tables are a more recent compilation. A comparison between the data of these tables and the values obtained in this study is given in Table II.

The agreement between the values given in the JANAF tables and those determined in this study is well within the experimental error of these measurements. Although the value of the free energy given in the N.B.S. tables differs from that determined in this study by more than the standard error of these measurements, this discrepancy is not considered significant. The magnitudes of the standard errors of the thermodynamic quantities calculated in this study are the same as those given in the JANAF tables for enthalpies and free energies calculated from aqueous electrochemical cell data and corrected to $25°$; the standard errors obtained in this study are, however, considerably greater than those obtained in the extremely precise calorimetric measurements of Rossini[26] on the same reaction at $25°$: $\Delta H°_{\text{measd}} = -22.063 \pm 0.012$ kcal./mole and $\Delta G°_{\text{calcd}} = -22.738 \pm 0.033$ kcal./mole.

(26) F. D. Rossini, *J. Res. Natl. Bur. Std.*, **9**, 679 (1932).

Table III. Standard Potentials at $450°$

Electrode system	$E°_M$, v.	$E°_m$, v.	$E°_X$, v.
Pt(II)–Pt	0.000	0.000	0.000
Ir(III)–Ir	−0.057	−0.062	−0.092
Rh(III)–Rh	−0.196	−0.201	−0.231
HCl(g)–H₂(g), Pt	−0.694	−0.710	−0.800

The combination of the half-reactions used to calculate these values requires that the standard state of Cl^- ion be defined as that which prevails in the pure molten electrolyte. For a more detailed discussion, the reader is referred to the thesis of the junior author.[1]

Standard potentials $E°_M$, $E°_m$, and $E°_X$, extrapolated to unit concentration on the molarity, molality, and mole fraction scales, calculated[3] from the data of this study, are given in Table III. The correction term is applied only to the reference electrode in the case of the hydrogen chloride–hydrogen data.

The Influence of Ionic Strength on Polarographic Half-Wave Potentials. III. Theoretical Considerations of Systems Involving Complex Ions and the Investigation of the Cadmium Nitrate–Lithium Chloride Lithium Nitrate System[1]

Douglas E. Sellers[2] and Nicholas E. Vanderborgh

Contribution from the Parkinson Laboratory of Southern Illinois University, Carbondale, Illinois. Received May 23, 1964

Previous investigations have shown the importance of including the effect of ionic strength of the system in considering the polarographic reduction of inorganic substances. This investigation is an attempt to correlate the effect of ionic strength on the equilibria involved in and on the interpretation of the polarographic data obtained from complex ion systems. In order to test these concepts, the half-wave potential of cadmium ion was determined in lithium nitrate–lithium chloride mixtures over the concentration range of 0–8 m including the various constant ionic strength systems. Application of theory indicates that above ligand concentrations of 1 m, a single complex system is present with an average number of bound ligands of 3.0 ± 0.1 and an over-all formation constant of 32 ± 5.

Introduction

The importance of ionic strength in the polarographic reduction of inorganic and complex species in solutions of high concentrations of inert (supporting) electrolyte

(1) Taken from the Ph.D. Thesis of N. E. V., Southern Illinois University, June 1964.
(2) Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio.

has been illustrated.[3–7] This work is an attempt to account for the effect of ionic strength in the polarographic investigation of complex ion systems, especially at electrolyte concentrations greater than 1 *m*.

Although the effect of ionic strength (usually constant) on the polarographic analysis of organic species has been known for some time,[8] similar importance has not been emphasized in the investigation of inorganic systems, even though it has been implied (rather strongly[7]) on occasion. This communication will illustrate why such determinations should be carried out in systems of constant ionic strength, where at all possible. Although they are to be pointed out in greater detail subsequently, three of the problems which arise in the investigation of systems of high ionic strength they *may* become negligible at constant μ are

(3) D. E. Sellers and N. E. Vanderborgh, *J. Am. Chem. Soc.*, **86**, 1934 (1964).
(4) N. E. Vanderborgh and D. E. Sellers, *ibid.*, **86**, 2790 (1964).
(5) D. D. DeFord and D. L. Anderson, *ibid.*, **72**, 3918 (1950).
(6) H. M. Hershenson, M. E. Smith, and D. N. Hume, *ibid.*, **75**, 507 (1953).
(7) H. Irving, "Advances in Polarography," Vol. I, I. S. Longmuir, Ed., Pergamon Press, New York, N. Y., 1960, pp. 42–67.
(8) P. J. Elving, J. C. Komyathy, R. E. Van Atta, C. S. Tang, and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

the change in the activity of the solvent (water), changes in the diffusion current constant, and the misinterpretation of data used for the evaluation of p (the average number of ligands associated with the central metal ion) and the formation constant of the complex. In order to provide data necessary to test the theoretical concepts proposed, the $Cd(NO_3)_2$–$LiCl$–$LiNO_3$ complex ion system was investigated.

