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Potential Dependence of the Elementary Steps in the Kinetics of Electrode Reactions Involving Amalgam Formation

by

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The Potential Dependence of the Elementary Steps in the Kinetics of Electrode Reactions Involving Amalgam Formation

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Abstract

The effect of the double layer on the kinetics of the possible elementary steps in amalgam formation reactions are described in detail. The steps considered are electron transfer, ion transfer, adsorption, and metal incorporation. It is shown that the rate equations for all elementary steps have the same form, but that they differ considerably with respect to their kinetic parameters, namely, the standard rate constant and apparent transfer coefficient. As the location of the elementary step moves closer to the interface, its potential dependence increases and larger values of the apparent transfer coefficient are observed. Double layer effects are also considered for a more complex mechanism in which more than one step is rate determining.

Introduction

The reaction of metal amalgam formation constitutes an important class of electrode processes whose kinetics have been studied extensively, especially in aqueous solutions.[1] The overall process which may be written

$$M^{+n} + ne + Hg \longrightarrow M(Hg) \qquad (1)$$

involves the transfer of the metal ion M^{+n} from an electrolyte solution where it is solvated by solvent molecules or other ligands to the metallic phase where the product metal atom M is solvated by mercury atoms. This reaction has been traditionally treated as an electron transfer process involving the transfer of one or more electrons to the metal ion in the double layer as the rate determining step (r.d.s.).[1] Losev[2] argued that the r.d.s. is the transfer of the first electron to M^{+n}, subsequent electron and ion transfer steps being rapid in comparison. Accordingly, intermediate ions such as Cd^+, Zn^+, and Pb^+, and atoms such as Cd, Zn, Pb, Li, Na and K, which are normally considered to be highly unstable species in solution, are formed near the interface. Sluyters, et al.[3-5] have concluded on the basis of the potential dependence of the rate constants for reduction of Zn^{++} and Cd^{++} at mercury that the reaction mechanism is complex, involving both electron transfer and chemical steps in which the reactant or an intermediate loses some of its solvation sheath. Somewhat different conclusions were reached by Baranski and Fawcett[6,7] on the basis of a study of the kinetics of reduction of alkali metal cations in non-aqueous media. They presented evidence that more than one step is involved for these processes and proposed that ion transfer in the inner part of the double layer with partial desolvation was the r.d.s. They also concluded that electron transfer to a fully solvated cation in the double layer does not occur.

It is obvious that the solvent plays an important role in the kinetics of these reactions regardless of the details of the mechanism. Since the r.d.s. occurs near the electrode, its kinetics are strongly influenced by the double layer to an extent which increases with the charge on the reactant. The purpose of the present paper is to examine the role of double layer effects in each of the proposed elementary steps with the goal of identifying differences in their potential dependence. It should be emphasized that the discussion in this paper is limited to situations where the reactant is only solvated by solvent molecules in the bulk of the solution, reactions involving metal ions with anionic ligands or other molecules as ligands not being considered.

The Nature of the Elementary Steps in Amalgam Formation and Their Location In the Double Layer

One may distinguish four possible elementary steps in amalgam formation. The first is electron transfer in which an electron moves from the metal phase to a metal ion in the vicinity of the electrode. The metal ion, which may be the original reactant or an intermediate, is assumed to be totally surrounded by solvent molecules, and not to be in intimate contact with the electrode. It follows that the theory of electron transfer for simple redox reactions should be applicable to this step. The second step is ion transfer in which the reactant or an intermediate ion moves from one location in the double layer to another which is closer to the electrode. The ion experiences a change in electrostatic potential and may lose some of its solvation sheath in this step; however, it does not come in contact with the metal phase, and therefore, is not adsorbed as a result of ion transfer. An adsorption step is one in which the ion moves from a site in the inner part of the double layer where it is completely surrounded by solvent molecules to an adsorption site at the electrode where it is partially solvated by solvent molecules and partially by mercury atoms in the electrode. This step is assumed to be accompanied by partial charge transfer so that the net charge on the adsorbed species is intermediate between that on the original ion and zero. Finally, there is a metal incorporation step in which the adsorbed metal ion moves from the adsorption site where it is partially solvated by mercury atoms to the mercury phase where it is totally solvated by these species.

In order to consider the potential dependence of each of the above steps, a more detailed picture of the location of the reactant in its progress through the double layer must be developed. A possible description of the progress of a Na^+ ion through the double layer in a dimethylformamide (DMF) solution containing tetraethylammonium perchlorate (TEAP) is illustrated in Fig. 1. Each of the constituents of the double layer is represented as a sphere of radius appropriate to its relative size. Since the reduction of Na^+ ion occurs at very negative potentials the perchlorate ion concentration near the outer Helmholtz plane (o.H.p) is assumed to be negligible. The details of the description will vary with each system considered but one can recognize three general stages in the overall process. While the reactant remains fully solvated its distance of closest approach to the electrode is located at position 'c' in the diffuse layer, a distance x_c from the interface. In the present model, the electrode is assumed to be covered by a monolayer of solvent molecules, and the cationic counter ions (TEA^+ in the present example) define the position of the o.H.p. (position 'd'). Since the TEA^+ cations are assumed to share the solvation sheath of the electrode, they are located closer to the electrode than the fully solvated reacting ion. At position 'b', a distance x_b from the interface, the reactant has entered the inner layer by breaking out of its original solvation environment, and now shares the solvation sheath of the electrode in the direction of the electrode/solution interface. It is reasonable to assume that solvation of the reactant is weaker in this location since the orientation of surrounding solvent molecules is determined not only by the field due to the charge on the reacting ion, but also by the field due to the charge on the electrode. Finally, the reacting species moves to position 'a' where it is adsorbed at the interface, its solvation atmosphere consisting of mercury atoms on one side, and solvent molecules on the other.

The electrostatic potentials at each site in the double layer may be estimated on the basis of the usual models.[8] For sites in the inner layer in the absence of specific adsorption of non-reacting ions and solute molecules, the average potential on reaction plane 'r' is given by[9]

$$\phi^r = \phi^d + \lambda_r(\phi^m - \phi^d) \qquad (2)$$

where ϕ^d is the potential drop across the diffuse layer, normally estimated using the Gouy-Chapman theory, ϕ^m, the potential of the metal on the rational potential scale, and λ_r, a dimensionless fraction equal to K_{md}/K_{rd}, K_{md} being the integral capacity of the inner layer and K_{rd}, that between the reaction plane (r.p.) and the o.H.p. Thus, the value of λ_r depends both on the distance of the r.p. from the electrode and the dielectric permittivity profile in this region. On the basis of Fig. 1 and neglecting variation in dielectric permittivity with position in the inner layer, one may estimate that $\lambda_a \simeq 0.85$ and $\lambda_b \simeq 0.3$. Obviously, as the reaction site moves closer to the electrode, the value of λ_r increases, and ϕ^r approaches ϕ^m.

