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Inverse Photoemission Spectroscopy at the Pt/Acetonitrile Interface with Several Redox Couples

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Ten compounds with standard reduction potentials ranging from −0.60 to −2.22 V vs. SCE were used to study the inverse photoemission (IP) from a platinum electrode in MeCN/0.1 M $TBABF_4$. Only those with standard reduction potentials more negative than −1.90 V vs. SCE (benzophenone, *trans*-stilbene, benzonitrile) produced inverse photoemission. The emission spectra showed a blue shift as the reduction potential became more negative. Control experiments in Me_2SO and double potential pulse experiments make it unlikely that electrogenerated chemiluminescent (ECL) processes are responsible for the emission. The threshold potentials to obtain the IP for those compounds are also reported. The efficiency of the inverse photoemission with the benzophenone system was determined to be about 10^{-7}. The effects of the presence of oxygen and water on emission in this experiment are also described.

Introduction

McIntyre and Sass[1,2] have recently introduced the technique of inverse photoemission spectroscopy (IPS) at the metal/electrolyte solution interface. In this method the oxidation of an anion radical $A^{\bullet-}$ (e.g., of benzophenone) with a redox potential, E_R, at a sufficiently positive potential, E_f, produces very weak emission with an energetic threshold near (within 0.1–0.2 eV) that corresponding to $E_f - E_R$. This emission was ascribed to transitions in the metal as shown schematically in Figure 1. Emission was also observed when a cation radical was reduced at a sufficiently negative potential.[2] Because of our long-standing interest in emission at electrode surfaces in electrogenerated chemiluminescence (ECL)[3] and especially in background processes that set the lower limit of detection when ECL is used as an analytical technique,[4] we have carried out additional experiments on IPS. These have been designed to eliminate the possibility that the observed IPS emission is attributable to very low level ECL, e.g., attributable to impurities or background processes in MeCN.[5] Additionally, we present an estimate of the efficiency of the IPS process and show that for a series of radical anions characterized by different standard (or redox) potentials, only those with a sufficiently negative value of E_R produce inverse photoemission.

Experimental Section

Materials. Most experiments were performed with MeCN/$TBABF_4$ as the solvent–electrolyte system with various redox species. Me_2SO was also used as a solvent to confirm the experimental results in MeCN, since Me_2SO does not produce any background ECL.[5] Although MeCN shows background ECL, MeCN has several advantages over Me_2SO; e.g., it is more easily purified and transferred on a vacuum line. Carefully purified MeCN will not generate ECL until background reduction of MeCN at potentials of −3.0 V vs. SCE.[5]

HPLC grade acetonitrile (Fisher Scientific Co., Fair Lawn, NJ) was purified and dried by continuous refluxing and then distillation from P_2O_5 under nitrogen. The solvent was further dried and degassed by three vacuum distillations over dry P_2O_5 and stored over Super I Woelm alumina N. Electrometric grade tetrabutylammonium tetrafluoroborate ($TBABF_4$) (Southwestern Analytical Chemical Co., Austin, TX) was recrystallized three times from ethyl acetate and then dried in a vacuum oven at 85–100 °C for 36 h. All the redox species were purified by the methods given in ref 6.

Apparatus. Cyclic voltammetric and inverse photoemission (IP) experiments were performed with a Princeton Applied Research (PAR) Model 175 universal programmer, Model 173 potentiostat/galvanostat, and Model 179 digital coulometer. A BAS 100 (Bioanalytical Systems, West Lafayette, IN) electrochemical analyzer was used to generate the normal pulse polarography potential wave in the measurement of IP intensity–potential relations. The IP intensity vs. potential curves were measured through the optical window of the electrochemical cell with a Hamamatsu Model R928 photomultiplier tube (PMT) (available range ca. 200–900 nm). A Nicolet Model 1090 A digital oscilloscope was used to record the photomultiplier tube output during the double potential pulse. A one-compartment electrochemical cell was used in the experiment. Two different kinds of platinum electrodes were used as working electrodes: a platinum disk electrode and an electrode made from platinum film sputtered on a mica substrate (ca. 1 cm^2).[7] A Pt wire auxiliary electrode and an Ag wire quasi-reference electrode (AgRE) were used.

