

THE MIXED ADSORPTION LAYERS OF BUTANOL/THIOUREA AND BUTANOL/TOLUIDINE AT THE INTERFACE Hg/AQUEOUS PERCHLORATE SOLUTION

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Properties of mixed, two-component adsorption layers of butanol/thiourea, butanol/*m*-toluidine and butanol/*p*-toluidine in 1 M NaClO₄ were investigated. The systems were characterized by the measurements of differential capacity, zero charge potential and surface tension at this potential. The data were analyzed to obtain the surface pressure and relative surface excess of thiourea, *m*-toluidine or *p*-toluidine as a function of charge and bulk concentration of these substances. The standard Gibbs energy of adsorption $\Delta\bar{G}^0$ and parameters *a*, *B* obtained from the Frumkin and virial isotherms were compared. The electrostatic parameters of the inner layer were determined.

Key words: Mixed adsorption; Mercury; Differential capacity; Surface tension.

The adsorption of neutral organic molecules from aqueous electrolyte solutions on metal electrodes primarily involves the inner layer of the metal/solution interface, and hence its study can provide significant information on the structure and intermolecular interactions in this layer.

Adsorption of molecules containing sulfur as well as of aromatic compounds on the mercury electrode in connected with a partial charge transfer, i.e. with formation of a very weak covalent bond. The group of compounds thiourea (TU), *m*-toluidine (mT) and *p*-toluidine (pT) was chosen for investigations. These substances accelerate electroreduction of Zn(II) ions on the mercury electrode^{1,2} but on the other hand butanol (BU) is a typical inhibitor of this reaction³. The different effect of these substances on reduction of Zn(II) ions has decided about their choice for studies of the mixed adsorption layers on mercury. This paper is a continuation of the earlier investigations^{4,5} and includes a thermodynamic description of the mixed adsorption layers studied in 1 M NaClO₄.

The adsorption behaviour will be discussed in terms of the inner potential distribution and the adsorption isotherm constants resulting from the surface pressure data as a function of electrode charge density and bulk concentration of the studied substances.

EXPERIMENTAL

Analytical grade reagents thiourea, butanol, *m*-toluidine and *p*-toluidine (Merck) were used without further purification. High-purity sodium perchlorate (Merck) was used as a background electrolyte. Water and mercury were triply distilled. Solutions were deaerated using nitrogen passed through vanadous sulfate solution.

A three-electrode cell, containing a dropping mercury electrode (DME) with a drawn-out capillary as a working electrode, a saturated calomel electrode (SCE) with sodium chloride and a platinum spiral were used, as the reference and the counter electrodes, respectively. The reference electrode was connected to the cell via a salt bridge filled with the cell solution. Height of the mercury column was 0.70 m. The flow rate of mercury was determined by weighing the mercury collected during a given time.

The measurements were carried out at 25 ± 0.1 °C.

The differential capacity was measured using a computer acquisition unit with EIM-2 impedance meter manufactured at the Lodz University. Measurements were carried out at 800 Hz. The reproducibility of the average capacity measurements was $\pm 1\%$ over the studied range of potentials. Some measurements were carried out at 275–1 990 in order to check the frequency dependence. In the potential range studied no dispersion of the capacitance was observed. The potential of zero charge E_z was measured using the streaming mercury electrode^{6,7}. Interfacial tension at E_z was measured by the maximum bubble pressure method according to Schiffrin⁸.

RESULTS AND DISCUSSION

Analysis of Experimental Data

Differential capacity curves were measured for TU concentrations from 0.0055 to 0.55 mol l⁻¹ and for mT or pT concentrations from 0.0015 to 0.05 mol l⁻¹ at selected constant concentration of BU (0.44, 0.55 or 0.88 mol l⁻¹). Figure 1 presents the values of E_z as a function of logarithm of concentration of TU, mT and pT in 1 M NaClO₄ without and with the addition of BU.

