Summary

Controlled potential electrolyses have been used for the preparation of Ru(III) and Ru(IV) in perchloric acid. The analytical identification, absorption spectra and stabilities of these states are described. Conditions for the oxidation of Ru(III) and Ru(IV) by perchloric acid are discussed.

Evidence from absorption spectra and electrode behavior is cited for the complex nature of the ionic species present in solutions of Ru(III) and Ru(IV). The slowness of equilibria involving these species is discussed. Limits have been placed on the formal oxidation potential of the Ru(III) → Ru(IV) + e^- couple.

The formal oxidation potential of the couple Ru(IV) → RuO_4 + e^- has been estimated as -1.40 ± 0.05 v. (1 *M* $HClO_4$), -1.43 ± 0.05 v. (6 *M* $HClO_4$) and -1.51 ± 0.05 v. (9 *M* $HClO_4$).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Effect of Ionic Strength on Polarographic Half-wave Potentials[1]

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The half-wave potential for the polarographic reduction of simple ions of metals soluble in mercury is given[3,4,5] by the equation

$$E_{1/2} = E_a^0 + \frac{RT}{nF}\ln f_s - \frac{RT}{2nF}\ln\left(\frac{D_s}{D_a}\right) \qquad (1)$$

where E_a^0 is the standard potential of the metal amalgam electrode, f_s is the activity coefficient of the metal ions in the solution, D_s is the diffusion coefficient of the metal ions in the solution and D_a is the diffusion coefficient of the metal atoms in the mercury. In the derivation of this equation it has been assumed that both the activity of the mercury and the activity coefficient of the metal atoms in the amalgam are equal to unity. Since the amalgams formed at the dropping mercury electrode are extremely dilute, these assumptions are reasonable. It has also been assumed that the Ilkovic equation is valid for the reduction under consideration.

If the measurement of the half-wave potential is made in the customary manner by employing an external reference electrode as the anode, the observed half-wave potential will also include the junction potential between this reference electrode and the solution being studied. Furthermore, even though one selects a supporting electrolyte which has very little tendency to form complexes with the reducible metal ion, it is often impossible to find a suitable supporting electrolyte which exhibits completely negligible tendency toward complex-formation. If complex-formation does occur, the half-wave potential is shifted by an amount which is given[6] by

$$\Delta E_{1/2} = \frac{RT}{nF}\ln\left(1 + \frac{C_x^p f_x^p f_s}{K_c f_c}\right) \qquad (2)$$

where C_x represents the concentration of the complex-forming substance, K_c represents the dissociation constant of the complex, p represents the number of moles of complex-forming substance per mole of metal ion in the complex, and f_x, f_s and f_c represent the activity coefficients of the complex-forming substance, of the simple (hydrated) metal ion and of the complex, respectively.

If the effects of liquid-junction potential and of complex-formation are included in the equation for the half-wave potential, equation (1) becomes

$$E_{1/2} = E_a^0 + \frac{RT}{nF}\ln f_s - \frac{RT}{2nF}\ln\left(\frac{D_s}{D_a}\right) - E_L - \frac{RT}{nF}\ln\left(1 + \frac{C_x^p f_x^p f_s}{K_c f_c}\right) \qquad (3)$$

where E_L is the liquid junction potential. Since the values of f_s, D_s and E_L are functions of the ionic strength and of the ionic environment, it may be expected that the half-wave potential will be significantly affected by changes in ionic strength or ionic environment.

The only previous study of the effect of ionic strength on half-wave potentials is that of Lingane,[1] who studied the half-wave potentials of thallous, zinc, lead and cadmium ions in a supporting electrolyte of potassium nitrate. The range of ionic strengths studied was quite narrow, 0.02 to 1.0 *M*, but the data indicated that the influence of ionic strength on the half-wave potentials was indeed significant.

The present paper reports the results of measurements of the half-wave potential of cadmium in various nitrate supporting electrolytes for a range of ionic strengths extending up to 12 *M*. Cadmium was chosen as the reducible ion since it is particularly easy to study by the polarographic method. Nitrates were chosen as supporting electrolytes in order to keep complex-formation at a minimum.

