The Octyltrimethylamonium Bromide Adsorption at the Mercury Electrode / NaClO$_4$ Solution Interface

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Abstract

The behaviour of octyltrimethylammonium bromide electrosorption on the mercury electrode in 1 mol/L NaClO$_4$ was determined by means of double layer differential capacity measurements. The adsorption constants were derived from surface pressure data as a function of electrode charge density and cationic surfactant bulk concentration. Adsorption of octyltrimethylammonium bromide was analyzed using constants obtained from Frumkin, corrected Flory-Huggins and virial isotherms. It was found that the repulsive interactions for electrode charges close to 0 were the weakest between the adsorbed cations C$_{11}$H$_{26}$N$^+$. In these conditions the surface concentration of the studied surfactant was the greatest.

Keywords: adsorption isotherm, cationic surfactant, differential capacity, mercury electrode

1. Introduction

The electrosorption of surfactants is important in a variety of fields, since they are used in electrocatalysis and electroanalysis. The fundamental and practical aspects of surfactant adsorption at various interfaces have received considerable attention thanks to their importance in many industrial processes. Quaternary ammonium compounds as cationic surfactants are used as inhibitors of steel corrosion in the acidic environment.[1–3]

In most cases the application of surfactants is dominated by empirical knowledge. However, for new technologies basic knowledge of the mode of their adsorption mechanism is required. One of the main aspects concerning the use of surfactants is the control of surface energy of the adsorbent. Based on adsorption isotherms the changes of such energy, the amount of surfactant adsorbed per unit area of adsorbent and the adsorption mechanism can be determined.[4–8] Some authors investigated the adsorption of cationic surfactants on mercury.[9,10] Mercury surface homogeneity and purity provide excellent reproducibility of adsorption phenomena. Solid electrodes (noble metals, different forms of carbon) have much narrower cathodic potential windows and thus cannot compete with mercury in this region.[11]The adsorption of phenols,[12] thiourea derivatives,[13–17] and tert-butanol[18] as well as coadsorption of butan-1-ol and I$^-$ ions[19] at the mercury electrode from sodium perchlorate solutions were studied.

The aim of this work was to study the adsorption of octyltrimethylammonium cation, C$_{11}$H$_{26}$N$^+$ at the dropping mercury electrode from 1 mol/L NaClO$_4$ solution. We chose NaClO$_4$ as a supporting electrolyte because ClO$_4^-$ ions cause the strongest disruption in water structure.[20] The chosen surfactant concentrations are lower than its critical micellar point. The double capacitance was chosen as the primary experimental quantity. It was proved that the inhibiting effect of octyltrimethylammonium bromide on the electrode reaction rate is caused not only by blocking the electrode surface.[21]

2. Experimental

The differential capacity of the double layer C was measured using the ac impedance technique with an Autolab frequency response analyzer (Eco Chemie, Netherlands). The measurements were carried out at frequencies: 400, 800, 1200, 1600 and 2000Hz with the amplitude 5 mV. The equilibrium capacities were obtai-

ned by extrapolation of the measured capacity versus square root of the frequency to zero frequency.

The experiments were performed in a three-electrode system with a dropping mercury electrode as a working electrode, Ag/AgCl with saturated sodium chloride as a reference electrode, and a platinum spiral as a counter electrode. A controlled growth mercury drop electrode (CGMDE) manufactured by MTM Anko Poland was used.

The potential of zero change, 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.[22] The charge density and surface tension for the studied systems: 1 mol/L $NaClO_4$ + increasing concentration of $C_{11}H_{26}NBr$ from 1×10^{-5} mol/L to 7.5×10^{-4} mol/L were derived by the back integration of differential capacity-potential dependencies.

Analytical grade $C_{11}H_{26}NBr$ (Sigma, 98%) and $NaClO_4$ (Fluka) were used without any further purification. Water and mercury were double distilled before use. The solutions were deaerated by passing high purity nitrogen over the solutions during the measurements which were carried out at 298 ± 0.1K.