For reaction sites in the diffuse layer, ϕ^r may be estimated using the Gouy-Chapman theory according to which

$$\ln \tanh(f\phi^r/4) = \ln \tanh(f\phi^d/4) - \kappa(x_r - x_d) \qquad (3)$$

where x_r and x_d are the distances of the r.p. and o.H.p. from the electrode/solution interface, respectively, κ, the Debye-Huckel reciprocal length, and $f = F/RT$. It should be remembered that κ, which is equal to $(2F^2c_s/\varepsilon\varepsilon_oRT)^{1/2}$ for 1-1 electrolytes, depends on salt concentration c_s and the dielectric permittivity of the solvent ε. For locations in the diffuse layer which are close to the o.H.p. such as position 'c', $\ln \tanh(f\phi^r/4)$ may be replaced by its Taylor's series expansion about $\ln \tanh(f\phi^d/4)$. When this function is approximated by the first two terms in the Taylor's series, the expression for ϕ^r becomes[10]

$$\phi^r = \phi^d - \frac{2\kappa\ RT}{F}\ (x_r - x_d)\ \sinh(f\phi^d/2) \qquad (4)$$

Recalling that, on the basis of the Gouy-Chapman theory,

$$\sinh(f\phi^d/2) = \sigma/2A = K_{md}(\phi^m - \phi^d)/2A \qquad (5)$$

where σ is the charge density on the electrode and $A = (2RT\ \varepsilon\varepsilon_oc_s)^{1/2}$, the Gouy-Chapman constant, it is easily shown that ϕ^r is related to $(\phi^m - \phi^d)$ by eq. (2). The parameter λ_r is now negative and is given by the ratio $-K_{md}/K_{dr}$ where $K_{dr} = \varepsilon\varepsilon_o/(x_r - x_d)$ is the capacity of the region in the diffuse layer between the r.p. and o.H.p. The approximate nature of eq. (2) for estimating ϕ^r in the diffuse layer is clearly recognized, the approximations made being valid only when $|\phi^d|$ is greater than 100 mV. However, for the sake of convenience, eq. (2) will be used for the potential ϕ^r for all locations in the double layer, it being recognized that the estimation of λ_r for sites in the diffuse layer is more complex than suggested by the approximate relationship given here.

Values of ϕ^r for the sites in the double layer illustrated in Fig. 1 are tabulated in Table I as a function of electrode charge density for the mercury/DMF system with 0.1M TEAP as electrolyte on the basis of data obtained earlier.[11] It is clear that the average potential on planes parallel to the interface becomes significantly larger as the site in the double layer moves closer to the interface. Thus, the role of the double layer in determining kinetic parameters increases as the reaction site moves closer to the electrode. It should also be noted that λ_c for reaction sites in the diffuse layer varies significantly with electrode potential as a result of the non-linear variation in potential with distance in this region.

On the basis of the above discussion, the electrochemical potential for a species, i, may be estimated for any location, 'r', in the double layer. In general, $\tilde{\mu}_i^r$ is given by the expression

$$\tilde{\mu}_i^r = \mu_{io} + RT \ln a_i^r + z_i F \phi^r + g_i^r \qquad (6)$$

where μ_{io} is the standard chemical potential for unit activity of species i in the bulk of the solution, a_i^r, the activity of species i at location 'r', z_i, the charge on species i and g_i^r, any non-electrostatic work done in bringing this species into the double layer.[12] The local activity a_i^r is, in general, not equal to the activity in the bulk, a_i^s for equal concentrations ($c_i^r = c_i^s$) because of variation in the activity coefficient with position in the double layer. The local activity coefficient, γ_i^r is related to the discreteness-of-charge potential ζ_i^r through the relationship[9]

$$RT \ln \gamma_i^r = z_i F \zeta_i^r \qquad (7)$$

Thus, γ_i^r is related to the extent to which the local potential experienced by species i differs from the average potential on the plane, ϕ^r, just as the bulk activity coeffient γ_i^s is related to the departure of the local potential experienced in the bulk of the solution from the average value ϕ^s. Since the discussion here is limited to cases where specific adsorption is absent, γ_i^r is approximately independent of potential over a limited range provided the location of 'r' does not change with respect to the electrode/solution interface. The term g_i^r is zero for location 'c' or other locations further from the interface. For sites closer to the interface, its value depends on the non-electrostatic work done in moving species i out of its original solvation sheath to sites 'a' or 'b' in the inner layer.

On the basis of the simple model discussed here, the potential dependence of each of the elementary steps described above may now be analyzed. In this regard, the potential dependence of heterogeneous electron transfer is well known but it is presented again here in order to describe carefully the double layer efects and compare them with those found for the other elementary steps considered.

The Electron Transfer Step

For ease of notation, the overall reaction will be written

$$A_s + ne \longrightarrow B_m \qquad (8)$$

where A_s represents the metal ion in solution and B_m, the metal atom in mercury. In the following discussion it is assumed that transfer of one electron to species A at a reaction site in the double layer is the r.d.s.. The mechanism of the reaction can then be written as

$$A_s \rightleftharpoons A_r \qquad (9)$$

$$A_r + e \longrightarrow X_r \qquad (10)$$

$$X_r + (n-1)e \rightleftharpoons B_m \qquad (11)$$

where X_r is the intermediate ion or atom formed at the reaction site. Following the transition state theory of electron transfer[13], the free energy of activation for the forward process is given by

$$\Delta G_f^{\ddagger} = \Delta G_o^{\ddagger} + \alpha(\tilde{\mu}^r_{Xo} - \tilde{\mu}^r_{Ao} - \tilde{\mu}^m_{eo}) \qquad (12)$$

where $\Delta G_o^{\ddagger}$ is the free energy of activation at the formal potential, $\tilde{\mu}^r_{io}$, the electrochemical potential of species i at the reaction site when its local concentration is unity, $\tilde{\mu}^m_{eo}$, the electrochemical potential of the electron in the metal, and α, the transfer coefficient. Assuming that[14]

$$\tilde{\mu}^r_{Xo} = \mu_{Xo} + RT \ln \gamma^r_X + z_X F \phi^r \qquad (13)$$

and

$$\tilde{\mu}^m_{eo} = \mu_{eo} - F\phi^m \qquad (14)$$

the expression for $\Delta G_f^{\ddagger}$ becomes

$$\Delta G_f^{\ddagger} = \Delta G_o^{\ddagger} + \alpha[\Delta G_{ro} + RT \ln(\gamma_X^r/\gamma_A^r) - F(\phi^r-\phi^m] \tag{15}$$

where ΔG_{ro} is the standard free energy change associated with the r.d.s. and is given by

$$\Delta G_{ro} = \mu_{Xo} - \mu_{Ao} - g_A^r - \mu_{eo} \tag{16}$$

The rate of the forward reaction v_f may be written

$$\ln v_f = \ln Z + \ln c_A^r - \Delta G_f^{\ddagger}/RT \tag{17}$$

where Z is the collision frequency associated with this process. On the basis of equilibrium (9), the concentrations of A in the bulk and at the reaction site may be related as follows:

$$RT \ln(\gamma_A^s c_A^s) = RT \ln(\gamma_A^r c_A^r) + z_A F\phi^r + g_A^r \tag{18}$$

