JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 84 FEBRUARY 27, 1962 NUMBER 4

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

Polarography of Copper Amine Complexes at the Dropping Copper Amalgam Electrode

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RECEIVED JULY 31, 1961

Polarographic anodic–cathodic waves obtained with dropping copper amalgam electrodes in amine solutions were investigated under a large range of conditions. In solutions containing a large excess of polydentate amines, the polarograms consist of single reversible waves which involve equilibria between copper(II) complexes and free copper in the amalgam while in solutions containing a large excess of monoamines they consist of reversible stepwise waves which involve intermediate stable copper(I) complexes. The wave for the equilibrium between free copper in the amalgam and aquocopper(II) is reversible if the solution has a *p*H smaller than about 3 to prevent the formation of Cu_2O. The anomalous appearance of certain waves was shown to be due to changes in the concentrations of free ligand at the electrode surface as a consequence of electrolysis even in reversible electrode reactions. This effect was observed in ligand deficient solutions and at *p*H values close to acidity equivalence points of basic ligands where the buffering capacity is small even with an excess of the ligand present. Equations for the application of Leden's method and optimum experimental conditions for application of the amalgam electrode to complex equilibria are discussed. Stepwise complexity constants calculated from either the half-wave or the spontaneous potentials are in good agreement with those obtained by other established methods provided stable intermediates are not formed during the electrode reaction.

Introduction

The dropping amalgam electrode has the advantages of both the dropping mercury electrode and the quiet metal or amalgam electrodes in the investigation of complex equilibria since it can be used to obtain equilibrium potential data with or without electrolytic current flow. It has a further advantage over quiet electrodes in that a fresh amalgam surface of constant composition is constantly exposed to the aqueous phase.

The behavior of the dropping copper amalgam electrode in amine solutions was investigated because the electrode reactions have been shown to be reversible under a large range of conditions.[1,2] Furthermore, both stepwise reduction and reduction directly to the free metal can be investigated because a stepwise electrode reaction involving copper(I) occurs in monoamine solutions of copper(II) and the electrode reaction involving only the copper(II) complexes and the free metal occurs in polydentate amine solutions of copper(II).

Lingane first obtained anodic polarographic waves with dropping amalgam electrodes containing 0.01% cadmium.[3] Heyrovsky and Kalousek[4] reported that dropping amalgam electrodes containing copper, lead, cadmium and zinc in concentrations of less than 0.005% yielded anodic waves having diffusion currents which were proportional to the concentration of metal in the amalgam and discussed theoretical aspects of the waves in some detail. Recently, Strehlow and Stackelberg[5] have modified the Ilkovic equation for amalgams by considering the stirring which takes place within the drop as the amalgam flows. Turner and Winkler,[6] who worked with lead and cadmium amalgams, verified their equation. Furman and Cooper[7] studied the characteristics of dropping amalgam electrodes containing copper, zinc, cadmium, thallium and lead. They obtained stepwise anodic waves with copper amalgams in solutions containing ammonia and ammonium chloride. They also measured the diffusion coefficients of zinc, cadmium, lead, copper, thallium, tin and bismuth and found that, except for copper and bismuth, the diffusion coefficients were an inverse

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[1] M. V. Stackelberg and H. V. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[2] J. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955).

[3] J. J. Lingane, *J. Am. Chem. Soc.*, **61**, 976 (1939).

[4] J. Heyrovsky and M. Kalousek, *Coll. Czech. Chem. Comm.*, **11**, 464 (1939).

[5] H. Strehlow and M. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[6] R. S. Turner and C. A. Winkler, *Can. J. Chem.*, **29**, 467 (1951).

[7] N. H. Furman and W. C. Cooper, *J. Am. Chem. Soc.*, **72**, 5667 (1950); **74**, 6183 (1952).

linear function of the atomic radii. Tockstein[8] obtained irreversible waves when he used copper amalgam electrodes in the presence of chloride, sulfate, oxalate, cyanide and tartrate. Pecsok[9] cited the continuity of an anodic–cathode polarogram of a copper ethylenediaminetetraacetate solution as evidence that the electrode reaction was reversible.

In common with many metals, copper forms a two phase amalgam. It is evident that mechanical difficulties will be encountered unless a pure liquid phase amalgam is used in the dropping electrode. Richards[10] found that the liquid phase which passed through leather under pressure contained 0.00235% by weight. The second phase is a solid for which a large range of composition has been reported. Cohen[11] and his co-workers applied pressure to the two phase amalgams to remove the liquid and found that the solid phase had a composition corresponding to the formula, CuHg, or 23.2% copper by weight. Russell, Cazalet and Irvin[12] presented evidence for the formation of the compound, CuHg, in copper amalgams and stated that five other compounds varying from Cu_7Hg to $CuHg_4$ also may form.

Theoretical

DeFord and Hume[13] have derived equations for Leden's function in terms of conventional polarographic data with excess ligand present while Ringbom and Eriksson[14] have derived equations applicable to polarographic data obtained in the presence of relatively low ligand concentrations. The derivation of Leden's function for the dropping amalgam electrode is similar to that of the former authors provided the concentrations of the various ligands are large enough so that no appreciable ligand concentration changes occur at the drop's surface as a consequence of the formation or reduction of the various complex species. The general procedure for applying Leden's function to mixed complexes has been discussed in previous papers.[15,16]

The anodic diffusion current can be limited either by the concentration of reducible metal in the amalgam electrode or by the concentration of free ligand in the aqueous solution. If the concentration of free ligand in the aqueous solution limits the anodic current its concentration at the drop surface must decrease greatly as the anodic current increases and cause the equilibrium to shift toward lower complexes. The waves obtained under these conditions are not well suited for investigation of complex stability. Consequently, the following equations will involve the equilibrium between any reducible metal ion in the aqueous solution and the free metal in the amalgam in which the anodic diffusion current is limited by concentration of the metal in the amalgam.

Assuming the amalgam concentrations to be so dilute that the activity of free mercury is unchanged, the equations for the electrode reaction of aquo metal ions in equilibrium with the dissolved metal in an amalgam and the electrode potential are

$$\mathrm{M}^{n+} + n\epsilon \rightleftharpoons \mathrm{M}_{\mathrm{am}}$$

$$E = E_0 + S \log (\mathrm{M})_s f_m/(\mathrm{M}_{\mathrm{am}})_s f_{\mathrm{am}} \qquad (1)$$

where E is the measured electrode potential *versus* the standard hydrogen electrode, E_0 is the standard potential for the electrode reaction of the aquo ion and S indicates 2.303 RT/nF. M^{n+} or simply M indicates the aquo metal ion in solution, M_{am} indicates the metal dissolved in mercury and f_m and f_{am} are their respective activity coefficients. Throughout this paper brackets indicate activities and parentheses indicate concentrations. The subscripts s and b after concentrations indicate concentrations at the electrodes surface and in the bulk of the solutions, respectively, while the subscript t, as in (M_t), indicates the total concentration of the species in all forms. Primes or the subscript, aq., will be placed after symbols to indicate the absence of complexing agents.

