Spectrophotometric Investigation of Equilibria Between Silver(II) and 2,2′-Bipyridine

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A spectrophotometric study has been made of an aqueous solution of silver(II) containing nitric acid and an excess of 2,2′-bipyridine over the wavelength range 350—550 nm. The data are consistent with the existence of only two complexes related by the equilibrium $[Ag(bipy)_2]^{2+} + H^+ \rightleftharpoons [Ag(bipy)]^{2+} + Hbipy^+$. At I = 1.00 mol dm^{-3} and at 25 °C, K_h for this equilibrium is found to be (3.3 ± 0.5) × 10^{-3}. From the variation of K_h with temperature the values for the enthalpy and entropy of the above reaction are found to be 11.5 ± 2.6 kJ mol^{-1} and −9 ± 10 J K^{-1} mol^{-1} respectively.

BIS(2,2′-BIPYRIDINE)SILVER(II) peroxodisulphate, $[Ag(bipy)_2][S_2O_8]$, was first prepared by Morgan and Burstall,[1] who also reported $[Ag(bipy)_3]X_2$ with X = NO_3^- or ClO_4^-. Later work [2] has confirmed that all these complexes contain two bipy ligands and not three. The spectrum of aqueous $[Ag(bipy)_2]^{2+}$ in the visible region shows a maximum at 455 nm with values for $\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1} reported as 1 600,[3] 1 980,[4] and 2 160 ± 40.[5] Balzani *et al.*[3] suggested that the ion $[Ag(bipy)_2(OH_2)_2]^{2+}$ was present in aqueous solution, but Banerjee and Basu [4] showed that the band at 455 nm could be resolved into three Gaussian components, consistent with square-planar $[Ag(bipy)_2]^{2+}$. Several e.s.r. studies of $[Ag(bipy)_2]^{2+}$ compounds in solution have been made.[2,6-8] Halpern *et al.*[7] dissolved $[Ag(bipy)_2][S_2O_8]$ in a minimum quantity of concentrated nitric acid and froze the solution at 77 K. The e.s.r. spectrum showed hyperfine interaction with two (not four) equivalent nitrogen atoms. The model proposed to explain the spectrum assumed co-ordination with two nitrogens and two solvent oxygens in alternate sequence. Po [5,9] suggested that the sigmoidal pH dependence found in a kinetic study [5] of the reduction of $[Ag(bipy)_2]^{2+}$ by hydrogen peroxide in aqueous solution could be explained by the occurrence of reaction (1), and this would be consistent

$$[Ag(bipy)_2]^{2+} + 2H^+ \rightleftharpoons [Ag(Hbipy)_2]^{4+} \quad (1)$$

with the *trans* model adopted by Halpern *et al.*[7] for the complex in frozen acidic solution. However, Thorpe and Kochi [2] showed that the dissociation of bipyridine ligands from $[Ag(bipy)_2]^{2+}$ does not occur under non-acidic conditions, since successive dilutions in aqueous solution showed no deviation from Beer's law in the range $<10^{-5}$—5×10^{-4} mol dm^{-3} of the complex. Moreover, their e.s.r. spectrum of an aqueous solution showed a hyperfine-splitting pattern of 11 lines which they interpreted as two sets of nine N hyperfine lines, similar to the e.s.r. spectrum of Ag^{II} complexed with tetraphenylporphyrin.[10] This latter complex is forced to adopt a square-planar configuration, and these authors [2] suggested that the results in acidic solution [7] could be due to dissociation of a bipyridine as in (2),

$$[Ag(bipy)_2]^{2+} + H^+ \rightleftharpoons [Ag(bipy)]^{2+} + Hbipy^+ \quad (2)$$

leaving the two remaining nitrogen atoms at *cis* positions.

In this paper, spectrophotometric evidence is presented which supports the latter view that reaction (2) is the correct interpretation in acidic solutions.

EXPERIMENTAL

Materials.—Silver carbonate, silver nitrate, and cerium(III) carbonate were of reagent grade. 2,2′-Bipyridine, nitric acid, sodium nitrate, and sulphuric acid were all of A.R. grade. Water was distilled once in an all-glass still.

