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Structural Factors Involved in Ionic Adsorption

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This paper deals with the adsorption of simple inorganic anions on metallic electrodes. Thesis was made that adsorption may be regarded as a co-ordination reaction similar to complex formation in solution.

Pearson's Principle of Soft and Hard Acids and Bases (SHAB) was applied. It suggests that adsorption is a typical soft co-ordination reaction (*i. e.* metal surfaces are soft acceptors) in which an electron pair on the anion is shared with a vacant orbital on a surface metal atom. Thus soft anions and electrodes with high φ_M or E. A. adsorb strongest.

Variations in adsorption order of anions and electrodes can be understood in terms of the symmetry of surface and anion orbitals and by the change in the balance between solvation and bonding energies which can occur on electrodes of different bonding propensity.

INTRODUCTION

This paper deals with the adsorption of simple inorganic anions on metallic electrodes. The thesis will be developed that adsorption of this nature may be regarded as a co-ordination reaction similar to complex formation in solution. It is anticipated that this approach will have greater success in rationalising adsorption phenomena than had previous hypotheses based on the formation of a normal covalent bond or on the supposition that the principal limitation to adsorption is the extent of solvation of the anion. The distinction between a coordinate and normal covalent bond is that the former may be regarded, in solutions of high dielectric constant, as resulting from the heterolytic combination of ions while the latter results from the homolytic combination of atoms.

Like co-ordination reactions between cations and ligands, all that may be achieved at present is an understanding of the *relative* variations in adsorption behaviour of anions and electrodes rather than quantification of the adsorption free energy ($\Delta G_{ADS.}$) in terms of a theoretical model. Thus it is required to elucidate the properties which lead to the order of adsorptivity of anions at the potential of zero charge, E_Z:

$$S^{2-} > I^- > CN^- > NCS^- > Br^- > S_2O_3^{2-} \sim N_3^-$$
$$> NO_3^- > ClO_4^- > Cl^- > NO_2^- > CO_3^{2-} > SO_4^{2-} > F^-$$

** Present address: »Croatia« Research Laboratory, Koturaška 69, 41000 Zagreb, Croatia, Yugoslavia and of electrodes[1]

Au, Ag, Cu > Pt > Hg > Sb, Bi > Tl, In, Ga

Softness and Adsorptivity

It has previously been shown that soft anions are the most strongly adsorbed on mercury[2]. As the order, unlike the degree, of adsorption of anions given above does not vary significantly with the electrode material — some exceptions will be discussed — this relationship between softness and adsorptivity can be generalised for all metallic electrodes. Because Pearson[3] developed his Principle of Soft and Hard Acids and Bases (SHAB) mainly to rationalise the co-ordination properties of ions in solution this correlation suggests that adsorption is a typical soft co-ordination reaction (*i. e.* metal surfaces are soft acceptors) in which an electron pair on the anion is shared with a vacant orbital on a surface metal atom. While no quantitative explanation has been given which can account in detail for the SHAB principle, a treatment due to Klopman[4] indicates that soft interactions occur as a result of a balance between the energy spent in partial desolvation of the reacting particles and the energy gained in formation of a co-ordinate covalent bond. Soft interactions, and hence adsorption, are favoured by weak solvation *and* by the energies of the frontier orbitals on the donor and acceptor being nearly equal. The problem then is to determine the relative value of these properties as a function of electrode and anion.

Variation in Adsorption with Electrode Material

The approximately linear relationship between E_Z in the absence of specific adsorption and the work function, φ_M, *in vacuo* suggests that the surface potential due to adsorbed water is sensibly constant on most metals[5], indicating that the variation in adsorption with electrode material does not arise from the difference in desolvation energies of electrodes. This conclusion is borne out to some extent by the results of calculations on the dispersion interaction between adsorbed water molecules and electrodes[6]. The relative adsorption properties of electrodes may then be regarded as being determined by the electronic properties of the surface metal atoms.

