

# Patterns of Ionic and Molecular Adsorption at Electrodes

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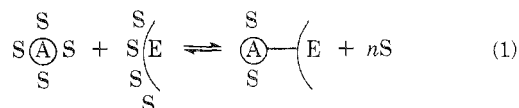
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Studies of the adsorption of ions and molecules at electrodes have occupied electrochemists for many years for reasons that are both important and obvious: all electrode processes involve an electronic interaction between reactants and the electrode surface which can be drastically altered by the presence of adsorbed ions and molecules. Adsorption can greatly enhance electrode reaction rates (e.g., the oxidation and reduction reactions of many cations are accelerated by barely detectable quantities of adsorbed anions) or eliminate the electrode reaction altogether (e.g., certain organic amines prevent metal deposition reactions from proceeding when they are adsorbed on electrode surfaces).

The classical methods for studying adsorption on electrodes are based on the Gibbs adsorption equation and involve the determination of the interfacial tension at the electrode–electrolyte interface, either directly by means of capillary electrometer measurements or indirectly from experimentally determined double-layer capacitances which can be doubly integrated to obtain the interfacial tension.<sup>1</sup> Many highly precise data have been obtained by these methods, although they require much labor and patience from the experimenter.<sup>2,3</sup>

More recently, an alternative method for determining the quantities of adsorbed species has been developed which, while lacking the full thermodynamic rigor of the classical methods, offers much greater ease and speed in execution. This method, chronocoulometry,<sup>4–6</sup> depends upon a measurement of the charge consumed in the electrode reactions of adsorbed species and is therefore restricted to electroactive adsorbates. However, the method has provided considerable new data on the adsorption of a variety of electroactive molecules and ions which would have been much more difficult to obtain by the classical techniques. The combination of the recent chronocoulometric results with the extensive earlier data obtained in conventional ways is providing new insight into the surface chemistry associated with molecular and ionic adsorption at electrodes. This Account is an attempt to show that the presently available data can be understood and classified on the basis of differences in the surface chemistry exhibited in the adsorption reactions.

The equilibrium involved in adsorption at an electrode can be represented as in eq 1, where A is the adsorbate, S is the solvent in which the adsorption is



being observed, and E is the electrode on the surface of which the adsorption occurs. The important feature to note in equilibrium 1 is the prominent role played by the solvent: the adsorbate, A, sheds some, if not all, of its solvation sheath in the act of adsorption and some of the solvent molecules which were initially adsorbed on the electrode surface are displaced by the adsorbate to form the adsorbate–electrode bond.

The remainder of this Account will be devoted to a discussion of the chemical factors that influence equilibrium 1 and cause the adsorption to be more or less favored. The discussion will be restricted to adsorption from aqueous solutions onto mercury electrodes, but the principles and reasoning involved have general applicability. The subject of adsorption at electrodes has received considerable attention from both experimentalists and theorists. Numerous quantitative analyses have been made of the extensive data available on simple inorganic and organic adsorbates.<sup>7</sup> Without intending to slight this previous body of work, my present intent is to present an almost entirely qualitative description of the adsorption reactions in order to focus on the interfacial chemistry involved.

A very large number of adsorption equilibria has been examined but the surface chemistry exhibited throughout almost all of the cases seems to fall naturally into five distinguishable classes which form a convenient basis for dividing the discussion. To emphasize the similarities and differences among the five classes it will be useful to examine the adsorption by means of plots which show how the extent of adsorption depends upon the sign and magnitude of the excess electronic charge present on the electrode surface.

## Class I Adsorbates

Figure 1 is an adsorption vs. charge diagram for the first class of adsorbates which consists of simple inorganic anions and cations. This class is best subdivided into the two subclasses, IA and IB, identified in the figure. Class IA is comprised of ions whose solva-

<sup>†</sup> Contribution No. 5032.

(1) D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).

(2) D. M. Mohilner, *Electroanal. Chem.*, **1**, 1 (1966).

(3) R. Payne, *Tech. Electrochem.*, **1**, Chapter 2 (1972).

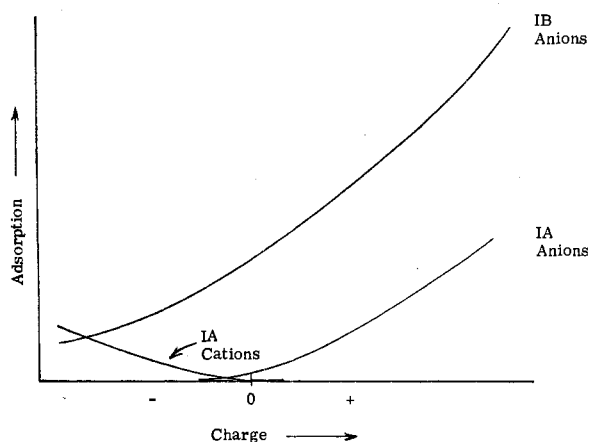
(4) F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

(5) B. Case and F. C. Anson, *J. Phys. Chem.*, **71**, 402 (1967).

(6) J. H. Christie, R. A. Osteryoung, and F. C. Anson, *J. Electroanal. Chem.*, **13**, 236 (1967).

(7) For recent reviews, see R. Payne, *J. Electroanal. Chem.*, **41** 277 (1973); R. Reeves, *Mod. Aspects Electrochem.*, **9** (1974).

