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Solvent Effects on the Kinetics of Electroreduction of Cu(I) at Mercury

by

W.R. Fawcett and C.A. Foss, Jr.

Prepared for Presentation

at

The Symposium honoring Professor E. Yeager

ACS Central Regional Meeting
Cleveland, Ohio, June 1989

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SOLVENT EFFECTS ON THE KINETICS OF ELECTROREDUCTION OF Cu(I) AT MERCURY.

W.Ronald Fawcett and Colby A. Foss, Jr. Department of Chemistry, University of California, Davis, CA 95616.

The solvent plays an important role in amalgam formation reactions when it forms the primary solvation sheath of the reactant. In the present paper we report a study of the role of the solvent in the kinetics of reduction of Cu(I) in nitrile solvents where the monovalent ion is stable. The standard rate constants for reduction of Cu(I) in acetonitrile (AN) and benzonitrile (BN) are virtually identical (0.13 and 0.16 cm s⁻¹, respectively) at Hg with 0.1 M TEAP as supporting electrolyte. The apparent transfer coefficients are close to unity for the reduction process in both solvents in spite of the fact that the double layer structure is very different. Kinetic parameters including heats of activation in these solvents and other nitriles will be presented and discussed with respect to intrinsic asymmetry of the reaction barrier.

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Solvent Effects on the Kinetics of Electroreduction of Cu(I) at Mercury

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Two fundamental parameters in any electrochemical kinetic study are the standard rate constant, k_s , which is the rate constant at zero overpotential, and the charge transfer coefficient, α , which is a unitless quantity that determines the degree to which the general rate constant, k , is affected by the electrode potential, E , according to

$$k = k_s \exp(-\alpha n f (E - E^\circ)) \quad (1)$$

where n is the number of electrons involved in the reaction, $f = F/RT$, and E° the electrode potential corresponding to the standard potential of the reaction (the quantity $E - E^\circ$ is also referred to as the "overpotential").

The quantity, α , is of physical significance in that it describes the symmetry of the activation barrier region of the reaction coordinate. The reaction coordinate is often conceptualized in terms of two Gibbs energy surfaces corresponding to the reactants and products (see Figure 1).¹ The activation barrier ΔG^\ddagger is determined by the height of the intersection point of the reactant and product surfaces relative to the equilibrium energy on the reactant side. Since the reactant includes the energy of the electron(s) in the electrode phase, the reaction free energy ΔG° and hence the activation barrier ΔG^\ddagger are functions of the overpotential. If the curvature of these surfaces is similar the activation barrier is symmetrical and $\alpha \approx 1/2$. Surface curvature is a function of the strength of solvent-metal interactions, and for a simple electron transfer system where reactants and products are in the same phase, and where the metal center does not experience a ligand loss or exchange, the assumption that the barrier is symmetrical is a reasonable one. Indeed, so many electrode reactions yield a value of α equal to $1/2$ that

deviations from this value are often attributed to instrumental or method artifacts or complex multi-step mechanisms.²

We have recently completed an AC admittance analysis of the reduction kinetics of Cu^+ at the solution/mercury interface in two solvents, acetonitrile and benzonitrile. In these two solvents Cu^+ reduction is extremely interesting because the charge transfer coefficients are consistently large (0.9 to 1.2), regardless of variations in temperature, analyte concentration and supporting electrolyte identity and concentration. In a preliminary note³, we discussed how these large α values could be due to severe differences in reactant and product surface curvature (see Figure 2). These differences are reasonable when one considers the fact that Cu^+ -nitrile interactions are strong⁴ (indeed, Cu^+ is stabilized in nitrile and nitro solvents⁵, whereas in water it disproportionates to Cu^{2+} and Cu^0), and Cu^0 -mercury interactions are weak.^{6,7}

The data obtained and discussed in this presentation are summarized in the tables given on the following three pages.

References

1. A.J. Bard and L.R. Faulkner, "Electrochemical Methods" John Wiley and Sons (1980) pp. 86-101.
2. M. Saakes, M. Sluyters-Rehbach, and J.H. Sluyters, *J. Electroanal. Chem.*, 259 (1989) 265.
3. W.R. Fawcett and C.A. Foss, Jr., *J. Electroanal. Chem.*, 250 (1988) 225.
4. M. Kubota and D.L. Johnston, *J. Inorg. Nucl. Chem.*, 20 (1967) 769.
5. J.A. Altermatt and S.E. Manahan, *Anal. Chem.* 40 (1968) 655.
6. The solubility of Cu^0 in mercury is quite low (see Ref. 8). The product surface curvature is also a function of solvent dipole - electrode field interactions, but since Cu^+ reduction occurs near the potential of zero charge in acetonitrile and benzonitrile, we would expect this contribution to be small.
7. F. Vydra, K. Stulik and E. Julakova, "Electrochemical Stripping Analysis" John Wiley and Sons (1976) p. 59.

