

AN ELECTROCHEMICAL STUDY OF SOLVATED ELECTRONS IN LIQUID AMMONIA

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ABSTRACT. — The electrochemical behavior of solvated electrons in liquid NH_3 was investigated by cyclic voltammetry, coulometry, and the galvanostatic single pulse technique. The cyclic voltammetric results suggest that the electrogeneration and collection of solvated electrons in liquid NH_3 occurs in simple diffusion controlled, Nernstian, electron transfer reactions. The formal potential for the generation of solvated electrons was found to be -2.69 ± 0.01 V relative to Ag/AgNO_3 (0.1 M) reference electrode. The exchange current density of a 0.12 mM solution of solvated electrons in liquid NH_3 as determined by the single galvanostatic pulse method was 6 ± 2 mA/cm². The diffusion coefficient of solvated electrons in 0.4 M KI was 2.5×10^{-5} cm²/s at -55°C .

Introduction

Solvated electrons can be generated electrochemically in a variety of solvents, such as liquid ammonia, hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide, and propylene carbonate¹. Interest in the production and properties of solvated electrons dates from before the turn of the century, when the electrolysis of solutions containing salts of alkali metal ions in liquid NH_3 was shown to produce the blue color characteristic of solvated electrons². The primary interest in these early studies was limited to synthetic uses of solvated electrons which are extremely strong reducing agents, rather than to studies of the nature of the electrode reaction. During the last decade a number of investigations of solvated electrons have been reported; several reviews on this subject have recently appeared³⁻⁵. The electrochemical behavior of solvated electrons can be studied most easily in solvents in which the solvated electrons are stable. A number of studies have been reported using HMPA, since this solvent has a convenient liquid range and is able to solvate a variety of organic and inorganic compounds. Several reviews dealing with the electrochemical behavior of solvated electrons in HMPA have appeared recently which provide contrasting viewpoints on the interpretation of the results⁶⁻⁸. Kanzaki, and Aoyagui^{9,10} studied the behavior of solvated electrons in HMPA extensively and were the first to attempt to deal with the kinetics of the electrode reaction in this solvent. By assuming the electrode reactions to be



they were able to treat this electron transfer process as any other simple redox system and to evaluate the kinetic parameters (exchange current and the transfer coefficient)⁹.

We report here studies of the electrochemical behavior of solvated electrons in liquid ammonia. Earlier papers from this laboratory have dealt with liquid ammonia as a solvent in the study of the electrochemical reductions of a variety of organic compounds¹¹⁻¹⁴. Although organic compounds in general are not as soluble in NH_3 as they are in HMPA, ammonia offers

clear advantages in ease of purification, low viscosity and its ability to stabilize solvated electrons for a long period of time. Solvated electrons generated by the dissolution of alkali metals in liquid NH_3 have long been used for specific chemical transformations in the Birch reduction. While numerous reports dealing with the physical and chemical properties of solvated electrons in liquid NH_3 have been published, only a few actually deal with the electrode reaction. Makishima¹⁵ was the first to summarize the cathodic electrode reactions occurring during electrolysis in anhydrous NH_3 . Later Laitinen, and Nyman^{16,17} performed polarographic reductions of alkali metals in liquid NH_3 and used a dropping mercury electrode to measure the current-voltage characteristics of the solvated electrons. Gordon, and Sundheim¹⁸ used chronopotentiometry to determine the diffusion coefficient of solvated electrons in liquid NH_3 and to study the electrode double layer capacitance. Lagowski, and Quinn¹⁹ developed techniques for the electrolytic generation and spectroscopic characterization of various quaternary ammonium radicals in liquid NH_3 .

We also report more detailed studies of the electron transfer process in liquid NH_3 by cyclic voltammetry, chronocoulometry, coulometry and galvanostatic methods and report new values for the diffusion coefficient, formal potential and rate constants for the electrogeneration and collection of solvated electrons in liquid NH_3 .

Experimental

CHEMICALS

The ammonia (Matheson Gas 99.9%) was purified by condensation in a trap containing several small pieces of clean sodium metal. The condensed ammonia was allowed to stand overnight in contact with the Na and was then redistilled into an adjacent trap also containing small pieces of sodium. This was then distilled directly into the electrochemical cell. The supporting electrolyte used in the experiments, reagent grade potassium iodide (Fisher Scientific Company), was dried in an oven at 120°C for several days then stored in a desiccator.