Fred C. Anson received his B.S. degree from the California Institute of Technology and the Ph.D. from Harvard University (in 1957). His research has concerned various aspects of electrode kinetics, especially with adsorbed reactants. He and his students have focused on the role of adsorption in the catalysis of electrode processes, ligand bridging in heterogeneous electron-transfer reactions, and effects of the structure and composition of the electrical double layer on electrode reaction rates and mechanisms.



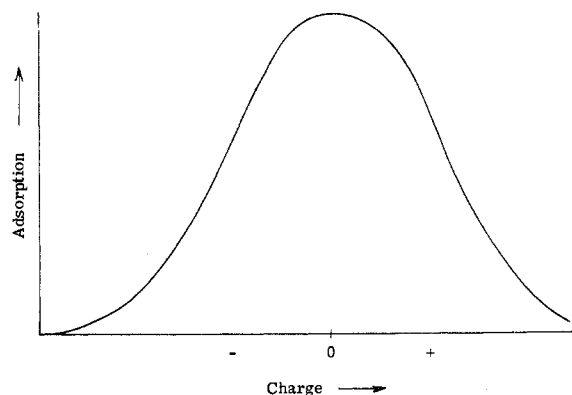
Examples: IA:  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{Cs}^+$ ,  $\text{R}_4\text{N}^+$ ,  $\text{R}_3\text{NH}^+$ , etc.  
 IB:  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ ,  $\text{HS}^-$ , etc.

**Figure 1.** Dependence of the adsorption of class I adsorbates on the electronic charge density on the electrode.

tion energies are not great enough to prevent their undergoing reaction 1 in response to the electrostatic interaction between the charge of the ion and the opposite charge on the electrode surface. An additional factor that contributes to the adsorption of certain of the class IA anions, such as  $\text{ClO}_4^-$  and  $\text{PF}_6^-$ , is their tendency to break up the local structure in the solvent when they dissolve in water. This property conveys some hydrophobic character to these ions which causes them to accumulate at the air-water interface as well as the electrode-water interface. Note that the adsorption of class IA ions decreases toward zero when the electrode charge has the same sign as that of the ion, the point at which complete desorption occurs depending on the concentration of the anion.

The preponderance of anions over cations in class IA is a reflection of the important role of solvation in equilibrium 1. The smaller, more highly hydrated alkali and alkaline earth cations exhibit little or no adsorption because their large hydration energies strongly oppose their adsorption. Only the most weakly hydrated cesium cation shows significant adsorption on negatively charged electrodes, while a large number of polyatomic anions exhibit extensive adsorption on positive electrode surfaces, as is indicated in Figure 1. In fact, the only anions which resist adsorption on positive electrodes are the very strongly hydrated fluoride and hydroxide ions.

The anions of class IB in Figure 1 differ from those in class IA in the strength of their adsorption. Class IB anions are adsorbed to a much greater extent than class IA anions on positive electrode surfaces, and on negatively charged electrodes their adsorption persists even in the face of fairly substantial negative charge densities. The forces that hold class IB anions on the surface involve more than the simple coulombic attractions or solvent structure-breaking factors that are primarily responsible for the adsorption of the class IA anions. Covalent bonding with the electrode surface seems to be much more prominent among the class IB anions. Electrons on the adsorbing anions are donated to available orbitals in the electrode surface. Examples of relative extents of adsorption which highlight this feature of the surface chemistry include the following sequences of increas-



Examples: Aliphatic and aromatic alcohols, amines, ethers, ketones, carboxylic acids, etc.

**Figure 2.** Dependence of the adsorption of class II adsorbates on the electronic charge density on the electrode.

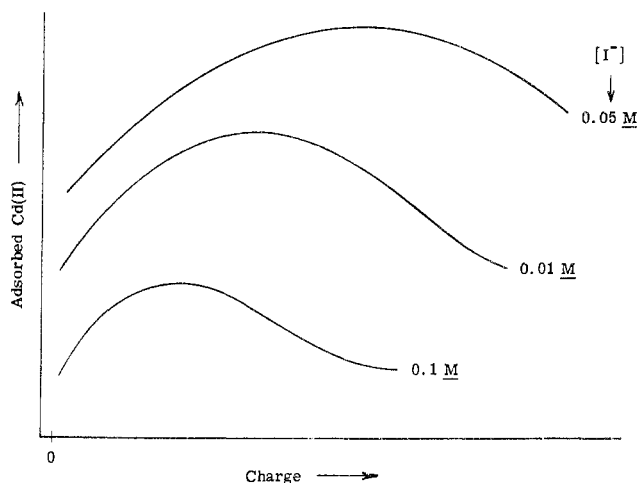
ing adsorbability:  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ;  $\text{SO}_4^{2-} \ll \text{S}_2\text{O}_3^{2-}$ ;  $\text{NCO}^- \ll \text{NCS}^-$ . The lack of cationic examples in class IB is also understandable on this basis.

As might be anticipated, this classification scheme is not free of oversimplifications. There are some relatively simple ions (e.g., guanidinium cation) whose adsorption depends only mildly on the electrode charge density. Such ions do not fit neatly into class IA or class IB. However, the primary features shown for the two subclasses in Figure 1 are representative of the behavior of most simple ions.