The complex $[Ag(bipy)_2]^{2+}$ was prepared by the anodic oxidation of 4 × 10^{-3} mol dm^{-3} Ag^+ (derived from $Ag_2[CO_3]$) and 8 × 10^{-3} mol dm^{-3} 2,2′-bipyridine in 1.0 mol dm^{-3} nitric acid. This stock solution was diluted about ten fold with thermostatted solutions having $[H^+]$ = 0.1—1.0 mol dm^{-3} (HNO_3) and ionic strength I adjusted to 1.00 mol dm^{-3} ($Na[NO_3]$).

Procedure.—As the observed absorption coefficient, $\varepsilon_{obs.}$, depends on the concentration of the excess of 2,2′-bipyridine (Table 1), a standard excess of 4.0 × 10^{-3} mol dm^{-3} was always employed. The spectrum was recorded in the region 350—550 nm using a Unicam SP 500 spectrophotometer equipped with a thermostatted cell compartment; the blank solution contained 4.0 × 10^{-3} mol dm^{-3} 2,2′-bipyridine at the appropriate acidity and ionic strength. Values for the optical density were extrapolated back to the time of dilution to allow for the oxidation of water by Ag^{II}. At least two, and usually four or more, determinations were made for each wavelength. The complex $[Ag(bipy)_2]^+$ does not absorb light significantly above 400 nm, but a correction was made to $\varepsilon_{obs.}$ at 350 and 375 nm. Solutions were used immediately after preparation and the total $[Ag^{II}]$ was determined by the oxidation of Ce^{III} in 15 mol dm^{-3} H_2SO_4 [11] with spectrophotometric estimation of $[Ce^{IV}]$ at 360 and 380 nm.

TABLE 1

Variation of $\varepsilon_{obs.}$ (dm^3 mol^{-1} cm^{-1} × 10^{-3}) with $[Hbipy^+]$ for $[H^+]$ = 0.10 mol dm^{-3}, I = 1.00 mol dm^{-3}, $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-3}, and 25 °C

10^3[Hbipy$^+$]/ mol dm^{-3}	λ/nm		
	400	450	500
0.00	1.36	1.58	1.10
1.00	1.66	1.94	1.41
2.00	1.76	2.06	1.50
4.00	1.80	2.10	1.53

RESULTS AND DISCUSSION

A solution of $[Ag(bipy)_2]^{2+}$ in aqueous nitric acid exhibits a maximum in its spectrum at about 450 nm and a minimum at about 400 nm (Figure 1). Table 2

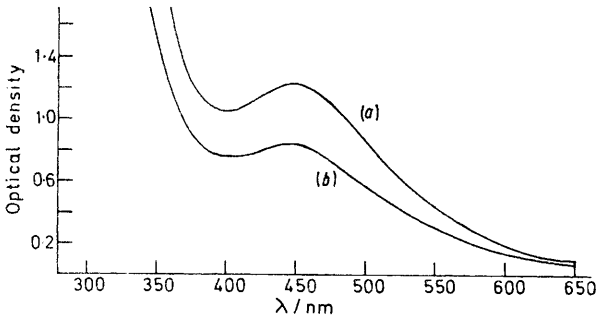

FIGURE 1 Spectrum of $[Ag(bipy)_2]^{2+}$ with varying acidity, $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-3}, and $[Hbipy^+] \approx 4.0 \times 10^{-3}$ mol dm^{-3} (excess). $[H^+] = 0.10$ (*a*) or 1.00 mol dm^{-3} (HNO_3) (*b*)

shows that Beer's law is obeyed at a constant excess of 2,2′-bipyridine for a fixed wavelength and constant acidity, and Tables 3 and 4 show that the observed

TABLE 2

Independence of $\varepsilon_{obs.}$ (dm^3 mol^{-1} cm^{-1} $\times$ 10^{-3}) on $[Ag^{II}]$ (mol dm^{-3} $\times$ 10^4) at 450 nm for $[Hbipy^+] \approx 4.0 \times 10^{-3}$ mol dm^{-3} (excess), $I = 1.00$ mol dm^{-3}, and 25 °C with a range of acidities

