

Underpotential Deposition of Metals: Structural and Thermodynamic Considerations

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The dependence of underpotential deposition (UPD) shift on work function differences, lattice coordination numbers, solvent desorption energies, and surface coverages is analyzed. The transport processes that govern monolayer formation and bulk deposition are incorporated. The parameteric dependence of the UPD shift on different thermodynamic quantities and adsorbate charge densities is reported. The validity of the formalism is demonstrated by comparison with the experimental data.

1. Introduction

The phenomenon of underpotential deposition (UPD) indicating the onset of deposition of metal adatoms at various types of substrates in potential ranges positive to the reversible Nernst potential has been a topic of intense research activity during the past few decades.^{1–3} The analysis of UPD is especially useful in view of the fact that (sub)monolayer formation of species on different single-crystal surfaces or polycrystalline metals can lead to diverse electrocatalytic applications.⁴ At a fundamental level, too, UPD presents a system wherein density functional formalism of metals can be coupled with statistical mechanical theory of electrolyte solutions, in conjunction with kinetics of electrode processes. While a rigorous theoretical analysis encompassing the above features is in itself complex, the experimental characterization of UPD is even more involved because it requires not only the application of transient electrochemical techniques such as cyclic voltammetric studies but also a combination of various spectroscopic and scattering methods.⁵ Further, the study of UPD finds applicability in the investigation of self-assembled monolayers for developing desirable surface architectures.⁶

The occurrence of UPD is, in general, inferred from cyclic voltammetric studies wherein peaks corresponding to (sub)monolayer adsorption are observed at potentials more positive than Nernst potential. Thus, the charge involved in the adsorption and deposition processes can be conveniently analyzed by integrating the observed current response (which is a measure of the rate) over the entire time domain. Because the origin of this phenomenon lies in the enhanced interaction of depositing metals (M) with foreign substrates (S), the work function differences play a predominant role in dictating the potential shift.

Because of the specificity of UPD with regard to the substrate crystal structures as well as influence of the supporting electrolyte, it has become possible to investigate several types of two-dimensional phase transformations (commensurate vs incommensurate) using diverse spectroscopic techniques⁷ as well as statistical mechanical models.⁸ In effect, UPD offers a system wherein the deposition of M on S can be controlled or influenced

by factors such as potential window, adsorption of ions, nature of single-crystal faces, and interaction between adatoms.

Early investigations of UPD were concerned with estimating the potential shift involved for different metallic couples in aqueous and nonaqueous solvents and its interpretation in terms of work function differences.¹ However, recent studies emphasize (i) observation of different cyclic voltammetric peaks pertaining to UPD on single-crystal surfaces and their origin in surface topography,^{9–13} (ii) morphological changes brought about by additives and the nature of the electrolytes,^{14,15} (iii) correlation of electrochemical data with structural analysis, such as binding energies in X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) patterns, resolution of scanning tunneling microscopy (STM) images,^{16,17} and (iv) density functional methods employing jellium and related models with pseudopotentials.^{18–23}

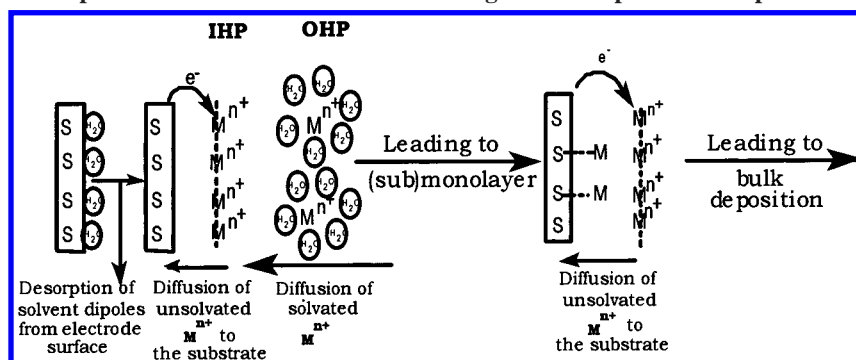
The purpose of this communication is to (i) evaluate the potential of adsorption and bulk deposition using various transport processes and the corresponding energetic contributions, (ii) rationalize the UPD shift in terms of work function differences, and (iii) calculate the UPD shift for various couples using thermodynamic parameters. Our essential input in this endeavor consists of incorporating the constituent terms into the overall Gibbs free energy changes so as to exploit the availability of different thermochemical data after correcting for the interface effects.

2. Underpotential Deposition of Metals on Foreign Substrates

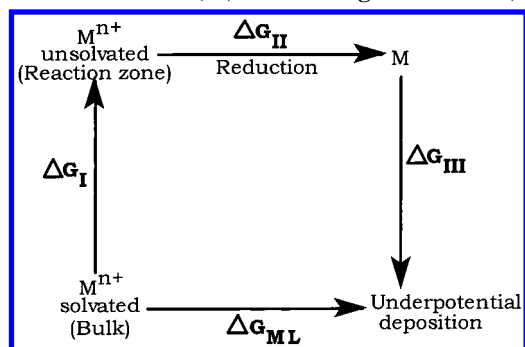
For obtaining the total Gibbs free energy change involved in UPD, it is imperative to consider various processes contributing to the potential of (sub)monolayer adsorption and bulk deposition, separately. The monolayer formation of M on S can be envisaged as follows: (i) movement of solvated ions from the bulk to the reaction zone, getting rid of their solvation sheath and (ii) electron transfer from the substrate to the metal ions leading to the subsequent bond formation with the substrate (S). It has been well-documented that the underpotential deposition of metals is dictated by crystal imperfections.¹ Hence, the S–M bond formation involves knocking off the adsorbed solvent dipoles from the appropriate sites of the substrate.²⁴ We note here that, because the electrode is solvated, the nature of the arrangement of solvent dipoles at electrode surfaces also needs

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SCHEME 1: Schematic Representation of Processes Constituting the Adsorption of M upon S



SCHEME 2: Thermochemical Cycle Denoting Different Energetic Contributions Involved in the Monolayer Formation of a Metal (M) on a Foreign Substrate (S)



to be included. Scheme 1 depicts the constituent processes involved in the formation of M on S. On the basis of Scheme 1, a thermochemical cycle can be constructed, which leads to

$$\Delta G_{ML} = \Delta G_I + \Delta G_{II} + \Delta G_{III} \quad (1)$$

where ΔG_{ML} denotes the Gibbs free energy change in the monolayer formation (Scheme 2). In eq 1, ΔG_I denotes the work done in bringing the solvated metal ions, M^{n+} , from bulk to the reaction zone represented as

$$\Delta G_I = W_{M^{n+}} \quad (2)$$

and ΔG_{II} consists of the free energy change of electron transfer from the substrate to the metal ions represented as ΔG_{et}^S as well as the contribution of ΔG° governed by the standard reduction potential of M^{n+}/M ,

$$\Delta G_{II} = \Delta G_{et}^S + \Delta G^\circ \quad (3)$$

It is necessary to introduce ΔG° in the expression for ΔG_{II} because it takes into account the inherent ability of the depositing species to get reduced, while ΔG_{et}^S is the contribution from the substrate, which is the source of electrons. On the other hand, ΔG_{III} involves the desorption of solvent dipoles and formation of the substrate–metal (S–M) bond. Hence, ΔG_{III} is written as

$$\Delta G_{III} = \theta(\Delta G_{desor}^S + \Delta G_{S-M}^{(inter)}) \quad (4)$$

where ΔG_{desor}^S represents the free energy change in the desorption of solvent dipoles from the substrate while $\Delta G_{S-M}^{(inter)}$ is that involved in the formation of the S–M bond and θ denotes the surface coverage of the underpotentially deposited metal adatoms on the substrate lattice. Because adsorption is visualized as the replacement of solvent molecules by the depositing

species, θ is introduced in ΔG_{desor}^S as well as in $\Delta G_{S-M}^{(inter)}$. Substituting eqs 2, 3, and 4 in 1, we obtain

$$\Delta G_{ML} = W_{M^{n+}} + \Delta G_{et}^S + \Delta G^\circ + \theta \Delta G_{desor}^S + \theta \Delta G_{S-M}^{(inter)} \quad (5)$$

In the preceding eq, the terms $W_{M^{n+}}$ and ΔG° for a chosen depositing species are independent of the substrate used.

