Studies of the solvated electron in Li salt + HMPA solutions using the rotating ring-disk electrode technique. Part 1. Non-uniform current distribution and determination of the solvated electron diffusion coefficient

Citation for published version (APA):

Andel-Scheffer, van, P. J. M., Wonders, A. H., & Barendrecht, E. (1991). Studies of the solvated electron in Li salt + HMPA solutions using the rotating ring-disk electrode technique. Part 1. Non-uniform current distribution and determination of the solvated electron diffusion coefficient. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 301(1-2), 87-100. [https://doi.org/10.1016/0022-0728\(91\)85461-W](https://doi.org/10.1016/0022-0728(91)85461-W)

DOI:

[10.1016/0022-0728\(91\)85461-W](https://doi.org/10.1016/0022-0728(91)85461-W)

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 26. Apr. 2023

J. Electroanal. Chem., 301 (1991) 87–100
Elsevier Sequoia S.A., Lausanne

Studies of the solvated electron in Li salt + HMPA solutions using the rotating ring–disk electrode technique

Part 1. Non-uniform current distribution and determination of the solvated electron diffusion coefficient

P.J.M. van Andel, A.H. Wonders and E. Barendrecht

Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (Netherlands)

(Received 30 January 1990; in final form 4 December 1990)

Abstract

Solvated electrons (e_s^-) which are generated at the disk of a rotating ring–disk electrode (RRDE) can be oxidized at the ring electrode; the electrons were generated at different electrode materials in a 0.3 M Li salt + hexamethylphosphortriamide (HMPA) solution. By means of this RRDE technique the current distribution during e_s^- generation at glassy carbon was investigated: a uniform current density distribution could not be obtained during e_s^- generation. Also passivation of different ring electrode materials in this medium was studied. During cathodic polarization at Pt, a film, probably from the electrocatalytically destroyed solvent, was formed. This film is impermeable for e_s^- . At glassy carbon, however, this type of passivation was not observed. The e_s^- diffusion coefficient in a 0.3 M LiBr + HMPA solution was calculated at different temperatures from e_s^- transit time measurements. The activation energy of diffusion was found to be 5.9 kJ mol^{-1} .

INTRODUCTION

Interest in hexamethylphosphortriamide (HMPA) as a solvent with a high stability towards the solvated electron (e_s^-) was prompted by qualitative observations of benzene reduction by Sternberg et al. [1]. Ever since, the electrochemical generation of e_s^- in HMPA has been investigated thoroughly [2–5].

Cathodic generation of e_s^- takes place at -3.1 V (vs. SCE) in a solution of LiCl in HMPA and should be independent of the electrode material used if no adsorption is involved.

Two models for the structure of e_s^- are proposed to interpret the results. In the “cavity model”, the electron is trapped in a cavity created in the bulk solvent. Orientation of solvent dipoles appears to be important for stabilization. In the

“expanded metal model”, the electron occupies an expanded orbital defined by the hydrogen atoms of the first solvent sphere.

For the generation of e_s^- , two theoretical mechanisms can be distinguished: chemical dissolution of electrons and electron thermoemission [6–9]. The former can be compared to an electrochemical process: the metal electron is transferred to an acceptor. The latter has no electrochemical equivalent: the electrons enter the solution in a delocalized form and are subsequently solvated.

Alpatova and co-workers [10] have already noted that the mechanism of e_s^- generation depends on the state of the electrode surface. Measurements of the double-layer capacitance [11] have revealed that cathodic polarization of electrodes in alkali metal solutions can lead to passivation which decreases the ability for and the rate of e_s^- generation. Anodic polarization reactivates the surface. The probable formation of an organic film increases the tunnelling barrier for e_s^- generation. Spectral methods [12] have shown that films of different compositions may be formed depending on the type of electrode material used and the solution purity. It was concluded that a different degree of electrode passivation can explain why different authors obtained qualitatively and quantitatively different results.

When one compares the mobility of e_s^- to that of other charged species, it can be noted that the movement of e_s^- is anomalous. Different studies leading to different e_s^- diffusion coefficients are known and one may say that in the literature some controversy about the e_s^- transport mechanism exists.