APPARATUS

The cell used for all the electrochemical measurements was a standard three compartment cell with a Ag/AgNO₃ (0.1 M) reference electrode isolated from the test solution by a fine-porosity sintered-glass disk. The working electrode was a platinum disk with a projected area of 0.039 ± 0.001 cm². This electrode was polished with alumina slurry (0.3 μm particle size) before use. For the bulk generation of solvated electrons a 3.8 by 2.8 cm platinum foil was used as the working electrode. Details of the components and design of a similar cell have been previously described¹². The cell assembly was thermostated using a Model LC-100 liquid cooler equipped with a Model TCH-1 temperature controller (FTS Systems Inc., Stone Ridge, New York). All electrochemical experiments were carried out with a PAR Model 173 potentiostat with a Model 179 digital coulometer equipped with positive feedback for *iR* compensation and a Model 175 universal programmer (Princeton Applied Research Corporation, Princeton, N. J.). A Model 2000 X-Y recorder (Houston Instruments, Austin, Texas) was used to record the current-potential curves. A PAR Model 5204 lock-in amplifier was used in the measurement of cell resistance. A model 1090A digital oscilloscope (Nicolet Instrument Corporation, Madison, Wisconsin) was employed for data acquisition in the galvanostatic pulse, chronocoulometric and potential step experiments.

PROCEDURE

The electrochemical cell containing a weighed amount of supporting electrolyte in each compartment was connected to the vacuum line (10⁻⁵ Torr) and evacuated for approximately 24 hours. The required volume of ammonia was distilled from the trap into the cell, which was cooled by a dry ice-isopropanol bath. The temperature of the solution was maintained at the desired temperature (±0.1°C) by the cryostat.

Results and discussion

CYCLIC VOLTAMMETRY

Theory. — The cyclic voltammetric (cv) generation and, on reversal, removal of solvated electrons in liquid ammonia can be represented by the equation



The cv behavior for this reaction scheme differs from that in the usual cv studies of a soluble oxidant²⁰, since diffusion of reactant to the electrode is not a factor. Thus we first derive the theory for the cv *i*-*E* curves for this case. Diffusion of the generated solvated electrons to a planar electrode is governed by equation (2) where *C*(*x*, *t*) and *D* are the concentration and

$$\partial C(x, t)/\partial t = D(\partial^2 C(x, t)/\partial x^2), \quad (2)$$

diffusion coefficient of solvated electrons, respectively. *t* is the time, and *x* is the distance from the electrode surface. *C*(*x*, *t*) is related to the potential, *E* by:

$$t = 0, \quad x \geq 0, \\ C(x, 0) = \exp[(F/RT)(E^\circ - E_i)], \quad (3)$$

$$t \geq 0, \quad x = 0, \\ C(0, t) = \exp[(F/RT)(E^\circ - E)], \quad (4)$$

where *E*[°] and *E_i* are the standard redox potential for the reaction in equation (1) and the initial potential, respectively. The use of equations (3) and (4) assume that the reaction in equation (1) is rapid so that the electrode process is governed by the Nernst equation in which the electron number, *n*, is 1. This assumption is justified by the reaction rate measurements described in a later section.

For linear potential sweeps, the electrode potential is given by the relations

$$0 < t \leq \lambda, \quad E = E_i - vt, \quad (5a)$$

$$\lambda \leq t, \quad E = E_i - 2v\lambda + vt, \quad (5b)$$

where *v* is the scan rate (V/s) and *λ* is the time when the potential scan is reversed. The total current flowing through the electrode interface is given by

$$i(t) = FAD[\partial C(x, t)/\partial x]_{x=0}. \quad (6)$$

With the procedure developed by Nicholson *et al.*²⁰, the total current can be expressed as

$$i(t) = FA\sqrt{\pi Da}\chi(at), \quad (7)$$

where *a* = *Fv*/*RT* and *A* is the electrode area.

χ(*at*) in equation (7) is given by the following integral equation²¹:

$$\int_0^{at} (\chi(Z)/\sqrt{at-Z})dZ = 1/\theta((1/S_\lambda(at)) - 1), \quad (8)$$

$$\theta = \exp\{F/RT(E_i - E^\circ)\}, \quad (9)$$

$$S_\lambda(t) = \begin{cases} \exp(-at) & \text{for } t \leq \lambda, \\ \exp(at - 2a\lambda) & \text{for } t \geq \lambda. \end{cases} \quad (10a)$$

$$(10b)$$

Kanzaki, and Aoyagi derived the analytical solution [equation (10), reference⁸] for only the forward scan *t* ≤ *λ*. The numerical solutions, of equation (8) were obtained with a NEAC7000, digital computer at Tohoku University using different values of initial and switching potentials²¹. The numerical solution was strongly affected by the initial potential when its value was near *E*[°]. However, there was no change in the calculated currents for initial potentials chosen to be at least 0.3 V positive of *E*[°]. A typical calculated cyclic voltammogram for the reversible generation of solvated electrons is given in Figure 1. Numerical solutions obtained for various switching potentials (*E_λ*) at a given value of initial potential yield the following predicted characteristics for this reaction:

1. The Tafel plot (ln *i* vs *E*) for the forward scan has a slope of *RT*/*F*.

2. The ratio of the current at the switching potential (*i_{sλ}*) to the peak anodic current (*i_{pa}*) is a constant, independent of *E_λ* and *v*, and has a value of 0.196.

