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

A Reversible Dropping Gallium Amalgam Electrode

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A dropping gallium amalgam electrode has been used successfully to obtain anodic and composite polarographic waves. Polarographic irreversibility was observed for the gallium couple in KNO_3, but anodic, composite and cathodic waves obtained in 7.5 *M* KSCN satisfied accepted criteria for a polarographically reversible 3 electron reaction. Ga^{+3} reduction waves obtained with the d.m.e. in 7.5 KSCN are diffusion controlled, and $i_d/C_{Ga^{+3}}$ is a constant above 0.3 mmolar gallium.

Introduction

According to Fogg[1] studies on the electrochemistry of gallium prior to 1934 dealt either with measurements of E^0 for the gallium electrode or with conditions for the irreversible electrolytic deposition of gallium. Later, Stelling[2] obtained reproducible null-point values for E_{Ga} with a dropping gallium amalgam electrode and concluded that this indicated reversibility for the gallium couple. However, some current–voltage curves[3] were obtained with large surface electrodes, but the curves were not adaptable to rigorous testing for reversibility of the reaction. A thermodynamic study[4] of the gallium electrode in halide and perchlorate solutions has shown potentiometric reversibility for the solid metal but has indicated the liquid electrode to be irreversible.

Early work[5-10] on the reduction of gallium (III) at the dropping mercury electrode (d.m.e.) had shown irreversibility in perchlorate, nitrate, sulfate, ammoniacal, halide, acetate, citrate, sulfosalicylate and EDTA solutions. In addition the authors have demonstrated irreversibility for the reaction in oxalate, formate, tartrate and malonate solutions. Vinogradova and Chudinova[9] and Zelyanskaya and Bausova[11] have reported finding well-defined polarographic waves for gallium(III) in salicylate and in thiocyanate solutions buffered with salicylate but they give no evidence of the independent effect of thiocyanate on the reaction.

It was the purpose of this study, therefore, to investigate the preparation and use of a dropping gallium amalgam electrode and to use this electrode in conjunction with the d.m.e. to examine the polarography of gallium in strong solutions of thiocyanate. The criteria inherent in the equation for the polarographic wave were used as a test to determine the extent of polarographic reversibility.

Experimental

Apparatus.—Current–voltage curves were obtained with a manual instrument in which the potential applied to the cell was taken from a bridge of fixed resistors. Potential increments of 0.02 and 0.20 volt in the range + 0.40 to −2.40 volts were available. A standard resistor and K-1 type potentiometer were used to calibrate the circuit.

The reservoir and stand-tube used for the dropping gallium electrode were patterned after the apparatus of Cooper and Wright and Furman and Cooper.[12] Cells were constructed from 100 and 180-ml. electrolytic type beakers and were capped with a rubber stopper drilled to accommodate the dropping electrode, nitrogen inlet tube, salt bridge and glass electrode. Connection was made to the saturated calomel electrode with a 10-mm. diameter bridge containing saturated KCl in 4% agar or with a bridge containing saturated KNO_3 *via* a saturated KCl–KNO_3 reservoir. High purity dry-pumped tank nitrogen was used without further purification for deaeration of the polarographic test solutions and for the exclusion of oxygen in the amalgam work.

Data were taken at 25.0 ± 0.1° and applied potentials were corrected for cell resistance which was measured with an Industrial Instruments Inc. conductance bridge, Model RC-1B. The potential of the calomel electrode was established by comparing the observed value of −0.461 ± 0.003 volt *vs.* S.C.E., which was obtained in 0.1 *M* KNO_3, for the $E_{1/2}$ of the Tl^+ reduction wave with the accepted value −0.459 ± 0.003 volt *vs.* S.C.E. given by Kolthoff and Lingane.[13] Measurements of *p*H were made with a Beckman Model H-2 meter calibrated with potassium bitartrate buffer (*p*H 3.56 at 25.0°).[14]

Reagents.—Gallium metal and gallium nitrate octahydrate, both "spectroscopically pure" were obtained from Johnson, Matthey and Company, Ltd. Mercury and other chemicals were of reagent grade. The mercury was "pinholed" at least once before use. Potassium thiocyanate was prepared as a 10 *M* stock solution and was standardized by titration with silver nitrate solution. Demineralized, doubly distilled water was used throughout the work.

