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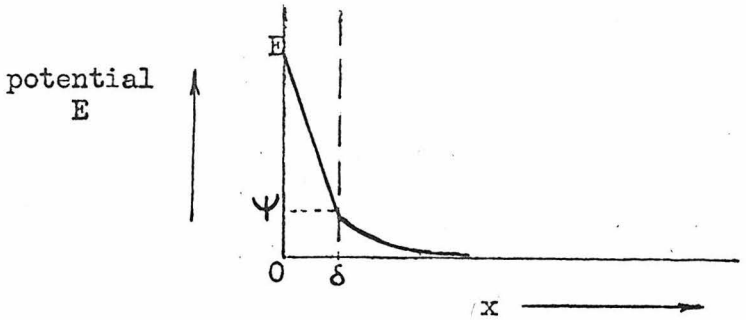
Attempted Determination of the Mechanism of the Reduction of Cobalt(III) trisethylenediamine to the Cobalt(II) Complex

In this experiment the author attempted to determine polarographically the mechanism for the reduction of $Co(III)(en)_3$ to $Co(II)(en)_3$ by a method utilizing double layer considerations.

In most electrochemistry it is assumed that ions exist continuously op to the surface fo the electrode. This assumption is however incorrect. Consider the following illustration:



distance from the electrode surface

Ions actually do not exist closer to the electrode than a distance, δ, one to three molecular diameters long. Thus the measured potential, E, may differ from the potential, Ψ, where the electrochemistry takes place. This "double layer" phenomenon effects the system in two ways. First the measured potential is not the same as the potential required for the oxidation or reduction. Second the concentration at the place where the electrochemistry occurs is not the same as the bulk concentration due to an electrostatic repulsion or attraction of the ions.

The equation for the system thus becomes:

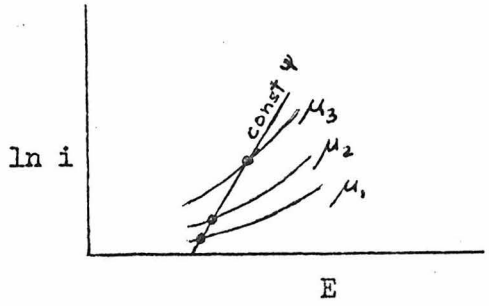
$$\ln i = \ln knFAC_o - \frac{\alpha nF}{RT}E + \frac{\alpha nF}{RT}\left(1 - \frac{Z}{\alpha n_a}\right)\Psi \qquad (1)$$

where i= current, n= number of electrons transferred, k= rate constant, F= Faraday, A= area of electrode, C_o= concentration, α= constant depending on the system, R= gas constant, T= temperature, and n_a= number of electrons in the rate determining step. Ψ depends on things such as the ionic strength of the solution, μ, the specific electrolite, and the potential. Ψ is given by the Gouy-Chapman equation:

$$\Psi = \frac{2RT}{FZ} \sinh^{-1} \frac{\sqrt{\pi} q}{\sqrt{\epsilon kTC}} \qquad (2)$$

In most cases the double layer effect is small. However if the reaction is irreversible and the rate is slow, the effect can be observed.

In practice one might plot ln i against E for various μ as follows:



Then if $\Psi = \Psi(E,\mu)$ is known, one can determine a line of constant Ψ. This line will have the slope of αn_a.

By making appropriate substitutions in equation (1) one can see that

$$\Delta E_{\frac{1}{2}} = \left(1 - \frac{Z}{\alpha n_a} \right) \Delta \Psi \qquad (3)$$

where $E_{\frac{1}{2}}$ is the potential at which the current is one half the limiting current. Thus it is possible to determine $\frac{Z}{\alpha n_a}$ by varying Ψ and observing the resulting shift of the half wave potential, $E_{\frac{1}{2}}$.

EXPERIMENTAL

In general the solution of supporting electrolite was deoxygenated by passing nitrogen gas through it for several minutes. Then a

polarogram was taken to determine the background current. $Co(III)(en)_3(ClO_4)_3$ was added (concentration of the test solution was .0005 M in the cobalt complex). More nitrogen was passed through the solution and another polarogram was taken. $E_{\frac{1}{2}}$ was determined.

The first attempt at observing a shift in $E_{\frac{1}{2}}$ was made by varying Ψ through changing the ionic strength of the supporting electrolite. Electrolite solution were made up of reagent grade sodium nitrate in tripple distilled water. This experiment yielded the following results:

Concentration of $NaNO_3$	$E_{\frac{1}{2}}$	
1.000 M	-.395 V vs. saturated calomel electrode	
.100	-.372	($E_{\frac{1}{2}}$ correct to a precision of $\pm$.01 V)
.010	-.362	
.001	-.365	

The observed shifts were considerably smaller than expected. Therefore this experiment was considered to be inconclusive.

Another attempt of observing the shift was made by mantaining the ionic strength constant and changing the nature of the electrolite. The concentration of salt was held at one molar; however, varying ratios of $NaNO_3$ to KSCN were tried. This technique is merely another method for changing Ψ. The results were as follows:

$NaNO_3$	KSCN	$E_{\frac{1}{2}}$ vs. SCE
1.000 M	.000 M	-.395 V ($\pm$.01 V)
.999	.001	-.393
.990	.010	-.397
.900	.100	-.380

Again the expected shift was not observed and the results were inconclusive.

It was decided that the reaction might possibly be more reversible than was believed at the outset of the experiment. With the help of Peter Lingane the author employed the technique of cyclic voltometry to examine the reversibility of the reaction. This experiment acknowledged the belief that the reaction was too revesible to observe the double layer effect of the shifting $E_{\frac{1}{2}}$.