The general expression for the equilibrium of the aquo-metal ion with several ligands, assuming that only mononuclear complexes are formed, is

$$\mathrm{M} + i\mathrm{A} + j\mathrm{B} + k\mathrm{C} = \mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k$$

$$\beta_{ijk} = \frac{(\mathrm{MA}_i\mathrm{B}_j\mathrm{C}_k)}{(\mathrm{M})(\mathrm{A})^i(\mathrm{B})^j(\mathrm{C})^k} \qquad (2)$$

As proposed by Deford and Hume[13] the diffusion current can be described approximately by a single expression in terms of a mean diffusion current constant I_m instead of a summation of the contributions of all species in terms of their specific diffusion current constants. This term may be expected to change continuously as the concentration of ligand increases. It will usually decrease as bound water molecules are replaced by larger ligands.

The substitution of equations for the conservation of metal ion and diffusion near the drop surface and within the drop yield the following equation for the polarographic wave in a complex containing solution.

$$E_c = E_0 + S \log f_m I_{\mathrm{am}}/f_{\mathrm{am}} I_m + S \log (i_{d_c} - i)/(i - i_{d_{an}})$$
$$- S \log \sum_{i=0}^{N} \sum_{j=0}^{N} \sum_{k=0}^{N} \beta_{ijk}(\mathrm{A})^i(\mathrm{B})^j(\mathrm{C})^k \qquad (3)$$

The corresponding equation for the wave in a complex-free solution is

$$E_{\mathrm{aq}} = E_0 + S \log f_m' I_{\mathrm{am}}/f_{\mathrm{am}} I_m +$$
$$S \log (i_{d_c}' - i')/(i' - i_{d_{an}}') \qquad (4)$$

Combining equations 3 and 4, yields the following expression for Leden's function F_0 which is valid if the electrode reaction is diffusion controlled.

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[8] A. Tockstein, *Coll. Czech. Chem. Comm.*, **16**, 101 (1951).

[9] R. L. Pecsok, *Anal. Chem.*, **25**, 561 (1953).

[10] T. W. Richards, "Electrochemical Investigation of Liquid Amalgams," Carnegie Institute of Washington, 1909.

[11] E. Cohen, F. D. Chattaway and W. Tombrock, *Z. Physik. Chem.*, **60**, 706 (1907).

[12] A. S. Russell, P. V. F. Cazalet and N. M. Irvin, *J. Chem. Soc.*, 852 (1932).

[13] D. DeFord and D. H. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

[14] A. Ringbom and L. Eriksson, *Acta Chem. Scand.*, **7**, 1105 (1953).

[15] J. I. Watters and J. G. Mason, *J. Am. Chem. Soc.*, **78**, 285 (1956).

[16] J. I. Watters, J. G. Mason and O. E. Schupp, *ibid.*, **78**, 5782 (1956).

$$F_0 = (f_m'/f_m)(I_m/I_m') \text{ antilog } \Delta E/S = \sum_{i=0}^{N} \sum_{j=0}^{N} \sum_{k=0}^{N} \beta_{ijk}(A)^i(B)^j(C)^l \quad (5)$$

ΔE is the shift of the potential at any point on the complex wave from the corresponding point on the wave for the complex free solution containing the same metal ion and amalgam concentration, or it may be the shift in the half-wave potential regardless of the metal ion or amalgam concentration. In the former case the current terms in equations 3 and 4 cancel. In the latter case these terms are equal to zero. If all solutions contain the same large excess of supporting electrolyte, the activity coefficient term, f_m'/f_m, is a small constant. When the ligand is a neutral molecule the complex and aquo ions will have the same ionic charge so this term may be dropped. In other cases adequate approximate values may be obtained in a variety of ways. Often the magnitudes of I_m and I'_m are quite similar. If the size of the aquo and complex ion differ appreciably, these terms may be calculated from diffusion current or conductance data. Furthermore, these terms do not appear when spontaneous potentials are measured since the electrode process is not diffusion controlled.

If only one ligand is added in a stepwise manner, the following functions may be used to solve the over-all complexity constants, β_1 and β_2. In general, as many polarographic waves or spontaneous potentials with varied $(A)_t$ are required as there are unknown complexity constants, and these data must be obtained in solutions in which the distribution of all complex species vary greatly. A method of using determinants to solve equation 5 has been described in previous papers.[15,16]

$$F_1 = (F_0 - 1)/(A) = \beta_1 + \beta_2(A) \quad (6)$$

$$F_2 = (F_1 - \beta_1)/(A) = \beta_2 \quad (7)$$

The reversibility of certain electrode reactions even though the waves have an anomalous appearance can be confirmed by calculating the predicted potential shift, ΔE, using known complexity constants. Since the equilibrium concentration of free ligand may differ greatly from that in the bulk of the solution under these conditions, the following expression due to Ringbom and Eriksson[14] can be applied. Thus

$$(M^{n+})_s = (M^{n+})_b\,(i_{d_c} - i)/i_{d_c} \quad (8)$$

This expression is also valid for anodic currents obtained with amalgams since the total concentration of metal ion at the electrode surface is that already present, $(M^{n+})_b$, plus that produced anodically, $(i_{an}/i_{d_c})(M^{n+})_b$. It is further assumed that the total concentration of the ligand at the electrode surface is equal to that in the bulk of the solution. The equilibrium concentration of free ligand at the electrode surface is then calculated by means of Bjerrum's formation function.

The predicted potential of the electrode for any current on the wave can finally be calculated by substituting the complexity constants and the free ligand concentrations into equation 3 after solving the sum of the first three terms on the right by means of a known half cell in which the spontaneous potential of the same electrode is measured using the same amalgam and total copper ion concentration with a known excess of free ligand present. The predicted shift in potential from that for the corresponding point on the reversible aquocopper(II) wave can be solved by equation 5 if similar cells and concentrations of metal ion and supporting electrolyte are used.