The Ag quasi-reference electrode has the advantage of not introducing traces of water, halide, or alkali metal ions into the test solution. All potentials were later referenced to the saturated calomel electrode (SCE) by observation of the voltammetry of ferrocene in the test solution. Solutions were prepared by transferring solvent under vacuum into the electrochemical cell containing purified and predried $TBABF_4$ and redox species.

IP spectra were taken by using a single-photon-counting system (Pacific Precision Instruments, Concord, CA 94518), RCA Model 31034 GaAs photomultiplier, cooled by Pacific Precision Instruments cooler controller. The photomultiplier output was amplified by a Pacific Precision Instruments amplifier–discriminator and the final output was read as number of photons per second. A lens was used to focus the emission at the electrode onto the inlet slit of the spectrometer to minimize any loss in light intensity. Due to the weak intensity, the spectra were obtained point by point as the average of the emission intensities at each different wavelength (with a set of 16 narrow band interference filters) (Oriel, Stratford, CT); the emission intensity was the average of 8–10 measurements at each wavelength. The IP efficiency was determined relative to $Ru(bpy)_3^{2+}$, the ECL efficiency of which has been determined in several studies.[3b–d]

Results

Several different approaches are possible in IPS. With a given radical ion precursor, A, the potential can be stepped to one negative of the redox potential of the $A/A^{\bullet-}$ couple (E_R) to produce $A^{\bullet-}$ and then stepped to various more positive potentials until emission (within a given range of wavelength, λ) is observed. The

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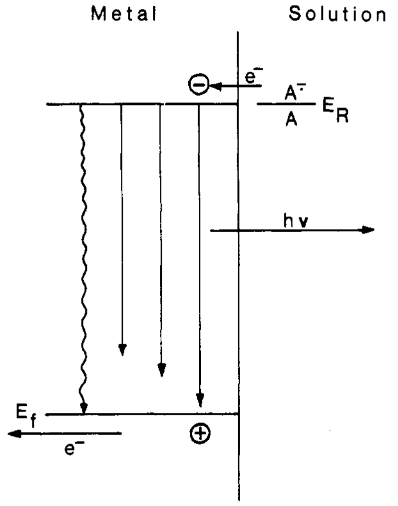

Figure 1. Model of IP process at metal/electrolyte interface.

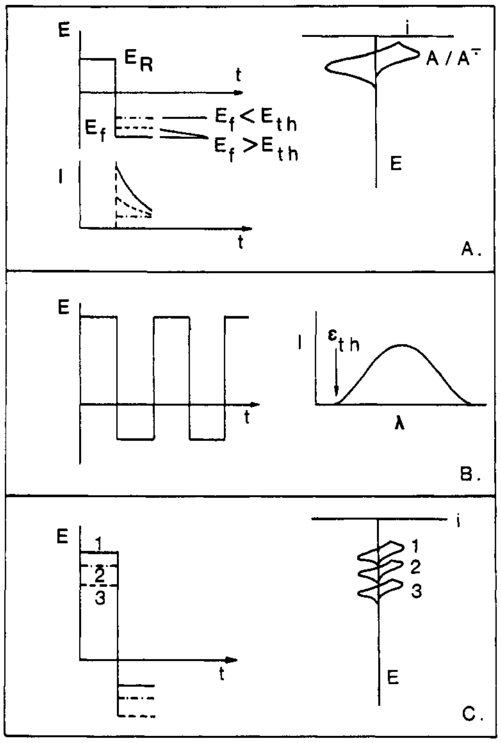

Figure 2. Definitions of (A) E_{th}, (B) ϵ_{th}, and (C) $E_{R,th}$.