Preparation of Oxide-free Amalgams.—Surface oxide films were removed from the as-received gallium metal pellets by immersing them in 1 *M* hydrochloric acid solution on a small watch glass. The system was warmed until the gallium melted (approx. 30°). The adherent oxide film quickly dissolved in the acid solution leaving a bright, shiny globule of liquid gallium which was then quickly frozen in cold ethanol. The resulting hard, shiny pellet could thus be handled and weighed conveniently.

The solid, oxide-free pellet of gallium was added with the exclusion of air to a weighed quantity of mercury which had been evacuated and washed several times with high purity nitrogen. The gallium dissolved in the mercury within a few minutes. The flask holding the amalgam then was evacuated and shaken periodically for an hour. After this treatment the stoppered, evacuated 250-ml. suction flask containing the amalgam was inverted and the liquid metal transferred to the evacuated reservoir of the dropping electrode assembly *via* a short length of *dry* Tygon tubing. Pressure then was restored to the reservoir with high purity nitrogen and mineral oil added to cover the surface of the amalgam. After each run, the nitrogen pressure in the reservoir was adjusted to atmospheric and the amalgam

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allowed to drop continuously into ethanol or acidified distilled water.

Capillary Characteristics.—A Sargent "2–5 second" capillary was used for the dropping electrode throughout the work and was sealed into the glass sleeve at the bottom of the amalgam reservoir with Varno Cement. The $m^{2/3}t^{1/6}$ value for the capillary with pure mercury dropping into 7.5 M KSCN was 2.403 mg.$^{2/3}$ sec.$^{-1/2}$ at $E = -1.20$ volts *vs.* S.C.E.; for the amalgams, 2.143 mg.$^{2/3}$ sec.$^{-1/2}$ at $E = -1.00$ volt *vs.* S.C.E. in 7.5 M KSCN; 2.125 mg.$^{2/3}$ sec.$^{-1/2}$ at $E = -1.20$ volts *vs.* S.C.E. in 0.1 M KNO_3 containing 0.005% gelatin.

Results and Discussion

Dropping Gallium Amalgam Electrode.—Preliminary studies with the dropping gallium amalgam electrode proved that the usual arrangement of leveling bulb and standtube with connecting Tygon tubing was unsuitable (because of contamination) for maintaining a stable amalgam. Replacement of the Tygon with glass eliminated this difficulty. However, if the amalgam were not allowed to drop continuously between runs the anodic current would decrease and finally increase to approximately its former constant value. Occasionally, the anodic current would exceed its former constant value but would return eventually. The first runs would then show a smaller current, later runs a higher current and eventually a constant current. At higher amalgam concentrations the capillary showed a tendency to clog near the tip because of oxide formation. At amalgam concentrations of 0.0005% gallium or less, clogging did not occur and the characteristics remained constant.

Polarography in HCl and KNO_3 Solution.—Normal maxima were observed in anodic current–voltage curves obtained with the dropping gallium amalgam electrode in 1 M hydrochloric acid solutions. These maxima could be eliminated by addition of sufficient Triton X-100 but not without a positive shift in $E_{1/2}$. Triton X-100 also suppressed the flat anodic maximum observed in 0.1 M potassium nitrate. Gelatin in concentrations greater than 0.0025% was found satisfactory for suppression of maxima. Later it was observed that maxima were entirely suppressed in strong (7.5 M) thiocyanate solution and no additional suppressor was needed.

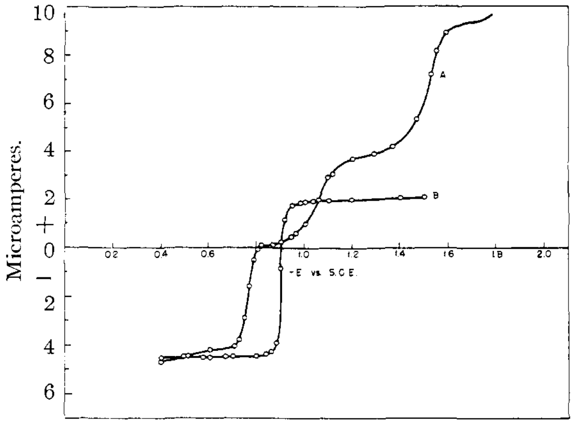

Fig. 1.—Polarograms taken with the dropping gallium amalgam electrode (0.0002% Ga) of 0.5 mM $Ga(NO_3)_3$: curve A, in 0.1 M KNO_3; curve B, in 7.5 M KSCN.