Experimental

Apparatus and Reagents.—Most of the apparatus, experimental techniques and chemicals have been described in a previous publication.[15] As has been emphasized by Furman and Cooper,[7] it was found to be necessary to use an all glass assembly for the dropping amalgam electrode in order to avoid oxidation of the dissolved copper. In this Laboratory, attempts to use a leveling bulb connected to the capillary by tygon, polyethylene or rubber tubing resulted in a steadily decreasing anodic diffusion current of copper amalgram electrodes over a period of several days. A dark coating of copper oxide on the interior surface of translucent tubing was observed after several weeks. The amalgam column, from 30 to 97.5 cm. in height and 6 mm. in inside diameter, had a glass reservoir bulb, 7.5 cm. in diameter, at its top and a standard taper glass stopcock just above a 10/30 female standard taper joint at the bottom. A Sargent 2 to 5 second capillary was ground down somewhat to fit into a short section of the male portion of this joint and was sealed into it with Varno cement. A 6 mm. layer of degassed Nujol was placed over the amalgam in the reservoir. When the amalgam was not in use, the stopcock was closed and the tip was immersed in distilled water. The stopcock was always opened and the amalgam allowed to flow for about 1 hr. before use.

The dropping amalgam half cell consisted of a tall 200 ml. Berzelius beaker without spout fitted with a rubber stopper bored to accommodate accessories. The salt bridges consisted of inverted U tubes constructed of glass tubing, 12 mm. in inside diameter, slightly constricted to prevent expulsion of a 3% agar. The first bridge also contained 1 *M* KNO_3 and dipped into a beaker containing 1 *M* KNO_3. The second contained saturated KCl and dipped into the S.C.E. half cell. To minimize liquid junction effects, the potentials of the dropping copper amalgam electrode in the aqueous and complexing media were measured, insofar as possible, in the presence of the same excess of the same supporting electrolyte with the same cell. The ionic strength was adjusted to unity with KNO_3.

Copper amalgams of known composition were readily prepared by the cathodic reduction of a known weight of $CuSO_4 \cdot 5H_2O$ (Mallinckrodt Analytical Reagent Grade) dissolved in 0.1 *M* HCl solution. The reduction was performed in a stoppered tall 200 ml. Berzelius beaker, without spout, containing a known weight of mercury as the cathode and a platinum flag electrode as the anode. Near the end of the electrolysis, which required about 3 hr. at 3 volts, the solution was diluted and flushed with nitrogen to remove oxygen. The amalgam was separated by means of a separatory funnel and stored under Nujol in an air-free flask. The reliability of the procedure was confirmed by weighing the mercury before and after the electrolysis. The absence of copper in the electrolysis solution was shown by the absence of any blue color when the solution was made ammoniacal. More dilute amalgams were prepared by mixing known weights of the amalgam and pure mercury. The air-free mixture was then stirred for several hours to insure homogeneity.

Results and Discussion

The Amalgam Concentration.—In order to establish the optimum concentration of copper and to confirm its concentration in the saturated liquid phase amalgam, the potentials of amalgams of varied concentrations were measured *versus* a pure copper electrode in solutions containing the ethylenediamine (en) complex of copper(II). This electrolyte was chosen in preference to one containing the aquocomplex because the electrode has been shown by Poulsen and Bjerrum[2] to be particularly well poised and to behave reversibly over a large range of *p*H. Many investigators[17] have observed that the potential of a copper electrode tends to drift over rather long periods of time in the absence of complexing agents presumably as a result of the formation of copper(I) ions or the red Cu_2O precipitate. The electrolyte contained 0.00101 M $CuSO_4$, 0.1 M en, and sufficient KNO_3 to produce an ionic strength of unity. The reference copper electrode was prepared by plating copper on a 1 cm. square platinum flag electrode, which was then dipped momentarily into 1 M $Hg(NO_3)_2$ solution according to the procedure of Muller and Reuther.[18] Photomicrograms and the electrode potential indicate that the film of mercury formed on the electrode is too thin to form a true amalgam but allows the massive free copper to make contact with the solution without any interference as a result of oxide formation. Both the amalgam electrode and the copper electrode were immersed in the same solution to eliminate liquid junction potentials.

As one would predict for a reversible two phase electrode and in agreement with published results,[18] the two phase amalgam electrode retained the constant potential of +0.0051 volts relative to the copper flag electrode until the concentration of copper was reduced to 0.0027% copper by weight or $5.75 \times 10^{-3} M$, based on a mercury density of 13.534 g. per ml. at 25°. The voltage then increased as a linear function of the negative logarithm of the amalgam concentration. The slope, $\Delta E/\Delta \log(\mathrm{Cu})$, equal to -0.030 ± 0.001 volts, is in good agreement with the theoretical value -0.0296 volts, for a two electron electrode reaction. Duplicate data are not included for the dropping amalgam electrode since the spontaneous potentials were practically identical with those of quiet pools having the same amalgam concentrations. It is evident that the dropping copper amalgam electrode containing less than 0.0027% or $5.75 \times 10^{-3} M$ copper fulfills the conditions of a single phase liquid amalgam discussed in the theoretical section for anodic or zero currents. In the cathodic region the original amalgam concentration must be decreased by the fraction, $i_c/i_{d_{an}}$ below saturation if two phase amalgam formation is to be prevented. The composition of 0.0027% copper in the saturated amalgam at 25° obtained in the present study is in fair agreement with the value 0.00235% obtained by Richards,[10] especially when the low concentration and the possibility of air oxidation are considered.

TABLE I

RELATION OF ANODIC DIFFUSION CURRENT TO COLUMN HEIGHT USING 0.00405% COPPER AMALGAM

Column height, cm.	Drop time, sec.	Flow rate, mg./sec.	$m^{2/3}t^{1/6}$, mg.$^{2/3}$ sec.$^{-1/2}$	$i_{d_{an}}$, μamp.	I_{an}
22.2	11.10	0.636	1.108	3.39	3.55
27.1	9.09	0.7919	1.240	3.84	3.59
32.0	7.62	0.9026	1.313	4.16	3.68
64.0	3.78	1.7999	1.847	7.28	4.57

TABLE II

RELATION OF FLOW RATE, DROP TIME, CAPILLARY CHARACTERISTIC AND ANODIC DIFFUSION CURRENT TO CONCENTRATION OF COPPER IN THE AMALGAM AT THE POTENTIAL OF THE SATURATED CALOMEL ELECTRODE