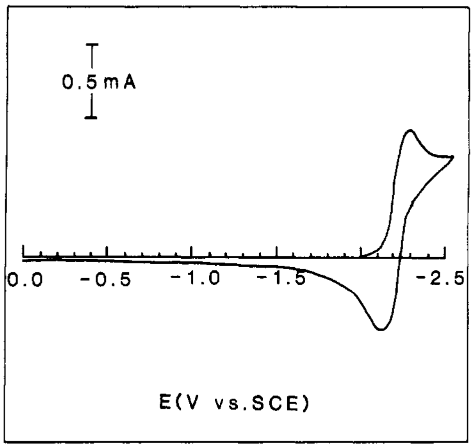

Figure 3. Cyclic voltammogram of 50 mM *trans*-stilbene in MeCN/0.1 M TBABF$_4$. The working electrode is Pt on mica. Scan rate = 100 mV s^{-1}.

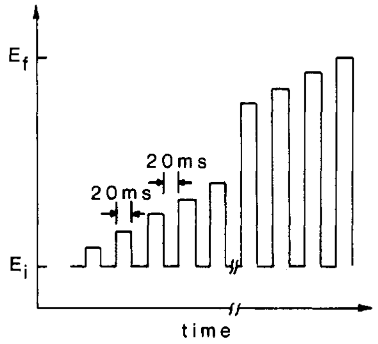

Figure 4. Excitation potential wave for inverse photoemission. In each successive potential step, the potential is changed by 4 mV.

TABLE I

redox couple	$-E°$, V vs. SCE	detection of light	E_{th}, V vs. SCE	E_T,[a] eV
p-dinitrobenzene	0.60	no		
m-nitrobenzonitrile	0.905	no		
p-chloronitrobenzene	0.985	no		
nitrobenzene	1.17	no		
phenazine	1.39	no		
azobenzene	1.42	no		
quinoxaline	1.72	no		
benzophenone	1.90	yes	+0.2	3.0
trans-stilbene	2.17	yes	−0.2	2.0
benzonitrile	2.22	yes	−0.3	3.3

[a] E_T is the energy of triplet state.

threshold potential for this emission is denoted E_{th} (Figure 2A). At any given potential more positive than E_{th}, an IPS spectrum can be recorded. The shortest wavelength (highest energy) emission is the threshold energy,[1,2] denoted here ϵ_{th} (Figure 2B). Finally a series of different precursors of different E_R can be employed. As shown below, for redox couples with E_R more positive than a given value, no emission is produced. We denote this redox threshold as $E_{R,th}$ (Figure 2C). Results of experiments of this type are given below.

Cyclic Voltammetric Behavior. Eleven compounds were used in the inverse photoemission (IP) study at the platinum electrodes: *p*-dinitrobenzene, *m*-nitrobenzonitrile, *p*-chloronitrobenzene, nitrobenzene, phenazine, azobenzene, quinoxaline, benzophenone, *trans*-stilbene, benzonitrile, and pyridine. These were selected because they form reasonably stable radical anions in well-defined voltammetric waves and do not luminesce strongly in the visible region. This latter property is important in the elimination of the possibility that solution redox processes of the type that occur in conventional ECL will lead to emission via the formation of A*. All these compounds undergo Nernstian one-electron reduction at different potentials on the platinum electrode in rigorously dried nonaqueous solvents. A typical cyclic voltammogram of 50 mM *trans*-stilbene in MeCN/0.1 M TBABF$_4$ is shown in Figure 3. In this experiment, the working electrode was a Pt film on mica. All of the redox species used with their redox potentials (defined as the average of the peak cathodic and anodic potentials) are given in Table I. Pyridine is not included in the table, since its standard reduction potential (−2.6 V vs. SCE) is close to the cathodic potential limit of MeCN/0.1 M TBABF$_4$ (−3.0 V vs. SCE).