In this study, first some attention is paid to the electrochemical properties of HMPA and to the general characteristics of e_s^- generation in this solvent. Then the electrochemical oxidation of e_s^- by means of the rotating ring-disk electrode (RRDE) technique is reported. This technique gives us the possibility of studying the current distribution during e_s^- generation and of estimating e_s^- transit times. The transit times obtained were used to calculate the e_s^- diffusion coefficient ($D_{e_s^-}$). $D_{e_s^-}$ measurements at different temperatures gave an insight into the way the electrons move in this medium. Because electrode passivation is a major problem when e_s^- are electrochemically generated in HMPA, this subject will also receive attention.

EXPERIMENTAL

Reagents

Commercial granular phosphorus pentoxide (J.T. Baker) and silver nitrate (H. Drijfhout & Zoon's) were used as received. Commercial glassy carbon (C_g) (Highways International) and pyrolytic graphite (C_p) were used to manufacture the electrodes. Commercial HMPA (99%, Janssen Chimica), LiCl (ultrapure 99.99%, Alfa), LiBr (99 + %, Janssen Chimica), BTS catalyst (BASF) and argon (Hoekloos) were purified as described below.

Preparation of the solution

Investigation of e_s^- requires a well-purified system. The impurities in HMPA are amines, chlorides (especially HCl), water and HMPA peroxides. HMPA was re-

fluxed in an argon atmosphere under reduced pressure (0.1 Torr) over granular phosphorus pentoxide.

The argon used was first deoxygenated at 150 °C by means of a BTS catalyst, which consists of dispersed copper. This catalyst was deoxygenated by hydrogen gas before use. The argon was subsequently dried over molecular sieves, which, in turn and before use, were dried under vacuum (0.1 Torr) at 200 °C. As the conducting salt, LiCl or LiBr was used. The Li salt was pre-dried in an oven at 150 °C for at least 24 h and dried again in the distillation apparatus under reduced pressure at 180 °C for 4 h. The first fraction of HMPA was collected after 4 h of refluxing. Only the middle fraction (56 °C, 0.1 Torr) was used for the 0.3 M Li salt solution. The solution was brought to and kept under atmospheric pressure with the dried argon.

The purity of HMPA can be checked qualitatively by adding silver nitrate [12]: the appearance of instantaneous white cloudiness and of a brown colour after a few minutes indicates the presence of chloride anions and amines, respectively. Conductivity measurements can be used as a quantitative check, since it has been shown that the conductivity is related to the total amount of impurities [6]. The conductivity of the undistilled solvent was $1.14 \times 10^{-6} \text{ mS cm}^{-1}$. After the first distillation, the HMPA conductivity was $10^{-7} \text{ mS cm}^{-1}$, and this distillate was used for the preparation of the Li salt solution.

Cell

The three-compartment electrochemical cell used is shown in Fig. 1. The cell was pre-cleaned with a $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ solution, rinsed thoroughly with distilled water and stored in a drying oven at 120 °C until just before use. The specifications and geometric parameters of the rotating ring-disk working electrodes used are

Fig. 1. The electrochemical cell.

TABLE 1

Rotating ring-disk electrode characteristics

RRDE No.	Disk ^a	Ring ^a	r_1 /cm	r_2 /cm	r_3 /cm	α	β	N_t
1	C _g	C _g	0.350	0.464	0.599	1.322	2.690	0.358
2	C _p	Pt	0.401	0.440	0.489	0.321	0.492	0.238
3	C _p	Pt	0.405	0.437	0.495	0.256	0.566	0.268
4	Pt	Pt	0.4001	0.4393	0.4882	0.324	0.4921	0.238

^a C_g = glassy carbon; C_p = pyrolytic graphite.

given in Table 1. The electrodes were polished with aluminium oxide, rinsed with distilled water and dried before use. A Pt foil (2.5 cm²) served as the counter-electrode. A silver wire, which had a potential of -0.96 V (vs. SCE) in the medium studied, was used as the reference electrode. All potentials were measured with respect to this reference electrode unless otherwise stated. The electrochemical cell was filled first with dried argon, then with 8 ml of the Li salt + HMPA solution by means of pressurized argon. During the experiments, argon was bubbled through the solution. The cell temperature was controlled by a Huber Variostat and measured by a Ru/Pt thermocouple.

Transient measurements

Figure 2 shows the instrument set-up for the transient measurements.

Measuring devices

The potentials and currents of the electrode were controlled by a Tacussel bipotentiostat of the type Bi-Pad and a Wenking model VSG 72 Voltage Scan Generator. For the transient measurements a Nicolet 310 digital scope was used. The currents were recorded using a Kipp & Zonen BD91 dual pen X-Y₂ recorder.