Experimental

A Sargent Model XXI visible recording polarograph was used for recording all polarograms. The initial and span voltages of the polarograph were measured by means of a

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conventional potentiometer circuit, which permitted standardization of the voltage scale on the recorded polarogram to within ±1.0 mv. An external saturated calomel electrode, making contact with the solution through a saturated potassium chloride salt bridge and a sintered glass disc, was used as a reference electrode for all measurements. All measurements were made at 25 ± 0.1°. All solutions were purged of dissolved oxygen by means of nitrogen which was bubbled through the solution prior to the analysis. Capillaries were carefully and frequently standardized; *m* values were in the vicinity of 2.5 mg. $sec.^{-1}$ and drop times were of the order of 4 sec. Residual currents for all supporting electrolytes were determined and proper corrections for this factor were made. Proper correction for the *iR* drop across the current-measuring resistor was applied in all cases. The resistance of the cell was found to be small enough that no correction for *iR* drop in the solution was necessary for the currents employed. All half-wave potentials were determined from the relationship[5]

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF}\ln\frac{i}{i_d - i} \qquad (4)$$

by plotting a series of values of $E_{d.e.}$ against the corresponding log term. The use of this technique permitted a higher degree of precision than was possible by using the original recorded polarograms directly for the determination of the half-wave potential.

In order to minimize migration current the normality of the supporting electrolyte was maintained at a value at least twenty-five times the normality of the cadmium ion. Except for the measurements at the lowest ionic strengths, all solutions were 1.00 millimolar in cadmium ion and contained 0.001% gelatin as a maximum suppressor. For the measurements in the most dilute solutions the concentration of gelatin was reduced by an amount proportional to the reduction in cadmium ion concentration. Preliminary experiments indicated that the half-wave potential of cadmium was independent of the concentration of both gelatin and reducible ion for the concentration ranges employed in this study. C. P. or reagent grade chemicals were used for the preparation of all solutions.

Results and Discussion

The curves obtained by plotting $E_{d.e.}$ as a function of log $[i/(i_d - i)]$ were all straight lines with slopes varying from 29 to 32 mv., in good agreement with the value of 30 mv., predicted by equation (4).

The observed half-wave potentials, plotted as a function of the square root of the total ionic strength, are shown in Fig. 1. The reproducibility of the half-wave potentials which are shown is excellent; the average deviation of single measurements from the mean of duplicate measurements was approximately 0.5 mv.

The changes in half-wave potential which accompany changes in the ionic strength or changes in the nature of the supporting electrolyte are much larger than has been tacitly assumed previously. Although this variation in half-wave potential is of little importance in the application of the polarograph to ordinary analytical determinations, it is very significant in any application which involves measurement of changes in half-wave potential. An example of the latter type of application is the study of complex ions in solution. The results reported here indicate that careful attention must be paid to the effect of ionic strength and of ionic environment in studies of this type in order to avoid serious misinterpretation of experimental data. Many investigators in this field have attempted to eliminate all changes in half-wave potential except those resulting from complex-formation by working with solutions of constant ionic strength. It is apparent from the results shown in Fig. 1, however, that this technique may prove ineffective at ionic strengths exceeding approximately 0.1 *M*, although it would appear to be valid at lower ionic strengths where the half-wave potential is relatively independent of the nature of the ionic environment and is a function of the total ionic strength only.

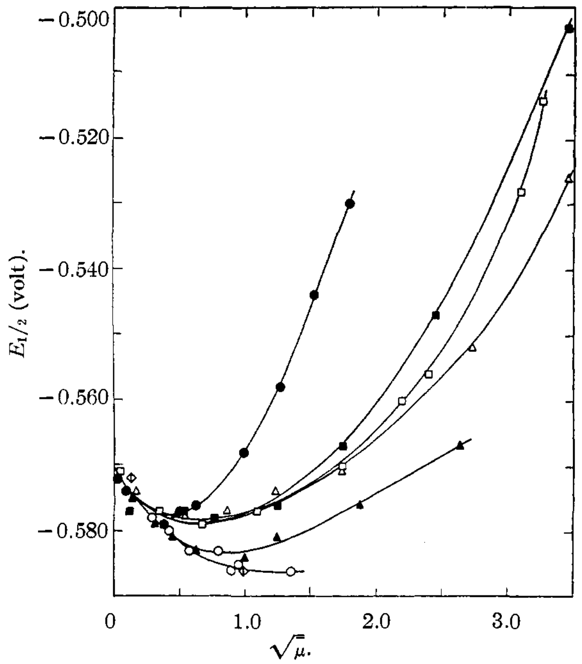

Fig. 1.—Half-wave potential of cadmium in nitrate supporting electrolytes as a function of the total ionic strength: ○, HNO_3; ●, $LiNO_3$; △, $Mg(NO_3)_2$; ▲, NH_4NO_3; □, $Al(NO_3)_3$; ■, $Ca(NO_3)_2$; ◇, KNO_3 (Lingane[1]).