2.1. Estimation of Work Terms and Desolvation Energies at the Interface. The solvation energy of ions is a measure of the work involved during the transfer of an ion from a point in a vacuum to the bulk, and in this case, the vacuum–solution interface needs to be considered.²⁵ On the other hand, during desolvation, ions surmount the energy barrier, which is governed by the surface potential, $\chi_{M^{n+}}$. Therefore, the total work of transfer may be written as

$$W_{M^{n+}} = F\chi_{M^{n+}} + \Delta G_{desolv}/S_N \quad (6)$$

where ΔG_{desolv} is the bulk desolvation energy of M^{n+} ions and S_N denotes their solvation number. The rationale behind the division of the bulk desolvation energy by the solvation number is as follows: When the solvated ions get transported from the bulk to the inner Helmholtz plane (IHP) in relation to the reaction zone, they get rid of their solvation sheath.^{26,27} An ion under consideration can get rid of S_N number of solvent molecules in view of the fact that S_N is its solvation number. Thus, $1/S_N$ denotes the factor by which ΔG_{desolv} is diminished from its bulk value. Although such a division is ad hoc, it incorporates the fact that S_N molecules are removed during the desolvation process.²⁸

ΔG_{et}^S representing the free energy change involved in the heterogeneous electron transfer from the substrate to the metal adatoms depends on the work function of the substrate. ΔG_{et}^S can be represented as²⁹

$$\Delta G_{et}^S = nF\mu_S^{el(inter)} \quad (7)$$

$\mu_S^{el(inter)}$ represents the electrochemical potential of the substrate S at the electrochemical interface. μ_S^{el} is a measure of electrical and chemical forces to which M^{n+} ions are exposed. μ_S^{el} at the interface is influenced by discreteness of charge effects, electron density profile, and dipolar orientation; hence, an exact value of $\mu_S^{el(inter)}$ is not easy to obtain. However, it is inferred^{26,29} that the electrochemical potential at the interface is considerably diminished from its bulk value. Hence, the electrochemical potential experienced by an M^{n+} ion at the interface is assumed to be μ_S^{el}/CN_S where CN_S is the coordination number of the substrate obtainable from interatomic distances.³⁰ $1/CN_S$ denotes the probability of one metal ion experiencing the electrochemical force exerted by the substrate. Thus, the factor $1/CN_S$ takes into

TABLE 1: Thermodynamic Parameters Employed for Calculating the UPD Shift Using Eq 36

system	$\Delta H_{S-H_2O}^{36}$ (kJ mol ⁻¹)	$T\Delta S_{S-H_2O}^{25}$ (kJ mol ⁻¹)	$\Delta G_{S-H_2O}^a$ (kJ mol ⁻¹)	$\Delta H_{M-H_2O}^{36}$ (kJ mol ⁻¹)	$T\Delta S_{M-H_2O}^{25}$ (kJ mol ⁻¹)	$\Delta G_{M-H_2O}^b$ (kJ mol ⁻¹)
Au/Cu ²⁺	292.00	125.52	83.24	277.80	125.52	76.14
Pt/Cu ²⁺	335.00	125.52	104.74	277.80	125.52	76.14
Ag/Tl ⁺	215.00	12.55	101.22	346.00 ^c	12.55	333.45
Ag/Cd ²⁺	215.00	12.55	101.22	69.00	125.52	-28.26 ^d
Ag/Pb ²⁺	215.00	12.55	101.22	382.00	125.52	256.48
Cu/Tl ⁺	277.80	125.52	76.14	346.00 ^c	12.55	333.45
Au/Pb ²⁺	292.00	125.52	83.24	382.00	125.52	256.48

^a ΔG_{S-H_2O} for d metals is obtained from $(\Delta H_{S-H_2O} - T\Delta S_{S-H_2O})/2$ leading to the entries of column 4. ^b ΔG_{M-H_2O} for d metals is evaluated from $(\Delta H_{M-H_2O} - T\Delta S_{M-H_2O})/2$, while for sp metals $\Delta G_{M-H_2O} = \Delta H_{M-H_2O} - T\Delta S_{M-H_2O}$. ^c ΔH_{Tl-O} is obtained using Pauling's arithmetic mean formula (eq 17) by substituting ΔH_{Tl-Tl} as 60.7 kJ mol⁻¹ and ΔH_{O-O} as 498.36 kJ mol⁻¹ from Weast et al.,³⁶ while the electronegativities of thallium and oxygen in Pauling's scale are 1.8 and 3.5, respectively.³⁸ ^d The negative value of ΔG_{M-H_2O} for cadmium indicates that the desorption of water molecules from the cadmium surface is facile in contrast to other metals. This fact is supported by the recent self-consistent density functional calculations of the cadmium–water interface,⁵⁰ which indicate that no tightly bound molecules are attached to the cadmium surface.

account the extent to which the bulk electrochemical potential of the metal is diminished at the electrode/electrolyte interface. Hence,

$$\mu_S^{el(inter)} = \mu_S^{el}/CN_S \quad (8)$$

where μ_S^{el} is given as³¹

$$\mu_S^{el} = \mu_S + \chi_S \quad (9)$$

where μ_S and χ_S denote the chemical potential and surface potential of the substrate, respectively. Further,

$$\mu_S = -\Phi_S - \chi_S \quad (10)$$

Φ_S being the work function of the substrate. Upon substituting eq 10 in eq 9, we obtain $\mu_S^{el} = -\Phi_S$. Hence,

$$\mu_S^{el(inter)} = -\Phi_S/CN_S \quad (11)$$

Equation 7 now becomes

$$\Delta G_{et}^S = -nF\Phi_S/CN_S \quad (12)$$

The preceding equation illustrates the influence of the *substrate* upon the reduction of M^{n+} and has important implications in analyzing the influence of electrode surfaces upon heterogeneous electron-transfer reactions. Note that ΔG° in relation to E° , the reduction potential of the depositing ions—a tabulated parameter, is introduced separately in eq 5.

