hydroxide ion effect also supports the argument that the rate is primarily controlled by the positioning of the cyanide ions around the nickel rather than just the unfolding of Y^{-4}.

Previous exchange studies[3,4] of radionickel complexes with $Ni(CN)_4^{-2}$ have proposed a direct bimolecular exchange of the nickel complexes. How the ligands rearranged themselves was not clear. The inert character of $Ni(CN)_3$ type intermediates postulated in this study offers a more plausible explanation for the observed kinetics and also explains salt effects. Thus, the true behavior of $Ni(CN)_4^{-2}$ and $Ni(gly)_2$ was obscured by the fact that the experiments[4] were performed

in an excess of glycine (proportional to $Ni(gly)_2$) which could react with $Ni(CN)_4^{-2}$. Similarly, the dissociation mechanism with $Ni(en)_3^{+2}$ was ruled out because the reaction was still very fast in excess en[3]. In fact, excess en speeds up the reaction. This is to be expected if en attacks $Ni(CN)_4^{-2}$ in a manner similar to the EDTA mechanism. Direct bimolecular exchange of nickel complexes is not disproved but an alternate mechanism involving inert nickel cyanide complexes seems more likely.

Some Mixed Ligand Complexes with the Cyanide Complexes of Mercury[1]

By Leonard Newman and David N. Hume

Equilibria of the type $Hg(CN)_3^- + X^- = Hg(CN)_3X^-$ have been studied polarographically at a temperature of 30° and an ionic strength of 2.0. When the ligand X^- is chloride, bromide and thiocyanate, the values of the formation constants are 0.4, 2.3 and 2.9, respectively. From a spectrophotometric study at an ionic strength of 4.0 the formation constant for the addition of one chloride ion to mercuric cyanide was found to be 0.56 ± 0.05.

Introduction

In previous investigations the formation constants of $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^-$ were measured polarographically[2] and the formation constant of $HgOHCN$ was measured by both polarographic and solubility methods.[3] The knowledge that was obtained about the polarography of mercuric cyanide is utilized in the present paper for a polarographic investigation of mixed ligand complexes of the type $Hg(CN)_3X^-$. Equations previously developed for a spectrophotometric approach[4] are utilized to demonstrate that an anion, other than cyanide, can be added on to mercuric cyanide.

Polarographic Study of Complexes of the Type $Hg(CN)_3X^-$.

—It was demonstrated previously that, in basic solutions, the cyanide liberated by the reduction of mercuric cyanide can complex with more mercuric cyanide diffusing toward the surface of the drop.[2] It was thought that this might, in part, be prevented if a ligand (X^-) were added that could complex the mercuric cyanide. If the ligand were in large excess, the possible mixed anion complexes that could be formed directly are $Hg(CN)_2X^-$ and $Hg(CN)_2X_2^-$. The species $Hg(CN)_3X^-$ could also be formed as a consequence of the electrode reaction.

Utilizing the same apparatus, technique, conditions and reagents as previously described,[2] polarograms were obtained of solutions containing

(1) Taken in part from the Ph.D. Thesis of Leonard Newman, Massachusetts Institute of Technology, June, 1956. This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)905.

(2) L. Newman, J. de O. Cabral and D. N. Hume, This Journal, 80, 1814 (1958).

(3) L. Newman and D. N. Hume, ibid., 81, 5901 (1959).

(4) L. Newman and D. N. Hume, ibid., 79, 4571 (1957).

10^{-3} M mercuric cyanide with 1 M chloride, bromide, thiocyanate or iodide. The ionic strength was maintained at 2.0 with sodium nitrate, the pH at 11.0 ± 0.1, the temperature at 30 and gelatin at 0.004%. The drop time was 4.3 seconds at the limiting current. In all cases except that of iodide a discrete cathodic wave was observed. The anodic wave for mercurous iodide is so close to the cathodic wave that the residual current cannot be measured, making it impossible to analyze the wave.