3. The potential difference between the anodic peak potential (*E_{pa}*) and the potential at zero current (*E_{i=0}*) is a constant, given by

$$E_{pa} - E_{i=0} = 0.96(RT/nF). \quad (11)$$

4. The difference between the switching potential (*E_λ*) and *E_{i=0}* is also constant:

$$E_{i=0} - E_\lambda = 0.409(RT/nF). \quad (12)$$

Typical theoretically calculated values are given in Table I.

Experimental results. — The cv background current in liquid NH₃ at a Pt-electrode over a wide potential range is shown in Figure 2. The anodic current at the positive potential limit at +0.6 V vs Ag/AgNO₃ (0.1 M), is due to the discharge of the iodide ion rather than to the oxidation of NH₃²². The sharp increase in current at -2.4 V is attributed to the generation of solvated electrons and occurs with the formation of a blue color at the electrode surface^{16,17}. An expanded

Table I. - Theoretically predicted characteristics for cyclic voltammetric generation of solvated electrons ^a.

Cathodic		Anodic					
$(E_{\lambda} - E^{\circ})$ (mV)	$j_{c\lambda} = \sqrt{\pi\chi} (at)$	$(E_{pa} - E^{\circ})$ (mV)	$j_{pa} = \sqrt{\pi\chi} (at)$	$(E_{i=0} - E^{\circ})$ (mV)	$(E_{pa} - E_{i=0})$ (mV)	$(E_{pa} - E_{\lambda})$ (mV)	$j_{pa}/i_{c\lambda} = i_{pa}/i_{c\lambda}$
128.5	0.671×10^{-2}	163.7	-0.131×10^{-2}	139.0	24.7	35.2	0.195
179.8	0.908×10^{-2}	215.0	-0.177×10^{-2}	190.4	24.7	35.2	0.195
205.5	0.334×10^{-2}	240.7	-0.652×10^{-4}	216.1	24.7	35.2	0.195
231.2	0.123×10^{-2}	266.4	-0.240×10^{-4}	241.8	24.7	35.2	0.196
256.9	0.451×10^{-4}	292.1	-0.888×10^{-5}	267.4	24.7	35.2	0.197
282.6	0.165×10^{-4}	317.8	-0.331×10^{-5}	292.9	24.7	35.2	0.200

^a, temperature 25°C; E_{λ} , cathodic switching potential; $j_{c\lambda}$, cathodic current function at the switching potential; E_{pa} , anodic peak potential; E° , standard potential; j_{pa} , anodic peak current function; $E_{i=0}$, potential at zero current.

cyclic voltammogram in the cathodic region where the solvated electrons are generated at the Pt-cathode (Fig. 3) has a wave-shape which is almost identical with the theoretical calculated curve shown in Figure 1. The rising portion of the curve at -2.4 V is so sharp that the measured values discussed below are greatly affected by the amount of uncompensated ohmic resistance between the working and the reference electrodes. To minimize this effect, the amount of iR compensation was selected using an oscilloscope to find the amount of positive feedback which just did not cause current oscillations.

The experimental results for scan rates of (0.01 to 0.2 V/s) agree very well with the theoretical characteristics described above:

1. A Tafel plot for the forward generation of solvated electrons is shown in Figure 4. The straight line obtained has the predicted slope (43 mV; $T = -55^{\circ}\text{C}$).

2. The current ratio $i_{pa}/i_{c\lambda}$, equal to 0.20 ± 0.01 , does not show any dependence on the switching potential [which was less than -2.57 V vs Ag/AgNO_3 (0.1 M)] or scan rate.

