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ORIGINAL PAPER

# Effects of viscosity-dependent diffusion in the analysis of rotating disk electrode data

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**Abstract** This paper demonstrates the application of a modified Levich equation for chemical systems with varying viscosity. A commonly used technique to analyze rotating disc electrode (RDE) experiments is to fit the data to the Levich equation assuming a constant effective diffusion coefficient which may be valid for conditions where the viscosity does not vary significantly (less than an order of magnitude). However, most diffusion coefficient models (e.g. Stokes–Einstein) show an inverse relationship with viscosity which consequently indicates that a constant effective diffusion coefficient may result in poorer model-to-data agreement. Here, data are presented for a series of RDE experiments for the electrodissolution of Cu in phosphoric acid, water and glycerin based baths. Viscosity changes of greater than one order of magnitude allow for testing the assumption of a constant effective diffusion coefficient. The collected data, as well as data published elsewhere, can be explained by a modified Levich equation which takes into account the viscosity dependence of the diffusion coefficient.

**Keywords** Diffusion coefficient · Electrodissolution · Electropolishing · Levich analysis · Rotating disc electrode · Stokes–Einstein

## List of Symbols

| | |
|---|---|
| $C_A$ | Concentration of A in solution (mol $l^{-1}$) |
| D | Diffusion coefficient ($m^2$ $s^{-1}$) |
| $D_A$ | Effective diffusion coefficient of A ($m^2$ $s^{-1}$) |
| $D^{\circ}_{AB}$ | Mutual diffusivity at infinite dilution of A in B ($m^2$ $s^{-1}$) |
| $D_{AB}$ | Mutual diffusivity ($m^2$ $s^{-1}$) |
| $F$ | Faraday's constant (C $mol^{-1}$) |
| $I_{lim}$ | Limiting current per unit area (A $m^{-2}$) |
| k | Boltzman's constant (J $K^{-1}$) |
| m | Molality of solute (mol (kg of solvent)$^{-1}$) |
| $n$ | Ionic charge |
| r | Effective radius (m) |
| $s$ | Solvent coordination number |
| T | Absolute temperature (K) |
| V | Molar volume ($m^3$ $mol^{-1}$) |
| $\gamma_{\pm}$ | Mean ionic activity coefficient of solute |
| $\mu$ | Absolute viscosity (cP) |
| $\nu$ | Kinematic viscosity ($m^2$ $s^{-1}$) |
| $\varphi_B$ | Association factor for solvent B for Wilke-Chang equation |
| $\psi_B$ | Parachor parameter for component B for Tyn-Calus equation |
| $\omega$ | Rotational speed (rad $s^{-1}$) |

## 1 Introduction

Rotating disk electrodes (RDE) are used in electrochemical kinetic experiments due to the specific momentum and mass transfer characteristics [1]. The hydrodynamics of the

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system have been solved analytically by assuming spatially constant transport properties [2, 3]. In addition, analytic solutions for the momentum equations in the case of an infinite disk have been obtained by Rogers and Lance [4]. By solving the convective diffusion equation with the boundary conditions of the hydrodynamic velocity profile, the Levich [5–8] equation can be used to describe the relationship of limiting current, $I_{lim}$, to the physical properties of the electrolyte bath:

$$I_{\mathrm{lim}} = \frac{0.62n}{s_{\mathrm{A}}} F D_{\mathrm{A}}^{2/3} \omega^{1/2} \nu^{-1/6} C_{\mathrm{A}} \tag{1}$$

One analysis technique is to assume a spatially uniform diffusion coefficient (as assumed in the derivation of the Levich equation itself) for a given system and then plot $I_{lim}$ versus $\omega^{1/2}\nu^{-1/6}C_{\mathrm{A}}$. A linear-regression is then done to determine the diffusion coefficient from the slope. The aim of this work is to asses the validity of this assumption and develop an improved model with an *a posteriori* treatment of viscosity variations. Limiting current data have been collected for a variety of phosphoric acid based electrolyte baths with varying water concentrations and physical properties, such as density and viscosity, for a given copper RDE system of interest. Additionally, literature data have also been analyzed to test the validity of the constant diffusion coefficient assumption. Based on the analysis presented here, a unified or general model correlating the limiting current to the physical properties of the electrolyte bath can be obtained by taking into account the viscosity dependence of the diffusion coefficient.

