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Study of Ion Transport Models for Electroanalytical Simulation. Part 2: Experimental Comparison[†]

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Ion transport models are compared by simulating the limiting current density of copper deposition from aqueous $CuSO_4$ solutions on a rotating disk electrode. The first ion transport model is the pseudoideal solution model, on which many commercial electroanalytical simulation tools are built. The second, more rigorous model consists of the linear phenomenological equations for which the activity coefficients and Onsager coefficients are calculated locally with the mean spherical approximation (MSA). The influence of the formal association constant in the pseudoideal solution model is also investigated.

Introduction

In a previous paper,[1] we compared the pseudoideal solution model and the mean spherical approximation (MSA) on a theoretical basis and found that the first model predicts a lower limiting current density than the second. Even though a statistical mechanical model like the MSA is expected to be more accurate than a semiempirical model like the pseudoideal solution model, this expectation needs to be verified by comparison with experiments. Limiting current densities on a rotating disk electrode were measured by Hsueh and Newman[2] for copper deposition from aqueous $CuSO_4$ solutions and are used here to validate the ion transport models.

Aqueous $CuSO_4$ solutions have the additional complication of ion association:[3]

$$\mathrm{Cu}^{2+} + \mathrm{SO_4}^{2-} \rightleftharpoons \mathrm{CuSO_4} \tag{1}$$

The equilibrium concentrations are dictated by a formal association coefficient, K', which depends on the concentrations themselves via their activity coefficients. To investigate the importance of the formal equilibrium coefficient, three versions of pseudoideal solution model are used: (a) without ion association

$$K' = 0 \tag{2}$$

(b) with the thermodynamic association constant

$$K' = K \tag{3}$$

and (c) with a formal association constant that incorporates the activity coefficients to ensure the correct equilibrium composition:

$$K' = K\frac{y_{\mathrm{Cu}^{2+}}y_{\mathrm{SO_4}^{2-}}}{y_{\mathrm{CuSO_4}}} \tag{4}$$

Results and Discussion

The electrolyte solution contains three dissolved species: Cu^{2+}, SO_4^{2-}, and $CuSO_4$. For each of them we can write down a stationary material balance equation:

$$\vec{\nabla}\cdot(c_i\vec{v} + \vec{J}_i) + \nu_i J = 0 \tag{5}$$

where J is the rate of the association reaction 1 and ν_i is the stoichiometric coefficient of the species in that reaction. The formula for the diffusion fluxes, $\vec{J}_i$, was given in our previous paper.[1] The reaction rate is given by a classical rate law:

$$J = k_f' c_{\mathrm{Cu}^{2+}}c_{\mathrm{SO_4}^{2-}} - k_b' c_{\mathrm{CuSO_4}} \tag{6}$$

where the forward and backward rate coefficients are modeled by

$$k_f' = k_f y_{\mathrm{Cu}^{2+}}y_{\mathrm{SO_4}^{2-}} \tag{7}$$

$$k_b' = k_b y_{\mathrm{CuSO_4}} \tag{8}$$

such that the correct formal association coefficient is satisfied:

$$K' = K\frac{y_{\mathrm{Cu}^{2+}}y_{\mathrm{SO_4}^{2-}}}{y_{\mathrm{CuSO_4}}} = \frac{k_f'}{k_b'} = \frac{c_{\mathrm{CuSO_4}}}{c_{\mathrm{Cu}^{2+}}c_{\mathrm{SO_4}^{2-}}} \tag{9}$$

In the MSA the rate coefficients are calculated locally, while in the pseudoideal solution model they are constant.

The material balance equations together with the electroneutrality condition

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$$\sum_{i=1}^{I} z_i c_i = 0 \qquad (10)$$

are solved for each model with the finite element method with upwind contributions for the convection term. The domain of calculation for the simulations is located within the first 100 μm from the electrode. The grid is made up of 801 points, defining 800 elements exponentially contracting toward the electrode. The refinement factor is set to 1.011, which corresponds to a ratio of 1:10 000 between the size of the first and the last element. At the limiting current density, the concentration of the reacting ion becomes zero on the electrode. On the solution side, bulk concentrations and zero potential are imposed. The simulations are performed at 300 rpm and at concentrations of 0.02, 0.05, 0.10, and 0.30 mol/L. Literature values for the viscosity and density are used to compute the flow field and the reference frame correction for the Onsager coefficients.[5]