3. The potential separation ($E_{pa} - E_{i=0}$) is 14 ± 2 mV as compared with a theoretical value of 18 mV (-55°C).

4. The value of $E_{i=0} - E_{\lambda}$ is 6 ± 1 mV compared to the predicted value, 7.7 mV.

From the comparison of the experimental and theoretical results, we can conclude that the generation of solvated electrons in liquid NH_3 is essentially reversible in the time scale of the cyclic technique. Cyclic voltammetric studies of solvated electrons in HMPA show differing, less well-behaved, results in different reports. Avaca, and Bewick ⁶ reported an unusual loop at a vitreous carbon electrode in HMPA. The cathodic current during the initial part of the anodic sweep ($t > \lambda$) exceeded the corresponding current for the cathodic sweep. Krishtalik, and Alpatova ⁷ reported that the Pt electrode surface passivates during the generation of solvated electrons. On the other hand, Kanzaki, and Aoyagui ⁸⁻¹⁰ in their comprehensive study of solvated electrons in HMPA obtained cyclic voltammetric behavior which was quite similar to that shown in Figure 1. Recent results ²³ have suggested that the observed unusual loop and the passivation of the electrode surface are caused by impurities in the solvent. The reproductibility of data in liquid NH_3 is excellent and such current loops or electrode passivation were never observed in this solvent.

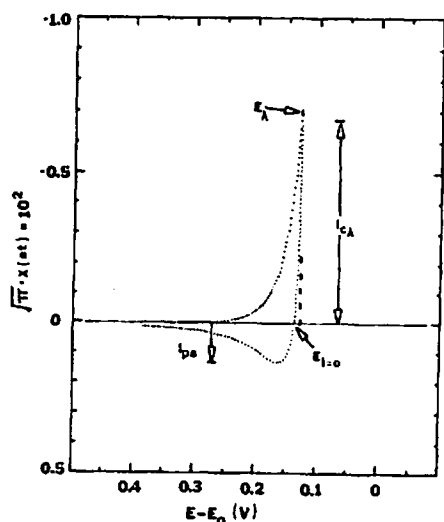


Figure 1. - Theoretical cyclic voltammogram for the generation of solvated electrons. Initial potential ($E_i - E^{\circ} = 370$ mV), the switching potential ($E_{\lambda} - E^{\circ} = 128.5$ mV) at 25°C .

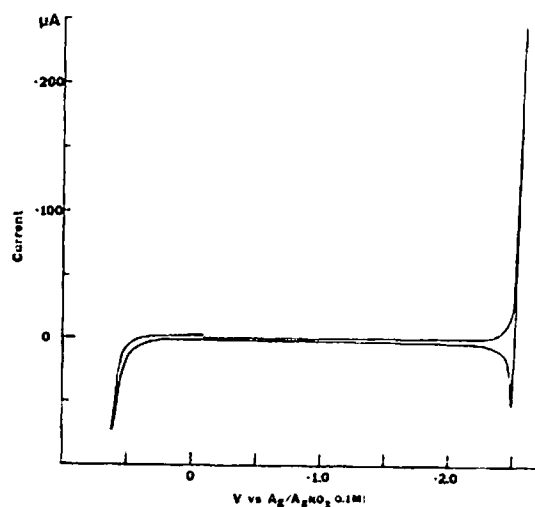


Figure 2. - Current-potential curve for Pt-electrode in liquid NH_3 . Scan rate, 0.2 V/sec; temperature, -55°C ; supporting electrolyte, 0.1 M KI; electrode area, 0.039 cm^2 .

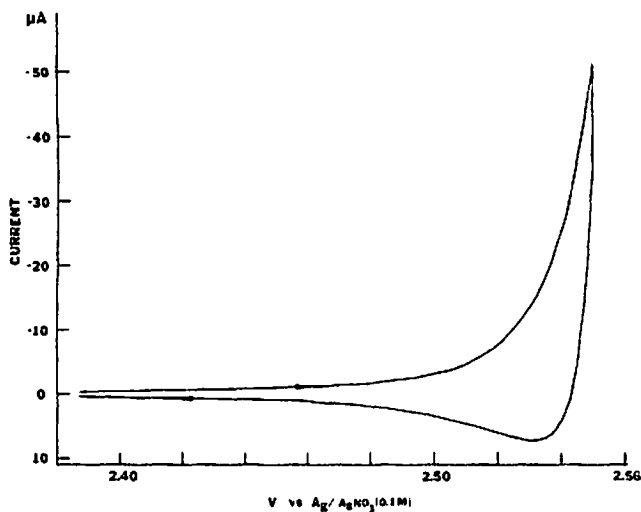


Figure 3. — Current-potential curve for Pt-electrode in liquid NH_3 in the potential region of generation of solvated electrons. Scan rate, 20 mV/sec; temperature, -55°C ; supporting electrolyte, 0.1 M KI; electrode area, 0.039 cm^2 .

