

PHOTOELECTRON EMISSION FROM A METAL ELECTRODE IN LIQUID AMMONIA

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Photoemission of electrons from platinum into liquid ammonia has been demonstrated. In the absence of electron scavengers a small photocurrent, attributed to the presence of impurities, was observed. With n-BuCl as scavenger a large photocurrent was observed with both He/Ne and Ar ion laser illumination which obeyed the "five-halves law". From the threshold potentials the energy level of the emitted electron was found to be -1.13 eV with respect to vacuum, 0.22 eV more negative than the solvated electron energy level, indicating that the electron is emitted initially as a delocalized or "dry" species.

1. Introduction

There has been much recent interest in the properties of chemically stable and metastable excess electron states in polar solvents [1,2]. Techniques used to investigate the chemical and physical properties of these solvated electrons include electronic absorption, ESR and NMR spectroscopy, as well as thermodynamic and electrochemical techniques [3,4]. A recent study of solvated electrons in liquid ammonia from this laboratory showed their formal potential ($E^0(e_s^-)$) to be -2.69 V (versus Ag/AgNO₃, 0.1 M) [4]. We have also demonstrated the photogeneration of solvated electrons on p-GaAs electrodes in ammonia at an underpotential of approximately 0.9 V with respect to $E^0(e_s^-)$ [5].

Photoelectron emission from metal electrodes into electrolyte solutions on photoexcitation of the electrode surface has received considerable attention since its discovery by Becquerel in 1839 [6] and characterization by Barker [7]. Numerous investigations have been carried out with a view to understanding this phenomenon and its relationship to double-layer structure, electrode kinetics and electron-transfer reactions [8]. Most of these studies, however, were carried out on aqueous solutions where the excess electrons are short-lived, thus allowing only an estimation of their standard potential [9,10].

In this paper we report the observation of a photocurrent from a platinum electrode in liquid ammonia under laser illumination and discuss the energy levels of excess electron states in this medium.

2. Experimental

The ammonia, supporting electrolyte (0.1 M KI) and general apparatus and procedures have been previously described [4,11]. n-butyl-bromide and -chloride used as scavengers of emitted electrons, were purified by distillation and injected into the electrochemical cell with a micro-syringe. The platinum disk working electrode (projected area 0.04 cm²) was polished prior to use with a 0.5 μ m alumina slurry.

Electrochemical measurements were carried out with a PAR 173 potentiostat and PAR 175 universal programmer (Princeton Applied Research Corp.) and current-potential curves recorded on a Houston 2000 X-Y recorder (Houston Instruments, Austin, Texas). The light sources were a 1.7 mW He/Ne laser (Spectra Physics, model 132, $\lambda = 632.8$ nm) and an Ar ion laser (Spectra Physics, model 164, $\lambda = 488.0$ nm). To aid detection of the small photocurrents these were chopped at 100 Hz with a PAR 192 variable frequency chopper and the resulting currents synchronously detected with a PAR 5204 lock-in amplifier.

All potentials are reported relative to the Ag/AgNO₃, 0.1 M reference electrode. Experiments were carried out at -55°C.

3. Results and discussion

The wide potential range, particularly cathodic, of liquid ammonia until the commencement of electrochemical generation of solvated electrons at approximately -2.4 V, is shown in fig. 1A and is in agreement with previous studies [4]. On illumination of the electrode immersed in this solution (free of added electron scavengers) with the He/Ne laser, a photocurrent, commencing at about -1.0 V was observed (fig. 1B). This photocurrent increased to a limiting value at -1.6 V before decreasing to zero at -2.2 V. The magnitude of this photocurrent was irreproducible for different experiments with solutions prepared at different times and was considerably reduced, but still observable, after repetitive coulometric generation of solvated electrons. This probably indicates that trace amounts of an adventitious impurity, acting as electron scavengers is responsible for the current, with the small current remaining after solvated electron generation being caused by residual impurities on or near the electrode surface. Significantly the onset of electrochemical sol-

vated electron generation at approximately -2.2 V results in a decrease in photocurrent probably due to direct reduction of these impurities. Clearly the limiting photocurrent observed between -1.6 V and -2.2 V could be due to the controlled rate of diffusion of impurities to the electrode surface. An alternate explanation, that the current is caused by photoemitted solvated electrons that avoid recapture by the electrode is also possible, although the variations observed make this appear unlikely.