Weight % copper	Flow rate, mg./sec.	Drop time, sec.	$m^{2/3}t^{1/6}$, mg.$^{2/3}$ sec.$^{-1/2}$	$i_{d_{an}}$, amp.	I_{an}
0.00000	1.465	5.21	1.698	0.000	..
.00050	1.465	5.21	1.698	3.90	3.66
.00100	1.459	5.40	1.704	7.75	3.64
.00220	1.452	5.75	1.716	16.60	3.58
.00250	...	..	...	19.35	3.66

The relation of column height to anodic diffusion current is shown in Table I. The decrease in I_{an}, the diffusion current constant, with decreasing capillary characteristic supports the contention of Strehlow and Stackelberg,[5] that stirring within the drop has an appreciable effect on the apparent diffusion current. These authors found that the flow rate influenced the internal stirring more than did the drop time. Our results are consistent with theirs for the same capillary characteristic in which some internal stirring is indicated. The data in Table I indicate that the capillary characteristic should be less than 1.1 mg.$^{2/3}$ sec.$^{-1/2}$ if the effect of internal stirring is to be essentially eliminated. Stirring produces no effect on the spontaneous potential at zero current since the composition of the interior of the drop is the same as that of the surface. However, with a current flowing, stirring may produce a noticeable effect on the shift of the half-wave potential due to complex formation if different capillaries are used in the aquo and complex solution. The errors will tend to cancel if the same capillary is used for both waves since the electrode will have the same composition at corresponding points on similar waves. Stirring can produce some deviation of the slope from the theoretical in conventional wave analysis which requires that the linear diffusion gradient at the drop's surface persist in the drop as well as in the solution. Although these effects are most easily observed in anodic currents in which the amalgam composition is current limiting, they are also present and produce a similar effect in conventional cathodic polarograms.

The effects of amalgam concentration on drop time, flow rate and anodic diffusion current were also investigated using a particular dropping electrode assembly. The results are given in Table II. The 10% increase in drop time and the 1% decrease in flow rate produce less than 0.5% change in the capillary characteristic and the diffusion current is strictly proportional to the amalgam concentration, even though the I_{an} value of 3.64 μamp M^{-1} mg.$^{-2/3}$ sec.$^{1/2}$ indicates a slight amount of stirring. These observations permit the calculation of amalgam concentrations from diffusion current measurements after a known amalgam has been investigated using the same capillary assembly.

The Aquocopper(II)/Copper Electrode.—The present study indicates that, in general, reasonably accurate values have been used by previous workers for the half-wave potential of the drop-

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[17] A. R. Tourky and S. E. S. El-Wakkad, *J. Chem. Soc.*, 3536 (1950).

[18] F. Muller and H. Reuther, *Z. Elektrochem.*, **48**, 682 (1942); **52**, 44 (1943).

ping mercury electrode in aqueous solution of copper(II) in calculations of complex stabilities. However, the sources of potentials have not usually been discussed in detail. In the present study, the necessary conditions for experimentally observing the reversible electrode potential of the aquo-copper(II) ion/copper couple were readily established because the reversible waves were continuous without inflection across the zero current axis. As illustrated by curve 1, Fig. 1, the anodic-cathodic waves of aquocopper(II) obtained below a pH of about 3.5 fulfill this condition. Furthermore, the slope $(\Delta E)/\frac{i_{d_c} - i}{i - i_{d_a}}$, had the theoretical value 0.030 ± 0.001 volts and the half-wave potentials of the composite wave had the same value as that of the pure cathodic or anodic waves obtained in initial absence of copper in the amalgam and in the solution, respectively, after correcting for the cell's *ir* drop, regardless of the concentration of copper in the amalgam or in solution. An essentially constant half-wave potential of + 0.017 ± 0.001 v. *vs.* the s.c.e. was obtained using dropping mercury electrodes containing zero to 0.0010% copper in a half cell containing zero to 2 millimolar copper(II), 0.001 M HNO_3 and 0.1 M KNO_3 separated from the s.c.e. by a 3% agar salt bridge containing 0.1 M KNO_3, a solution of 0.1 M KNO_3 and a 3% agar salt bridge containing saturated KCl. This value is very close to those reported by Laitinen and co-workers[19] for pure cathodic waves. However, the composition of the solution and the intervening salt bridges is important. For example, values 0.005 and 0.007 v. more positive were obtained in this Laboratory when 0.1 M KNO_3 was replaced by 1 M potassium nitrate and 1 M tetramethylammonium nitrate, respectively. In contrast with the half-wave potential the spontaneous potential of the amalgam electrode is, of course, a function of both the amalgam and the copper ion concentration. In the pH range of 3.0 ± 0.1, the half-wave potential was essentially constant. In more acidic solutions the spontaneous or half-wave potentials became less positive just as would be predicted on the basis of the liquid junction potential for a strongly acidic half cell having a liquid junction with a neutral solution. In unbuffered solutions containing 4 mM Cu^{2+}, 1 M KNO_3 and various concentrations of nitric acid, the dropping electrode containing 0.0022% copper had the following spontaneous potentials *versus* the s.c.e.: at $p\text{H} = 3.02$, $E_{\text{sp.}} = 0.0143$ v.; at $p\text{H} = 2.07$, $E_{\text{sp.}} = 0.0137$ v.; and at $p\text{H} = 1.07$, $E_{\text{sp.}} = 0.0060$v. These experiments prove that the half-wave or spontaneous potential of the aquo ion can be experimentally determined in each laboratory in any noncomplexing electrolyte and a particular cell assembly at a pH of 3.0 ± 0.1. This is of considerable practical importance since the use of salt bridges containing different electrolytes between the half cells produces significant differences in the cell voltage.[2] In this Laboratory the spontaneous or half-wave potential of the aquo-copper(II)/dropping copper amalgam electrode is always determined for each series of experiments using a particular electrode and cell assembly.

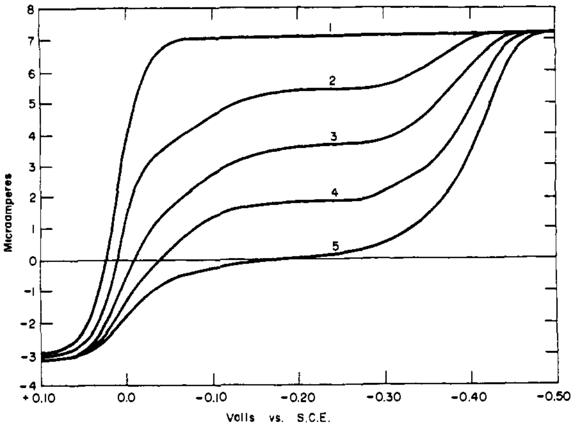

Fig. 1.—Anodic–cathodic polarograms of copper(II) in the presence of limited concentrations of en. $C_{cu} = 0.001$ M, 1 M KNO_3, 0.0005% methyl red, 0.0004% copper in amalgam $m^{2/3}t^{1/6} = 1.70$ mg.$^{2/3}$ sec.$^{-1/2}$. (1) No en; (2) 0.0005 M en; (3) 0.0010 M en; (4) 0.0015 M en; (5) 0.0020 M en.