Then, combining eqs. (15), (17), and (18), the following expression is obtained for the logarithm of the forward rate constant, k_f:

$$\ln k_f = \ln(v_f/c_A^s) = \ln k_{fo} + \ln(\gamma_A^s/\gamma_{\ddagger}) - z_A f\phi^r + \alpha f(\phi^r-\phi^m) \tag{19}$$

k_{fo} is the forward rate constant at $\phi^m = 0$ in the absence of double layer effects ($\phi^r=0$) and is given by

$$\ln k_{fo} = \ln Z - \Delta G_o^{\ddagger}/RT - g_A^r/RT - \alpha\Delta G_{ro}/RT \tag{20}$$

$\gamma_{\ddagger}$ is the activity coefficient of the activated complex which is related to the activity coefficients of A and X at the reaction site as follows:

$$\ln\gamma_{\ddagger} = (1-\alpha) \ln \gamma_A^r + \alpha \ln \gamma_X^r \tag{21}$$

Since the position of the reaction site in the double layer is unknown it is more convenient to write eq. (19) in terms of the o.H.p potential ϕ^d. Using eq. (2), the expression for the logarithm of the forward rate constant becomes

$$\ln k_f = \ln k_{fo} + \ln(\gamma_A^s/\gamma_{\ddagger}) - z_A f\phi^d - \alpha_a n f(\phi^m-\phi^d) \tag{22}$$

where α_a is the apparent transfer coefficient for the overall forward reaction given by

$$\alpha_a = [\alpha+\lambda_r(z_A-\alpha)]/n \qquad (23)$$

This result shows that α_a which is determined from the slope of a corrected Tafel plot (c.T.p.) depends on the location of the reaction site in the double layer, the charge on the reactant, and the total number of electrons involved.

For the backward process, the free energy of activation is given by

$$\Delta G_b^{\ddagger} = \Delta G_o^{\ddagger} + (1-\alpha)[-\Delta G_{ro} + RT\ \ln(\gamma_A^r/\gamma_X^r) + F(\phi^r-\phi^m)] \qquad (24)$$

and the rate of reaction, by

$$\ln v_b = \ln Z + \ln c_X^r - \Delta G_b^{\ddagger}/RT \qquad (25)$$

In order to relate the concentration of the intermediate X to the product B, the condition for equilibrium (11) is used:

$$\mu_{Xo} + RT\ \ln(\gamma_X^r c_X^r) + z_X F\phi^r + (n-1)\mu_{eo} - (n-1)F\phi^m$$
$$= \mu_{Bo} + RT\ \ln(\gamma_B^m c_B^m) \qquad (26)$$

Now, combining eqs. (24)-(26) and remembering that $z_A = z_X+1 = n$, the following expression for the backward rate constant is obtained:

$$\ln k_b = \ln(v_b/c_B^m) = \ln k_{bo} + \ln(\gamma_B^m/\gamma_{\ddagger}) + (n-\alpha)f(\phi^m-\phi^r) \qquad (27)$$

In this equation,

$$\ln k_{bo} = \ln Z - \Delta G_o^{\ddagger}/RT - g_A^r/RT - \alpha\Delta G_{ro}/RT + \Delta G_o/RT \qquad (28)$$

where ΔG_o is the standard free energy change for the overall reaction. Replacing ϕ^r by its expression in terms of ϕ^d and ϕ^m (eq.(2)), eq. (27) becomes

$$\ln k_b = \ln k_{bo} + \ln(\gamma_B^m/\gamma_{\ddagger}) + (n-\alpha_a n)f(\phi^m-\phi^d) \qquad (29)$$

and the expression for the apparent transfer coefficient for the backward process,

$$\beta_a = 1 - \alpha_a \qquad (30)$$

The condition for equilibrium in this system is that $v_f = v_b$. On the basis of eqs. (19) and (27), it is easily shown that the equilibrium potential is

$$\phi_e^m = \frac{-\Delta G_o}{nF} - \frac{RT}{nF} \ln \frac{a_B^m}{a_A^s} \qquad (31)$$

which is the Nernst equation for reaction (8) as expected. Eqs. (19) and (27), or (22) and (29) could be written with the potential expressed as an overpotential with respect to the formal potential but not much is to be gained by such a change. This follows from the fact that the standard potential for the r.d.s. is different from that for the overall reaction.

It is clear from the description presented earlier that, if electron transfer is the r.d.s., it occurs at position 'b' or 'c', that is, in the inner layer, or at a position in the diffuse layer close to the o.H.p. (Fig. 1). It is instructive to estimate values of the apparent transfer coefficient α_a as a function of charge on the reactant and its location in the double layer. In order to do this one must assume a value for the intrinsic transfer coefficient α. On the basis of well known arguments related to the fact that the atmospheres of the reactant and product are essentially the same, this quantity is usually assumed to be 0.5.[15] Values of α_a estimated at positions 'b' and 'c' for reactants of different charge are given in Table II. Two trends are immediately apparent. As the reaction site moves further from the electrode the value of α_a decreases.

Since α_a is determined experimentally from the slope of the c.T.p. calculated assuming that the reaction site is the o.H.p., values of α_a greater than 0.5 for a reactant with a charge of +1 indicate that the reaction site is in the inner layer, and those less than 0.5, that the reaction site is in the diffuse layer. For a given reaction site, the value of α_a decreases markedly with charge on the reactant. This result reflects the fact that the r.d.s. involves the transfer of one electron whereas the transfer coefficient is calculated on the basis of the overall reaction which involves n electrons.

Earlier treatments of electron transfer[1] have considered the case that the r.d.s. involves more than one electron. If this were the case then the expressions for α_a and β_a would be different. However, the simultaneous transfer of more than one electron does not seem probable on quantum mechanical grounds. Therefore, the discussion here has been limited to the transfer of one electron. Moreover, it has been assumed that the transfer of the first electron is the r.d.s. If transfer of a subsequent electron is the r.d.s., then the equations presented in this section are not applicable. Of course, the appropriate relationships could be derived, but the probability of their applicability seems very small. This conclusion follows from the fact that intermediates resulting from transfer of the first electron are normally unstable and, therefore, should undergo reduction much more rapidly.

The Ion Transfer Step

As defined above, ion transfer involves the movement of the reactant or an intermediate ion without electron transfer from a site in the double layer to one closer to the electrode but not in contact with it. In terms of the model used here, this process involves moving this species from position 'c' to position 'b'. In previous literature[3-5], this step has often been called partial desolvation and referred to as a chemical step whose rate does not depend on potential. It seems highly likely that partial desolvation will also involve movement of the charge center of the reactant because the reacting species is located in the attractive field of the electrode, most amalgam formation reactions occurring negative of the p.z.c. Thus, the term ion transfer seems more appropriate to describe what has previously been called a partial desolvation or chemical step.

