THE CORRECT INTERPRETATION OF TETRAMETHYLTHIOUREA ELECTROSORPTION DATA IN 3 M $NaClO_4$ SOLUTION

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Tetramethylthiourea (TMTU) electrosorption behaviour at the mercury electrode in 3 M $NaClO_4$ has been examined. Using a new concept of adsorption isotherm, new theoretical expressions have been proposed. The application of these equations shows evident influence of the electrode charge on the TMTU adsorption. It can be concluded that TMTU molecules are largely specifically bonded and at zero electrode charge the change of adsorbed TMTU molecules orientation is observed.

Keywords: Tetramethylthiourea; Standard free energy of adsorption; Flory–Huggins isotherm; Non-random two liquid model.

The addition of organic compounds to aqueous solutions with a polarizable surface makes it possible to easily control the electrical variables. For example, thiourea, tertbutanol or tetramethylthiourea (TMTU)[1–5] can significantly affect the kinetics of ions electroreduction at the mercury electrode. Small additions of those substances can increase or decrease the rate of electrode processes. Such behaviour is commonly explained by the adsorption of organics at the electrode surface. In the chemical structure of thiourea and its derivatives a double bond is preesent between carbon and sulfur atoms. They adsorb at the mercury electrode through covalent bond formation. Earlier studies[6,7] showed that the standard free energy of adsorption ΔG^0 of TMTU is evidently larger than for thiourea. Undoubtedly, four $-CH_3$ groups which are typically hydrophobic significantly affect TMTU adsorption. Its molecular structure also suggests the possibility of an insignificant change of vertical orientation at the electrode surface.

The investigation of organic compounds adsorption can provide a lot of important information helpful to understand the phenomena which occur during ion electroreduction at the electrode[8–14]. For example, the adsorp-

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tion of organic compounds on the electrode surface causes the decrease of differential capacity and surface tension. Then, following a thorough analysis of differential capacity curves the role and possible applications of adsorption phenomena in the electroanalysis can be recognized.

To describe the adsorption equilibria at the solid|solution interface the Frumkin isotherm is commonly applied. It seems that in many cases it is sufficient to use that isotherm. However, it should be remembered that the Frumkin isotherm is based on the lattice model of adsorption and mean field approximation (MFA). Sometimes during adsorption some additional effects may occur, for example the reorientation of the adsorbed molecules or the change in electron density of the adsorbed molecules. The adsorption of organics at the electrode surface may be of a competitive character – solvent molecules can also adsorb at the electrode surface. This is due to the fact that a base electrolyte at a sufficiently large concentration is commonly added to the solution. This in turn makes it possible to avoid all the undesirable artifacts that arise as a result of too low conductivities.

The application of MFA assumes random distribution of the adsorbed species at the surface. However, it seems that during the process of adsorption the adsorbed molecules sometimes form clusters[15–17]. In such a case another isotherm expression must be used that would better correspond to the investigated adsorption system.

The aim of the present paper is to obtain quantitative results of the adsorption of organic compounds at the mercury electrode surface. We show a simple way to determine new isotherm expressions. Now anybody can adjust the form of theoretical isotherm to the analyzed adsorption system. The determined new adsorption isotherms have been used to investigate TMTU adsorption at the dropping mercury electrode. The analysis of adsorption equilibria by using a few theoretical isotherm expressions can complement each other.

THEORY

The most popular expression used to describe the adsorption equilibrium is the Langmuir isotherm[18]

$$\beta x = \theta/(1 - \theta) \tag{1}$$

where $\theta = \Gamma'/\Gamma_s$ is the fractional coverage, Γ' is the actual surface excess, Γ_s is the surface excess at saturation, β is the equilibrium constant and x is the molar fraction.

The above expression is based on the lattice formalism. It means that above the surface there exists the lattice of energetically identical adsorption centers and the adsorbed molecule occupies only one adsorption site – the adsorbed species form a monolayer at the electrode surface each molecule replacing one solvent molecule.