2.2. Desorption of Solvent Dipoles from the Substrate and Substrate–Metal Bond Enthalpies. ΔG_{desor}^S indicates the Gibbs free energy change involved in the desorption of solvent dipoles from the substrate. A rigorous procedure to estimate ΔG_{desor}^S within the framework of statistical mechanical models would require analyzing infinite orientations of water dipoles interacting via long-range Coulombic and short-range nearest-neighbor interactions aided by an external electric field and influenced by the electronic density profile of the metal.^{32–34} Because this is a formidable task, we propose a simple methodology for calculating ΔG_{desor}^S incorporating the gross differences in the adsorption behavior at different electrodes. It is well-known that³⁵ adsorption behavior of water dipoles on sp and d metals are dissimilar because of the varying surface charge densities and extent of spillover of electronic density profiles. In the case of sp metals, the coordination of water occurs via the oxygen atoms because of positive surface charge densities, whereas for d metals, water dipoles adsorb via any one of the hydrogen atoms because of negative charge densities.

Thus, in the case of hydrated electrodes, $\Delta G_{desor}^S = \Delta G_{S-H_2O}/a$ where a equals 2 for d metals and unity for sp metals. The value of a is 2 for d metals because the probability of a water dipole coordinating with the substrate S via H atoms is $1/2$. ΔG_{S-OHH} (where the subscript S–OHH indicates bonding via the oxygen atom) is assumed as the free energy change for substrate–oxygen bond formation and ΔG_{S-HOH} (where the subscript S–HOH indicates bonding via the hydrogen atom) as that pertaining to substrate–hydrogen bond. On account of the availability of bond enthalpies between various metal–hydrogen bonds, we convert ΔG_{S-H_2O} into ΔH_{S-H_2O} using the reported ΔS_{S-H_2O} values pertaining to water. Thus, for sp metals,

$$\Delta G_{S-H_2O} = \Delta H_{S-H_2O} - T\Delta S_{S-H_2O} \quad (13)$$

while for d metals

$$\Delta G_{S-H_2O} = (\Delta H_{S-H_2O} - T\Delta S_{S-H_2O})/2 \quad (14)$$

The enthalpy of bond formation, ΔH_{S-O} or ΔH_{S-H} , for various substrates, S, are available in tabular compilations,³⁶ while $T\Delta S_{S-H_2O}$ for monovalent and polyvalent metals are given as 12.55 and 125.52 kJ mol⁻¹, respectively, on the basis of Born charging process.²⁵ The computed ΔG_{S-H_2O} values for different substrates are given in Table 1.

Consequent upon electron transfer by the substrate to the depositing metal ions, S–M bond formation occurs. Because a metal adatom is involved in the formation of a coordinate bond with any of the CN_S number of substrate atoms, we may write

$$\Delta G_{S-M}^{(inter)} = \Delta G_{S-M}/CN_S \quad (15)$$

Because the $T\Delta S_{S-M}$ term is, in general, ca. 10% of ΔH_{S-M} ,³⁷ ΔG_{S-M} is replaced by ΔH_{S-M} yielding

$$\Delta G_{S-M}^{(inter)} = \Delta H_{S-M}/CN_S \quad (16)$$

The enthalpy of formation of the substrate–metal bond is generally obtainable from tabular compilations.³⁶ Alternatively, Pauling's arithmetic mean version can also be employed for an approximate estimate. The dissociation energy corresponding to the bond between the substrate and metal, DE_{S-M} in Pauling's analysis,³⁸ is given by

$$DE_{S-M} = (DE_{S-S} + DE_{M-M})/2 + 23(x_S - x_M)^2 \quad (17)$$

where DE_{S-S} refers to the dissociation energy of the substrate–substrate bond and DE_{M-M} denotes that involved in the M–M bond. The quantities x_S and x_M are, respectively, the electro-

TABLE 2: Estimation of Enthalpy of Formation of the Substrate–Metal Bond Using Eq 17^a

system	DE _{S–S} ³⁶ (kJ mol ^{–1})	DE _{M–M} ³⁶ (kJ mol ^{–1})	x_S^{38}	x_M^{38}	DE _{S–M} (kJ mol ^{–1})
Pt/Cu ²⁺	357.30	195.00	2.2	1.9	278.22
Ag/Tl ⁺	163.00	60.70	1.9	1.8	112.08
Ag/Cd ²⁺	163.00	11.30	1.9	1.7	88.07
Ag/Pb ²⁺	163.00	86.60	1.9	1.8	125.03
Cu/Tl ⁺	195.00	60.70	1.9	1.8	128.08

^a For the other two UPD systems of Table 1, Au/Cu²⁺ and Au/Pb²⁺, the respective DE_{S–M} values are available directly from Weast et al.³⁶ (235.60 and 130.00 kJ mol^{–1}, respectively). Further, DE_{S–M} = –ΔH_{S–M} where ΔH_{S–M} is the enthalpy of formation of S–M bond.

negativities of S and M in Pauling's scale.³⁸ Obviously, the enthalpies of formation of S–M or M–M bonds are the negative of the dissociation energies (Table 2).

2.3. Potential for (Sub)Monolayer Formation. Upon substituting eqs 6, 12, 14, and 16 in eq 5, we obtain

$$\Delta G_{ML} = \Delta G_{desolv}/S_N + F\chi_{M^{n+}} - nF\Phi_S/CN_S + \Delta G^\circ + \theta\Delta G_{S-H_2O} + \theta\Delta H_{S-M}/CN_S \quad (18)$$

Further, ΔG_{ML} = –nFE_{ML} where *n* is the number of electrons involved in the reduction of Mⁿ⁺ and E_{ML} denotes the potential at which adsorption occurs. Thus,

$$E_{ML} = -\Delta G_{desolv}/(nFS_N) - \chi_{M^{n+}}/n + \Phi_S/CN_S + E_0 - \theta\Delta G_{S-H_2O}/(nF) - \theta\Delta H_{S-M}/(nFCN_S) \quad (19)$$

The value of *n* is, in general, not directly obtainable from the appropriate valencies in view of partial charge transfer in relation to electrosorption valency notions.²⁷ However, the number of electrons required for the reduction of Mⁿ⁺ by electron transfer from the substrate will equal the partial charge on the adsorbate (*z*_{ad}). Hence, eq 19 becomes

$$E_{ML} = -\Delta G_{desolv}/(z_{ad}FS_N) - \chi_{M^{n+}}/z_{ad} + \Phi_S/CN_S + E_0 - \theta\Delta G_{S-H_2O}/(z_{ad}F) - \theta\Delta H_{S-M}/(z_{ad}FCN_S) \quad (20)$$

The preceding equation enables the computation of E_{ML} using parameters such as work function of the substrate, free energy change of desorption of water dipoles, the desolvation energy of the depositing ions, and the enthalpy of bond formation between S and M.

It is instructive to enquire whether the above potential of monolayer formation is consistent with the potential (or charge of) adsorption customarily analyzed in the context of adsorption of ions or organic compounds at electrode surfaces.²⁴ A direct comparison is precluded in view of the fact that, in this case, detailed considerations regarding (a) the transport of ions from the bulk, (b) reduction of depositing species, and (c) explicit influence of substrate have been invoked. In contrast, the above details are not incorporated, in general, in electrosorption of ions, the emphasis therein being the competition between the solvent and adsorbate for occupancies and potential distribution.