Figure 1, curve A shows a complete polarogram obtained with the gallium amalgam electrode (0.0002% Ga) dropping into a solution containing 0.5 mM $Ga(NO_3)_3$, 0.1 M KNO_3 and 0.005% freshly prepared gelatin. The observed $E_{1/2}$ value, −0.76 volt *vs.* S.C.E., of the anodic wave falls within the range expected for an amalgam of this concentration based upon the standard oxidation potential of +0.58 volt at 29.78° for the liquid gallium–gallium ion couple reported by Challenger.[6] The cathodic portion agrees well with that observed by Challenger who used 0.5 mM $GaCl_3$ in 0.1 M potassium chloride containing 0.005% gelatin. However Challenger's $E_{1/2}$ value of −1.11 volts is more negative than the −1.05 volt observed by the authors in nitrate solutions. Excellent agreements with Challenger's values for the *cathodic* diffusion current and the diffusion current constant in 0.5 mM solutions were obtained. Challenger's more negative values for $E_{1/2}$ may be explained in part as the result of complexing in chloride solution or as a difference in junction potential. From Fig. 1 it appears that the overpotential for the gallium couple in 0.1 M KNO_3 is approximately 0.29 volt.

Cathodic waves obtained with the dropping mercury electrode in solution containing 0.5 mM $Ga(NO_3)_3$, 0.1 M KNO_3 and 0.005% gelatin were essentially the same as those obtained with the dropping amalgam electrode.

Polarography in Thiocyanate Solutions.—A series of cathodic current–voltage curves obtained with the mercury electrode dropping into a solution 0.5 mM in $Ga(NO_3)_3$, 0.005% in gelatin, a range of 0–0.5 M KSCN and enough KNO_3 to maintain an ionic strength of 0.5 M showed a progressive improvement in the shape of the wave as well as a shift of $E_{1/2}$ to more positive values *vs.* S.C.E. as the concentration of KSCN increased. At 0.5 M KSCN the reduction wave was well defined and had an $E_{1/2}$ of −0.88 volt *vs.* S.C.E.

A plot of E_{applied} *vs.* log $[(i - i_{d_a})/i]$ for the anodic wave obtained with the gallium electrode (0.0002% Ga) dropping into a solution containing only 7.5 M KSCN gave a straight line with reciprocal slope of 0.022 volt and an $E_{1/2}$ equal to -0.905 ± 0.003 volt *vs.* S.C.E. when log $[(i - i_{d_a})/i] = 0$. This slope agrees well with the theoretical value 0.020 predicted by the Nernst equation for a three electron change.

Composite current–voltage curves were obtained with a gallium amalgam (0.0024% Ga) electrode in a solution 5.0 mM in $Ga(NO_3)$, 1.0 M in KSCN, 0.1 M in KNO_3 which was also 0.002% in gelatin. The natural pH was 3.4. In addition to a well-defined anodic wave the data indicated two irreversible cathodic waves the first of which corresponds to the reduction of Ga(III) to the metal while the second, at $E_{1/2} = -1.45$ volts *vs.* S.C.E., is comparable in height to the first wave and is probably the hydrolysis wave noted by Challenger.

Curve B in Fig. 1 shows the composite wave obtained with the dropping amalgam electrode (0.0002% Ga) in 7.5 M KSCN containing 0.5 mM $Ga(NO_3)_3$ but no suppressor. The cathodic diffusion current is approximately one-half that observed in 0.1 M KNO_3 (Fig. 1), and this decrease in

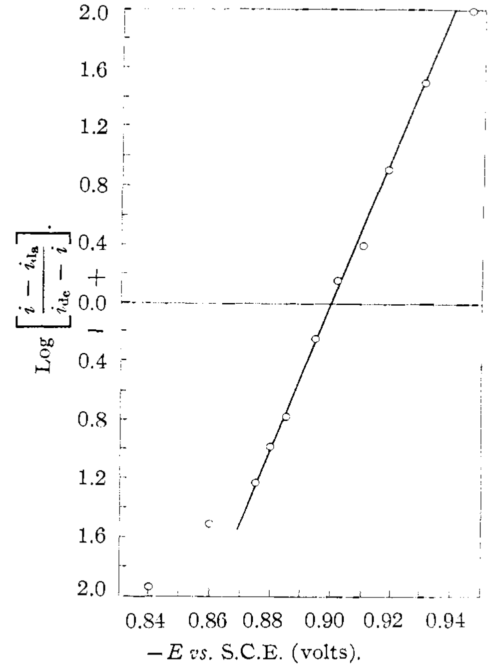

Fig. 2.—Plot of E *vs.* log $[(i - i_{d_a})/(i_{d_c} - i)]$ for composite curve in Fig. 1.