Fig. 2. Instrument set-up for transient measurements.

Fig. 3. Current-potential characteristic of a C_g disk electrode (No. 1) in 0.3 M LiBr + HMPA obtained by the triangular potential sweep method. Scanning rate: 200 mV s^{-1} ; $T = 1.5^\circ \text{C}$.

RESULTS AND DISCUSSION

Electrochemical properties of HMPA and the electrochemical generation of solvated electrons

The current-potential characteristic of a 0.3 M Li salt + HMPA solution is shown in Fig. 3, corresponding to the results presented in the literature [2,11]. The electrolytic generation of e_s^- can be represented by

in which e_M^- denotes the electron present in the electrode material. At the disk electrode of a C_g/C_g RRDE this generation starts at -2.1 V . A reversible anodic current, due to e_s^- oxidation, was observed after scanning back positively. For lithium salt solutions the shape of the anodic curve pertains to the oxidation of

Fig. 4. Tafel slope of e_s^- generation at a C_g disk electrode (No. 1) in 0.3 M LiBr + HMPA. Scanning rate: 10 mV s^{-1} ; $T = 1.5^\circ \text{C}$.

mono-electrons. When excess salt is present, ion pairs can be formed which differ only slightly in their properties from non-associated electrons. Lithium cations never form associates with two electrons.

For the generation of e_s^- a Tafel slope of 60 mV/dec is found (see Fig. 4; for a comparison, see refs. 2,3,4,7 and 8). Mechanisms involving the discharge of base electrolyte cations either with the formation of a alkali-metal phase or with the formation of adatoms, or a mechanism involving barrierless reduction of solvent molecules were refuted by the independence of the generation rate on the type of cation and on the type of electrode material [8]. The absence of a rotation dependence excludes concentration polarization. The Tafel slope of 60 mV/dec corresponds to the electron thermoemission escape mechanism mentioned earlier [7].

Collection efficiency N and current distribution

It is known that e_s^- are rather stable in HMPA. So, in a solution of 0.3 M LiBr in HMPA, it was possible to generate e_s^- at the disk electrode of a RRDE and collect them at the ring electrode. The disk current I_D was controlled galvanostatically; the ring potential E_R was kept constant at 0 V, while the ring current I_R was measured for different values of I_D . The experimental I_R - I_D curve is shown in Fig. 5. The measured collection efficiency N_m does not coincide with the theoretical collection efficiency N_t [13]: N_m exceeds N_t . A possible explanation follows from assuming a non-uniform current distribution on the disk electrode during e_s^- generation [14].

Fig. 5. Experimental and calculated I_R - I_D curves for the generation and oxidation of e_s^- at a RRDE (No. 1; with wide gap) 0.3 M LiBr + HMPA; $\omega = 2.55 \text{ rad s}^{-1}$, $T = 1.5^\circ \text{C}$, $E_R = 0 \text{ V}$. (+) Experimental; (Δ) calculated. $N_m = 0.385$; $N_t = 0.358$.

Fig. 6. Experimental and calculated I_R-I_D curves for the generation and oxidation of e_s^- at a RRDE (No. 2; with small gap). 0.3 M LiBr+HMPA; $\omega = 2.55 \text{ rad s}^{-1}$, $T = 1.5^\circ \text{C}$, $E_R = 0 \text{ V}$. (+) Experimental; (Δ) calculated. $N_m = 0.347$; $N_t = 0.268$.

The degree of non-uniformity can be assessed by calculating Newman's dimensionless parameter J :

$$J = j_{\text{avg}}(nFr_1/RT\kappa) \quad (1)$$

where j_{avg} is the average disk current density, r_1 is the disk radius, κ is the specific conductance, and n , F , R and T have their usual meaning. As has been shown [15], a uniform current density cannot be achieved at currents below the limiting current density or when J exceeds 0.1. The latter can, for example, be caused by a high solution resistance. As for 0.3 M LiBr in HMPA, $\kappa = 5.22 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$; further, $nF/RT = 42.27 \text{ C J}^{-1}$ and $r = 0.35 \text{ cm}$; the range of J is from 2.9 to 11.2. Current density profiles at a disk electrode are known for different J values [15]. High J values result in higher current densities at the edge of the disk electrode. This is reflected in higher collection efficiencies. The deviation from N_t is less when a RRDE with a wider gap is used. Indeed, it was found that the N_m/N_t ratio depends on the gap width. The I_R-I_D curve for an electrode with a small gap (electrode No. 2) is shown in Fig. 6. It is, however, difficult to relate quantitatively measured collection efficiencies to J values.