Theory

Consider first the simplified approach taken in the polarographic investigation of systems involving a single complex species and at low concentrations of electrolytes where the hydration and activity of the water may be neglected. The shift in the half-wave potential has been shown to obey the relation[9]

$$(E_{1/2})_c - (E_{1/2})_{\mu=0,k} = \frac{RT}{nF} \left\{ \frac{1}{2} \ln \frac{D_H}{D_c} - \ln \beta_p + \ln \frac{\gamma_c}{\gamma_H} - p \ln m_x\gamma_x \right\} \quad (1)$$

(expressed in terms of molalities and neglecting liquid-junction potentials) where each of the terms possess its usual significance but will be defined again subsequently. More often than not in systems such as these, the approximate form is used, i.e.

$$(E_{1/2})_c - (E_{1/2})_{\mu=0,k} = -\frac{RT}{nF} \left\{ \ln \beta_p + p \ln m_x \right\} \quad (2)$$

where $\gamma_c \cong \gamma_H$, $D_c \cong D_H$, and γ_x is essentially unity. The plot of $(E_{1/2})_c - (E_{1/2})_{\mu=0,k}$ as a function of the logarithm of the ligand concentration, log m_x, yields a linear curve whose slope is equal to $-0.0591p/n$, or (at 25°)

$$\frac{(d\Delta E_{1/2})}{d \log m_x} = \frac{0.0591}{n} p \quad (3)$$

and an intercept which has been used in the evaluation of β_p. The change in the half-wave potential, $\Delta E_{1/2}$, has been determined by the subtraction of $(E_{1/2})_{\mu=0}$ or $(E_{1/2})_{\mu=k}$ from $(E_{1/2})_c$, where $(E_{1/2})_{\mu=0}$ and $(E_{1/2})_{\mu=k}$ are the half-wave potentials of the metal ion in a system of zero ionic strength and where an inert electrolyte is present at a specified concentration (such as systems of constant ionic strength), respectively. Variations of this approach have been used in the investigation of systems involving successive formation constants.[10] As has been stated previously,[3] it is extremely doubtful that such simplifying assumptions may be made when systems of high ionic strength are being investigated; Irving[7] has already shown that certain discrepancies arise when such generalizations are made concerning the diffusion current constants or diffusion coefficients. In all of these investigations the effect of the changing activity of the solvent (water) has been scarcely mentioned.

Again, considering the simple complex system where only a single complex is being formed, but considering hydration of the various species, leads to the analysis of the following equilibria which are present: (1) for the

hydration of the simple metal ion

$$M^{n+} + xH_2O = M(H_2O)_x^{n+}$$
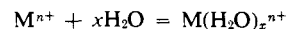
and (2) for the complexation of the metal ion

$$M(H_2O)_x^{n+} + pX(H_2O)_r^{b-} = M(X)_p(H_2O)_z^{n-pb} + (x + pr - z)H_2O$$
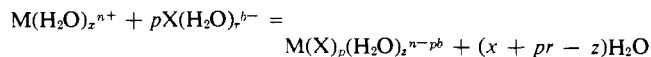
where the terms in these equations and those of future discussion, for simplicity sake, are defined as follows.

M = simple metal ion, M^{n+}
H = hydrated simple metal ion, $M(H_2O)_x^{n+}$
C = hydrated metal complex ion, $M(X)_p(H_2O)_x^{n-pb}$
X = hydrated ligand species, $X(H_2O)_r^{b-}$
i = inert electrolyte
m = molality; m_x is the molality of the ligand, m is the total molality of the solution, $m_i + m_x$
ϕ = osmotic coefficient; ϕ_t is the osmotic coefficient of a solution of mixed electrolytes, i.e., 1 m LiCl plus 1 m LiNO$_3$
a_w = water activity
β_H, β_p = hydration and complex formation constants, respectively
N = mole fraction
n^+, b^- = charge of the metal ion and ligand, respectively
x, r, z, p = reaction coefficients
ν = number of ions produced by the electrolytes(s)
E_L = liquid junction potential
D = diffusion coefficient; D_a is the diffusion coefficient of the metal in mercury; D_a' is the diffusion coefficient of the hydrated metal ion at zero ionic strength
n = number of electrons involved in the reduction of the metal ion at the mercury drop
γ = molal activity coefficient; γ_x is the molal activity coefficient of the ligand
$E_{1/2}$ = half-wave potential; $(E_{1/2})_c$ and $(E_{1/2})_{\mu=0}$ are the half-wave potentials of the complex and of the hydrated metal ion (at zero ionic strength), respectively
R, T, and F possess their usual significance.

The expression for the hydration and formation constants, in terms of molality, are

$$\beta_H = \frac{m_H\gamma_H}{m_M\gamma_M(a_w)^x} \quad (4)$$

and

$$\beta_p = \frac{m_c\gamma_c(a_w)^{(x+pr-z)}}{m_H\gamma_H(m_x)^p(\gamma_x)^p} \quad (5)$$

The multiplication of eq. 4 and 5 yields

$$\beta_p\beta_H = \frac{m_c\gamma_c}{m_M\gamma_M(m_x)^p(\gamma_x)^p(a_w)^{z-pr}} \quad (6)$$

such that at the electrode surface

$$m_M^0\gamma_M = \frac{m_c^0\gamma_c}{\beta_p\beta_H(m_x)^p(\gamma_x)^p(a_w)^{z-pr}} \quad (7)$$

Actually eq. 7 is only an approximation since it is not known if $m_x\gamma_x$, or the activity of the ligand in the bulk of the solution, adequately describes the activity of the same at the electrode surface.[11] However, for the lack of any known, accurate method for the correction of the activity of the ligand at the electrode surface, this approximation will be used. Inserting eq. 7 into the polarographic equation for $E_{d.e.}$ (in terms of molality)

$$E_{d.e.} = \epsilon - E_L - \frac{RT}{nF} \ln (m_a^0\gamma_a/m_M^0\gamma_M) \quad (8)$$

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 214.

