# An overview of Electron Transfer Processes at Electrochemical Interfaces - Theoretical Studies and Experimental Validation

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**Abstract:** The present status of the theoretical analysis pertaining to the equilibrium properties of the metal/electrolyte interfaces is pointed out with the emphasis on several un-resolved issues. The semi-phenomenological estimation of the exchange current densities in terms of the parameters pertaining to the metal, solvent and reactant is indicated. The importance of liquid/liquid interfaces in the chemical and electrochemical synthesis of nanomaterials is highlighted. The electrochemical reduction of carbon-halogen bonds using convolution potential sweep voltammetry is discussed.

**Keywords:** Electron transfer; interfaces; electrical; double layer

## 1. Introduction

The analysis of any electrochemical systems is focussed towards two central themes: (i) interfacial potential distribution and (ii) kinetics of charge transfer. The former aspect customarily designated as the electrical double layer theory has a chequered history, commencing from the Lippman equation to the modern-day density functional theories. The latter aspect *viz* kinetics of electron transfer processes is often based on the classical Butler-Volmer equation or its phenomenological and microscopic variants. It is of interest to note that the de-coupling of double layer theories from electron transfer formalism is not possible since the interfacial potential distribution influences the rate constant as well as the symmetry factors of charge transfer reactions.

This manuscript will provide an overview of the equilibrium properties of electrified Interfaces and electron transfer processes from diverse perspectives. Since research on these topics continues to be expanding in a dynamic manner, the emphasis herein is on a few topics wherein more extensive studies are warranted.

## 2. Electrical Double layer theories

The preliminary version of the electrical double layer consists of the postulate of the inner and diffuse layers spanning the entire interfacial region. More sophisticated approaches invoke a multilayer model of the interface wherein the electrostatic equations are formulated and solved self-consistently for deducing the dipole potential and differential capacitance.

### 2.1 Solvent structure at electrode/electrolyte interfaces

The early experimental emphasis pertaining to the potential distribution at metal/electrolyte interfaces began with the electrocapillary and differential capacitance measurements of Hg/NaF interfaces, obviously on account of their strict compliance with the non-polarizable nature. The point of interest in these studies was on the temperature-dependence of the potential of zero charge and location of the potential at which the maximum in the differential capacitance arises. These are direct quantitative measures of the organisation of water diploes at Hg

electrodes. Since the interfacial dielectric constant of water has to be substantially different from that at the bulk, quantitative models of dipolar liquids in conjunction with hydrogen bonding became non-negotiable. Recalling that a quantitative fundamental understanding of bulk water from first principles is still lacking, the difficulties pertaining to the study of water structure at electrode/electrolyte interfaces can be comprehended. The classical review by Grahame in 1947 [1] on the solvent structure at electrochemical interfaces is a valuable source of information on account of its critical summary of the experimental patterns for Hg/NaF interfaces under various 'control variables'. This review of Grahame has been cited ~ 4100 times and is considered as a 'historic paper'.

During the past few decades, the experimental data pertaining to the modelling of solvent structure has been carefully acquired on many polycrystalline and single crystal surfaces. These have now provided a platform for the study of interfacial water at a variety of electrodes. In a simultaneous manner, the advent of density functional theories has made the task of electrochemists simpler by incorporating electronic structure of metals into the classical electrostatic theory of electrical double layer. Table 1 provides a partial list of potential of zero charge (pzc)of different metal/electrolyte interfaces. While the work function pertains to metal/vacuum interfaces, the pzc values are pertinent for metal/electrolyte interfaces. However, a linear correlation of the pzc with work function has been deduced [2].

**Table 1 – Potential of zero charge values for a few metals (For brevity, the electrolyte is not indicated)**

| System | Potential of zero charge (V vs SHE) |
|---|---|
| Bi | - 0.39 |
| Ni | - 0.33 |
| Co | - 0.43 |
| Sn | - 0.38 |
| Pb | - 0.60 |
| Cd | - 0.75 |
| In | - 0.65 |
| Cu | -0.73 |