### Class II Adsorbates

Most neutral organic molecules are adsorbed on electrode surfaces from aqueous solutions primarily because of hydrophobic forces. In general, the less soluble an organic molecule is in aqueous media the more strongly it is adsorbed. Figure 2 shows the way in which the adsorption of most neutral organic molecules depends on the electric charge of the electrode. Unlike the ionic adsorbates of class I, organic adsorbates tend to exhibit their largest adsorptions near the point where the electrode bears no net charge; the adsorption decreases as the charge is increased in both the negative and positive directions. This behavior is readily explained by referring to equilibrium 1 and recalling the previously mentioned role of the solvent molecules in the overall adsorption reaction. The absorbing organic molecule must displace water molecules from the electrode surface, and at high charge densities on the surface the interaction energy of the water dipole with the electric field at the surface becomes so large that the water molecules are preferentially adsorbed and the organic molecules thereby desorbed from the surface. Very often the maximum in the adsorption of neutral organic molecules appears when the electrode charge is slightly negative rather than zero. This is a reflection of a preferred orientation of the water dipoles (at least on mercury electrodes) with the oxygen next to the metal surface. At slightly negative surfaces (e.g.,  $-2 \mu\text{C cm}^{-2}$ ) the water-electrode interactions are the weakest so that organic adsorbates are most strongly adsorbed.

Besides the common hydrophobic interactions, bonding to the electrode can also involve sharing of  $\pi$  electrons and nitrogen lone-pair electrons with the metal surface. Included among the adsorbates of



**Figure 3.** Adsorption of Cd(II) from iodide solutions as a function of the electronic charge density on the electrode.

class II are numerous organic ligands which form metal ion complexes, such as bipyridyl and *o*-phenanthroline. In some instances the organometallic complexes formed retain sufficient hydrophobic character to adsorb strongly on electrodes even when the complexes bear net ionic charges. Thus, class II adsorbates can sometimes be used to produce high concentrations of metal complexes on electrode surfaces where changes in the oxidation state of the metal center are readily achieved to yield intermediate species with potentially high reactivities. There is much greater variety in the details of the adsorption of organic molecules than can be discussed in this brief article. However, the topic has been studied extensively, and a rich literature on this subject is available.<sup>8-10</sup>

### Class III Adsorbates

The first two classes that have been mentioned represent the classical cases of adsorption at electrodes on the basis of which much of our understanding of the factors which influence adsorption has been worked out. The remaining three classes have been delineated much more recently and their characteristics are noteworthy because of the ways in which they depart from those of the classical adsorbates comprising classes I and II. Class III adsorbates are cations from the triads which immediately follow the transition metals, in particular Zn(II), Cd(II), Hg(II), In(III), Tl(I), and Pb(II). These cations show very little tendency to adsorb on mercury electrodes when they are present in solutions containing a nonadsorbing anion such as fluoride or anions from class IA, such as nitrate, perchlorate, or sulfate. (Tl(I) is somewhat exceptional in showing weak adsorption in the presence of nitrate.<sup>11</sup>) However, extensive adsorption of these cations is induced by the presence of class IB anions.<sup>12-21</sup> Figure 3 shows the

(8) A. N. Frumkin and B. B. Damaskin, *Mod. Aspects Electrochem.*, **3**, Chapter 3 (1964).

(9) B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes", Plenum Press, New York, N.Y., 1971.

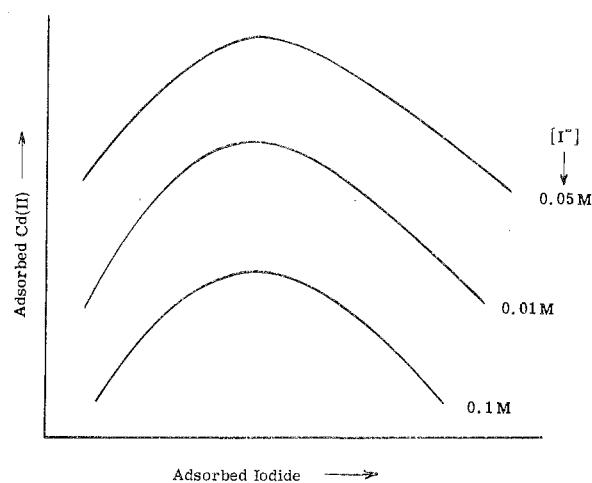
(10) For a recent review, see S. Trasatti, *J. Electroanal. Chem.*, **53**, 335 (1974).

(11) P. Delahay and G. G. Susbielles, *J. Phys. Chem.*, **70**, 647 (1966); G. G. Susbielles, P. Delahay, and E. Solon, *ibid.*, **70**, 2601 (1966).

(12) R. W. Murray and D. J. Gross, *Anal. Chem.*, **38**, 392 (1966).

(13) F. C. Anson, J. H. Christie, and R. A. Osteryoung, *J. Electroanal. Chem.*, **13**, 343 (1967).

(14) G. W. O'Dom and R. W. Murray, *Anal. Chem.*, **39**, 51 (1967).