n-butyl-chloride was used as an electron scavenger on the basis of its previously determined properties [12]. Its reduction peak at -2.4 V (fig. 2A) barely decreased the available potential range (as opposed to n-butyl-bromide whose reduction commenced at approximately -1.7 V [13]). In the presence of scavenger the photocurrent was much larger than in the scavenger-free solution (fig. 2B). The theory of photoemission at the metal-electrolyte interface, given by Brodsky et al. [8,14], predicts that the photocurrent, i , is governed by the "five-halves law":

$$i = A(h\nu - h\nu_0 - eV)^{5/2}, \quad (1)$$

where V is the electrode potential, ν the frequency of the excitation source, ν_0 the threshold frequency at $V = 0$ versus the reference electrode, and A a proportionality constant. Note that this same "five-halves

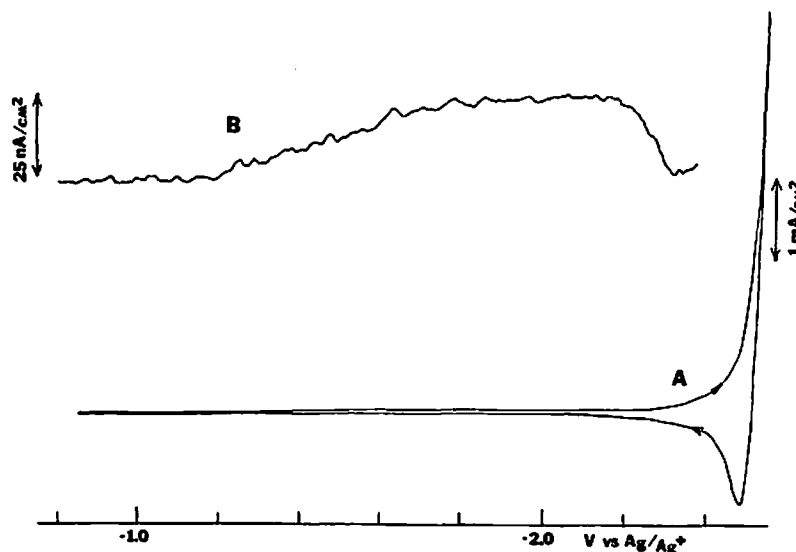


Fig. 1. (A) Current-potential curve for Pt-electrode in liquid NH₃. Scan rate 0.1 V/s; temperature, -55°C; supporting electrolyte, 0.1 M KI. (B) Photocurrent-potential curve with He/Ne laser in liquid NH₃ in the absence of scavenger. Scan rate, 10 mV/s.