The most pioneering work of including the local density approximation (viz *jellium* models) into the electrical double layer theories should be ascribed to Schmickler [3] in view of the first systematic approach for the study of metal-dependence of the electrical double layer properties. A careful delineation of the contribution of the metal to the interfacial capacitance was carried out, by extending the rigorous analysis of Smith [4] pertaining to the estimation of the work function of about 40 different metals. The trial function employed by Smith for the electron density profile n(z) at metal/vacuum interface is as follows:

$$n(z) = n_{+} [\, 1 - (\tfrac{1}{2})\, e^{-\alpha z}] \text{ for } z>0 \quad (1)$$

$$n(z) = n_{+} (\tfrac{1}{2})\, e^{\alpha z}] \text{ for } z < 0 \quad (2)$$

with $n_{+}$ being the bulk electron density of metals. The parameter α is a measure of the extent of spill over of the electron density. Other versions of the trial functions with inclusion of pseudopotentials have also been postulated. Using a self-consistent approach, Leiva and Schmickler [5] were able to estimate the contribution offered by the metal surface alone to the measured differential capacitance.

To mark the occasion of the completion of nearly 50 years of Grahame's article, a critical review by Schmickler highlighting the progress and prospects of interfacial electrochemistry has been published in Chemical Reviews[6]. It should be emphasized that despite the availability of sophisticated computational tools, only a partial understanding of the interfacial solvent structure is rendered feasible. This signifies that the satisfactory incorporation of various interfacial interactions, mediated by the external electric field is indeed a formidable task. There is a need for entirely new concepts and analysis.

While the statistical thermodynamic approaches in conjunction with density functional calculations do provide a satisfactory framework in comprehending double layer data of single crystalline and polycrystalline surfaces, an alternate view has been expounded by Groβ in a recent perspective article [7].The subtle distinction between potentials of reversible hydrogen electrode (RHE) and standard hydrogen electrode(SHE) has been highlighted using cyclic voltammetric data by Feliu et al. [8] of Pt(111) in KBr solutions**.** The need for an atomistic view point

of the electrode/electrolyte interfaces in contrast to the thermodynamic-inspired formalism has been emphasized.

## 2.2 Adsorption of ions and organic compounds

Since the corrosion inhibition is often accomplished by coating the electrode surface with the appropriate inhibitors, studies on the adsorption of species occupy a pivotal role in electrochemical technologies. In contrast to the adsorption of gaseous species at different surfaces, electro sorption is governed by (i) the replacement of solvent molecules by the ionic or organic adsorbate (ii) potential-dependence of the adsorption equilibrium constants and (iii) occurrence of two-dimensional phase transitions. Hence, the formulation of adsorption isotherms at electrode/ electrolyte interfaces warrants new approaches with satisfactory incorporation of adsorbate-adsorbate, adsorbate-solvent, solvent-solvent, electrode-solvent and electrode-adsorbate interactions.

In this context, two different approaches can be envisaged viz. from (a) the two-dimensional equation of state and (b) system Hamiltonian. The option (a) is often employed to derive the adsorption isotherm since there is a direct prescription to deduce the adsorption isotherm from the two-dimensional equation of state [ 9]. It is well known that the ideal gas equation of state corresponds to Langmuir adsorption isotherm. The most celebrated adsorption isotherm almost often employed by electrochemists is the Frumkin isotherm derived in 1925 [10]viz

$$\frac{\theta}{1-\theta} = \beta(E) C_{ads} e^{-2a\theta} \qquad (3)$$

where $C_{ads}$ denotes the bulk concentration of the adsorbate relative to that of the solvent; the adsorption equilibrium constant β is a *quadratic* function of the applied potential (E) and the magnitude of the Frumkin constant ('a') is a parameter describing the intermolecular interactions. Its value has important implications regarding the onset of two-dimensional condensation of organic adsorbates.

The wide applicability of the Frumkin Isotherm (FI) for ions as well as neutral organic compounds bears testimony to its validity; nevertheless, its molecular interpretation has remained elusive till recently. In order to overcome this limitation, microscopic modelling using two-dimensional Ising models has been accomplished [11] leading to a statistical mechanical interpretation of FI and quantitative interpretation of two-dimensional condensation of organic adsorbates (adenine, uracil, thymine, camphor-10-sulphonic acid etc). The signature of two-dimensional condensation of neutral organic compounds consists in the occurrence of the 'capacitance pit' in the differential capacitance-potential plots at electrode surfaces [12]. The onset of a sudden discontinuity in the surface coverage vs potential plots indicates the occurrence of condensation. The critical properties of the interfaces can be analysed using any of the three control variables viz (i) bulk concentration of the adsorbate;(ii) electrode potential and(iii) temperature.

