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Non-adiabaticity in Electrochemical Reactions

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We consider the effects of nonadiabaticity on electron and proton transfer reactions at a metal electrode. We use simple model hamiltonians for the description of processes. The continuem of electron-hole excitations is accounted for by treating them as bosons. Non-adiabaticity is found to modify the rates. In the case of proton transfer, we consider the tunelling of a proton from H_3O^+ in water to the surface of a metal electrode and calculate the tunelling probability using the semi-classical approaches. We show that typically, tunelling probability can be decreased by one to two order of magnitude by non-adiabaticity.

Design and Fabrication of a Simple, Inexpensive Scanning Tunneling Microscope

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Scanning Tunneling Microscope (STM) has become indispensable tool for surface characterisation and studies involving absorption and monolayer formation on metals. However the commercial STMs are quite expensive and very few laboratories can afford to own one. In Raman Research Institute, a simple and inexpensive STM has been designed and fabricated.

In scanning tunneling microscope, the tunneling current between a sharp probe (which is usually an electrochemically etched Pt-Ir or W wire) and the flat sample is measured while the surface of the probe is rapidly scanned over by a piezo element, at distance of about 1 mm or less (called tunneling range). The tunneling current is extremely sensitive to separation between the probe and the sample - varying by one order of magnitude for every 0.1 mm change in the gap separation. This current is amplified and measured to gather topographic information. This method of collecting image data is called **constant height imaging**. In yet another mode of operation, known as **the constant current imaging**, the measured current is fed back to the scanning piezo controller in order to maintain the gap separation constant and aquire the topographic image from the feedback voltage.

In this STM, the course positioning of the tip close to the sample is accompanied by a motorless mechanism known as slip-stick or inertial positioning mechanism. The fine positioning is accomplished using piezo tubes controlled by high voltage amplifiers. Using the STM, images of nm resolution has been achieved in real time data aquisition. Image processing of the raw data obtained by scanning highly oriented pyrolytic

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graphite shows atomic scale features. Further work is on to improve the system to gather atomic scale image in real time.

Scanning Tunneling Microscopy (STM) Currents in the Presence of Chemisorbates

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The influence of chemisorbates on the STM current at electrochemical interface is elucidated. The potential and temperature dependence of the current are analysed. It is shown how such studies are relevent for distinguishing weak chemisorption from the strong one. Finally a comparative study between the adsorbate mediated Faradaic and STM currents are provided.

Surface Modification Technologies

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Surface Engineering relates to modification of surfaces by coating or by other methods to improve surface properties and thereby enhance life / performance of components. The surface engineering group of NAL has been active in this area for the past 25 years and has successfully developed several surface modification technologies. These have been used by industries saving large amounts of foreign exchange. Some of these have contributed to country's self-reliance in strategic and critical area. Soft nickel coated seal discs for nuclear power plant, and passive radiative cooler (used in INSAT series of satellites for IR detector of the IR camera that gives satellite pictures of earth) belong to this category. High efficiency black chromium coating (for solar energy harvesting) saves the country several thousand MW-hr electrical energy. The group has pioneered the development of electrochemical machining technology and has presently demonstrated successfully a cutting machine that combines the advantages of electrochemical machining and arc machining. Two major developments are underway to develop technologies for the manufacture of diamond discs, by electroplating and CVD, for polishing coloured gem stones, which is a large export oriented trade. The science based approach in solving many of the technological problems for getting the desired final product is discussed in detail.

Electroless Nickel

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Electroless nickel is a promising engineering coating with unique properties. Both the process and coating offer specific advantages. The process produces quite uniform coatings even on complex geometries and the coatings can be applied on a variety of substrates with appropriate pretreatment. EN coatings exhibit better corrosion resistance compared to electroplated nickel and has comparable wear resistance as that of hard chromium. Though the process was reported about five decades back, its penetration into the

engineering industries is rather slow. Only recently (within a decade) the facination with EN has turned into industrial excitement in the west. The unique properties are being tapped for a large number of advanced material applications. Aerospace / Aviation, Automotive, Chemical processing, Food processing, Oil & gas, Electronics and a host of other industries have already turned to EN. Development of ternary alloys, EN composites and low phosphorous EN has widened the prospects of EN.

In India, the scenario is not as green as in west, but the awareness about EN has crept into the industrial sector. Though the full potential of EN technology has not been exploited, it is proving to be a rising star in the engineering world. Though the introduction of EN into industries is at a low pace, the situation will improve and EN will find a unique place in the future, if the knowledge and understanding on this special coating penetrates into the industrial sector.

