

## Bond Formation in Electrosorbates

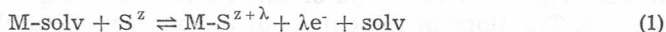
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The electrosorption valency  $\gamma$  is defined and its meaning is thoroughly discussed. Exptl. dent. of  $\gamma$  is demonstrated for systems Au/Bi<sup>3+</sup> and Pt/Cu<sup>2+</sup>. It is found that for homonuclear ions in aq. solns. the ratio  $\gamma/z$ , where  $z$  stands for Nernst valency, is successfully correlated with the electronegativity difference  $|\chi_M - \chi_S|$  of the electrode metal  $M$  and the sorbate  $S$ . For small electronegativity differences,  $\gamma/z$  is close to unity indicating large covalency. Bond formation in electrosorbates in non-aq. solvents and at single crystal planes of various orientations are briefly discussed.

### DEFINITION AND INTERPRETATION OF THE ELECTROSORPTION VALENCY, $\gamma$

In electrosorption reactions a substance,  $S^z$ , from the electrolyte comes in direct contact with the electrode metal,  $M$ :



Solvent molecules are desorbed, and  $\lambda$  electrons ( $\lambda \geq 0$ ) are transferred to the metal. Reaction (1) can be characterized by the electrosorption valency,  $\gamma$ . In case of excess supporting electrolyte,  $\gamma$  is defined by the partial derivatives<sup>1</sup>

$$\gamma = \frac{1}{F} \left( \frac{\partial \mu_S}{\partial \varepsilon} \right)_{\Gamma_S} = - \frac{1}{F} \left( \frac{\partial q_m}{\partial \Gamma_S} \right)_{\varepsilon} \quad (2)$$

According to this equation,  $\gamma$  can be determined experimentally, as was demonstrated for several anionic and cationic adsorption systems<sup>2</sup>. In general,  $\gamma$  is in the range between 0 and the charge of the ion,  $z$ . An electrostatic model<sup>1</sup> of the partially discharged substance with the charge,  $z_{ad} = z - \lambda$ , yields the correlation between the thermodynamic value,  $\gamma$ , and the microscopic data of the electrosorption reaction:

$$\frac{\gamma_N}{z} \approx g - \frac{\lambda}{z} (1 - g) \quad (3)$$

$\gamma_N$  is the electrosorption valency at the potential of zero charge,  $\lambda$  is the partial charge transfer coefficient and  $g$  is a geometric factor characterizing the relative penetration of the sorbate into the double layer.  $g$  is defined by the electric potentials at the adsorption site,  $\Phi_{ad}$ , in the metal,  $\Phi_m$ , and in the electrolyte,  $\Phi_e$ :

$$g = (\Phi_{ad} - \Phi_e) / (\Phi_m - \Phi_e) \quad (4)$$

In Eq. (3) the small dipole terms of the adsorbed substance and of the desorbed solvent molecules are neglected, which is possible in the case of ionic adsorption where the charge terms dominate<sup>3,4</sup>. Since Eq. (3) involves the two unknown values,  $g$  and  $\lambda$ , a direct determination of these values from the experimental data of a single system is not possible. However, a comparison of the experimental data of different systems permits an estimation of  $g$  and  $\lambda$ , respectively<sup>2</sup>.

#### EXPERIMENTAL DETERMINATION OF $\gamma$ FOR THE SYSTEMS Au/Bi<sup>3+</sup> AND Pt/Cu<sup>2+</sup>

To demonstrate the possibilities of electroadsorption experiments, galvanostatic and potentiostatic experiments were carried out with gold electrodes in diluted solutions of Bi<sup>3+</sup> with an excess of HClO<sub>4</sub> as supporting electrolyte. The electroadsorption equilibrium was reached by potentiostatic prepolarization of the gold electrode at a potential of  $\varepsilon > \varepsilon_{\text{Bi/Bi}^{3+}}$ . Then the adsorbed Bi<sup>3+</sup>-atoms were desorbed anodically by galvanostatic or potentiodynamic polarization. The charge  $Q$ , which is necessary for the desorption of bismuth, was obtained from the total anodic charge after subtraction of the small double layer charge. Such values are plotted in Figure 1 *versus* the logarithm of the bismuth concentration for different values of the prepolarization potential  $\varepsilon_1$ , as a parameter. Since constant  $Q$  means also a constant surface concentration  $\Gamma_{\text{Bi}}$  of adsorbed bismuth atoms, the electrode potential  $\varepsilon$  as a function of  $\mu_{\text{Bi}^{3+}}$  (or  $\log c_{\text{Bi}^{3+}}$ ) at constant  $\Gamma_{\text{Bi}}$  can be obtained from Figure 1. Figure 2 shows the  $\varepsilon/\log c$  diagram obtained in this manner. For comparison the equilibrium potential of the bismuth electrode is plotted which is given by Nernst's equation. The slope of this curve is  $d\varepsilon/d \log c = 20$  mV corresponding to  $z = 3$ . The slope of the curves of the adsorption equilibrium ranges between 18 and 37 mV, which means that  $\gamma$  ranges between 3.1 and 1.6. At large coverages  $\gamma$  differs from the Nernst valency,  $z = 3$ .