Model Parameters. The IUPAC recommended value of 0.224 L/mol is taken for the thermodynamic association constant of $CuSO_4$. Because ion association is generally very fast, the forward and backward rate constants, k_f and k_b, are taken on the order of 10^6 (SI units). The limiting diffusion constants, D_i^0, and the diameters, σ_i, are listed in Table 1. Literature values were taken for the limiting diffusion constants of Cu^{2+} and SO_4^{2-}.[6] The remaining model parameters were fitted with a least-squares algorithm on the mean activity coefficient, the equivalent conductivity, the cation transport number and the mutual diffusion coefficient reported by Miller et al.[7]

As can be seen in Figures 1−4, the quality of the fit is surprisingly good. Undoubtedly, the MSA benefits from a favorable cancelation of errors, because the continuous solvent approximation cannot be justified any more at molar concentrations, as there is almost no free water present between the ions. Furthermore, the $CuSO_4$ ion pairs that are formed cannot be considered spherical, so their diameter should be regarded as an average interaction parameter for all orientations. To expect this nice cancelation of errors for all aqueous electrolyte solutions would be wishful thinking, but the MSA has been successfully applied also to alkali and earth-alkali chlorides.[8−10]

Comparison with Experiment. The limiting current density is plotted in Figure 5 for the experiments and for the different ion transport models. The MSA predicts the limiting current density quite well, with a maximum overestimation of 8%. Given the experimental uncertainty of 2% on the current and 1% on the imposed rotation speed together with the difficulties related to surface roughness and the determination of the current plateau,[2] we think that the MSA simulations are still acceptable. The deviations in the mean activity coefficient with increasing concentration in Figure 1 are probably still small enough to not impair the limiting current density at 0.30 mol/L (0.55 $\sqrt{\text{mol/L}}$).

The best pseudoideal solution model is the one with a formal association constant that incorporates the activity coefficients. Roughly speaking, the limiting current density depends on the bulk concentrations and the Nernst layer thickness. Due to the activity coefficients in the formal association constant, this pseudoideal solution model predicts the correct concentrations of the species in the bulk. In turn, the effective diffusion constants depend on the bulk concentrations via the conductivity correction factor.[1] That could explain why this pseudoideal solution model performs the best. However, it still underestimates the limiting current density up to 18%, which lies almost surely outside the experimental uncertainty. The main reasons for this are (1) the absence of local concentration dependence of the effective diffusion constants and (2) the fact that the conductivity correction factor makes the effective diffusion constants more appropriate or migration but not for diffusion.

TABLE 1: Limiting Diffusion Constants and Diameters of the Species

	D_i^0 (10^{-9} m^2/s)	σ_i (Å)
Cu^{2+}	0.714	4.56
SO_4^{2-}	1.065	4.61
$CuSO_4$	0.731	6.48

The other two pseudoideal solution models show huge deviations from experiment, so it is clear that the choice of formal association constant has a big influence. This is because the effective diffusion constants are obtained from the limiting diffusion constants by a correction factor for the conductivity.[1] Since the ion pair, $CuSO_4$, does not contribute to the conductivity, this correction is sensitive to the choice of formal association constant, as shown in Figure 6. Complete dissociation leads to a too-high conductivity and consequently to a small correction factor, which brings down the limiting current density. The use of the thermodynamic association constant shifts the reaction toward too much association and a too-low conductivity. The correction factor is then greater than 1 and the limiting current

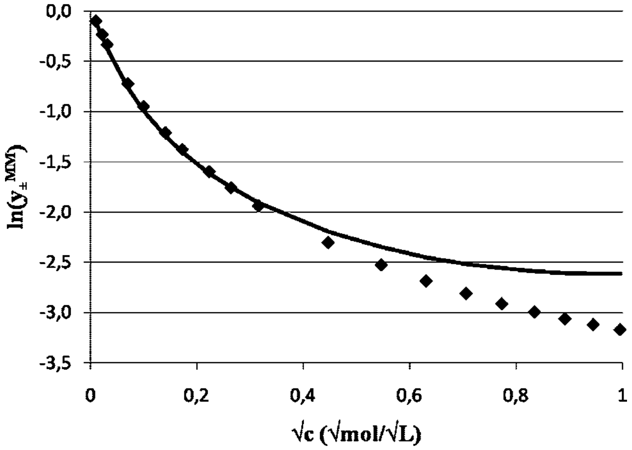

Figure 1. Natural logarithm of the McMillan−Mayer mean activity coefficient as a function of the square root of the $CuSO_4$ concentration. Symbols are experimental values reported by Miller et al.[7] The solid line is the MSA fit.

