

STUDIES OF A MIXED ADSORPTION LAYER OF BUTAN-1-OL AND *o*-TOLUIDINE ON MERCURY ELECTRODE

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The results of thermodynamic analysis of *o*-toluidine adsorption on a mercury electrode in the presence of various butan-1-ol amounts complete our previous studies on properties of mixed adsorption layers of toluidine isomers–butan-1-ol. The values of the relative surface excess Γ'_{or} obtained for *o*-toluidine show that adsorption of this compound decreases with increasing of butan-1-ol concentration. Analysis of adsorption parameters derived from the Frumkin isotherm indicates that in the presence of 0.33 M BuOH in 1 M NaClO₄ with adjusted pH 3 as supporting electrolyte, ΔG^0 values for *o*-toluidine are the highest and, at the same time, the strongest repulsive interaction occurs. In the presence of 0.11 M butan-1-ol, smaller values of ΔG^0 for *o*-toluidine correspond to weaker repulsive interaction. Therefore the change of the Γ'_{or} value for *o*-toluidine as a function of butan-1-ol concentration is the result of mutual changes of ΔG^0 and interaction constant *A* between adsorbate molecules.

Keywords: Adsorption isotherm; Surface pressure; Surface charge density; Thermodynamics; Alcohols; Butanol; Toluidine.

Experimental studies carried out in our laboratory have resulted in rich materials concerning the influence of mixed adsorption layers containing two organic substances on the rate of electrode processes. It was found that in solutions containing a suitable inhibitor and a substance accelerating Zn²⁺ electroreduction, *e.g.* butan-1-ol and thiourea¹, butan-1-ol and *m*-toluidine, and butan-1-ol and *p*-toluidine², inhibition, acceleration or compensation of these effects take place upon changing the relative concentration of these substances. Studies concerning butan-1-ol (BuOH) adsorption show a flat orientation of the BuOH molecule at the maximum electrode coverage in an aqueous solution of Na₂SO₄³ while perpendicular orientation takes place in 0.1 M NaF solution⁴. An inhibiting effect of butan-1-ol on metal ion reduction on mercury is commonly known; thiourea, *m*-toluidine and *p*-toluidine accelerate the Zn²⁺ reduction^{5–8}.

Capacitance and electrocapillary data for *o*- and *p*-toluidines in Na_2SO_4 and H_2SO_4 solutions have been reported by Damaskin *et al.*⁹ They observed a change in orientation of the adsorbed molecule upon changing the charge of mercury. Differential capacity curves of toluidine isomers differ slightly but Joshi *et al.*¹⁰ and Mahajan¹¹ showed quantitative differences in adsorption of these isomers. In 0.01 M KI and KClO_4 , their adsorption increases in the order of $p < o < m$ -toluidine. A larger adsorption for the same concentration of the adsorbate at the same charge value is observed for KClO_4 than for KI. This paper is a continuation of the earlier investigations^{2,12} of mixed adsorption layers: butan-1-ol and *p*-toluidine, and butan-1-ol and *m*-toluidine. The adsorption behavior for the system butan-1-ol and *o*-toluidine (*oT*) will be discussed in terms of the adsorption isotherm constants resulting from the surface pressure data as a function of electrode charge density and the bulk concentration of studied substances. Adsorption parameters, interaction constant *A* and standard Gibbs energy of adsorption for *oT* on mercury electrode in 1 M NaClO_4 solution are presented. The data are complementary to those presented in literature and allow us to explain the behavior of toluidine isomers in the presence of butan-1-ol.

EXPERIMENTAL

Measurements were carried out using a three-electrode cell containing a static drop mercury electrode (SMDE) of the area 0.017 cm^2 (Electronics Industry MTM, Cracow, Poland), platinum cylinder electrode of the area *ca* 2 cm^2 as a counter and Ag/AgCl with saturated NaCl solution as a reference electrode. The reference electrode was connected to the electrolytic cell *via* a bridge filled with the investigated solution. Measurements were taken at 25 ± 0.1 °C. The solutions were prepared from freshly twice-distilled water and analytical grade chemicals (Merck, Darmstadt, Germany). All solutions were deoxygenated by high-purity nitrogen. The double layer capacity was measured using the ac impedance technique at a frequency of 800 Hz with a 9121 Frequency Response Analyzer and 9131 electrochemical interface using an appropriate program (Electronic System Plants, Atlas-Sollich, Gdańsk, Poland). The capacitance was measured with an accuracy of $\pm 1\%$. A few measurements were also carried out in the frequency range 200–2 000 Hz to check the frequency dependence of the results. In the potential range studied, no dispersion of the capacitance was observed. The potential of zero charge E_z was measured for each solution with an accuracy of ± 0.2 mV using the streaming mercury electrode. The interfacial tension at the E_z was measured by the maximum bubble pressure following Schiffrin's method. Measurements were carried out in 1 M NaClO_4 solution of pH 3 adjusted with HClO_4 in the BuOH concentration range from 0.11 to 0.55 mol l^{-1} and that of *oT* from 0.0015 to 0.05 mol l^{-1} as well as with their mixtures. The choice of the *oT* maximum concentration 0.05 mol l^{-1} was given by its solubility.