Corresponding experiments were carried out with platinum electrodes in solutions of Cu<sup>2+</sup> with an excess of H<sub>2</sub>SO<sub>4</sub><sup>5</sup>. The electroadsorption valency  $\gamma \approx 1.7$ , was obtained for small coverages.

Further,  $\gamma$  was obtained for the same system from combined coulometric/analytic measurements which yielded the derivative  $(\partial q_m/\partial I)_t$ . Finally, kinetic

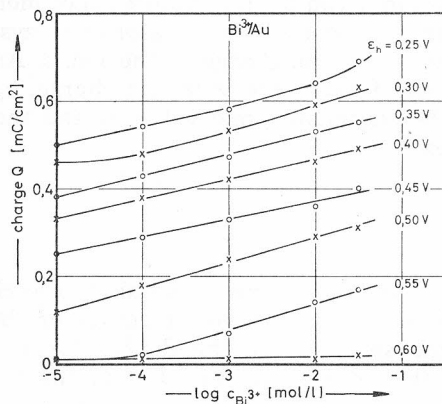


Figure 1. Charge,  $Q$ , for the desorption of Bi<sup>3+</sup>-atoms adsorbed at gold electrodes in dependence on  $\log c_{\text{Bi}^{3+}}$  at different values of  $\varepsilon_h$  as a parameter. Supporting electrolyte 1 M HClO<sub>4</sub>.

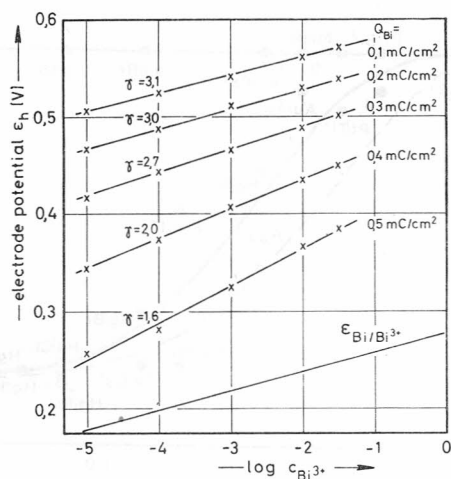


Figure 2. Electrode potential,  $\epsilon_N$ , as a function of  $\log c_{\text{Bi}^{3+}}$  at constant  $Q$ , i.e., constant  $\Gamma_{\text{Bi}}$ . The values have been taken from Figure 1.

measurements of the adsorption/desorption process yielded the transfer coefficients and according to Eq. (5), the electroadsorption valency  $\gamma$ :

$$\gamma/z = \alpha + \beta \quad (5)$$

All these experiments show that in the Pt/Cu<sup>2+</sup> system the electroadsorption valency,  $\gamma \approx 1.7$ , is somewhat smaller than the Faraday or Nernst valency,  $z$ , indicating a slightly polarized bond<sup>5</sup>.

#### CORRELATION BETWEEN THE ELECTROSORPTION VALENCY AND PAULING'S ELECTRONEGATIVITY FOR AQUEOUS SOLUTIONS

Experimental values of  $\gamma_N$  have been summarized for about 50 systems in aqueous solution<sup>3</sup>. For correlation purposes, only values at the potential of zero charge,  $\epsilon_N$ , and small coverages,  $\theta \approx 0.1$ , are used. Mixed adsorption<sup>6</sup> and phase formation must be excluded. For homonucleus ions, a simple correlation has been established between the ratio,  $\gamma/z$ , and the electronegativity difference,  $|\Delta\chi| = |\chi_M - \chi_S|$ , of the metal, M, and the sorbate, S<sup>3</sup>. This is shown in Figure 3.