(10) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(11) H. Irving, ref. 7, p. 58.

and solving for the half-wave potential of the complex $(E_{1/2})_c$ by a method similar to that described by Kolthoff and Lingane[12] yields

$$(E_{1/2})_c = \epsilon - (E_L)_c - \frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_c}{D_a} - \ln\gamma_c + \right.$$
$$\left. p\ln m_x\gamma_x + \ln\beta_p\beta_H + (z - pr)\ln a_w\right\} \quad (9)$$

at a specified concentration, m_x, of the ligand and when the ligand also acts as the inert electrolyte for the polarographic system. The expression for the half-wave potential at zero ligand concentration, and for that matter zero ionic strength, has previously been shown to be[3]

$$(E_{1/2})_{\mu=0} = \epsilon - (E_L)_{\mu=0} -$$
$$\frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_H'}{D_a} + \ln\beta_H'\right\} \quad (10)$$

such that the change of the half-wave potential, as a function of ligand concentration, m_x, only becomes

$$(E_{1/2})_c - (E_{1/2})_{\mu=0} = [(E_L)_{\mu=0} - (E_L)_c] -$$
$$\frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_c}{D_H'} - \ln\gamma_c + p\ln m_x\gamma_x + \right.$$
$$\left. \ln\frac{\beta_p\beta_H}{\beta_H'} - (z - pr)\ln a_w\right\} \quad (11)$$

where D_H' and β_H' are the diffusion coefficient and hydration constant of the metal ion at zero ionic strength, respectively. It can be seen that eq. 11 reduces to the simpler form, eq. 2, when the usual polarographic assumptions are made ($\beta_H' \cong \beta_H$, $D_H' = D_H$, $\gamma_c \cong \gamma_x = a_w \cong 1$, and the change in the liquid junction potential is negligible). Even so, since the hydration parameter of the metal ion, x, remains essentially constant over fairly wide ranges of electrolyte concentrations,[13] then $\beta_H' = \beta_H$ and eq. 11 becomes essentially identical with eq. 1 with the exception of the water activity term. (Similar arguments may be proposed concerning ligands which are not electrolytes but will not be discussed at the present.)

In the analysis of eq. 11, at high ligand concentrations the change in the half-wave potential would be different for systems of different ligand constituents (*i.e.*, LiCl, NaCl, or KCl where Cl⁻ is the ligand) as was observed in the effect of differing inert electrolytes on the reduction of metal ions.[3,4] Although similar in magnitude, the effect would be opposite in direction in the case of complex ions since generally $pr > z$. When systems of mixed electrolytes are considered, such as systems of constant ionic strength, the half-wave potential of the metal ion is *not* as described by eq. 10 but rather as[3]

$$(E_{1/2})_\mu - (E_{1/2})_{\mu=0} = [(E_L)_{\mu=0} - (E_L)_\mu] -$$
$$\frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_H}{D_H'} - \ln\gamma_H + x\ln a_w\right\} \quad (12)$$

where $(E_{1/2})_\mu$ is the half-wave potential of the metal ion in a system containing m_i concentration of inert electrolyte ($\beta_H \cong \beta_H'$). Thus, when considering systems of mixed electrolytes, the change in the half-wave potential

is bounded by two limits, eq. 11 and 12. It can be shown that the equation which will describe any point (or mixture of m_i and m_x) is

$$(E_{1/2})_{sys} - (E_{1/2})_{\mu=0} = (\Delta E_{1/2})_{sys} = [(E_L)_{\mu=0} -$$
$$(E_L)_{sys}] - \frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_cD_H}{(D_H')^2} - \ln\gamma_c\gamma_H + \ln\beta_p + \right.$$
$$\left. p\ln m_x\gamma_x + (x + pr - z)\ln a_w\right\} \quad (13)$$

This results from the following reasoning: if $y = f(x)$ and $y = F(x)$ then any point within these boundaries can be represented by $y = f(x) + F(x)$, assuming no interaction between $f(x)$ and $F(x)$. It is to be noted that

$$(E_{1/2})_{sys} - (E_{1/2})_{\mu=0} \neq (E_{1/2})_c - (E_{1/2})_\mu \quad (14)$$

unless the inert electrolyte used is of such a nature as to result in eq. 12 being equal to zero; then

$$(E_{1/2})_{sys} - (E_{1/2})_{\mu=0} = (E_{1/2})_c -$$
$$(E_{1/2})_{\mu=0} = (E_{1/2})_c - (E_{1/2})_\mu \quad (15)$$

This result raises the question of the validity of the formation constants which have been determined by eq. 15 but are bounded by the conditions of eq. 14. Equation 13 can be simplified further upon consideration of the coefficient of the water activity term. The coefficient, $(x + z - pr)$, for many complex ion systems may be estimated as being quite small, if not zero, if z[14] is quite small and $x \cong pr$[13,15]; of course, how general and valid such an approximation is depends on the individual system. Thus

$$(\Delta E_{1/2})_{sys} \cong [(E_L)_{\mu=0} - (E_L)_{sys}] -$$
$$\frac{RT}{nF}\left\{ \tfrac{1}{2}\ln\frac{D_cD_H}{(D_H')^2} - \ln\gamma_c\gamma_H + \right.$$
$$\left. \ln\beta_p + p\ln m_x\gamma_x\right\} \quad (16)$$