Conductometric Studies on Ion-solvation behaviour of Bromamine-B in various Single & Mixed solvents and Temperatures

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Electrical conductivity measurements is one of the most sensitive and widely used physical methods for the study of behaviour of electrolytes in solutions. Conductance studies of electrolytes in mixed solvents have received considerable attention in recent years. Studies of ion - solvation interactions reflect on ion-solvent interaction, solvent - solvent interactions and a brief idea about solvation numbers, size of solvated ion, the strength of ion-solvent bond, thermodynamics of solvation, etc.

Present paper reports the result obtained in the investigations on the ion-solvation behaviour of N-bromo-N-sodio benzene sulphonamide (Bromamine-B, BAB) in water, various non-aqueous and partially aqueous media from 283K to 313k by conductometry. Data were analysed by various conductivity models to identify limiting conductance, association/ dissociation constants, Walden product etc. Born relations were used to determine thermodynamics of solvation. Solvation number and thermodynamics of rate process are computed. Ionic conductance, ionic mobility and transport number of cation and anion of BAB in the case of pure solvents (water, methanol, acetonitryle and DMSO) are also calculated. From these computed values, it is observed that ion-solvent interaction of BAB is more in DMSO and least in CH_3CN.

Cyclic Voltammetric Behaviour of Silver in Alkaline Medium in the presence of Some azole compounds

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Cyclic voltammetric studies of Silver in 0.1 M NaOH are carried out and the effect of addition of some azole compounds such as

MBT, BTA and BIMD are studied. It was found that these compounds are adsorbed on the electrode surface. This adsorption was studied by two methods:

(i) by adding them directly to NaOH solution
and
(ii) by adsorption onto silver from their ethanolic solutions.

We find that all the three compounds reduce both the cathodic and anodic peak currents of the CV. The extent of suppresion is also dependent on the time of immersion in solution. We have also studied the effct of repeated cycling and different potential ranges on the cyclic voltammograms.

Solvation Behaviour of Potassium Thiocyanate in various Aqueous & Non-Aqueous Solvents and their Mixtures by Conductometry

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Principle of Electrical Conductivity is used in the study of solvtion behaviour of potassium thiocyanate in water, DMF, DMSO and their mixtures at temperature range of 288 - 313K. Even water - dioxane was used as a solvent in the study. The conductance data were analysed by D.H.O., Kraus-Bray and Shedlovsky model. Limiting molar conductance and dissociation / association constants were evaluated for all solvent compositions. The walden product has been determined under all conditions. Stoke's molecular radius was calculated by primitive model (r_s) and Evan's semi-emperical relationship (r_j). Born relations were used to compute thermodynamics of solvation. Activation energy of the rate process is also calculated. These data were used to investigate the nature of ion-solvent and solute-solvent interaction exisiting in the system under prevailing conditions.

Effect of Substituents on the Adsorption of Organic Molecules at the Mercury / Solution Interface

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The adsorption of organic compounds such as Thiophenol, Methylphenylsulphide, Methyl p-nitro phenyl-sulphide and Methyl p-tolyl-sulphide have been studied at mercury / solution interface using 1M NaCl as the base electrolyte. It is found that all the compounds are adsorbed more on the positively charged mercury surface. Thermodynamic parameters like charge on metal surface (q_m), surface excess of organic molecule adsorbed (Γ_{org}), surface coverage (θ) and free energy of adsorption ($-\Delta G$) have been evaluated. It is found that the various substituents present in the organic

molecules influence the extent of adsorption. The order of adsorption among the compounds being Methyl p-tolyl-sulphide > Methyl phenyl-sulphide > P-Nitro phenyl-sulphide _ Thiophenol

The adsorption characterics of all these compounds can be explained using only the Langmur's adsorption isotherm.

Influence of Anions on the Adsorption of Thiophenol at the Mercury/Aqueous Interface

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Electrocapillary curves for 1M solutions of NaCl, $NaNO_3$ and Na_2SO_4 in the presence of different concentrations of thiophenol show that the compound is adsorbed more on the positively charged metal surface. The extent of adsorption from these base electrolytes follows the order Na_2SO_4 > $NaNO_3$ > NaCl. Thermodynamic parameters like charge on the metal surface(q^M), surface excess or organic molecules adsorbed (Γ_{org}), surface coverage (θ) and free energy of adsorption ($-\Delta G$) have been evaluated and presented. The adsorption of thiophenol at the mercury / solution interface obeys Langmuir's adsorption isotherm in all cases, irrespective of the nature of the base electrolyte used.

Electrochemical Growth Behaviour of Poly Diphenylamine

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The electrochemical growth behaviour of poly diphenylamine film was studied under varying experimental conditions such as different concentrations of diphenylamine (DPA) and number of cycles using cyclic voltammetric experiment at a constant scan rate of 100 mV/Sec. The anodic peak potentials remain totally unaffected with increase in the number of cycles for the polymerisation with any concentration of DPA in the range of 10 mM to 50 mM. The anodic peak current values for the well defined second redox process increase progressively with increase in the number of cycles for any fixed [DPA]. Using the anodic charges obtained from the cyclic voltammograms recorded during the polymerization of DPA for 5, 10, 15 and 20 cycles and for different concentration of DPA, a growth expression was deduced.