The surface potential of Mⁿ⁺ can be estimated by invoking the concept of electronic equilibrium under which $\chi_{M^{n+}} = z_{ad}\chi_e^{(s)}$ where $\chi_e^{(s)}$ is the surface potential of electrons in solution.³⁵ Further, $\chi_e^{(s)}$ equals χ_e^S where χ_e^S denotes the surface potential of electrons in the substrate. If surface anisotropic effects are ignored, simple jellium model calculations provide χ_e^S as approximately equal to –0.4 eV for all metals.³⁵ The

potential step experiments pertaining to the UPD of Ag⁺ on Au yield E_{ML} as 0.44 V,³⁹ and if we use this value, θ may be obtained with help of the following parameters: the desolvation energy of Ag⁺ and its solvation number are reported²⁵ as 422.58 kJ mol^{–1} and 4; the work function³⁵ of Au and the enthalpy of formation for the Au–Ag bond are taken³⁶ as 4.80 eV and –202.9 kJ mol^{–1}, respectively; the coordination number of Au is given³⁸ as 5.56; the standard reduction potential⁴⁰ of Ag⁺/Ag is 0.49 V; ΔG_{Au–H₂O} = 83.24 kJ mol^{–1} (see section 2.2). If complete charge transfer is assumed, *z*_{ad} equals unity. The surface coverage θ , estimated using eq 20, yields 0.45, which is in good agreement with the experimental value of 0.40 reported by integrating the stripping current peaks and dividing it by *q*_{ml} where *q*_{ml} is the charge equivalent of a monolayer of the depositing species.⁴¹

The present phenomenological formalism provides an insight into the various system parameters influencing θ in relation to the potential of adsorption. Equation 20 may be rewritten as

$$E_{ML} = A + B\theta \quad (21)$$

where

$$A = -\chi_{M^{n+}}/z_{ad} - \Delta G_{desolv}/(z_{ad}FS_N) + \Phi_S/CN_S + E_0 \quad (22)$$

and

$$B = -\Delta G_{S-H_2O}/(z_{ad}F) - \Delta H_{S-M}/(z_{ad}FCN_S) \quad (23)$$

Interestingly, the linear dependence of E_{ML} upon θ has also been noticed in the experimental study of UPD of Cu²⁺ on Au(111).⁴² Further, the slope is characteristic of the desorption energetics of water molecules from the substrate and the enthalpy of formation of the substrate–metal bond, while the intercept is dependent upon the work function of the substrate, desolvation energy, surface potential, and standard reduction potential of metal ions.

3. Bulk Deposition of Metals and UPD Shift

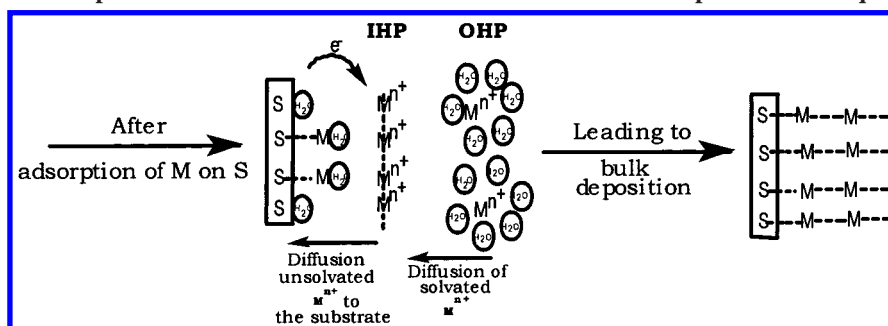
To evaluate the UPD shift, the potential at which the deposition occurs after the formation of M upon S is required. Scheme 3 envisages the processes involved in bulk deposition and enables the calculation of E_B, employing a thermochemical cycle (Scheme 4).

From the cycle in Scheme 4, ΔG_B pertaining to the bulk deposition can be written as the sum of ΔG_I^B, ΔG_{II}^B and ΔG_{III}^B. The free energy change in step I (ΔG_I^B) consisting of the work done in bringing the ions from bulk to the reaction zone is given by W_{Mⁿ⁺} as before. Thus,

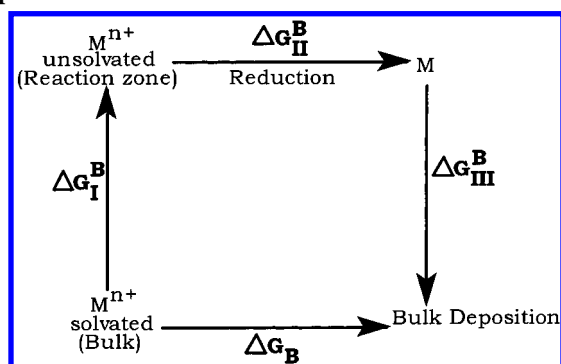
$$\Delta G_I^B = W_{M^{n+}} \quad (2)$$

W_{Mⁿ⁺} needs to be incorporated because the phenomenon of bulk deposition involves the transport of metal ions from the bulk, once again. The free energy change in step II (ΔG_{II}^B) involves (a) electron transfer from the metal to the depositing species, Mⁿ⁺, which leads to M–M bond formation (obviously this would occur only from the sites covered by adatoms of M, θ , and hence ΔG_{et}^M is multiplied by θ), (b) electron transfer from the substrate to the adsorbed ions, which would involve only the vacant sites of S (hence ΔG_{et}^S needs to be multiplied by

SCHEME 3: Schematic Representation of Various Processes Involved in Bulk Deposition Subsequent to Adsorption



SCHEME 4: Thermochemical Cycle Representing Different Energetic Contributions Pertaining to the Bulk Deposition



(1 - θ)), and (c) electron transfer for the reduction of metal ions governed by the standard electrode potential of the M^{n+}/M couple in relation to ΔG° . Thus,

$$\Delta G_{II}^B = \theta \Delta G_{et}^M + (1 - \theta) \Delta G_{et}^S + \Delta G^\circ \quad (24)$$

Analogously, ΔG_{III}^B may be expressed as follows: The substrate may be visualized as a modified electrode consequent upon adsorption of M on S. It is worth pointing out that the bulk deposition will occur not only on the sites covered by M

initially but also on the vacant sites caused by desorption of solvent dipoles from the substrate (see Scheme 5). Consequently, for further deposition, the adsorbed solvent dipoles on S with coverage (1 - θ) as well as the adatoms on S, of which the coverage is θ , get replaced by the depositing species M thereby leading to substrate-metal and metal-metal bond formation. Hence, the free energy changes ΔG_{desor}^S and ΔG_{desor}^M need to be multiplied by factors of (1 - θ) and θ , respectively. Thus, the contribution arising from the formation of S-M and M-M bonds are represented as (1 - θ) $\Delta G_{S-M}^{(inter)}$ and $\theta \Delta G_{M-M}^{(inter)}$. Therefore, ΔG_{III}^B becomes