The evaluation of the number of ligands, p, associated with the central metal ion can be made utilizing the slope of the $(\Delta E_{1/2})_{sys}$ as a function of $\log m_x$ curve; however, in systems of high, constant ionic strength, p no longer bears the simple relationship of eq. 3 to $d(\Delta E_{1/2})_{sys}/d \log m_x$. Since it has been shown that the change in the half-wave potential of the metal ion is a function of both the inert electrolyte, m_i, and the ligand, m_x, concentration, then

$$d(\Delta E_{1/2})_{sys} = \left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_i}\right)_{m_x} dm_i +$$
$$\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_x}\right)_{m_i} dm_x \quad (17)$$

and in systems of constant ionic strength $dm_x = -dm_i$. It follows then

$$\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_x}\right)_{\mu=k} = -\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_i}\right)_{\mu=k} =$$
$$\left[\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_x}\right)_{m_i} - \left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_i}\right)_{m_x}\right] \quad (18)$$

(12) I. M. Kolthoff and J. J. Lingane, ref. 9, pp. 212 and 213.
(13) R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, 70, 1870 (1948).
(14) Since the hydration parameter is known to decrease with the size of the ionic species and that this parameter for large simple ions is of the order 1–2, it was felt that this would be a logical assumption.
(15) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Amsterdam, 1952, p. 131.

The evaluation of $(\partial(\Delta E_{1/2})_{sys}/\partial m_x)_{m_i}$ and $(\partial(\Delta E_{1/2})_{sys}/\partial m_i)_{m_x}$ may be made from eq. 16; thus, differentiating eq. 16 first with respect to m_x at constant m_i gives

$$\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_x}\right)_{m_i} = -\left(\frac{\partial(\Delta E_L)_{sys}}{\partial m_x}\right)_{m_i} -$$
$$\frac{RT}{nF}\left\{\frac{1}{2D_cD_H}\left(\frac{\partial(D_cD_H)}{\partial m_x}\right)_{m_i} -\right.$$
$$\left.\frac{1}{\gamma_c\gamma_H}\left(\frac{\partial\gamma_c\gamma_H}{\partial m_x}\right)_{m_i} + \frac{p}{m_x} + \frac{p}{\gamma_x}\left(\frac{\partial\gamma_x}{\partial m_x}\right)_{m_i}\right\} \quad (19)$$

where $(\Delta E_L)_{sys} = [(E_L)_{\mu=0} - (E_L)_{sys}]$. It can be shown that the differentiation of eq. 16 with respect to m_i at constant m_x gives

$$\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_i}\right)_{m_x} = -\left(\frac{\partial(\Delta E_L)_{sys}}{\partial m_i}\right)_{m_x} -$$
$$\frac{RT}{nF}\left\{\frac{1}{2D_cD_H}\left(\frac{\partial(D_cD_H)}{\partial m_i}\right)_{m_x} -\right.$$
$$\left.\frac{1}{\gamma_c\gamma_H}\left(\frac{\partial(\gamma_c\gamma_H)}{\partial m_i}\right)_{m_x} + \frac{p}{\gamma_x}\left(\frac{\partial\gamma_x}{\partial m_i}\right)_{m_x}\right\} \quad (20)$$

Substitution of eq. 19 and 20 into eq. 18, and remembering that γ_c, γ_H, γ_x, D_c, and D_H are all functions of m_i and m_x, yields

$$\left(\frac{\partial(\Delta E_{1/2})_{sys}}{\partial m_x}\right)_{\mu=k} = \left(\frac{\partial(\Delta E_L)_{sys}}{\partial m_x}\right)_{\mu=k} -$$
$$\frac{RT}{nF}\left\{\frac{1}{2D_cD_H}\left(\frac{\partial(D_cD_H)}{\partial m_x}\right)_{\mu=k} -\right.$$
$$\left.\frac{1}{\gamma_c\gamma_H}\left(\frac{\partial(\gamma_c\gamma_H)}{\partial m_x}\right)_{\mu=k} + \frac{p}{m_x} + \frac{p}{\gamma_x}\left(\frac{\partial\gamma_x}{\partial m_x}\right)_{\mu=k}\right\} \quad (21)$$

or, at 25°

$$\left(\frac{\partial(\Delta E_{1/2})_{obsd}}{\partial \log m_x}\right)_{\mu=k} = -\frac{0.0591}{n}p\left\{1 +\right.$$
$$\frac{1}{\gamma_x}\left(\frac{\partial\gamma_x}{\partial \log m_x}\right)_{\mu=k}\right\} - \frac{0.0591}{n}\left\{\frac{1}{2D_cD_H}\times\right.$$
$$\left.\left(\frac{\partial(D_cD_H)}{\partial \log m_x}\right)_{\mu=k} - \frac{1}{\gamma_c\gamma_H}\left(\frac{\partial(\gamma_c\gamma_H)}{\partial \log m_x}\right)_{\mu=k}\right\} \quad (22)$$

where $(\Delta E_{1/2})_{obsd}$ has been previously defined.[3] A plot of $(\Delta E_{1/2})_{obsd}$ vs. log m_x yields an intercept from which the formation constant, β_p, may be evaluated. The number of ligands, p, may be made from

$$p = \left\{\frac{1}{\gamma_c\gamma_H}\left(\frac{\partial(\gamma_c\gamma_H)}{\partial \log m_x}\right)_{\mu=k} - \frac{1}{2D_cD_H}\left(\frac{\partial(D_cD_H)}{\partial \log m_x}\right)_{\mu=k} -\right.$$
$$\left.\frac{n}{0.0591}\left(\frac{\partial(\Delta E_{1/2})_{obsd}}{\partial \log m_x}\right)_{\mu=k}\right\}\Big/\left[1 + \frac{1}{\gamma_x}\left(\frac{\partial\gamma_x}{\partial \log m_x}\right)_{\mu=k}\right]$$
$$(23)$$

In review, eq. 16 and 21 are valid only if (1) only a single complex species is formed; (2) the activity of the ligand in the bulk of the solution adequately describes the activity at the electrode surface; (3) the hydration parameters remain essentially constant over the ranges of ionic strength investigated (β_H is constant); (4) the ligand concentration is sufficiently high so that the original concentration expresses its concentration in solution $[(m_x)_{orig} = m_x + pm_c \cong m_x]$; and (5) the hydration parameter of the metal ion approximates p

times the hydration parameter of the ligand, z being small.