Passivation

As has been noted, passive films are formed on the electrode during the electrochemical generation of e_s^- , even when the solvent/electrolyte is well purified.

There are several possible causes of passivation. The electrochemical reduction of traces of water leads to the precipitation of lithium hydroxide on the electrode. Also the solvent can be destroyed electrocatalytically by the electrode material. In any case, the formation of a passive film increases the barrier thickness for e_s^- generation and may change the e_s^- escape mechanism or promote electrodeposition of the alkali metal [8,9].

The influence of water was studied by means of a C_g/C_g RRDE. When traces of water are introduced during galvanostatic e_s^- generation at the disk, lithium hydroxide precipitates on the disk and on the ring electrode ($E_R = 0$ V) as a result of the reaction of water with e_s^- ($k = 16 \text{ l mol}^{-1} \text{ s}^{-1}$ [5]). A thin layer does not affect the e_s^- generation potential at the disk or the e_s^- oxidation current at the ring, so the film seems to be permeable for e_s^- .

When the film becomes thicker, the e_s^- generation potential at the disk increases as a result of increasing barrier thickness and the oxidation current at the ring decreases because the e_s^- cannot reach the ring electrode properly. The film cannot be removed by anodic polarization. Possible formation of an organic film through electrocatalytic destruction of the solvent was studied by means of a C_g/C_g and a C_p/Pt RRDE. First, the effect on the e_s^- oxidation current was investigated; then the effect on the e_s^- generation Tafel slope. The ring e_s^- oxidation current was measured while E_R was scanned negatively. I_D was kept constant galvanostatically. The ring electrode materials C_g and Pt were anodically polarized before scanning. The results are shown in Fig. 7 (represented by the solid lines).

The C_g ring electrode (see Fig. 7A) showed no decrease in e_s^- oxidation current during negative polarization until the e_s^- redox potential was reached. However, similar scanning of the Pt electrode potential leads to a drastic decrease in the e_s^- oxidation current before the e_s^- redox potential was reached (see Fig. 7B, path 1). A reverse scan, where the Pt potential was scanned to -1 V, shows the e_s^- oxidation current at -0.3 V to be revived, represented by path 2. The cyclic voltammogram of an active Pt electrode shows a faradaic current peak at -0.9 V, corresponding to the potential at which the e_s^- oxidation rate decreases. When the Pt electrode is not anodically polarized before scanning, different results are obtained, as can be seen by the dotted line, path 3, in Fig. 7B. A high positive potential (2 V) is then necessary to regain the limiting e_s^- oxidation current.

At Pt, a film, probably from the electrocatalytically destroyed solvent, is formed. This film is not permeable for e_s^- and its formation potential seems to be determined by the surface state.

The effects of the film formed on the e_s^- generation remain. Using the C_g electrode, no decrease was observed (see Fig. 7A). Probably, the solvent is not electrocatalytically destroyed at C_g . Generation of e_s^- at a passive Pt electrode can still take place, though the range of Tafel slopes measured, ranging from 93 to 200 mV, are hard to reproduce. In general, an anodically polarized Pt electrode gives the lowest Tafel slope, and a cathodically polarized one the largest. It was assumed that an increasing film thickness lowers the tunnelling probability of the electron for

Fig. 7. I_R - E_R curves in 0.3 M LiBr+HMPA for electrode No. 1 (A) and electrode No. 2 (B). Scanning rate: 200 mV s^{-1} ; $T = 1.5^\circ \text{C}$, $I_D = 1 \text{ mA}$, $\omega = 2.55 \text{ rad s}^{-1}$.

thermoemission. A different film thickness may therefore lead to different Tafel slopes and may explain the poor reproducibility.