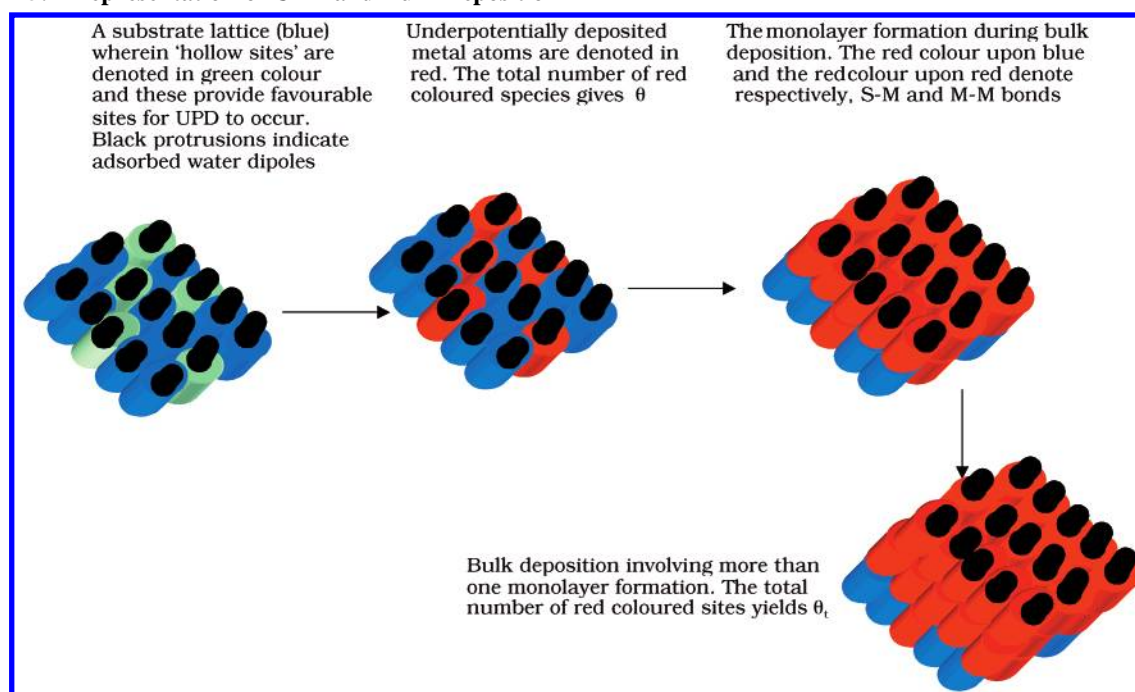
$$\Delta G_{III}^B = (1 - \theta) \Delta G_{desor}^S + \theta \Delta G_{desor}^M + (1 - \theta) \Delta G_{S-M}^{(inter)} + \theta \Delta G_{M-M}^{(inter)} \quad (25)$$

Combining eqs 2, 24, and 25 gives

$$\Delta G_B = W_{M^{n+}} + (1 - \theta) \Delta G_{et}^S + \theta \Delta G_{et}^M + \Delta G^\circ + (1 - \theta) \Delta G_{desor}^S + \theta \Delta G_{desor}^M + (1 - \theta) \Delta G_{S-M}^{(inter)} + \theta \Delta G_{M-M}^{(inter)} \quad (26)$$

The Gibbs free energy changes, ΔG_{et}^M , ΔG_{desor}^M , and $\Delta G_{M-M}^{(inter)}$ in the case of bulk deposition, can be obtained by extending the methodology indicated earlier. Thus, we obtain

SCHEME 5: Representation of UPD and Bulk Deposition



$$\Delta G_{\text{ct}}^{\text{M}} = -nF\Phi_{\text{M}}/\text{CN}_{\text{M}} \quad (27)$$

$$\Delta G_{\text{M-M}}^{(\text{inter})} = \Delta H_{\text{M-M}}/\text{CN}_{\text{M}} \quad (28)$$

instead of eqs 12 and 17, respectively. $\Delta G_{\text{M-H}_2\text{O}}$ is again represented as

$$\Delta G_{\text{M-H}_2\text{O}} = \Delta H_{\text{M-H}_2\text{O}} - T\Delta S_{\text{M-H}_2\text{O}} \quad (29)$$

and

$$\Delta G_{\text{M-H}_2\text{O}} = (\Delta H_{\text{M-H}_2\text{O}} - T\Delta S_{\text{M-H}_2\text{O}})/2 \quad (30)$$

for sp and d metals, respectively, as indicated earlier (see section 2.2). The computed $\Delta G_{\text{M-H}_2\text{O}}$ values using eqs 29 and 30 are listed in Table 1. Hence, eq 26 becomes

$$\Delta G_{\text{B}} = \Delta G_{\text{desol}}/S_{\text{N}} + F\chi_{\text{M}^{n+}} + \Delta G^{\circ} - (1 - \theta)nF\Phi_{\text{S}}/\text{CN}_{\text{S}} - \theta nF\Phi_{\text{M}}/\text{CN}_{\text{M}} + (1 - \theta)\Delta G_{\text{S-H}_2\text{O}} + \theta\Delta G_{\text{M-H}_2\text{O}} + (1 - \theta)\Delta H_{\text{S-M}}/\text{CN}_{\text{S}} + \theta\Delta H_{\text{M-M}}/\text{CN}_{\text{M}} \quad (31)$$

Analogously, the potential at which bulk deposition (E_{B}) occurs is now given by

$$E_{\text{B}} = -\Delta G_{\text{desol}}/(nFS_{\text{N}}) - \chi_{\text{M}^{n+}}/n + E_0 + (1 - \theta)\Phi_{\text{S}}/\text{CN}_{\text{S}} + \theta\Phi_{\text{M}}/\text{CN}_{\text{M}} - (1 - \theta)\Delta G_{\text{S-H}_2\text{O}}/(nF) - \theta\Delta G_{\text{M-H}_2\text{O}}/(nF) - (1 - \theta)\Delta H_{\text{S-M}}/(nFCN_{\text{S}}) - \theta\Delta H_{\text{M-M}}/(nFCN_{\text{M}}) \quad (32)$$

The quantity n equals z_{ad} as mentioned earlier,⁴³ and $\chi_{\text{M}^{n+}} = z_{\text{ad}}\chi_{\text{e}}^{(\text{s})}$. Thus,

$$E_{\text{B}} = -\Delta G_{\text{desol}}/(z_{\text{ad}}FS_{\text{N}}) - \chi_{\text{e}}^{(\text{s})} + E_0 + (1 - \theta)\Phi_{\text{S}}/\text{CN}_{\text{S}} + \theta\Phi_{\text{M}}/\text{CN}_{\text{M}} - (1 - \theta)\Delta G_{\text{S-H}_2\text{O}}/(z_{\text{ad}}F) - \theta\Delta G_{\text{M-H}_2\text{O}}/(z_{\text{ad}}F) - (1 - \theta)\Delta H_{\text{S-M}}/(z_{\text{ad}}FCN_{\text{S}}) - \theta\Delta H_{\text{M-M}}/(z_{\text{ad}}FCN_{\text{M}}) \quad (33)$$

The preceding eq is valid if the bulk deposition is presumed to be of one monolayer comprising (a) depositing species of coverage θ on the underpotentially deposited metal and (b) initially vacant sites of S given by $(1 - \theta)$, now being occupied by the depositing species.