Cu⁺ Reduction in Acetonitrile[Cu⁺] = 0.50mM T = 25 °C

ELECTROLYTE/CONC.(M)	k_s (cm s ⁻¹)	α_{exp}	
TEAP	0.063	0.127	1.07
	0.100	0.113	1.06
	0.160	0.106	1.07
	0.250	0.103	1.06
	0.400	0.099	1.04
TPAP	0.063	0.103	1.09
	0.100	0.091	1.07
	0.160	0.082	1.07
	0.250	0.074	1.07
	0.400	0.062	1.04
TBAP	0.063	0.074	1.06
	0.100	0.062	1.02
	0.160	0.054	1.02
	0.250	0.048	0.99
	0.400	0.040	0.99

Cu⁺ Reduction in Acetonitrile

Electrolyte (conc. = 0.10M)	$\ln A_{\text{exp}}$	$\Delta H_{r,\text{exp}}^{\ddagger}$ (kJ mol ⁻¹)
TEAP	4.27 ± 0.32	15.5 ± 0.8
TPAP	5.23 ± 0.54	18.9 ± 1.3
TBAP	12.21 ± 0.18	36.9 ± 0.4

Electrolyte (conc. = 0.10M)	$\ln A_{\text{corr}}$	$\Delta H_{r,\text{corr}}^{\ddagger}$ (kJ mol ⁻¹)
TEAP	3.03 ± 0.27	11.8 ± 1.9
TPAP	6.77 ± 0.32	22.6 ± 1.9
TBAP	11.8 ± 4.8	37.4 ± 11.1

Electrolyte (conc. = 0.10M)	ΔS_{rc}° (J mol ⁻¹ K ⁻¹)	ΔH_i^{\ddagger} (kJ mol ⁻¹)
TEAP	159 ± 4	59.2 ± 2.2
TPAP	174 ± 3	74.5 ± 2.1
TBAP	172 ± 5	89 ± 11

Cu⁺ Reduction in Benzonitrile

ELECTROLYTE/CONC.(M)		$k_s(\text{cm s}^{-1})$ $\pm 2\%$	α_{exp} $\pm 5\%$
TEAP	0.100	0.106	0.91
TBAP	0.063	0.144	1.02
	0.100	0.164	1.12
	0.160	0.195	1.29
	0.250	0.221	1.23
	0.400	0.281	1.27

ELECTROLYTE	$\ln A_{\text{exp}}$	$\Delta H_{r,\text{exp}}^{\ddagger}(\text{kJ mol}^{-1})$
TEAP	5.68 ± 0.39	19.6 ± 1.0
TBAP	6.80 ± 0.79	21.1 ± 1.9

ELECTROLYTE	$\ln A_{\text{corr}}$	$\Delta H_{r,\text{corr}}^{\ddagger}(\text{kJ mol}^{-1})$
TEAP	6.26 ± 0.42	20.6 ± 1.0
TBAP	4.68 ± 0.74	16.0 ± 0.2

ELECTROLYTE	$\Delta S_{rc}^{\circ}(\text{J mol}^{-1}\text{K}^{-1})$	$\Delta H_i^{\ddagger}(\text{kJ mol}^{-1})$
TEAP	146 ± 4	64.1 ± 1.6
TBAP	144 ± 8	58.9 ± 2.4