## 2.3 Ising model formalism for electrosorption

The usefulness of the two-dimensional Ising (or lattice gas) models whose Hamiltonian is given below

$$H_T = -\frac{H}{2}\sum_{\langle i \rangle} s_i - \frac{J}{4}\sum_{\langle ij \rangle} s_i s_j \qquad (4)$$

plays a crucial role in this context. Within a two-state version where the spin variable $s_i$ can assume either +1 or – 1, the above Hamiltonian has the ability to provide an unified description of various interfacial processes.

In the case of adsorption of organic compounds at electrode surfaces, the parameter 'H' in the above eqn consists of the chemical potentials μ(org) and μ(water) while 'J' is a composite parameter, comprising the solvent-solvent($J_{ss}$), adsorbate-solvent ($J_{as}$) and adsorbate-adsorbate ($J_{aa}$) interaction energies. Under typical mean field approximation, H may be deduced as [11]

$$H \approx \Delta\alpha(\langle\xi\rangle)^2 + \Delta p\langle\xi\rangle + \mu(org)\text{-}\mu(water) \qquad (5)$$

Δα denotes the difference in the polarizabilities of the organic adsorbate and solvent molecules, while "p denotes the permanent dipole moment differences in an analogous manner. <ξ> denotes the mean field whereby the decoupling between various spins has been accomplished using an average 'electric field'. The Frumkin interaction constant 'a' of eqn (3) is directly proportional to the nearest neighbour interaction energies. Table 2 provides the critical(condensation) temperature of a few typical

adsorbates exhibiting two-dimensional condensation at Hg/NaF interfaces. The critical temperatures vary from 260 to 320 K in general.

**Table 2 – Typical adsorbates undergoing two-dimensional condensation at mercury electrodes**

| Adsorbate | Condensation Temperature (K) | Ref. no. |
|---|---|---|
| Camphor | 322 | [13] |
| Coumarin | 308 | [14] |
| Uracil | 294 | [15] |
| 5-nitrocytosine | 278 | [16] |
| 5-methylcytosine | 305 | [17] |

Onsager's exact solution [18] of two-dimensional nearest neighbour Ising models provides an explicit relation between the interaction energy $J_{nn}$ and critical temperature $T_c$ viz

$$\sinh (2J_{nn}/ kT_c) = 1 \quad (6)$$

for square lattices. The above eqn is of extreme significance since it enables the theoretical prediction of the critical temperatures of the organic adsorbates, if nearest neighbour interaction energies ($J_{nn}$) are ferreted out from density functional calculations or spectroscopic data. This has been accomplished for predicting the critical temperatures of a few organic adsorbates at Hg/NaF interfaces [19] using the molecular parameters of the adsorbate and solvent dipoles.

### 2.4 Electrical double layer at liquid/liquid interfaces

While the classical Gouy Chapman models were extensively pursued for metal/electrolyte interfaces, the analysis of the potential distribution between immiscible electrolyte solutions caught the attention of researchers on account of its significance in ion transport across membranes and synthesis of nanostructured materials.

It is customary to assume sharp and diffuse boundary models for the potential distribution. The terminologies of sharp and diffuse boundary essentially refer to the crossing of the species viz a sharp boundary assumption implies that the reactants or species present in one (aqueous) phase cannot cross over to the other (organic) phase.

The diffuse layer models pertaining to metal/electrolyte interfaces can be extended in this case as a zeroth order approximation. The major difference in the case of electrical double layer at L/L interfaces is the thickness and it is customary to assume different types of trial functions for the variation of the density profiles with interfacial thickness for solvent mole fractions [20].The subsequent minimisation of the Helmholtz free energy in conjunction with the interfacial dielectric constant profile leads to theoretical construction of differential capacitance plots of various L/L interfaces e.g. water/dichloroethane, water/hexane, water/dimethylformamide, water/acetonitrile, etc.

## 3. Electron transfer reactions at electrode surfaces

### 3.1 New perspectives into the Butler-Volmer equation

#### *(a) Phenomenological thermodynamics*

The theoretical and experimental study of electron transfer processes at metal/electrolyte interfaces is often centred around the Butler-Volmer (B-V) equation (also referred to as Erdey-Gruz-Volmer equation). Its phenomenal success lies in the ease with which the two crucial parameters viz standard exchange current density and symmetry factor can be extracted from any steady state or transient electrochemical techniques.