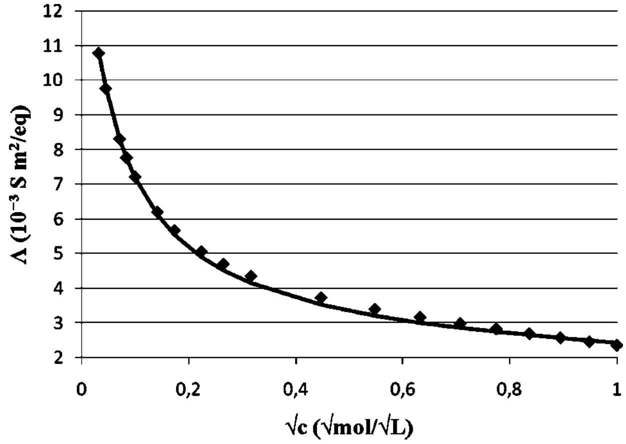

Figure 2. Equivalent conductivity as a function of the square root of the $CuSO_4$ concentration. Symbols are experimental values reported by Miller et al.[7] The solid line is the MSA fit.

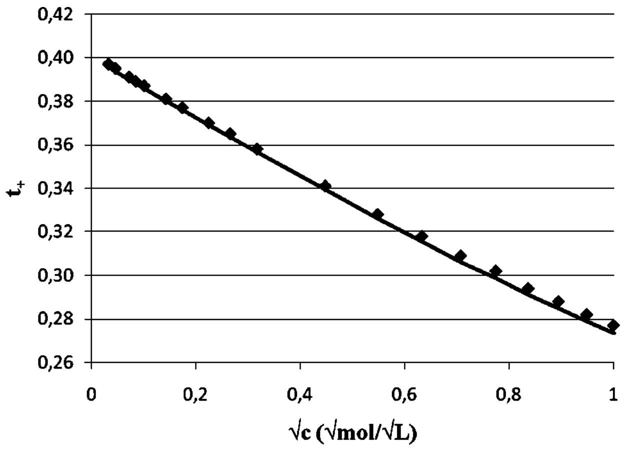

Figure 3. Solvent-fixed cation transport number as a function of the square root of the $CuSO_4$ concentration. Symbols are experimental values reported by Miller et al.[7] The solid line is the MSA fit.

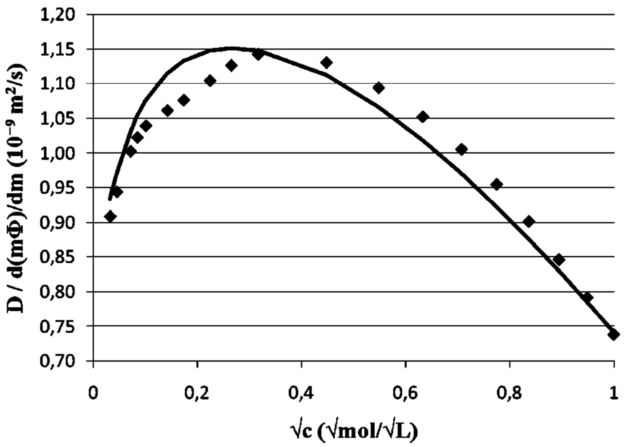

Figure 4. Volume-fixed mutual diffusion coefficient divided by the thermodynamic factor [d($m\Phi$)/dm] as a function of the square root of the $CuSO_4$ concentration. Symbols are experimental values reported by Miller et al.[7] The solid line is the MSA fit.

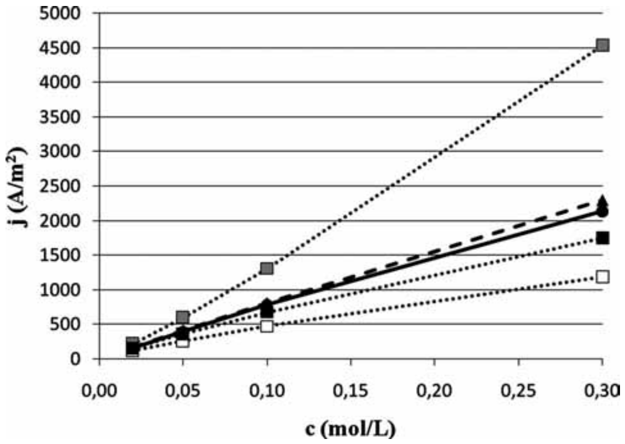

Figure 5. Limiting current density at 300 rpm as a function of $CuSO_4$ concentration: experimental (●), MSA (▲), and pseudoideal solution model, without association (white squares), with thermodynamic association constant (gray squares), and with a formal association constant that incorporates activity coefficients (black squares).

