

Experimental Determination of the Standard Reduction Potential of the Gold(i) Ion

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Summary Changes in potential observed on diluting solutions of $\text{Au}(\text{MeCN})_2^+$ in acetonitrile with 0.1 M aqueous HClO_4 up to 99.6% water at 25 °C are consistent with a value of $E^\circ = 1.695 \pm 0.01$ V for the standard reduction potential of the Au^{I} ion.

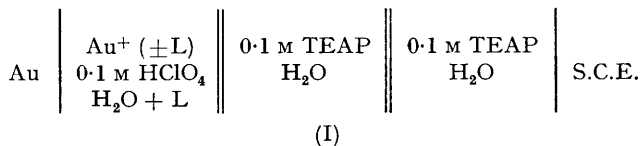
sumably owing to catalysis of the decomposition of Au^{I} by traces of other metal ions). Under these conditions about half of the AuL_2^+ is dissociated to the simple aquated Au^+ . We report here the use of this approach for the first experimental determination of the standard reduction potential of Au^{I} .

THE d^{10} Au^{I} ion is of great interest as the archetype of the class-b or 'soft' Lewis acid, but the inability to prepare and study the simple aquated ion in the absence of strong ligands (such as cyanide or thiourea) has severely restricted our knowledge of the co-ordination chemistry of Au^{I} and prevented determination of its standard reduction potential.^{1,2} Estimates of the latter vary widely from +1.67³ and 1.68¹ through 1.88⁴ up to 2.12,⁵ all apparently based on equally impeccable assumptions. Such a wide variation introduces a very large uncertainty into the values of the equilibrium constants for the co-ordination of ligands, which provide the basis for comparing class-a with class-b (or hard with soft) co-ordination behaviour.

Gold can be anodically dissolved in acetonitrile (L) to give solutions of the complex $\text{AuL}_2^{+2,6}$. We now find that we can measure potentials, which are stable for at least 5 min, when such solutions are diluted with 0.1 M aqueous HClO_4 (but not with water alone) down to about 0.4% L (below which the potentials become increasingly unsteady); unstable readings were also observed when using a microsyringe with a stainless steel needle (pre-

The potential shown by solutions of Au^{I} in water without L should be related directly to E° , and the variation in potential observed with increasing L should be explicable in terms of the two equilibria corresponding to K_1 ($= [\text{AuL}^+]/[\text{Au}^+][\text{L}]$) and K_2 ($= [\text{AuL}_2^+]/[\text{AuL}^+][\text{L}]$) or β_2 ($= K_1K_2$). The variation of the activity coefficients of the different species with solvent composition is, of course, not known; we therefore operate over as narrow a range of solvent composition as possible (0–4% L), assume that the activity coefficients do not vary significantly, and use concentrations instead of activities. To evaluate the experimental data we select a range of possible values for E° , calculate the 'apparent' concentration of free (*i.e.*, Au^+) and of bound (*i.e.*, $\text{AuL}^+ + \text{AuL}_2^+$) gold for each value of E° , and plot $\log ([\text{AuL}^+] + [\text{AuL}_2^+])/[\text{Au}^+]$ against $\log [\text{L}]$. Reasonable values of E° should give plots which either curve between asymptotes with slope $n = 1$ at low [L] and $n = 2$ at high [L] (when $K_1 \geq K_2$) or are linear over the whole range with $n = 2$ (when $K_1 \ll K_2$). The problem of determining E° then resolves itself into finding a value of E° which is consistent with the existence of such equilibria and with the observed changes in potential. The data may then be used to determine K_1 and K_2 (or β_2).

Solutions containing either 2.01 or 9.42×10^{-4} M AuL_2^+ in pure L were diluted with successive additions of 0.1 M aqueous HClO_4 to give final compositions of 96.2–99.6% water (*i.e.*, from 3.8 down to 0.4% L) in four separate experiments. The potentials were measured using



the cell (I), where TEAP is tetraethylammonium perchlorate. For convenience in visualising the extrapolation, the observed potentials (E_{obs} , vs S.C.E.) have been corrected for dilution using the Nernst equation to give 'apparent' standard reduction potentials (E_{app}° vs. standard hydrogen electrode) for each solvent composition. Merck UVASOL (spectrophotometrically pure) acetonitrile was used throughout, and all solutions were thermostatted at 25 °C.