3. Results and Discussion

3. 1. Analysis of Experimental Data

Figure 1 presents differential capacity curves obtained experimentally in 1 mol/L $NaClO_4$ solution and with the addition of $C_{11}H_{26}N^+$ to the solution. A decrease of differential capacity in a wide range of potentials from

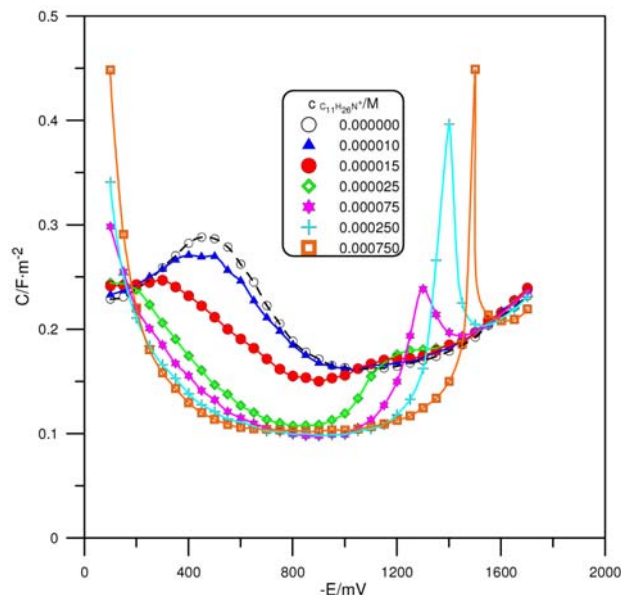**Figure 1.** Differential capacity-potential curves of the double layer Hg/1 mol/L $NaClO_4$ aqueous solution and with the addition of $C_{11}H_{26}N^+$ (concentrations as in the legend).

–200mV to –1150mV was caused by the addition of $C_{11}H_{26}N^+$. The increase of the concentration of $C_{11}H_{26}N^+$ caused a widening of that area of potentials towards negative values. At the same time, the value of the potential –200mV practically did not change. The obtained results showed strong adsorption of $C_{11}H_{26}N^+$ on the mercury electrode. With the maximum concentration of $C_{11}H_{26}N^+$, its desorption took place at the potential of E = –1550mV. This effect was undoubtedly the result of electrostatic interactions of the cation $C_{11}H_{26}N^+$ with the differently charged surface of the mercury electrode.
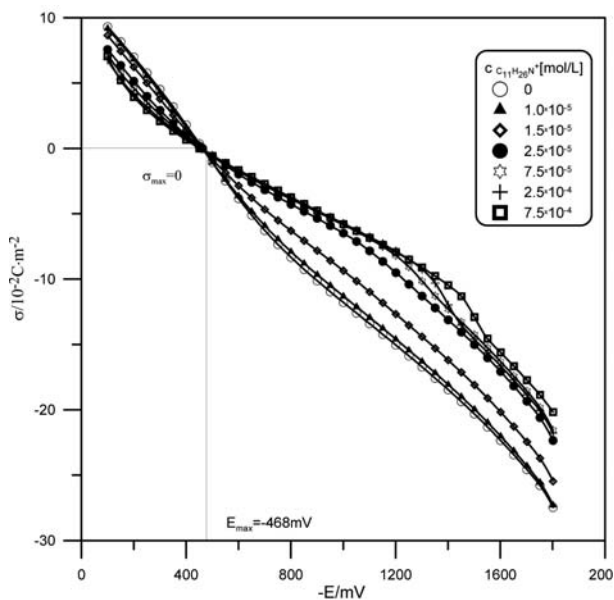

Figure 2. Dependences of the electrode charge versus the electrode potential for the studied $C_{11}H_{26}NBr$ concentrations.

As not all of the obtained C-E curves converge at sufficiently negative potentials with the corresponding curve for the base solution the capacity versus potential data were numerically integrated from the point of E_z. The value of E_z changed from –461mV, for 1 mol/L $NaClO_4$, to – 447mV for the base solution containing 7.5×10^{-4} mol/L $C_{11}H_{26}N^+$. Such changes of E_z indicate the mechanism of cation adsorption $C_{11}H_{26}N^+$ with the ammonium group directed to mercury. At the same time the Γ_z value decreased from 421mN · m^{-1} for 1 mol/L $NaClO_4$ to 402 mN · m^{-1} for the base solution containing 7.5×10^{-4} mol/L $C_{11}H_{26}N^+$. Figure 2 presents the dependences of the electrode charge versus the electrode potential for the studied $C_{11}H_{26}N^+$ concentrations. The point of intersection of the obtained curves allows one to determine the parameters of the maximum adsorption for $C_{11}H_{26}N^+$: E_{max} = –468mV, the surface charge of the electrode, σ_{max} = 0. At the same time, such a course of dependences $\sigma_{max} = f(E)$ confirms the physical character of adsorption $C_{11}H_{26}N^+$ on the mercury electrode.