## 2 Experimental

The experiments were performed in the three-electrode cell constructed from a Pyrex 200 mL beaker, a rotating Teflon coated copper rod (99.999% purity, Johnson Matthey) as a working electrode, a platinum coil counter electrode, and a saturated calomel reference electrode (SCE). The diameter of the copper electrode is 7 mm. A variable speed rotator 616 RDE and PARSTAT 2273 controlled by PowerCORR software (Princeton Applied Research) were used. The electrolytes were prepared using 85% ortho-phosphoric acid and glycerin (Fisher Scientific, Certified ACS).

Polarization sweeps were carried out to obtain limiting current between 0 and 2.2 V versus SCE at a scan rate of 10 mV $s^{-1}$ and a rotation speed of 400 rpm. A Brookfield DV II viscometer was used for viscosity measurements.

Data were collected for electrodissolution of copper in phosphoric acid with varying concentrations of glycerin and water to alter the physical properties of the bath. The electrolyte baths were prepared by mixing 85% $H_3PO_4$ with glycerin in three ratios: 63:37, 53:47, and 43:57. The resulting solutions were then diluted with water to alter the physical properties. For a series of 53:47 $H_3PO_4$:glycerin solutions, additional $KH_2PO_4$ was added to increase the $H_2PO_4^-$ concentration. The bath compositions and measured data are listed in Table 1.

## 3 Results and discussion

### 3.1 Levich analysis

As proposed elsewhere [6, 8, 9], water is assumed to be the limiting acceptor species in the removal mechanism. With this assumption the water concentration should approach zero near the surface. The data are plotted (Fig. 1) in a Levich analysis assuming that the effective diffusion coefficient for water is constant among the different experimental conditions and using the bulk concentration of the acceptor species. The linear fit has an $R^2$ value of 0.94. Using the slope of the linear regression, the effective diffusion coefficient (assuming $s_A = 6$) is $5.3 \times 10^{-8}$ $cm^2$ $s^{-1}$ which is similar to previously reported values [6, 8, 9]. However, over the range of data collected, a curvature results when a regression analysis is performed suggesting additional factors exist which are not captured by the Levich model.

### 3.2 Modified Levich analysis

We propose that the assumption of a constant diffusion coefficient is one source of the deviation from a purely linear relationship. Many fundamental and empirical diffusion coefficient models show an inverse relationship between the diffusion coefficient and the absolute viscosity. For example, the Stokes–Einstein relationship for diffusion of hard spheres in a simple fluid is as follows:

$$D = \frac{kT}{6\pi r \mu} \tag{2}$$

In our data, the absolute viscosity of the electrolyte varies by greater than an order of magnitude; thus one may expect that the diffusion coefficient would vary over the range of experimental conditions. With the relationship between absolute and kinematic viscosity ($\mu = \nu\rho$), we have modified the Levich equation to analyze the data where the diffusion coefficient is replaced by the Stokes–Einstein relationship.

$$I_{\mathrm{lim}} = \frac{0.62n}{s_{\mathrm{A}}} \left(\frac{kT}{6\pi r}\right)^{2/3} F \omega^{1/2} \rho^{-2/3} \nu^{-5/6} C_{\mathrm{A}} \tag{3}$$

Other authors [10, 11] have proposed that the concentrated phosphoric acid/water system is not a