During last decades many modifications of the Langmuir isotherm has been proposed. The Flory–Huggins (FH) isotherm is popular in theoretical description of the adsorption at the electrode|electrolyte interface[19]

$$\beta x = \theta / r(1 - \theta)^r \tag{2}$$

which is based on a model in which adsorbed species replace r solvent molecules (r is the relative size factor). Dhar et al.[20] suggested using the modified form of Eq. (*2*).

$$\beta x = \theta / e^{r-1}(1 - \theta)^r \tag{3}$$

For the readers' convenience we call here the above expression as the Flory–Huggins–Dhar (FHG) isotherm.

The use of the above equilibrium isotherms allows to determine the standard free energy of adsorption ΔG^0 which can be calculated from the experimental coverage or the surface excess measurements.

$$\Delta G^0 = -RT \ln \beta \tag{4}$$

Of course the correct calculation of the standard free energy ΔG^0 of the solvent-substitution adsorption process of the charged interface from the experimental coverage data cannot be made unless the configurational term (r.h.s. of Eqs (*1*)–(*3*)) is properly formulated. It seems that from the above adsorption isotherms (*1*)–(*3*), the Langmuir equation is the simplest and will be accompanied with the largest error in determining of ΔG^0. Obviously the correctness of ΔG^0 calculation is also connected with taking into account the additional effects accompanying adsorption phenomena.

It is well known that the interactions between the adsorbed species can lead to strong deviations from ideal behaviour. It is particularly important in the region of high surface coverage. The most popular extension of Eq. (*1*) for that case has the following form

$$\beta x = [\theta / (1 - \theta)] \exp \{-A\theta\} \tag{5}$$

where A is the interaction parameter. Equation (*4*) is a well-known Fowler–Guggenheim, Bragg–Williams or Frumkin isotherm and can be determined by using statistical thermodynamics and assuming MFA as the model of interactions in the adsorbed phase.

While comparing Eqs (*1*) and (*5*), it can be stated that the theoretical adsorption isotherm based on the lattice formalism can be written as follows

$$\beta x = \Lambda_{entr} \times \Lambda_{ther} \tag{6}$$

where Λ are the entropic and thermal contributions to adsorption. It can be seen that Λ_{entr} is one of the r.h.s. of Eqs (*1*)–(*3*) and in the case of MFA Λ_{ther} has the following form.

$$\Lambda_{ther} = \exp\{A\theta\} \tag{7}$$

In that way we can obtain well-known modification of the Langmuir or Flory–Huggins adsorption isotherms.

The general purpose of the present paper is to show a simple way to generalize isotherms (*1*)–(*3*) to different models of non-ideality. In other words, we will show the way how to determine the thermal term in expression (*6*) by taking into account a few models of non-ideality in the adsorbed phase. It is due to the fact that the commonly applied MFA sometimes can lead to incorrect results. It follows from the assumption of random distribution of the adsorbed molecules across the surface. It means that the interaction parameter A is the product of the interaction energy between two molecules adsorbed on two nearest-neighbour adsorption sites and of the number of the nearest-neighbour adsorption sites on a given lattice of sites. It seems that with the growing surface coverage the interactions between the adsorbed molecules can lead to smaller or greater deviations from the mean field theory (MFT). The same concerns the difference in sizes of solvent and adsorbed molecules.

A convenient theoretical tool to generalize the adsorption isotherm for the case of any model of non-ideality in the adsorbed phase is the vacancy solution theory (VST). It was introduced into literature in 1980 by Suwanayuen and Danner[21] and is based on the assumption that the bulk and surface phases are the solutions of adsorbed molecules and hypothetical 'vacancies'. Thus, the one component adsorption system is considered to be a binary vacancy solution $i + v$, where vacancies are occupied by solution species.

The general VST expression for the case of lattice model of adsorption has the following form[21]

$$\mathrm{d}\ln x = -\frac{1}{\theta}\left(\frac{\partial \ln \gamma_v^s}{\partial \theta} - \frac{1}{1-\theta}\right)\mathrm{d}\theta \tag{8}$$

where γ_v^s is the activity coefficient in "vacancy" formalism.