Above a pH of about 4.0, the waves became increasingly drawn out and showed some tendency to separate into two waves. In order to account for the limited pH range in which the electrode reaction of the aquo species is reversible the various ways for hydroxyl ion to become involved in the electrode reaction through the formation of oxides or complex ions of copper(I) and copper(II) were explored. Even in fairly acidic solutions, hydroxyl ion reacts with copper in either valence state to produce oxide precipitates. It also combines with copper(II) to form hydroxyl complexes. Calculations based on tabulated data in the literature[20-22] show that the red Cu_2O precipitate is formed by a reaction of copper(II) with free copper at the electrode surface even in fairly acidic solutions, and this reaction determines the alkaline limit of the pH range, somewhat above 4.0, in which the electrode reaction is reversible. Similar calculations involving the complex ions formed with ethylenediamine or ammonia indicate that the pH must exceed 13 before Cu_2O will form in the presence of millimolar copper(II) and tenth molar ligand. However, Cu_2O may form in the presence of weaker ligands or lower concentrations of strongly bound ligands.

The Effect of Ligand Deficiencies.—As mixtures of copper(II) ion and en are soluble in all ratios, it was possible to study the effect of ligand deficiencies on the polarographic waves. The polarograms shown in Fig. 1 were obtained in solutions in which a constant copper(II) ion concentration of 0.001 M was maintained and the en concentration was varied from zero to twice that of copper(II) by 0.0005 M increments. The tendency of the polarogram to break up into two widely separated

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[19] H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann, Jr., *J. Am. Chem. Soc.*, **71**, 1550 (1949); **72**, 4729 (1950).

[20] C. Berecki Biedermann, *Arkiv. Kemi*, **9**, 175 (1956).

[21] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Part II, The Chemical Society, Burlington House, W. 1. London, 1958.

[22] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Inc., New York, N. Y.

waves, the first of which appears to be a composite wave is evident. Although it follows from Leden's equation 3 that all species contribute to the potential, the $Cu{\cdot}aq^{2+}$ term, unity, is predominant until $p$en approaches log β_1 or 10.7. At smaller $p$en values the Cu en^{2+} term, β_1(en), becomes predominant until $p$en becomes equal to $^1/_2$ log β_2 or 10.0, beyond which the Cu en_2^{2+} term becomes predominant. As a consequence, the first cathodic wave is due largely to an electrode reaction involving the aquo copper ion. The second wave, which coalesces with the first, is due largely to the monoamine complex and the final separate wave is due to the diamine complex. In all of the waves the anodic portion is due, largely, to the oxidation of copper to aquocopper(II) ion or to the monocomplex if any of the dicomplex is present. The stepwise nature of the wave is not the consequence of sluggish equilibria since the wave heights differ greatly from the corresponding concentrations in the bulk of the solution. Instead, the equilibrium potentials associated with increasing currents are consistent with those calculated for a rapid reversible equilibrium. The displacement of the waves along the voltage axis is due to the increase in concentration of the ligand set free and the decrease in the concentration of copper(II) at the electrode surface during the reduction of the complex. In the stepwise waves, the concentration gradient after the first diffusion current is attained corresponds to that for the final diffusion current. However, only part of this flux of ions is reduced. The balance are converted to higher complexes and diffuse out from the electrode until their reduction potential is reached.

In Fig. 1, the shift of all of the anodic waves of curves 2 to 5 to more negative potentials than curve 1 is due to decrease in the contribution of the Cu aq^{2+} term and the increase in the contribution the Cu en^{2+} and Cu en_2^{2+} terms to the equilibrium potential. In curve 5, Fig. 1, there is only one cathodic wave having a half wave potential in the range 0.3 to 0.4 v. *vs.* s.c.e. This wave is due largely to the reduction of the species, Cu en_2^{2+}, which is predominant in this solution containing $(Cu^{2+}{}_t)$: (en_t) in the ratio of 1:2. The anodic wave is due largely to the reaction

$$Cu + Cu\ en_2^{2+} \rightleftarrows 2Cu\ en^{2+} + 2e$$

In curve 2 there is a cathodic portion of the aquocopper(II) wave with a half wave potential close to zero. This wave is followed very closely by a second small wave in the region -0.05 to -0.15 v. which is due to the reduction of Cu en^{2+}. The final wave is due to the reduction of Cu $(en)_2^{2+}$ as in curve 5. The first cathodic wave of curve 2 approaches a diffusion current of one half the final diffusion current just as would be predicted since one half of the copper(II) is present as the aquo complex. Although the remaining half of the copper(II) is present largely as Cu en^{2+}, the second diffusion current resulting from the reduction of this species only accounts for one-fourth of the final diffusion current. This apparent anomaly is readily accounted for in terms of the conversion of one ion of Cu en^{2+} to Cu en_2^{2+} by reaction with the molecule of en liberated for each Cu en^{2+} ion reduced. Similar arguments account for the two waves in curves 3 and 4. In unbuffered solutions of copper(II) containing a deficiency of en, such that $(en_t) < 2(Cu_t{}^{2+})$, the following generalization can be made. The first diffusion current at -0.2 to -0.3 volts occurs when $(Cu_t{}^{2+})_s$ is reduced to one-half the total en concentration. At this point $\bar{n}$ becomes essentially equal to 2 and $(en)_s$ exceeds a value of about $10^{-7.61}$, so that the $\beta_2(en)^2$ term in Leden's equation becomes predominant. The height of the final wave always corresponds to that calculated by assuming all of the en present at the electrode surface forms Cu en_2^{2+}.