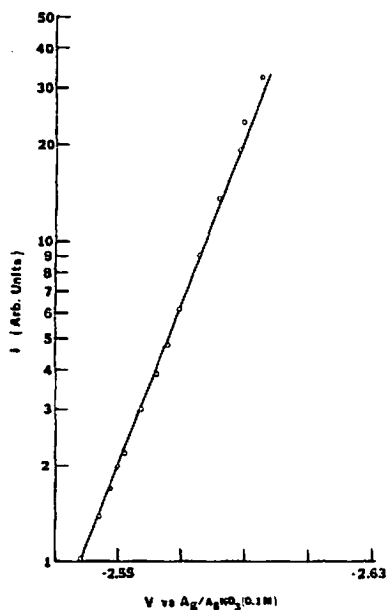


Figure 4. — Tafel plot for the generation of solvated electrons in the forward scan as shown in Figure 3. Slope of the line $40 \pm 2 \text{ mV/decade}$.

Coulometric generation and removal of solvated electrons

The stability of solvated electrons in 0.1 M KI, was determined experimentally by repeated generation and removal of solvated electrons. A typical experiment involved the electrochemical generation of a precise amount of solvated electrons in a coulometric cell. The solution was allowed to stand for 3 hours, (average time required for an experiment), followed by coulometric oxidation. The integrated current resulting from oxidation was approximately $95 \pm 2 \%$ of that measured during the initial generation for solvated electron concentrations of 10^{-4} to $2.5 \times 10^{-2} \text{ M}$.

The formal potential of solvated electrons

Potential measurements of solvated electrons in liquid NH_3 has been subject to a number of investigations. Kraus²⁴

measured the e.m.f. in concentration cells containing Na in liquid NH_3 while Laitinen, and Nyman¹⁷ determined the potential of solvated electrons at a dropping mercury electrode through analysis of current-potential curves. The potentials of galvanic cells containing solvated electrons were measured by Russell, and Sienko²⁵ and more recently by Ichikawa, and Thompson²⁶. With the exception of the Laitinen and Nyman study, the reported potential measurements were carried out in solutions in the absence of excess supporting electrolyte, so that changes in the activity of the electrons with ionic strength were significant. In this section we report a detailed investigation of the potential of liquid NH_3 solutions containing varying concentrations of solvated electrons in the presence of excess KI.

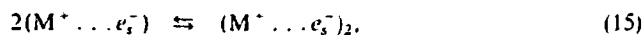
The cv behavior of solvated electrons showed that the electrode process can be essentially described by equation (1). Unfortunately, a precise value of E° cannot be obtained from cv experiments described above. Since solutions of solvated electrons in liquid NH_3 containing excess KI are very stable, as shown by the coulometric experiments, accurate concentrations can be prepared using coulometry rather than a chemical method. If the electrode reaction is represented by equation (1), then the electrode potential should follow the appropriate Nernst equation:

$$E = E^\circ - (RT/F) \ln(\gamma_e [e_s^-]) = E^\circ - (RT/F) \ln [e_s^-]. \quad (13)$$

where γ_e and $[e_s^-]$ are the activity coefficient and the concentration of solvated electrons, respectively, and E° is the formal potential. The experimental results obtained by preparing solutions with total solvated electron concentrations, C_T , between 10^{-4} and 10^{-2} M and measuring the potential of the Pt electrode are shown in Figure 5. The slope of the linear portion at lower concentrations is $35 \pm 2 \text{ mV}$ as compared with a predicted value (if $[e_s^-] = C_T$) of 43 mV at -55°C . Besides the variation from the predicted slope, there is also a small downward bending of the data points in the high concentration region. Although γ_e should depend upon the concentration of solvated electrons, the effect of the generated electrons on the ionic strength and the slope should be minimal because of the large concentration of supporting electrolyte. Ion-pair formation of solvated electrons with a counter cation, equation (14),



is well-known in liquid NH_3 ²⁷, but this cannot explain the bending behavior, because in these experiments, the concentration of supporting electrolyte cation was always much larger than $[e_s^-]$. There is also the possibility of dimer (or electron pair) formation in liquid NH_3 , such as^{27, 28},



or



Demortier, and Lepoutre³⁴ reported an equilibrium constant for this reaction in liquid NH_3 , where M is potassium, of about 10^3 . The effect of ion pairing and dimerization on the measured potentials was investigated by employing the following values for the equilibrium constants ($\text{M}^- = \text{K}^+$): Reaction (14)³⁴, $K = 1 \times 10^{-3}$, reaction (15)³⁴, $K = 10^3$; and $K = 10^{-3}$ for the ion pair formation reaction³⁵ $\text{K}^+ \text{I}^- \rightleftharpoons \text{K}^+ \text{I}^-$. The sixth order equation in free electron concentration, $[e_s^-]$, derived from these equilibrium constant