An increase of TU concentration causes the shift of E_z values towards negative potentials. A similar shift is observed in the presence of BU, however, the dependence on $\log c$ is not linear. This fact confirms an adsorption of TU molecules on mercury with the negative and i.e. the sulfur atom. Significantly smaller changes of E_z values towards positive potentials are observed in 1 M NaClO₄ when the concentration of mT and pT increases which also holds for BU. Contrary to the common belief presented in literature⁹ that the aromatic compounds shift E_z values towards negative potentials it was found that in the electrolyte with a weak adsorption of ClO₄⁻ anion, E_z potentials shift towards positive values. However, in the presence of BU, E_z potentials shift towards negative values with the concentration increase of mT or pT. A similar behaviour of toluidine was observed by Joshi et al.¹⁰ who studied adsorption of toluidine in 0.1 M KI. This fact can be explained by a mixed adsorption layer formation. It should be noted that the dependence of E_z values on logarithm of mT and pT concentrations are linear. At the same time the plots are parallel. This effect is due to the co-adsorption of BU

and toluidine which may cause mutual reorientation of the molecules of these substances in the adsorption layer.

The capacity against potential data were numerically integrated from the point of E_z . The values of integration constants were presented earlier^{4,5}. The data obtained from the integration of differential capacity curves were then used to calculate Parsons' auxiliary function $\xi = \gamma + \sigma E$ and the surface pressure $\Phi = \Delta\xi = \xi^0 - \xi$ where ξ^0 represents the mean value for supporting electrolyte with the determined constant concentration of BU without TU or toluidine^{11,12}.

According to the Gibbs adsorption isotherm, the relative surface excess of TU, mT or pT is given by

$$\Gamma'_A = \frac{1}{RT} \left(\frac{\partial \Phi}{\partial \ln c_A} \right)_{\sigma, c_{\text{BU}}} \quad (1)$$

where the subscript A means TU, mT or pT. In Eq. (1) it is assumed that the mean activity coefficients of individual solution components do not change with the increase of TU, mT or pT concentration. The estimated error of these calculations is approximately 10 times higher than that of the capacity data which is ranging from ± 2 to $\pm 5\%$.

Figure 2 shows the characteristic plots of Φ vs $\log c_A$ for the mixture at constant concentration of 0.55 M BU and $\sigma_M = 0$. The variations of the relative surface excess Γ'_A for TU, mT or pT at $\sigma_M = 0$ in the same solutions as a function of the bulk concentration of TU, mT or pT are shown in Fig. 3. As can be seen in this figure, the adsorption of toluidine isomers is stronger compared with TU at the same concentration of BU

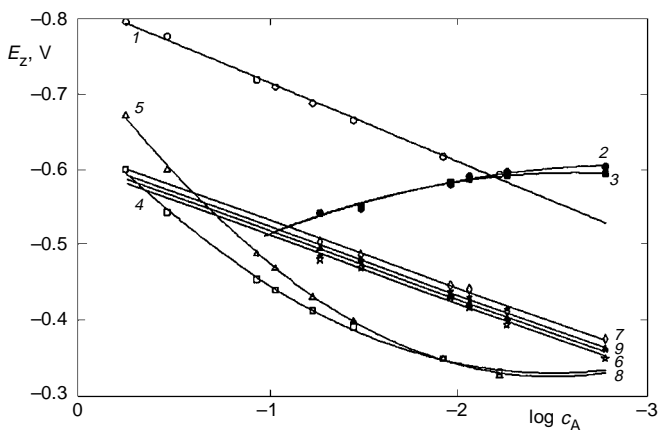


FIG. 1

Dependence of potential of zero charge E_z on concentration of TU (1), mT (2), pT in 1 M NaClO₄ (3), TU + 0.88 M BU (4), TU + 0.55 M BU (5), mT + 0.55 M BU (6), mT + 0.44 M BU (7), pT + 0.55 M BU (8), pT + 0.44 M BU in 1 M NaClO₄ (9)

and at much lower concentration of toluidine compared with TU. Flat orientation of aliphatic alcohols on the electrode surface¹³ is justified, particularly in the case of BU, by the distribution of electron density on carbon atoms. The highest electron density is found in a BU molecule on the first and third carbon atoms possessing some hydrophilicity, they are oriented to the solution, along with the oxygen atom¹⁴. The difference in adsorption of TU and toluidine isomers on such preliminary covered electrode surface is undoubtedly due to the different affinity of toluidine aromatic ring and TU sulfur atom to mercury. In turn, higher values of Γ'_A obtained for mT compared with pT result