The potentials corresponding to all currents in Fig. 1 agree reasonably well with those calculated by assuming that all reactions, including hydrolysis of the en and its association with H^+ as well as Cu^{2+} reach equilibrium rapidly compared to the rates of diffusion. For example, in curve 2 the calculated shift in potential of the first wave from that for the aquo complex at $i = {}^1/_2\ i_{d_c}$ is 0.017 v. compared to the observed shift of 0.025 v. The corresponding shift of the second half-wave potential is calculated to be 0.328 v. compared to an observed shift of 0.334 volts. In curve 4 the corresponding shift of the first and second waves are 0.092 v. and 0.390 compared to calculated values of 0.065 and 0.395 v., respectively. The agreement is satisfactory when the exceedingly poor poise of the electrode in the presence of these exceedingly low concentrations of unbuffered free en is considered. The general agreement between calculated and observed potentials at varied currents improves with an increase in (en). For example, the calculated shift of the half-wave potential of the final wave from that for the aquo ion in curve 5 is 0.407 v. compared to the observed value of 0.405 v. At this point the concentration of en which is not complexed is 0.001 *M* of which 33% is hydrolyzed to Hen^+. Both the observed and calculated slope of this wave are 0.067 v. from $i = {}^1/_4 i_d$ to $i = {}^3/_4 i_d$ instead of the usual 0.296 v. This is due to the increase in concentration of free en from 0.00025 to 0.00108 *M* at the electrode surface due to the reduction of the complex.

The series of polarograms obtained in solutions of varied pH containing 0.001 *M* Cu^{2+} and an excess of en close to 0.1*M* are shown in Fig. 2. The ionic strength was maintained at unity with KNO_3 and the pH was varied by increasing concentrations of HNO_3. Although curves 2 to 4 and especially 3 appear drawn out, the electrode reaction is essentially reversible. The apparent anomalous appearance of these waves is readily accounted for in terms of the buffering capacity of the solution as illustrated by the acid titration curve of ethylenediamine.[23] Since the pK_a's for the successive addition of two hydrogen ions to en are 10.20 and 7.52 ± 0.03, the first and second equivalence points are reached at a pH of 8.9 and 4.3. The solution is poorly buffered in the pH range of 9.4 to 8.4 and nearly or entirely unbuffered at pH values smaller than about 6.8. Curve 4, Fig. 2, obtained at a pH of 5.08 has the most

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(23) J. I. Watters, *J. Am. Chem. Soc.*, **81**, 1560 (1959).

anomalous appearance. At this low (en) 84% of the copper(II) ion in the bulk of the solution is present as Cu en_2^{2+}. When the current reaches 80% of its diffusion value, 1.44×10^{-3} M en is released at the electrode surface. This concentration of en is sufficient to change (en) to $10^{-6.62}$ at this proximity to the acidimetric equivalence point. The calculated potential shift is 0.201 v. compared to the observed shift of 0.221 v. Curve 3 was obtained at a pH of 4.02 slightly beyond the acidimetric equivalence point of en which is in the region of maximum pH change on the titration curve. When the current reaches about 90% of its diffusion value, (en) reaches the critical value of $10^{-7.61}$ corresponding to $\bar{n}$ approaching 2. The final small wave is due to the reversible reduction of the Cu en_2^{2+} formed at these currents and is not, as one might surmise, due to a small concentration of a difficultly reduced species in sluggish equilibrium with more easily reduced species.

The slightly greater slope of 0.035 v. observed in curve 8 is due to the decreased buffering capacity of en in the pH range of 8.4 to 9.4. This deviation has also been observed at the acidimetric equivalence point in polyphosphate buffers and is to be anticipated even though the system behaves reversibly. If the buffering effect were responsible, the inclusion of a second buffer with enhanced buffering capacity should improve the shape of the waves. The addition of 0.1 M sodium acetate which has a good buffering capacity at pH of 5 yielded single continuous waves at pH's of 5.03, 6.03 and 7.01. A small terminal wave persisted at the pH of 5.03 and the slope was large at a pH of 6.03. Both effects are accounted for in terms of the increased buffering capacity. The use of this buffer in complex stability studies is limited by the formation of acetato complexes in en deficient solutions.

To confirm the conclusion that the electrode reaction in the poorly shaped waves is essentially reversible and that sluggish equilibrium plays no part, polarograms of the solution having a pH of 5.08 were obtained in the temperature range of 15 to 46.5° and with mercury heights from 42.9 to 93.5 cm. The shapes of the waves and relative currents at various potentials remained practically unchanged, confirming the absence of any kinetic effect. As will be shown next, the spontaneous potentials at zero current were within ±1 millivolt of the predicted value in all of the buffered but acetate-free solutions.

To test the application of Leden's method, to spontaneous potential data, an experiment was performed in which the pH and the spontaneous potentials of a dropping 0.0005% copper amalgam electrode were measured in a mixture of two solutions, one of which was acidified with 0.2461 M HNO_3 while both contained 0.01 M copper(II), 0.1143 M en and sufficient KNO_3 to produce an ionic strength of unity. Periodically, portions of the solution were removed in order to obtain a continuously changing ratio from the acidic to an essentially acid free solution but with all other concentrations unchanged. An intermediate agar salt bridge containing 1 M KNO_3 separated the half cell from the saturated calomel reference electrode.

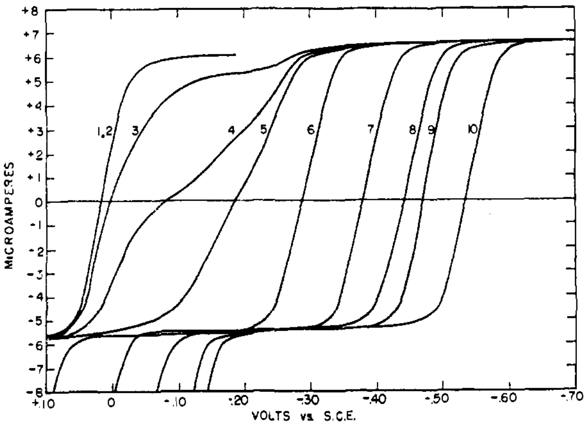

Fig. 2.—The effect of varying pH on anodic–cathodic polarograms of copper(II) in the presence of excess en. $C_{cu} = 0.001$ M, $C_{en} = 0.09846$ M, 0.0005% methyl red, sufficient KNO_3 to produce unit ionic strength, 0.00073% copper in amalgam, $m^{2/3}t^{1/6} = 1.70$ mg.$^{2/3}$ sec.$^{-1/2}$. (1) No en, pH = 3.00; (2) pH = 3.00; (3) pH = 4.02; (4) pH = 5.08; (5) pH = 6.02; (6) pH = 6.99; (7) pH = 8.03; (8) pH = 9.00; (9) pH = 10.01; (10) pH = 11.44.