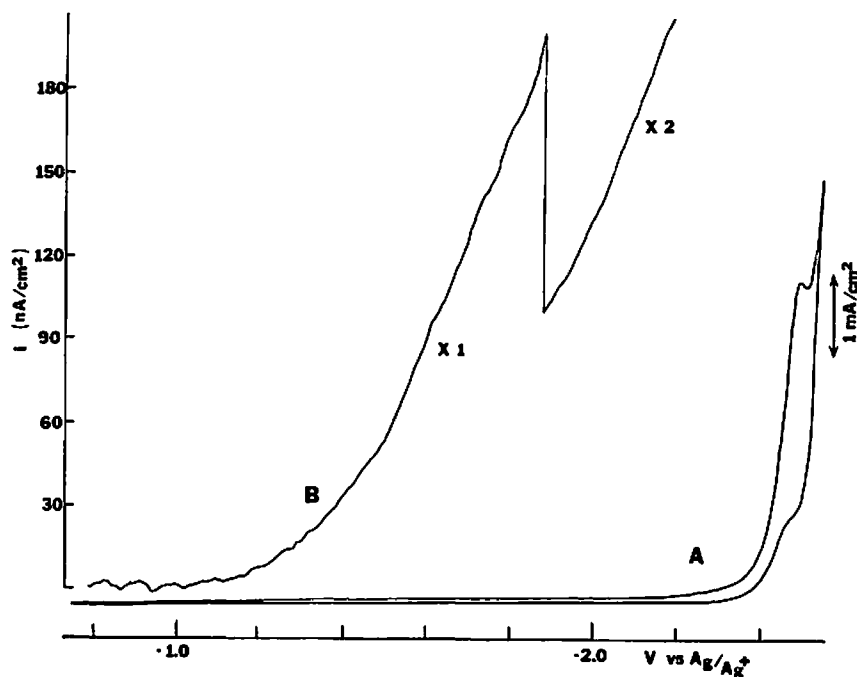


Fig. 2. (A) Cyclic voltammogram of a solution of n-butyl-chloride (5mM). Scan rate, 0.1 V/s. (B) Photocurrent-potential curve with He/Ne laser in a 60 mM n-butyl-chloride solution. Scan rate, 10 mV/s.

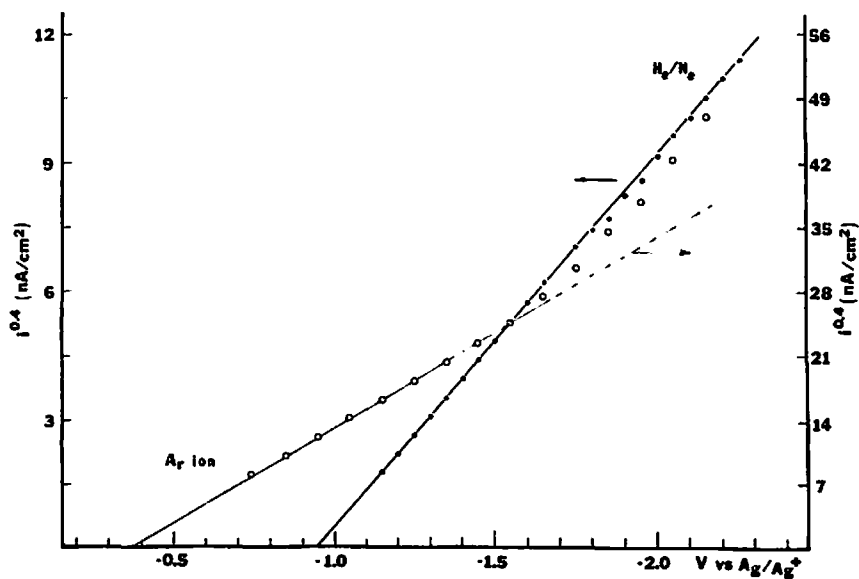


Fig. 3. Dependence of photocurrent ($i^{0.4}$) on electrode potential and illumination wave length for a 60 mM n-butyl-chloride solution. (●): He/Ne laser ($\lambda = 632.8$ nm). (○): Ar ion laser ($\lambda = 488.0$ nm).

law" is also predicted for photoemission at the metal–vacuum interface with the assumptions that the potential energy $V(x) = -V_0$ (constant) for $x < 0$ and $V(x) = 0$ for $x > 0$ [15]. From the above law a plot of $i^{0.4}$ against V yields an intercept with the V axis equal to the potential for the onset of photoemission for a given energy of photoexcitation (the "threshold potential"). Such a plot for the experimental data reported here is shown in fig. 3. With the He/Ne laser (1.96 eV) a linear plot was observed over a potential range of -1.1 V to -2.3 V versus Ag/Ag^+ yielding a threshold potential of -0.95 V. For the Ar ion laser (2.54 eV) linearity was observed between -0.7 V and -1.65 V yielding a threshold potential of -0.37 V. The difference between these two values exactly equals the difference in photon energy between the lasers; this agrees with the results of Rotenberg et al. [16] who reported that a plot of threshold potential versus photon energy for an aqueous 1 M HCl solution has a unit slope. The plot for the Ar ion laser showed an appreciable positive deviation (upward bending) at more negative potentials but apart from this irregularity, which is difficult to interpret at present, the current data appears to adequately fit the theory.