**Table 1** Compositions and measured data for phosphoric acid electrolyte baths

| Base Solution ($H_3PO_4$/Glycerin) | % $H_3PO_4$ (85 wt%) | % Glycerin | % Water | Additional $KH_2PO_4$ | M $H_2O$ | Density (measured)/g cm$^{-3}$ | Viscosity (measured)/cP | Limiting current (measured)/mA cm$^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| 63%/37% | 63 | 37 | 0 | | 9.0 | 1.55 | 161 | 6.2 |
| | 57 | 33 | 10 | | 14.5 | 1.49 | 64 | 15.2 |
| | 50 | 30 | 20 | | 20.1 | 1.45 | 29 | 33.2 |
| | 44 | 26 | 30 | | 25.6 | 1.40 | 17 | 63.6 |
| 53%/47% | 53 | 47 | 0 | | 7.5 | 1.51 | 262 | 4.0 |
| | 52 | 47 | 1 | | 8.1 | 1.51 | 234 | 5.7 |
| | 52 | 46 | 2 | | 8.7 | 1.50 | 214 | 5.7 |
| | 50 | 45 | 5 | | 10.3 | 1.49 | 139 | 7.6 |
| | 48 | 42 | 10 | | 13.1 | 1.47 | 76 | 11.7 |
| | 42 | 38 | 20 | | 18.7 | 1.42 | 33 | 28.4 |
| | 37 | 33 | 30 | | 24.2 | 1.37 | 20 | 58.1 |
| 43%/57% | 43 | 57 | 0 | | 6.1 | 1.46 | 462 | 3.0 |
| | 39 | 51 | 10 | | 11.7 | 1.42 | 145 | 6.8 |
| | 34 | 46 | 20 | | 17.2 | 1.37 | 44 | 22.1 |
| | 30 | 40 | 30 | | 22.8 | 1.34 | 18 | 44.3 |
| 53%/47% | 53 | 47 | 0 | 99.5 g L$^{-1}$ | 7.5 | 1.54 | 300 | 4.4 |
| | 48 | 42 | 10 | 89.7 g L$^{-1}$ | 13.1 | 1.49 | 104 | 10.8 |
| | 42 | 38 | 20 | 79.6 g L$^{-1}$ | 18.7 | 1.47 | 43 | 23.6 |

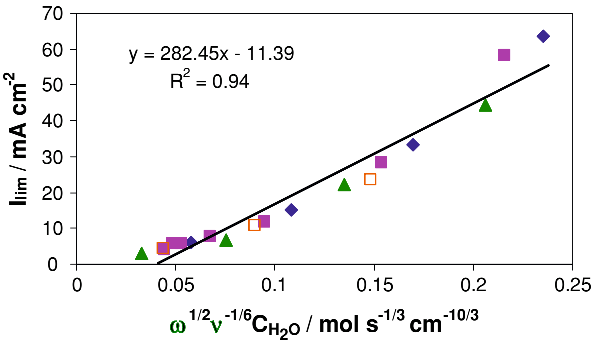

**Fig. 1** Plot of limiting current versus $\omega^{1/2}\nu^{-1/6}C_A$. Here, the diffusion coefficient is assumed to be constant. The result of a linear regression predicts that the diffusion constant has a value of 5.3 × 10$^{-8}$ c m$^2$ s$^{-1}$ (Assuming $s_A = 6$). ◆ 63%/37% ■ 53%/47% ▲ 43%/57% □ 53%/47% w/ $KH_2PO_4$

hydrodynamically simple fluid. The hard sphere and simple fluid assumptions used in the Stokes–Einstein relationship suggest the equation does not physically model the diffusion of water in the phosphoric acid system. More complex models [12] exist which may better predict the diffusion coefficient in liquids and electrolytes, e.g.

Wilke-Chang:

$$D^{\circ}_{AB} = \frac{7.4 \times 10^{-8} (\phi_B C_B)^{1/2} T}{\mu_B V_A^{0.6}} \tag{4}$$

Tyn-Calus:

$$D^{\circ}_{AB} = \frac{8.93 \times 10^{-8} \left(\frac{V_A}{V_B^2}\right)^{1/6} \left(\frac{\psi_B}{\psi_A}\right)^{0.6} T}{\mu_B} \tag{5}$$

Gordon:

$$D_{AB} = D^{\circ}_{AB} \frac{1}{C_B \overline{V}_B} \frac{\mu_B}{\mu} \left(1 + \frac{\ln \gamma_{\pm}}{\ln m}\right) \tag{6}$$

However, these models still maintain the inverse relationship between diffusion coefficient and absolute viscosity where the exponent of viscosity is of order 1 (O(1)). As such, the viscosity dependence of the effective diffusion coefficient can be tested using the Stokes–Einstein model with the caveat that the effective radius for the solute would represent a non-physical dimension. In this analysis the bulk electrolyte bath viscosity is used to compare different experimental conditions when assessing whether the assumption of a constant diffusivity in a Levich analysis is valid.