Equation (*8*) is the main equation which makes it possible to determine the generalization of the Langmuir isotherm (*1*) for any model of interactions between the adsorbed molecules. For example, if we use MFA recalled above, the activity coefficient of the vacancy reads

$$\ln \gamma_v^s = \frac{A}{RT}\theta^2 \tag{9}$$

and the integration of Eq. (*8*) with γ_v^s defined by Eq. (*9*) leads to the Frumkin isotherm (*5*). If we use the Flory–Huggins activity

$$\ln \gamma_v^s = \frac{a_{1v}\theta}{1 + a_{1v}\theta} - \ln(1 + a_{1v}\theta) \tag{10}$$

where a_{1v} is the Flory–Huggins interaction parameter. The integration of Eq. (*8*) leads to the following expression of thermal term Λ_{ther}

$$\Lambda_{ther} = \exp\left\{\frac{a_{1v}^2\theta}{1 + a_{1v}\theta}\right\} \tag{11}$$

which, for example, combined with the FHD isotherm (*3*) leads to the following new expression.

$$\beta x = \frac{\theta}{e^{r-1}(1-\theta)^r}\exp\left\{\frac{a_{1v}^2\theta}{1 + a_{1v}\theta}\right\} \tag{12}$$

To distinguish the new isotherm expressions we call the above as N-FHD–FH isotherm.

As the third example the non-random two liquid (NRTL) model is used. NRTL was proposed by Ranon and Prausnitz[15–17] and is based on the assumption that the local concentration around a molecule is different from the bulk concentration (non-randomness is caused by energetic differences). The authors developed a new equation for the excess Gibbs energy by introducing a constant characteristic of the non-randomness of the mixture into the expression for the local mole fractions. Then, the NRTL activity coefficient for vacancy reads

$$\ln\gamma_v^s = \theta^2\left\{\tau_{1v}\frac{\exp\{-2\alpha_{1v}\tau_{1v}\}}{\left[(1-\theta)+\theta\exp\{-\alpha_{1v}\tau_{1v}\}\right]^2}+\tau_{v1}\frac{\exp\{-\alpha_{1v}\tau_{v1}\}}{\left[\theta+(1-\theta)\exp\{-\alpha_{1v}\tau_{v1}\}\right]^2}\right\} \qquad (13)$$

where

$$\tau_{1v} = \frac{g_{1v}-g_{vv}}{RT}$$
$$\tau_{v1} = \frac{g_{v1}-g_{11}}{RT} \qquad (14)$$

g_{1v} and g_{v1} are, the energies of interactions between 1 – v and 1 – 1 pair of molecules $g_{1v} = g_{v1}$ respectively, whereas α_{1v} is, as mentioned above, a constant characteristic of the non-randomness of the mixture. While integrating Eq. (*8*) with ln γ_v^s defined in Eq. (*13*), we arrive at the following form of Λ_{ther}[23,24].

$$\Lambda_{ther} = \exp\left\{\frac{\tau_{v1}\exp\{-2\alpha_{1v}\tau_{v1}\}}{(1-\exp\{-\alpha_{1v}\tau_{v1}\})\left[\theta+(1-\theta)\exp\{-\alpha_{1v}\tau_{v1}\}\right]^2}+\right.$$
$$\left.+\frac{\tau_{1v}\exp\{-2\alpha_{1v}\tau_{1v}\}}{(\exp\{-\alpha_{1v}\tau_{1v}\}-1)\left[1+(\exp\{-\alpha_{1v}\tau_{1v}\}-1)\theta\right]^2}\right\} \qquad (15)$$

Summing up, we showed a simple way to generalize adsorption isotherms based on lattice formalism to any model of non-ideality used to describe the interaction effects between the adsorbed molecules. The MFA, Flory–Huggins activity coefficients and NRTL model combined with isotherms (*1*)–(*3*) give the possibility to determine nine different expressions describing the adsorption isotherms. A few of them have never been reported in literature. The next section will be devoted to the verification of their accuracy in theoretical description of adsorption phenomena at the electrode|electrolyte interface.