If ion transfer is the r.d.s., the mechanism of the overall process can be written as

$$A_s \rightleftharpoons A_c \qquad (32)$$

$$A_c \longrightarrow A_b \qquad (33)$$

$$A_b + ne \rightleftharpoons B_m \qquad (34)$$

It follows that the free energy of activation for the forward reaction is

$$\Delta G_f^\ddagger = \Delta G_o^\ddagger + \alpha(\tilde{\mu}_{Ao}^b - \tilde{\mu}_{Ao}^c) \qquad (35)$$

where $\Delta G_o^\ddagger$ is the free energy of activation when $\tilde{\mu}_{Ao}^b = \tilde{\mu}_{Ao}^c$, and α the transfer coefficient for ion transfer. On the basis of eq.(6) this may be rewritten as

$$\Delta G_f^\ddagger = \Delta G_o^\ddagger + \alpha[RT \ln(\gamma_A^b/\gamma_A^c) + g_A^b + z_A F(\phi^b-\phi^c)] \qquad (36)$$

The rate of the forward reaction is now given by

$$\ln v_f = \ln Z + \ln c_A^c - \Delta G_f^{\ddagger}/RT \qquad (37)$$

where the concentration of A at location 'c' is estimated on the basis of equilibrium (32)

$$RT \ln(\gamma_A^c c_A^c) + z_A F \phi^c = RT \ln(\gamma_A^s c_A^s) \qquad (38)$$

Combining eqs. (36)-(38) and using equation (2) to express the potentials ϕ^b and ϕ^c in terms of ϕ^d and $\phi^m-\phi^d$, the following expression is obtained for the logarithm of the forward rate constant

$$\ln k_f = \ln(v_f/c_A^s) = \ln k_{fo} + \ln(\gamma_A^s/\gamma_{\ddagger}) - z_A f \phi^d - \alpha_a n f(\phi^m-\phi^d) \quad (39)$$

The quantities k_{fo}, $\gamma_{\ddagger}$ and α_a are defined by the equations:

$$\ln k_{fo} = \ln Z - \Delta G_o^{\ddagger}/RT - \alpha g_A^b/RT \qquad (40)$$

$$\ln \gamma_{\ddagger} = (1-\alpha) \ln \gamma_A^c + \alpha \ln \gamma_A^b \qquad (41)$$

and

$$\alpha_a = \lambda_c + \alpha(\lambda_b-\lambda_c) \qquad (42)$$

In a similar way, it is easily shown that the logarithm of the backward rate constant is given by

$$\ln k_b = \ln(v_b/c_B^m) = \ln k_{bo} + \ln(\gamma_B^m/\gamma_{\ddagger}) + (n-\alpha_a n) f(\phi^m-\phi^d) \qquad (43)$$

where

$$\ln k_{bo} = \ln Z - \Delta G_o^{\ddagger}/RT - \alpha g_A^b/RT + \Delta G_o/RT \qquad (44)$$

When one compares eqs. (39) and (43) with the corresponding equations for electron transfer (eqs. (22) and (29)), it is immediately apparent that the form of the potential dependence for ion transfer and electron transfer is exactly the same. The only way one can distinguish between these steps is via the kinetic parameters, namely, the standard rate constant k_s and the apparent transfer coefficients α_a and $\beta_a = 1-\alpha_a$. The latter aspect is now considered in more detail. Ion transfer as described above involves the reactant ion moving from a solvation environment where it more strongly interacts with surrounding solvent molecules to one where it interacts more weakly. If one examines this process within the context of theory of reactions in polar media[15,16], then the vibrational energy of the reactant in its environment can be described by a parabola with a larger force constant than that for the product in its environment (Fig. 2). As a result, the rate of ion transfer is determined by an asymmetrical free energy barrier, the extent of asymmetry depending on the relative values of the vibrational force constants for the reactant and product free energy surfaces.[17] On the basis of models developed earlier[15,16] it is easily shown that the intrinsic transfer coefficient for the forward process at the standard potential is given by[17]

$$\alpha = \frac{k_i^{1/2}}{k_i^{1/2} + k_f^{1/2}} \tag{45}$$

where $2k_i$ is the vibrational force constant for the initial state, and $2k_f$, that for the final state. In the case that the free energy barrier is completely symmetrical so that $k_i = k_f$, the intrinsic transfer coefficient is equal to 0.5. As k_i increases with respect to k_f, α also increases; for example when $k_i = 10\ k_f$, α is equal to 0.76. Thus, one expects α to increase with increase in the strength of reactant solvation in the bulk of the solution.

Values of the apparent transfer coefficient α_a estimated according to eq. (42) for ion transfer from location 'c' to 'b' are listed in Table III for various values of the intrinsic transfer coefficient α. First of all, it should be noted that α_a does not depend explicitly on the charge on the reactant, any dependence due to reactant nature and charge being contained in the intrinsic transfer coefficient α. Secondly, the values of α_a are small, mainly because the rate controlling step occurs in the vicinity of the o.H.p without the participation of electrons. As the intrinsic transfer coefficient increases, a small increase in α_a is found, but for the chosen values of λ_b and λ_c, α_a remains small even when the value of α is very large. Low values of α_a are not uncommon for amalgam formation reactions, a good example being the Cd(II) system for which low values of α_a are found in both aqueous and non-aqueous media.[18-20] However, these results could also be attributed to an electron transfer step occurring further from the electrode at position 'c' (see Table II). Another way of distinguishing ion transfer from other elementary steps is in terms of the standard rate constant and the associated free energy barrier at the standard potential. This has been discussed to some extent from a theoretical point of view[21,22] but not in detail with respect to the solvent which must play an important role in determining these parameters.

The equations derived above are for the case that the moving species is the original reactant A. If an intermediate species X is involved in ion transfer, which is also the r.d.s., then the mechanism becomes

$$A_s + me \rightleftharpoons X_c \tag{46}$$

$$X_c \longrightarrow X_b \tag{47}$$

$$X_b + (n-m)e \rightleftharpoons B_m \tag{48}$$

The intermediate is formed at location 'c' by the transfer of m electrons to A where m is less than n, and in most cases would equal one. On analyzing this mechanism, one obtains the expected results that the expression for the forward rate constant can be written exactly as above (eq. (39)) but with new definitions of the kinetic parameters k_s and α_a. In fact, the apparent transfer coefficient is then defined by the equation

$$\alpha_a n = m + z_X\lambda_c + z_X\alpha(\lambda_b - \lambda_c) \qquad (49)$$

where z_X is the charge on the intermediate species, X. On the basis of this result, the apparent transfer coefficient for reaction (47) is considerably larger than that for reaction (33). For instance, for the reduction of a divalent species with transfer of one electron at site 'c' (m=1), and assuming $\lambda_b = 0.3$ and $\lambda_c = -0.1$, the value of α_a is equal to 0.55. The higher value of α_a reflects the fact that the equilibrium constant for reaction (46) is potential dependent, and is expressed in eq. (49) through the term 'm'. However, it seems highly unlikely that mechanism (46)-(48) would be important in amalgam formation reactions. This conclusion follows from the fact that the strength of solvation of the intermediate species X is generally less than that of the original reactant A because of its lower charge. Thus, one would usually not expect an ion transfer step following electron transfer at location 'c' to be rate controlling. The details of the most probable mechanism are discussed further below.