With this in mind the data were then plotted in a fashion consistent with the modified Levich equations (Fig. 2). The data now fall on a straight line with an R$^2$ value of 0.98. The points which deviate from the fit are data for low-viscosity, high-limiting current baths where uncertainties in measuring the low viscosity and high current values may contribute to the error. The limiting current for the baths with additional phosphate ion (open squares) are correctly

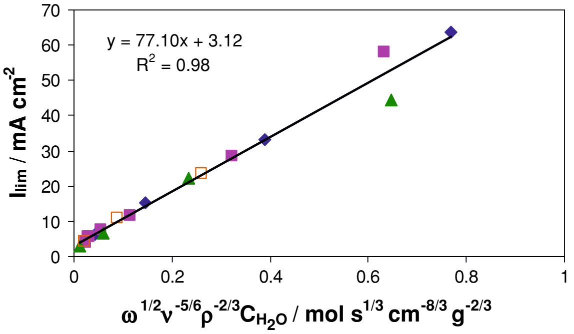

**Fig. 2** Plot of limiting current versus $\omega^{1/2}\nu^{-5/6}\rho^{-2/3}C_A$. Here, the diffusion coefficient is defined by the Stokes–Einstein relationship. The result of a linear regression predicts that the effective radius has a value of 2.9 × $10^{-9}$ m (Assuming $s_A$ = 6). ◆ 63%/37% ■ 53%/47% ▲ 43%/57% □ 53%/47% w/ $KH_2PO_4$

modelled by the water acceptor form of the modified Levich equation. From the slope of the linear regression an effective radius of 2.9 × $10^{-9}$ m is obtained for the solute.

### 3.3 Analysis of published data

Previously published data have also been fitted using the modified Levich equation to test the validity of the viscosity dependence. For comparison, Fig. 3 shows the published data [8, 9] plotted assuming a constant diffusion coefficient using the Levich analysis. Here the $R^2$ value is 0.90 with significant scatter in the data. Assuming $s_A$ = 6, a diffusion constant of 5.5 × $10^{-8}$ $cm^2$ $s^{-1}$ is calculated from the linear regression, which is in agreement with previous results.

By accounting for the viscosity dependence of the diffusion coefficient using the Stokes–Einstein relationship an improved linear fit of the data is obtained (Fig. 4). The $R^2$ value of 0.98 suggests that the data are better described by taking into account a viscosity-diffusion coefficient relationship. From Fig. 4 the effective radius of the water solute is calculated to be 1.9 × $10^{-9}$ m.

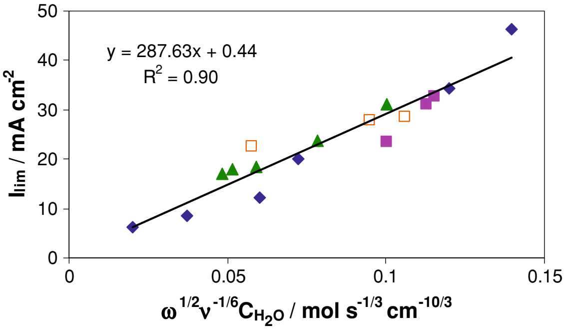

**Fig. 3** Plot of limiting current versus $\omega^{1/2}\nu^{-1/6}C_A$ from published data [8]. Here, the diffusion coefficient is assumed to be constant. The result of a linear regression predicts that the diffusion constant has a value of 5.5 × $10^{-8}$ $cm^2$ $s^{-1}$ (Assuming $s_A$ = 6). ◆ $H_3PO_4/H_2O$ ■ $CuSO_4$ ▲ EtOH □ Other

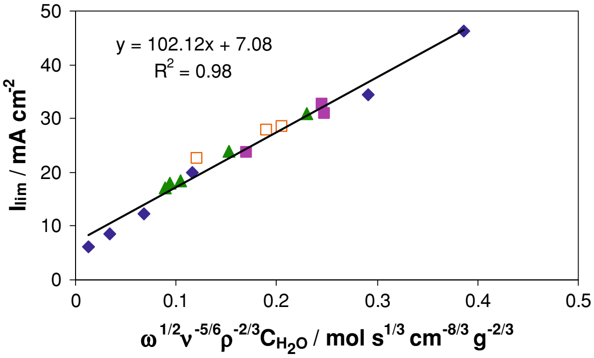

**Fig. 4** Plot of limiting current versus $\omega^{1/2}\nu^{-5/6}\rho^{-2/3}C_A$ from published data [8]. Here, the diffusion coefficient is defined by the Stokes-Einstein relationship. The result of a linear regression predicts that the effective radius has a value of 1.9 × $10^{-9}$ m (Assuming $s_A$ = 6). ◆ $H_3PO_4/H_2O$ ■ $CuSO_4$ ▲ EtOH □ Other

For both sets of data the y-intercept is not zero as predicted by the model. For the cases where the effective diffusion coefficient is assumed to be constant (i.e. traditional Levich analysis) this is expected because of model limitations. For the modified Levich analysis (Figs. 2, 4) the exact cause of the deviation was not determined. However, possible sources of the error might be the finite size of the electrode and bath compared to the infinite dimensions used in the derivation of the Levich equation or electrode kinetics becoming competitive with the mass transfer limitation assumption.