It is of interest to note that the exchange current density is related to the standard heterogeneous rate constant (kinetic parameter) while the symmetry factor is associated with the activation energy ('thermodynamic property'). While Tafel polarization was the preferred technique initially to extract these two quantities, the present-day experiments make use of either the Electrochemical Impedance Spectroscopy or Convolution Potential Sweep Voltammetry.

The pedagogical formulation of the B-V eqn starts with the expressions for the anodic and cathodic current densities in terms of the Gibbs free energies. The most fascinating feature of B-V eqn is its ability to yield Nernst eqn and Tafel eqns as limiting cases. Despite its popularity, the B-V eqn has the following shortcomings: (i) explicit dependence on the nature of the electrode;(ii) role of the solvent molecules on the kinetic parameters;(iii) limited applicability for electron transfer reactions of organic compounds; (iv) dependence of the symmetry factor on electrode potentials and (v) lack of any rigorous microscopic derivation.

In order to partially overcome the above limitations, a phenomenological thermodynamic approach has been advocated by including quantitative parameters for the interfacial dehydration of reactants, work function of the metals, desorption of the solvents. The resulting eqn for the exchange current density is given in [21]

$$\ln [i_o] = \text{constant} + [-\Delta G_{desor}/aRT - F\chi_r/RT + FX\Phi_M/RT] \quad (7)$$

where the quantitative parameters pertaining to the solvent dipoles (Gibbs free energy of desorption $\Delta G_{desor}$), ionic reactant (surface potential $\chi_r$) and electrode surfaces (work function $\phi_M$) have all been included, thus enabling the computation of the exchange current density in an effortless manner.

Its validity for the experimental data on hydrogen evolution reaction and interpretation of the volcano plots has been discussed [21].

### *(b) Statistical and non-equilibrium Thermodynamics version of the Butler-Volmer eqn*

An entirely new perspective on B-V eqn has been provided by Keizer [22] employing the concepts of non-equilibrium statistical thermodynamics in conjunction with a canonical rate process. A complimentary approach for the B-V eqn arises by employing Onsager's non-equilibrium thermodynamics concepts which yields the Onsager's phenomenological coefficient as well as rate of entropy production for electrochemical reactions. Onsager's phenomenological coefficient L is related to $i_0$ as [ 23]

$$L = \frac{i_0}{RTnFA} \quad (8)$$

where A denotes the area of the electrode. A notable feature of the above is that L is a constant, independent of the driving force and hence, the prediction of the exchange current density at any temperature becomes feasible. Also, the entropy production of any electron transfer reactions at electrodes can be estimated effortlessly, using the linear flux-force formalism of Onsager [24].

### 3.2 Electron transfer at Liquid/Liquid interfaces

The field of Liquid/Liquid (abbreviated as L/L) interfaces continues to be a frontier area of research on account of its immense implications in electrocatalysis, analytical and medicinal chemistry and biosensors. The electron and ion transfer processes at L/L interfaces involve many fascinating aspects such as(i) potential distribution;(ii) nature of the boundary;(iii) validity of Gouy-Chapman theory;(iv) nature of the dielectric profile and (v) influence of the interfacial thickness.

Interestingly, the earlier-mentioned phenomenological and non-equilibrium thermodynamic approaches are applicable *mutatis mutandis* to electron transfer at L/L interfaces, as a zeroth order approximation. Furthermore, the methodology that led to the molecular interpretation of the B-V eqn has directly been applied to compute the exchange current densities assuming both sharp [25] and diffuse [26] boundary versions for the interfacial region. A qualitative agreement with the experimental rate constants has indeed been obtained, for various redox couples in the aqueous and organic phases. The major difficulty in this thermodynamic calculation is the magnitude of the solvation numbers pertaining to the redox couples in the bulk and at the interface. Figure 1 schematically depicts the various parameters involved in the electron transfer processes at L/L interfaces.

The work terms are denoted as $W_{r1}$ and $W_{r2}$ pertaining to the two reactants and analogously for products. The solvation number of the reactant in each phase is denoted as $SN^{bulk}$. The diminished solvation numbers at the interface are represented as $SN^{inter}$ and these need to be calculated in a self-consistent manner.

