PHOTOELECTRON EMISSION FROM A PLATINUM ELECTRODE INTO LIQUID AMMONIA SOLUTIONS

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Photoelectron emission from a Pt electrode into liquid NH_3 under Ar-ion laser illumination at wavelengths corresponding to 2.41, 2.54, 2.71 and 3.41 eV is described. Plots of photocurrent (i) versus electrode potential (V) in the "five-halves law" ($i^{0.4}$ versus V) form show "two-slope" plots that yield threshold potentials and electron injection levels. Based on these, an energy level diagram involving injection of electrons at energies 0.13–0.97 eV above the solvated electron level (which is −1.3 eV versus vacuum) is proposed.

1. Introduction

We have been investigating the energies of electrons in liquid ammonia by electrochemical and photoelectrochemical (PEC) methods [1–3]. The PEC studies involved determination of the photocurrent that arises upon irradiation of a platinum electrode immersed in a liquid NH_3 solution of 0.1 M KI as a function of potential; the experimental and theoretical basis for such measurements, based mainly on studies of aqueous solutions, are well documented [4–6]. The previous studies [1,2] involved irradiation with a He–Ne (632.8 nm, 1.96 eV) and an Ar-ion (488.0 nm, 2.54 eV) laser, and produced straight-line "five-halves" law plots ($i^{0.4}$ versus V) which yielded a threshold for electron photoemission at −2.91 V versus Ag/Ag$^+$ (0.1 M) (compared to the standard potential for solvated electrons in this solution of −2.74 V versus AgRE [2,7]). This photoemission threshold, originally assigned to the quasi-free electron level [1], was later attributed by Krohn and Thompson [8,9] to injection into pre-existing solvent trap states of the bulk solvent or at the interface. This explanation was reinforced by the fact that the $i^{0.4}$ − V plot with the Ar ion laser in the earlier study [1] showed two straight line portions, with the portion at higher potentials corresponding to a threshold at −3.64 V versus AgRE or 0.9 eV above the solvated electron level; this corresponds more closely to that expected

for the quasi-free electron in liquid NH_3. The Thompson model has also been supported by recent measurements of photoelectron emission into ammonia vapor at different densities, where "two-slope" plots are also found [10,11]. To obtain additional experimental evidence for the location of trap states and to see if two-slope plots were obtained at other wavelengths of irradiation (especially at higher energies where a larger range of electrode potentials can be investigated), PEC studies with wavelengths down to 363.8 nm were carried out. The results of these investigations are reported here.

2. Experimental

The solvent (anhydrous NH_3), the supporting electrolyte (0.10 M KI), and general apparatus and procedures have been previously described [12,13]. The *n*-butyl chloride, used as scavenger for photoemitted electrons, was purified by distillation and injected into the electrochemical cell with a micro-syringe. The working electrode was a platinum disk (projected area 0.031 cm^2). It was polished prior to use with a 0.3 μm alumina slurry.

Electrochemical measurements were carried out with a Princeton Applied Research (PAR) 173 potentiostat, a PAR 179 current-to-voltage converter and a PAR 175 universal programmer. Current–potential curves were

recorded on a Houston Instruments 200 $X-Y$ recorder. The light sources were: (a) an Ar-ion laser (Spectra Physics, model 164, wavelengths (nm): 514.5; 457.9 and 488.0) and (b) a 70 mW (total power) Ar-ion laser (Spectra Physics, model 171, $\lambda = 363.8$ nm). To obtain a more stable intensity with the model 164 laser, it was operated at 100 mW; the intensity impinging on the Pt electrode was decreased with a 1.0 neutral density filter. The laser radiation was chopped at 100 Hz with a PAR 192 variable frequency chopper and the resulting photocurrents synchronously detected with a PAR 5204 lock-in amplifier.

All the potentials were measured relative to a silver wire quasi-reference electrode (AgRE) [12–14]. Experiments were carried out with 0.1 M KI solutions at $-55°C$.

3. Results and discussion

Photocurrent—potential curves for a Pt electrode immersed in a liquid NH_3 solution containing the supporting electrolyte (0.1 M KI) and an electron scavenger (60 mM n-butyl chloride) are shown in fig. 1. This scavenger has been shown to be an appropriate one in liquid NH_3, since its cyclic voltammogram only exhibits a reduction peak at the onset of the solvated electron wave (≈ -2.4 V versus AgRE) so that the available potential range of this solvent (+0.5 to -2.5 V versus AgRE) is decreased only slightly [1].

