The Influence of Ionic Strength on Polarographic Half-Wave Potentials. II. The Investigation of the Reduction of Zinc and Nickel Nitrates and the Effect of Mixed Uni-univalent Inert Electrolytes on the Reduction of Cadmium Nitrate

By Nicholas E. Vanderborgh and Douglas E. Sellers

Application of previous theoretical considerations concerning the influence of high ionic strength on polarographic investigations has been applied to systems of mixed, uni-univalent nitrate inert electrolytes and to systems whose reduction potential is different from that of the electrocapillary maximum. It is shown that hydration in such systems is an important consideration in the interpretation of the effect of high ionic strength on polarographic data.

Previous work by these authors[1] has shown that the observed change in the half-wave potential for cadmium nitrate (assuming no complexation between the reducible species and the inert electrolyte) is a function of the activity coefficient of the inert electrolyte and the activity of water. The more usable approximate form has been stated as

$$(\Delta E_{1/2})_{obsd} = \{29.5 \log \gamma_{\pm} + 4.62 m\phi\} \text{ mv.} \quad (1)$$

at 25° where $\gamma_{\pm}$ is the mean molal activity coefficient of the inert electrolyte and ϕ is the osmotic coefficient of the solution at molality m; the constant 4.62 corresponds to systems such as cadmium nitrate where the number of electrons involved in the reduction is two, the inert electrolyte is of the uni-univalent type, and the hydration parameter for the reducible species is 10.

It was of interest to determine whether or not eq. 1 could be applied to systems involving mixed inert electrolytes and also to systems whose half-wave potentials were not in the vicinity of the electrocapillary maximum.

The experimental procedure followed in this investigation was essentially the same as that mentioned in the previous study.[1] The three major exceptions follow. (1) The polarographic test solution was degassed for 10 min. prior to placing it in the polarographic cell. An additional 1–2-min. degassing period was used after the sample had been placed in the cell and prior to the determination of the current–voltage curve. (It was felt that this change would lessen the possibility of chloride contamination, from the salt bridge, in the test solution.) (2) Gelatin, 0.005%, was used as a maximum suppressor in zinc and nickel systems. (3) The salt bridge(s) were prepared following the procedure suggested by Meites.[2] The capillary used had a constant of 1.54 mg.$^{2/3}$ sec.$^{-1/2}$ as measured in distilled water and open circuit. Duplicate determinations of each polarogram were run and the average result was reported.

The initial investigations of the mixed electrolyte systems were suggestive that the over-all effect of the inert electrolyte was extensive in nature. Thus, as a first approximation, the relationship between $(\Delta E^{1/2})_{obsd}$ and the molal concentrations of the mixed inert electrolytes may be broken into two factors: (1) $(\Delta E_{1/2})_a$ or the change attributed to electrolyte a; and (2) $(\Delta E_{1/2})_b$, the change caused by electrolyte b. These two factors

may be combined to represent the $(\Delta E_{1/2})_{obsd}$ in terms of a function of the mole fraction, or

$$(\Delta E_{1/2})_{obsd} = \frac{m_a}{m_a + m_b} (\Delta E_{1/2})_a +$$
$$\frac{m_b}{m_a + m_b} (\Delta E_{1/2})_b \text{ mv.} \quad (2)$$

The observed half-wave potential may thus be represented as

$$(E_{1/2})_{obsd} = (E_{1/2})_{\mu = 0} + (\Delta E_{1/2})_{obsd} = (E_{1/2})_{\mu = 0} +$$
$$\frac{m_a}{m_a + m_b} (\Delta E_{1/2})_a + \frac{m_b}{m_a + m_b} (\Delta E_{1/2})_b \text{ mv.} \quad (3)$$

This result, eq. 3, is not necessarily to be unexpected. Although known not to be accurate in all instances, there does exist a linear relationship between the over-all osmotic coefficient and the composition of the solution.[3] The relationship between the individual mean and over-all mean activity coefficients is not nearly so simple. However, in the concentration range investigated here, the osmotic coefficient term of eq. 1 is the more important term except at the lower ionic strengths, i.e., less than 1 m. Thus, eq. 3 should be at least adequate in the representation of the observed shift in the half-wave potential.

The reason for the choice of cadmium as the reducible species along with the utilization of a nitrate medium for this investigation was illustrated in the earlier work.[1] The results of this investigation are illustrated in Fig. 1 and Table I. The values of $(\Delta E_{1/2})_a$ and $(\Delta E_{1/2})_b$ used were the experimental values determined in our earlier work rather than those which may be obtained from eq. 2; it has been shown that eq. 1 begins to deviate from the experimental above concentrations of 5 m and it was felt that a better experimental–theoretical fit would be obtained from the experimentally determined $(\Delta E_{1/2})$ values. As can be seen from the data presented, eq. 3 is an adequate representation of the observed shift in the half-wave potential of cadmium in uni-univalent inert electrolyte media.