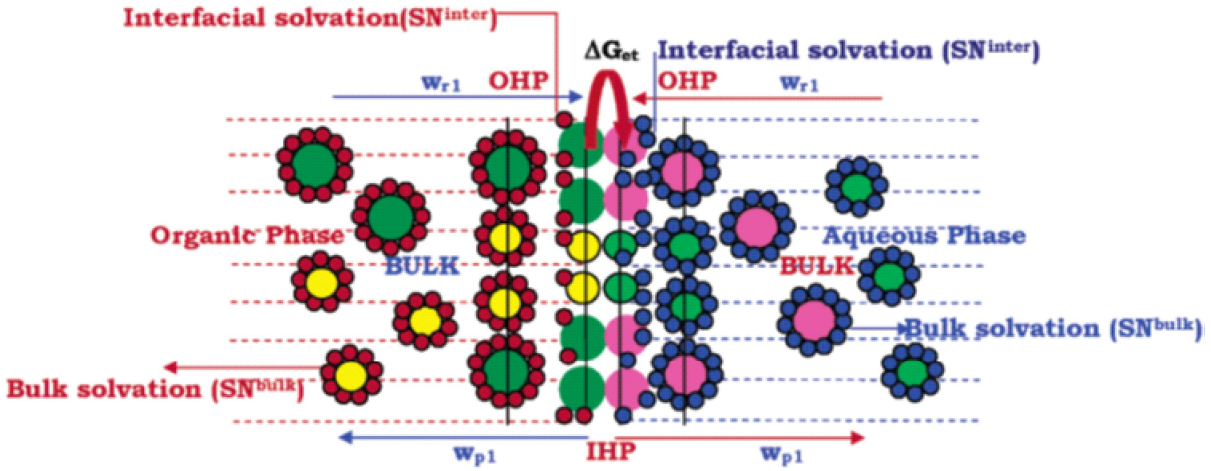



**Fig 1: Electron transfer at L/L interfaces using a sharp boundary model [25]. IHP and OHP denote respectively, the inner and outer Helmholtz planes. Reproduced with permission from American Chemical Society Copyright 2004**

An important milestone in this context was achieved by Marcus [27] whereby the electron transfer rate constants at L/L interfaces can be predicted using the corresponding data at the homogeneous phases or at electrode surfaces. While a qualitative trend arises from Marcus theory for a few redox couples, the quantitative agreement is still lacking.

It is imperative at this stage to point out a subtle difference between electron transfer at metal/electrolyte and L/L interfaces [28]. In the former, the potential between working and reference electrodes is controlled and the current is recorded in voltammetric experiments. On the other hand, at L/L interfaces, the potential is controlled between two reference electrodes, the steady state or transient current being measured between the two counter electrodes. Hence, it was customary to employ 'four-electrode assemblies' in *early* studies of voltammetry at L/L interfaces.

### 3.3 Novel Synthetic protocols using L/L interfaces

During the past few decades, the scope of L/L interfaces has been considerably expanded, especially for the preparation of diverse nanostructured materials [29] as well as conducting polymers [30]. The two pioneering works in this context are (i) synthesis of thin films of Ag,Au and various metal oxides and chalcogenides[29]and (ii)a simple and facile synthesis of nanostructured polyaniline at various L/L interfaces[30].

An entirely novel concept has recently been explored for the synthesis of nanostructures of conducting polymers ***'using'*** L/L interfaces in contrast to the hitherto-existing synthetic protocols ***'at'*** L/L interfaces. This approach has been demonstrated for obtaining diverse morphologies of conducting polymers such as polyaniline, polyindole, polythiophene, polypyrrole etc, almost effortlessly [31]. This can be termed as 'triple diffuse layer' methodology in view of the two diffuse layers existing at the organic/aqueous phases in addition to the Gouy Chapman diffuse layer at metal/electrolyte interfaces [31].

The three diffuse layers in Fig 2 are between (i) the electrode/electrolyte (stainless steel/aqueous $LiClO_4$) and (ii) the two immiscible electrolyte solutions (Tetra butyl ammonium perchlorate (org.) /lithium perchlorate (aq). Here, the surfactant sodium tetradecyl sulphate plays the role of a molecular pump in transporting aniline from one phase to another.