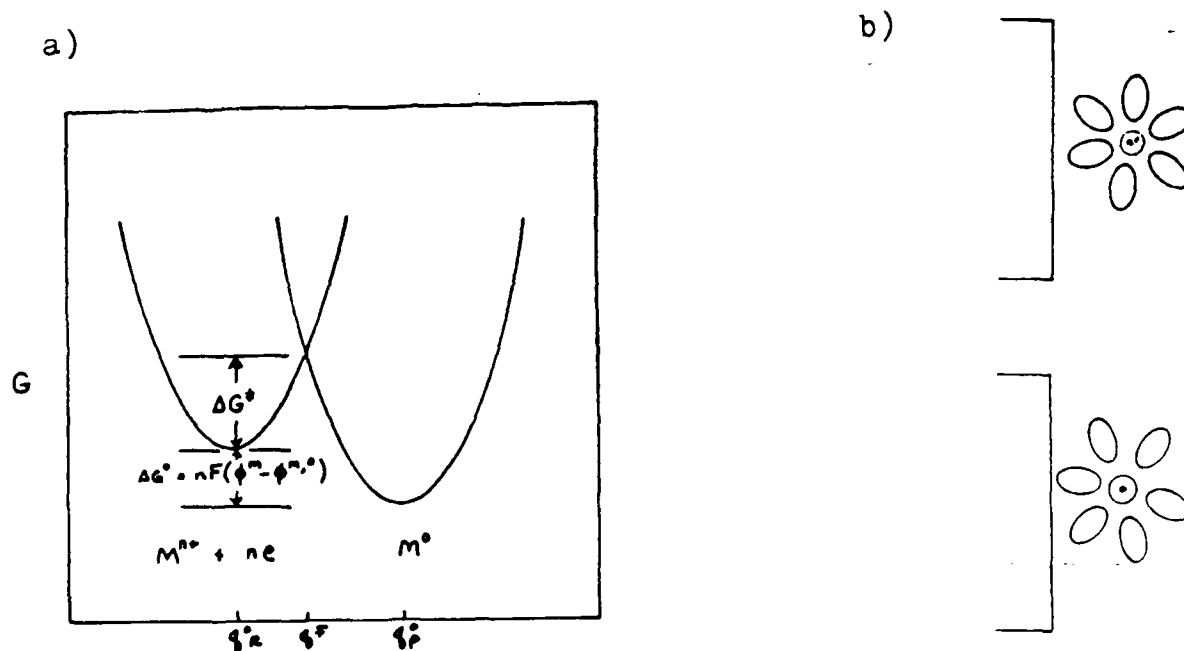


Figure 1. a) Reaction coordinate for a simple electron transfer reaction. b) Schematic of the metal center environment at the electrode for reactant and product.

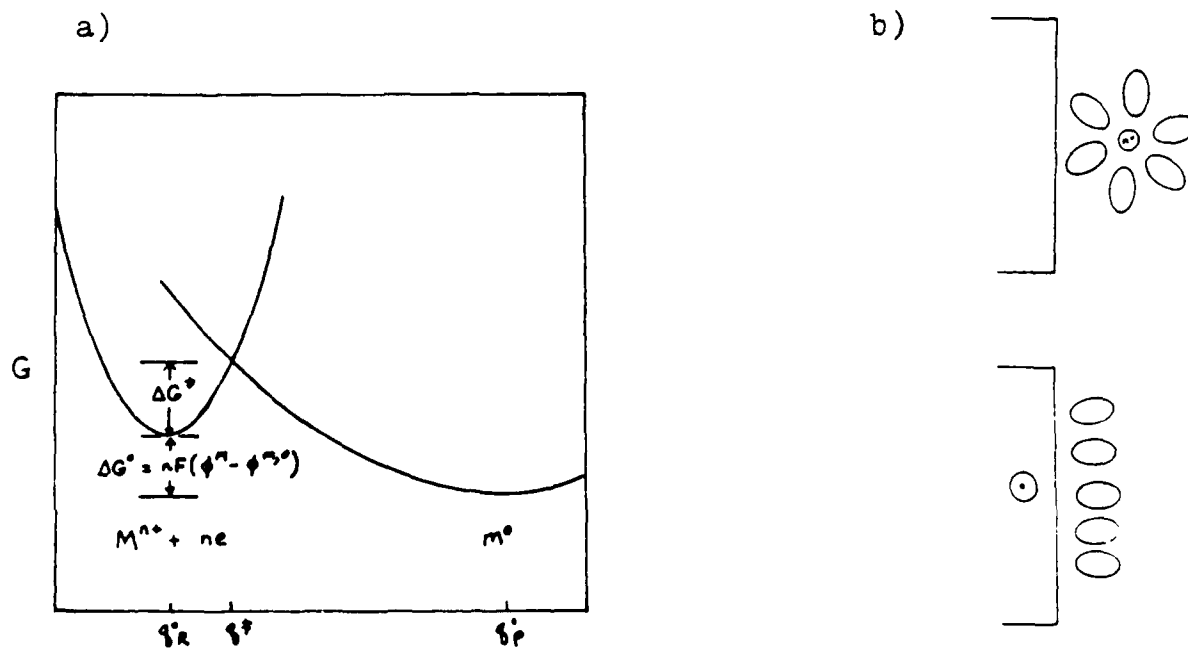


Figure 2. a) Reaction coordinate for amalgam formation reaction where reactant and product environments (b) are different.