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Solvent Donicity and Dielectric Continuum Effects in Amalgam Formation Reactions.

A Study of the Reduction of Cu(I) in the Nitrile Solvents

by

W. Ronald Fawcett and Colby A. Foss, Jr.

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# Solvent Donicity and Dielectric Continuum Effects in Amalgam Formation Reactions - A Study of the Reduction of Cu(I) in Nitrile Solvents

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The standard rate constants and charge transfer coefficients for the reaction

$$Cu^+ + e = Cu^-(Hg)$$

have been obtained using AC admittance voltammetry in the four solvents acetonitrile, propionitrile, butyronitrile and benzonitrile under conditions of varying temperature and supporting electrolyte identity and concentration. In all cases, the experimental charge transfer coefficient $\alpha_{ex}$ is close to unity. Corrections for the $\phi_2$ potential effect do not lead to lower transfer coefficients, and hence double layer effects, at least in the context of Frumkin theory do not account for the $\alpha_{ex} \approx 1$ result.

The most plausible explanation for the large transfer coefficient involves a reaction site inside the inner layer at the electrode surface. The "close reaction plane" model [1] will be discussed in detail, along with the consequences of applying the standard $\phi_2$ correction to systems where the reaction plane is not coincident with the outer Helmholtz plane. The relative merits of two other models, namely the asymmetric intrinsic barrier model [2,3] and the electro-chemical-chemical ("EC") mechanism [4] will also be considered.

Previous studies of alkali metal and alkaline earth cation reduction have shown a systematic dependence on the solvent donor number (DN) of both formal potentials [5] and kinetic rate constants [6]. For the $Cu^+$ system, the formal potentials measured against the reference redox couple cobalticinium/cobaltacene do correlate with DN, whereas the standard rate constants do not (Figure 1). Since the donicity range in the four nitriles chosen is small (12 in benzonitrile to 16.6 in butyronitrile), it is reasonable to assume that the dielectric properties of the solvents may be important. Dielectric effects are considered in two contexts. First, the simple Born theory is combined with classical ion-electrode imaging models to estimate a Gibbs energy of transfer quantity $\Delta G_{tr}$(bulk -> reaction site). In the second case, the Marcus Dielectric continuum expression [7] used to calculate $\Delta G^*_{os}$ for an electron transfer step. Using either $\Delta G_{tr}$, $\Delta G^*_{os}$, or both , so - called "continuum corrected" standard rate constants can be plotted against DN (Figure 2). The continuum corrected rate constants show an improved correlation with DN, particularly if they are also adjusted for a local potential equal to the rational $\phi^{m,r}$ quantity, which would be appropriate for a reaction plane at the electrode surface.

The shortcomings of the simple continuum models will be discussed, especially with regard to recent developments in the theory of ion - electrode imaging effects [8,9]. Also, the nature of the reaction coordinate for an amalgam formation reaction involving electron transfer will be discussed, with connections drawn between the empirical DN and the inner sphere reorganizational energy $\Delta G^*_{is}$.

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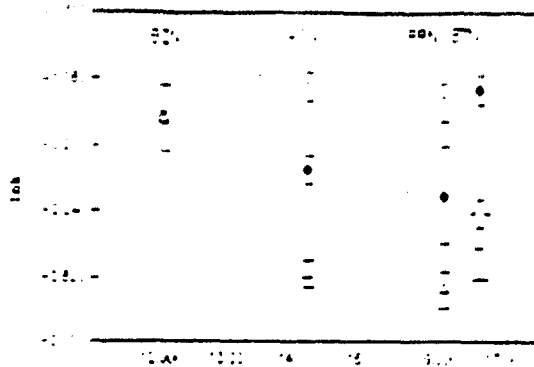
**DN**

Figure 1. Uncorrected standard rate constants for Cu^{+} reduction versus solvent donor number (DN). Key: TEAP: (O); TPAP: (●); TBAP: (c). All concentrations 0.10M.
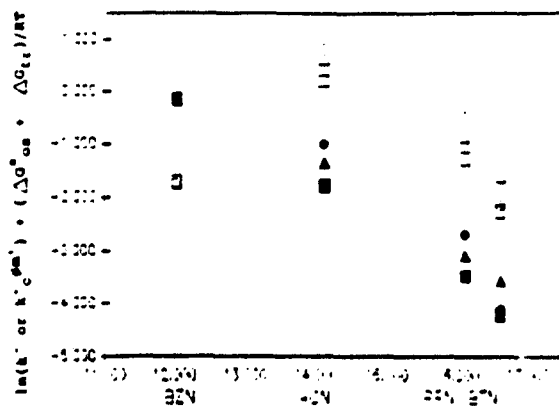


**DN**

Figure 2. Uncorrected and $\phi^m$ - corrected standard rate constants for Cu^{+} reduction summed with both $\Delta G_{tr}$ and $\Delta G^{\#}_{os}$ versus solvent donor number. Electrolyte key: TEAP: (⊃,●); TPAP: (△,▲); TBAP: (□,■). Open symbols are uncorrected rate constants. Solid symbols are $\phi^m$ - corrected rate constants.

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