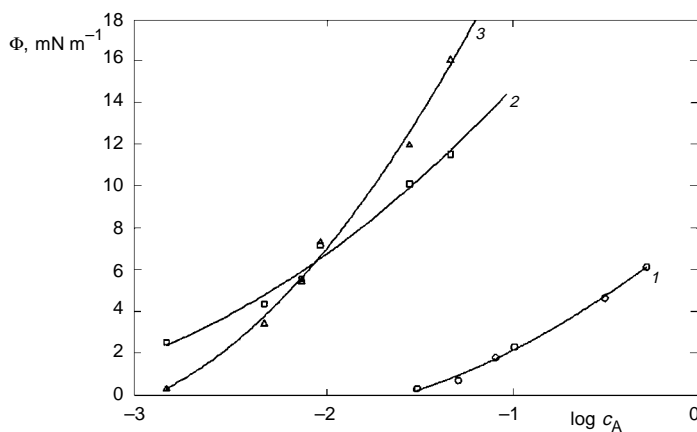


FIG. 2

Surface pressure as a function of concentration in bulk of TU (1), pT (2), mT (3) in 1 M NaClO_4 + 0.55 M BU at $\sigma_M = 0$

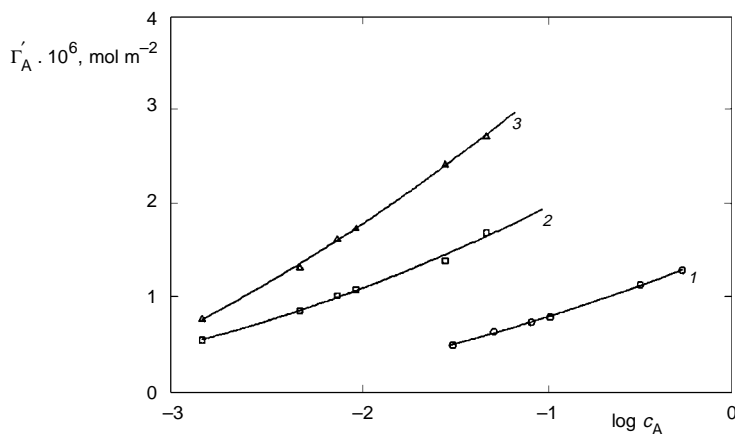


FIG. 3

Relative surface excess of TU (1), pT (2), mT (3) as a function of bulk concentration of these substances in 1 M NaClO_4 + 0.55 M BU at $\sigma_M = 0$

from the arrangements of the hydrophilic group $-\text{NH}_2$ in relation to the hydrophobic group $-\text{CH}_3$ in the ring. Stronger adsorption of mT compared with pT is confirmed by the adsorption studies in KCl solution¹⁰. These different adsorption properties of mT compared with pT and TU are confirmed by the values of Γ'_A in 0.44 and 0.55 mol l⁻¹ solutions and additionally for TU in 0.88 M BU. Adsorption of pT and TU increases with rising BU concentration but adsorption of mT practically does not depend on BU concentration.

Adsorption Isotherms

To illustrate the possible changes of the isotherm parameters with the electrode charge, the linear test of the Frumkin isotherm was applied. The surface excess at saturation Γ_s was estimated by extrapolation of the $1/\Gamma'_A$ vs $1/c_A$ plot to $1/c_A = 0$ at different charges and different values of c_{BU} .

The values of Γ_s obtained for TU in 0.55 and 0.88 M BU differ insignificantly being $5 \cdot 10^{-6}$ and $4.54 \cdot 10^{-6}$ mol m⁻², respectively.