If a complex were not formed with the ligand, or if the cyanide liberated at the surface of the drop displaced all other ligands from the complex, then the analysis of the wave would not be dependent upon the concentration of the ligands. On examination of the results in Table I it can be seen that the analyses of the waves are dependent upon the presence of the added ligands. If $Hg(CN)_2X_2^-$ or $Hg(CN)_2X^-$ were the predominating species being reduced, a plot of $E_{d.e.}$ vs. log $[(i_d - i)/i^2]$ would have a slope of 30 mv.,[2] the added ligands being in large excess. However, if $Hg(CN)_3X^-$ were the predominating species, a plot of $E_{d.e.}$ vs. log $[(i_d - i)/i^3]$ would have a slope of 30 mv. The data in Table I show the latter to be true. There are two possibilities through which $Hg(CN)_3X^-$ can become the predominating species. The first is that $Hg(CN)_2X^-$ is formed by the addition of one ligand to mercuric cyanide with the cyanide liberated at the surface of the drop complexing this species further. The second is that $Hg(CN)_2X_2^-$ is first formed, from which the liberated cyanide displaces one X^-. No differentiation between these mechanisms can be made.

The stepwise formation constant for $Hg(CN)_3X^-$ can be calculated from the observed concentration-
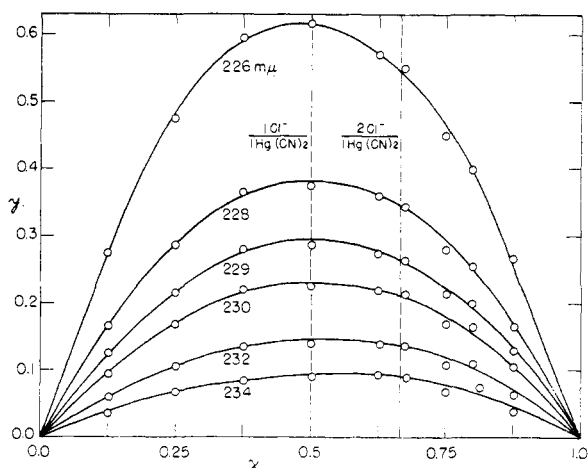
Fig. 1.—Continuous variations plot for mixtures of mercuric cyanide and sodium chloride.

independent potential. This potential for a mixed ligand complex is defined as

$$E_{f,x} = E_0 + 0.030 \log \frac{d_1}{d_n K_{3,x}[X^-]} \quad (1)$$

where d_1 and d_n are the proportionality constants between diffusion current and concentration for cyanide and $Hg(CN)_3X^-$, respectively, and where

$$K_{3,x} = \frac{[Hg(CN)_3X^-]}{[Hg^{++}][CN^-]^3[X^-]} \quad (2)$$

subtracting $E_{f,x}$ from E_f for $Hg(CN)_3^-$ (see ref. 2), we obtain

$$E_f - E_{f,x} = 0.030 \log k_{3,x} \quad (3)$$

where $k_{3,x}$ is the stepwise formation constant defined as

$$k_{3,x} = \frac{[Hg(CN)_3X^-]}{[Hg(CN)_3^-][X^-]} \quad (4)$$

The value of -300 mv. for the E_f of $Hg(CN)_3^-$, which was used for the calculation, was obtained from a previous publication.[2] With the measured values of $E_{f,x}$ presented in Table I, the stepwise formation constants for each of the mixed ligand complexes were calculated utilizing equation 3. The results are summarized in Table I. It is

TABLE I

POLAROGRAPHIC EVIDENCE FOR THE FORMATION OF $Hg(CN)_3X^-$

1 M	Slope (mv.) 2 CN⁻/Hg	$-E_{f,x}$ (mv.)	Slope (mv.) 3 CN⁻/Hg	$-E_{f,x}$ (mv.)	$k_{3,x}$
Cl⁻	43	298	33	287	0.4
Br⁻	40	323	31	311	2.3
SCN⁻	40	325	31	314	2.9

interesting to note how weak the complexes are. However, since the over-all formation constants for the cyanide complexes of mercury are much greater than for any anion other than sulfide, it might be expected to be difficult to add chloride, bromide or thiocyanate onto $Hg(CN)_3^-$. This probably also accounts for the slope of 33 mv. instead of 30 mv. obtained in the chloride system. In this case the stepwise formation constant for the addition of chloride is so small that the cyanide liberated at the surface of the drop can compete

successfully with chloride and form some $Hg(CN)_4^=$.