Further investigation of the application of eq. 1 to species whose half-wave potentials were more negative than that of cadmium was also undertaken. Lithium nitrate was chosen for the inert electrolyte in this investigation since it yielded the largest influence on the half-wave potential of cadmium and was expected to give the most critical test of eq. 1. From results

(1) D. E. Sellers and N. E. Vanderborgh, J. Am. Chem. Soc., 86, 1934 (1964).

(2) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, pp. 21 and 22.

(3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, p. 437.

TABLE I

COMPARISON BETWEEN OBSERVED, PREDICTED, AND THEORETICAL VALUES OF THE HALF-WAVE POTENTIAL OF CADMIUM NITRATE AS A FUNCTION OF THE CONCENTRATION AND COMPOSITION OF THE INERT ELECTROLYTE

Conditions: 1 mM cadmium nitrate, no gelatin, s.c.e. reference electrode

Inert electrolyte composition	Total molality	$-E_{1/2}$, mv. Obsd.	$-E_{1/2}$, mv. Pre-dicted[a]	Slope, mv./molal Obsd.	Slope, mv./molal Pre-dicted	Slope, mv./molal Theor.[b]
NH$_4$NO$_3$	1.0	580	577			
	3.0	577	576			
	5.0	575	571	1.7	1.7[b]	1.7
	7.0	573	567			
	9.0	570	565			
3:1 NH$_4$NO$_3$–	1.0	579	577			
LiNO$_3$	3.0	572	569			
	5.0	566	564	2.8	2.8	3.7
	7.0	562	558			
1:1 NH$_4$NO$_3$–	1.0	576	575			
LiNO$_3$	3.0	567	565	4.1	4.2	5.6
	5.0	558	556			
	7.0	551	547			
1:3 NH$_4$NO$_3$–	1.0	573	573			
LiNO$_3$	3.0	563	561	5.8	5.7	7.4
	5.0	550	549			
	7.0	539	535			
LiNO$_3$	1.0	571	571			
	3.0	554	556			
	5.0	542	537	7.7	9.4[b]	9.4
	7.0	528	517			
	9.0	516	497			
1:1 NH$_4$NO$_3$–	1.0	576	577			
NaNO$_3$	3.0	570	568			
	5.0	566	565	2.4	2.6	2.5
	7.0	561	(560)[c]			
	9.0	557	(556)			
NaNO$_3$	1.0	572	573[d]			
	2.0	569	569			
	3.3	563	565	3.7	3.3[b]	3.3
	4.1	561	563			
	5.1	555	559			
	6.0	553	554			
1:1 KNO$_3$–	1.0	574	575			
LiNO$_3$	3.0	565	569			
	4.0	561	(565)[c]	4.0	4.3	4.7
	5.0	558	(562)			
	6.0	554	(558)			
	7.0	551	(553)			
KNO$_3$	1.0	578	579			
	2.0	579	580	−1	−0.8[b]	−0.8
	3.0	580	581			
	3.5	578	581			
1:1 Mg(NO$_3$)$_2$–	1.0	567	569			
LiNO$_3$	3.0	543	549	11.9	13.0	17.4
	5.0	519	534			
	7.0	500	517			
Mg(NO$_3$)$_2$	1.0	561	570[c]			
	2.0	541	551	19.7	25.5[b]	25.5
	3.0	522	526			
	4.0	503	501			
	4.5	492	489			