The values $S \equiv (1/\Gamma_s)$ describing the surface occupied by TU molecule are 0.33 and 0.37 nm², respectively, i.e. slightly larger than the area 0.29 nm² calculated from the molecular dimensions of TU molecule^{15,16}. The values Γ_s obtained in the 0.44 and 0.55 M BU solutions for mT and pT differ insignificantly and are $4.17 \cdot 10^{-6}$ and $3.57 \cdot 10^{-6}$ mol m⁻², respectively. These values are much lower compared with Γ_s obtained from an estimate of cross-sectional area of the molecules based on the knowledge of bond angles and bond lengths¹⁰. The values Γ_s obtained in this way for mT and pT are $9.4 \cdot 10^{-6}$ and $9.7 \cdot 10^{-6}$ mol m⁻², respectively. The discrepancy between calculated and experimental values of Γ_s can be ascribed to the presence of the BU molecules and residual water molecules in the adsorbed film at the maximum coverage^{13,17}.

Figure 4 presents the linear test of the Frumkin isotherm for TU and mT in the presence of 0.55 M BU. As follows from the figure, the values of parameter a change significantly depending on the charge only in the case of TU. For mT the value a 1.53 remains constant. A similar situation is with pT but the value of a is 3.1. In the presence of 0.44 M BU the values of a for mT and pT are smaller and depend on the electrode charge to some extent. Figure 5 presents the change of parameter a depending on the electrode charge for TU in the presence of 0.55 and 0.88 M BU. As follows from the figure the influence of BU concentration on the parameter a is significant. However, the repulsion between thiourea molecules decreases with the increase of the electrode charge in both cases. Probably the latter effect is connected both with the increase of the amount of ClO_4^- anions occupying the positions adjacent to the positive end of the TU dipoles and with the presence of BU molecules.

The maximum change of parameter a in Fig. 5 is the same in both cases which can be taken as an evidence for a similar change in orientation of TU molecules. In the case

of toluidine isomers, however, the molecular orientation is constant in the studied range of electrode charge.

Figure 6 shows the plots of the standard Gibbs energy of adsorption at zero coverage $\Delta\bar{G}^0$ against σ_M . The value of $\Delta\bar{G}^0$ was determined from the extrapolation of the linear plot $\ln [(1 - \theta)x/\theta]$ vs θ for $\theta = 0$.

Much higher values of $\Delta\bar{G}^0$, up to over 20 kJ mol⁻¹ for toluidine isomers compared with TU indicate stronger interactions of mT and pT with the mercury surface than that of TU molecules. The linear dependence of $\Delta\bar{G}^0$ on σ_M for mT and pT suggests that a chemical interaction takes place via the π -electron system of the aromatic ring with partial charge transfer to the metal^{18,19}. The lack of linearity in the dependence of $\Delta\bar{G}^0$ on σ_M for TU for the whole concentration range is surprising. However, this behavior

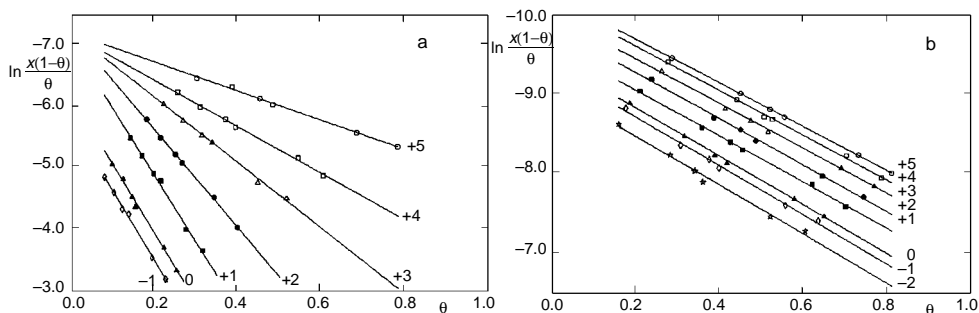


FIG. 4

Linear test of the Frumkin isotherm for TU (a) and mT (b) in presence of 0.55 M BU, the electrode charges σ_M (in 10^{-2} C m^{-2}) indicated by each line

