coefficient.

The linear test for the virial isotherm was performed in the system: log(*Γ*′/*c*) *vs.* *Γ*′ using the standard state 1 mol dm⁻³ in the bulk solution and 1 mol cm⁻² on the surface. The values of the obtained virial isotherm constants are presented in Table 3.

The trend of changes of these values is similar to the above-described isotherms. Noteworthy is the fact that there is a virtual lack of dependences of repulsive interactions in the potential function.

CONCLUSION

On the basis of the obtained results the following conclusions could be drawn:

- The changes of *E*z values indicate the mechanism of the surfactant adsorption with the alkyl radical - C₁₀H₂₁ directed to the mercury surface.
- The small value of the surface occupied by one surfactant molecule, *S*, indicates the perpendicular orientation of its molecules.
- The highest *Γ*′ values occur in the vicinity of the potential of maximal adsorption *E*ₘₐₓ They are accompanied by the highest values of the free adsorption energy (in absolute terms) which determine the adsorption size.

Table 4. The constants of Frumkin (F), corrected Flory-Huggins (H) and virial (V) isotherms for the system: 1mol dm^{-3} NaClO$_4$ + C$_{11}$H$_{26}$N$^+$

$10^2 \sigma$ / C m^{-2}	ΔG_F°/kJ mol^{-1}	$-A_F$	ΔG_H°/kJ mol^{-1}	$-A_H$	ΔG_V°/kJ mol^{-1}	B
−3	31.2	4.5	32.5	4.0	110.6	1.0
−2	31.3	5.5	32.7	3.2	110.7	0.8
−1	31.5	2.8	32.9	2.4	110.8	0.6
0	32.5	3.5	34.0	3.2	111.9	0.8
+1	32.9	5.0	34.4	4.6	112.4	1.1
+2	32.9	6.3	34.4	5.5	112.4	1.3
+3	34.6	12.0	36.0	11.2	114.2	2.4
+4	34.6	17.3	36.0	17.1	114.2	3.4

- Trends of constant changes of the applied adsorption isotherms are similar. With the sufficiently negative potentials of the electrode the $\Delta G°$ values clearly decrease together with the Γ' values.

- The C$_{17}$H$_{35}$NO$_6$ adsorption is of physical nature, which is evidenced by the shape of the dependence Γ' *vs. E* and the possibility of precise determination of the maximal adsorption parameters. However, $\Delta G°$ values are relatively high as compared with other systems describing the physical adsorption.

Comparison of Adsorption Properties of Various Surfactants

Comparison studies of adsorption on the mercury electrode of three surfactants: cationic (C$_{11}$H$_{26}$N$^+$) (Table 4), anionic (C$_{10}$H$_{21}$SO^{3-}),[4] and non-ionic (C$_{17}$H$_{35}$NO$_6$) made possible the comparative evaluation of their adsorption values.

- The greatest potential area of the decreased differential capacity occurs in the case of the cationic surfactant, whereas the narrowest one occurs for the anionic surfactant.[31]

- The greatest changes of the zero charge potential, E_z, for comparable concentrations of the surfactant occur in the case of the anionic surfactant. In each case, with the increase of the surfactant concentration the E_z values shift towards less negative potentials. This indicates the adsorption with the alkyl radical directed to the mercury. In the case of ionic surfactants, depending on the electrode charge, there is the probability of the adsorbed ions reorientation.

- Noteworthy is the stability of maximal adsorption parameters, E_{max} and σ_{max} irrespectively of the surfactant type. This may confirm the assumption that in the adsorption process the main role is played by the alkyl radical, and not by the functional groups of surfactants.

- The highest values of the relative surface excess occur in the case of non-ionic surfactants. For ionic surfactants, the Γ' values are comparable.

- The constant changes of the applied adsorption isotherms for each surfactant are different.

For the anionic surfactant, the maximal Γ' values correspond to the lowest $\Delta G°$ parameter values and the lowest A parameter values.[4] For cationic surfactant, the $\Delta G°$ values increase with the increase of the electric charge of the electrode, but at the maximal Γ' they do not reach the maximum value. Values the repulsive interactions, A, between the adsorbed surfactant cations are the weakest. Thus, in the case of ionic surfactants their adsorption is determined by the mutual repulsive interaction. In the case of non-ionic surfactants, the maximal Γ' values are accompanied by the highest $\Delta G°$ values and the strongest repulsive interaction. Thus, the adsorption of this surfactant is determined by the adsorption energy, however here is no simple relation between a surface excess and the values of repulsive interactions parameter, A.

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