Pulse Potentiostatic Electrochemical Polymerization of Diphenylamine

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The electrochemical polymerization of diphenylamine was carried out by pulse

potentiostatic method on platinum working electrode in aqueous sulphuric acid mediun under different experimental conditions. Polymerization was performed by varying the switching potentials and pulse widths. Polymer was grown on platinum working electrode in aqueous sulphuric acid medium for various number of pulses also. A close comparison of electrochemical growth behaviour was made between the electrochemical polymerization of diphenylamine through cyclic voltammetry and pulse technique.

Electrochemical Studies of Mangesium - The Effect of Addition of Aluminium

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The use of magnesium as a battery anode is gaining importance due to its comparatively higher negative electrode potential, higher energy density and higher abundance than the commonly used battery anode materials. Aluminium addition is reported to promote the formation of finer granular sludge which is less adherent to magnesium surface. So, for most of the battery applications, magnesium is alloyed with aluminium.

A systematic investigation was carried out to understand in detail the effect of alloying magnesium with aluminium, by preparing various binary Mg-Al alloys and carrying out the following studies in sodium chloride electrolyte:

a. Open circuit potential - time studies;
b. Polarisation studies;
c. Anode efficiency and
d. Impedance studies.

The results of the investigation are presented in this paper. The studies indicate that alloying magnesium with aluminium does not improve the open circuit corrosion behaviour of magnesium. The faradaic efficiency at various current drains increases with addition upto 3% aluminium and then decreases with further addition of aluminium.

Studies on Ion Plating of Brass Watch Case Parts

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The study deals with experimental investigations pertaining to the **ION GOLD PLATING OF BRASS base metal components** (such as watch case parts) with suitable undercoats, for the decorative applications. Besides, the high hardness and increased wear resistance property of PVD coating of TiN (which has been extensively used in engineering applications -tools- thus far) has been studied in connection with this work for effective application for decorative purpose.

The experimental work consists of preparation of undercoats of Nickel or Pd-Ni or Gold or in combination to different base metals. PVD of TiN/ION GOLD plating

over the various undercoats were carried out to the same extent. The reproducibility of results were checked. The parameters chosen for **ION GOLD PLATING <IGP>** were in conformity with those reported in the literature.

The watch cases coated differently were subjected to various test methods as per the standards - mainly to ascertain adhesion, corrosion and wear.

a. The adhesion test were conducted by tape and thermal shock methods.

b. Corrosion resistance was assessed by means of porosity, synthetic perspiration, synthetic sea water and CASS test.

c. The wear resistance is determined by tumbling, lapping and buffing methods. For the purpose of lapping wear, a small reciprocating test fixture was fabricated during the study.

In each case, the results of IGP are compared with **Conventional Gold Plating <CGP>**.

The test performance characteristics was observed in coating system comprising Electroplating of bright nickel, flash gold followed by palladium nickel (consists of 80% Pd and 20% Ni) of 2 to 3 micron thickness and then Ion cating of 0.5 micron TiN and 0.1 micron gold.

The colour, appearance, reflectivity and adhesion of finishes by IGP matches well with the CGP. Corrosion resistance of IGP under severe test condition was found better than CGP. The wear resistance performance of IGP is far superior to CGP and therefore opens an interesting avenue of decorative high hardness with low thickness coating system.

It is also observed that there is substantial cost saving with the added value of better performance characteristics in Ion Plating as compared to the conventional gold plating. It is also interesting to note that ion gold plating is considerably less hazardous, less polluting and hence an environmenmental friendly process.

Economical Alternatives for Nickel Free Gold Coatings

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The study pertains to the selection and investigation of suitable process for **nickel free gold plating** for decorative applications. The study has been prompted due to the impending ban by European union countries *on Nickel and Nickel containing coatings* (due to the Skin Contact Allergy) for applications in jewellary and watch parts. Various processes comprising of acid copper, acid tin, palladium and gold undercoats have been studied, with respect to its performace characteristics such as adhesion, corrosion and wear resistance on watch cases of brass base and zinc base metals.

Adhesion is evaluated by Tape test, Thermal Shock and Bend test. Corrosion resistance testing and rating are done by Porosity test and Synthetic Perspiration test conforming to ISO 3160.

Wear resistance is evaluated by a novel method by which both corrosion and wear are simultaneously evaluated.

The economy of various processes are discussed for suitable adoptation.