Steady-State Voltammetry at a Rotating Disk Electrode in the Absence of Supporting Electrolyte

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Steady-State Voltammetry at a Rotating Disk Electrode in the Absence of Supporting Electrolyte

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Predictions have been made of how total withdrawal of supporting electrolyte affects the steady-state limiting current at a rotating disk electrode. Incorporating transport by diffusion, migration, and convection, the treatment is restricted to a three-ion system under the assumption that all the ions share the same diffusivity. The results predict qualitative, but not quantitative, agreement with similar studies relating to steady-state voltammetry at a hemispherical microelectrode. The experimental findings of Gao and White are discussed in the light of the new treatment.

Introduction

The modeling of voltammetry when supporting electrolyte is absent is difficult because the migration that this introduces adds complications. By removing the time variable, however, restriction to the steady state provides a welcome simplification that has permitted some unsupported systems to be modeled exactly. Thus Amatore et al.[1] and, later, Cooper et al.[2] treated the voltammetry of the

$$R(\text{soln}) - (z_P - z_R)e^- \longrightarrow P(\text{soln, absent from bulk}) \quad (1)$$

reaction at a hemispherical microelectrode and showed that the steady limiting current density differed from that in a fully supported experiment by the factor

$$\frac{z_R - z_C}{z_C}\left[\frac{z_R z_P}{z_C(z_P - z_R)}\ln\left\{\frac{z_R(z_P - z_C)}{z_P(z_R - z_C)}\right\} - 1\right] \quad (2)$$

where z_R, z_P, and z_C are the charge numbers of the reactant, product, and an electropassive counterion.[3] It is of interest to enquire whether factor 2 is equally applicable to other steady-state systems and, if not, what other factor applies. To throw light on this question, the present study examines the behavior of reaction 1 in an unsupported system at a rotating disk electrode. Attention is restricted to the steady-state limiting current density. The limiting current is of paramount importance experimentally because it alone can be measured without corruption from ohmic polarization ("IR drop"), which is always more severe when supporting electrolyte is absent.

There have recently been a number of publications addressing systems in which migration augments the two transport modes, convection and diffusion, that are always operative in a rotating disk experiment. Many of these, involving plating onto[4−7] or dissolution of[8] the disk do not match reaction 1. Nor do the reactions considered by Nechiporuk and Elgurt[9] or by Pritzker.[10] Feldberg et al.[11] have discussed the simulation of rotating disk electrodes when contributions to transport are made by all three modes. All three transport modes are also considered in an interesting article by Gao and White[12] which reports the behavior of a small disk electrode, both rotating and stationary, when various levels of electrolyte support are present.

Model Conditions

An electrolyte solution is envisaged in which there are three solute ions: R, P, and C. The product ion P is absent from the bulk solution, which has a density d and a viscosity η. The reactant and product, R and P, have charge numbers, z_R and z_P, of the same sign, but opposite to z_C, the charge number of the counterion C. The case in which $z_R = 0$ is explicitly excluded from consideration because, in principle, no current whatsoever can flow in an unsupported solution of such an uncharged electroreactant. Cases in which z_R and z_P have opposite signs are also excluded because no limiting currents can be attained in such systems.

The rotating disk electrode is of standard design with radius a and a constant angular velocity ω. As in the classic Levich derivation,[13] the velocity of the solution, in the x-direction normal to the disk, is taken to obey the equation

$$v_x = -Kx^2\sqrt{\omega^3 d/\eta} \quad (3)$$

over the entire region $0 \leq r \leq a$, $0 \leq x \leq X$ where r is the radial dimension and X is an axial distance beyond which the solution is effectively of bulk composition. K is the von Kármán constant, equal to 0.510. It is assumed, following Levich, that the ionic concentrations c_i ($i = $ R, P or C) are functions only of x in $0 \leq r \leq a$, $0 \leq x \leq X$ and independent of both r and time, t. A consequence is that the current density i is constant and uniform over the area πa^2 of the electrode disk.