RESULTS AND DISCUSSION

Analysis of the Experimental Data

On the curves of differential capacity obtained for different *o*T concentrations in 1 M NaClO₄ a well-defined desorption peak is observed. Its potential is shifted from -0.70 to -1.25 V with rising *o*T concentration (Fig. 1). For less negative potentials, a significant drop in differential capacity is observed. For the maximum *o*T concentration 0.05 mol l⁻¹ this drop was found in the potential range from -0.25 to -1.10 V. In the case of BuOH adsorption, a significant decrease in the differential capacity takes place in a wider potential range compared with the supporting electrolyte. The range increases with an increase of BuOH concentration. On these curves, well-defined desorption peak appears with the peak potential shifted from -1.00 to -1.25 V with an increasing BuOH concentration. Figure 2 presents the differential capacity curves of a mixture of 0.11 M BuOH with addition of various amounts of *o*T. Introduction of *o*T into the 0.11 M BuOH solution resulted in higher differential capacity in the potential range from -0.30 to -0.70 V as well as in a number of potentials of desorption peaks. A similar effect occurs in solutions containing 0.33 and 0.55 M BuOH. With the increase of *o*T concentration, the height of desorption peaks distinctly increases. The greatest increase in desorption peak as well as the largest change in its potential occur in the presence of 0.11 M BuOH. For the maxi-

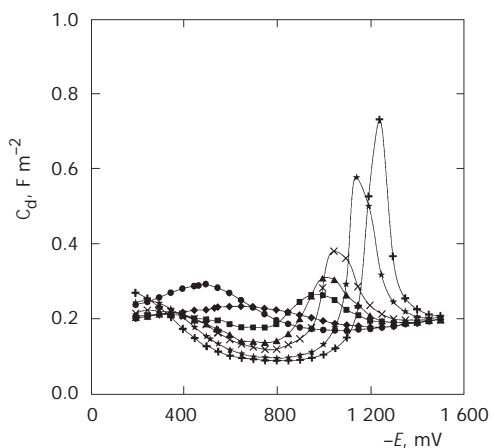


FIG. 1

Differential capacity curves of Hg/1 M NaClO₄ with various concentrations of *o*-toluidine in mol l⁻¹: 0 (●), 0.0015 (◆), 0.005 (■), 0.008 (▲), 0.01 (×), 0.03 (★), 0.05 (✦)

imum *o*T concentration of 0.05 mol l^{-1} , the potential of desorption peak remains virtually independent on BuOH concentration and remains constant in the solution without BuOH. This can suggest *o*T domination in the formation of balanced mixed BuOH-*o*T adsorption layer. Table I presents the values of zero charge potentials E_z for solutions containing *o*T, BuOH, and their mixtures. An increase of BuOH concentration causes a significant shift

TABLE I
Potential of zero charge $-E_z$, V vs Ag/AgCl for *o*-toluidine, butan-1-ol and their mixtures

c_{oT} , mol l^{-1}	c_{BuOH} , mol l^{-1}			
	0	0.11	0.33	0.55
0.00	0.469	0.327	0.253	0.227
0.0015	0.536	0.435	0.341	0.296
0.005	0.548	0.462	0.404	0.354
0.008	0.548	0.476	0.421	0.384
0.010	0.544	0.485	0.429	0.393
0.030	0.516	0.486	0.466	0.447
0.050	0.501	0.482	0.477	0.449