**Figure 4.** Adsorption of Cd(II) as a function of the quantity of adsorbed iodide ion.

behavior of Cd(II) in iodide solutions which is representative of the behavior exhibited by this class of adsorbates. The data are restricted to positive values of the electronic charge on the electrode because Cd(II) is reduced to the metal amalgam ahead of the potential at which the charge changes sign.

The maxima in the plots of Cd(II) adsorption vs. electrode charge and in the dependence of the adsorption on the concentration of iodide ion in the solution are the result of the simultaneous action of two opposing factors. The first of these is the extent of adsorption of the class IB anion, iodide, which induces the adsorption of Cd(II). Figure 4 shows that, when the quantity of adsorbed Cd(II) is plotted against the quantity of adsorbed iodide rather than the electrode charge, the maxima in the resulting curves line up, suggesting that the adsorbed iodide is more directly involved in controlling the adsorption of Cd(II) than is the electronic charge on the electrode. The second factor influencing the adsorption is the complexation of Cd(II) by iodide. The concentrations of the various cadmium(II)-iodide complex species present in the solution rise and fall as the iodide concentration is increased, while the quantity of adsorbed iodide increases monotonically. A clearer picture of the processes involved on the electrode surface can be obtained by maintaining the first of the two opposing factors constant while varying the second. Figure 5A shows how the adsorption of Cd(II) depends on the bulk concentration of iodide when the quantity of adsorbed iodide is kept constant. To obtain the data in Figure 5A, advantage was taken of the previously discussed dependence of the adsorption of class IB anions on the electrode charge (Figure 1). As the bulk concentration of iodide was increased the positive charge on the electrode was decreased (by changing its potential) so as to keep the quantity of adsorbed iodide constant.

The rise and fall of the adsorption shown in Figure 5A can now be correlated with the changes in the spe-

(15) F. C. Anson and D. J. Barclay, *Anal. Chem.*, **40**, 1791 (1968).

(16) G. W. O'Dom and R. W. Murray, *J. Electroanal. Chem.*, **16**, 327 (1968).

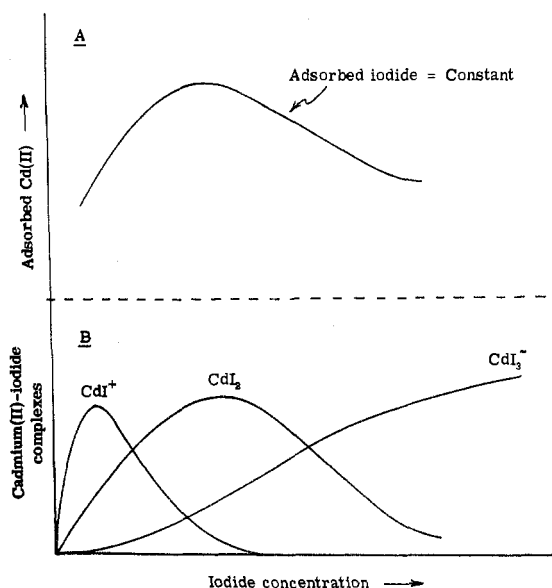
(17) D. J. Barclay and F. C. Anson, *J. Electrochem. Soc.*, **116**, 438 (1969).

(18) Z. Kowalski and F. C. Anson, *J. Electrochem. Soc.*, **116**, 1208 (1969).

(19) G. Lauer and R. A. Osteryoung, *Anal. Chem.*, **41**, 1882 (1969).

(20) M. Caselli and P. Papoff, *J. Electroanal. Chem.*, **23**, 41 (1969).

(21) D. J. Barclay and F. C. Anson, *J. Electroanal. Chem.*, **28**, 71 (1970).

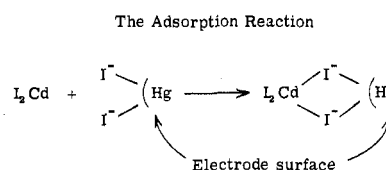


**Figure 5.** (A) Adsorption of Cd(II) as a function of the concentration of iodide with the quantity of adsorbed iodide held constant. (B) Speciation among the Cd(II)-iodide complexes as a function of the concentration of iodide.

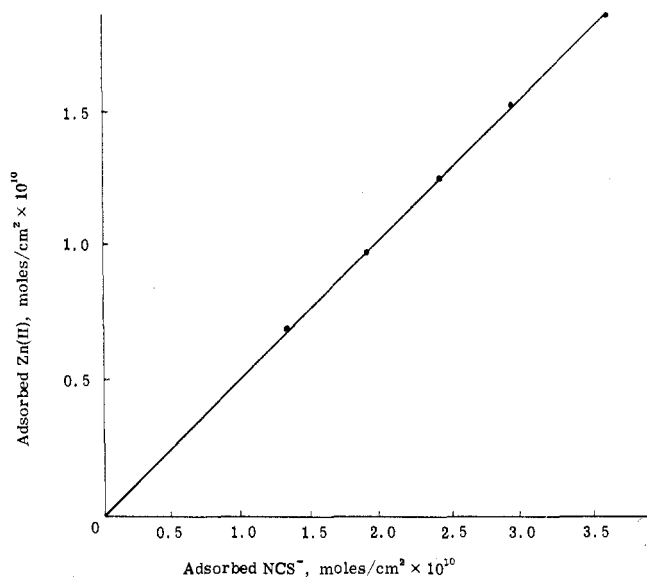
ciation of cadmium(II)-iodide complexes as the iodide concentration increases. Figure 5B shows these calculated changes. Note that the rise and fall of the concentration of the uncharged complex,  $\text{CdI}_2$ , matches the rise and fall of the adsorption of Cd(II) (Figure 5A) fairly closely. Thus, it appears that the preferentially adsorbed species is  $\text{CdI}_2$  and that its adsorption is induced by adsorbed iodide ions. The surface reaction believed to be responsible for the adsorption is shown in Figure 6 for the case where two adsorbed iodide ions act as bridges to hold the  $\text{CdI}_2$  on the electrode surface. (At higher coverages of the surface, when the adsorbed complexes are more closely packed, single iodide ion bridges appear to suffice to bind the complex to the electrode.<sup>15</sup>)