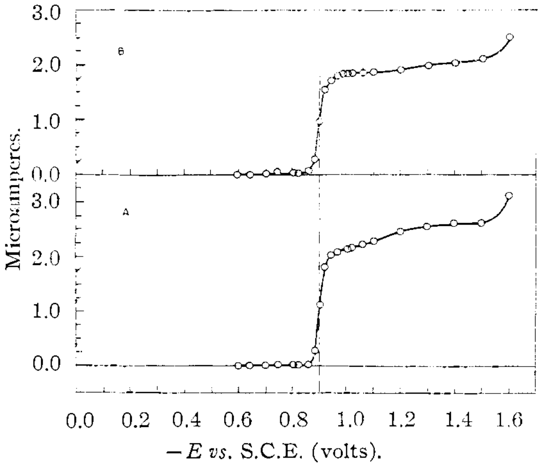

Fig. 3.—Cathodic current–voltage curve obtained with dropping mercury electrode in 7.5 M KSCN and 0.50 mM $Ga(NO_3)_3$. Curve B recorded 24 hours after curve A.

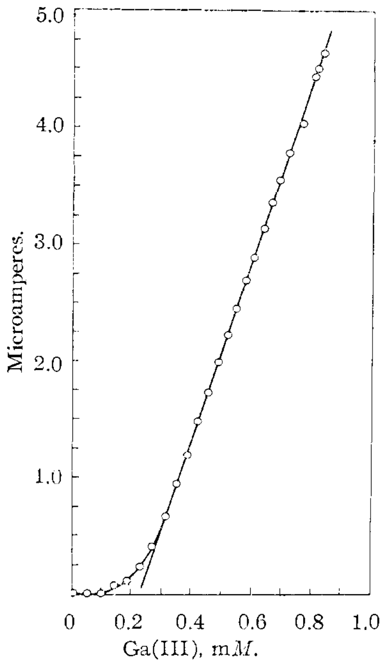

Fig. 4.—Plot showing constancy of i_d/c for gallium nitrate concentrations 0.30–0.83 mM.

current probably reflects the combined effects on the diffusion process of complexing and increased viscosity in the strong thiocyanate solution as well as the effect of adsorption of thiocyanate on the electrode surface. No hydrolysis wave was observed in 7.5 M KSCN. A plot of E_{applied} *vs.* log $[(i - i_{d_a})/(i_{d_c} - i)]$ for this wave is shown in Fig. 2. The curve is linear with reciprocal slope of 0.020 volt and indicates an $E_{1/2}$ of 0.900 ± 0.003 volt *vs.* S.C.E.

Figure 3 shows typical current–voltage curves for 0.50 mM $Ga(NO_3)_3$ in 7.5 M KSCN obtained with the d.m.e. Curve B was recorded 24 hours after curve A. The first wave of curve A was shown to be the polarographically reversible three-electron reduction of Ga(III) to the metal whose $E_{1/2} = -0.900 \pm 0.003$ volt *vs.* S.C.E. The diffusion current constant for this wave $I_A = i_d/Cm^{2/3}t^{1/2}$ is 1.67. The diffusion coefficient D calculated from this relationship and the assumption that $n = 3$ is equal to 0.84×10^{-6} cm.^{2}/sec. The small second wave with $E_{1/2} = -1.13$ volts *vs.* S.C.E. observed prior to the final current rise is pronounced in A but is less so in curve B indicating that the concentration of this species (probably a hydroxy or thiocyanate–hydroxy complex) is time dependent. The proximity of these two reduction waves may account for the "irreversibility" previously noted for the reduction wave at lower thiocyanate and higher gallium concentrations.

The half-wave potentials of current–voltage curves at gallium concentrations 0.23 to 0.83 mM taken with the d.m.e. in 7.5 M KSCN were constant at 0.900 ± 0.003 volt *vs.* S.C.E. and agree well with $E_{1/2} = -0.902 \pm 0.003$ volt *vs.* S.C.E. for 2.5 mM gallium in the same supporting electrolyte.