The Adsorption Step

In the adsorption step, the reactant or an intermediate moves from position 'b' in the inner layer where it is solvated by solvent molecules to the interface at position 'a' where it is partially solvated by the solvent and partially by mercury atoms. This step is probably accompanied by the transfer of some charge from the metal phase with which the reacting species is in contact. Adsorption is expected to be rate determining only when solvation by solvent molecules is much stronger than that by mercury atoms. Since it occurs very close to the electrode, its potential dependence is expected to be large.

When adsorption is the r.d.s., the mechanism of the reaction is

$$A_s \rightleftharpoons A_b \qquad (50)$$

$$A_b + pe \longrightarrow X_a \qquad (51)$$

$$X_a + (n-p)e \rightleftharpoons B_m \qquad (52)$$

Thus, the free energy of activation for the forward step is

$$\Delta G_f^{\ddagger} = \Delta G_o^{\ddagger} + \alpha(\tilde{\mu}_X^a - \tilde{\mu}_A^b - p\tilde{\mu}_e^m) \qquad (53)$$

where X designates the species at the interface whose charge is intermediate between z_A and zero, and α is now the transfer coefficient for the adsorption step. Substituting for the electrochemical potentials of the components of reaction (51), the following expression is obtained for $\Delta G_f^{\ddagger}$:

$$\Delta G_f^{\ddagger} = \Delta G_o^{\ddagger} + \alpha[\Delta G_{ro} + RT\ \ln(\gamma_X^a/\gamma_A^b) + z_X F\phi^a - z_A F\phi^b + pF\phi^m] \qquad (54)$$

where

$$\Delta G_{ro} = \mu_{Xo} - \mu_{Ao} - g_A^b - p\mu_{eo} \qquad (55)$$

Using the expression for the forward rate of reaction and equilibrium condition (50) given earlier for the case that the initial reaction location is 'b' (eqs. (17) and (18)), and recognizing that $z_X = z_A - p$, one may show that

$$\ln k_f = \ln(v_f/c^s_A) = \ln k_{fo} + \ln(\gamma^s_A/\gamma_\ddagger) - z_A f \phi^b - \alpha z_A f(\phi^a - \phi^b) - \alpha p f(\phi^m - \phi^a) \qquad (56)$$

where

$$\ln k_{fo} = \ln Z - \Delta G^\ddagger_o/RT - g^b_A/RT - \alpha \Delta G_{ro}/RT \qquad (57)$$

When the potentials ϕ^a and ϕ^b are written in terms of ϕ^d and $\phi^m - \phi^d$ using eq. (2), eq. (56) reduces to the equation derived earlier for the logarithm of the forward rate constant (eq. (22) or (39)). However, the apparent transfer coefficient is now given by the expression

$$\alpha_a n = z_A[\alpha \lambda_a + (1-\alpha)\lambda_b] + \alpha p(1-\lambda_a) \qquad (58)$$

Similarly, it is easily shown that the logarithm of the backward rate constant is given by eq. (29) or (43), but with the constant k_{bo} defined as follows:

$$\ln k_{bo} = \ln Z - \Delta G^\ddagger_o/RT - g^b_A/RT - \alpha \Delta G_{ro}/RT + \Delta G_o/RT \qquad (59)$$

It is not surprising that the expressions for the potential dependence of the adsorption step have exactly the same form as those for electron transfer and ion transfer. Adsorption combines ion transfer with partial electron transfer at a location closer to the interface where double layer effects are greater. Since the solvation atmosphere of the reactant changes significantly on adsorption, it is quite possible that the intrinsic transfer coefficient for this step is significantly different from 0.5. Values of α_a estimated according to eq. (58) assuming ion transfer from site 'b' ($\lambda_b = 0.3$) to site 'a' ($\lambda_a =$

0.85) for varying extents of partial charge transfer are given in Table IV. The values of α_a are much larger than those estimated for ion transfer, reflecting the fact that the reaction site is much closer to the electrode and double layer effects more pronounced. The effect of partial charge transfer is not very large because the electron charge density experiences only a small change in potential on interaction with the adsorbed species. In this regard, on the basis of experimental data[23], the extent of partial charge transfer varies considerably with the nature of the reactant, the electrode material and the solvent, but for most systems, p probably lies between 0 and 0.5 z_A. When one compares the values of α_a for the adsorption step assuming an intrinsic transfer coefficient of 0.5, with those for electron transfer at location 'b' (Table I), it is clear that this kinetic parameter cannot be used to distinguish between the two steps. If one is to differentiate between these steps one must rely on other parameters such as the standard rate constant or the heat of activation.

One could also write the reaction mechanism with the adsorption of an intermediate species as the r.d.s. Such a mechanism is very unlikely considering the instability of the intermediate species. Moreover, on the basis of the analysis given above for ion transfer, the apparent transfer coefficient would be exceedingly high under these circumstances so that preceding steps with comparable rates but lower transfer coefficients would rapidly become rate determining as the electrode potential is made more negative.

The Metal Incorporation Step

In the last step in the reduction reaction, the adsorbed intermediate moves from location 'a' where it is partially solvated by solvent molecules and partially by mercury atoms (Fig. 1) into the metal phase where it is totally solvated by mercury atoms. This step has the greatest dependence on potential, and therefore, under most circumstances, it is least likely to be rate controlling. However, the possibility that it is the r.d.s. is now examined in more detail.

When metal incorporation is the r.d.s., the mechanism of the reduction reaction can be written

$$A_s + pe \rightleftharpoons X_a \tag{60}$$

$$X_a + (n-p)e \longrightarrow B_m \tag{61}$$

The free energy of activation for the r.d.s. is

$$\Delta G_f^\ddagger = \Delta G_o^\ddagger + \alpha[\tilde{\mu}_B^m - \tilde{\mu}_X^a - (n-p)\tilde{\mu}_e] \tag{62}$$

After the usual substitutions, this equation becomes

$$\Delta G_f^\ddagger = \Delta G_o^\ddagger + \alpha[\Delta G_{ro} + RT\ \ln(\gamma_B^m/\gamma_X^a) - z_X F\phi^a + (n-p)F\phi^m] \tag{63}$$

where

$$\Delta G_{ro} = \mu_{Bo} - \mu_{Xo} - (n-p)\mu_{eo} \tag{64}$$

The condition for equilibrium (60) can be written

$$RT\ \ln\ \gamma_X^a c_X^a + z_X F\phi^a = -\Delta G_o + \Delta G_{ro} + RT\ \ln\ \gamma_A^s c_A^s - pF\phi^m \tag{65}$$

where ΔG_o is the standard free energy change for the overall reaction (eq. (8)). Substituting eqs. (63) and (65) into the appropriate expression for the forward rate of reaction, the following equation is obtained for the logarithm of the forward rate constant:

$$\ln k_f = \ln(v_f/c_A^s) = \ln k_{fo} + \ln(\gamma_A^s/\gamma_\ddagger) - z_X(1-\alpha)f\phi^a - p(1-\alpha)f\phi^m - \alpha n f\phi^m \quad (66)$$

where

$$\ln k_{fo} = \ln Z - \Delta G_o^\ddagger/RT - \Delta G_o/RT + (1-\alpha)\Delta G_{ro}/RT \quad (67)$$

When ϕ^a is expressed in terms of ϕ^d and $\phi^m - \phi^d$ using eq. (2), one obtains the same equation for the forward rate constant derived for all the other proposed elementary steps except that the apparent transfer coefficient is now given by the equation

$$\alpha_a n = z_A[\alpha + \lambda_a(1-\alpha)] + p(1-\alpha)(1-\lambda_a) \quad (68)$$

As one would expect the equation for the backward reaction has the same form as those for the other elementary steps, but with k_{bo} given by the equation

$$\ln k_{bo} = \ln Z - \Delta G_o^\ddagger/RT + (1-\alpha)\,\Delta G_{ro}/RT \quad (69)$$

and $\alpha_a n$ by eq. (68).