$[H^+]$/mol dm^{-3}							
0.10		0.30		0.50		0.70	
$[Ag^{II}]$	$\epsilon_{obs.}$	$[Ag^{II}]$	$\epsilon_{obs.}$	$[Ag^{II}]$	$\epsilon_{obs.}$	$[Ag^{II}]$	$\epsilon_{obs.}$
1.45	2.13	1.91	1.83	2.48	1.70	1.32	1.40
2.53	2.11	5.26	1.90	13.15	1.69	1.82	1.40
5.07	2.03	7.90	1.82			5.38	1.43
9.21	2.17					6.67	1.41
13.41	2.10					12.03	1.41
16.24	2.14						

absorption coefficient, $\varepsilon_{obs.}$, at a constant acidity and for a fixed wavelength and temperature is independent of ionic strength and added Ag^I. Table 5 demonstrates that $\varepsilon_{obs.}$ at a fixed wavelength decreases with increasing

TABLE 3

Independence of $\varepsilon_{obs.}$ (dm^3 mol^{-1} cm^{-1} $\times$ 10^{-3}) on ionic strength for $[Hbipy^+] \approx 4.0 \times 10^{-3}$ mol dm^{-3} (excess), $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-3}, and 25 °C for a range of acidities and wavelengths

$[H^+]$/ mol dm^{-3}	I/ mol dm^{-3}	λ/nm					
		375	400	425	450	475	500
0.10	0.10				2.06		
0.10	0.50				2.11		
0.10	1.00				2.12		
0.10	2.00				2.10		
0.50	0.50	1.66	1.45	1.58	1.66	1.52	1.18
0.50	1.00	1.72	1.46	1.58	1.69	1.52	1.18
0.50	2.00	1.72	1.48	1.61	1.61	1.51	1.18
1.00	1.00				1.40		
1.00	2.00				1.39		

acidity at 25 °C and that the wavelength of maximum absorption shifts slightly towards the u.v. as the acidity increases: in 0.1 mol dm^{-3} HNO_3 the maximum is at 450 nm and in 1 mol dm^{-3} HNO_3 it is at 446 nm (*cf.* Figure 1). Table 5 also shows that the decrease of $\varepsilon_{obs.}$ with increasing $[H^+]$ at a fixed wavelength also occurs at other temperatures.

If only one 2,2′-bipyridine molecule is lost as in (2)

TABLE 4

Independence of $\varepsilon_{obs.}$ (dm^3 mol^{-1} cm^{-1} $\times$ 10^{-3}) on added $[Ag^I]$ at $[H^+] = 0.50$ mol dm^{-3}, $I = 1.00$ mol dm^{-3}, $[Hbipy^+] \approx 4.0 \times 10^{-3}$ mol dm^{-3} (excess), $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-3}, and 25 °C for a range of wavelengths

$[Ag^I]$/ mol dm^{-3}	λ/nm		
	400	450	500
	1.48	1.69	1.22
0.10	1.48	1.69	1.20
0.20	1.47	1.67	1.23
0.50	1.49	1.70	1.21

with $K_h = [Ag(bipy)^{2+}][Hbipy^+]/[Ag(bipy)_2^{2+}][H^+]$, it can be shown that equation (3) will apply, which relates

$$[H^+]\left(1 - \frac{\varepsilon_1}{\varepsilon_{obs.}}\right) = \frac{\varepsilon_2}{K_h'\varepsilon_{obs.}} - \frac{1}{K_h'} \qquad (3)$$

$\varepsilon_{obs.}$ to the absorption coefficients ε_1 and ε_2 for $[Ag(bipy)]^{2+}$ and $[Ag(bipy)_2]^{2+}$ respectively: $K_h' = K_h/[Hbipy^+]_T$, where $[Hbipy^+]_T$ is the total excess of

TABLE 5

Values of $\varepsilon_{obs.}$ (dm^3 mol^{-1} cm^{-1} $\times$ 10^{-3}) for $[Hbipy^+] \approx 4.0 \times 10^{-3}$ mol dm^{-3} (excess), $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-3}, and $I = 1.00$ mol dm^{-3} for various temperatures and a range of acidities