Transient measurements

A known non-steady approach to electrochemical processes is the determination of the transit time τ of a species generated at the disk of a RRDE [16]. The time required for a species generated at the outer edge of the disk electrode to reach the inner edge of the ring electrode is called the transit time τ . Transit time measurements are useful in determining adsorption processes at the disk [17] or can be used to calculate the diffusion coefficient of the disk-generated species. If nothing is adsorbed at the disk, a disk-generated species will immediately be transferred to the ring by convective diffusion. For this case, Bruckenstein and Feldman [16] derived the expression

$$\omega\tau = 4.51(\nu/D)^{1/3}[\log(r_2/r_1)]^{2/3} \quad (2)$$

where ω is the rotation frequency of the RRDE, ν is the kinematic viscosity, D is the diffusion coefficient, and r_1 and r_2 are the radius of the disk and the inner radius of the ring, respectively. For the determination of the e_s^- transit times in a 0.3

Fig. 8. I_D-t and I_R-t curves for transit time measurements in 0.3 M LiBr + HMPA.

M LiBr/HMPA solution, the ring current transient was recorded after a current step at the disk electrode. Figure 8 shows the corresponding I_D-t and I_R-t curves.

In order to investigate whether the system was practically suitable for the determination of diffusion coefficients, it was tested by measuring the diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{4-}$ in 1 M aqueous KOH. The diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{4-}$ in this medium is known from literature [18]: $0.59 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 20°C . Mean $\omega\tau$ values were calculated from transit time measurements in this medium, using a Pt/Pt RRDE (RRDE nr. 4) the radii of which could be measured with great accuracy, i.e. with r_2/r_1 known exactly. At 20°C , a value of $0.56 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was found, agreeing well with the value from literature, and it was concluded that this method can be used for D determination. Measuring the radii of a carbon RRDE with the same accuracy is not easy. Sometimes the disk radius is not a perfect constant, and moreover, in the case of pyrolytic graphite, the surface is rough, which is a reason to gauge these electrodes as described above. The r_2/r_1 values, so obtained, see Table 2, were used for further calculations. To determine the diffusion coefficient of e_s^- in LiBr + HMPA, transit times curves were recorded at different rotation frequencies. Figure 9 gives the corresponding $\tau-\omega$ and $\omega\tau-\omega$ curves for RRDE No. 1.

For all rotation frequencies $\omega\tau$ must be constant. The mean of $\omega\tau$ was used to calculate $D_{e_s^-}$, being $1.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 21°C .

Information on the mobility of e_s^- is available for a few polar liquids only. In general, e_s^- mobilities are slightly greater than ionic mobilities. For water, the observed mobility of e_s^- is $1.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [19], corresponding to a

TABLE 2

Measured and calculated r_2/r_1 ratios for the different electrodes

Electrode No.	$(r_2/r_1)_{\text{measured}}$	$(r_2/r_1)_{\text{calculated}}$
1	1.3257	1.3521
2	1.0972	1.1206
3	1.0774	1.1120

Fig. 9. τ - ω (+) and $\omega\tau$ - ω (◆) obtained in a 0.3 M LiBr+HMPA solution at 21°C using RRDE No. 1.

diffusion coefficient of $0.49 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ (the mobility is related to the diffusion coefficient by the Nernst–Einstein relation $\mu = eD/kT$). This value is higher than those of nearly all ions in water, but comparable to that of OH^- . In ammonia the mobility of e_s^- is even higher, being $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [20] ($2.6 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$).

The transport seems not to be ionic and it was suggested that the electron can jump or tunnel from its cavity to a neighbouring site. In ethers, which are only slightly polar, the electron mobility is even larger and migration via the conduction band is indicated [21].

To our knowledge the value of $D_{\text{e}_s^-}$ in Li-salt + HMPA solutions is not unequivocal. In ref. 22, a value of $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was reported. This value was later considered as being much solvent by means of conductivity experiments and found to be $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at room temperature. In refs. 26 and 27 this value was criticized and in ref. 26 $D_{\text{e}_s^-}$ was calculated by means of diffusion controlled rate constant determinations in HMPA at room temperature: a value of $9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was found. Because little interaction exists between e_s^- and Li^+ , only small deviations, if any, from $D_{\text{e}_s^-}$ in pure HMPA are expected for $D_{\text{e}_s^-}$ in Li-salt + HMPA solutions. The values we found do not differ much from the values in ref. 24. It is not clear why Delaire et al. [27] found a different value. The absolute value of $D_{\text{e}_s^-}$ must reflect the mechanism of transport. Considering the diffusion coefficients of other species in HMPA at room temperature ($D_{\text{Li}^+} = 2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{anthracene}} = 5.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), the displacement of e_s^- seems anomalous. Considering