Although trace amounts of water and oxygen in the solvent influenced the observed emission (see below), such traces usually did not affect the cyclic voltammetric behavior of the redox species, especially since high concentrations of redox species were used in these studies. No adsorption of the redox species was observed for these species at these concentrations (from the shape of the cyclic voltammetric waves).

Observation of Inverse Photoemission. The excitation potential wave shown in Figure 4 was applied to the electrode in an IP experiment. A pulse width of 20 ms was usually used. The initial potential, E_i, was chosen to be negative of the reduction peak potential of the redox species used. E_f, the final potential, was scanned to progressively more positive potentials, and the threshold

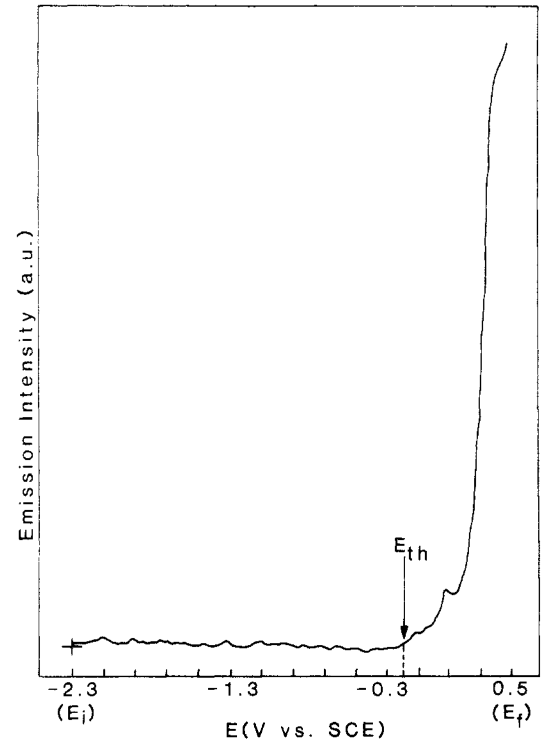

Figure 5. Emission intensity–potential relation. Same system as Figure 3. The emission is the unfiltered response of the photomultiplier tube.

potential, E_{th}, for onset of emission at any wavelength detected with the PMT located. A scan rate of 100 mV/s was used, so the difference in E_f per step was 4 mV. A typical emission intensity (I)–E profile obtained in this manner is shown in Figure 5. As shown in Table I, only benzophenone, *trans*-stilbene, and benzonitrile gave rise to the IP. Pyridine also produced emission, but we felt that its reduction was too close to MeCN background reduction to ascribe the emission unequivocally to IP rather than an ECL process. The other compounds, *p*-dinitrobenzene, *m*-nitrobenzonitrile, *p*-chloronitrobenzene, nitrobenzene, phenazine, azobenzene, and quinoxaline, did not show IP for values of E_f up to the MeCN background oxidation. Thus, species with E_R more negative than about -1.9 V vs. SCE produce IP, while those more positive than -1.9 V vs. SCE do not. Therefore we place $E_{R,th}$ at -1.9 V vs. SCE.

Threshold Potential. For those redox species which do give rise to IP, the positive pulse potential, E_f, must reach a threshold value, E_{th}, which is positive enough to generate IP. We define E_{th} as the potential at which IP appears for the total emission (at all wavelengths below 900 nm), i.e., for unfiltered emission within the range of sensitivity of the PMT, when the pulse potential is scanned in the positive direction. From the emission–potential curve shown in Figure 5 for 50 mM *trans*-stilbene in MeCN/0.1 M TBABF$_4$, with an initial potential of -2.3 V vs. SCE and a scan rate of 100 mV/s, E_{th} was -0.2 V vs. SCE. For $E > E_{th}$, the IP intensity increased sharply. The IP intensity did not continually increase as the potential became more and more positive, however, but declined at more positive potentials ($E >$ ca. 1.2 V). Similar results were obtained for the other redox species that showed IP; the threshold potentials are listed in Table I.