ILLUSTRATIVE CALCULATIONS

To perform the theoretical analysis of adsorption isotherms we used the data reported in our recent paper[6]. Then we studied TMTU electrosorption in the concentrated $NaClO_4$ solutions at the dropping mercury electrode. The experimental systems studied with such a working electrode have unquestionable advantage – its surface is fully renewable and ideally polarizable. The experimental data are characterized by high recurrence and practically exclusion of the errors resulting from the pollution existence on the electrode surface. Such properties of the dropping mercury electrode create a great possibility to perform thermodynamically consistent studies of electroreduction processes. All segments of the apparatus work in closed systems so the harmful influence of the mercury vapours on the operator's health is minimized.

Detailed description of the experimental procedure can be found elsewhere[5]. Briefly, it was performed in a three electrode system with the dropping mercury electrode as a working electrode, Ag|AgCl as a reference and platinum spiral as a counter electrode. The differential capacity–potential curves were determined at 298 K for different concentrations of TMTU and $NaClO_4$ used as a base electrolyte. The relative surface excess Γ' of TMTU has been determined by using the relative surface pressure Φ.

As TMTU is composed of nitrogen and sulfur atoms (which are strongly electronegative) it is a polar molecule: sulfur atom has a negative charge and nitrogen atom has a positive charge. It has been shown that organic compounds containing both nitrogen and sulfur atoms give better inhibition effects than those containing nitrogen or sulfur alone. As the molecule approaches the electrode surface, the electric field of double layer increases the polarization of molecules and induces additional charges on sulfur and nitrogen atoms, a condition that enhances the adsorption of molecules.

The experimental adsorption isotherms of TMTU were analyzed using two new expressions which are the combination of Dhar–Flory–Huggins Eq. (*3*) as the entropic contribution to the adsorption isotherm and thermal contribution described by Eqs (*11*) and (*15*). One of them is given by N-FHD–FH Eq. (*12*) whereas the other one is as follows.

$$\beta x = \frac{\theta}{e^{r-1}(1-\theta)^r}\exp\left\{\frac{\tau_{v1}\exp\{-2\alpha_{1v}\tau_{v1}\}}{(1-\exp\{-\alpha_{1v}\tau_{v1}\})\left[\theta+(1-\theta)\exp\{-\alpha_{1v}\tau_{v1}\}\right]^2}+\right.$$

$$\left.+\frac{\tau_{1v}\exp\{-2\alpha_{1v}\tau_{1v}\}}{(\exp\{-\alpha_{1v}\tau_{1v}\}-1)\left[1+(\exp\{-\alpha_{1v}\tau_{1v}\}-1)\theta\right]^2}\right\} \qquad (16)$$

We call the above expression the N-FHD–NRTL isotherm.

Before starting numerical calculations we discuss some of the details connected with theoretical applications of equilibrium isotherms (*12*) and (*16*). Namely, it is possible to minimize the number of best-fit parameters in the above mentioned expressions. The surface excess at saturation Γ_s can be estimated by extrapolating $1/\Gamma'$ vs $1/c$ dependence at different charges to $1/c = 0$, where c is the TMTU concentration. Further, the value of $S \equiv 1/\Gamma_s$ is equal to the surface occupied by one TMTU molecule. Then, the number of ClO_4^- ions replaced by one adsorbate molecule r is equal to the ration of S for TMTU (0.39 nm^2) to S for the projected area of ClO_4^- (0.31 nm^2). In the case of base electrolyte concentration equal to 3 mol l^{-1} the relative size factor r is equal to 1.26.

The numerical adjustment of the N-FHD–FH adsorption isotherm (*12*), to the experimental TMTU adsorption isotherms makes it possible to determine two values of best-fit parameters β and a_{iv}. The case of N-FHD–NRTL isotherm (*16*) is undoubtedly more numerically complicated – while adjusting Eq. (*16*) to the experimental equilibrium adsorption isotherms we can determine four values of the best-fit parameters: τ_{v1}, τ_{1v}, α_{1v} and β. The meaning of the used subscripts is as follows: '1' means the adsorbed TMTU molecule and '*v*' means the other molecules or ions (vacancies) which exist in the bulk phase: solvent (H_2O) molecules or ClO_4^- ions. Then g_{11} means the energy of interaction between two TMTU molecules; g_{vv} is the interaction energy between two water or ClO_4^- particles and g_{lv} is the interaction energy between TMTU and vacancy.