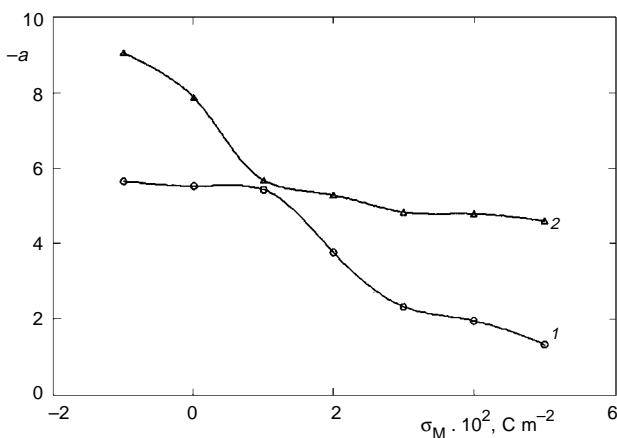


FIG. 5

Variation of the interaction parameter a due to the surface charge density for TU in presence of 0.55 M BU (1) and 0.88 M BU (2)

is typical for TU (refs^{11,20}) in the range of positive charges. A sudden decrease of $\Delta\bar{G}^0$ values for TU in proximity of E_z confirms more physical interactions of TU molecules with the electrode surface compared with the adsorption at positive charges. It should be emphasized that the increase of BU concentration is accompanied by the increase of $\Delta\bar{G}^0$ for all the systems studied in this work. This effect contrasts with the results presented earlier²¹ on the adsorption properties of TU in presence of polyethylene glycols. The facilitated adsorption of the studied substances in presence of higher BU concentration is probably connected with higher order of arrangement of the molecules adsorbed on the electrode surface.

As Γ_s values for the studied substances differ from the theoretical values, the virial isotherm was used for the description of TU, mT and pT adsorption. Figure 7 shows the linearity test of the virial isotherm for TU and mT in presence of 0.55 M BU. Values of two-dimensional second virial coefficient B calculated from the slopes of lines in Fig. 7 and the corresponding $\Delta\bar{G}^0$ values obtained from their intercepts²² are listed in Table I.

The values of the virial coefficient B for toluidine do not depend on the electrode charge and are 0.78 for mT + 0.44 M BU, 0.92 for mT + 0.55 M BU, 0.80 for pT + 0.44 M BU and 1.60 nm² per 1 molecule for pT + 0.55 M BU. The presented values of $\Delta\bar{G}^0$ and B are in an agreement with the results obtained from the Frumkin isotherm. The $\Delta\bar{G}^0$ for TU in presence of 0.55 M BU at E_z are somewhat lower than the values yielded in water ($\Delta\bar{G}^0 = 95.7$ kJ mol⁻¹ ref.²³) and slightly higher than values in water-ethanol and water-methanol mixtures^{24,25}. The virial coefficient B for TU at E_z is higher than for water ($B = 1.2$ nm² per 1 molecule, ref.¹¹). It indicates an effect of BU molecules on the interaction of adsorbed TU molecules.

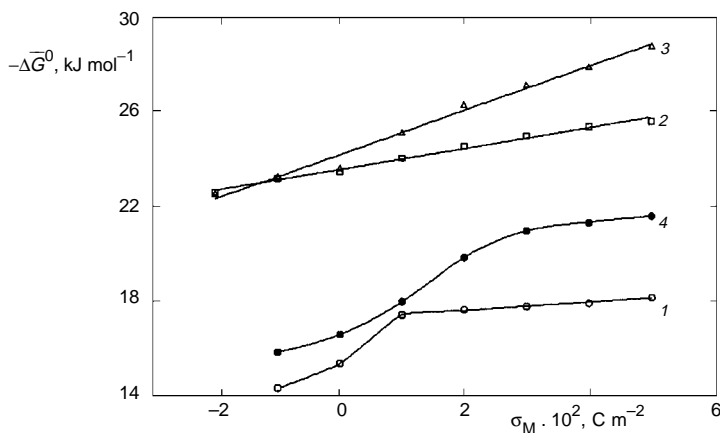


FIG. 6

Variations of the $-\Delta\bar{G}^0$ vs surface charge density for TU (1), mT (2), pT (3) in presence of 0.55 M BU and for TU (4) in presence of 0.88 M BU