Obedience to the electroneutrality condition

$$z_R c_R + z_P c_P + z_C c_C = \sum z_i c_i = 0 \quad (4)$$

is assumed. $\sum$ is being used to imply a sum over all three ions. The Nernst−Einstein relationship

$$RTu_i = |z_i|FD_i \quad (5)$$

interrelating the mobility u_i of ion i and its diffusivity (diffusion coefficient) D_i, is also taken to hold. R, T, and F have their usual significances.

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It will be assumed that the diffusivities of the three ions share a common value D. This enables us to invoke the principle of unchanging total concentration[14]

$$c_R + c_P + c_C = \sum c_i = \text{constant} = c_R^b + c_C^b = c_P^s + c_C^s \quad (6)$$

Note our use of the superscripts b and s to indicate conditions in the bulk solution and at the electrode surface. The last two equalities in (6) reflect the absence of P from the bulk and, on account of the extreme concentration in the limiting current region, the absence of R at the surface. The need to assume equidiffusivity is a severe weakness of the present model. Notice that the derivation of factor 2 required only the assumption $D_P = D_R$, which is much more credible than the assertion that the counterion diffuses at the same rate as the electroactive species.

Properties of the Electrolyte Solution

As advocated elsewhere,[14,15] the ionic strength

$$\mu = \frac{1}{2}\sum z_i^2 c_i \quad (7)$$

may provide a more convenient dependent variable than selecting any one of the ionic concentrations for this role. The three equations (4), (6), and (7) permit the local concentration of each ion to be expressed in terms of the local ionic strength μ and either the bulk, or the surface, ionic strength

$$c_i = \frac{2z_R z_C \mu - 2z_j z_k \mu^b}{z_R z_C(z_i - z_j)(z_i - z_k)} = \frac{2z_P z_C \mu - 2z_j z_k \mu^s}{z_P z_C(z_i - z_j)(z_i - z_k)} \quad (8)$$

In these equations the subscripts j and k denote the two ions other than i.

The local conductivity of the solution is given by the first equality[16] below

$$\kappa = F\sum |z_i| u_i c_i = \frac{F^2}{RT}\sum z_i^2 D_i c_i = \frac{2F^2 D\mu}{RT} \quad (9)$$

The second and third equalities then follow from eqs 5 and 7 and from the assumption of common diffusivity. Because Ohm's law asserts proportionality between the current density i, here constant and uniform, and the local field strength $-\partial\phi/\partial x$, the conductivity being the proportionality constant, eq 9 leads to

$$-\frac{d\phi}{dx} = \frac{i}{\kappa} = \frac{RTi}{2F^2 D\mu} \quad (10)$$

Here ϕ is the local potential, measured with respect to the bulk solution.

Transport Model

The diffusive and migratory components of the flux density of solute i toward the electrode are represented respectively by the first and second right-hand terms in the equation

$$-j_i = D_i \frac{\partial c_i}{\partial x} + \frac{z_i u_i c_i}{|z_i|}\frac{\partial\phi}{\partial x} - (j_{conv})_i \quad (11)$$

It is not possible to easily elaborate the convective term $(j_{conv})_i$ in this flux equation, because convection is not solely along the x-axis. However, because we have defined v_x as the component of the solution velocity in the x-direction, convective transport is represented by the third right-hand term in the equation

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{z_i u_i}{|z_i|}\frac{\partial}{\partial x}\left\{c_i \frac{\partial\phi}{\partial x}\right\} - v_x \frac{\partial c_i}{\partial x} \quad (12)$$

The whole equation expresses the rate of local concentration change brought about by each of the three transport modes: diffusion, migration, and convection. Equation 12 follows from (11) by exploiting the conservation relationship

$$\frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} = 0 \quad (13)$$

Because of the restriction to the steady state, the left-hand term is zero and the spatial dimension x becomes the sole independent variable in eq 12. Replacement of u_i via eq 5 and v_x via eq 3 now leads to

$$0 = \frac{d^2 c_i}{dx^2} + \frac{z_i F}{RT}\left[c_i \frac{d^2\phi}{dx^2} + \frac{dc_i}{dx}\frac{d\phi}{dx}\right] + \frac{K}{D}\sqrt{\frac{\omega^3 d}{\eta}}x^2\frac{dc_i}{dx} \quad (14)$$