Although the expression for α_a is rather complex involving several parameters, it is seen on inspection that α_a is approximately unity under most circumstances because the reaction site is so close to the interface. Values of α_a are recorded in Table V for the case that $\lambda_a = 0.85$, and for varying extents of partial charge transfer. In all cases, the apparent transfer coefficient is very high, and is exactly unity when $p = z_A$. The latter would correspond to a situation in which the reactant was completely discharged in the preceding adsorption step; as a result, the transfer coefficient reflects the potential dependence of the preceding equilibrium which determines the concentration of the intermediate X in the r.d.s. It is also apparent that α_a depends very little on the value of the intrinsic transfer coefficient α. These results confirm that the metal incorporation step has the greatest potential dependence of all the elementary steps considered, and would only be rate controlling if the associated standard rate constant is exceedingly low. Under most circumstances, this seems to be highly unlikely.

Discussion

The above analysis shows clearly that the potential dependence of all the elementary steps discussed can be described by one equation when one of these steps is rate determining. The values of the kinetic parameters, namely, the standard rate constant k_s and apparent transfer coefficient α_a depend on the nature of the r.d.s., the latter quantity increasing significantly as the location of the r.d.s. moves closer to the electrode. It should be remembered that the apparent transfer coefficient can be defined as the value of the transfer coefficient that would be obtained if the reaction site were located on the o.H.p. Strictly speaking, this definition can only be applied to the electron transfer step, since all of the other elementary steps involve movement of an ion from one location in the double layer to another or into the metal phase. In any case, it is easily seen that the free energy of the components of the elementary step are much more influenced by a change in electrode potential, as their location in the double layer moves closer to the interface. Thus, the value of α_a provides useful information regarding the location of the r.d.s.

The elementary steps have been disucssed here mainly from the point of view of the reduction reaction. When one focuses on the oxidation process, then the two elementary steps involving interaction with the metal phase are properly called the desorption step and the metal expulsion step. The kinetic equations describing all of the reverse reactions have been given above. Just as in the case of reduction, one equation describes the potential dependence of the oxidation process when one of the elementary steps is rate determining. The apparent transfer coefficient for the oxidation process increases as the location of the r.d.s. moves from the interface towards the electrolyte solution. In the above treatment, the properties of the metal phase have been assumed to be independent of position within this phase and composition These assumptions will not be valid in systems in which metal atoms are adsorbed at the metal amalgam surface such as thallium[24] and indium amalgams[25], or when intermetallic compounds are formed.[26] Complications resulting from these phenomena are not considered in this paper.

There is an increasing body of evidence that the nature of the r.d.s. changes with potential for some amalgam formation reactions.[3-7,20,27,28] Observations which support this conclusion are that the slopes of Tafel plots or c.T.p. for the reduction of metal ions at mercury often decrease with increase in electrode potential in the negative direction[5,7,20,27], and that the apparent transfer coefficients for oxidation and reduction measured in different potential regions do not sum to unity.[28] It is important to recognize that the apparent transfer coefficients derived above for mechanisms with one r.d.s do not apply for mechanisms in which more than one step is rate determining.

In order to illustrate the significance of the apparent transfer coefficient when the electrode process is complex, the mechanism proposed earlier[6,7] for the electroreduction of alkali metal ions is considered in more detail. Accordingly, one may describe the electrode reaction in terms of an ion transfer step, followed by adsorption[29]:

$$A_s \rightleftharpoons A_c \tag{70}$$

$$A_c \longrightarrow A_b\text{, reaction 1} \tag{71}$$

$$A_b + pe \longrightarrow X_a\text{, reaction 2} \tag{72}$$

$$X_a + (n-p)e \rightleftharpoons B_m \tag{73}$$

If one assumes a steady state with respect to the intermediate A_b, then the expression for the overall forward rate of reaction is

$$v_f = \frac{k_{1f}\, k_{2f}\, c_A^s}{k_{1b} + k_{2f}} \tag{74}$$

and that for the overall backward reaction

$$v_b = \frac{k_{1b}\, k_{2b}\, c_B^m}{k_{1b} + k_{2f}} \tag{75}$$

where k_{1f} and k_{2f} are the forward rate constants for reaction 1 (71) and reaction 2 (72), respectively, and k_{1b} and k_{2b}, the corresponding backward rate constants. Applying the analysis described above, the equation giving the potential dependence of k_{1f} is

$$\ln k_{1f} = \ln (v_{1f}/c_A^s) = \ln k_{1fo} - z_A f \phi^d - \alpha_{a1} f(\phi^m - \phi^d) \tag{76}$$

where k_{1fo} is the potential independent portion of k_{1f} including activity coefficients, and

$$\alpha_{a1} = z_A \lambda_c + z_A \alpha_1 (\lambda_b - \lambda_c) \tag{77}$$

α_1 being the intrinsic transfer coefficient for reaction 1 (71).

Similarly for k_{1b},

$$\ln k_{1b} = \ln(v_{1b}/c_A^b) = \ln k_{1bo} + \beta_{a1}\, f(\phi^m - \phi^d) \qquad (78)$$

where

$$\beta_{a1} = z_A(1-\alpha_1)(\lambda_b - \lambda_c) \qquad (79)$$

When the apparent transfer coefficients for the forward and reverse parts of reaction 1 are added, one obtains

$$\alpha_{a1} + \beta_{a1} = z_A\lambda_b \qquad (80)$$

This result indicates that the equilibrium constant for reaction 1 is potential dependent as one would expect, but to a degree which depends on the fact that the rate constant for the forward reaction is referenced to the concentration of A in the bulk of the solution. In addition, the apparent transfer coefficient for the reverse reaction is different than that derived above for the case that reaction 1 is the r.d.s. (eq. (43)) because this rate constant is now defined with respect to the concentration of the intermediate, A_b. In the case of reaction 2 (eq. (72)), the equation for the logarithm of the forward rate constant is

$$\ln k_{2f} = \ln(v_{2f}/c_A^b) = \ln k_{2fo} - \alpha_{a2} f(\phi^m - \phi^d) \qquad (81)$$

where

$$\alpha_{a2} = \alpha_2 z_A\ (\lambda_a - \lambda_b) + \alpha_2\ (1-\lambda_a)p \qquad (82)$$

α_2 being the intrinsic transfer coefficient. For the backward reaction

$$\ln k_{2b} = \ln(v_{2b}/c_B^m) = \ln k_{2bo} + \beta_{a2} f\ (\phi^m - \phi^d) \qquad (83)$$

where

$$\beta_{a2} = [n - z_A\alpha_2\lambda_a - z_A(1-\alpha_2)\lambda_b - \alpha_2 p(1-\lambda a)] \qquad (84)$$