$\gamma/z$  is about 1 for small differences,  $|\Delta\chi| < 0.5$ , and about 0.2 for large differences,  $|\Delta\chi| > 1.0$ . These two ranges are interpreted as the range of an almost covalent bond ( $\gamma/z \approx 1$ ;  $-\lambda/z \approx 1$ ) and of ionic adsorption ( $\gamma/z \approx 0.2$ ,  $-\lambda/z \approx 0$ ). In the mean range,  $0.5 < |\Delta\chi| < 1.0$ , the partial charge transfer ( $1 > \gamma/z > 0.2$ ;  $1 > -\lambda/z > 0$ ) with the formation of polarized bonds is important. The interpretation of the empirical correlation in Figure 3 can be based on Pauling's formula for the covalent contribution to a chemical bond:

$$-\lambda/z = \exp[-a(\Delta\chi)^2] \quad (6)$$

where «a» is a constant. The dashed line in Figure 3 was calculated according to Eq. (3) and (6) using  $a = 3$  and  $g = 0.16$ . A better fit of the experimental points was obtained using a geometric factor  $g$  increasing with increasing electronic interaction between M and S<sup>3</sup>.

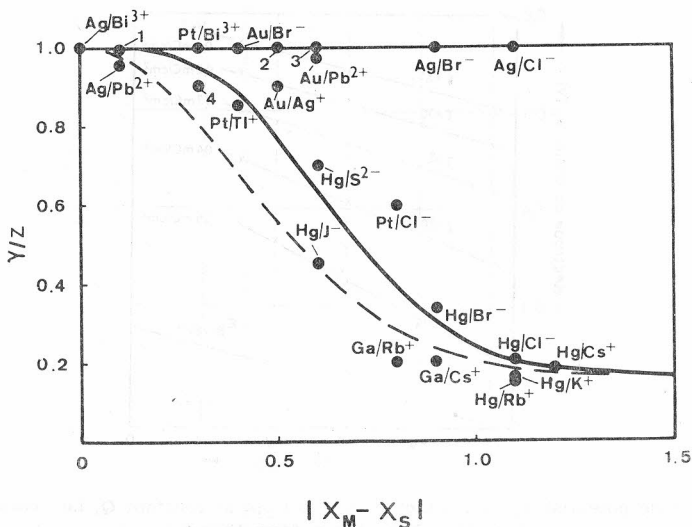


Figure 3. Electroadsorption valency ratio,  $\gamma/z$ , versus the absolute difference of electronegativities,  $|X_M - X_S|$ , for aqueous solution<sup>3</sup>. 1 = Pt/H<sup>+</sup>; Cu/Pb<sup>2+</sup>; Ag/Tl<sup>+</sup>; 2 = Au/Cu<sup>2+</sup>; Au/Bi<sup>3+</sup>. 3 = Au/Tl<sup>+</sup>, Au/Cl<sup>-</sup>. 4 = Pt/Cu<sup>2+</sup>.

The systems Au/Bi<sup>3+</sup> and Pt/Cu<sup>2+</sup> mentioned in Section 2 are representative for the »metallic monolayers« which can be characterized by  $\gamma/z \approx 1$ , *i. e.* a covalent bond with a small or negligible polarity. In these layers the electrostatic repulsion between adsorbed atoms is small, and monolayers can be built up with quasi-metallic properties. Small differences in the bond polarity may be important for the catalytic effects of these layers studied by Adzić and Despić<sup>8</sup>.

The electrostatic adsorption, on the other hand, is represented by various anionic and cationic systems, *e. g.* Hg/Cl<sup>-</sup>, Bi/K<sup>+</sup> and others. In these systems the charge transfer is negligible because of the large difference in electronegativity. The adsorbed ions retain their charge,  $z$ , and, consequently, the electrostatic repulsion between these adsorbed ions is important. Hence, in general, with these systems small coverages are observed. According to Eq. (3) the small  $\gamma/z$ -values of these systems can be identified as geometric factors, since  $-\lambda/z = 0$ .

Heteronucleus ions can be discussed qualitatively. The influence of the geometric factor seems to be dominant for these ions. Only SCN<sup>-</sup> or S<sub>2</sub>O<sub>3</sub><sup>2-</sup> have larger  $\gamma/z$ -values indicating some charge transfer<sup>3</sup>.

#### BOND FORMATION IN ELECTROSORBATES IN NON-AQUEOUS SOLVENTS

In the non-aqueous solvents, changes occur both in the structure of the double layer and the solvation of ions. Both effects must be discussed separately.