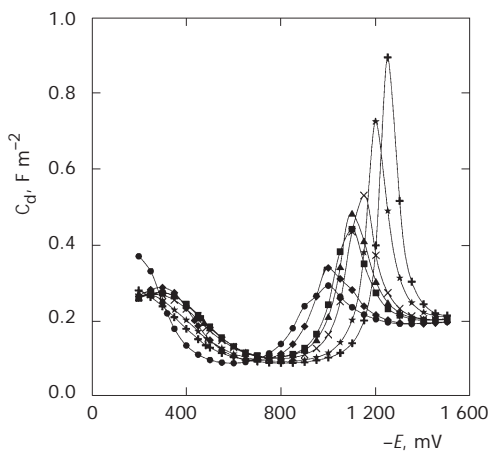


FIG. 2

Differential capacity curves of Hg/1 M NaClO_4 -0.11 M BuOH with various concentrations of *o*-toluidine as indicated in Fig. 1

of E_z towards positive potentials. An addition of *o*T into 1 M NaClO₄ causes at first a distinct shift of E_z towards negative potentials. Further increase of *o*T concentration is accompanied by a shift of E_z towards positive potentials. The changes of E_z values in this case are much smaller than those for BuOH. In a mixture containing a constant amount of *o*T, a small shift of E_z with rising concentration of BuOH is observed. The shift decreases further for higher *o*T contents. This may indicate a predominant influence of *o*T on the formation of a mixed adsorption layer, despite the fact that its concentration is much lower compared with that of BuOH. At low *o*T concentrations, the π -systems of *o*T lie flat on the metal surface. An increase in the adsorbate amount led to a negative shift of the point of zero charge. At higher concentrations, a positive E_z shift indicates a skew position of the *o*T molecules. This is also true for the mixture 0.11 M BuOH–0.05 M *o*T.

Table II presents the values of surface tension γ at E_z for *o*T and BuOH solutions and for their mixtures. Predominant role of *o*T in formation of mixed adsorption layer is shown at maximum *o*T concentration of 0.05 mol l⁻¹, when the increase of BuOH concentration causes only a slight decrease in the γ value. This relation confirms the above observation concerning potentials of desorption peaks in these systems.

The capacity vs the potential data were numerically integrated starting from the point of E_z . The integration constants are presented in Tables I and II. The data obtained from the integration of differential capacity plots were then used to calculate Parsons auxiliary function¹³ $\xi = \gamma + \sigma E$ (where

TABLE II
Surface tension γ , mN m⁻¹ at E_z of *o*-toluidine, butan-1-ol and their mixtures

c_{oT} , mol l ⁻¹	c_{BuOH} , mol l ⁻¹			
	0	0.11	0.33	0.55
0.00	422.4	411.5	398.7	393.6
0.0015	419.2	411.3	398.2	392.3
0.005	416.0	410.6	395.5	390.4
0.008	408.9	405.1	391.7	387.2
0.010	406.4	400.0	389.1	386.2
0.030	401.3	392.3	385.3	384.0
0.050	385.9	385.9	380.2	379.5

σ is the electrode charge, E is the electrode potential) and the surface pressure¹⁴ $\Phi = \Delta\xi = \xi^0 - \xi$ (ξ^0 represents average values of 1 M NaClO₄ or 1 M NaClO₄ with the determined constant concentration of BuOH without oT, ξ is the same but with addition of oT).

Figure 3 shows characteristic plots of Φ vs $\ln c_{oT}$ for 1 M NaClO₄ and 1 M NaClO₄-0.11 M BuOH. According to the Gibbs adsorption isotherm, the relative surface excess of oT is given by

$$\Gamma'_{oT} = -\frac{1}{RT} \left(\frac{\partial \Phi}{\partial \ln c_{oT}} \right)_{\sigma, c_{BuOH}}, \quad (1)$$