The surprising results of eq. 16 and 21, which are valid only for systems of constant ionic strength, are the similarity to eq. 1 and 3 (when γ_H, γ_c, γ_x, D_c, and D_H are not approximated out of eq. 2); the fact that the activity of the solvent (water) is of little consequence, in contrast to eq. 11; and that $(\Delta E_{1/2})_{sys} \neq (E_{1/2})_c - (E_{1/2})_\mu$. This analogy can be extended to any systems of the mixed electrolytes (m_i and m_x) provided the corresponding values of the activity and diffusion coefficients are used. Equation 14 in no way hinders the evaluation of p since $(\Delta E_{1/2})_{sys} = (E_{1/2})_c - (E_{1/2})_{\mu\mu=k}$ but it does place restrictions on the evaluation of the formation constant of such systems. Of course, the eventual utility of eq. 16 and 21 as applied to systems of high ionic strength depends on the ability to evaluate or estimate γ_c, γ_H, and γ_x (D_H and D_c can be estimated experimentally at m_i and m_x, each in the absence of the other). The evaluation of γ_c and γ_H is the most difficult since γ_x may be approximated as being proportional to $\gamma_\pm$,[16] the mean activity coefficient of the ligand electrolyte, when uni-univalent electrolytes are investigated.

The $Cd(NO_3)_2$–$LiCl$–$LiNO_3$ System

Earlier work indicated that this cadmium complex system could possibly produce a single complex, a condition which is imposed on the use of eq. 1, 2, and/ or 3, above 1 m,[17] and previous information was

Table I. Tabulation of Experimentally Determined Half-Wave Potentials and I_d Values of Cadmium in the $Cd(NO_3)_2$–$LiCl$–$LiNO_3$ System at Various Constant Ionic Strengths[a]

$\dfrac{m_{LiCl}}{m_{LiNO_3}}$	$-E_{1/2}$, mv.	I_d	$\dfrac{m_{LiCl}}{m_{LiNO_3}}$	$-E_{1/2}$, mv.	I_d
0:1	572[b]	3.89	0:6	535[b]	
0.5:0.5	600		0.5:5.5	574	
1:0	628[b]	3.89	1:5	603[b]	2.64
			2:4	630	
0:2	565[b]	3.61	3:3	644[b]	
0.5:1.5	600		4:2	656	
1:1	616[b]	3.59	5:1	666[b]	2.81
2:0	644[b]	3.76	6:0	676	
0:3	557[b]	3.34	0:7	528[b]	2.41
0.5:2.5	592		0.5:6.5	570	
1:2	612		1:6	600	
1.5:1.5	624		2:5	628	
2:1	634[b]	3.51	3:4	644	
3:0	654[b]	3.51	4:3	654	
			5:2	664	
0:4	550[b]	3.08	6:1	674	
0.5:3.5	586		7:0	682[b]	2.55
1:3	611[b]	3.11			
2:2	632[b]		0:8	520[b]	
3:1	650[b]	3.29	0.5:7.5	562	
4:0	657[b]	3.28	1:7	598[b]	2.24
			2:6	626[b]	2.25
0:5	542[b]	2.84	3:5	643[b]	2.28
0.5:4.5	580		4:4	655[b]	2.30
1:4	606[b]	3.12	5:3	666[b]	2.34
2:3	630		6:2	672[b]	2.35
3:2	646		7:1	680[b]	2.39
4:1	658[b]	3.04	8:0	687[b]	2.38
5:0	670[b]	3.03			

[a] Conditions: 0.5 mM $Cd(NO_3)_2$, 0.005% gelatin, s.c.e. reference electrode. [b] These values were experimentally determined.

(16) J. Guggenheim, *J. Am. Chem. Soc.*, **52**, 1315 (1930).
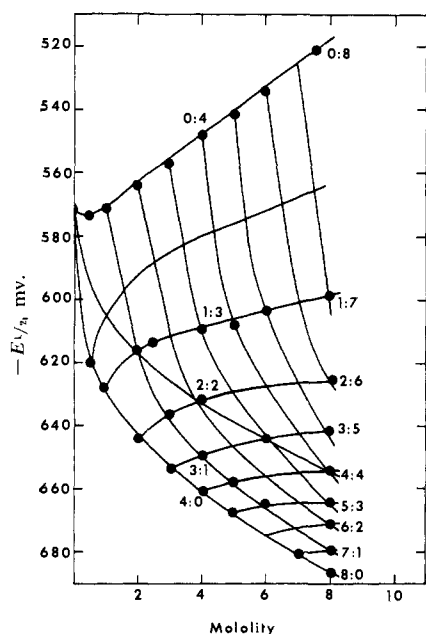(17) L. Eriksson, *Acta Chem. Scand.*, **7**, 1146 (1953).

Figure 1. Investigation of the change in half-wave potential for the system $Cd(NO_3)_2$–$LiNO_3$–$LiCl$ as a function of the total molality. Vertical lines (not drawn) represent solutions of constant ionic strength; the two vertical lines represented are at constant ionic strength of 4 and 8 m, respectively, and the notation corresponds to $m_{LiCl}:m_{LiNO_3}$. Dotted points represent experimentally determined half-wave potentials.