Experimental

Spectrophotometric Evidence for $Hg(CN)_2Cl^-$.—In a continuous variations experiment a series of equimolar mixtures was prepared by adding (x) liters of chloride to $(1 - x)$ liters of mercuric cyanide. The chloride and mercuric cyanide were each originally at 0.2 M and the ionic strength adjusted to 4.0 with sodium perchlorate. In a second experiment solutions containing 0.01 M mercuric cyanide were prepared containing sodium chloride varying between 0 and 4 M with the ionic strength again maintained at 4.0 with sodium perchlorate. The absorbance of each solution was measured against blanks containing all the constituents other than mercuric cyanide. The instrument used was a Beckman DU Quartz Spectrophotometer equipped with a hydrogen lamp and photomultiplier attachment.

Results

It was observed that a solution containing sodium chloride in great excess over mercuric cyanide began to absorb at 240 mμ and the absorption continued to rise until 215 mμ, the limit of the instrument. The method of continuous variations was employed to establish the combining ratio of chloride and mercuric cyanide. The limitations to this method[5,6] are not significant in this case; at the concentrations of mercuric cyanide and sodium chloride employed, only one complex is formed.

In Fig. 1 a plot of y (the difference between the value of the absorbance found and the value calculated for no reaction) vs. x has a maximum at a ratio of 1/1. This clearly indicates that one chloride is attached per mercuric cyanide yielding $Hg(CN)_2Cl^-$.

Since mercuric cyanide is so slightly ionized, the addition of chloride can be considered as a case of $M + X = MX$ where M = mercuric cyanide and X = chloride, and we obtain

$$k_{2,Cl^-} = \frac{[Hg(CN)_2Cl^-]}{[Hg(CN)_2][Cl^-]} \quad (5)$$

Since $Hg(CN)_2$ absorbs to some extent, the system has to be considered as a one ligand, two species with two absorbing case.[4]

In Fig. 2, a plot of absorbance vs. chloride concentration shows that it is impossible to attain a leveling-off value of the absorbance and still main-
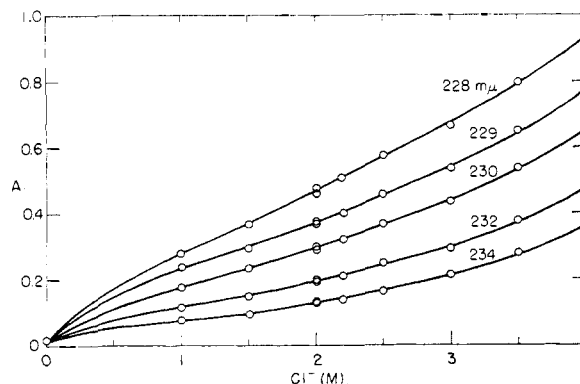

Fig. 2.—Absorbance data showing the formation of mixed ligand complexes of mercuric cyanide with chloride.

(5) L. I. Katzin and E. Gebert, THIS JOURNAL, 72, 5455 (1950).
(6) F. Woldbye, Acta Chem. Scand., 9, 299 (1955).

tain the ionic strength at 4.0. This means that the extinction coefficients for the chloride complex cannot be obtained directly. However, there appears to be a slight inflection in the curve at approximately 2 M chloride which indicates that at least two complexes are being formed under these conditions. Since the inflection is so slight, the difference between the formation constants and the difference between extinction coefficients must be small.