after division by the common diffusivity D. Next, substitution for c_i from eq 8 and for $(d\phi/dx)$ from eq 10 produces

$$0 = \frac{d^2\mu}{dx^2} + \frac{z_i i}{2FD}\left[\left(\mu - \frac{z_j z_k}{z_R z_C}\mu^b\right)\frac{1}{\mu^2}\frac{d\mu}{dx} - \frac{1}{\mu}\frac{d\mu}{dx}\right] + \frac{K}{D}\sqrt{\frac{\omega^3 d}{\eta}}\frac{d\mu}{dx} \quad (15)$$

As it must, this equation adopts the same form irrespective of the choice of i.

Further simplification results from defining a new independent variable

$$\chi = x\left(\frac{K}{3D}\sqrt{\frac{d}{\eta}}\right)^{1/3}\sqrt{\omega} \quad (16)$$

a new dependent variable

$$\rho = \frac{\mu}{\mu^b} = \frac{\mu}{z_R(z_R - z_C)c_R^b} \quad (17)$$

and a dimensionless parameter

$$\lambda = \frac{i}{2F\mu^b\sqrt{\omega}}\left(\frac{3}{KD^2}\sqrt{\frac{\eta}{d}}\right)^{1/3} \quad (18)$$

Note that the sign of λ is that of the current density i: positive if $z_P > z_R$, negative if $z_P < z_R$. These substitutions convert eq 15 into the compact differential equation

$$0 = \frac{d^2\rho}{d\chi^2} + \left[3\chi^2 - \frac{z_P\lambda}{\rho^2}\right]\frac{d\rho}{d\chi} \quad (19)$$

Its solution is addressed in the next section.

Without solving eq 19, one can see from definition 18 that the steady limiting current obeys the equation

$$i = 2\lambda F\mu^b\left(\frac{KD^2}{3}\sqrt{\frac{d}{\eta}}\right)^{1/3}\sqrt{\omega} \quad (20)$$

in which λ appears as a (presently unknown) numerical coefficient. Note that exactly the same proportionalities—to the square root of the rotation rate, to the two-thirds power of the diffusivity, and to the minus one-sixth power of the viscosity— are obeyed as in fully supported transport-controlled rotating-

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disk voltammetry. It remains to find λ, the value of which will reflect the magnitudes of the charge numbers z_R, z_P, and z_C.

Solution of the Differential Equation

To find λ, the solution of eq 19 is sought subject to the boundary conditions

$$\rho = \rho^s = \frac{z_P}{z_R} \quad \text{at} \quad \chi = 0 \tag{21}$$

which is a consequence of the second equality in (8), and

$$\rho \rightarrow \rho^b = 1 \quad \text{as} \quad \chi \rightarrow \infty \tag{22}$$

A third boundary condition is required for the efficient solution of (19), and one can be found by considering the flux density j_R^s at the electrode surface. This flux density can have no convective component at $x = 0$ because of the presence of the x^2 factor in v_x. Moreover, because c_R^s is zero under total concentration polarization, eq 11 shows that the migratory flux density vanishes too. Accordingly, the surface flux density of R is wholly diffusive and obeys Fick's first law

$$-j_R^s = D \left(\frac{dc_R}{dx} \right)^s \tag{23}$$

By Faraday's law, the left-hand member of (23) is proportional to current density and equals $i/[(z_P - z_R)F]$. The right-hand member can be expressed as proportional to $(d\rho/d\chi)^s$ by taking advantage of eqs 8, 16, and 17. One discovers that

$$\frac{i}{(z_P - z_R)F} = \frac{2\mu^b}{(z_R - z_P)(z_R - z_C)} \left(\frac{KD^2}{3} \sqrt{\frac{d}{\eta}} \right)^{1/3} \left(\frac{d\rho}{d\chi} \right)^s \tag{24}$$

The surprisingly simple result

$$\left(\frac{d\rho}{d\chi} \right)^s = -\lambda(z_R - z_C) \tag{25}$$

follows when eq 18 is invoked. Equation 25 serves as a third boundary condition.