The strongest co-ordinate covalent bond occurs when the energies of the donor and acceptor orbitals on the anion and electrode respectively are equal and a bond is only formed when these orbitals have the same symmetry properties. This is simply expressed in an equation suggested by Basolo and Pearson[7] for evaluation of the stabilisation of soft-soft interaction:

$$\Delta E = H_A - H_M + (\Delta H^2 + 4\beta^2)^{1/2} \tag{1}$$

Where the negative quantities H_A, H_M are Coulomb Integrals on the anion and electrode, ΔH is the difference between them, and β is the Exchange Integral. Maximum stabilisation obtains if $H_A = H_M$ when

$$\Delta E_{MAX} = 2\beta \tag{2}$$

where β may be expressed as[8]:

$$\beta = -2\,SH_{AV} \tag{3}$$

S being the Overlap Integral and H_{AV} the average value of the Coulomb Integrals. S, and hence ΔE, is nonzero only for orbitals of the same symmetry.

H_M essentially expresses the capability of surface atoms to accept electrons in a bond with the anion and may be taken as roughly proportional to their electron affinity, E. A., with atoms of the highest E. A. forming the strongest bond. As previously pointed out the E. A. of surface atoms may be approximated either by φ_M of the metal or by the E. A. of isolated metal atoms[9]. These respectively take the extreme views of regarding the surface atoms as having the properties of the bulk or as atoms free from the influence of the crystal. The true state of surface atoms will differ from either of these extremes though there is accumulated evidence, specially from gas-phase adsorption studies, that adsorption properties may be related to the chemical behaviour of individual metal atoms[10].

Table I lists values of φ_M of selected metals[11] together with the E. A. of the isolated metal atoms[12]. The strongest adsorbing electrodes have the highest value of these parameters as would be expected if they represent the relative value of H_M and a co-ordinate bond is formed on adsorption. The experimental evidence available is not, in general, of sufficient quality to allow us to determine what factors contribute to the increased adsorptivity of certain metals. However, the lack of the Esin-Markov effect in the adsorption of chloride and bromide on platinum[13] may be interpreted as indicating greater electron transfer in the Pt—Cl and Pt—Br adsorption bonds than in the corresponding mercury systems where the Esin-Markov effect is observed. The latter effect is the shift in E_Z resulting from specific adsorption and will be greatest when no electron-sharing occurs between the adsorbed ion and the electrode.

TABLE I

Work Functions and Electron Affinities for Selected Metals

M	φ_M (eV)	E. A. (eV)
Cu	4.5	2.0 (1.1)[a]
Ag	4.7	2.2 (1.0)[a]
Au	4.8	2.7 (2.2)[a]
Pt	5.4	1.6
Zn	3.7	0.7
Cd	4.0	0.6
Hg	4.5	1.0
Ga	3.8	(—0.1)[b]
In	—	(0.0)[b]

[a] — Taken from 12 (b)

[b] — H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, 55 (1955) 745. For comparison, Ag had an E. A. of 1.0 eV on this compilation.

It is assumed that the surface orbitals have the same symmetry as the directional orbitals of the bulk metal atoms. Thus, for transition metals *dsp* hybrids occur and empty and filled orbitals with σ and π symmetry project at the metal surface allowing σ and π donor and acceptor bonds to be formed. Non-transitional metals will evolve *sp* hybrids and σ donor and acceptor properties should predominate. The greater adsorptivity of anions over cations suggest that the acceptor mode of surface orbitals is energetically more favourable. However, the greater solvation of cations is also associated with their generally weak adsorption.

This distinction in terms of symmetry between the types of orbitals emerging at transition and non-transition metal surfaces immediately allows an explanation for the reversal of the degree of adsorption of certain anions on mercury and platinum. For example, cyanide is more strongly adsorbed than iodide on platinum[14] while the reverse is true on mercury. The cyanide ion is a good π-electron acceptor as well as being σ donor and hence extra stabilisation is obtained on metals, such as platinum, which are π-donors through filled t_{2g} levels (see Fig. 1). The back-bonding capabilities of iodide are much less than cyanide.

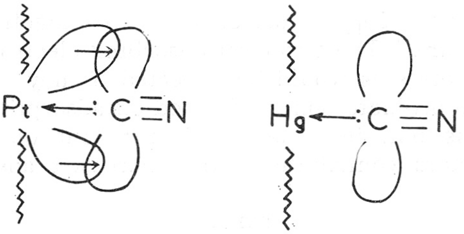

Fig. 1. Illustration of difference in bonding mode of cyanide to platinum and mercury. The filled t_{2g} orbitals on platinum can overlap with vacant orbitals on cyanide. Arrows indicate direction of electron transfer.