Figure 2. The graphical evaluation of S ($[\partial(\Delta E_{1/2})_{sys}/\partial \log m_x]_\mu = k$. Each line represents a constant ionic strength system; ◓, ◖, ●, and ○ represents constant ionic strength systems of 2, 3, 5, and 8 m, respectively.

known concerning the effect of high concentrations of lithium nitrate on the half-wave potential of the central metal ion, cadmium.[3,5] The procedure followed in this investigation has been described previously.[4] The capillary used in this investigation had a constant of 1.61 mg.$^{2/3}$ sec.$^{-1/2}$ measured in distilled water and with an open circuit.

The experimentally measured half-wave potentials are presented in Table I and Figure 1. The values marked with a superscript b and circled points represent cadmium in the $Cd(NO_3)_2$–$LiCl$–$LiNO_3$ system. The other values represent the half-wave potentials estimated from a plot similar to Figure 1 and should be within experimental error, ± 1 mv., of the actual value except possibly for the 0.5 m LiCl systems where p is variable.[17]

Before eq. 16, 22, and/or 23 can be applied to this system, the existence of a single complex ion system must be established. In this investigation the condition that p was constant for the various constant ionic strength systems could be established if the slope(s) of $(\Delta E_{1/2})_{obsd}$ as a function of $\log m_x$ was constant and if the various partial terms in the right side of eq. 22 were either constant, negligible, or zero. As can be seen from Figure 2, all of the systems investigated gave a constant slope of 90.0 $\pm$ 4.6 mv. for a $(\Delta E_{1/2})_{obsd}$ as a function of $\log m_x$ plot. However, the numerical evaluation of the partial terms of eq. 22 presents a problem which is not easily solved. In conjunction with this, these problems will have to be solved or approximated if the numerical values of p (and eventually β_p) are to be obtained for these systems of high ionic strength. Although the approach to be presented is known to be subjected to criticism, it is the only one which is presently known.

First, consider the partial term involving the diffusion coefficients of the hydrated and complex species.
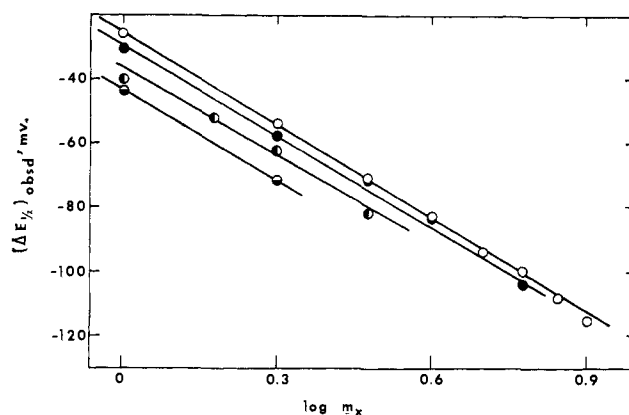
When there is little change in the viscosity of the system in going from m_i to m_x, at constant ionic strength, and when there is little difference in the size of the two species, one would expect little change in D_c and D_H[18] such that they may be considered to be constant, and the partial term would be essentially zero. The calculated diffusion coefficients of the two species were not calculated during this investigation; however, since a direct relationship exists between the diffusion coefficient and the square of the diffusion current constant (Ilkovic equation), analogies involving I_d were used. Values of I_d listed in Table I indicate that there is less than 5% change in going from a system involving only $LiNO_3$ to one involving only $LiCl$. Thus, for the first approximation, the partial term in eq. 22 involving the diffusion coefficients was neglected.

Second, consider the partial term in eq. 22 involving the activity coefficient of the ligand γ_x. If $\log \gamma_x$ is considered to be a linear function of $\log (\gamma_\pm)_x$, where $(\gamma_\pm)_x$ is the mean activity coefficient of LiCl, this relationship can be inserted in the corresponding partial term and can be rearranged to yield

$$\frac{1}{\gamma_x}\left(\frac{\partial \gamma_x}{\partial \log m_x}\right)_{\mu=k} = m_x\left(\frac{\partial \log (\gamma_\pm)_x}{\partial m_x}\right)_{\mu=k} \quad (24)$$

Harned's rule[19-21] states that

$$\log (\gamma_\pm)_x = \log (\gamma_\pm)_x^0 + \alpha_x m_x \quad (25)$$

where $(\gamma_\pm)_x^0$ is a constant and is the mean activity coefficient of the ligand electrolyte at zero m_x in inert electrolyte, at some specified constant ionic strength, and α_x can be determined by

$$(\alpha_x)_{\mu=k} = \frac{\phi_x - \phi_i}{2.303m} \quad (26)$$

where ϕ_x and ϕ_i are the osmotic coefficients of the ligand and inert electrolytes, respectively. (This ap-

(18) D. M. Brasher and F. R. Jones, Trans. Faraday Soc., 42, 775 (1946).
(19) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., Chapter 14, pp. 585–632.
(20) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, pp. 432–456.
(21) This is not the strict expression for the mean activity coefficient for LiCl in this system (see R. A. Robinson and C. K. Lim, Trans. Faraday Soc., 49, 1144 (1953)); however, the difference is small and up to about 8 m the discrepancy may be neglected in the evaluation of p.