		$[H^+]$/mol dm^{-3}				
θ_c/°C	λ/nm	0.10	0.30	0.50	0.70	1.00
25.0	350	3.88	3.38	3.29	2.93	2.67
	375	2.15	1.90	1.73	1.64	1.49
	400	1.79	1.59	1.48	1.39	1.26
	420	1.92	1.69	1.56	1.44	1.29
	425	1.95	1.75	1.59	1.48	1.32
	430	2.01	1.77	1.62	1.51	1.34
	440	2.09	1.83	1.68	1.55	1.39
	445	2.11	1.85	1.69	1.57	1.40
	450	2.12	1.86	1.69	1.57	1.40
	455	2.11	1.84	1.68	1.56	1.38
	460	2.09	1.83	1.67	1.54	1.36
	465	2.04	1.79	1.63	1.51	1.32
	475	1.90	1.70	1.55	1.44	1.28
	500	1.55	1.34	1.22	1.10	0.96
	525	1.16	0.98	0.91	0.82	0.71
	550	0.81	0.71	0.65	0.60	0.52
5.0	400	1.79	1.68	1.58	1.47	1.38
	450	2.28	2.03	1.87	1.73	1.62
19.4	400	1.81	1.63	1.57	1.43	1.36
	450	2.20	1.94	1.75	1.65	1.49
35.0	400	1.76	1.65	1.48	1.35	1.27
	450	2.16	1.86	1.71	1.55	1.41
45.0	400	1.71	1.53	1.43	1.25	1.26
	450	2.08	1.71	1.65	1.43	1.34

2,2′-bipyridine since the acid dissociation constant of $Hbipy^+$ is *ca.* 4×10^{-5} mol dm^{-3}.[12] If $(\varepsilon_1/\varepsilon_{obs.}) \ll 1$ at any particular wavelength, λ, then a plot of $h = [H^+]$ against $\varepsilon_{obs.}^{-1}$ for that wavelength should be linear. Figure 2 shows that such plots at 25 °C are linear at 550, 525, and 500 nm but become increasingly curved towards the h axis as λ decreases below 475 nm: curvature is just detectable at the latter wavelength. With such curves, $h[1 - (\varepsilon_1/\varepsilon_{obs.})]$ was plotted against $\varepsilon_{obs.}^{-1}$

for a range of values for ε_1 until the best linear plot was obtained as judged visually: Figure 3 shows an example of this type of fit for 455 nm at 25 °C. Values for K_h' and ε_2 are then calculated from the intercept and slope of the best linear plot using a least-squares procedure.

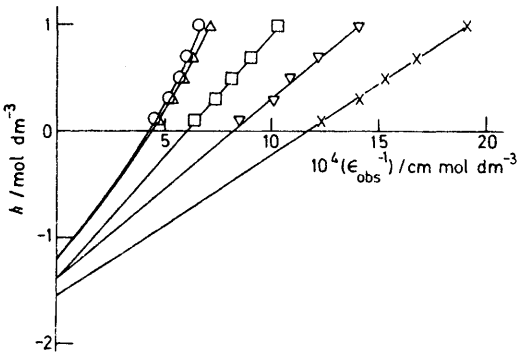

FIGURE 2 Plots of $h = [H^+]$ against $\epsilon_{obs.}^{-1}$ at $I = 1.00$ mol dm^{-3} and at 25 °C for $\lambda = 375$ (○), 450 (△), 500 (□), 525 (▽), and 550 nm (×)

The results of such an analysis for 16 wavelengths at 25 °C are given in Table 6. The errors quoted for ε_1 represent the range of ε_1 values which give a linear fit from graphical analyses such as that in Figure 3, and the values for ε_2 and K_h' are those derived from the application of the least-squares procedure to the plot for the value of ε_1 quoted, together with their standard deviations. In the last column the mean value of K_h' for $I = 1.00$ mol dm^{-3} and 25 °C is given. Similar