Analytic solutions, namely

$$\rho = \frac{z_P}{z_R} \left[1 - \left(\frac{z_R - z_C}{z_R} \right) \left(\exp\left\{ \frac{\lambda z_R^2 \chi}{z_P} \right\} - 1 \right) \right] \quad \text{as} \quad \chi \rightarrow 0 \tag{26}$$

and

$$\rho = \frac{\gamma(1/3; \chi^3)}{\Gamma(1/3)} \quad \text{as} \quad \chi \rightarrow \infty \tag{27}$$

are available close to the electrode and far from it, but a numerical approach is needed at intermediate distances. In eq 27 $\gamma(;)$ and $\Gamma( )$ are the incomplete and complete gamma functions.[17]

A "shooting" method,[18] similar to one that we have described previously,[15] was used in a computer-implemented numerical solution of eq 19. The idea is to guess λ and then, starting with the known value of ρ^s, progressively compute ρ for larger and larger χ up to a $\chi = 2.5$ limit,[19] corresponding to the bulk solution. If condition 22 is met within $\pm 1 \times 10^{-5}$ at $\chi = 2.5$, the value of λ is accepted as correct. Otherwise the previous λ estimate is automatically adjusted and the process is repeated until a satisfactory λ is found. Extrapolation through $0 < \chi \leq 2.5$

TABLE 1: Values of the Current Ratio $(i/i_{levich})_{lim}$ for the Cases $z_C = \mp 1$

	$z_R = \pm 1$	$z_R = \pm 2$	$z_R = \pm 3$	$z_R = \pm 4$	$z_R = \pm 5$	$z_R = \pm 6$
$z_P = \pm 1$		1.2980	1.6078	1.9211	2.2360	2.5517
$z_P = \pm 2$	0.8201		1.1917	1.3863	1.5820	1.7781
$z_P = \pm 3$	0.7339	0.8604		1.1423	1.2854	1.4287
$z_P = \pm 4$	0.6828	0.7775	0.8873		1.1134	1.2269
$z_P = \pm 5$	0.6495	0.7221	0.8123	0.9058		1.0943
$z_P = \pm 6$	0.6265	0.6824	0.7584	0.8383	0.9191	

TABLE 2: Values of the Current Ratio $(i/i_{levich})_{lim}$ for the Cases $z_C = \mp 2$

	$z_R = \pm 1$	$z_R = \pm 2$	$z_R = \pm 3$	$z_R = \pm 4$	$z_R = \pm 5$	$z_R = \pm 6$
$z_P = \pm 1$		1.2048	1.4239	1.6481	1.8747	2.1027
$z_P = \pm 2$	0.8697		1.1463	1.2980	1.4523	1.6078
$z_P = \pm 3$	0.7983	0.8904		1.1152	1.2327	1.3515
$z_P = \pm 4$	0.7523	0.8201	0.9072		1.0952	1.1917
$z_P = \pm 5$	0.7204	0.7707	0.8422	0.9199		1.0813
$z_P = \pm 6$	0.6974	0.7339	0.7938	0.8604	0.9296	

TABLE 3: Values of the Current Ratio $(i/i_{levich})_{lim}$ for the Cases $z_C = \mp 3$

	$z_R = \pm 1$	$z_R = \pm 2$	$z_R = \pm 3$	$z_R = \pm 4$	$z_R = \pm 5$	$z_R = \pm 6$
$z_P = \pm 1$		1.1561	1.3259	1.5010	1.6786	1.8578
$z_P = \pm 2$	0.8978		1.1184	1.2428	1.3702	1.4993
$z_P = \pm 3$	0.8373	0.9097		1.0967	1.1965	1.2980
$z_P = \pm 4$	0.7960	0.8489	0.9211		1.0821	1.1660
$z_P = \pm 5$	0.7665	0.8046	0.8638	0.9303		1.0715
$z_P = \pm 6$	0.7442	0.7706	0.8201	0.8772	0.9377	