3.1. Number of Monolayers Involved in Bulk Deposition.

In principle, the bulk deposition of M consists of a large number of monolayers dictated essentially by the packing and bonding considerations; consequently, eq 33 needs to be rewritten incorporating the number of monolayers formed under the given experimental conditions for a chosen system. Let us represent the surface coverage in the bulk deposition as θ_{t} , while θ denotes the surface coverage in the adsorption of M upon S. During the bulk deposition, the substrate sites $(1 - \theta)$, which were unoccupied during the (sub)monolayer formation, now become populated by metal atoms resulting in one complete monolayer (see Scheme 5). Further, the coverage $(\theta_{\text{t}} - 1)$ denotes the surface coverage *after* a complete monolayer of M upon S is formed, and consequently, $\theta_{\text{t}} - 1 = \theta_{\text{b}}$. Equation 33 can now be rearranged by introducing θ_{b} as

$$E_{\text{B}} = -\Delta G_{\text{desol}}/(z_{\text{ad}}FS_{\text{N}}) - \chi_{\text{e}}^{(\text{s})} + E_0 + (1 - \theta)\Phi_{\text{S}}/\text{CN}_{\text{S}} + \theta_{\text{b}}\Phi_{\text{M}}/\text{CN}_{\text{M}} - (1 - \theta)\Delta G_{\text{S-H}_2\text{O}}/(z_{\text{ad}}F) - \theta_{\text{b}}\Delta G_{\text{M-H}_2\text{O}}/(z_{\text{ad}}F) - (1 - \theta)\Delta H_{\text{S-M}}/(z_{\text{ad}}FCN_{\text{S}}) - \theta_{\text{b}}\Delta H_{\text{M-M}}/(z_{\text{ad}}FCN_{\text{M}}) \quad (34)$$

To obtain an insight into various terms of the preceding equation, we rewrite the same in a more transparent form:

$$z_{\text{ad}}F(E_{\text{B}} - E_0 + \chi_{\text{e}}^{(\text{s})}) = -\Delta G_{\text{desol}}/S_{\text{N}} - [\theta_{\text{b}}\Delta G_{\text{M-H}_2\text{O}} + (1 - \theta)\Delta G_{\text{S-H}_2\text{O}}] + z_{\text{ad}}F[\theta_{\text{b}}\Phi_{\text{M}}/\text{CN}_{\text{M}} + (1 - \theta)\Phi_{\text{S}}/\text{CN}_{\text{S}}] - [\theta_{\text{b}}\Delta H_{\text{M-M}}/\text{CN}_{\text{M}} + (1 - \theta)\Delta H_{\text{S-M}}/\text{CN}_{\text{S}}] \quad (35)$$

The terms containing surface coverage on the right hand side of eq 35 can be interpreted as follows: whenever the role of the substrate arises either via desorption characteristics or via bond formation with the depositing species, the factor $(1 - \theta)$ appears. Similarly, whenever the depositing species is involved during its displacement of adsorbed solvent dipoles or in the course of bond formation with M, the factor of θ_{b} occurs.

It is of interest to employ eq 35 for the UPD of Ag^+ on Au studied recently by Walters et al.⁴¹ The surface coverage θ is estimated to be 0.4 using potential step experiments.⁴¹ However, the bulk deposition is reported as consisting of 3.62 monolayers deduced by the mean values of charges calculated at two different time intervals $((q_{\text{t1}} + q_{\text{t2}})/2)$ obtained after integrating the appropriate stripping current peaks and dividing the integral by q_{ml} , q_{ml} being the charge equivalent of a monolayer of the depositing species. Thus, θ_{t} corresponds to 3.62 monolayers, while θ equals 0.4. Hence, we obtain θ_{b} as 2.62 monolayers.⁴⁴ The parameters employed for calculating E_{B} using eq 35 pertaining to Au/ Ag^+ are as follows: Gibbs free energy of desolvation of Ag^+ and its solvation number are given²⁵ as 422.58 kJ mol⁻¹ and 4, respectively; 4.80 and 4.3 eV are the work functions³⁵ of Au and Ag; the enthalpies of formation³⁶ of the Au-Ag and Ag-Ag bonds are -202.9 and -163 kJ mol⁻¹; the coordination number³⁸ of Au and Ag is 5.56; standard reduction potential⁴⁰ of $(\text{Ag}^+/\text{Ag}) = 0.49$ V. The value of z_{ad} is assumed to be unity, as before. The free energy changes, $\Delta G_{\text{Au-H}_2\text{O}}$ and $\Delta G_{\text{Ag-H}_2\text{O}}$, are 83.24 and 101.22 kJ mol⁻¹, respectively. E_{B} calculated using eq 35 is 0.096 V, which is in good agreement with 0.10 V estimated from potential step experiments.⁴¹

3.2. Underpotential Deposition Shift. UPD shift is usually obtained as a difference between the potential of (sub)monolayer formation and bulk deposition. Hence,

$$\Delta E_{\text{upd}} = \theta(\Phi_{\text{S}}/\text{CN}_{\text{S}} - \Phi_{\text{M}}/\text{CN}_{\text{M}}) + (1 - 2\theta)\Delta G_{\text{S-H}_2\text{O}}/(z_{\text{ad}}F) + \theta\Delta G_{\text{M-H}_2\text{O}}/(z_{\text{ad}}F) + (1 - 2\theta)\Delta H_{\text{S-M}}/(z_{\text{ad}}FCN_{\text{S}}) + \theta\Delta H_{\text{M-M}}/(z_{\text{ad}}FCN_{\text{M}}) \quad (36)$$

If the depositing ions and the substrate have identical coordination numbers, $\text{CN}_{\text{S}} = \text{CN}_{\text{M}} = \text{CN}$, eq 36 yields

$$\Delta E_{\text{upd}} = \theta(\Phi_{\text{S}} - \Phi_{\text{M}})/\text{CN} + (1 - 2\theta)\Delta G_{\text{S-H}_2\text{O}}/(z_{\text{ad}}F) + \theta\Delta G_{\text{M-H}_2\text{O}}/(z_{\text{ad}}F) + (1 - 2\theta)\Delta H_{\text{S-M}}/(z_{\text{ad}}FCN) + \theta\Delta H_{\text{M-M}}/(z_{\text{ad}}FCN) \quad (37)$$

Equation 36 indicates that the UPD shift depends not only on the work function differences but also on other substrate-metal and metal-metal bond enthalpies such as $\Delta H_{\text{S-M}}$ and $\Delta H_{\text{M-M}}$ apart from solvent desorption energies. The terms involving solvent energetics become crucial because the reduction of depositing species and subsequent bond formation with the electrode surface occur by replacement of the adsorbed solvent dipoles. This role of adsorption of solvent dipoles in

electron-transfer reactions at electrode surfaces have been recently pointed out.²⁴

4. Discussion

The foregoing analysis indicates the potential of monolayer adsorption and bulk deposition in terms of system parameters. Although eq 36 yields the explicit dependence of the UPD shift on energetics pertaining to the substrate, solvent, and depositing species, the demonstration of its validity for all of the couples studied in the UPD process is hindered because of the non-availability of (i) the surface coverage θ of the depositing ions, (ii) the number of electrons transferred in relation to the charge on the adsorbate during UPD, and (iii) the number of monolayers constituting bulk deposition. Hence, we consider seven UPD systems for which most of the required parameters have been extracted from hitherto-available experimental data obtained with the help of various transient electrochemical techniques. The systems considered are Au/Cu²⁺, Pt/Cu²⁺, Ag/Tl⁺, Ag/Cd²⁺, Ag/Pb²⁺, Cu/Tl⁺, and Au/Pb²⁺, as discussed below.