3. 2. Adsorption Isotherms

Due to the ionic nature of the surfactant for calculating the relative surface excess, Γ', we used the Parsons' auxiliary function: $\varsigma = \gamma + \delta E$, described in our previous studies.[23] As the adsorption of ClO_4^- ions was demonstrated earlier,[20] the obtained values Γ' describe the surface concentration only of $C_{11}H_{26}N^+$ ions. The Γ' values were determined according to Gibbs adsorption isotherm:

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

where c is the bulk concentration of $C_{11}H_{26}N^+$ and Φ is the surface pressure $\Phi = \Delta\varsigma = \varsigma_0 - \varsigma$ (ς_0 and ς are the values of the Parsons' auxiliary function for the base electrolyte and ς is the same function for the solution with $C_{11}H_{26}N^+$. The obtained Γ' values are presented in Fig. 3. The maximum Γ' values near the electrode charge $\delta = 0$. The shape of curves in Fig. 3 shows competitive electrostatic interactions: cation $C_{11}H_{26}N^+$– water dipoles.

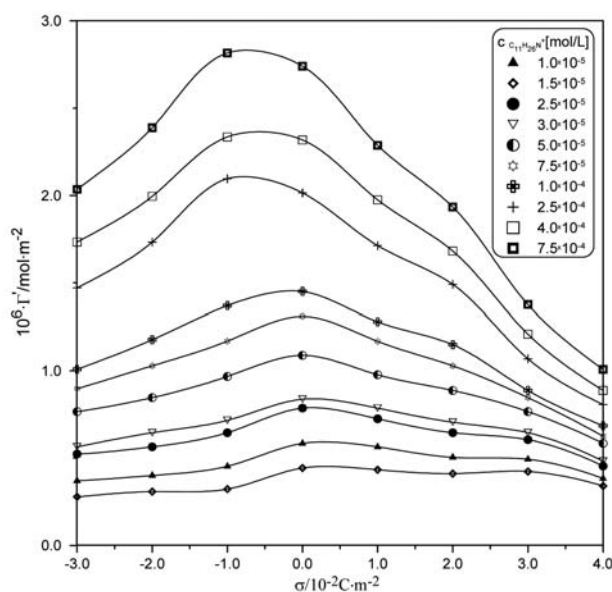**Figure 3.** Relative surface excess of $C_{11}H_{26}N^+$ as a function of the electrode charge and $C_{11}H_{26}N^+$ concentration in the bulk.

The adsorption of $C_{11}H_{26}N^+$ was further analyzed on the basis of the Frumkin and modified Flory-Huggins[24–26] isotherms. The Frumkin isotherm constants were determined on the basis of the equation:

$$\beta x = \left[\frac{\Theta}{1-\Theta}\right]\exp(-2A\Theta) \qquad (2)$$

where x is the mole fraction of $C_{11}H_{26}N^+$ in the solution, β is the adsorption coefficient: $\beta = \exp(-\Delta G^o/RT)$, ΔG^o is the standard Gibbs energy of adsorption, A is the interaction parameter, and Θ is the coverage value $\Theta = \Gamma'/\Gamma_s$. The

surface excess at saturation, Γ_s, was estimated by extrapolating the $1/\Gamma'$ vs. $1/c$ lines at different electrode charges to $1/c = 0$. The obtained Γ_s value was 7.7×10^{-6} mol · m^{-2}. The surface occupied by one $C_{11}H_{26}N^+$ cation, S (S≡$1/\Gamma_s$), was 0.216 nm^2. Such a small S value may indicate the perpendicular orientation of the adsorbed cation.

Figure 4 shows the linear test of the Frumkin isotherm for electrode charges $-3 \leq \sigma \leq 4$ 10^{-2} C · m^{-2}. The A_F parameter values were calculated from the slopes of the lines on the linear test in Fig.4.