non-ion-like transport mechanisms, we can distinguish three different ways of displacements for the electron: by means of tunneling, by means of a hopping mechanism or via a quasifree state. This was investigated further by measuring $D_{e_s^-}$ at different temperatures. For most hydrocarbon liquids, the electron mobility μ increases with temperature described by an Arrhenius-like equation:

$$\mu = \mu_0 e^{-E_a/RT} \quad (3)$$

To get more insight into the transport mechanism of e_s^- in HMPA, the temperature dependence of the diffusion coefficient was investigated. As an upper limit 21°C was taken because at higher temperatures the collection efficiency decreased as a result of e_s^- decay reactions. The mean $\omega\tau$ values, the calculated kinematic viscosities and the obtained $D_{e_s^-}$ for the different temperatures are shown in Table 3. Figure 10 shows the corresponding Arrhenius plot. The activation energy of the diffusion process was found to be 5.9 kJ mol⁻¹. The activation energy for electrons

TABLE 3

$\overline{\omega\tau}$ values, calculated kinematic viscosities (ν) and experimental e_s^- diffusion coefficients in 0.3 M LiBr + HMPA for RRDE Nos. 1–3 at different temperatures

$T/^\circ\text{C}$	$\overline{\omega\tau}$	$10^2 \nu/\text{cm}^2 \text{ s}^{-1}$	$10^5 D_{e_s^-}/\text{cm}^2 \text{ s}^{-1}$
<i>RRDE No. 1</i>			
-8.5	36.95 ± 0.44	14.75	0.46
-4.8	33.80 ± 0.82	13.12	0.53
-3.3	32.36 ± 0.62	12.51	0.46
0.0	29.85 ± 0.13	11.25	0.66
1.2	29.37 ± 0.04	10.82	0.67
5.0	28.81 ± 0.13	9.58	0.64
8.0	25.74 ± 0.25	8.72	0.8
12.0	24.57 ± 0.19	7.73	0.82
15.0	24.06 ± 0.25	7.11	0.8
18.0	23.50 ± 0.19	6.59	0.8
21.0	20.48 ± 0.19	6.18	1.13
<i>RRDE No. 2</i>			
-7.4	18.10 ± 0.44	14.25	0.54
-5.0	17.15 ± 0.44	13.21	0.59
0.0	15.77 ± 0.25	11.25	0.64
5.0	14.70 ± 0.13	9.58	0.68
10.0	13.07 ± 0.25	8.20	0.82
15.0	12.38 ± 0.25	7.11	0.84
<i>RRDE No. 3</i>			
-7.6	16.86 ± 0.06	14.34	0.58
-5.0	16.15 ± 0.19	13.21	0.61
0.0	14.29 ± 0.13	11.25	0.75
5.0	13.26 ± 0.06	9.58	0.8
10.0	12.21 ± 0.06	8.20	0.88
15.0	11.44 ± 0.13	7.11	0.93
20.0	10.62 ± 0.19	6.31	1.03

Fig. 10. Temperature dependence of $D_{e_s^-}$. RRDE No. 1 (+), 2 (O), 3 (Δ).

to reach the bottom level of a quasi-free state from the ground level of a localized state is determined by the gap between them. According to ref. 28, which provides the energy parameters of excess electrons in HMPA, the photoionisation energy is approximately 132 kJ mol^{-1} . Thus, our experimental results exclude a transport mechanism via a quasi-free state. Since tunnelling implies temperature independence of the mobility, a hopping mechanism seems the most plausible explanation for the observed phenomena.

LIST OF SYMBOLS

D	diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)
e_M^-	electron present in the electrode material
e_s^-	solvated electron
E_a	activation energy (kJ mol^{-1})
E_D	disk potential (V vs. Ag wire)
E_R	ring potential (V vs. Ag wire)
F	Faraday constant (96485 C mol^{-1})
I_D	disk current (mA)
I_R	ring current (mA)
j	current density (mA cm^{-2})
j_{avg}	average current density (mA cm^{-2})
J	Newman's dimensionless parameter

n	number of electrons involved in the electrochemical reaction
N_t	theoretical collection efficiency of the RRDE
N_m	measured collection efficiency of the RRDE
R	gas constant ($8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$)
r_1	disk radius (cm)
r_2	inner ring radius (cm)
r_3	outer ring radius (cm)
t	time (s)
T	temperature ($^{\circ}\text{C}$ or K)
α	$(r_2/r_1)^3 - 1$
β	$(r_3/r_1)^3 - (r_2/r_1)^3$
κ	specific conductance ($\Omega \text{ cm}^{-2}$)
μ	mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
ν	kinematic viscosity ($\text{cm}^2 \text{ s}^{-1}$)
τ	transit time (s)
ω	rotation frequency (rad s^{-1})