As shown in Table III, the spontaneous potentials, increase slightly to a value of 0.0556 v. at a pH of 2.80 indicating no complex formation in this pH range. This value was taken as the spontaneous potential of the aquo copper(II)/copper couple having this particular composition. Below this pH the voltage increases in a regular way.

TABLE III

SPONTANEOUS POTENTIALS OF THE DROPPING COPPER AMALGAM ELECTRODE IN COPPER(II) EN SOLUTION WITH VARIED pH

pH	$E_{sp.}$ vs. s.c.e.	ΔE	pen	Log F_0	Log F_1	Log F_2
1.88	+0.0545					
2.38	.0555					
2.80	.0556					
3.28	.0552					
3.58	.0533	0.0023	11.45	0.0778	10.75	
3.88	.0478	.0078	10.87	.2637	10.75	
4.18	.0358	.0198	10.29	.6694	10.76	
4.50	.0171	.0385	9.68	1.302	10.96	
5.49	− .0802	.1418	7.71	4.794	12.50	20.21
6.10	− .1564	.2120	6.51	7.167	13.68	20.19
6.42	− .1939	.2492	5.89	8.425	14.31	20.20
7.85	− .3299	.3855	3.50	13.03	16.53	20.03
11.45	− .4786	.5342	1.03	18.06	19.09	20.12

The limiting value of F_1 as (en) decreases is equal to β_1 or $10^{10.75}$ while the constant value of F_2 is $10^{20.20}$ using Bjerrum's[2] values for the acidity constants of en. However, the final value of $10^{20.12}$ is independent of the values taken for the acidity constants since the extent of hydrolysis is negligible. The excellent agreement of these results with published and confirmed values illustrates the advantage of the dropping copper amalgam electrode in the investigation of complex equilibria provided stable intermediates are not involved in the electrode reaction. Measuring the potential zero current instead of at the residual current is permissible only if sufficient metal ion, *i.e.* one millimolar, is present in the solution so that these potentials are essentially equal.

Stepwise Monoamine Waves.—It has been shown by Stackelberg and Freyhold[1] that copper(II) in ammoniacal solutions yields two reversible stepwise cathodic waves which involve the intermediate formation of a stable amminocopper(I) complex. They solved the complexity constants of the ammonia complexes of copper in both valence states on the basis of the shift in half-wave potentials as a function of ammonia concentration. Furman and Cooper[7] observed an analogous two step oxidation wave using the dropping copper amalgam in ammoniacal solutions. The present study was extended to include the composite anodic–cathodic waves obtained with copper(II) in solution using a copper amalgam dropping electrode in order to establish the nature of the electrode process determining the spontaneous electrode potential at zero current. Several series of polarograms were obtained in which the copper(II) ion concentration was varied from zero to 0.001 *M* and the concentration of free copper dissolved in mercury was varied from zero to 0.00085%. By increasing the amalgam concentration and decreasing the copper(II) ion concentration, it was possible to shift the waves continuously along the current axis from the cathodic to anodic–cathodic and finally entirely to the anodic region. For a given concentration of ammonia, all three half-wave potentials for corresponding cathodic, composite and anodic waves were practically identical proving the electrode reactions to be completely reversible. Both the first and second diffusion currents in all cathodic waves reached a maximum value in approximately 0.2 *M* $\mathrm{NH_3}$ indicating that intermediates, especially the tetrammino-species, have a larger diffusion coefficient than either the aquo or the final pentaamine species. In contrast, all of the corresponding diffusion currents of purely anodic waves had exactly the same values for all ammonia concentration since the diffusion of copper within the amalgam was the current limiting process.

The rising portion of the first cathodic wave if obtained with a pure mercury dropping electrode is due to the reduction of copper(II) to copper(I) while the second wave is due to the reduction of copper(I) to the free state. With no copper(II) in solution, the corresponding anodic waves obtained with dropping copper amalgam electrodes are due to the reverse processes. With copper(II) ion present in solution and free copper in the amalgam, both processes can occur simultaneously so the net current flow is the algebraic sum of the two. It was experimentally proved that the composite wave is equal to the algebraic sum of the simple anodic wave and the simple cathodic wave for the same copper(II) and amalgam concentrations after correcting for residual currents and differences in capillary characteristics.

When the sum of the anodic and cathodic waves is equal to zero or more exactly to the residual current, the electrode assumes its so-called spontaneous potential. This potential will be maintained even though the electrode is disconnected. Furthermore, the simultaneous diffusion of free copper from the interior of the drop to the surface where it is oxidized to copper(I) and diffusion of copper(II) from bulk of the solution where it is reduced to copper(I) will also continue. By varying the proportions of the copper(II) ion concentrations and copper amalgam concentration, the polarogram may be made to cross the zero current axis at any potential between the final anodic diffusion current and the final cathodic diffusion current.

If the copper concentration in the amalgam is relatively small so that $3I_{\mathrm{am}}(\mathrm{Cu_{am}}^0)_\mathrm{b} = I_\mathrm{m}(\mathrm{Cu}^{2+})_\mathrm{b}$, the spontaneous potential and the first half-wave potential of the cathodic wave coincide. The $\mathrm{Cu}^{2+}/\mathrm{Cu}^{1+}$ couple determines the electrode potential because the free copper in the amalgam is essentially quantitatively oxidized to copper(I) as it reaches the surface by the copper(II) ion which diffuses to the surface at one-third of its maximum rate. By increasing the copper concentration in the amalgam so that $I_{\mathrm{am}}(\mathrm{Cu_{am}}^0)_\mathrm{b} = I_\mathrm{m}(\mathrm{Cu}^{2+})_\mathrm{b}$, the plateau between the waves crosses the zero current axis. At this point the electrode is essentially unpoised because copper(II) from the solution reacts nearly quantitatively with the free copper in the amalgam producing the copper(I) complex so that only small equilibrium concentrations of the copper(II) complex and free copper remain in the solution and the electrode, resp., at the interphase. If the concentration of the copper in the amalgam is further increased so that $I_{\mathrm{am}}(\mathrm{Cu_{am}}^0)_\mathrm{b} = 3\,I_\mathrm{m}(\mathrm{Cu}^{2+})_\mathrm{b}$, the spontaneous potential and the second half-wave potential of the cathodic wave coincide. The copper(II) complex diffuses to the electrode surface at its maximum rate and is quantitatively reduced to copper(I). Copper within the mercury drop diffuses to the surface at one-third its maximum rate where it forms copper(I). The equilibrium concentration of free copper at the amalgam surface is two thirds that in the interior of the drop. Thus, the $\mathrm{Cu}^{1+}/\mathrm{Cu}^0$ couple determines the spontaneous potential even though copper(II) is present in the bulk of the solution.