It follows that the sum of the apparent transfer coefficients for the forward and backward parts of reaction 2 is

$$\alpha_{a2} + \beta_{a2} = n - z_A\lambda_b \qquad (85)$$

Adding eqs. (80) and (85), one finds that the sum of the transfer coefficients for the two reactions add to n, as required for the overall reaction. As expected, the exact values of the transfer coefficients for each step depend on the charge on the reactant and its position in the double layer. Obviously they will also depend on the mechanism of the overall reaction. However, it is clear that the transfer coefficients in the reduction direction increase as the reaction site moves closer to the interface, α_{a2} being considerably larger than α_{a1} for the mechanism presented assuming α_1 is equal to α_2. As a result, although the adsorption step may be rate determining at more positive potentials, its free energy of activation decreases more rapidly than that for ion transfer so that the ion transfer step becomes the r.d.s. at the most negative potentials. This situation was convincingly demonstrated by Baranski and Fawcett[7,27] in a study of the electroreduction of Na^+ in dimethylformamide solutions at mercury and indium amalgam electrodes. By using indium amalgam as the electrode material, the potential range over which kinetic data could be obtained was ~500 mV, and the overall apparent transfer coefficient was observed to fall from 0.5 to close to zero.

As more precise data become available for amalgam formation reactions over a wider potential range, it should be possible to obtain mechanistic descriptions of a wider variety of systems. It is clear from the work presented here that double layer effects are very important for these reactions, and that they must be considered carefully in deducing a mechanism. In this regard, the equations presented here have considered both the traditional double layer effect expressed through the average potential on the reaction plane, ϕ^r, and the discreteness-of-charge effect expressed through the local activity coefficients which appear in the kinetic equations as the activity coefficient of the activated complex, $\gamma_\ddagger$. As pointed out above, variation in $\gamma_\ddagger$ with potential can be neglected over limited potential ranges when specific adsorption is absent. However, in the presence of the specific adsorption of ions or molecules, $\gamma_\ddagger$ definitely does vary with potential.[9,30] This variation must be considered if correct rate parameters are to be extracted from the kinetic data.

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Table I. Electrostatic Potential for Various Locations in the Double Layer at the Mercury/Dimethylformamide Interface with 0.1M TEAP as Electrolyte[a]

Electrode Charge Density	Inner Layer Integral Capacity	Electrode Potential	Electrostatic Potential at			
			O.H.P.	Position 'a'[b]	Position 'b'[c]	Position 'c'[d]
σ, μC cm^{-2}	K_i, μF cm^{-2}	ϕ^m, V	ϕ^d, V	ϕ^a, V	ϕ^b, V	ϕ^c, V[e]
-4	20.6	-0.258	-0.064	-0.231	-0.123	-0.043 (-0.11)
-8	15.7	-0.605	-0.096	-0.535	-0.252	-0.060 (-0.07)
-12	13.1	-1.032	-0.116	-0.905	-0.396	-0.068 (-0.05)
-16	11.8	-1.487	-0.131	-1.298	-0.546	-0.073 (-0.04)
-20	11.0	-1.960	-0.142	-1.707	-0.698	-0.076 (-0.04)

a. The thickness of the inner layer was assumed to be 0.72 nm

b. Located 0.10 nm from the interface where $\lambda_a = 0.86$

c. Located 0.50 nm from the interface where $\lambda_b = 0.31$

d. Located 0.94 nm from the interface

e. Calculated according to eq. (3); the numbers in parentheses give the values of λ_c calculated according to eq. (2)

Table II. The apparent transfer coefficient α_a for the transfer of one electron to a metal ion in solution as r.d.s. assuming the intrinsic transfer coefficient α is 0.5

Charge on Reactant z	Apparent Transfer Coefficient α_a	
	at position 'b' ($\lambda_b = 0.3$)	at position 'c' ($\lambda_c = -0.1$)
1	0.65	0.45
2	0.48	0.18
3	0.42	0.08

Table III. The apparent transfer coefficient α_a for ion transfer from location 'c' (λ_c = -0.1) to location 'b' (λ_b = 0.3) in the double layer for various values of the intrinsic transfer coefficient α

Intrinsic Transfer Coefficient α	Apparent Transfer Coefficient α_a
0.5	0.10
0.7	0.18
0.9	0.26

Table IV. The apparent transfer coefficient α_a *for adsorption of* a reactant with charge z_A from location 'b' ($\lambda_b = 0.3$) to location 'a' ($\lambda_a = 0.85$) in the double layer for various values of the intrinsic transfer coefficient and various extents of partial charge transfer.

Intrinsic Transfer Coefficient α	Apparent Transfer Coefficient α_a		
	Extent of Partial Charge Transfer		
	$p = 0$	$p = 0.5z_A$	$p = z_A$
0.5	0.58	0.61	0.65
0.7	0.69	0.74	0.79
0.9	0.80	0.86	0.93

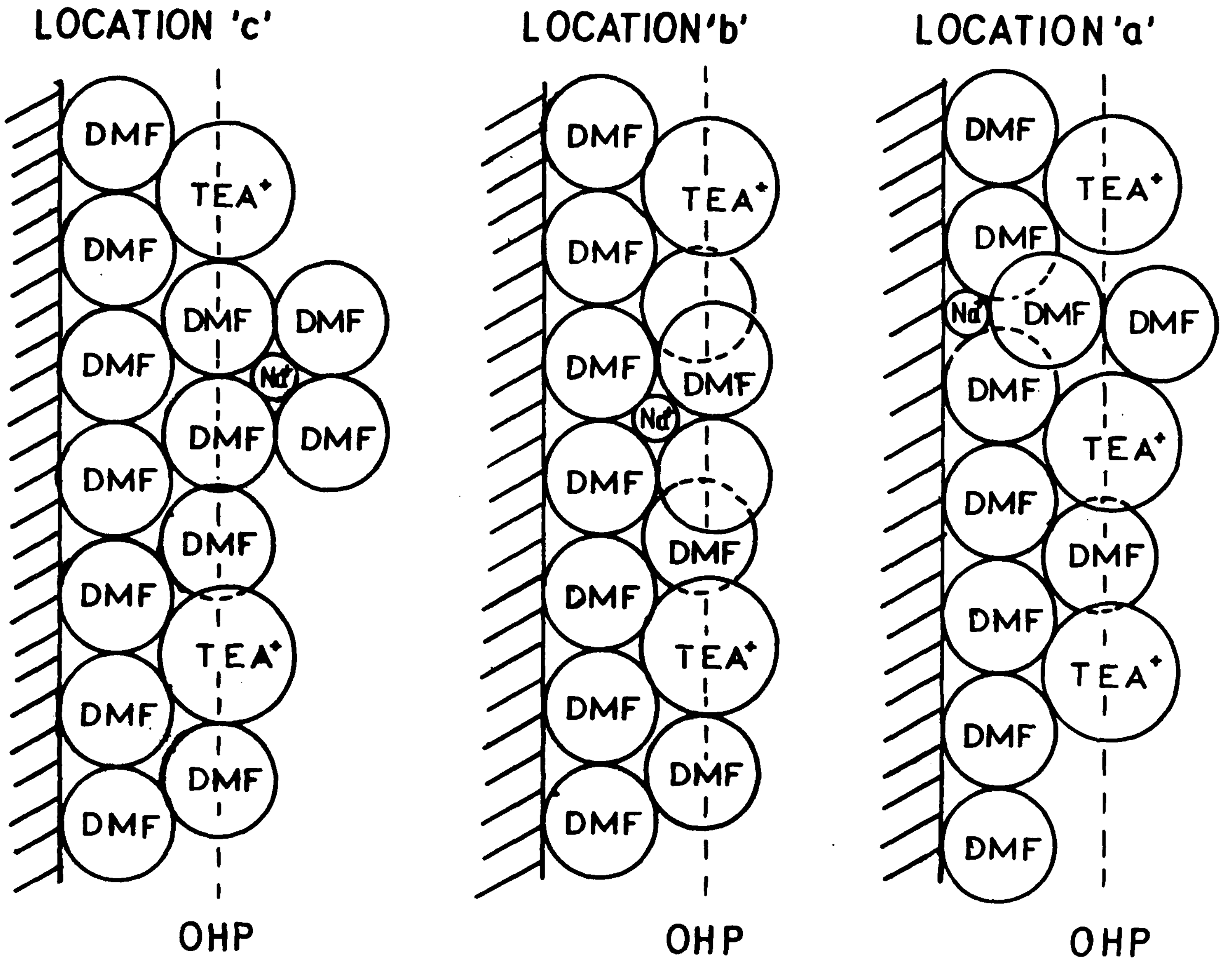
Table V. The apparent transfer coefficient α_a for the metal incorporation step from location 'a' ($\lambda_a = 0.85$) in the double layer to the bulk of the metal for various values of the intrinsic transfer coefficient and various extents of partial charge transfer