The applicability of new expressions will be illustrated by the analysis of a few experimental isotherms determined at different electrode charges and constant $NaClO_4$ concentration. To compare the fit quality, we use the average absolute deviation AAD (in %) function defined as

$$\mathrm{AAD} = \frac{1}{n}\sum_{i=1}^{n}\frac{x^{exp}-x^{calc}}{x^{exp}}\times 100 \qquad (17)$$

where x^{exp} and x^{calc} are the experimentally measured and theoretically calculated mole fractions and n is the number of experimental points.

The results of adjustment of Eqs (*12*) and (*16*) to the experimental TMTU adsorption isotherms are shown in Figs 1 and 2.

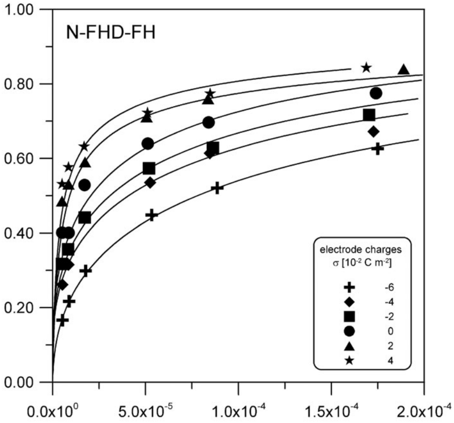

FIG. 1

Comparison of the experimental isotherms for the systems TMTU–3 M $NaClO_4$ with the theoretical isotherms calculated using the modified N-FHG–FH isotherm (*12*). The values of the obtained best-fit parameters are collected in Table I

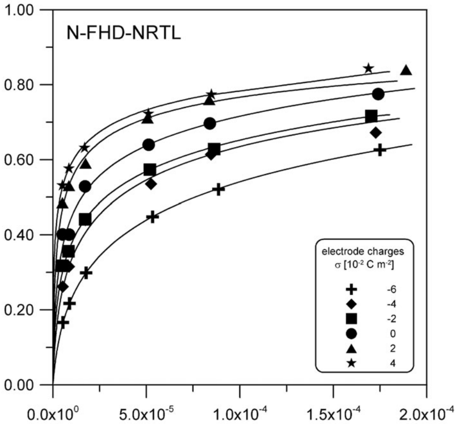

FIG. 2

Comparison of the experimental isotherms for the systems TMTU–3 M $NaClO_4$ with the theoretical isotherms calculated using the N-FHD–NRTL isotherm (*16*). The values of the obtained best-fit parameters are collected in Table II

For the readers' convenience the best-fit values collected in Tables I and II are shown graphically in Figs 3–6. It makes easier to give their theoretical interpretation. The discussion concerning the results of theoretical analysis of TMTU adsorption at the mercury electrode will be divided into two subsections.

TABLE I
Values of the N-FHD–FH isotherm (*12*) best-fit parameters obtained when fitting the measured equilibrium isotherms presented in Fig. 1

Electrode charge σ 10^{-2} C m^{-2}	a_{1v}	β	AAD, %
–6	3.76	1.38×10^5	0.68
–4	8.98	3.48×10^7	1.90
–2	10.13	1.41×10^8	1.62
0	9.72	1.42×10^8	1.60
2	–0.84	1.82×10^5	1.17
4	–0.82	2.40×10^5	2.70

TABLE II
Values of the N-FHD–NRTL isotherm (*16*) best-fit parameters obtained when fitting the measured equilibrium isotherms presented in Fig. 2

Electrode charge σ 10^{-2} C m^{-2}	α_{1v}	τ_{1v}	τ_{v1}	β	Error
–6	0.062	9.48	–6.37	3.25×10^7	0.46
–4	0.058	8.71	–6.71	5.20×10^7	9.20
–2	0.081	9.45	–6.10	6.57×10^7	0.90
0	0.195	6.29	–3.30	5.10×10^6	5.50
2	0.191	3.36	–3.36	2.90×10^6	4.40
4	0.037	0.86	–3.45	1.90×10^6	4.60

Interaction Parameters

Figures 3 and 4 show that the electrode charge has evident impact on the interaction energy between the adsorbed molecules. The values of interaction parameters determined by using both theoretical models of adsorption suddenly change in the region of zero electrode charge σ.