The relatively weak adsorption of the nitrite ion on mercury, even though it is classified as being intermediately soft, may be due in part to its softness being determined by its acceptor capabilities. It should be noted that orbitals of varying symmetry will emerge from different crystallographic faces of the electrode[10] and that π-bonding in the adsorption of acceptor anions should be demostrable by measuring their adsorption as a function of crystal orientation.

Variation in Adsorption with Anion

Unlike metal surfaces, where the degree of solvation is regarded as being invariant with the nature of the electrode, the relative co-ordination — or in the present context, adsorptivity — properties of anions are dependent on the solvation as well as the orbital energy. Generally speaking, the solvation contribution to ΔG_{ADS} will favour the adsorption of weakly solvated anions although strong adsorption of highly solvated anions (*e. g.* S^{2-} and $S_2O_3^{2-}$) sometimes occur. In the latter instances the stabilisation brought about by the covalent bond more than compensates for the loss in solvation energy. On the other hand weakly solvated anions such as ClO_4^- and PF_6^- show little tendency to form covalent bond and do not adsorb strongly.

H_A in equation (1) is related to the 1st and 2nd ionisation potentials (I. P.)[15] of the adsorbing anion and most often anions with low I. P.'s will be best matched in energy with the relatively high energy acceptor orbitals at the metal surface. This facet is illustrated in Fig. 2 where the adsorption stabilisation obtained with an easily ionisable anion is contrasted with that for a difficult to ionise anion.

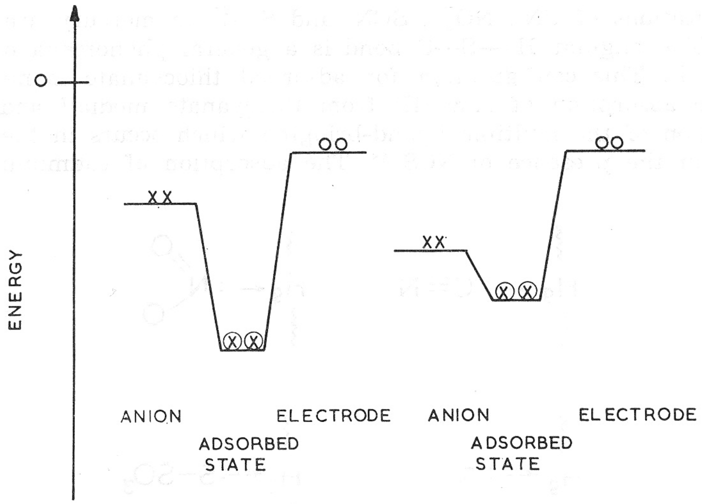

Fig. 2. Diagrammatic representation of the increased stabilisation obtained by an anion of high orbital energy. The crosses represent electron pairs on the anion, and the circles vacant orbitals on the electrode.

It is not yet feasible to predict on the basis of ionic parameters how the balance between solvation and orbital energies will influence the adsorptivity of anions. At this point the SHAB principle becomes most useful. In Table II the extreme combinations of solvation and energy and orbital energy (~ H_A) are given with examples of the adsorption behaviour of ions with these properties. Pearson's classification, determined empirically from the co-ordination trends of ions in solution best describes the result of the interplay between solvation and bonding tendencies. This interplay can result in a variation in the order of adsorptivity of ions on different electrodes. For example, on platinum chloride adsorbs to a greater extent than perchlorate[16] (at E_Z) while the reverse is true on mercury. This may be explained as follows. The adsorption of perchlorate, with little or no bonding capabilities, is determined by its weak solvation and is unlikely to vary with electrode, whereas chloride, though much more strongly solvated, has good bonding ability and its adsorption will be enhanced on electrodes such as platinum.