The phocurrents are significant only at potentials more negative than -0.8 V, and increase rather slowly up to ≈ -1.2 V. After this point the increase is more
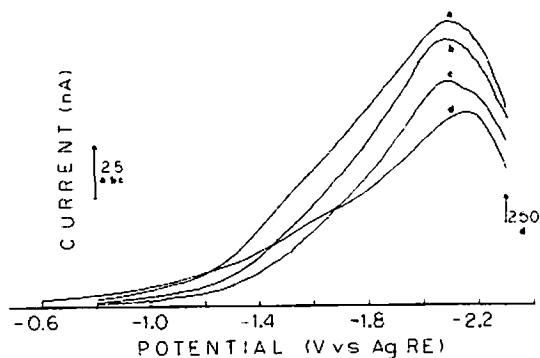

Fig. 1. Photocurrent-electrode potential curves for Ar-ion laser irradiation in liquid NH_3 containing 0.1 M KI and 60 mM n-butyl-chloride. Wavelengths (nm), (a) 457.9, (b) 488.0, (c) 514.5 and (d) 363.8. Scan rate, 20 mV/s. Temperature, $-55°C$.

pronounced and reaches a peak at ≈ -2.1 V. The decrease in photocurrent beyond this potential is probably due to a direct reduction of the scavenger at the surface of the electrode and the onset of solvated electron production. Plots of the photocurrent (i) versus potential (V) following the equation of Brodsky and Gurevich [4–6,15]:

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

where V is the electrode potential versus the reference electrode, ν is the frequency of the excitation source, ν_0 is the threshold frequency at $V = 0$, and A is a proportionality constant, which depends on the nature of metal electrode, are shown in fig. 2. For all irradiation wavelength, plots of $i^{0.4}$ versus V exhibit two linear regions. Thus the previous "two-slope" plot with irradiation at 2.54 eV seems to be general and the single slope line with a He—Ne laser (1.96 eV) only arises because of the restricted range of potentials available with this wavelength. The intercepts of each plot on the potential axis yield two threshold potentials, V_t (I and II), one in the low-photocurrent region (solid line) and the other in the high-photocurrent region (dashed line). The threshold potential values along with the corresponding excitation energies are shown in table 1. The results for the He—Ne laser [1] are also included.

Since the five-halves law predicts the same functionality of the photocurrent on the radiation energy ($h\nu$) and the potential of the electrode (V), their effects should be additive, so that a change in $h\nu$ leads to a concomitant change in the magnitude of the threshold potential. Note that a plot of plot V_t (I) versus $h\nu$ is linear, with a slope close to unity. However, the point for ultraviolet radiation (3.41 eV) lies at more negative values than that expected from the plot.

The lowest energy level for the photoemitted electrons in liquid NH_3 can be calculated from the sum of the threshold potential (I) and the photon energy (table 1). From the visible radiation results, the level is -2.86 ± 0.04 V versus AgRE. This is approximately 0.15 eV above the energy level for the solvated electron, e_s^-, ($E^{0'} = -2.74 \pm 0.01$ V versus AgRE) and in general agreement with the level previously reported for liquid NH_3 [2,7] and NH_3 vapor [10,11]. Based on the Thompson model, we ascribe this level to emission into preexisting solvent trap states. The intercepts of the visible light plots, V_t(II) also yield the same level (-3.28 V versus AgRE), corresponding to a level 0.54 eV above that for e_s^-. However, again the UV plot yields
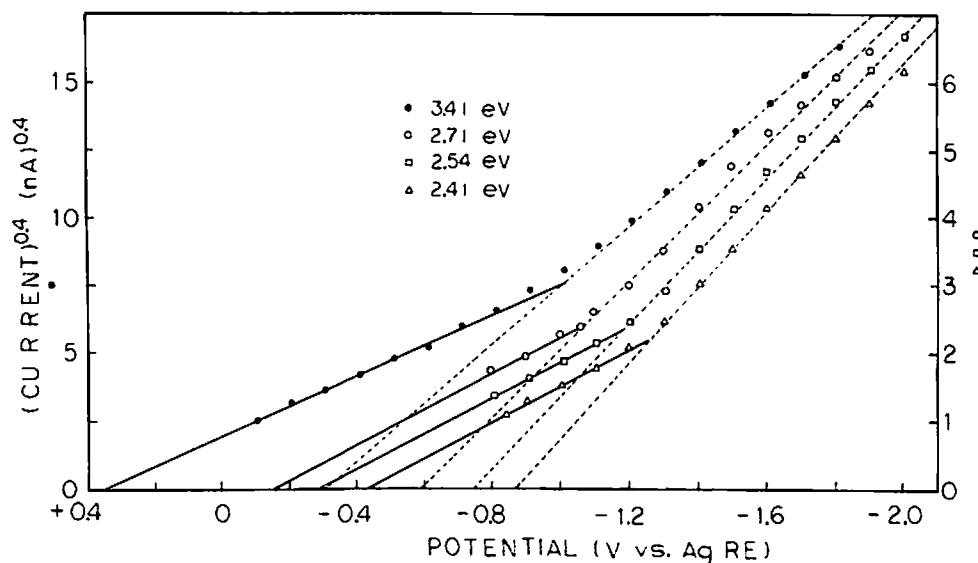
Fig. 2. Dependence of photocurrent ($i^{0.4}$) on electrode potential and wavelength (conditions as in fig. 1). Ar-ion laser wavelengths in nm, ● 363.8, ○ 457.9, □ 488.0, △ 514.5.