Double Potential Step Experiments. We also investigated the generation of IP by a double potential step, rather than with continuous pulsing, with E_f swept toward more positive potentials. This can be carried out between any two potentials, E_i and E_f, as shown in Figure 6, with *trans*-stilbene. When the potential was stepped to a potential E_i at which the stilbene was reduced for 20 ms and then to a potential E_f (more positive than the threshold potential) at which the reduced stilbene was oxidized back to neutral compound with a large excess potential, emission was detected during the time when $E = E_f$. However, when the potential was first stepped to the positive potential and then to the negative one, no emission was detected. This demonstrates that injection of electrons into the electrode is necessary for the emission to occur and decreases the likelihood that ECL processes of trace solution species are the cause of the emission.

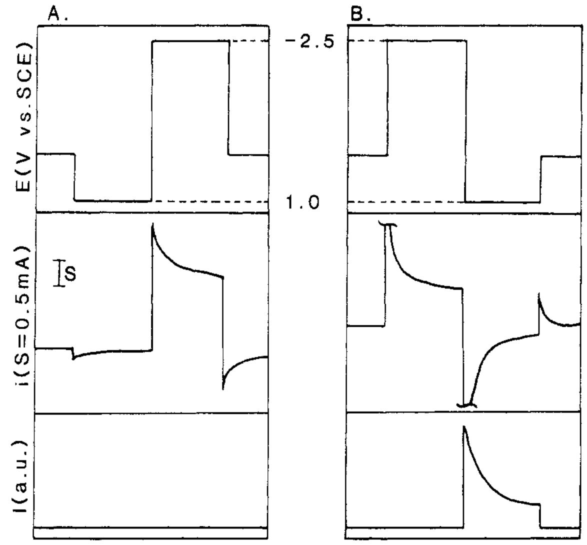

Figure 6. Emission–potential response during double potential pulse. Same system as Figure 3. Pulsing width is 20 mS. (A) Potential steps to positive, then negative; (B) potential steps to negative, then positive.

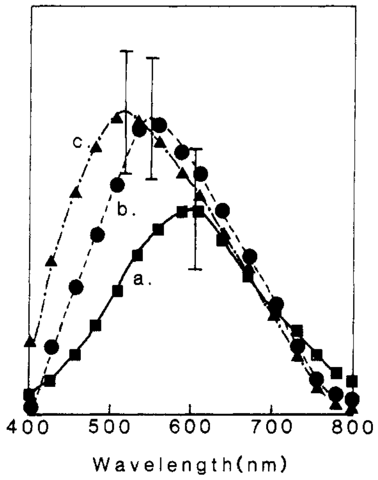

Figure 7. Inverse photoemission spectra for (a) benzophenone, (b) *trans*-stilbene, and (c) benzonitrile. Potential pulses between -2.5 and $+1.0$ V vs. SCE. Points are the average on measurements at each wavelength. The error bars are estimates of the standard deviation.

Inverse Photoemission Spectra. IP spectra were obtained by continuous pulsing of the potential and recording with interference filters and single-photon-counting apparatus. Spectra for benzophenone, *trans*-stilbene, and benzonitrile are shown in Figure 7. All three compounds produce spectra in the visible region. They perhaps show a small blue shift as the redox potential of the species becomes more negative. However, the emission is very weak and accurate peak positions could not be obtained; the spectra were taken point by point with averaging of the intensities at each different wavelength. Two different platinum electrodes were used, a platinum disk electrode and a platinum thin film on mica. The platinum disk electrode has a polycrystalline structure while the platinum thin film on mica has a (111) surface.[7] Both electrodes gave the same emission–potential response.