Table II. The Comparison of the Magnitude of the Activity and Osmotic Coefficient Terms of Eq. 30

$\dfrac{m_{LiCl}:}{m_{LiNO_3}}$	ϕ_x [a]	ϕ_i [a]	$\dfrac{N_x \times (\phi_x - \phi_i)}{(2.303)}$	$(\gamma_\pm)_x'$ [a]	$(\gamma_\pm)_i'$ [a]	$\dfrac{N_x \log \dfrac{(\gamma_\pm)_x'}{(\gamma_\pm)_i'}}{}$	$\dfrac{3N_x \times (\phi_x - \phi_i)}{(2.303)}$	$\dfrac{2N_x \log \dfrac{(\gamma_\pm)_x'}{(\gamma_\pm)_i'}}{}$
0:1	1.018	0.997	...	0.774	0.743	...	...	...
0.5:0.5			0.005			0.009	0.013	0.018
1:0			0.009			0.018	0.027	0.036
0:2	1.142	1.088	...	0.921	0.835	...	...	...
0.5:1.5			0.006			0.011	0.018	0.022
1:1			0.011			0.021	0.035	0.042
2:0			0.023			0.042	0.069	0.084
0:3	1.286	1.181	...	1.156	0.966	...	...	...
0.5:2.5			0.008			0.013	0.023	0.026
1:2			0.015			0.026	0.047	0.052
1.5:1.5			0.022			0.039	0.068	0.078
2:1			0.030			0.052	0.091	0.104
3:0			0.046			0.078	0.138	0.156
0:4	1.449	1.270	...	1.510	1.125	...	...	...
0.5:3.5			0.010			0.016	0.029	0.032
1:3			0.019			0.032	0.058	0.064
2:2			0.039			0.064	0.117	0.128
3:1			0.058			0.096	0.175	0.192
4:0			0.078			0.128	0.234	0.256
0:5	1.619	1.352	...	2.020	1.310	...	...	...
0.5:4.5			0.011			0.019	0.034	0.038
1:4			0.024			0.038	0.070	0.075
2:3			0.046			0.075	0.139	0.150
4:1			0.092			0.150	0.278	0.301
5:0			0.116			0.188	0.348	0.376
0:6	1.791	1.420	...	2.72	1.506	...	...	...
0.5:5.5			0.013			0.021	0.040	0.043
1:5			0.027			0.043	0.081	0.086
2:4			0.054			0.085	0.161	0.170
3:3			0.081			0.128	0.242	0.256
4:2			0.107			0.171	0.321	0.342
5:1			0.134			0.213	0.402	0.426
6:0			0.161			0.256	0.483	0.512
0:7	1.965	1.485	...	3.71	1.723	...	...	...
0.5:6.5			0.015			0.024	0.045	0.047
1:6			0.030			0.048	0.089	0.095
2:5			0.060			0.095	0.179	0.190
3:4			0.090			0.143	0.269	0.286
4:3			0.119			0.190	0.358	0.380
5:2			0.149			0.237	0.447	0.474
6:1			0.179			0.283	0.537	0.566
7:0			0.209			0.332	0.627	0.664
0:8	2.134	1.541	...	5.10	1.952	...	...	...
0.5:7.5			0.016			0.026	0.049	0.052
1:7			0.033			0.052	0.098	0.105
2:6			0.065			0.104	0.196	0.208
3:5			0.098			0.157	0.293	0.314
4:4			0.130			0.209	0.390	0.418
5:3			0.163			0.261	0.489	0.522
6:2			0.196			0.314	0.588	0.628
7:1			0.228			0.366	0.684	0.732
8:0			0.261			0.418	0.783	0.839

[a] Values from tables listed in ref. 13.

proach assumes that $(\gamma_\pm)_x$ and ϕ are linear functions of m_x, at constant ionic strength, which is known not to be the case for all electrolyte mixtures[20].) Thus

$$m_x \left(\frac{\partial \log (\gamma_\pm)_x}{\partial m_x} \right)_{\mu = k} = \frac{1}{\gamma_x} \left(\frac{\partial \gamma_x}{\partial \log m_x} \right)_{\mu = k} =$$

$$\frac{m_x}{m} \left(\frac{\phi_x - \phi_i}{2.303} \right)_{\mu = k} = N_x \left(\frac{\phi_x - \phi_i}{2.303} \right)_{\mu = k} \quad (27)$$

Table II lists various values for this term as a function of N_x for the system investigated here. It can be seen that for concentrations less than 5 m and for greater concentrations when N_x is small this term is quite small and has little effect on the determination of

p. The point to be stressed at this time is that the neglect of this term is not to be considered generally possible; if it is neglected too often, erroneous interpretations of the obtained p values may follow. Actually, such results may be seen in Figure 2; even though p is supposedly a constant, the slope of the curve begins to decrease at the higher m_x concentrations, within a single constant ionic strength system, indicating that this term is not negligible and should be included in the calculations.