a threshold which corresponds to a higher energy (−3.71 V versus AgRE or 0.97 eV above the e_s^- level). If we assume that all of these represent actual energy levels, we can construct the diagram shown in fig. 4. The values with respect to vacuum were estimated following the previously described procedure [1,2]. This model implies that the highest level, at about −0.3 eV versus vacuum or 0.97 V above the e_s level represents the quasi-free electron or the conduction band edge, and that a distribution of solvent trap levels exists. The

lowest of these would represent pre-existing states of configuration near that of the thermalized solvated electron, while higher levels represent solvent states of less-ordered configurations. In all cases very rapid (< psec) thermalization of the emitted electron would occur; of course, under conditions of the photoemission experiments those electrons not captured by the scavenger return to the Pt electrode.

The results thus appear consistent with the existence of solvent traps in ammonia, distributed over a range of

Table 1
Threshold potentials and energy levels for electron photoemission at different wavelengths [a]

Laser energy eV	Threshold potential (I) V [b]	Injection level		Threshold potential (II) V [b]	Injection level (II)	
		(±0.04)V [b]	(±0.04)eV [c]		(±0.04)V [b]	(±0.04)eV [c]
1.96 [d]	−0.95	−2.91	−1.13	−	−	−
2.41	−0.45	−2.86	−1.18	−0.86	−3.27	−0.77
2.54	−0.28	−2.82	−1.22	−0.74	−3.28	−0.76
2.71	−0.15	−2.86	−1.18	−0.58	−3.29	−0.75
3.41	0.34	−3.07	−0.97	−0.30	−3.71	−0.33

[a] 0.1 M KI, liquid ammonia.
[b] V versus AgRE.
[c] With respect to vacuum.
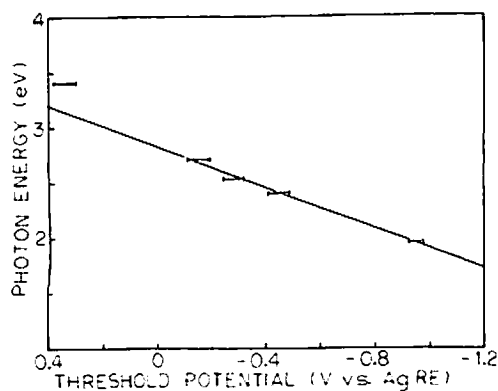[d] Values taken from ref. [4].

Fig. 3. Threshold potential as a function of the light excitation energy.

energies as suggested by Thompson. A similar model also probably applies to aqueous solutions, where the first photoemission level is only ~0.2 eV above the solvated electron. Indeed, Wiesenfeld and Ippen have recently provided more direct evidence of the preexisting solvent traps in water [16]. The visible absorption of solvated electrons was found to appear less than 0.3 ps after UV photolysis of $Fe(CN)_6^{4-}$ in water. This appears to be too short a time for molecular reorientation to occur in the solvation process. The alternative mecha-

nism would be electron capture by pre-existing solvent traps.

The results presented in this letter show that electron photoemission from a metal electrode into ammonia solution is a useful tool in studying the local liquid structure and the energy levels of electrons in the medium. More experiments with other electrodes (metal and semiconductor) with different supporting electrolytes and other scavengers at various concentrations should be informative. Emission into binary solvent mixtures might also be of interest.
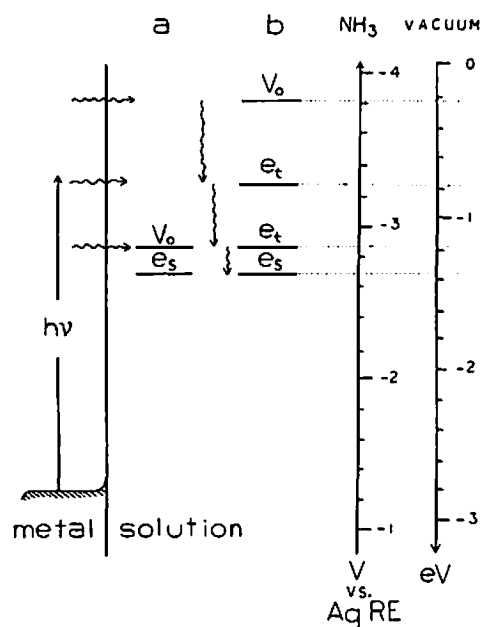
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Fig. 4. Energy levels of electron states in liquid NH_3 in V versus AgRE and estimated versus vacuum.

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