According to the principles outlined in Section 3, the electroadsorption valencies of various systems in non-aqueous solvents were summarized<sup>4</sup>. For methanol as solvent,  $\gamma/z$  was plotted in dependence on  $|\Delta\chi|$  corresponding to the analysis for water. This is shown in Figure 4. Complete charge transfer is observed for  $|\Delta\chi| < 0.3$ , and electrostatic adsorption without charge transfer takes place for large  $|\Delta\chi|$ -values. In the mean range of  $|\Delta\chi|$ , *e. g.*,

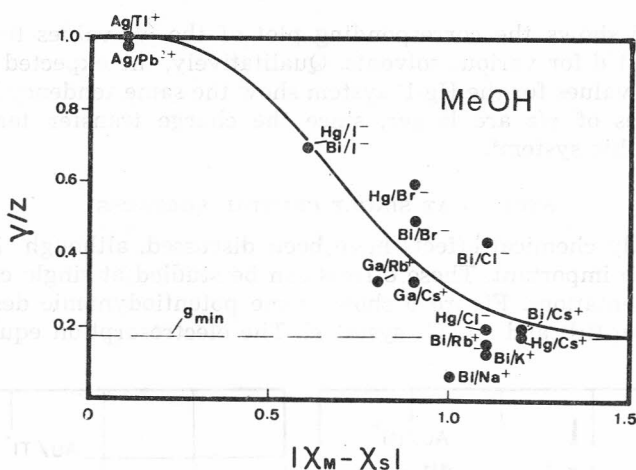


Figure 4.  $\gamma/z$  in dependence on  $|\Delta\chi|$  for MeOH as solvent<sup>4</sup>.

in the iodide systems, partial charge transfer takes place. This behaviour is observed in all solvents. The influence of the solvation properties of the solvent on the partial charge transfer can be discussed only qualitatively. It is concluded that a strong solvent-ion interaction facilitates the electrostatic adsorption, while increasing charge transfer is enhanced by a decreasing solvent-ion interaction, e. g., in the case of anion adsorption from aprotic solvents.

$\gamma/z$ -values of ions adsorbed electrostatically can be taken as geometric factors,  $g$ , which characterize the relative penetration of the ions into the double layer according to Eq (4). For different solvents,  $g$  should increase with increasing double layer thickness, since the M—S distance is constant. Assuming a double layer thickness given by the diameter of the solvent molecule,  $d$ , the geometric factor should decrease with increasing reciprocal double layer thick-

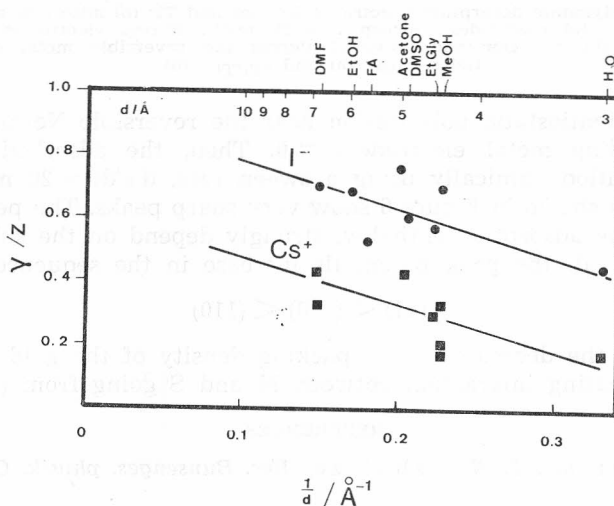


Figure 5.  $\gamma/z$  of an electrostatic system (Hg/Cs<sup>+</sup>) and of a system with partial charge transfer (Hg/I<sup>-</sup>) in dependence on the reciprocal diameter of the solvent molecules,  $1/d$

ness. Figure 5 shows the corresponding plot of the  $\gamma/z$ -values for the Hg/Cs<sup>+</sup> system *versus*  $1/d$  for various solvents. Qualitatively, the expected behaviour is observed. The values for the Hg/I<sup>-</sup> system show the same tendency however, the absolute values of  $\gamma/z$  are larger, since the charge transfer term,  $-\lambda/z$ , is important in this system<sup>4</sup>.