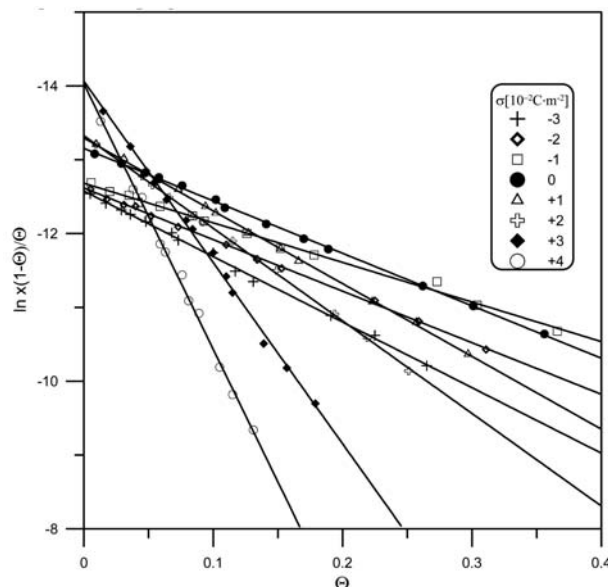**Figure 4.** A linear test of the Frumkin isotherm in the system 1 mol/L $NaClO_4 + C_{11}H_{26}N^+$ for various electrode charges.

The corresponding ΔG_F^o was determined by the extrapolation of the lines of $\ln\left[\frac{1-\Theta}{\Theta}\right]$ vs. Θ to the value $\Theta = 0$. The obtained values are presented in Table 1. The ΔG_F^o values change monotonically, characteristically for the ion adsorption. The values of the A_F parameter indicate the repulsive interactions between the adsorbed $C_{11}H_{26}N^+$ cations. This interaction is the weakest for the electrode charge, for which the Γ' values are maximum ones (Fig. 3). This repulsive interaction is particularly promoted with the positive electrode charge. The $C_{11}H_{26}N^+$ adsorption was further analyzed based on the constants: ΔG_H^o and A_H (Table 1) obtained from the modified Flory-Huggins isotherm. The linear test was prepared in the system: $\ln\left[\frac{x(1-\Theta)^n}{\Theta}\right]$ vs. Θ where $n = 1.76$ is the number of water molecules replaced by one $C_{11}H_{26}N^+$ cation. In the presented case the projected area for water[27] is 0.123 nm^2. As ClO_4^- ions cause the strongest disruption in

water structure,[20] the surface of one water molecule instead of the water cluster was used in the calculations. The changes of the obtained values ΔG_H^o and A_H show similar tendencies to the changes of the values of ΔG_F^o and A_F, respectively (Table 1).

Table 1. The constants of Frumkin (F), corrected Flory-Huggins (H) and virial (V) isotherms for the system: 1 mol/L NaClO$_4$ + C$_{11}$H$_{26}$N$^+$; 10^2 σ[C · m^{-2}], ΔG^o[kJ · mol^{-1}]

σ	$-\Delta G_F^o$	$-A_F$	$-\Delta G_H^o$	$-A_H$	$-\Delta G_V^o$	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

The obtained data from the above-mentioned isotherms were verified using the virial isotherm. The application of the virial isotherm does not require knowing the Γ_s value. The virial isotherm equation is:

$$\ln \beta c = \ln \Gamma + 2B\Gamma \qquad (3)$$

where β is the two-dimensional (2D) second virial coefficient. The 2D second virial coefficient values were calculated from the slopes of lines on the linear test log(Γ'/c) *vs.* Γ' of the virial isotherm. The corresponding ΔG_V^o values were obtained from the intercepts of those lines with the axis log(Γ'/c) using the standard state 1mol · dm^{-3} in the bulk solution and 1mol · cm^{-2} on the surface. Like the previous isotherms, the values of ΔG^o increased (in absolute terms) with the increase of the electrode charge. With the most positive electrode charges there occurred strong repulsive interactions between the absorbed cations C$_{11}$H$_{26}$N$^+$. The weakest repulsive interactions took place for the electrode charges for which the Γ' values were the largest (Fig. 3). With those electrode charges it was possible to reorganise the adsorbed cations C$_{11}$H$_{26}$N$^+$. This effect can cause the increase of surface concentration of the adsorbate. As it results from Table 1, the increase of the Γ value is due to weak repulsive interactions between the cations of the adsorbate. The most negative ΔG^o values occurring for $\sigma > 0$ may be the effect of the inductive movement of the charge in the C$_{11}$H$_{26}$N$^+$ cation. This is accompanied by strong repulsive interactions and small Γ' values.