IP Efficiency. The IP emission intensity was very low in comparison with most ECL processes. The low intensity prevented the direct measurement of IP efficiency (e.g., by actinometry). However, the efficiency (photons emitted per electron transferred at the metal/solution interface) could be estimated indirectly by comparing the benzophenone IP system with ECL of the Ru(bpy)$_3^{2+}$ system (which has a known ECL efficiency of 5%[3]) with the same electrode and cell placement with respect to the photomultiplier tube window. The IP intensity at the same current

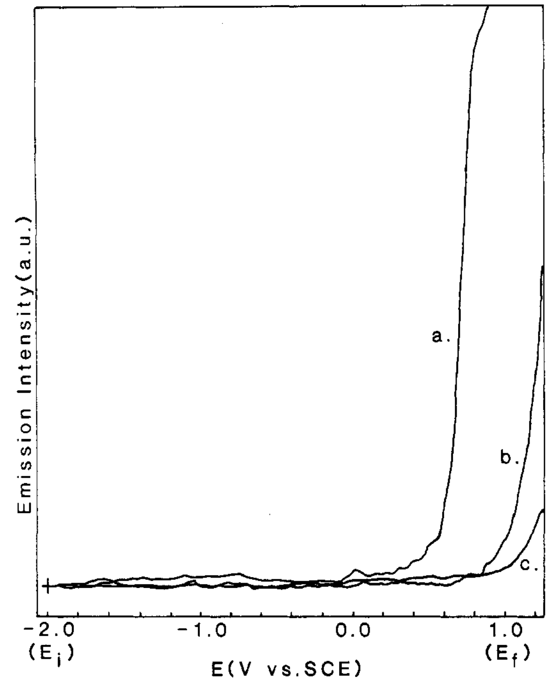

Figure 8. The emission–potential relation of benzophenone in the presence of *trans*-stilbene with different concentrations. (a) No *trans*-stilbene; (b) 25 mM *trans*-stilbene, and (c) 75 mM *trans*-stilbene.

was less than 10^{-5} times that of the ECL, so that we estimate the IP efficiency to be of the order of 10^{-7}.

Some Control Experiments. Several experiments were carried out to ascertain the possible role of solution processes in producing ECL. To examine the role of solvent and solvent impurities, similar experiments on benzophenone and *trans*-stilbene were performed with dimethyl sulfoxide (Me_2SO) with $TBABF_4$ as supporting electrolyte. The IP results were essentially the same as in MeCN. These results are significant because one would expect different impurities in Me_2SO, and Me_2SO does not show a background ECL process while MeCN does.[5] However, the presence of oxygen and water in the MeCN increased the observed emission. In fact, all of the redox species listed in Table I would show emission when the rigorously dried and vacuum-deoxygenated MeCN/0.1 M $TBABF_4$ solution was equilibrated with air (with addition of a drop of water). The process that results apparently involves the reduction of O_2, which occurs at −0.87 V vs. SCE under these conditions. Thus, all of the compounds, except *p*-dinitrobenzene, emit upon reduction and subsequent stepping to more positive potentials. With all of these compounds, setting the initial potential (E_i) at E_R also causes O_2 reduction. With *p*-dinitrobenzene, when E_i is more positive than −0.8 V vs. SCE, no emission was observed. However, when E_i was set beyond the O_2 reduction wave ($E_i < -0.87$ V vs. SCE) emission was detected upon stepping to positive potentials ($E_f > +0.60$ V vs. SCE).

Effect on the Emission of the Benzophenone System by trans-Stilbene. Addition of *trans*-stilbene affected the IP emission of a benzophenone (MeCN, 0.1 M $TBABF_4$) system; the results are given in Figure 8. In this experiment E_i was set at −2.0 V vs. SCE where benzophenone is reduced but *trans*-stilbene is not, and, as before, E_f was pulsed to progressively more positive potentials until emission was observed. Note that addition of 25 mM *trans*-stilbene shifts the E_{th} about 0.4 V toward more positive values, and E_{th} is even more positive in the presence of 75 mM *trans*-stilbene.