TABLE II

Adsorption of Anions as a Function of Solvation and Orbital Energy

Solvation	LOW	HIGH	HIGH	HIGH	LOW
Orbital Energy	HIGH	LOW	HIGH	HIGH	LOW
Example	I^-	F^-	OH^-	$S_2O_3^{2-}$	ClO_4^-
Pearson's Classification	SOFT	HARD	HARD	SOFT	HARD
Adsorptivity	HIGH	LOW	LOW	HIGH	LOW

The relationship between softness and adsorbability allows speculation on the orientation of ambidentate anions at electrode surfaces. Thus the most probable positions of CN^-, NO_2^-, SCN^- and $S_2O_3^{2-}$ on mercury are as shown in Fig. 3. The angular Hg—S—C bond is a general phenomena of sulphur-bonded SCN^-. This configuration for adsorbed thiocyanate is necessary to explain the adsorption of zinc (II) from thiocyanate media[17] and allows a rationalization of the multiple ligand-bridging which occurs in the oxidation of Cr (II) in the presence of NCS^-[18]. The adsorption of cadmium (II) from thiosulphate media is understoood on the basis of the proposed bonding of thiosulphate to the electrode[19]. The assignment for NO_2^- is rather more tentative than for the other anions as its weak adsorptivity on mercury suggests that the interaction may be non-specific.

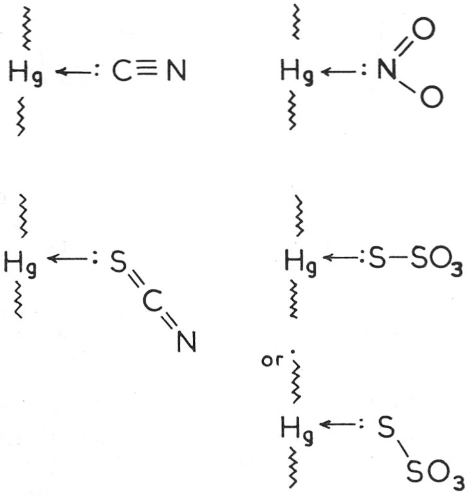

Fig. 3. Orientation of ambidentate ligands at a mercury electrode. The bonding atom is the one which normally co-ordinates to soft cations.

CONCLUSION

The proposal that adsorption of anions on metal electrodes be regarded as a co-ordination reaction allows the gross variations in adsorptive behaviour to be rationalised. Thus soft anions and electrodes with high φ_M or E. A. adsorb strongest. Variations in adsorption order of anions and electrodes can be understood in terms of the symmetry of surface and anion orbitals and by the change in the balance between solvation and bonding energies which can occur on electrodes of markedly different bonding propensity. On some electrodes (*e. g.* Ga) the relatively strong adsorption of water may have a significant influence on the extent of anion adsorption[20]. Reasonable assignments can be made of the orientation of adsorbed anions at electrode surfaces. A complete description of adsorption would have to include the influences of image and electron-repulsion forces. While the former do not vary greatly with the anion if no chemical bond is formed[21], the reduction in charge on the adsorbed anion resulting from electron transfer infers that the image energy gained when covalent bonding occurs will be less than for purely ionic adsorption. The correct model would maximise the covalent and image energy contribution. Electron-repulsion forces generally have a small influence on relative bond-energies. However, in the present context where ΔG_{ADS} results from differences in fairly large numbers it would be desirable to quantify them. It would not be correct to include an attractive polarisation term in an equation which also included covalent stabilisation.

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IZVOD

Strukturalni faktori pri jonskoj adsorpciji

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U ovom radu obrađuje se adsorpcija jednostavnih anorganskih aniona na metalnim elektrodama. Pretpostavljeno je da se adsorpcija može promatrati koordinacijskom reakcijom, slično kao što je reakcija stvaranja kompleksa u otopini.

Primijenjen je Pearsonov princip slabih i jakih kiselina i baza. Na osnovu toga adsorpcija se može razumjeti kao slaba koordinacijska reakcija (tj. metalne površine su slabi akceptori), prema kojoj anion dijeli elektronski par s praznom orbitalom atoma na površini metala. Zato se slabi anioni i elektrode s visokim φ_M i E. A. vrlo snažno adsorbiraju.

Simetrija orbitala aniona i površine te promjene u jakosti solvatacije i energije veze uzrokuju razliku u adsorbiranju serije aniona i elektroda.

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