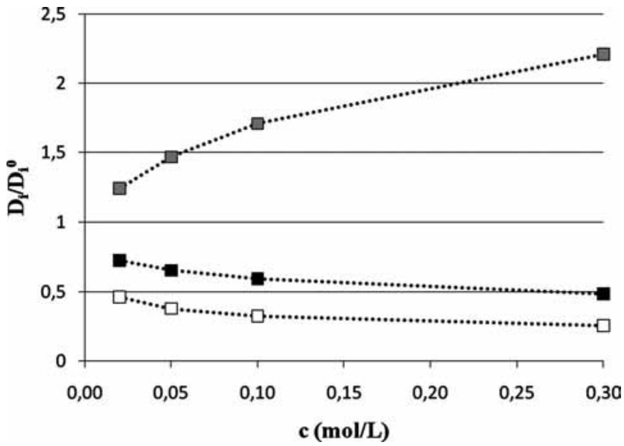

Figure 6. Ratio of effective diffusion constants to limiting diffusion constants as a function of $CuSO_4$ concentration for a pseudoideal solution model: without association (white squares), with thermodynamic association constant (gray squares), and with a formal association constant that incorporates activity coefficients (black squares).

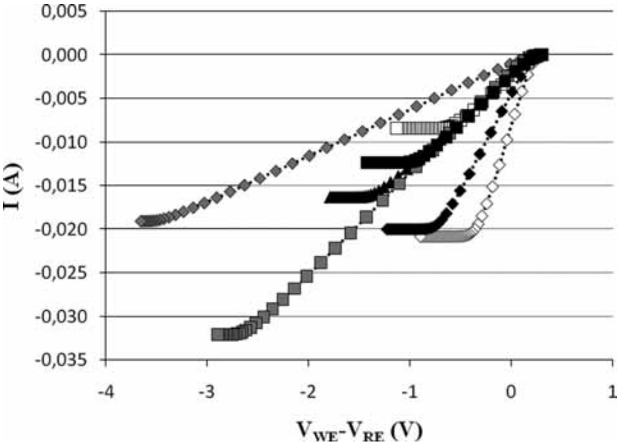

Figure 7. Simulated polarization curves at 300 rpm and 0.3 M $CuSO_4$ for MSA (▲) and for a pseudoideal solution model without association (white squares), with thermodynamic association constant (gray squares), and with a formal association constant that incorporates activity coefficients (black squares). The curves shown with corresponding diamonds instead of squares are with limiting diffusion constants instead of effective diffusion constants.

density becomes much too high. It is of course possible in this case to tune the effective diffusion constants such that both the conductivity and the limiting current density are correct. However, such a procedure is hard to generalize to electrolyte solutions in which multiple simultaneous electrode reactions occur, while a simple conductivity correction to all diffusion constants is always feasible.

To emphasize the importance of the conductivity correction, Figure 7 shows the simulated polarization curves at 0.30 mol/L also without this correction. The reference electrode (RE) is assumed to be positioned infinitely far away from the working electrode (WE). Butler−Volmer kinetics are assumed for the copper deposition reaction, for which the rate constants and symmetry factor are taken from Newman.[11] The slope of the polarization curve is strongly affected by the conductivity. Unfortunately, the paper of Hsueh and Newman did not reveal the complete experimental polarization curve to compare with.

Conclusion

Comparison of the pseudoideal solution model and MSA with experiments for copper electrodeposition on a rotating disk electrode from aqueous $CuSO_4$ solutions up to 0.30 mol/L confirms the conclusion from our previous theoretical comparison: the pseudoideal solution model underestimates the limiting current density. In this case the underestimation goes up to 18%.

The MSA overestimates the limiting current density in this case but probably still falls within the experimental uncertainty.

An activity coefficient correction for the formal association constant is important in the pseudoideal solution model to prevent too-extreme conductivity corrections on the diffusion constants, which would lead to completely unreliable limiting current densities.

This investigation has shown the limitations and pitfalls of the frequently used pseudoideal solution model for simulation of electrodeposition processes. A conductivity correction to the diffusion constants and activity coefficient corrections to the formal equilibrium constants are necessary but may still lead to an underestimation of the limiting current density. This should be kept in mind when the model is used for reactor design, but it could be advantageous that the model gives a “cautious prediction”. The MSA gives better results for aqueous $CuSO_4$ solutions and it has the advantage that concentrations can be changed without having to adjust any model parameters. However, there is no guarantee that the MSA will work so well for other aqueous electrolyte solutions, and the necessary experimental data are still incomplete.

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