Discussion

The results presented here support the findings of McIntyre and Sass[1,2] that electrochemical generation of IP occurs and that low-level ECL processes (e.g., radical ion annihilation, radical ion reaction with impurities) are not solely responsible for the observed emission. Evidence for this is the finding that IP occurs with several nonluminescent or weakly luminescent substances and that it occurs with similar properties with Me_2SO rather than MeCN as a solvent. The emission cannot be ascribed to phosphorescence for several reasons. For both benzophenone and benzonitrile, the emission occurs at wavelengths significantly longer than that corresponding to the triplet energy, E_T. Moreover, all three compounds that show IP have similar emission spectra, while E_T for *trans*-stilbene is much smaller than that of the other two compounds. The double potential step studies also support IP as opposed to an ECL process of an annihilation type. Only when the potential was first stepped to a negative value and then to the positive of the threshold value was emission observed. The opposite potential sequence (first positive, then negative) did not result in emission. A radical annihilation ECL process would usually produce some emission with either sequence. We should note, however, that selective quenching effects or a very unstable reactant generated during the anodic pulse would show an effect similar to that described above, even in an ECL-type process.[8] Thus, electrochemical IPS (or CTRIPS[1,2]) appears to be a useful approach to studies of emission from metals and joins previous studies of IP[9-13] and photoluminescence[14,15] of metals as approaches to study of the metal surface. We might note that the previous IP studies[9-13] involved electron beams of energies in the tens of electronvolts and hence involved considerably more energetic excitation than the McIntyre–Sass IPS experiments. Pendry[9] laid the theoretical foundation for IP and estimated yields of the order of 10^{-8} photons per incident electron. The yield we find here, ca. 10^{-7}, is of the order of this prediction. Since the penetration depth of low-energy electrons is small (e.g., an electron mean free path in a metal of about 5 Å[13]), IPS is a true surface sensitive technique. This, however, implies that the metal energy levels being probed are those at the metal/solution interface rather than those characteristic of the bulk metal, as discussed below.

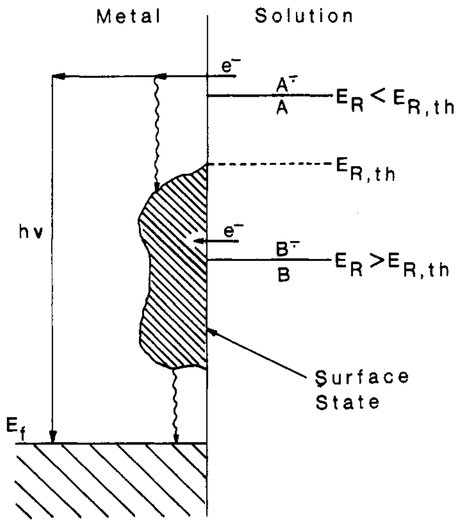

Figure 9. Proposed model and energy-level diagram involving inverse photoemission processes at the metal electrode/electrolyte interface.

A new feature of the work presented here is the existence of a redox threshold, $E_{R,th}$, implying that the energy of the injected electron (proportional to the standard or redox potential of the $A/A^{\bullet -}$ couple) must be above a certain level for IP to occur. To account for this finding, we propose the model illustrated in Figure 9. This involves the location of a distribution of surface states of energies in the region corresponding to potentials more positive

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(8) See, e.g.: (a) Cruser, S. A. and Bard, A. J. *J. Am. Chem. Soc.* **1969**, *91*, 567. (b) Chang, M. M.; Saji, T.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 5399.