Electrostatic Parameters of the Inner Layer

The change in potential drop across the electrode–solution interface is usually split into contributions from free charges and from oriented dipoles. In principle, no separation between the two effects is experimentally possible²⁶. As evidenced previously by Parsons¹⁰ the potential drop across the inner region Φ^{M-2} may be represented as a sum of the two terms depending upon σ_M and Γ'_A , respectively, and expressed as

$$\Phi^{M-2} = \frac{4\pi x_2}{\epsilon_i} \sigma_M + \frac{4\pi\mu_A}{\epsilon_i} \Gamma'_A, \quad (2)$$

TABLE I

Comparison of the virial isotherm constants for BU in systems containing mT, pT or TU. Concentration of BU in mol l⁻¹, ΔG in kJ mol⁻¹, B in nm² per molecule

$\sigma_M \cdot 10^{-2}$ C m ⁻²	0.44 BU	0.55 BU	0.44 BU	0.55 BU	0.55 BU + TU		0.88 BU + TU	
	+ mT	+ mT	+ pT	+ pT	$-\Delta G$	B	$-\Delta G$	B
+5	102.8	104.1	102.8	106.8	96.7	0.58	99.9	1.62
+4	102.5	103.9	102.2	106.1	96.7	0.79	99.7	1.73
+3	101.9	103.6	101.5	105.6	96.6	0.98	99.6	1.81
+2	101.7	103.1	100.9	104.5	96.5	1.33	98.2	1.87
+1	101.5	102.6	100.6	103.3	95.9	1.81	96.3	2.16
0	100.7	101.9	100.0	101.9	93.8	1.81	94.7	2.56
-1	99.9	101.1	99.4	101.2	92.7	1.81	94.2	2.96

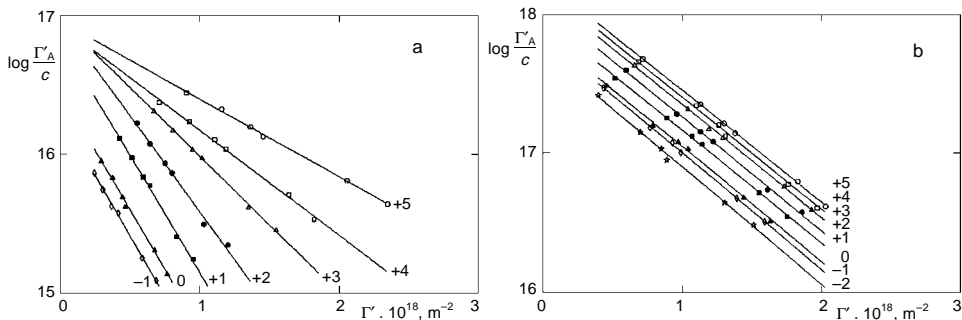


FIG. 7

Linearity test of the virial isotherms for TU (a) and mT (b) in presence of 0.55 M BU, the electrode charges σ_M (in 10⁻² C m⁻²) indicated by each line

where μ_A is the dipole moment of an isolated molecule of TU ($\mu = 16.31 \cdot 10^{-30}$ C m), mT ($\mu = 4.76 \cdot 10^{-30}$ C m, ref.²⁷) and pT ($\mu = 4.43 \cdot 10^{-30}$ C m, ref.²⁸). The apparent dielectric constant and the thickness of the inner region are represented by ϵ_i and x_2 , respectively. The value of $\Phi^{M-2} = E - E_z - \Phi^{2-s}$, where E and E_z are the potential and the potential of zero charge, respectively, measured in the absence of TU, mT or pT for the determined BU concentration.