The value of Flory–Huggins interaction parameter α_{1v} with the increasing σ somewhat increases and at $\sigma > 0$ changs jumpwise. A similar behaviour of interaction effects between the adsorbed molecules has been observed by using the Flory–Huggins adsorption isotherm (*2*)[6]. Also the values of NRTL interaction parameters τ_{1v} and τ_{v1} changed jumpwise in the region of zero

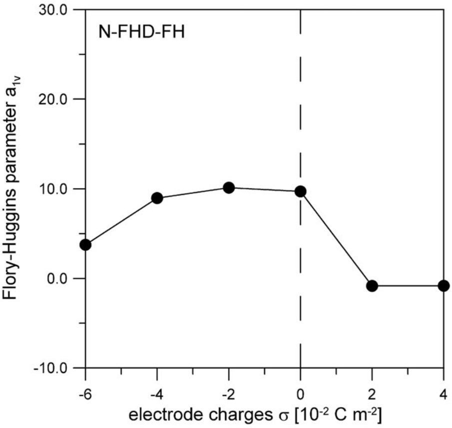

FIG. 3
Variation of the N-FHD–FH interaction parameter a_{1v} determined using the isotherm (*12*) due to charge density

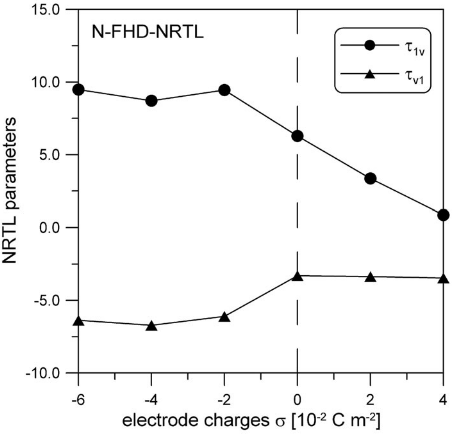

FIG. 4
Variation of the NRTL interaction parameters τ_{1v} and τ_{v1} determined using the isotherm (*16*) due to charge density

charge. Figure 4 shows that when $\sigma \geq -2$, the parameter τ_{1v} linearly decreases. Simultaneously, when $\sigma < 0$ τ_{v1} remains constant when the electrode charge is between –6 and –2 and slightly increases between –2 and 0. When $\sigma \geq 0$, τ_{v1} remains approximately constant. While looking at Eq. (*14*), we can state that with the increasing electrode density charge the energy of interaction between the molecules or ions adsorbed at the electrode surface g_{vv} increases more violently than the energy of interactions between the TMTU molecules g_{11}. Further, it probably means that at $\sigma \geq 0$ the number of vacancies adsorbed at neighbouring adsorption sites increases. It seems that at positive electrode charges the adsorption of ClO_4^- ions caused by electrostatic interactions increases. Then at the electrode surface there probably appears areas (patches) where many particles of the same type are adsorbed on neighbouring adsorption sites where water or TMTU molecule is adsorbed. Such conclusion confirms the change of nonrandomness parameter α_{1v}. Figure 5 shows, that in the region of zero electrode charge α_{1v} evidently increases and it means that the TMTU molecules are distributed at the electrode surface in more ordered (more nonrandom) way.

Summing up, it seems that the rapid changes of interaction energy between the adsorbed TMTU molecules (Figs 3 and 4) and the increase of the value of nonrandomness parameter α_{1v} (Fig. 5) can indicate a change of orientation of the adsorbed molecules. The possible change of the electron densities of the adsorbed species can also take place. Then, the electrode charge influence on the dipole moment of the adsorbed TMTU molecules.