The variation of E_{app}° (averages of four experiments) with the concentration of L (see Figure 1) suggests that

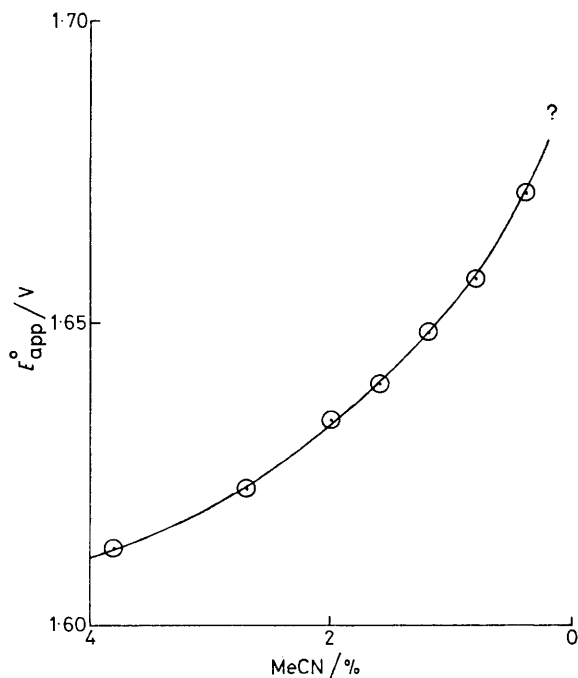


FIGURE 1. Variation of E_{app}° with the concentration of MeCN.

extrapolation to 0% L should give $E^{\circ} = 1.68$ – 1.71 . This was confirmed by plotting values of $\log \left(\frac{[\text{AuL}^+] + [\text{AuL}_2^+]}{[\text{Au}^+]} \right)$ against $\log [\text{L}]$ for values of E° between

+1.67 and 1.72 at 100 mV intervals. The plots for $E^{\circ} = +1.67$, 1.69, and 1.71 are shown in Figure 2. We can

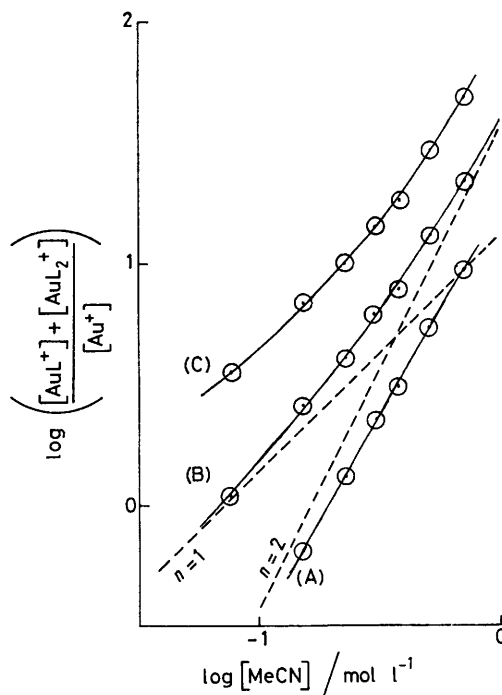


FIGURE 2. Plot of $\log \left(\frac{[\text{AuL}^+] + [\text{AuL}_2^+]}{[\text{Au}^+]} \right)$ against $\log [\text{MeCN}]$ for $E^{\circ} = +1.67$ (A), 1.69 (B), and 1.71 (C).

eliminate values of $E^{\circ} \geq 1.71$ (since $n < 1$ at low $[\text{L}]$), 1.68 ($n = \text{const.} = 1.6$), and ≤ 1.67 ($n \text{ ca. } 2$ at low $[\text{L}]$) and falls with increasing $[\text{L}]$, and the first point is meaningless). Reasonable and meaningful plots, which curve as expected between the asymptotes with $n = 1$ and $n = 2$, are obtained only for $E^{\circ} = 1.69$ and 1.70. We conclude that $E^{\circ} = +1.695 \pm 0.01$ V vs standard hydrogen electrode in 0.1 M HClO_4 at 25 °C, in good agreement with the lowest of the estimated values.^{1,3} It is interesting to note that the most accurate estimate was also the earliest (in 1938).

The asymptotes for the plots based on $E^{\circ} = 1.69$ and 1.70 gave values of $K_1 = 13.2$ and 26.3, respectively (average 19.8), *i.e.*, $\log K_1 = \text{ca. } 1.31 \text{ mol}^{-1}$, and $\beta_2 = 36.3$ and 52.5, respectively (average 44.4), *i.e.*, $\log \beta_2 = \text{ca. } 1.61^2 \text{ mol}^{-2}$, hence $\log K_2 = \text{ca. } 0.31 \text{ mol}^{-1}$.

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