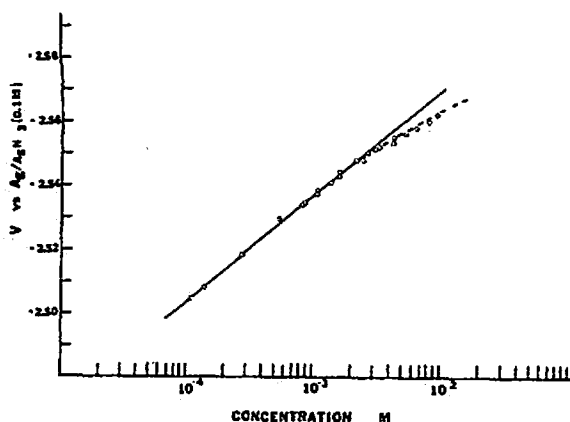


Figure 5. — The equilibrium potential of solvated electrons vs. concentration. Supporting electrolyte, 0.1 M KI; reference electrode, Ag/AgNO₃ (0.1 M); temperature, -55°C (solid line). The theoretical electrode potential vs. C_T (dashed curve).

expressions and the relevant material balance equations was solved numerically to yield values of $[e_s^-]$ as a function of C_T ($C_T = [e_s^-] + [M^+ \dots e_s^-] + 2[(M^+ \dots e_s^-)_2]$). The calculations demonstrate that extensive ion pair formation and dimerization of solvated electrons exists under the conditions of our experiment and yields the following values of $[e_s^-]$ at different C_T -values: $C_T = 10^{-4}$ M, $[e_s^-] = 8.4 \times 10^{-6}$ M; $C_T = 1.1 \times 10^{-3}$ M, $[e_s^-] = 5.8 \times 10^{-5}$ M; $C_T = 10^{-2}$ M, $[e_s^-] = 3.7 \times 10^{-4}$ M. This data was fit, using equation (13) to the measured E vs C_T results to yield the dashed line in Figure (5) and an E^0 value of -2.69 ± 0.01 V vs Ag/AgNO₃ (0.1 M) at -55°C. A plot of E vs $[e_s^-]$ produced a straight line over the whole C_T -region with a slope of 43 mV, in agreement with the theoretically predicted value. We might note that in less polar solvents, such as ethers and amines, species such as metal anion (M^-) have been described²⁹, but these have not yet been observed in liquid NH₃. The calculated value of the formal potential in our experiments compares quite well with the value obtained by Laitinen, and Nyman at mercury, where from polarographic measurements of a solution containing tetrabutylammonium iodide at -36°C they reported a value of -1.92 V vs standard hydrogen electrode which corresponds to about -2.60 V vs Ag/AgCl (satd.) KCl (satd.)³⁰.

Determination of diffusion coefficient

Gordon, and Sundheim¹⁸ examined the chronopotentiometric behavior of solvated electrons in liquid NH₃ containing excess supporting electrolyte and determined the diffusion coefficient. The accuracy of the chronopotentiometric technique strongly depends upon the accuracy in the evaluation of the transition time, τ , and correction for the effect of double layer charging^{31a}. We chose to use chronocoulometry³² as a more accurate technique to determine the diffusion coefficient. In the absence of adsorption and for a potential step into the mass transfer limiting region, the integrated current (Q) is given by³²,

$$Q = 2nFAC(Dt/\pi)^{1/2} + Q_{dl} \quad (17)$$

where Q_{dl} is the charge consumed in charging the double layer

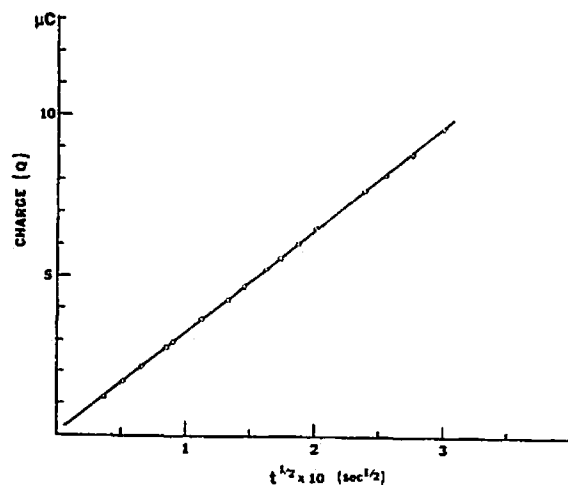


Figure 6. — Chronocoulometric charge vs $t^{1/2}$ obtained in a solution of 1.12 mM solvated electrons. Reference electrode, Pt/ e_s^- ; the electrode potential was changed abruptly from 0 to +0.1 V; supporting electrolyte, 0.1 M KI; electrode area, 0.039 cm²; temperature, -55°C. The slope of the line is $31.74 (\pm 0.04) \mu\text{C}/\text{sec}^{1/2}$.