#### STUDIES AT SINGLE CRYSTAL SURFACES

So far, only chemical effects have been discussed, although the structural effects are also important. These effects can be studied at single crystal planes of various orientations. Figure 6 shows some potentiodynamic desorption spectra for the Au/Bi<sup>3+</sup> and Au/Tl<sup>+</sup> systems<sup>7</sup>. The electroadsorption equilibrium was

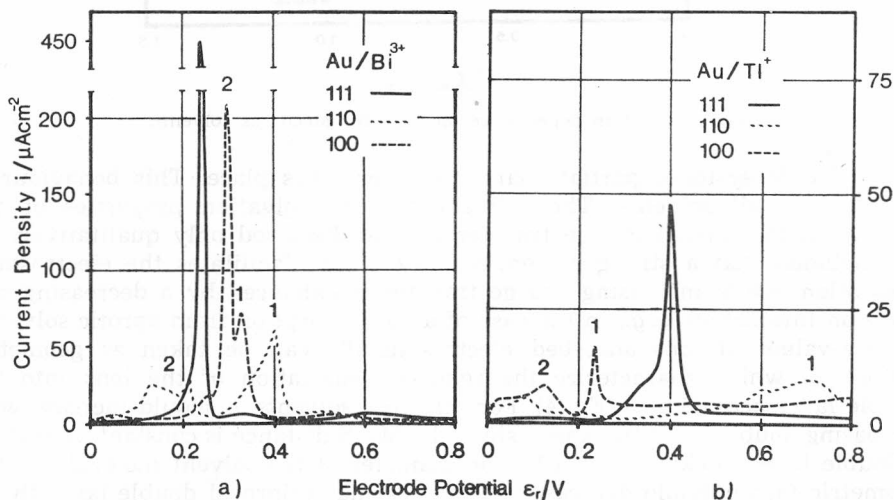


Figure 6. Potentiodynamic desorption spectra of Bi<sup>3+</sup> (a) and Tl<sup>+</sup> (b) adsorbed at various planes of gold single crystal electrodes<sup>7</sup>. Sweep rate 20 mV/s. Excess electrolyte: 1M HClO<sub>4</sub> (a) and 1M NaClO<sub>4</sub> (b).  $\epsilon_r$  = electrode potential *versus* the reversible metal electrode potential  $\epsilon_{\text{Bi/Bi}^{3+}}$  (a) and  $\epsilon_{\text{Tl/Tl}^{+}}$  (b).

reached by potentiostatic polarization near the reversible Nernst-potential of the corresponding metal electrode  $\epsilon_r = 0$ . Then, the adsorbed atoms were desorbed potentiodynamically using a sweep rate,  $d\epsilon/dt = 20$  mV/s. The desorption curves shown in Figure 6 show very sharp peaks. The peak potentials, representing the adsorption enthalpy, strongly depend on the substrate orientation. In general, the peak potentials increase in the sequence

$$(111) < (100) < (110)$$

This is due to the decrease of the packing density of the gold atoms, which yields an increasing interaction between M and S going from (111) to (110)<sup>7</sup>.

#### REFERENCES

1. K. J. Vetter and J. W. Schultze, *Ber. Bunsenges. physik. Chem.* **67** (1972) 920, 927.
2. J. W. Schultze and K. J. Vetter, *J. Electroanal. Chem.* **44** (1973) 63.
3. J. W. Schultze and F. D. Koppitz, *Electrochim. Acta*, **21** (1976) 326.

4. F. D. Koppitz and J. W. Schultze, *ibid.* **21** (1976) 337.
5. J. W. Schultze, *Ber. Bunsenges. physik. Chem.* **74** (1970) 705.
6. J. W. Schultze and K. J. Vetter, *Electrochim. Acta* **19** (1974) 913.
7. J. W. Schultze and D. Dickertmann, *Surf. Science* **54** (1976) 489.
8. R. R. Adzić and A. R. Despić, *Z. Phys. Chem. Neue Folge* **98** (1975) 95.

### SAŽETAK

#### Stvaranje veze kod elektrosorbata

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Definirana je elektrokemijska valencija  $\gamma$  i diskutirano je njeno značenje. Eksperimentalno određivanje  $\gamma$  ilustrirano je na sistemima Au/Bi<sup>3+</sup> and Pt/Cu<sup>2+</sup>. Ustanovljeno je da se za homonuklearne ione u vodenim otopinama omjer  $\gamma/z$  može uspješno korelirati s razlikama elektronegativnosti metala M elektrode i sorbata S. Oznaka z označava Nernstovu valenciju. Za male razlike u elektronegativnosti omjer  $\gamma/z$  je blizak jedinici što znači da je postotak kovalentnosti veze vrlo velik. Ukratko je diskutirano formiranje veze kod elektrosorbata u bezvodnim otopinama i na plohama kristala.

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