The obtained ΔG^o values are comparable with those calculated for tetramethylthiourea[16,26] where chemisorption occurs on the mercury electrode. That is why in the case of physically adsorbed C$_{11}$H$_{26}$N$^+$ considerably high ΔG^o values are quite surprising. However, in this case the discussion of chemical interactions between the adsorbate and the electrode is not justified, first of all because of the

structure of the surfactant molecule. Namely, the surfactant molecule does not possess the atoms that could form any bonds, or even pseudo-bonds with mercury, as is the case for tetramethylthiourea (TMTU). In the case of TMTU, the S atoms possessing lone electron pairs that are able to form chemical bonds with mercury, are responsible for the above-mentioned interactions. Moreover, the possibility of determining maximum adsorption parameters is an important argument that confirms physical adsorption of C$_{11}$H$_{26}$N$^+$ on the mercury electrode. Another proof of physical adsorption is the shape of curves of relative surface excess of C$_{11}$H$_{26}$N$^+$ as a function of the electrode charge (Fig. 3). As can be seen, the curves are bell-shaped. In the case of chemical adsorption of tetramethylthiourea the curves are constantly increasing.[16]

The problem of physical adsorption of surfactants on various materials is generally well known. Mercury offers a highly reproducible and smooth surface for adsorption of surfactants and can be used as a model study.

4. Conclusions

The following conclusions can be drawn;

– Adsorption of the cationic surfactant C$_{11}$H$_{26}$N$^+$ on the mercury electrode has the physical character. However, it is quite strong, as evidenced by the ΔG^o values. The new important achievement of the present study is that we managed to question the hitherto-existing opinions stating that physical adsorption is determined by low ΔG^o values. Namely, we showed that on the mercury electrode at physical adsorption of surfactant molecules with high molar mass the ΔG^o values are not at all small but are comparable with those obtained for the chemisorption of tetramethylthiourea.

– The highest values of surface concentrations Γ' are found in the vicinity of the electrode charge $\sigma = 0$. Under these conditions the repulsive interactions between the adsorbed cations are the weakest ones and they facilitate the adsorption C$_{11}$H$_{26}$N$^+$.

– The intensity of repulsive interactions between the adsorbate cations for the distant charges from $\sigma = 0$ may be the result of the adsorbate reorientation. This reorientation is more pronounced for $\sigma > 0$ than for $\sigma < 0$.

– In the extreme negative potential region, the positively charged surfactant headgroups are bound to mercury and there are strong interactions between the surfactant alkyl chains that are oriented parallel to each other. The bromide ions may form bridges between the ammonium groups, stabilizing the adsorption film electrostatically.

5. References

1. T. Y. Soror, M. A. El-Ziady, *Mater. Chem. Phys.* **2002**, *77*, 697–703. http://dx.doi.org/10.1016/S0254-0584(02)00129-3

2. T. Vasudevan, S. Muralidharan, S. Alwarappan, S.V. K. Iyer, *Corros. Sci.* **1995**, *37*, 1235–1244. http://dx.doi.org/10.1016/0010-938X(95)00028-I

3. M. M. Saleh, *Mater. Chem. Phys.* **2006**, *98*, 83–89. http://dx.doi.org/10.1016/j.matchemphys.2005.08.069

4. M. J. Rosen, Surfactants and Interfacial Phenomena, 2nd ed., Wiley, New York, **1989**.

5. M. Klin, J. Nieszporek, D. Sieńko, D. Gugała-Fekner, J. Saba, *Acta Chim. Slov.* **2011**, *58*, 26–32.

6. J. Nieszporek, *S. Afr. J. Chem.* **2014**, *67*, 1–5.

7. D. Gugał-Fekner, J. Nieszporek, D. Sieńko, *Monatsh. Chem.* **2015**, *146*, 541–545. http://dx.doi.org/10.1007/s00706-014-1382-7

8. J. Nieszporek, D. Sieńko, D. Gugał-Fekner, M. Klin, *Turk. J. Chem.* **2012**, *36*, 841–851.

9. A. Avranas, A. Komnianou, U. Retter, *J. Colloid Interface Sci.* **2003**, *264*, 407–413. http://dx.doi.org/10.1016/S0021-9797(03)00534-4