capacitance during the potential step. Equation (17), predicts that a plot of Q vs $t^{1/2}$ is linear, with intercept Q_{dl} and a slope determined by the diffusion coefficient and concentration. Chronocoulometric oxidations of solutions of solvated electrons prepared coulometrically were carried out for potential steps at least 100 mV positive of the equilibrium solution potential; a typical $Q-t^{1/2}$ plot is shown in Figure 6. The linearity of such plots for times between 0.1 ms and 1.0 second was excellent. The average value of D for a series of three experiments at a C_T of 1.12×10^{-3} M was $4.47 (\pm 0.08) \times 10^{-5}$ cm²/sec in 0.1 M KI and $2.5 (\pm 0.1) \times 10^{-5}$ cm²/sec in 0.4 M KI at -55°C. This corresponds to mobilities (μ) of 2.38×10^{-3} and 1.33×10^{-3} cm² · V⁻¹ · sec⁻¹ for 0.1 M and 0.4 M KI, respectively. The calculated diffusion coefficient values are, in fact, weighted average or "formal" ones, since there are several species diffusing to the electrode. At a $C_T = 1.12 \times 10^{-3}$ M in 0.1 M KI, we calculate the following concentrations of free-electron species: $[K^+ e^-]$, 5.20×10^{-4} M; $[(K^+ e^-)_2]$, 2.71×10^{-4} M; $[e_s^-]$, 5.77×10^{-5} M. The D value can be compared with the reported value¹⁸, in the order of 5×10^{-5} cm²/sec obtained for solutions containing excess KI. C_{dl} , taken as $Q_{dl}/\Delta E$ was $33 \pm 1 \mu\text{F}/\text{cm}^2$ in 0.4 M KI ($\Delta E = 0.1$ V).

Electrode kinetics of solvated electrons

The cv results clearly indicate that the electrode process of solvated electrons in liquid NH₃ is a fast one; even at scan rates as high as 100 V/s, the oxidation of solvated electrons shows reversible behavior. An exchange current of 1.8×10^{-2} A/cm² has been reported for a 1 mM HMPA solution of solvated electrons⁹. This value is sufficiently large to consider the electrode process polarographically reversible. We applied the single galvanostatic pulse method for the determination of the exchange current of solvated electrons in liquid NH₃ on a Pt-electrode. A convenient way of obtaining the exchange current density, i^0 , from the overpotential (η) - t data was developed by Berzins, and Delahay³³. The theoretical equations for a single galvanostatic pulse technique are:

$$\eta = \eta_{i^0} + \delta(t^{1/2} - t_i^{1/2}), \quad (18)$$

Table II. — Data for single galvanostatic pulse experiment.

Concentration (10^{-3} M)	δ (V/sec $^{1/2}$)		$t_i^{1/2}$ (ms) $^{1/2}$	$\eta_i^{1/2}$ (mV)	i (mA/cm 2)	i^0 (mA/cm 2)
	Experimental	Theoretical				
0.12	0.36	0.28	12.0	2.5	0.77	6 (\pm 2)
0.15	0.41	0.38	8.9	1.8	1.32	13 (\pm 5)
0.25	0.385	0.36	5.3	1.0	2.06	40 (\pm 20)

^a The values in parenthesis show the deviation of the exchange current in a series of experiments.