4.1. Estimation of the UPD Shift and Correlation with Work Function Differences. Equation 36 can be written as

$$\Delta E_{\text{upd}} = \theta(\Phi_S/\text{CN}_S - \Phi_M/\text{CN}_M) + \text{terms involving solvent energetics, substrate-metal bond enthalpies, etc} \quad (38)$$

The classical analysis of a variety of bimetallic couples carried out by Kolb et al.⁴⁵ indicates that a plot of ΔE_{upd} vs $(\Phi_S - \Phi_M)$ is linear although a strict quantitative explanation has been unavailable until now. It is of interest to consider the prediction of eq 36 as regards this issue. For this purpose, let us assume that $\text{CN}_S \approx \text{CN}_M$ as is the case for couples such as Au/Ag⁺ and Au/Cu²⁺. Hence, eq 38 becomes

$$\Delta E_{\text{upd}} = \theta(\Phi_S - \Phi_M)/\text{CN} + \text{correction terms} \quad (39)$$

The preceding equation shows that a plot of ΔE_{upd} vs θ will be linear with a slope of θ/CN provided all other terms involving substrate and depositing species are not work function dependent. This possibility is rather remote in view of the fact that (i) organization of solvent dipoles at electrode surfaces is strongly influenced by work function differences as demonstrated using density functional calculations^{32,33} and (ii) bonding characteristics between S and M are also dictated by appropriate work functions. Consequently, the observed slope of 0.5 deduced on the basis of experimental data is an interplay of various factors and may require further detailed analysis.

In view of the fact that z_{ad} crucially depends on the nature of the couples, it is instructive to discuss its influence in a systematic manner. In the case of Au/Cu²⁺, $n = z_{\text{ad}} = 2$, which indicates a complete charge transfer,¹ whereas for Pt/Cu²⁺, $n = z_{\text{ad}} = 1$, leading to partial charge transfer.¹ Consider the UPD of Tl⁺, Cd²⁺, and Pb²⁺ on Ag. In these cases, a parameter designated as δ , which is related to z_{ad} , has been estimated. The parameter δ denotes the change in the number of free electrons per adsorbed atom on the surface of the substrate and is given by⁴⁶

$$\delta = (z_{\text{ad}} - z_{\text{sub}})^2 \quad (40)$$

where z_{sub} representing the charge on the substrate equals unity for these couples. Hence, the preceding equation enables the computation of z_{ad} . For the couples Ag/Tl⁺, Ag/Cd²⁺, and Ag/Pb²⁺, δ values are reported as 6.38, 3.79, and 9.96, respectively, and hence, z_{ad} turns out to be 3.53, 2.95, and 4.16. In the case

TABLE 3: Parameters Employed in the Calculation of the UPD Shift Using Eq 36 and Comparison with the Experimental Data^a

system	Φ_S (eV) ³⁵	Φ_M (eV) ³⁵	z_{ad}	θ^1	CN_S^{38}	CN_M^{38}	ΔE_{upd} (calcd) (V)	ΔE_{upd} (exptl) (V) ¹
Au/Cu ²⁺	4.80	4.55	2.00 ¹	0.18	5.56	5.56	0.18	0.22
Pt/Cu ²⁺	5.03	4.55	1.00 ¹	0.23	6.00	5.56	0.43	0.44
Ag/Tl ⁺	4.30	4.10	3.53 ⁴⁶	0.22	5.56	3.56	0.25	0.28
Ag/Cd ²⁺	4.30	4.12	2.95 ⁴⁶	0.17	5.56	4.56	0.16	0.16
Ag/Pb ²⁺	4.30	4.24	4.16 ⁴⁶	0.10	5.56	2.56	0.12	0.16
Cu/Tl ⁺	4.55	4.10	2.76 ^b	0.31	5.56	3.56	0.34	0.34
Au/Pb ²⁺	4.80	4.24	1.50 ^b	0.22	5.56	2.56	0.40	0.40

^a The desorption energies, such as ΔG_{S-H_2O} and ΔG_{M-H_2O} , and various ΔH_{S-M} and ΔH_{M-M} values are reported in Tables 1 and 2.^b For Cu/Tl⁺ and Au/Pb²⁺, z_{ad} values are assumed as indicated in the text.

of the UPD of Pb²⁺ on Au, the reduction of Pb²⁺ is represented⁴⁷ as $\text{Pb}^{2+} + (2 - y)e \rightarrow \text{Pb}^{y+}$, indicating that $z_{\text{ad}} < 2$. Hence, z_{ad} in our calculation is assumed to be 1.5. The UPD of Tl⁺ on Ag, Au, etc has been investigated by considering relative resistance changes using resistometric techniques.⁴⁶ The value of z_{ad} varies from 2.13 in the case of Au/Tl⁺ to 3.53 for Ag/Tl⁺. Hence, if z_{ad} is assumed to be 2.76 for Cu/Tl⁺, it leads to the experimentally observed UPD shift. The values of z_{ad} for these seven couples are listed in Table 3. The estimated UPD shifts using eq 36 are in good agreement with the experimental values (Table 3).

4.2. Calculation of Surface Coverages. The usual method of estimating θ in this context consists of calculating the charge due to adsorbed species, q ($\mu\text{C cm}^{-2}$), from experimental cyclic voltammograms and subsequently carrying out a data reduction to obtain surface excess, Γ (mol cm^{-2}), with a priori knowledge of the maximum surface excess, (Γ_{max}) , using the underlying lattice structure of the substrate. The surface characterization studies, such as scanning tunneling microscopy (STM) and X-ray absorption spectroscopy (XAS), can also be used for the determination of surface coverages. On the other hand, the present phenomenological formalism provides an insight into the various system parameters that influence θ in relation to UPD shift. Using eq 36, we obtain

$$\Delta E_{\text{upd}} = B\theta + A \quad (41)$$

where

$$A = \Delta H_{S-M}/(z_{\text{ad}}FCN_S) + \Delta G_{S-H_2O}/(z_{\text{ad}}F) \quad (42)$$

and

$$B = \Phi_S/\text{CN}_S - \Phi_M/\text{CN}_M - 2\Delta G_{S-H_2O}/(z_{\text{ad}}F) + \Delta G_{M-H_2O}/(z_{\text{ad}}F) - 2\Delta H_{S-M}/(z_{\text{ad}}FCN_S) + \Delta H_{M-M}/(z_{\text{ad}}FCN_M) \quad (43)$$

The variation of ΔE_{upd} with θ is linear. Further, the intercept is composed of the free energy change involved in the desorption of water molecules from the substrate and enthalpy changes. However, the slope is crucially dependent upon work function differences as well as enthalpies of S–M and M–M bonds for a chosen solvent.

4.3. UPD Shift in Aqueous and Nonaqueous Solvents. It is of interest to verify the prediction of eq 36 concerning the UPD shift in nonaqueous solvents. The solvent energetics arise via the replacement of adsorbed solvent dipoles by the depositing species. Because water dipoles have enhanced attraction with electrode surfaces in general, the desorption energies pertaining to water, ΔG_{S-H_2O} and ΔG_{M-H_2O} , are crucial. On the other hand,

the interaction of the nonaqueous solvents with the electrode surfaces is weaker, and it is not incorrect to ignore the solvent-dependent terms in this case. Consequently, we may write $\delta(\Delta E_{\text{upd}}) = \Delta E_{\text{upd}}(\text{aqueous}) - \Delta E_{\text{upd}}(\text{nonaqueous})$, whereby

$$\delta(\Delta E_{\text{upd}}) = (1 - 2\theta)\Delta G_{\text{S-H}_2\text{O}}/(z_{\text{ad}}F) + \theta\Delta G_{\text{M-H}_2\text{O}}/(z_{\text{ad}}F) - (1 - 2\theta)\Delta G_{\text{S-S}}/(z_{\text{ad}}F) - \theta\Delta G_{\text{M-S}}/(z_{\text{ad}}F) \quad (44)$$

if θ and z_{ad} as well as various energy terms are assumed to be identical in both cases. In eq 44, $\Delta G_{\text{S-S}}$ and $\Delta G_{\text{M-S}}$ denote the Gibbs free energy change of desorption of nonaqueous solvent molecules from the substrate and metal, respectively. Consequently, we infer that the sign of $\delta(\Delta E_{\text{upd}})$ may be positive or negative depending upon the magnitude of θ , $\Delta G_{\text{S-S}}$, and $\Delta G_{\text{M-S}}$. In fact, the experimental data pertaining to the analysis of UPD shift of identical couples in different nonaqueous solvents¹ have indeed resulted in positive or negative potential shift in comparison with the corresponding value in aqueous solvents.