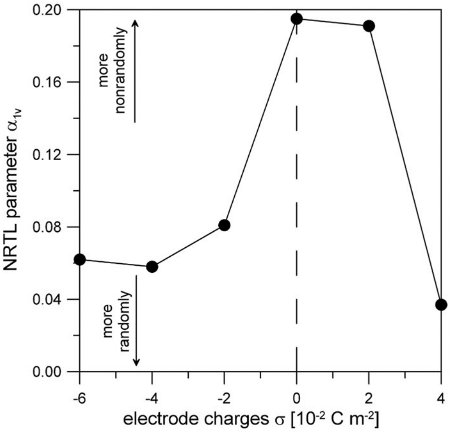

FIG. 5

The nonrandomness parameter α_{1v} determined using the N-FDH–NRTL isotherm (*16*) as the function of density charge

Gibbs Free Energy of Adsorption

The best-fit values collected in Tables I and II make it possible to calculate the Gibbs free energy of adsorption ΔG^0 as a function of charge density. Figure 6 shows that $-\Delta G^0$ calculated using both isotherms (*12*) and (*16*) increases with the increasing electrode charge and decreases jumpwise near $\sigma = 0$. The negative sign of the free energy of adsorption implies spontaneous adsorption and mainly electrostatic or chemical interactions between the dipole molecule TMTU and the electrode. It is due to the fact that the TMTU molecule can be bonded chemically with the mercury electrode by sulfur atom. As the values of $-\Delta G^0$ vary in the range 30–50 kJ mol^{-1}, it indicates the contribution of permanent dipole of TMTU to the free energy of adsorption. Only at zero electrode charge the adsorption forces bonding the TMTU molecules are of different from the electrostatic one. In the region of negative electrode charges $-\Delta G^0$ there is a quasi-linear function of σ. It is in agreement with the results obtained by Ikeda et al.[22].

The increase of the free energy of adsorption $-\Delta G^0$ in the region of negative electrode charges indicates the decrerase of the strength of electrostatic interactions between the TMTU and the electrode. The rapid decrease of the free energy $-\Delta G^0$ in the region where the electrode charge changes to positive can be explained again by the possibility of the reorientation of dipole TMTU molecules caused by the change of the sign of electrode charge. When the electrode charge is negative, the TMTU molecules bend and the

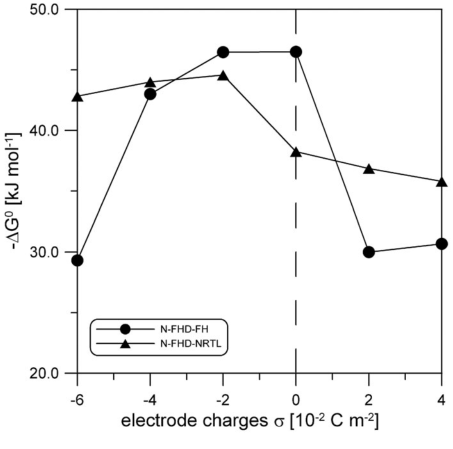

FIG. 6
The Gibbs energy of adsorption ΔG^0 calculated using the N-FHD–FH isotherm (*12*) and the N-FHD–NRTL isotherm (*16*) as the function of surface density

nitrogen atoms are close to the electrode surface. When the sign of the electrode charge changes to positive the dipole particles of TMTU change orientation and are bonded electrostatically with the electrode by sulfur molecules. It also seems also that with large positive or negative values of electrode charges there can appear a change of electron density in the TMTU molecules that is connected with the change of dipole moment.

CONCLUSIONS

The results of the theoretical analysis of TMTU adsorption at the dropping mercury electrode indicate the existence of rapid effects in the region of zero electrode charge. It has been shown that the adsorption isotherm equations can be expressed as the effect of entropic and thermal contributions. The application of the modified Flory–Huggins isotherm and two models of interactions between the adsorbed molecules results in two new adsorption isotherm equations. Both expressions applied to the experimental TMTU adsorption isotherms showed that the adsorbed molecules are largely specifically bonded. Such conclusions confirm the values of free energy of adsorption. Further, the best-fit parameters describing the strength of the energy of interactions between the adsorbed TMTU molecules suggest the existence of the orientation change of adsorbed species. The application of the NRTL equation confirms this conclusion – in the region of zero electrode charge the TMTU molecules are distributed onto the electrode surface in a more ordered (nonrandom) way. So, the simultaneous analysis of adsorption isotherms by two different models of adsorption gives more reliable results.

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