## 4. Electron transfer reactions of organic compounds

As mentioned earlier, the issues involved in the electron transfer processes involving organic compounds are entirely different. In the context of electro-organic reactions, the elucidation of the reaction mechanism (stepwise or concerted) and selective reduction (or oxidation) of reactants become a central issue. For unravelling the reaction mechanism, a commonly employed technique is the convolution potential sweep voltammetry (CPSV)

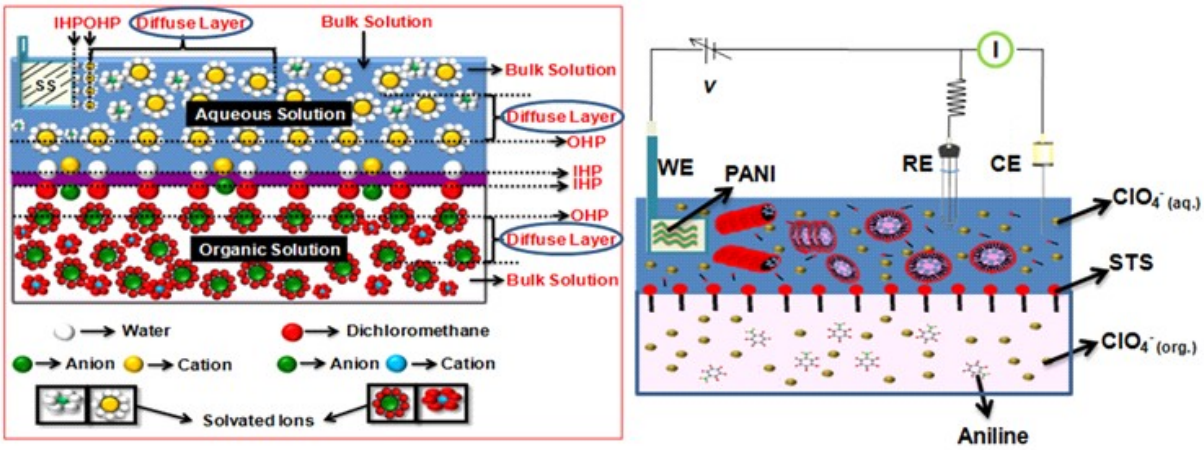



**Fig 2: Triple diffuse layer methodology for the synthesis of polyaniline on stainless steel electrode, in the presence of the surfactant sodium tetradecyl sulphate [ after ref. 31]**

where the scan rates ranging from millivolts per second to megavolts per second are customarily applied. This impressive feature is an outcome of the convolution techniques wherein all the cyclic voltammograms at various scan rates can be superimposed as a 'master curve'. Furthermore, it is straightforward to distinguish between the step wise and concerted mechanisms of various types of organic compounds.

While a variety of oxidation and reduction reactions can be studied using CPSV, its impressive features get unravelled when organic compounds with different functional groups are present in the molecule. Interestingly, in the case of 5-bromo-1,3-dichloro-2-iodobenzene ,the distinct peaks pertaining to various carbon-chlorine, carbon-bromine and carbon-iodine bonds can be deciphered

[32] as shown in Fig 3. The reduction mechanism of carbon-halogen bonds in halopentafluorobenzenes has also been analysed using Convolution Potential Sweep Voltammetry [33].

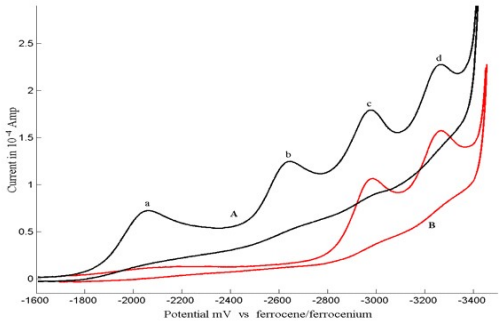



**Fig 3: Cyclic voltammograms of (A)5-bromo-1,3-dichloro-2-iodobenzene and (B)1,3 dichlorobenzene in dimethylformamide and 0.1 M $n$Bu$_4$NBr at the glassy carbon electrode. scan rate = 200 mVs$^{-1}$[32] Reprinted with permission from Elsevier (Copyright 2004)**

## 5. Summary

The salient features pertaining to the equilibrium properties of the metal/electrolyte and liquid/liquid interfaces are pointed out. The issues underlying the theoretical analysis of electrical double layer are pointed out. The composition of the exchange current density in terms of the parameters pertaining to the metal, solvent and reactant is highlighted. The importance of liquid/liquid interfaces in the synthesis of nanomaterials is indicated. The electrochemical reduction of carbon-halogen bonds using convolution potential sweep voltammetry is pointed out.

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