It was concluded that the dropping copper amalgam electrode offers no particular theoretical advantage over the dropping mercury electrode when copper(II) complexes which yield stepwise polarographic waves are present in the bulk of the solution, since equilibrium is never attained between the amalgam and the copper(II) ion in the bulk of the solution. Diffusion processes are involved both in the amalgam and in the solution even though no net current is flowing. There is, in fact, a possibility for a small error if, as is true in ammonia solutions, the diffusion coefficient of the copper(II) complex ion in solution changes with ammonia concentration. However, if stable copper(I) complexes are present in the bulk of the solution, spontaneous potentials correspond to equilibrium between the electrode and the complex copper(I) species present in the bulk of the solution and the advantages of the amalgam electrode are maintained.

Methylamine and ethylamine also yielded stepwise waves, but in the latter study the first cathodic wave was masked by the wave for the anodic dissolution of mercury. Monodentate ligands tend to favor the stepwise reduction while bi- or polydentate ligands favor the direct reduction. This enhanced stability of the copper(II) complex relative to copper(I) is reasonable when one considers that two linear sp bonds with copper(I) often appear to be more stable than four sp^3 bonds. Monodentate amines are as effective as dangling polydentate amines for forming these linear sp complexes. Copper(II) tends to form four square dsp^2 bonds so the copper(II) complexes with bidentate ligands are very stable. Consequently their reduction waves occur at more negative potentials than those of any of the possible intermediate sp linear copper(I) complexes.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON, EUGENE, OREGON]

Thermodynamics of Ion Hydration as a Measure of Effective Dielectric Properties of Water

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RECEIVED JULY 5, 1961

An improved method has been developed for evaluating the changes in thermodynamic properties associated with hydration of individual species of gaseous monatomic ions. Application of the method to entropy data leads to consistent results only by neglecting the contributions observed during solvation of neutral atoms of the same size. The partial molal entropy of hydrogen ion at 25° is estimated to be −3.3 cal./mole deg. in satisfactory agreement with thermocell calculations. For cations having the electronic structure of an inert gas, the free energies of hydration indicate effective dielectric constants that depend only on size of ion and are virtually independent of charge. These effective dielectric constants can be used to estimate local dielectric constant as a function of distance from the center of a cation, but the data are not sensitive enough to permit extrapolation beyond the radius of the largest cation studied. Cations not having an inert gas structure show larger absolute enthalpies and free energies of hydration as predicted by ligand field theory. The singly charged d^{10} ions Cu^+, Ag^+, and Au^+ exhibit extreme solvation effects that are not observed for any other ions, including the isoelectronic species Zn^{2+}, Cd^{2+}, and Hg^{2+}. Thermodynamic properties change more during the hydration of anions than for cations of the same size, and the few available data do not exhibit the monotonic variation with ionic size that is observed with cations.

Introduction

If a charge q is reversibly transferred from a conducting sphere of radius r in a vacuum to an identical sphere in a medium of dielectric constant ϵ, the change in electrostatic free energy is

$$\Delta F^0_{\text{el}} = -\frac{q^2}{2r}\left(1 - \frac{1}{\epsilon}\right) \qquad (1)$$

Also

$$\Delta S^0_{\text{el}} = -\left(\frac{\partial \Delta F^0_{\text{el}}}{\partial T}\right)_{\text{P}} = \frac{q^2}{2rT\epsilon}\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_{\text{P}} \qquad (2)$$

These equations are unquestionably valid for spheres of macroscopic dimensions. If they are applied to ions of absolute charge ze dissolved in water at 25° (for which[1] $\epsilon = 78.30$ and $(\partial \ln \epsilon)/\partial \ln T)_{\text{P}} = -1.357$), they predict the theoretical values

$$\Delta F^0_{\text{theo}} = -163.89 \frac{z^2}{r/\text{Å.}} \text{ kcal./mole} \qquad (3)$$

$$\Delta S^0_{\text{theo}} = -9.649 \frac{z^2}{r/\text{Å.}} \text{ cal./mole deg.} \qquad (4)$$

The absolute free energy changes observed for hydration of real ions are less than those predicted by equation 3. Latimer, Pitzer and Slansky[2] showed that an empirical fit with theory could be obtained by adding a constant factor to the crystallographic radii of the ions. Little attempt has been made to adopt an alternative treatment of experimental data by assuming that ion sizes are known and constant but that dielectric saturation effects occur in the neighborhood of solvated ions. Near the surface of an ion, the electrostatic potential gradient is of the order of millions of volts per cm. Such an intense field causes extreme polarization of the solvent, and it has long been recognized that it must be a very poor approximation to assume that the bulk dielectric constant of the medium can be used to describe effects at distances of the order of molecular dimensions. The purpose of the present paper is to show that thermodynamic measurements on solvated ions can be used to calculate effective dielectric properties of solvent in the neighborhood of these ions.

Formulation of Problem

Let monatomic cations and anions be represented by M^{+z} and X^{-z}, respectively. Let the hydration reaction be the transfer of ions from gas phase at a standard state of one atmosphere fugacity to aqueous solution at a standard state of one molal activity. Then

$$M^{+z}(g) \longrightarrow M^{+z}(aq) \quad (\Delta F^0_{\text{hyd}}, \text{cation}) \qquad (5)$$

$$X^{-z}(g) \longrightarrow X^{-z}(aq) \quad (\Delta F^0_{\text{hyd}}, \text{anion}) \qquad (6)$$

where the parentheses represent a convention to be followed in this paper to permit easy reference to reactions defining the subscripts applied to various changes in thermodynamic properties.

Let A be a monatomic inert species of the same radius as an ion of interest. The hydration of this neutral species is represented by

$$A(g) \longrightarrow A(aq) \quad (\Delta F^0_{\text{neut}}) \qquad (7)$$

The hydration of an ion can be conceived to proceed by discharging the gaseous ion, hydrating the resulting neutral species, and then recharging it. Then we can write

$$\Delta F^0_{\text{hyd}} = \Delta F^0_{\text{neut}} + \Delta F^0_{\text{el}} \quad \text{(cation or anion)} \qquad (8)$$

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[1] C. G. Malmberg and A. A. Maryott, *J. Res. Nat. Bur. Standards*, **56**, 1 (1956).

[2] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).