Intrinsic Transfer Coefficient α	Apparent Transfer Coefficient α_a		
	Extent of Partial Charge Transfer		
	$p = 0$	$p = 0.5z_A$	$p = z_A$
0.5	0.93	0.96	1.00
0.7	0.96	0.98	1.00
0.9	0.99	0.99	1.00

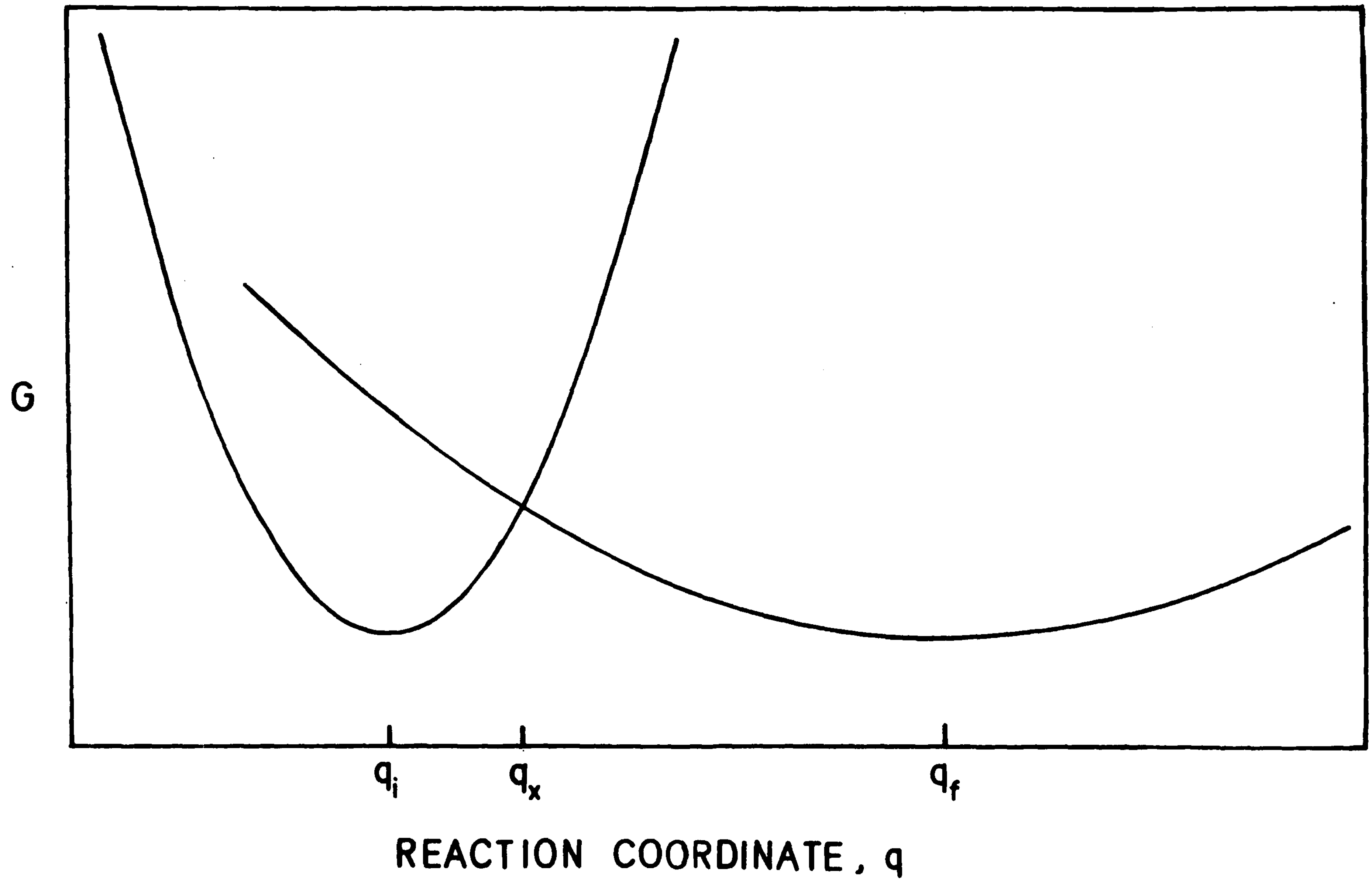
Legends for Figures

Figure 1. Model for passage of a reacting metal ion through the compact region of the double layer. The solvent (dimethylformamide), predominant base electrolyte ion (tetraethylammonium cation) and reactant (sodium ion) are represented as hard spheres with the following radii: DMF = 0.34, TEA^+ = 0.40, and Na^+ = 0.095 nm. Positions 'a', 'b', and 'c' correspond to passage of the reactant from a fully solvated ion at its distance of closest approach (position 'c') to an adsorbed species at the interface (position 'a').

Figure 2. Free energy G against reaction coordinate q for a system in which the reactant is more strongly bound to its solvation environment than the product. The parabola for the reactant is drawn with a force constant ten times that for the product. q_i and q_f define the positions of the minimum free energy on the surfaces for the reactant and product, respectively; q_x is the position on the reaction coordinate where these surfaces intersect.



Fawcett, Fig 1



Fawcett, Fig. 7