The same type of reaction as that shown in Figure 6 leads to the induced adsorption of other class III adsorbates by class IB anions. There appear to be two ingredients involved in this type of anion-induced adsorption: The adsorption-inducing anion must itself be adsorbed and it must also form complexes with the cation of the class III adsorbate. For example, the adsorption of zinc(II) is not induced by iodide ion because the complexation of zinc(II) by iodide is so weak that appreciable concentrations of iodozinc complexes are not formed. By contrast, thiocyanate anions complex zinc(II) much more strongly and produce extensive adsorption of the cation at positive values of the charge on the electrode.<sup>19</sup> However, if the electrode charge is made negative (a possibility with zinc(II) because of its more negative reduction potential) the adsorption of the thiocyanate anions is eliminated (Figure 1) and so is the adsorption of zinc(II), even in the presence of large bulk concentrations of  $\text{Zn}(\text{NCS})_2$ .

Figure 7 shows the adsorption of zinc(II) from thiocyanate solutions as a function of the quantity of adsorbed thiocyanate anions under conditions where the coverage of the surface by thiocyanate is high.<sup>21</sup> The line through the data points also passes through the origin and has a slope close to  $1/2$ . This behavior



**Figure 6.** Surface reaction leading to iodide-induced adsorption of Cd(II).



**Figure 7.** Thiocyanate anion induced adsorption of zinc(II). The quantity of adsorbed zinc(II) vs. the quantity of initially adsorbed thiocyanate anions at a constant bulk concentration of thiocyanate.<sup>21</sup>

matches that expected on the basis of the general reaction shown in Figure 6 in which  $\text{NCS}^-$  replaces  $\text{I}^-$  and  $\text{Zn}(\text{NCS})_2$  replaces  $\text{CdI}_2$ .

The tendency for preferential adsorption of the uncharged complexes of class III cations (one exception appears to be the chloride-induced adsorption of Pb(II) in which  $\text{PbCl}_3^-$  is the predominantly adsorbing species<sup>20,21</sup>) may be attributed chiefly to the effect of solvation. The uncharged complex gains less energy by shedding its solvation sheath than any of the charged species with which it is in equilibrium.

Quite recently halide anion induced adsorptions of Pb(II) and Tl(I) on mercury were studied in solutions containing halide and metal ion concentrations below those corresponding to the equilibrium precipitation of the bulk-phase metal halide.<sup>22,23</sup> Plots of the adsorption vs. the concentration of the halide anion or of the metal cation exhibit sharp discontinuities at values which correspond to an essentially constant product of the anion and cation concentrations, as if the discontinuity marked the formation of a new phase on the electrode surface with a solubility product smaller than that for the formation of the bulk-phase metal halide. The quantity of metal cation adsorbed beyond the discontinuity is close to the value calculated for a monolayer of adsorbed metal halide on the surface. For Tl(I) in bromide two discontinuities are observed and the adsorption increases by almost exactly twofold on going from the first to the second. For this reason the observed behavior has been interpreted as indicating the spontaneous for-

(22) C. M. Elliott and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3321 (1974).

(23) H. B. Herman, R. L. McNeely, P. Surance, C. M. Elliott, and R. W. Murray, *Anal. Chem.*, **46**, 1258 (1974).

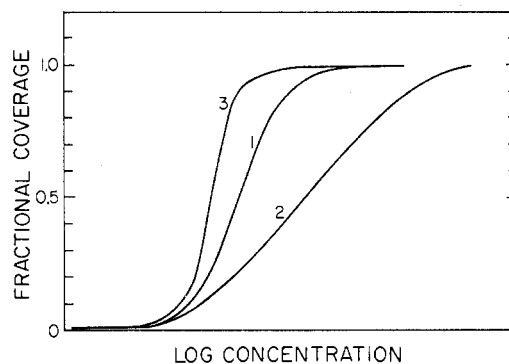


Transition Metal	d Electronic Configuration	Extent of Adsorption
$V^{3+}, d^2$		Moderate
$Cr^{3+}, d^3$		Strong
$Mn^{2+}, d^5$ (high spin)		None
$Ru^{3+}, d^5$ (low spin)		Strong
$Ni^{2+}, d^8$		Detectable

**Figure 9.** Examples of class IV adsorbates with their d-electronic configurations and extent of adsorption. The splitting of the d orbitals into an upper ( $e_g$ ) and a lower ( $t_{2g}$ ) set assumes octahedral coordination geometry.

tionally labile in solution so that aquation of the transition-metal center ensues upon reaction with  $Hg^{2+}$  with the formation of thiocyanato complexes of  $Hg(II)$  and destruction of the transition-metal complex. However, the adsorption of substitutionally labile isothiocyanato complexes on mercury electrodes can readily be measured without affecting the integrity of the complexes in solution, so that a more extensive test could be made of the prediction that the extent of adsorption of the complexes should correlate with the increase in ligand-field stabilization energy resulting from the proposed enhancement of the ligand-field strength about the transition metal caused by the adsorption.