Finally, the term involving the activity coefficients of the complex, γ_c, and hydrated, γ_H, ions may be approximated when these two terms are considered equal such that

$$\frac{1}{\gamma_c\gamma_H}\left(\frac{\partial(\gamma_c\gamma_H)}{\partial \log m_x}\right)_{\mu=k} = \frac{2}{\gamma_c}\left(\frac{\partial \gamma_c}{\partial \log m_x}\right)_{\mu=k} =$$

$$2m_x\left(\frac{\partial \log \gamma_c}{\partial m_x}\right)_{\mu=k} \quad (28)$$

and are related to the activity coefficient of the solution, γ_t. The reason for the equality approximation of γ_c and γ_H is an extension of the fact that the activity coefficient of one species, in a constant ionic strength solution of another at low concentrations, is essentially a constant and independent of the concentration of that species.[22]

The correlation between γ_c or γ_H and the mean activity coefficient of the inert electrolyte[3] and of mixtures of uni-univalent inert electrolytes[4] has already been demonstrated; it would appear that such a correlation could also be made in this case. The logarithm of the total mean activity coefficient of the solution, $\log \gamma_t$, can be estimated as a linear function of m_x, when the total osmotic coefficient is a linear function of m_x; then

$$2m_x\left(\frac{\partial \log \gamma_t}{\partial m_x}\right)_{\mu=k} = 2m_x\left(\frac{\log (\gamma_\pm)_x' - \log (\gamma_\pm)_i'}{m}\right) =$$

$$2N_x\left(\log \frac{(\gamma_\pm)_x'}{(\gamma_\pm)_i'}\right) \quad (29)$$

where $(\gamma_\pm)_x'$ and $(\gamma_\pm)_i'$ are the mean activity coefficients of m_x and m_i only and at the constant ionic strength specified. Thus, substituting eq. 27 and 29 into eq. 23 and rearranging yields

$$p = -\frac{nS}{0.0591}\left[\frac{\left(2N_x \log \frac{(\gamma_\pm)_x'}{(\gamma_\pm)_i'} - \frac{nS}{0.0591}\right)}{\left(-\frac{nSN_x}{0.0591}\left(\frac{\phi_x - \phi_i}{2.303}\right) - \frac{nS}{0.0591}\right)}\right] \quad (30)$$

where S is the slope of $(\Delta E_{1/2})_{obsd}$ as a function of $\log m_x$. Table II lists various values for $N_x \log [(\gamma_\pm)_x/(\gamma_\pm)_i]$. At the lower N_x and μ values this term is quite small. At higher constant ionic strengths, this term is not small; however, it can be seen from the tabulated values that twice this term is essentially equal to three ($nS/0.0591$) times the osmotic coefficient term such that the entire value within the brackets in eq. 30 is essentially unity. Thus, for this system the relationship between p and S is the same as that for dilute solutions, or

$$p = -\frac{n}{0.0591}\left(\frac{\partial(\Delta E_{1/2})_{obsd}}{\partial \log m_x}\right)_{\mu=k} \quad (31)$$

Such a simple relationship may or may not exist for other complex ion systems at high ionic strength. The evaluation of p for this system leads to a value of 3.0 ± 0.1, which is comparable to other literature values[17] determined at lower ionic strengths, and leads to the conclusion that $CdCl_3(H_2O)_r^-$ is the only major complex species existing in the system described.

(22) H. S. Harned and B. B. Owen, ref. 19, p. 598.

The evaluation of the formation constant, β_p, may be made by means of eq. 16; in terms of $\log \beta_p$, at 1 m ligand electrolyte concentration, it becomes

$$\log \beta_p = -\frac{n}{0.0591}[(\Delta E_{1/2})_{obsd}]_{m=1} + 2 \log \gamma_c +$$

$$2 \log \frac{D_H'}{D_c} - p \log \gamma_x \quad (32)$$

or for this system

$$\log \beta_p = -\frac{[(\Delta E_{1/2})_{obsd}]_{m=1}}{0.0296} - 2 \log (I_d)_c + 1.27 =$$

$$-\frac{[(E_{1/2})_{sys} + 0.572]}{0.0296} - 2 \log (I_d)_c + 1.27 \quad (33)$$

where $2 \log \gamma_c \cong 3 \log \gamma_x$ and $(I_d)_c = 4.28$ $\mu a./mmole$ $mg.^{2/3} sec.^{-1/2}$. Equation 33 is quite similar to that suggested by Irving[23] where various formation constants, as determined in different systems, have been corrected for changes in the diffusion coefficient of the complex species. Table III lists the various values of β_p as determined from eq. 33 for which the average value is 32 ± 5. This value shows the expected consistency from the proposed theory in contrast to 172 ± 94 as calculated by the usual polarographic techniques where $(\Delta E_{1/2}) = (E_{1/2})_c - (E_{1/2})_\mu$. If corrections of K_f were made for the change in the diffusion coefficient, the deviation would be even greater. The proposed value does not agree with the literature[17] for the cadmium–chloride system, but it must be remembered that the essential difference in the evaluation made by this method is due to the definition of $\Delta E_{1/2}$; one would not expect agreement between values determined by this procedure and any other technique where the activity coefficients and the effect of hydration have been neglected.

Table III. The Evaluation of the Over-All Formation Constant, β_p, for $CdCl_3^-$ as Determined from the $Cd(NO_3)_2$–$LiCl$–$LiNO_3$ System Using Eq. 33

Ionic strength	$-\Delta E_{1/2}$, mv.	$-\Delta E_{1/2}/$ 29.6	2 log $(I_d)_c$	log β_p	β_p	$K_f{}^a$
1	56	1.89	1.17	1.99	(97)	79
2	44	1.49	1.12	1.64	43	56
3	40	1.35	1.10	1.52	33	71
4	39	1.32	1.00	1.59	39	115
5	34	1.15	0.98	1.44	27	144
6	31	1.05	0.85	1.47	29	199
7	28	0.95	0.83	1.39	25	268
8	26	0.88	0.70	1.45	28	434
				Average	32	172
				Deviation	±5	±94

a The formation constant as determined by normal procedure where $(\Delta E_{1/2}) = (E_{1/2})_c - (E_{1/2})_\mu$ and neglecting corrections due to changes in D_c or D_H.

(23) H. Irving, ref. 7 p. 55.