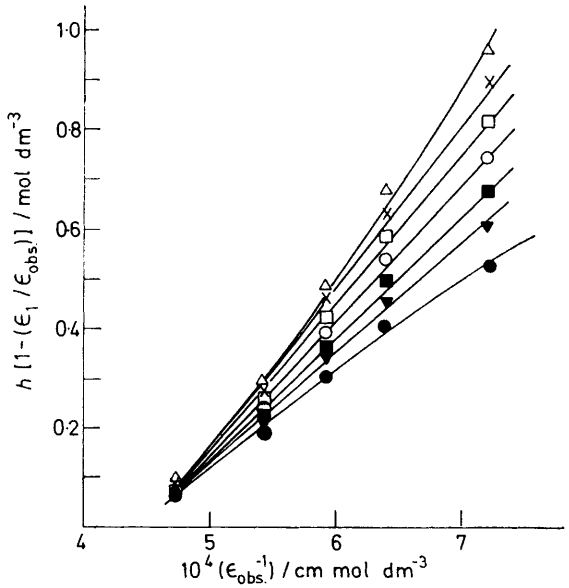

FIGURE 3 Plots of $h[1 - (\epsilon_1/\epsilon_{obs.})]$ against $\epsilon_{obs.}^{-1}$ at 455 nm, $I = 1.00$ mol dm^{-3}, and 25 °C using $\epsilon_1 = 50$ (△), 150 (×), 250 (□), 350 (○), 450 (■), 550 (▼), and 650 dm^3 mol^{-1} cm^{-1} (●)

analyses were carried out for $\epsilon_{obs.}$ values found at 400 and 450 nm at several temperatures in the range 5—45 °C, and the values found for ε_1, ε_2, and K_h' are also given in Table 6, together with the mean value of K_h' at $I = 1.00$ mol dm^{-3}. From an application of least squares to the plot of the logarithm of this mean value of K_h' against the reciprocal of absolute temperature the enthalpy change, ΔH, for (2) is 11.5 ± 2.6 kJ mol^{-1} and the entropy change ΔS is −9 ± 10 J K^{-1} mol^{-1} at $I = 1.00$ mol dm^{-3}. ε_2 For $[Ag(bipy)_2]^{2+}$ shows a maximum value of 2 240 ± 140 dm^3 mol^{-1} cm^{-1} at 450 nm and a minimum value of 1 900 ± 100 dm^3 mol^{-1} cm^{-1} at 400 nm.

The above analysis shows that the spectrophotometric data presented here are consistent with the operation of equilibrium (2). If either equilibrium (1) or (4) were

$$[Ag(bipy)_2]^{2+} \rightleftharpoons [Ag(bipy)_2(OH)]^+ + H^+ \quad (4)$$

responsible for these spectrophotometric data $\epsilon_{obs.}$ would be independent of the concentration of 2,2′-bipyridine, contrary to the variation given in Table 1. Moreover, the rates of redox reactions of $[Ag(bipy)_2]^{2+}$ with added substrates are dependent on the added excess

TABLE 6

Values for ε_1 (dm^3 mol^{-1} cm^{-1} × 10^{-2}), ε_2 (dm^3 mol^{-1} cm^{-1} × 10^{-3}), K_h' (dm^3 mol^{-1}), and mean K_h' (dm^3 mol^{-1})

θ_c/°C	λ/nm	ϵ_1	ϵ_2	K_h'	Mean K_h'
5.0	400	5.5 ± 2.0	1.84 ± 0.45	0.56 ± 0.14	0.59 ± 0.03
	450	3.5 ± 2.0	2.36 ± 0.53	0.62 ± 0.14	
19.4	400	6.5 ± 2.0	1.88 ± 0.25	0.77 ± 0.07	0.75 ± 0.02
	450	3.5 ± 2.0	2.31 ± 0.31	0.73 ± 0.10	
25.0	350	15 ± 2	4.14 ± 0.24	1.24 ± 0.07	0.82 ± 0.12
	375	10 ± 1	2.36 ± 0.20	1.72 ± 0.11	
	400	6.5 ± 1.0	1.90 ± 0.10	1.04 ± 0.06	
	420	4.5 ± 1.0	2.04 ± 0.08	0.89 ± 0.03	
	425	4.0 ± 2.0	2.08 ± 0.10	0.82 ± 0.04	
	430	3.75 ± 2.0	2.12 ± 0.07	0.81 ± 0.03	
	440	4.5 ± 1.0	2.22 ± 0.08	0.89 ± 0.03	
	445	4.5 ± 2.0	2.24 ± 0.07	0.89 ± 0.03	
	450	3.5 ± 2.0	2.24 ± 0.14	0.81 ± 0.05	
	455	3.5 ± 2.0	2.33 ± 0.15	0.81 ± 0.06	
	460	3.5 ± 2.0	2.22 ± 0.09	0.84 ± 0.04	
	465	2.5 ± 2.0	2.18 ± 0.12	0.79 ± 0.05	
	475	1.5 ± 1.0	2.01 ± 0.26	0.65 ± 0.09	
	500	0	1.63 ± 0.12	0.70 ± 0.05	
	525	0	1.23 ± 0.31	0.74 ± 0.19	
	550	0	0.91 ± 0.10	0.86 ± 0.10	
35.0	400	6.5 ± 2.0	1.92 ± 0.80	1.09 ± 0.50	1.02 ± 0.07
	450	4.5 ± 1.0	2.29 ± 0.12	0.94 ± 0.05	
45.0	400	*ca.* 6.5	1.83 ± 0.42	1.10 ± 0.25	1.07 ± 0.03
	450	*ca.* 4.5	2.21 ± 0.40	1.04 ± 0.19	