Figure 9 summarizes both the predictions and the experimental results for isothiocyanato complexes of several transition metals assumed to be octahedrally coordinated. The identity of the adsorbing complex is known only for the substitutionally inert complexes, but the general trends in the strength of the adsorption are nicely accommodated by the simple ligand-field argument outlined above. Thus, for example,  $V(III)$ , a  $d^2$  ion, is adsorbed on mercury from thiocyanate solutions<sup>24</sup> (in which it exists as  $VNCS^{2+}$  and  $V(NCS)_2^+$ ), but not as extensively as in  $Cr(NCS)_2^+$ ,<sup>25</sup> a  $d^3$  ion, which gains more stability from increases in ligand-field strength.  $Mn(II)$  forms isothiocyanate complexes in which the metal has a high-spin,  $d^5$  configuration with no possibility for ligand-field stabilization energy. One therefore predicts no adsorption of  $Mn(II)$  from thiocyanate solutions, and none was found.<sup>31</sup> By contrast,  $Ru(III)$ , which is also a  $d^5$  ion but with a low-spin configuration, has much to gain from increases in ligand-field strength, and the complex  $Ru(NH_3)_5(NCS)^{2+}$  is very strongly adsorbed on mercury, as is the corresponding  $d^6$  complex of  $Ru(II)$ ,  $Ru(NH_3)_5(NCS)^+$ .<sup>31,32</sup> Nickel(II), with a  $d^8$  configuration, has less to benefit from increases in



**Figure 10.** Adsorption isotherms: (1) Langmuir isotherm; (2) Frumkin isotherm with repulsive interaction between adsorbed molecules; (3) Frumkin isotherm with attractive interactions between adsorbed molecules.

the magnitude of the ligand field, and the adsorption of  $Ni(II)$  from thiocyanate electrolytes is evident but not extensive.<sup>31</sup> The examination of the adsorption of isothiocyanato complexes of  $Co(III)$  has so far been thwarted by their spontaneous reductive decomposition in the presence of mercury to yield  $Co(II)$  and mercury(II) thiocyanate species. However, in every case in which the ligand-field argument outlined above has been tested by measuring the adsorption of isothiocyanate<sup>25,26</sup> (and azido<sup>26</sup>) complexes there has been good agreement between the experimental results and the predictions of the argument.

The surface chemistry involved in promoting the adsorption of these class IV isothiocyanate complexes depends strongly on the specific nature of the electrode material: the adsorption observed at mercury electrodes depends upon the chemical properties of mercury, and different behavior would be expected at, say, carbon or platinum electrodes. It has been proposed<sup>33</sup> that the way in which the nature of the electrode affects its properties as an adsorbent for ions and molecules can be rationalized by regarding an electrode surface as a Lewis acid with a variable acidity determined by its electrical charge density. Some data have been marshalled in support of this appealing idea,<sup>34,35</sup> but more extensive experimental tests are needed.

A unique and intriguing aspect of the behavior of class IV adsorbates is the adsorption isotherms to which several members of this class conform. Curve 1 in Figure 10 represents a simple Langmuir adsorption isotherm which is derived by assuming that there are no interactions among the adsorbed molecules except that the occupancy of an adsorption site by one adsorbate molecule denies that site to all other molecules. Most ionic and molecular adsorbates obey Langmuir adsorption isotherms only at very low coverage. Intermolecular repulsions typically develop at modest coverages because of coulombic forces between ions of like charge or dipole-dipole forces between uncharged molecules. Curve 2 in Figure 10 shows a typical adsorption isotherm obeyed by adsorbates which repel each other on the surface. Note that the curve lies below the Langmuir isotherm. It will rise to meet the Langmuir isotherm when the

(31) D. J. Barclay and F. C. Anson, unpublished experiments.

(32) S. N. Frank and F. C. Anson, experiments to be published.

(33) D. J. Barclay, *J. Electroanal. Chem.*, **19**, 318 (1968).

(34) D. J. Barclay, *J. Electroanal. Chem.*, **28**, 443 (1970).

(35) D. J. Barclay and J. Caja, *Croat. Chem. Acta*, **43**, 221 (1971).

fractional coverage reaches unity, but this occurs at bulk concentrations of the adsorbate larger than those that are shown in the figure. The differences between the Langmuir isotherm and curves such as 2 in Figure 10 can be used to evaluate a repulsive "interaction parameter"<sup>36,37</sup> for each particular adsorbate.