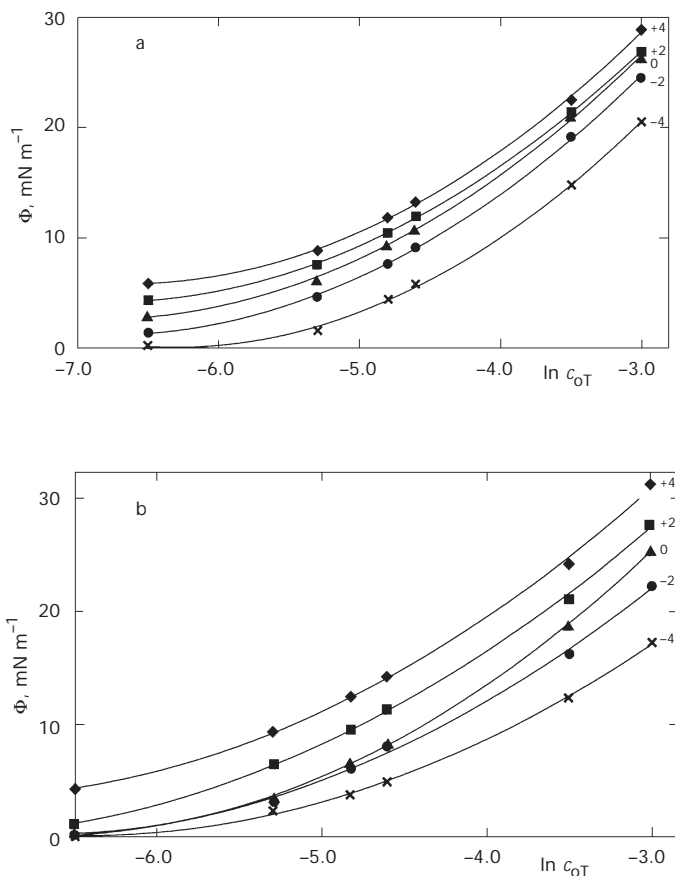


FIG. 3

Surface pressure as a function of *o*-toluidine concentration in the bulk: 1 M NaClO₄ (a), 1 M NaClO₄-0.11 M BuOH (b). The electrode charges (σ_M , 10^{-2} C m⁻²) are indicated for each curve

where c_{oT} is the bulk concentration of *o*T. The estimated error in these calculations is from ± 2 to $\pm 5\%$.

The obtained values of Γ'_{oT} at E_z (Fig. 4) indicate that the adsorption of *o*T in 1 M NaClO₄ is similar to that in the presence of 0.11 M BuOH, whereas Γ'_{oT} values decrease with the increasing BuOH concentrations. The most significant differences occur for the maximum *o*T concentration.

Adsorption Isotherm

The adsorption of *o*T was further analyzed on the basis of the relative surface excess data using the Frumkin isotherm. The constants of the Frumkin isotherm were determined from Eq. (2), where x is the mole fraction of *o*T, Θ is the coverage, A is the interaction constant, and β is the adsorption coefficient $\beta = \exp(-\Delta G^0/RT)$.

$$\beta x = [\Theta / (1 - \Theta)] \exp(-2A\Theta) \quad (2)$$

The surface excess at saturation $\Gamma_s = 9.4 \cdot 10^{-6} \text{ mol m}^{-2}$ (ref.¹⁰) was obtained from estimated cross-sectional area of the molecules based on the knowledge of bond angles and bond lengths.

Figure 5 presents the linear test of the Frumkin isotherm for *o*T in 1 M NaClO₄ and in 1 M NaClO₄-0.11 M BuOH. As follows from the figure,

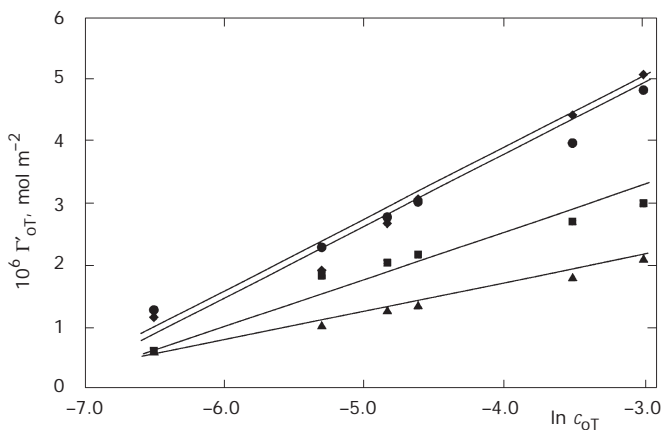


FIG. 4

Relative surface excess of *o*-toluidine in solutions: 1 M NaClO₄ (●), 1 M NaClO₄-0.11 M BuOH (◆), 1 M NaClO₄-0.33 M BuOH (■), 1 M NaClO₄-0.55 M BuOH (▲) as a function of bulk concentration of *o*-toluidine at $\sigma_M = 0 \text{ C m}^{-2}$

the value of the interaction constant A is practically independent of the electrode charge. A similar situation exists in other systems tested containing 0.33 or 0.55 M BuOH. Table III presents the values of parameter A and of standard Gibbs energy of adsorption at zero coverage ΔG^0 against σ_M . The value of ΔG^0 was determined from the extrapolation of the linear plot $\ln [(1 - \Theta)x/\Theta]$ vs Θ to $\Theta = 0$.