REFERENCES

- 1 H.W. Sternberg, R. Markby and I. Wender, *J. Electrochem. Soc.*, 110 (1963) 425.
- 2 Y. Kanzaki and S. Aoyagui, *J. Electroanal. Chem.*, 36 (1972) 297.
- 3 N.M. Alpatova, L.I. Krishtalik and M.G. Fomicheva, *Sov. Electrochem.*, 8 (1972) 516.
- 4 L.A. Avaca and A. Bewick, *J. Electroanal. Chem.*, 41 (1973) 395.
- 5 For a review see N.M. Alpatova, L.I. Krishtalik and Y.U. Pleskov, *Top. Curr. Chem.*, 138 (1987) 149.
- 6 L.I. Krishtalik, *Electrochim. Acta*, 21 (1976) 693.
- 7 L.I. Krishtalik and N.M. Alpatova, *J. Electroanal. Chem.*, 65 (1975) 219.
- 8 L.I. Krishtalik and N.M. Alpatova, *Sov. Electrochem.*, 12 (1976) 161.
- 9 L.I. Krishtalik, N.M. Alpatova and E.V. Ovsyannikova, *Sov. Electrochem.*, 12 (1976) 1365.
- 10 M.G. Fomicheva, N.M. Alpatova and S.E. Zabusova, *Sov. Electrochem.*, 13 (1977) 179.
- 11 G.W. Martin and R.W. Murray, *J. Electroanal. Chem.*, 98 (1979) 149.
- 12 M.G. Fomicheva, Yu.M. Kessler, S.E. Zabusova and N.M. Alpatova, *Sov. Electrochem.*, 11 (1975) 152.
- 13 W.J. Albery and S. Bruckenstein, *Trans. Faraday Soc.*, 62 (1966) 1920.
- 14 J. Newman, *J. Electrochem. Soc.*, 113 (1966) 1235.
- 15 W.J. Albery and M.L. Hitchman, *Ring-Disk Electrodes*, Clarendon Press, Oxford, 1971, pp. 29-37.
- 16 S. Bruckenstein and G.A. Feldman, *J. Electroanal. Chem.*, 9 (1965) 395.
- 17 S. Bruckenstein and D.T. Napp, *J. Am. Chem. Soc.*, 90 (1968) 6303.
- 18 R. Landsberg and R. Thiele, *Electrochim. Acta*, 11 (1966) 1243.
- 19 E.J. Hart and M. Anbar, *The Hydrated Electron*, Wiley-Interscience, New York, 1970.
- 20 J.L. Dye, R.F. Sankuer and G.E. Smith, *J. Am. Chem. Soc.*, 82 (1960) 4797.
- 21 J.-P. Dodelet and G.R. Freeman, *Can. J. Chem.*, 53 (1975) 1263.
- 22 Y. Kanzaki and S. Aoyagui, *J. electroanal. Chem.*, 36 (1972) 297.
- 23 L.A. Avaca and A. Bewick, *J. Electroanal. Chem.*, 41 (1973) 395.
- 24 E.I. Mal'tsev, A.V. Vannikov and N.A. Bakh, *Radiat. Eff.*, 20 (1973) 197.
- 25 A.V. Vannikov, E.I. Mal'tsev, V.I. Zolotarevsky and A.V. Rudnev, *Int. J. Radiat. Phys. Chem.*, 4 (1972) 135.
- 26 E.A. Shaede, L.M. Dorfman, G.J. Flynn and D.C. Walker, *Can. J. Chem.*, 51 (1973) 3905.
- 27 J.A. Delaire, M.O. Delcourt and J. Belloni, *J. Phys. Chem.*, 84 (1980) 1186.
- 28 D.A. Copeland, N.R. Kestner and J. Jortner, *J. Chem. Phys.*, 53 (1970) 1189.