The potential drop across the diffusion layer Φ^{2-s} can be calculated using the Gouy–Chapman theory²⁹. Following the analysis made by Parsons for similar systems in water^{11,23}, the electrostatic parameters of the inner layer ϵ_i , x_2 , and the integral capacity K_i were calculated for the studied mixtures and the constant quantity of adsorbed TU, mT or pT.

Figure 8 shows the dependence of Φ^{M-2} vs Γ'_A at constant σ_M for TU and mT in the presence of 0.55 M BU. This dependence is linear to the first approximation, similar to other systems containing TU (refs^{11,15,24}). The linear relationship of Φ^{M-2} vs Γ'_A obtained at each charge represents congruence with respect to the charge³⁰.

The values of ϵ_i for TU at E_z are about 3.3 lower than for water³¹, and also lower than for methanol³². However, the values ϵ_i for mT and pT are close to those obtained for TU in methanol.

The values of the integral capacity K_i at E_z in all systems are close to 30.6 obtained for TU in water¹¹. The values of 0.1–0.24 nm calculated for the thickness of the inner layer x_2 are low compared to the model¹¹. According to Fawcett³ the differences between the dipole moments can have various reasons such as the polarization of thiourea molecules at the charged electrode, orientation of solvent dipoles and TU molecules, the change of TU dipole moment and the chemical interactions of sulfur in TU molecule with mercury.

The decrease of x_2 value in the case of toluidine molecules is caused by the same factors. Therefore the analysis of electrostatic parameters of the inner layer can be treated as the first approximation.

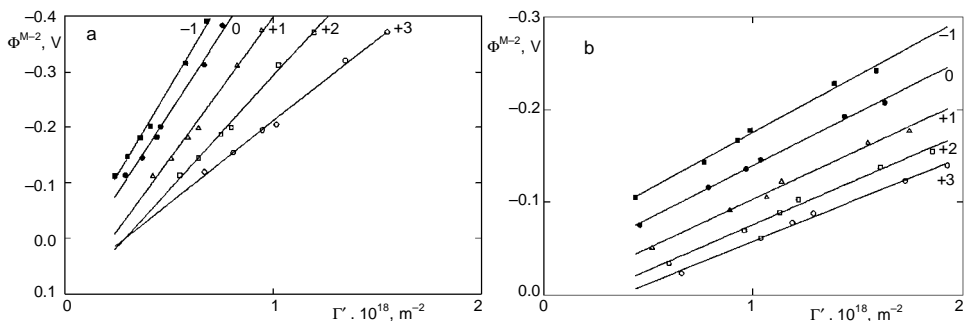


FIG. 8

Potential drop across the inner layer Φ^{M-2} as a function of Γ'_A for TU (a) and mT (b) in presence of 0.55 M BU, the electrode charges σ_M (in 10^{-2} C m^{-2}) indicated by each line

CONCLUSIONS

In the mixed adsorption layers, the effect of adsorbate can be studied by means of E_z , Γ'_A , a , $\Delta\bar{G}^0$ and electrostatic parameters. In the mixed adsorption layers in presence of BU, the molecules of TU, mT and pT are oriented with the negative end towards mercury electrode surface. Congruence of adsorption isotherms in relation to the charge for all the studied systems was observed. The discrepancy between the experimental and calculated values of Γ_s is caused by co-adsorption of the studied substances.

The differences were found between the adsorption properties of toluidine and TU molecules in solutions containing BU.

Higher values of Γ'_A were obtained for mT and pT. Parameter a in the Frumkin isotherm and parameter B in the virial isotherm have constant values in relation to the electrode charge or toluidine isomers. It confirms the stability of their molecular orientation on the electrode surface. In case of TU a significant change of these parameters was observed.

Higher values of $\Delta\bar{G}^0$ were obtained for both isotherms for mT and pT compared with TU. It gives us an evidence of stronger chemical interaction between the toluidine aromatic ring and the mercury surface compared with that of sulfur in TU molecule.

The values of the electrostatic parameters of the inner layer calculated on the basis of a simple electrostatic model of inner potential distribution are not correct in all cases indicating that a simple electrostatic model is not fully applicable to the description of the systems studied in this work.

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