5. Perspectives and Summary

The foregoing analysis has provided a thermodynamic interpretation of UPD phenomena taking into account various transport processes governing it and employing appropriate interfacial energetic contributions, in an approximate manner. In view of the UPD process being inherently complex, as can be gauged from Schemes 1–5, the need for phenomenological analysis has become inevitable. Further, although a large number of UPD systems have been studied as regards the UPD shift, relevant parameters that enter into the model analyzed here are not always unambiguously available, thereby restricting the validity of our formalism to only a few systems. Nevertheless, the roles of several factors in dictating the UPD shift such as (a) adsorbate charge densities, (b) surface coverages in UPD and the number of monolayers involved in bulk deposition, (c) lattice coordination number of the substrate and depositing species, and (d) solvent desorption energies have been explicitly indicated here for the first time in this context.

The significant feature emanating from this study is the interplay of various factors in dictating the magnitude of the UPD shift. In particular, the slope of 0.5 extracted from the UPD shift vs work function difference, first enunciated by Kolb et al.,⁴⁵ seems to arise from diverse contributions involving various enthalpy changes and solvent desorption energies, and a rigorous explanation of this behavior looks formidable. The fact that incorporation of work function differences alone are insufficient to interpret the UPD shift has been pointed out more than 2 decades ago,⁴⁸ and the influence of structural parameters in rationalizing the UPD shift has also been indicated.

Although one of the limitations of the present approach consists of the ad hoc incorporation of interfacial parameters in terms of the corresponding quantities in the bulk, the fact that none of these is adjustable lends credibility to the version. A second weakness concerns the omission of adsorbate–adsorbate interactions, which limits the applicability of the formalism to systems wherein no phase transitions occur. Because sophisticated statistical mechanical models employing diverse potential functions^{16,17} and kinetic Ising model approaches to analyze electrosorption and electron-transfer processes have become available in recent times,⁴⁹ this lacuna needs to be overcome.

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List of Symbols

CN_{S} , CN_{M} = coordination number of the substrate (S) and metal (M), respectively.

$\text{DE}_{\text{S-S}}$, $\text{DE}_{\text{M-M}}$ = dissociation energy (kJ mol^{-1}) of S–S and M–M bonds, respectively.

$\text{DE}_{\text{S-M}}$ = dissociation energy (kJ mol^{-1}) of the S–M bond.

E_0 = standard reduction potential (V) of the metal ions.

E_{B} , E_{ML} = potential (V) for bulk deposition and for (sub)-monolayer adsorption, respectively.

n = number of electrons involved in charge transfer.

S_{N} = solvation number of the depositing species.

$W_{\text{M}^{n+}}$ = work (kJ mol^{-1}) done in bringing the metal ions from the bulk to the reaction zone.

χ_{S} , χ_{M} = Pauling's electronegativities of the substrate and metal, respectively.

z_{sub} , z_{ad} = charge on the substrate (S) and adsorbate (M), respectively.

$\chi_{\text{e}}^{(\text{s})}$, $\chi_{\text{e}}^{\text{S}}$ = surface potential (eV) of electrons in solution and in substrate, respectively.

$\chi_{\text{M}^{n+}}$, χ_{S} = surface potential (eV) of the metal ions and the substrate, respectively.

δ = change in number of free electrons per adsorbed atom on the surface of the substrate.

μ_{S} = chemical potential (eV) of the substrate.

$\mu_{\text{S}}^{\text{el}}$ = electrochemical potential (eV) of the substrate.

$\mu_{\text{S}}^{\text{el}(\text{inter})}$ = electrochemical potential (eV) of the substrate at the interface.

Φ_{S} , Φ_{M} = work function (eV) of the substrate and metal, respectively.

θ = surface coverage in the UPD.

θ_{t} = total surface coverage after bulk deposition.

θ_{b} = surface coverage after a complete monolayer is formed.

ΔE_{upd} = underpotential deposition shift (V).

ΔG° = standard free energy change (kJ mol^{-1}) in the reduction of M^{n+} .

ΔG_{B} = Gibbs free energy change (kJ mol^{-1}) in bulk deposition.

ΔG_{ML} = Gibbs free energy change (kJ mol^{-1}) in (sub)-monolayer formation.

$\Delta G_{\text{desor}}^{\text{S}}$, $\Delta G_{\text{desor}}^{\text{M}}$ = Gibbs free energy change (kJ mol^{-1}) in desorption of water dipoles from the substrate and metal.

ΔG_{desolv} = desolvation energy (kJ mol^{-1}) of the metal ions.

$\Delta G_{\text{et}}^{\text{S}}$, $\Delta G_{\text{et}}^{\text{M}}$ = Gibbs free energy change (kJ mol^{-1}) involved in the heterogeneous electron transfer from the substrate and metal to the depositing species.

$\Delta G_{\text{S-H}_2\text{O}}$, $\Delta G_{\text{M-H}_2\text{O}}$ = change in Gibbs free energy (kJ mol^{-1}) of desorption of water dipoles from S and M.

$\Delta G_{\text{S-M}}^{(\text{inter})}$, $\Delta G_{\text{M-M}}^{(\text{inter})}$ = Gibbs free energy change (kJ mol^{-1}) in S–M and M–M bond formation at the interface.

$\Delta G_{\text{S-S}}$, $\Delta G_{\text{M-S}}$ = change in Gibbs free energy (kJ mol^{-1}) of desorption of nonaqueous solvents from S and M.

$\Delta H_{\text{S-H}_2\text{O}}$, $\Delta H_{\text{M-H}_2\text{O}}$ = enthalpy change (kJ mol^{-1}) in the desorption of water dipoles from the substrate and metal.

$\Delta H_{\text{M-M}}$, $\Delta H_{\text{S-S}}$, and $\Delta H_{\text{S-M}}$ = negative of the dissociation energies, $\text{DE}_{\text{M-M}}$, $\text{DE}_{\text{S-S}}$, and $\text{DE}_{\text{S-M}}$ (kJ mol^{-1}).

$\Delta S_{\text{S-H}_2\text{O}}$, $\Delta S_{\text{M-H}_2\text{O}}$ = entropy change (kJ mol^{-1}) in the desorption of water dipoles from the substrate and metal.

$\Delta S_{\text{S-M}}$ = entropy change (kJ mol^{-1}) during the S–M bond formation.

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- (44) Although the notations θ_b and θ_l in the context of UPD is somewhat confusing in view of their magnitude being greater than 1, we have resorted to their usage to maintain consistency with the notation of ref 41.
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