of 2,2′-bipyridine,[13] suggesting the existence of a pre-equilibrium (2) rather than (1) or (4). As $\epsilon_{obs.}$ is independent of the ionic strength (and hence of the added $[NO_3^-]$), as shown in Table 3, equilibrium (5) cannot be

$$[Ag(bipy)]^{2+} + H^+ \rightleftharpoons Ag^{2+} + Hbipy^+ \quad (5)$$

responsible for the spectrophotometric data, since the spectrum of Ag^{2+} has been shown to be markedly dependent on $[NO_3^-]$.[14] The similarity of the spectrum of $[Ag(bipy)_2]^{2+}$ found in this work with that observed by the dissolution of $[Ag(bipy)_2][NO_3]_2$ in water also supports the view that equilibrium (2) is responsible for these spectrophotometric data. Although the present values of ε_2 at 400 nm (1 900 ± 100 dm^3 mol^{-1} cm^{-1}) and at 455 nm (2 230 ± 150 dm^3 mol^{-1} cm^{-1}) agree well with those found by Po and Chen [5] at the same wavelengths (1 750 ± 90 and 2 160 ± 40 dm^3 mol^{-1} cm^{-1} respectively), values derived by other workers [3,4] are

lower probably because these were not corrected for the loss of Ag^{II} from its reaction with water.

We therefore suggest that the interpretation by Thorpe and Kochi [2] of the difference between their e.s.r. results and those of Halpern *et al.*[7] is correct.

In general, for two reversible redox systems (6) and (7) involving the same cations M^{z+} and $M^{(z+1)+}$ and a

$$ML_n^{(z+1)+} + e \rightleftharpoons ML_n^{z+} \quad (6)$$

$$M^{(z+1)+} + e \rightleftharpoons M^{z+} \quad (7)$$

ligand L, with standard electrode potentials $E_L^{\ominus}$ and $E^{\ominus}$, respectively, it can readily be shown that equation (8) holds, where K and K' are equilibrium constants for (9)

$$E_L^{\ominus} - E^{\ominus} = (RT/F)(\ln K - \ln K') \quad (8)$$

$$M^{z+} + nL \overset{K}{\rightleftharpoons} ML_n^{z+} \quad (9)$$

$$M^{(z+1)+} + nL \overset{K'}{\rightleftharpoons} ML_n^{(z+1)+} \quad (10)$$

and (10). For the Ag^{2+}–Ag^{+} system, $E^{\ominus} = 1.928\ 7$ V [15] in aqueous nitric acid at 25 °C and $E_L^{\ominus}$ for $n = 2$ is 1.453 V [16] in aqueous acidic media containing both nitrate and sulphate ions; for $n = 1$, $\log K = 3.70$ and for $n = 2$, $\log K = 7.22$.[17] Using the value determined here for K_h together with the acid-dissociation constant for 2,2′-bipyridine,[12] $E_L^{\ominus}$ for $n = 1$ is 1.65 V. However, in the determination of $E_L^{\ominus}$ by Scrocco *et al.*[16] the presence of sulphuric acid and the absence of an excess of 2,2′-bipyridine suggests that their value may refer to $n = 1$. Assuming this to be the case, $E_L^{\ominus}$ for $n = 2$ now becomes 1.05 V. This latter view is supported by the correlation [18] of rate constants and $E^{\ominus}$ data for the reactions of Fe^{II} with complexes of metal atoms with 2,2′-bipyridine and 1,10-phenanthroline [19] where Ag^{2+}–Ag^{+} only lies on the linear Marcus plot in aqueous sulphuric acid (where $n = 1$) if $E_L^{\ominus}$ is 1.4 V.[18]

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