[a] Calculated by eq. 3 where $(E_{1/2})_{\mu=0} = -572$ mv.   [b] See ref. 1.   [c] Contribution of NaNO$_3$ and KNO$_3$ estimated beyond the solubility of these electrolytes.   [d] $(E_{1/2})_{\mu=0}$ was chosen as -569[1] mv. vs. s.c.e.   [e] Calculated from eq. 12 in ref. 1 using $x = 10$, $\nu = 3$, $n = 2$, and $(E_{1/2})_{\mu=0} = -569$ mv. vs. s.c.e.
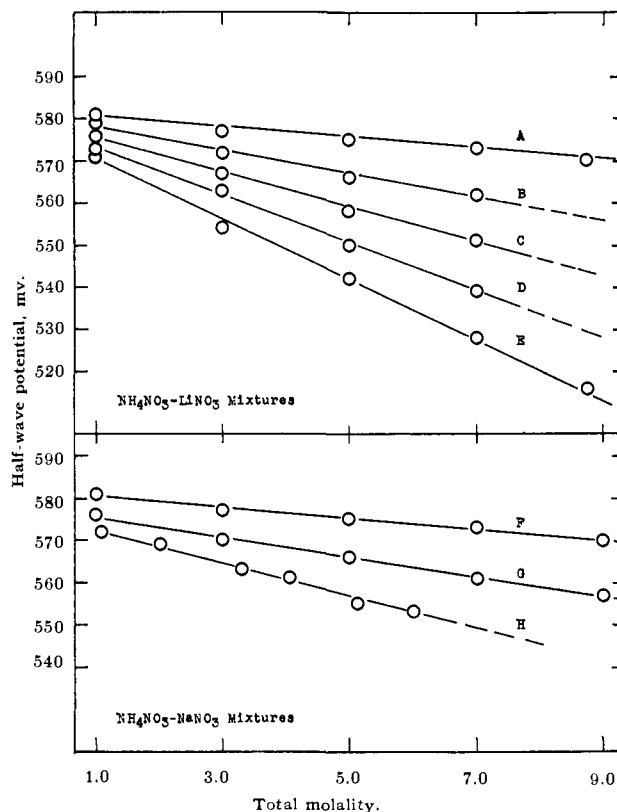

Fig. 1.—The effect of mixed electrolytes on the observed half-wave potential of cadmium. Conditions for curves A through H are: A, NH$_4$NO$_3$; B, 3:1 NH$_4$NO$_3$–LiNO$_3$; C, 1:1 NH$_4$NO$_3$–LiNO$_3$; D, 1:3 NH$_4$NO$_3$–LiNO$_3$; E, LiNO$_3$; F, NH$_4$NO$_3$; G, 1:1 NH$_4$NO$_3$–NaNO$_3$; and H, NaNO$_3$.

obtained in the earlier investigation, the use of gelatin was not expected to interfere with the results. As can be seen from the data presented in Table II, the change

TABLE II

COMPARISON BETWEEN THE THEORETICAL AND EXPERIMENTAL HALF-WAVE POTENTIALS OF ZINC AND NICKEL NITRATES IN HIGHLY CONCENTRATED SOLUTIONS OF LITHIUM NITRATE

Conditions: 1.0 mM reducible species, 0.005% gelatin, s.c.e. reference electrode

LiNO$_3$ concn., m	$-E_{1/2}$, mv. Obsd.	$-E_{1/2}$, mv. Theor.[a]
	Zinc nitrate ($x = 12$)[b]	
0		994
1.0	997	991
2.0	984	984
3.0	974	974
4.0	963	963
5.0	949	952
7.0	929	929
9.0	908	904
	Nickel nitrate	
0	1024[c]	1024[d]
0.5	1029	1028	1022
1.0	1018	1022	1019
1.5	1015	1016	1013
2.0	1009	1009	1006
3.0	988	992	992
4.0	975	974	975
5.0	958	955	957
6.0	936	935	940
7.0	912	914	921

[a] Calculated from eq. 1 in text.   [b] Hydration parameter.   [c] Hydration parameter equal to 10 and n equal to 1.   [d] Hydration parameter equal to 20 and n equal to 2.

in the half-wave potential as a function of the ionic strength can be described by eq. 1. Because of this agreement, one must conclude that hydration is more important than complexation in these systems.

The plot of log $(i/i_d - i)$ vs. $E_{d.e.}$ for the zinc systems yielded a linear curve with a slope of approximately 33 mv., a reversible two-electron reduction; the values approached the theoretical value of 30 mv. as the concentration of $LiNO_3$ was increased. The same plot for the nickel systems yielded a nonlinear curve with slope values in the vicinity of 120 mv. indicating a nonreversible reduction.

The use of hydration parameters for these ions in the vicinity of 10–15 appear to be the most probable.[4]

(4) R. A. Robinson and R. H. Stokes, ref. 3, pp. 62, 246.

The hydration parameters chosen for these systems were 12 for zinc and 10 or 20 for nickel. Since nickel shows a nonreversible reduction, either a one- or two-electron mechanism might be proposed for the primary electrode reaction. Calculations were made using a hydration parameter of 10 when a one-electron reduction was considered, and a hydration of 20 when a two-electron mechanism was proposed. In the case of nickel, a better experimental–theoretical fit of the data was obtained when the hydration parameter of 10 and a one-electron mechanism was used (see Table II).