was carried out by dividing χ-space into units of width Δ. A discretized version of eq 19 may be written

$$0 = \frac{\rho_{j+1} - 2\rho_j - \rho_{j-1}}{\Delta^2} + \left[3j^2\Delta^2 - \frac{\lambda z_P}{\rho_j^2} \right] \frac{\rho_{j+1} - \rho_{j-1}}{2\Delta} \tag{28}$$

where ρ_j denotes the value of ρ at $\chi = j\Delta$, and may be reorganized into

$$\rho_{j+1} = \rho_{j-1} + \frac{4(\rho_j - \rho_{j-1})}{2 + 3j^2\Delta^3 - (\lambda z_P \Delta / \rho_j^2)} \tag{29}$$

This latter equation enables each ρ value to be found from the two previous values. To start the process, ρ_2 was calculated via eq 29 from $\rho_0 = \rho^s = z_P/z_R$ and a ρ_1 value obtained by setting $\chi = \Delta$ in eq 26. The Δ interval was fixed at 10^{-4} after it was determined that smaller values had no effect on the computed λ.

Using this procedure, λ was calculated for various combinations of the charge numbers z_R, z_C, and z_P. Rather than report λ values as such, it is more instructive to compare the current in the absence of supporting electrolyte with the prediction of the Levich equation

$$i_{levich} = \frac{(z_P - z_R)Fc_R^b}{\Gamma(4/3)} \left(\frac{KD^2}{3} \sqrt{\frac{d}{\eta}} \right)^{1/3} \sqrt{\omega} \tag{30}$$

for fully supported solutions. The ratios of the two steady-state currents, calculated via

$$\frac{i}{i_{levich}} = \Gamma\left(\frac{4}{3} \right) \frac{\lambda z_R(z_R - z_C)}{(z_P - z_R)} = 0.892980 \frac{\lambda z_R(z_R - z_C)}{(z_P - z_R)} \tag{31}$$

are reported in Tables 1−3.

For the case $z_C = \mp 1$, Figure 1 compares the results of the present study with the ratios generated by expression 2.
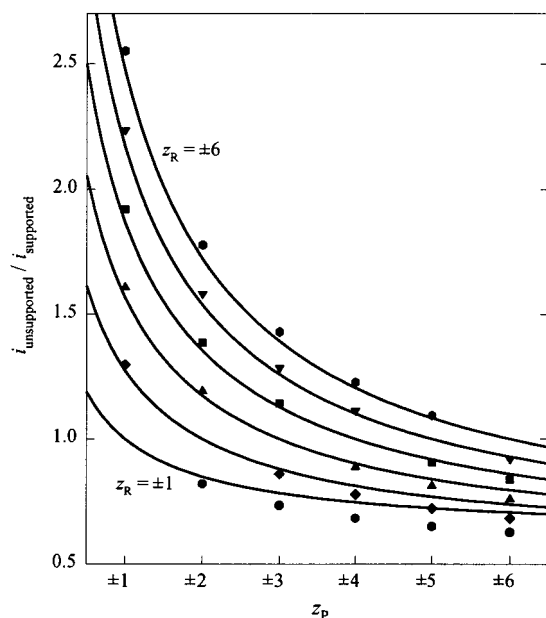
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Figure 1. Comparison of the ratio $i_{unsupported}/i_{supported}$, when $z_C = \mp 1$, as predicted by (full lines) eq 2 and (symbols) Table 1.

Evidently, the same trends in the ratio $i_{unsupported}/i_{supported}$ apply for steady states at a rotating disk electrode as at a hemispherical microelectrode. However, the numerical values differ somewhat.

Comparison with Experiment

It appears that the literature contains few examples of the limiting currents of electroactive ions at a rotating disk electrode in the absence of supporting electrolyte. Gao and White,[12] however, did perform such experiments and compared these results with those of similar supported experiments, and with experiments in which the disk was not rotated.

Plots of the limiting current versus $\sqrt{\omega}$ were found to be equally linear with or without supporting electrolyte, in line with the present prediction. Surprisingly, Gao and White found that the limiting currents of very weakly supported *neutral* decreased with ω, a circumstance not addressed by the present treatment.