Diffusion control[13] of the cathodic currents was shown by linear variation of the diffusion current at −1.0, −1.1 and −1.2 volts with $h_0^{1/2}$, the square root of the corrected mercury height, for a solution 2.5 mM in $Ga(NO_3)_3$ and 7.5 M in KSCN.

The variation of the corrected diffusion current with gallium concentration (in 7.5 M KSCN) over the range 0.0 to 0.83 mM gallium was found to be constant above 0.30 mM $Ga(NO_3)_3$. This behavior is shown in Fig. 4. It thus appears that the diffusion current–concentration relationship follows an Ilkovic-type equation in the concentration range above 0.3 mM gallium.

The half-wave potentials found in this work and reported here are, of course, formal values. They include an unknown junction potential which was reproducible in successive experiments.

These results indicate that the gallium couple is polarographically reversible in solutions high in thiocyanate and that under these conditions maximum suppressors are unnecessary for the elimination of anodic or cathodic maxima. The primary cathodic reaction in strong thiocyanate solution is the reversible reduction of gallium(III) to the metal, and the current is controlled by diffusion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

The Application of Light Scattering to the Study of the Hydrolytic Aggregation of Ions[1]

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The use of light scattering measurements on systems of polyelectrolytes in the presence of supporting electrolytes is discussed with particular emphasis on low molecular weight inorganic polymers of relatively high charge. Equations are developed for the determination of the degree of aggregation of charged species in the presence of supporting electrolyte. Estimates are made of the error caused by the assumption that the turbidities of the various components are additive under these conditions.

Although the theory of light scattering in multicomponent systems has been rather thoroughly discussed,[3-5] the application of light scattering measurements to the determination of molecular weights and degrees of aggregation of polymers with high charge to weight ratios has not been considered in detail.

Equations have been developed for the determination of molecular weights of charged protein molecules in the presence of supporting electrolyte[6]; however, the experimental conditions for the study of proteins are considerably different from those used in the study of ionic aggregation. The light scattering of these inorganic polyelectrolytes must be studied at relatively high concentrations to permit accurate turbidity measurements. This, in turn, necessitates the use of rather high concentrations of the supporting electrolyte. Since the differential refractive index of the supporting electrolyte is not negligible in comparison to that of the polymer, as is usually true with proteins, the contributions of all of the components in the system to the turbidity must be carefully considered. In many respects, this paper is a parallel of the discussion by Johnson, Kraus and Scatchard[7] of the application of sedimentation equilibrium in the ultracentrifuge to the study of similar systems.

Several workers have used light scattering measurements to determine approximate molecular weights of the isopoly and heteropoly acids and their salts[8-12] and aggregates formed by the hydrolysis of multivalent metal ions.[13]

It has been observed that the equation which describes the scattering in relatively dilute solutions of non-electrolytes

$$Hc/\tau = 1/M_w + 2Bc \qquad (1)$$

appeared to be obeyed when the measurements on the inorganic polyelectrolytes were made on solutions with a relatively large and constant concentration of supporting electrolyte.[11] Similar behavior also was observed with a large but variable concentration of supporting electrolyte.[12,13] In a study of the scattering by solutions of phosphotungstic acids,[10] it was observed that equation 1 failed, presumably because of charge effects. It was also observed that the scattering by these solutions followed equation 1 at very low values of the *p*H. This was probably a result of two factors, the reduction in charge of the species by protonation and also the presence of relatively high concentrations of the 1:1 supporting electrolyte $HClO_4$.

It has been suggested[10] that a separate determination of $(\partial \ln a_2/\partial c_2)$, where c_2 is the concentration in g./ml., by e.m.f. or isopiestic methods would allow the calculation of M_2 in a two component system when equation 1 is not obeyed, since the general relation describing the scattering in two component systems is given by the equation

$$\tau = \frac{HM_2}{(\partial \ln a_2/\partial c_2)} \qquad (2)$$

This method involves some difficulty in the separate determination of $(\partial \ln a_2/\partial c_2)$ which would limit it to very favorable systems.

In general light scattering measurements are most useful for studying systems at relatively high degrees of polymerization. The more usual methods of e.m.f. titrations, spectrophotometry, cryoscopy, etc., are particularly useful at the beginning of the aggregation where the degree of polymerization is low.

1. Turbidity of Multi-component Systems.—The equation for the turbidity τ in excess of that due to density changes, *i.e.*, in excess of that due to the scattering by the pure solvent, has been given by Stockmayer.[5]

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