A few adsorbates are known that obey adsorption isotherms which deviate from the Langmuir isotherm in the opposite sense from curve 2. Curve 3 in Figure 10 shows the kind of behavior that has been observed with certain hydrophobic, organic adsorbates.<sup>37</sup> This kind of positive deviation from the Langmuir isotherm reflects attractive interactions between the adsorbing species which results in cooperative adsorption—the presence of a few molecules of adsorbate on the surface makes the adsorption of additional molecules more favorable. It is not particularly surprising to observe this kind of behavior with hydrophobic adsorbates which prefer the less aqueous environment they can create by accumulating at surfaces. However, it was surprising to find that several of the isothiocyanato complexes of chromium(III) obey adsorption isotherms like curve 3 in Figure 10.<sup>26,27</sup> Complexes which display such behavior include *fac*-Cr(OH<sub>2</sub>)<sub>3</sub>(NCS)<sub>3</sub>, *cis*-Cr(NH<sub>3</sub>)<sub>4</sub>(NCS)<sub>2</sub><sup>+</sup>, *cis*-Cr(en)<sub>2</sub>(NCS)<sub>2</sub><sup>+</sup>, *trans*-Cr(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>4</sub><sup>-</sup>, and Cr(NCS)<sub>6</sub><sup>3-</sup>.

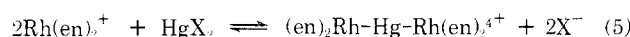
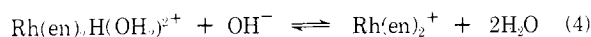
Almost all previously studied inorganic ions obey adsorption isotherms on mercury consistent with repulsive interactions between the adsorbed species, so that the origin of the attractive interactions for the chromium(III) isothiocyanato complexes apparently results from a new type of surface chemistry. One speculative proposal that has been made<sup>26</sup> attributes the intermolecular attractions to bonding interactions between the sulfur atoms of the isothiocyanate ligands which are themselves the site of the sulfur-to-mercury adsorption bonds. This proposal was inspired by an earlier interpretation offered by Stiefel et al.<sup>38</sup> to account for unusual structural features in some rhenium complexes with sulfur donor ligands. These authors observed unusually short distances between the ligand sulfur atoms that were bonded to the rhenium center along with a trigonal-prismatic coordination geometry of the sulfur atoms instead of the more usual octahedral geometry that would keep the sulfur atoms as far away from each other as possible. They proposed that these observations could be explained by bonding interactions between the coordinated sulfur atoms induced by their attachment to the oxidized metal center. The counterpart to such intramolecular attractions between nominally non-bonded sulfur atoms in a complex would be the proposed, sulfur-based, intermolecular attractions between the adsorbed isothiocyanato complexes.<sup>26</sup> The primary mercury-sulfur adsorption bond serves to hold the complexes closely enough together on the surface for sulfur-sulfur bonding to develop between adjacent, adsorbed complexes.

On the basis of the presently available experimental data, this interpretation can only be regarded as

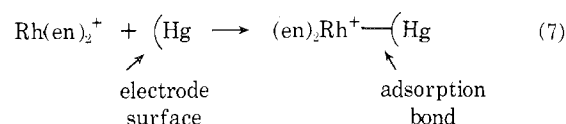
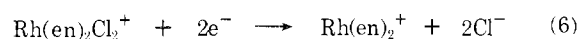
not ruled out. But whatever the source of the attractive forces between these adsorbed complexes proves to be, its existence seems indisputable, and its influence is evident in the kinetics of the electroreduction of the adsorbed complexes<sup>39</sup> as well as in the shapes of their adsorption isotherms.

### Class V Adsorbates

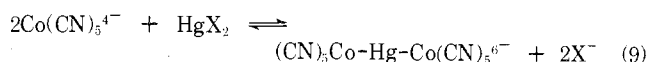
This final class has been described only recently, and as yet contains only a few members. The property which characterizes this class of adsorbates is metal-metal bonding between the adsorbing complex and the electrode surface. One example from this class is Rh(en)<sub>2</sub><sup>+</sup>, which can be generated by reduction of *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> at mercury electrodes, whereupon it binds tenaciously to the mercury surface by what is believed to be a rhodium-mercury bond.<sup>40</sup> The surface chemistry involved has its counterpart in some related homogeneous reactions of rhodium(I) and mercury(II) depicted in reactions 4 and 5.<sup>41</sup> Equilibrium 4 lies very far to the left, but at



sufficiently high pH values enough Rh(en)<sub>2</sub><sup>+</sup> is produced from the corresponding aquahydrido complex of rhodium(III), Rh(en)<sub>2</sub>H(OH)<sub>2</sub><sup>2+</sup>, for reaction 5 to ensue, with the formation of the trinuclear complex shown containing two rhodium-mercury bonds.<sup>41</sup> The analogous pair of reactions that proceed at a mercury electrode to produce an adsorbed product are



A second example of class V behavior is provided by some cyano complexes of cobalt. Reactions 8 and 9 have been shown to proceed in homogeneous solutions of hydridopentacyanocobaltate(III).<sup>42</sup> The tri-



nuclear ion formed in reaction 9 contains two cobalt-mercury bonds and again has a counterpart at the mercury electrode surface: exposing a mercury surface to pentacyanocobaltate(II) leads to the accumulation of a cobalt complex at the surface, and the reactions involved are believed to be (10) and (11).<sup>43</sup>

The rates at which the adsorbing species collect on the mercury surface are much smaller for class V adsorbates than for any of the other classes. (Diffusion-

(39) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem.*, **58**, 81 (1975); **58**, 95 (1975); **60**, 19 (1975).

