

## Adsorption of Thiourea on Monocrystalline Silver Electrodes

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The electrosorption of thiourea (TU) on single crystal electrodes: Ag(111), Ag(100) and Ag(110) was studied using electrochemical and radiochemical methods. A radiotracer method called „thin gap method” [1], with TU labeled with C-14 in 0.1 M HClO<sub>4</sub>, was used to determine the surface concentration of the adsorbate. The real surface area of the electrodes was estimated from the underpotential deposition of lead and also from the determination of capacitance of the electrodes. The hydrogen evolution as well as surface oxidation depend on the electrode plane – the Ag(111) is the most and Ag(110) the least active, respectively. From radiometric data it follows that adsorption of TU is reversible with respect to the bulk concentration and the potential in the range of ideal polarizability of electrodes. The maximum surface concentration of TU, determined radiometrically, follows the sequence: Ag(111) > Ag(100) > Ag(110), which is in agreement with the atom surface density of the silver planes. The surface concentration of TU on Ag(111) plane is nearly equal to that of calculated based on crystallographic data, assuming the perpendicular orientation of TU molecule towards the electrode surface. The experimentally determined adsorption isotherms were tested with different isotherm equations. The simple Langmuir equation describes experimental data the best up to 80% of surface coverage. This means that the lateral interaction of adsorbed TU molecules is weak. The Gibbs energy of adsorption is similar (25.5 ± 1 kJ/mol) for all studied planes. Hence, the energy of adsorption is practically independent of the electrode surface structure.

[1]. E.K.Krauskopf, A.Wieckowski, in: J.Lipkowski, P.N.Ross (Eds.), *Frontiers in Electrochemistry*, VCH, New York, 1992, p. 119

Table 1

Thermodynamic parameters of TU adsorption on Ag electrodes

	(111)	(100)	(110)
$10^{-15} \sigma_{\text{Ag}_2}$ atom cm <sup>-2</sup>	1.388	1.202	0.850
$10^{-14} \Gamma_{\text{max}}$ molec. cm <sup>-2</sup>	5.7 ±0.5	4.6 ±0.4	3.9 ±0.4
$\sigma_{\text{Ag}} / \Gamma_{\text{max}}$ atom molec <sup>-1</sup>	2.4 ±0.2	2.6 ±0.2	2.2 ±0.2
$\Delta G_{\text{L}}^{\circ} / \text{kJ mol}^{-1}$ (293 K)*	-25.3 ±0.5	-25.9 ±0.5	-25.9 ±0.5

$\sigma_{\text{Ag}}$  – surface atom density

\* The standard state:  $\Gamma^{\circ} = 0.5 \Gamma_{\text{max}}$ ,  $c^{\circ} = 1 \text{ mol dm}^{-3}$