The negative values of interaction coefficient A show repulsive effect between adsorbed oT molecules. In all the systems tested we observed virtually no dependence of A values on the electrode potential, which can suggest constant molecular orientation in the studied range of the electrode

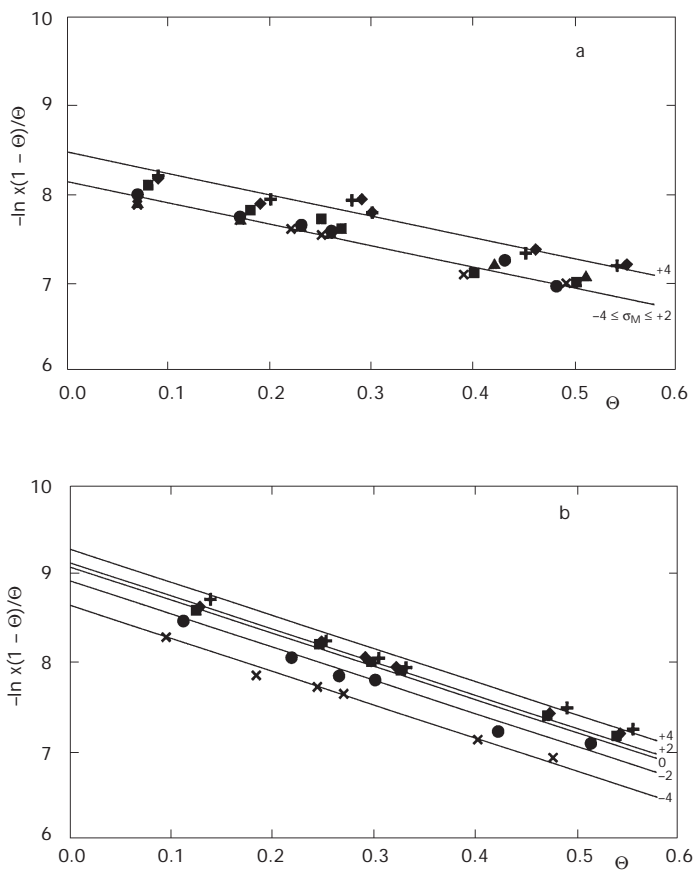


FIG. 5

Linearity test of the Frumkin isotherm: 1 M NaClO₄ (a), 1 M NaClO₄-0.11 M BuOH (b). The electrode charges (σ_M , 10^{-2} C m^{-2}) are indicated for each line

charge. However, the value of A depends on the presence of BuOH. In solutions containing 0.33 and 0.55 M BuOH the repulsive interaction between adsorbed molecules of *o*T is the strongest whereas the weakest interaction occurs in solution without BuOH.

The values of ΔG^0 obtained in 1 M NaClO₄ differ slightly from values obtained in 0.55 M BuOH solution. If the values of Γ'_{oT} for these systems are compared, a significant influence of repulsive interaction between adsorbed *o*T molecules is observed resulting in a decrease in their surface concentration. In solution containing 0.11 M BuOH, the values of Γ'_{oT} are comparable with those obtained in 1 M NaClO₄ solution, which can be associated with a simultaneous increase in A and ΔG^0 . A significant decrease in Γ'_{oT} in the presence of 0.33 M BuOH is a consequence of a continuous increase in ΔG^0 and A values. Comparing the *o*T adsorption in 1 M NaClO₄ with adsorption of *m*-toluidine and *p*-toluidine¹² the following conclusion can be stated: The greater surface excess of *o*T is followed by smaller ΔG^0 and a significantly smaller repulsive interaction.

The studies presented in this paper show clearly that parameter A contributes to surface concentration of *o*T in the presence as well as in absence of BuOH.

TABLE III

Comparison of the Frumkin isotherm constants for *o*-toluidine adsorption. Variable is σ_M , 10² C m⁻²; ΔG^0 , kJmol⁻¹

σ_M	1 M NaClO ₄		0.11 M BuOH		0.33 M BuOH		0.55 M BuOH	
	$-\Delta G^0$	$-A$	$-\Delta G^0$	$-A$	$-\Delta G^0$	$-A$	$-\Delta G^0$	$-A$
-4	20.19	1.05	21.35	1.75	23.08	7.00	19.34	6.85
-2	20.19	1.05	21.90	1.75	25.31	7.10	19.69	6.45
0	20.19	1.05	22.32	1.75	26.28	6.85	22.02	6.25
+2	20.19	1.05	22.42	1.70	26.55	6.85	-	-
+4	20.78	1.10	22.56	1.70	-	-	-	-

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