(40) J. Gulens, D. Konrad, and F. C. Anson, *J. Electrochem. Soc.*, **121**, 1421 (1974).

(41) J. Gulens and F. C. Anson, *Inorg. Chem.*, **12**, 2568 (1973).

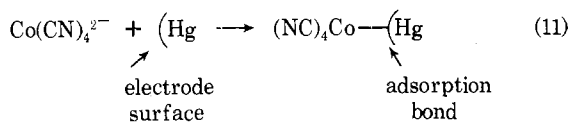
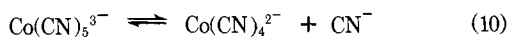
(42) H. S. Lim and F. C. Anson, *Inorg. Chem.*, **10**, 103 (1971).

(43) H. S. Lim and F. C. Anson, *J. Electroanal. Chem.*, **31**, 297 (1971).

(36) A. N. Frumkin, *Z. Phys.*, **35**, 792 (1926).

(37) Reference 8, p 182.

(38) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966).



controlled adsorption rates are usual except for class IV adsorbates which form more than a single isothiocyanate-to-mercury bond at the surface.<sup>44</sup>) This sluggishness in the adsorption rates may result from the small concentrations of the low-valent intermediates that are produced in the rapidly established equilibria which precede the formation of the metal-metal bond. The same slow rates are also observed during the homogeneous formation of the trinuclear complexes by the reactions between mercury(II) and the reactive rhodium(I) and cobalt(I) species shown in reactions 5 and 9.

Apart from their intrinsic interest as examples of heteronuclear metal-metal bonding on surfaces, these examples of class V adsorbates are intriguing because of their potential application as electrogenerated catalysts. For example, the cross sectional concentrations of  $\text{Rh(en)}_2^+$  that can be generated at a mercury electrode by rapidly changing its potential to desorb the  $\text{Rh(en)}_2^+$  that spontaneously coats the surface at selected initial potentials is very much larger than is obtainable by any other known means. The variety of cases in homogeneous solutions where  $\text{Rh(en)}_2^+$  serves as an effective catalyst<sup>45</sup> adds to the attractiveness of this line of pursuit.

## Concluding Remarks

The division of the patterns of adsorptive behavior exhibited by simple molecules and ions on mercury electrodes into the five classes that have been discussed is, of course, arbitrary. A larger number of subdivisions might have contributed to greater precision in drawing distinctions among classes, but the five classes chosen seem to suggest themselves quite naturally. In any case, the intent of this article has not been taxonomical. Rather it has been to elaborate the diversity of the surface chemistry that controls the tendencies for molecules to accumulate at charged, metallic interfaces. Increasingly, electrochemical kineticists and energy harvesters are striving to exploit the spontaneous adsorptive tendencies of reactants to enhance reactivities and reaction efficiencies, and an important component in such efforts is an understanding of the ways that are available for attaching molecules to electrode surfaces.

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(44) S. N. Frank, M. J. Weaver, and F. C. Anson, *J. Electroanal. Chem.*, **54**, 387 (1974).

(45) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals", *Interscience*, New York, N.Y., 1967, Chapter 6.

# Picosecond Spectroscopy in Chemistry and Biology

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In recent years picosecond spectroscopy has been applied to the study of both chemical and biological systems. Some of the results obtained have been predicted by extrapolation from nanosecond studies, while others reveal phenomena never realized or expected before.

The application of mode-locked lasers is now almost a decade old. The technology which makes it

possible to perform spectroscopic studies in the picosecond range is described in references 1-18. The

- (1) H. W. Mocker and R. J. Collins, *Appl. Phys. Lett.*, **7**, 270 (1965).
- (2) A. J. DeMarie, W. H. Glenn, M. J. Brienzu, and M. E. Mack, *Proc. IEEE*, **57**, 2 (1969).
- (3) N. Bloembergen, *Commun. Solid State Phys.*, **1**, 37 (1968).
- (4) P. M. Rentzepis, *Chem. Phys. Lett.*, **2**, 117 (1968).
- (5) C. V. Shank and E. P. Ippen, *Top. Appl. Phys.*, **1**, 121 (1973).
- (6) T. L. Netzel, W. S. Struve, and P. M. Rentzepis, *Rev. Phys. Chem. Jpn.*, **44**, 1 (1973).
- (7) D. J. Bradley and G. H. C. New, *Proc. IEEE*, **62**, 313 (1974).
- (8) J. A. Giordmaine, P. M. Rentzepis, S. L. Shapiro and K. W. Wecht, *Appl. Phys. Lett.*, **11**, 216 (1967).
- (9) P. M. Rentzepis, C. J. Mitschele, and A. C. Saxman, *Appl. Phys. Lett.*, **17**, 122 (1970).
- (10) R. Alfano and S. L. Shapiro, *Chem. Phys. Lett.*, **8**, 631 (1971).
- (11) G. E. Busch, R. P. Jones, and P. M. Rentzepis, *Chem. Phys. Lett.*, **18**, 178 (1973).
- (12) F. Shimizu, *IBM J. Res. Dev.*, **17**, 286 (1973).
- (13) C. A. G. O. Varma and P. M. Rentzepis, *Chem. Phys. Lett.*, **19**, 162 (1973).

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