10. A. Avranas, N. Sedlačkova, E. Malasidon, *J. Colloid Interface Sci.* **2005**, *285*, 665–673. http://dx.doi.org/10.1016/j.jcis.2004.12.015

11. J. Barek, *Port. Electrochim. Acta.* **2013**, *31*, 291–295. http://dx.doi.org/10.4152/pea.201306291

12. S. Sarangapani, V. K. Venkatesan, *Proc.Indian Natn. Sci. Acad.-A,* **1983**, *49(1)*, 124–142.

13. A. Nosal-Wiercińska, G. Dalmata, *Electrochim. Acta*, **2006**, *51(27)*, 6179–6185. http://dx.doi.org/10.1016/j.electacta.2006.01.062

14. G. Dalmata, A. Nosal-Wiercińska, *Croat. Chem. Acta*, **2008**, *81(4)*, 529–537.

15. N. Nosal-Wiercińska, G. Dalmata, *Electrochim. Acta*, **2006**, *51(27)*, 6179–6185.

16. http://dx.doi.org/10.1016/j.electacta.2006.01.062

16. D. Gugał, Z. Fekner, D. Sieńko, J. Nieszporek, J. Saba, *Electrochim. Acta*, **2004**, *49(14)*, 2227–2236. http://dx.doi.org/10.1016/j.electacta.2003.12.026

17. M. Klin, J. Nieszporek, D. Sieńko, D. Gugał-Fekner, J. Saba, *Croat. Chem. Acta*, **2011**, *84(4)*, 475–480. http://dx.doi.org/10.5562/cca1791

18. J. Nieszporek, *Cent. Eur. J. Chem.* **2013**, *11(1)*, 86–93. http://dx.doi.org/10.2478/s11532-012-0137-8

19. J. Saba, K. Sykut, J. Nieszporek, J. Szaran, *Collect. Czech. Chem. Commun.,* **1999**, *64(12)*, 1925–1936. http://dx.doi.org/10.1135/cccc19991925

20. J. Koryta, J. Dworak, V. Bohackova, Lehrbuch der Elektrochemie, Springer-Verlag Wien, New York, **1975.** http://dx.doi.org/10.1007/978-3-7091-8418-9

21. J. Nieszporek, *J. Electroanal. Chem.* **2013**, *706*, 108–116. http://dx.doi.org/10.1016/j.jelechem.2013.08.007

22. D. J. Schiffrin, *J. Electroanal. Chem.* **1969**, *23*, 168–171. http://dx.doi.org/10.1016/S0022-0728(69)80203-2

23. D. Sieńko, D. Gugał-Fekner, J. Nieszporek, Z. Fekner, J. Saba, *Collect. Czech. Chem. Commun.* **2009**, *74*, 1309–1321. http://dx.doi.org/10.1135/cccc2009007

24. W. R. Fawcett, R. C. Rocha-Filho, L. M. Doubova, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2967–2970. http://dx.doi.org/10.1039/FT9918702967

25. S. Trassati, *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, 28, 257–277. http://dx.doi.org/10.1016/S0022-0728(70)80120-6

26. D. Gugał-Fekner, D.Sieńko, J. Nieszporek, M. Klin, J. Saba, *J. Colloid Interface Sci.* **2009**, *332*, 291–297. http://dx.doi.org/10.1016/j.jcis.2008.12.067

27. J. Lawrence and J. Parsons, *J. Phys. Chem.* **1969**, *73*, 3577–3581. http://dx.doi.org/10.1021/j100845a008

Povzetek

Z meritvami diferencialne kapacitivnosti dvoplasti smo proučevali elektrosorpcijo oktil trimetil amonijevega bromida ($C_{11}H_{26}NBr$) na Hg elektrodo v vodni raztopini 1 M $NaClO_4$. Z uporabo Frumkinove, popravljene Flory-Hugginsove in virialne izoterme smo iz podatkov za površinski tlak v odvisnosti od gostote naboja na elektrodi in koncentracije surfaktanta določili konstante adsorpcije. Izkazalo se je, da so pri naboju na elektrodi blizu 0 odbojne interakcije med adsorbiranimi kationi $C_{11}H_{26}N^+$ najšibkejše. Pri teh pogojih je torej koncentracija preučevanega surfaktanta na površini največja.