Binding of Silver Ion by Adenine and Substituted Adenines

BY KEITH GILLEN, RONALD JENSEN, AND NORMAN DAVIDSON

Potentiometric, pH-Stat titrations reveal that silver ion forms insoluble compounds at pH values around 7 with 6-dimethylaminopurine, adenine, deoxyadenosine, and 9-methyladenine; and a soluble polymeric species with deoxyadenosine 5'-monophosphate. The binding by 9-methyl-6-dimethylaminopurine is much weaker. In the reaction with 6-dimethylaminopurine, a 1:1 compound is formed and the N-9 proton is displaced according to the reaction: $Ag^+ + BH \rightleftharpoons (AgB)_{ppt} + H^+$, $K = 5.0 \times 10^3$ M^{-1}. With 9-methyladenine and deoxyadenosine, the reaction is: $3Ag^+ + 2BH + ClO_4^- \rightleftharpoons [Ag_3B_2 \cdot ClO_4]_{ppt} + 2H^+$, $K = [H^+]^2/[BH]^2[Ag^+]^3 = 1.37 \times 10^4$ M^{-3} and 6.08×10^2 M^{-3}, respectively. The novel and unexpected result of this investigation is that with substances like adenosine and 9-methyladenine, the very weakly acidic amino hydrogens can be displaced by silver ions. With adenine, the reaction is complex; both N-9 and amino hydrogens are displaced. There is 1.5–2.0 Ag^+ bound per adenine and slightly less proton displacement. With deoxyadenosine 5'-monophosphate at pH ≥ 7, a soluble polymeric species is formed according to a reaction of the type: $2Ag^+ + BHP^{-2} \rightleftharpoons (1/n)[Ag_2BP]_n^{-n} + H^+$.

Introduction

Silver ion and mercuric ion form complexes with the nucleic acids and with polynucleotides which undoubtedly involve covalent bond formation with the purine and pyrimidine moieties, and most probably electron-pair bonds to σ-electron pairs of nitrogen atoms (although the possibility of π-bonding or some other exotic type of interaction is not absolutely excluded).[1-3] In order to understand these complexes more fully, we have investigated the reactions between silver ion and some monomeric adenine derivatives.

It is well known that silver ion forms precipitates with purines but not with pyrimidines in fairly acid solution.[4] (Although, so far as we know, the first measurement of a solubility product constant is that reported here.) A simple hypothesis as to the structure of the insoluble silver–purine complex is that it is a 1:1 compound, and a linear neutral polymer formed by replacement of the N-9 hydrogen atom of purine by silver, and then the formation of a second silver–nitrogen bond with one of the several basic nitrogen atoms of another purine molecule. In the sketch in Fig. 1, the polymerization involves the N-9 and N-7

(1) T. Yamane and N. Davidson, *J. Am. Chem. Soc.*, **83**, 2599 (1961).
(2) T. Yamane and N. Davidson, *Biochim. Biophys. Acta*, **55**, 609 (1962).
(3) S. Katz, *ibid.*, **68**, 240 (1963).
(4) A. Bendich, "The Nucleic Acids," Vol. I, E. Chargaff and J. N. Davidson, Ed., Academic Press, New York, N. Y., 1955, p. 124.

nitrogen atoms. It will be shown that the reaction to form a 1:1 compound does occur, but it is not the only possible reaction for adenine derivatives.

If the N-9 hydrogen were the only replaceable hydrogen, adenine derivatives which are blocked in the N-9 position, such as 9-methyladenine or adenosine, would be unable to form such neutral linear polymers, and would either form conventional, soluble 2:1 complexes (analogous to $H_3N:Ag:NH_3^+$), or, conceivably, charged linear polymers, $-Ads-Ag^+-Ads-Ag^+-$ (Ads being the neutral adenosine molecule).

The investigations reported here reveal that the predictions described in the previous paragraph are wrong. Silver ion can react with 9-methyladenine and with adenosine by displacement of one of the weakly acidic amino protons to form fairly insoluble compounds.

Experimental

Materials.—The adenine derivatives studied were the highest grade available from the sources indicated below. No further purification was attempted. The disodium salt of deoxyadenylic acid (5') (A grade), deoxyadenosine (A grade), adenine (A grade), and 6-dimethylaminopurine (A grade) were from Calbiochem. 9-Methyladenine was supplied by the Cyclo Chemical Co.[5]; and 9-methyl 6-dimethylaminopurine was kindly furnished by Prof. Roland K. Robbins of the University of Arizona.[6]

(5) Los Angeles 1, Calif.
(6) R. K. Robbins and H. H. Lin, *J. Am. Chem. Soc.*, **79**, 490 (1957).