Table 4 presents experimental $i_{unsupported}/i_{supported}$ data reported by Gao and White for the reduction of methyl viologen

$$MV^{2+} + e^- \rightarrow MV^+ \tag{32}$$
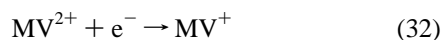
and the oxidation of [(trimethylammonio)methyl]ferrocene

$$TMAFc^+ - e^- \rightarrow TMAFc^{2+} \tag{33}$$

in acetonitrile with the singly charged hexafluorophosphate anion as counterion. Tetrabutylammonium hexafluorophosphate served as supporting electrolyte when any was used. In the table,

TABLE 4: Comparison between Experimental Values of the Ratio $i_{unsupported}/i_{supported}$, as Reported by Gao and White,[12] and Theoretical Predictions

	reaction 32		reaction 33	
ω/rad s^{-1}	0	378	0	378
experimental ratio	1.25	1.22	0.85	1.04
theory, factor 2	1.274		0.849	
theory, Table 1		1.2980		0.8201

the experimental ratios for the stationary disk are compared with the predictions of formula 2. The agreement is impressive for both reactions, even though the experiment was conducted with a disk electrode, while the theory relates to a hemisphere. Agreement for the rotating electrodes is disappointing, especially in the case of reaction 33, in which the experimental ratio *exceeds* unity, a counterintuitive observation. Part of the small discrepancy in the case of methyl viologen reduction may arise from the fact that the theory applies to *excess* supporting electrolyte, whereas Gao and White used a bulk solution in which as much as 15% of the ionic strength was provided by the electroactive cation itself.

References and Notes

(1) Amatore, C.; Fosset, B.; Bartelt, J.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1988**, *256*, 255.

(2) Cooper, J. B.; Bond, A. M.; Oldham, K. B. *J. Electroanal. Chem.* **1992**, *331*, 877.

(3) Reference (2) considered only cases of singly charged counterions, $|z_C| = 1$. Factor (2) is a new, more general, result.

(4) Danilov, A. I.; Molodkina, E. B.; Polukarov, Y. M. *Russ. J. Electrochem.* **1997**, *33*, 288.

(5) Roy, S.; Pintauro, P. N. *J. Electrochem. Soc.* **1993**, *140*, 3167.

(6) Bortels, L.; van den Bossche, B.; Deconinck, J. *J. Electroanal. Chem.* **1997**, *422*, 161.

(7) Krause, T.; Arulnayagam, L.; Pritzker, M. *J. Electrochem. Soc.* **1997**, *144*, 960.

(8) Barcia, O. E.; Mottos, O. R.; Tribollet, B. *J. Electrochem. Soc.* **1992**, *139*, 446.

(9) Nechiporuk, V. V.; Elgurt, I. L. *Soviet Electrochem.* **1991**, *27*, 520.

(10) Pritzker, M. D. *J. Electroanal. Chem.* **1994**, *373*, 39.

(11) Feldberg, S. W.; Goldstein, C. I.; Rudolph, M. *J. Electroanal. Chem.* **1996**, *413*, 25.

(12) Gao, X. P.; White, H. S. *Anal. Chem.* **1995**, *67*, 4057.

(13) Levich, V. G. *Phyicochemical Hydrodynamics*; Prentice Hall: Engelwood Cliffs, 1962.

(14) Oldham, K. B.; Feldberg, S. W. *J. Phys. Chem. B* **1999**, *103*, 1699.

(15) Myland, J. C.; Oldham, K. B. *Electrochem. Commun.* **1999**, *1*, 467.

(16) Oldham, K. B.; Myland, J. C. *Fundamentals of Electrochemical Science*; Academic Press: San Diego, 1994; p 147.

(17) Spanier, J.; Oldham, K. B. *An Atlas of Functions*; Hemisphere: Washington and Springer: Berlin, 1987; Chapters 45 and 43.

(18) Press: W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge; 1986.

(19) Equation 29 shows that ρ exceeds 0.999 999 8 at $\chi = 2.5$.