### 3.4 Effect of additives and diluents

For the experimental data presented here, as well as previously published data, the effect on limiting current of different diluents and additives was investigated. In the first case, glycerin and additional $KH_2PO_4$ were studied to determine the effect on limiting current. As seen in Fig. 2, these data are adequately modelled by the modified Levich analysis using a water acceptor model. For the data by Du and Suni [8, 9] the effect of $CuSO_4$, ethanol, glycerin, ethylene glycol and methanol was investigated. Again, with the modified Levich analysis, all the data collapse onto the same curve which suggests two important implications. First, additional phosphate, sulfate, or $Cu^{2+}$ ions do not change the fundamental behavior of the system implying that the water acceptor model is valid. Second, the impact of all the studied additives on the limiting current is restricted to changing the physical properties (viscosity and density) of the electrolyte bath and can be captured completely by our proposed modified Levich analysis for a water acceptor model. The additional ions and diluents do not modulate the removal mechanism;

hence, mass-transport limitations of the water acceptor play the key role in determining the limiting current for electrodissolution of copper in phosphoric acid based baths.

### 3.5 Validity of the Stokes–Einstein model

The concentrated phosphoric acid–water system has been shown to not be a hydrodynamically simple fluid. Therefore, the Stokes–Einstein model of diffusion is not strictly valid. This model was chosen because it captures the viscosity–diffusion coefficient inverse relationship which is also seen in more complex models. The limitation of using this model is that the predicted effective radius of the solute is not the physical dimension. From the modified Levich analysis of the data an effective radius of $1.9–2.9 \times 10^{-9}$ m is obtained, which is an order of magnitude larger than expected for a water molecule with an O–H bond length of approximately $0.1 \times 10^{-9}$ m. This agrees with the complex behavior of the concentrated phosphoric acid system as suggested by Chakrabarti [10] and Chung [11]. In effect, due to the electrostatic interactions between water and the electrolyte bath, the effective diffusivity is an order of magnitude less than the Stokes–Einstein model predicts for a hard sphere model.

Also, when using the Stokes–Einstien model (Eq. 2), the bulk electrolyte bath viscosity was used to modify the Levich equation. Due to the changing water concentration near the electrode, it can be expected that the viscosity near the surface also varies. An analysis done by Barton and West [13] accounts for the effects of varying physical properties near the electrode which could be included when correlating particular baths.

Despite the above limitations our studies indicate the importance of considering the effect of viscosity when modeling the limiting current. The better $R^2$ correlation values strongly suggest that explicit consideration of the viscosity dependence of the diffusivity coefficient is necessary to correctly model the RDE system where the viscosity changes significantly. Here, an *a posteriori* correction to the Levich equation was done to account for these effects. By using the effective radius as obtained by linear regression, the effective diffusivity is predicted to vary from $1.6 \times 10^{-9}$ to $4.4 \times 10^{-8}$ cm$^2$ s$^{-1}$.

## 4 Conclusion

We have shown for a series of phosphoric acid based electrolyte baths that the limiting current in electrodissolution of copper is better understood by using a modified Levich equation where the viscosity dependence of the diffusion coefficient is explicitly included. An improved model fit also resulted when applied to previously published data. In addition, it appears that chemical additives such as $KH_2PO_4$, $CuSO_4$, glycerin, ethylene glycol, methanol and ethanol do not have a primary affect on the dissolution mechanism. Instead, any change in the limiting current is due to secondary effects on the density and viscosity of the electrolyte. Finally, the diffusion coefficient for water in phosphoric acid is predicted to vary from $1.6 \times 10^{-9}$ to $4.4 \times 10^{-8}$ cm$^2$ s$^{-1}$ depending upon the viscosity of the solution. This range represents values more than order of magnitude less than the diffusion constant predicted by the Levich analysis.

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