$$\delta = 2RTi/(nF)^2 C(\pi D)^{1/2}, \quad (19)$$

$$t_i^{1/2} = \pi C_{dl} \delta / 4i, \quad (20)$$

$$\eta_{i^0} = (RT/nF)(i/i^0), \quad (21)$$

where η_{i^0} is the overpotential at $t_i^{1/2}$ given by equation (20). i is the constant current density, and C_{dl} is the differential capacitance of the electrode-solution interface. A plot of η vs $t^{1/2}$ should be linear with a slope δ . From the slope and the double layer capacitance, the time $t_i^{1/2}$ is calculated from equation (20). The magnitude of the exchange current can be obtained from the magnitude of i and the overpotential at the time $t_i^{1/2}$ equation (21). The uncompensated resistance between the working and reference electrodes was measured by superimposing a small ac potential variation (10 mV) for the electrode at potentials of -0.0 to -1.0 V vs Ag/AgNO $_3$ (0.1 M) and determining the resulting ac currents with a lock-in amplifier. For a 0.1 M KI solution, this resistance was about 200 Ω at -55°C . In the study of the kinetics of oxidation of solvated electrons, the resistance was decreased to 60 Ω by increasing the concentration of supporting electrolyte to 0.4 M KI (-55°C). The double layer capacitance in 0.4 M KI determined by chronocoulometry using a small potential step (0.1 V) was 33 ± 1 $\mu\text{F}/\text{cm}^2$ (-55°C). The rise time of the galvanostatic pulse (to attain 90% of the final value), which determines the resolution of data and the maximum value of i^0 obtainable, was approximately 8 μsec . Although the rise time of the current pulse is not as fast as that employed in the kinetic studies in HMPA, the diffusion coefficient, D , of solvated electrons in liquid NH $_3$ is much larger than that in HMPA⁸. Moreover, a stable relatively dilute solution of solvated electrons in 0.4 M KI can be prepared coulometrically. These factors extend the range for the determinations of the exchange current, since D and C contribute to the value of δ [equation (19)].

The η vs. $t^{1/2}$ plot obtained for a 0.12 mM solution of solvated electrons is shown in Figure 7. After subtracting the potential drop caused by the ohmic resistance, the exchange current was found to be 6 ± 2 mA/cm 2 . The $t_i^{1/2}$ value, calculated from the slope of the line in Figure 7 and the double layer capacitance, without taking into account the rise-time of the current pulse was 12×10^{-3} sec $^{1/2}$. The accuracy of the exchange current is directly dependent on the value of the overpotential at time, t_i . In these experiments, $t_i^{1/2}$ and t_i have an uncertainty within the rise-time of the current pulse. Consequently, the higher the concentration of solvated electrons, the more difficult it is to determine the exchange current (because at higher concentrations $t_i^{1/2}$ becomes comparable to the rise time). A summary of the results obtained in the single galvanostatic pulse experiments are shown in Table II. From the results it appears that the exchange current

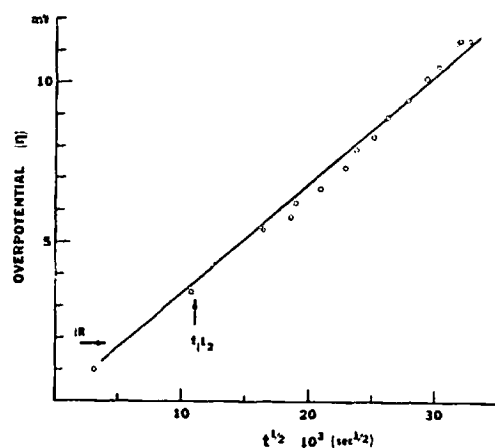


Figure 7. — Overpotential (η) vs $t^{1/2}$ obtained by galvanostatic single pulse method. Concentration of solvated electrons, 0.12 mM; supporting electrolyte, 0.4 M KI; current density, 0.77 mA/cm 2 ; uncompensated resistance between the working and the reference electrode was 60 Ω .

of solvated electrons in liquid NH $_3$ is fairly large and of almost the same magnitude as that in HMPA⁹. Although the transfer coefficient, α ^{31b}, should be obtainable from a plot of i^0 vs. concentration of solvated electrons, we were unable to measure precise i^0 -values over a sufficiently wide range of solvated electron concentrations to obtain such a plot, because of the limited rise time of the galvanostatic pulse. The slope of the line in Figure 7 is 0.36 which compares reasonably with the theoretical value, (0.28), calculated by equation (19) (see Table II).

The agreement between the observed and the theoretical slope clearly indicates that the electrode reaction of solvated electrons in liquid NH $_3$ is an apparently simple process with no interference of coupled chemical reactions. This is in contrast to the results in HMPA, where Kanzaki, and Aoyagi⁹ observed a discrepancy between the observed and the theoretically predicted slope. They also reported double peaks in the linear scan voltammograms¹⁰. These results were attributed to ion-pair formation, with slow dissociation reaction rates for these ion-pairs. Such double peaks were never observed in liquid NH $_3$.

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NOTE:

In the section on the formal potential of solvated electrons, a computational error exists. The correct results are given in *J. Phys. Chem.*, **84**, 1262 (1980) which lead to a formal potential of -2.74 rather than -2.69 V.