An attempt was made to apply Equation D12c[4] to the data presented in Fig. 2. The necessary conditions are that the chloride concentration be much greater than the mercuric cyanide concentration, that the extinction coefficient of mercuric cyanide be known and that only two complex species be present. The extinction coefficient of the mercuric cyanide is obtained by direct measurement when the chloride concentration is equal to zero. There appears, however, to be a contribution due to the formation of $Hg(CN)_2Cl_2^=$ because straight line plots were not obtained upon application of this equation. A straight line could be drawn asymptotically to the data at low chloride ion concentrations where the conditions stipulated by Equation D12c are best met. Because of the limited accuracy with which the slope of this line could be drawn, it was not usable for calculation of the formation constant of $Hg(CN)_2Cl^-$, but the intercept could be used to obtain reasonably good values for the extinction coefficient. The values so obtained for the extinction coefficients of $Hg(CN)_2Cl^-$, each good to approximately 5 units, were 80, 60, 50, 30 and 20 mole^{-1} cm.$^{-1}$ at 228, 229, 230, 232 and 234 mμ, respectively. The extinction coefficient of $Hg(CN)_2$ over this range was found to be constant at 1.5 mole^{-1} cm.$^{-1}$

With the aid of these extinction coefficients further information could be derived from the absorbance data of the continuous variations experiment. Because in this experiment the concentration of chloride is comparable to the mercuric cyanide concentration, the conditions imposed by equation E12[4] are met, namely, that two species be present, both absorbing, with both extinction coefficients known. A plot of the relationships specified by equation E12 for each of the five wave lengths is presented in Fig. 3. It was found that a straight line with a slope of 1.0 could be put through the data. This further indicates that under the conditions of the continuous variations experiment only one chloride adds onto the mercuric cyanide, forming $Hg(CN)_2Cl^-$. The spread of the data at the top of the curve is due to the small differences taken, whereas the deviations on the bottom of the curve can be attributed to the presence of the third species, $Hg(CN)_2Cl_2^=$.

The value of k_{2,Cl^-}, obtained from the intercept, was found to be 0.56 ± 0.05 at an ionic strength of 4.0 maintained with sodium perchlorate. Bourion and Rouyer[7] have observed by ebullioscopic means, a formation constant for $Hg(CN)_2Cl^-$ as 0.77 ± 0.07 (μ = 2 to 3). Considering the weakness of this complex, the agreement is exceedingly good.
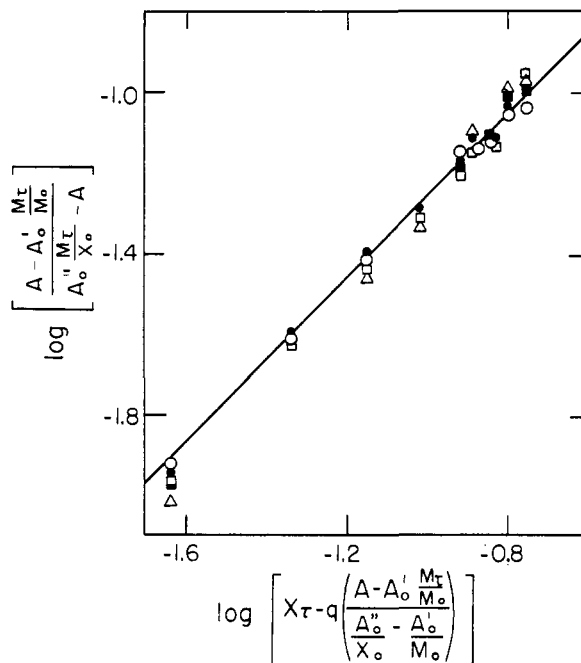

Fig. 3.—Plot for the determination of the stepwise formation constant of $Hg(CN)_2Cl^-$.

The agreement with the ebullioscopic determination is also highly gratifying in view of the fact that the methods employed differ radically. In both methods, the necessity of working at high ionic strengths to approximate a constant ionic environment results in the values obtained being formal or concentration constants, rather than the theoretically more desirable activity equilibrium constants. Although the values given include unknown and unestimable activity coefficients, the satisfactory agreement between different methods emphasizes again the intrinsic usefulness of the constant ionic environment approach in studying and comparing complexes which are not stable in solutions dilute enough to permit application of the conventional approximations for correcting to ideal standard states.

(7) F. Bourion and E. Rouyer, Ann. Chim., 10, 263 (1928).