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than $E_{R,th}$. Injection from a couple $(B/B^{\bullet-})$ directly into these surface states would lead to more rapid radiationless decay. Only couples $(A/A^{\bullet-})$ above this level would inject electrons that would lead to detectable emission. While we have no evidence for such states in these studies, we might note that previous experimental and theoretical studies of metals have shown the existence of a Shockley-type surface state.[16-18] This type of surface state has been reported for the Pt(111) surface located about 1 eV above the Fermi level.[19] This model is analogous to one that has been applied for studies of electroluminescence at the semiconductor/solution interface upon hole (or electron) injection from a solution species.[20]

Finally we should point out that it may be difficult to assign emission to IP processes unambiguously in many cases, because of the existence of many solution processes that can lead to emission. These include so-called "preannihilation ECL processes" attributed to redox processes involving adventitious impurities.[21] Although IP may be a factor in some of the emission previously reported as preannihilation ECL,[2,22] impurity effects are probably also important. The effects of oxygen and water on the emission seen here illustrate this problem. Chemiluminescence frequently is observed for processes involving oxygen or hydrogen peroxide in alkaline solution.[23,24] Very low level emission was also reported[25] at a Pt electrode in $Me_2SO/0.2$ M $LiClO_4$ containing dissolved oxygen, when the potential was scanned in a negative direction to the reduction of oxygen and then reversed to the positive direction. The present experiments gave the same results for MeCN/0.1 M $TBABF_4$ with dissolved oxygen and water. Processes involving oxygen frequently involve peroxy radicals or singlet oxygen, e.g., in a reaction sequence such as

cathodic

$$O_2 + e \rightarrow O_2^{\bullet-}$$

$$H_2O + O_2^{\bullet-} \rightarrow HO_2^{\bullet} + OH^-$$

$$HO_2^{\bullet} + e \rightarrow HO_2^-$$

anodic

$$HO_2^- \rightarrow HO_2^{\bullet} + e$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2^* \ (^1\Delta_g)$$

$$O_2^{\bullet-} \xrightarrow{\text{oxidant}} O_2^*$$

etc.[26]

Thus, IP experiments at the metal/solution interface probably will require highly purified solvents and electrolytes and rigorous removal of water and oxygen.

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Hydrophobic Interactions of Some Ionic Iron Complexes with Neutral Micelles. A Kinetic Study

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The effect of Triton X-100, Triton X-102, and Triton X-165 nonionic surfactants on the kinetics of the cerium(IV) oxidation of the iron(II) complexes FeL_3^{2+} (L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, and 5,6-dimethyl-1,10-phenanthroline) and of the reactions involving Fe^{2+} and the iron(III) complexes FeL_3^{3+} has been studied at 20.0 °C in the presence of $[H_2SO_4] = 0.050$ mol dm^{-3} by the stopped-flow technique. No kinetic evidence of interactions between neutral micelles and the triply charged iron complexes has been found, while binding of the corresponding iron(II) complexes with micellar aggregates occurs to some extent. The estimated binding constants of the last complexes increase with increasing both the hydrophobicity of the coordinated ligand and the number of the ethoxy units of the Triton surfactants examined. A binding site of the solubilizates in an intermediate region between the wet poly(ethylene oxide) sheath of the micelle and the hydrophobic core is suggested.

Introduction

In a previous paper[1] we have investigated the effect of charged and neutral micelles on the equilibria and kinetics of the electron-transfer reactions between ferrocene and some cobalt(III) complexes with phenanthroline-like ligands, the reaction products being the corresponding cobalt(II) complexes and ferrocenium ion. We have found, among other things, that, in the presence of nonionic Triton X-100 micelles, the balance between hydrophilic and hydrophobic effects is extremely delicate for the association of these species with nonionic micelles and that the reduction of the formal positive charge from 3+ to 2+ and from 1+ to 0 for the cobalt complexes and the ferrocenium ion, respectively, causes the predominance of the hydrophobic interactions, favoring the (partial) solubilization of the ionic cobalt(II) complexes and the

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(1) Carbone, A. I.; Cavasino, F. P.; Sbriziolo, C.; Pelizzetti, E. *J. Phys. Chem.* **1985**, *89*, 3578.