It is virtually impossible to compare the observed values of the half-wave potentials with the values which might be predicted by equation (3), since the activity coefficients and the liquid junction potential which are involved in this equation are not susceptible to independent experimental measurement. For very low ionic strengths the activity coefficients may be calculated with reasonable certainty, but the liquid junction potential may be quite large and cannot be calculated with any degree of confidence. At high ionic strengths neither of these variables may be calculated. Between these two extremes there is a range of ionic strengths for which the activity coefficients may be approximated with reasonable confidence and for which the liquid junction potential is sufficiently small that it may be neglected without serious error. It is of interest to compare observed values of half-wave potentials for an ionic strength lying within this range with those calculated by equation (3). Since the results of Guggenheim[7] and other investigators in this field indicate that the junction potentials between solutions of an ionic strength of 0.1 *M* and saturated potassium chloride solution probably do not exceed a few millivolts, this ionic strength seems quite suitable for such a comparison.

Using Harned and Fitzgerald's[8] value of −0.3515 volt for the standard potential of the saturated cadmium amalgam–cadmium ion electrode, together with Hamer's[9] value of −0.2415 volt for the potential of the saturated calomel electrode and Hulett and DeLury's[10] data for the potentials of very dilute cadmium amalgam electrodes, we calculate a value of −0.567 volt for the standard potential of the cadmium amalgam electrode. Employing 6.2 Å. as the radius of the cadmium ion,[11,12] we calculate, by means of the extended Debye–Hückel equation, a value of 0.41 as the activity coefficient of the cadmium ion at an ionic strength of 0.1 *M*. This result is in good agreement with the value of 0.38 given by Kielland.[13] Either of these activity coefficients gives a value of −0.012 volt for the activity term in equation (3). Lingane[1] has shown that the diffusion coefficient term in the equation has a magnitude of +0.005 volt. Righellato and Davies[14] have shown that cadmium forms a weak mononitrate complex, and report that the dissociation constant of this complex is 0.394. Employing this value, we find that the complex-formation term in equation (3) has a magnitude of −0.001 volt for all of the supporting electrolytes employed. In this calculation it was assumed that f_x was equal to f_c since the corresponding ions are both singly charged. Combination of all terms of the equation gives a calculated value of −0.575 volt for the half-wave potential, while the experimentally observed values were found to be −0.578, −0.579, −0.578, −0.577 and −0.576 volt in nitric acid and in ammonium, lithium, magnesium, calcium and aluminum nitrates, respectively. The agreement between calculated and observed values is probably better than could be reasonably expected in view of the uncertainties involved in the calculations. The slight differences in the observed half-wave potentials among the various supporting electrolytes are probably not significant at this ionic strength. The best value for the half-wave potential of cadmium in nitrate supporting electrolytes at a total ionic strength of 0.1 *M* is then −0.578 volt. Lingane[1] has previously reported this value for the half-wave potential in 0.1 *M* potassium nitrate. Very recent measurements by Meites,[15] who employed a considerably more refined technique, gave a value of −0.5777 ± 0.0002 v. for the half-wave potential in 0.10 *M* potassium nitrate without gelatin.

Summary

1. The half-wave potential of cadmium has been studied as a function of ionic strength in supporting electrolytes of nitric acid and of ammonium, lithium, calcium, magnesium and aluminum nitrates for a range of ionic strengths extending up to 12 *M*. It has been shown that the half-wave potential varies between wide limits as the ionic strength and the character of the ionic environment are altered.

2. The various factors responsible for changes in half-wave potential which occur as a result of changes in the composition of the solution have been discussed. Experimentally measured half-wave potentials have been compared with those calculated by means of the theoretical equation.

3. The necessity of considering the effects of ionic strength and ionic environment in the polarographic investigation of complex-formation has been emphasized.

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