The energy level of the emitted electrons (the bottom of the ammonia conduction band), calculated from the sum of the threshold potential and photoexcitation energy, is -2.91 ± 0.03 V versus Ag/AgNO_3 (0.1 M) at -55°C . The difference between this value and $E^0(e_s^-)$, 0.22 ± 0.03 V indicates that an electron emitted from the electrode surface into NH_3 exists initially as a delocalized state (i.e., a quasi-free, or "dry" electron) not fully relaxed by solvent reorganization. In aqueous solution, the energy difference between these two states has been estimated to be 0.2 eV [17].

A diagram of the excess electron energy levels is shown in fig. 4. The energy levels were related to vacuum by assuming that (a) the formal potential of the Ag/Ag^+ (0.01 M) couple in acetonitrile is -4.70 V versus vacuum [18] and (b) the redox potentials (with respect to an absolute scale) of ferrocene and naphthalene are independent of solvent [19]. The redox potentials for naphthalene and ferrocene are -2.20 V [20] and 0.8 V [19] versus Ag/AgNO_3 , 0.1 M respectively in ammonia and -2.87 V and 0.074 V versus Ag/AgNO_3 , 0.1 M respectively in acetonitrile[‡]. These values then yield an energy of the localized (solvated) state, e_s , of

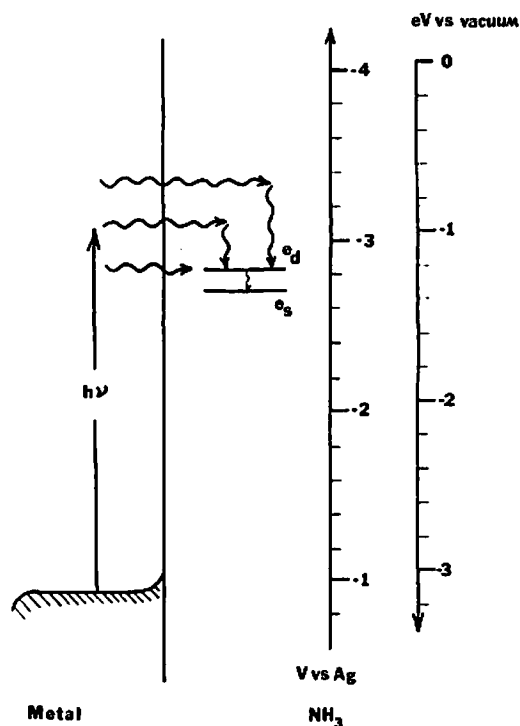


Fig. 4. Energy levels of localized and delocalized electron states in liquid NH_3 in V versus Ag/Ag^+ reference electrode and estimated versus vacuum.

-1.35 ± 0.03 eV versus vacuum, and an energy of the delocalized state (bottom of the conduction band), e_d , of -1.13 eV. Numerous theoretical attempts have been made to estimate these values thermodynamically [1, 2, 17]. Jortner et al., using an estimate for the absolute heat of solution of a proton in NH_3 , placed the heat of solvation of an electron in this solvent thermodynamically in the range of -1.0 to -1.7 eV [22, 23]. Since the entropy change for the solvation of electrons is probably small [17], the values reported here are within the range estimated by Jortner et al.

Finally studies of photoelectron emission are of interest in the investigation of chemical reactions involving very rapid electron transfer reactions of solvated electrons [8, 24–26]. Liquid ammonia may be especially useful for similar studies of organic compounds.

[‡] The value of naphthalene in acetonitrile was obtained in the present work. The other was taken from ref. [21].

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