Activation Volumes for Peroxodisulphate Oxidation of Low-spin Iron(II) Complexes in Aqueous Salt Solutions*

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Activation volumes are reported for peroxodisulphate oxidation of the four complexes of the Fe^{2+}-2,2'-bipyridyl–cyanide sequence, *viz.* $[Fe(bipy)_3]^{2+}$, $[Fe(bipy)_2(CN)_2]$, $[Fe(bipy)(CN)_4]^{2-}$ and $[Fe(CN)_6]^{4-}$ (abbr. bipy for 2,2'-bipyridyl), in aqueous solutions of a selection of nitrate, sulphate, and perchlorate salts of Li^+, Na^+, K^+, and Mg^{2+} containing up to 6 mol dm^{-3} of added salt. The dependences of activation volumes on the nature and concentration of the added salt, and on the nature of the iron(II) complex, are established and discussed. Ancillary information relevant to hydration of the substrate complexes in the initial state for peroxodisulphate oxidation has been obtained from solvatochromism (halochromism) of $[Fe(bipy)_2(CN)_2]$ and of $[Fe(bipy)(CN)_4]^{2-}$, and from the solubility of $[Fe(bipy)_2(CN)_2]$, in some of the electrolyte solutions used in the high pressure kinetic studies.

Key words: iron(II)-2,2'-bipyridyl–cyanide complexes, peroxodisulphate oxidation, activation volumes.

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.
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INTRODUCTION

Effects of added salts on rate constants for reactions of inorganic complexes and ions have been studied intensively for several decades.[1,2] However there has been much less activity in determining salt effects on enthalpies and entropies of activation,[2] and there have been almost no studies of pressure effects to determine the effects of added electrolytes on volumes of activation for such reactions. Indeed there have been rather few activation volumes reported for inorganic redox reactions.[3] Following the determination of activation volumes for peroxodisulphate oxidations of several cobalt(III), iron(II), and nickel(II) complexes,[4,5] we now report the results of a study of the effects of several nitrates and perchlorates on activation volumes for peroxodisulphate oxidation of a series of low-spin (and thus substitution-inert) iron(II) complexes. This series comprises the four binary and ternary complexes of the Fe^{2+}–2,2'-bipyridyl–cyanide sequence, *viz.* $[Fe(bipy)_3]^{2+}$, $[Fe(bipy)_2(CN)_2]$, $[Fe(bipy)(CN)_4]^{2-}$, and $[Fe(CN)_6]^{4-}$ (bipy: 2,2'-bipyridyl). Rate constants determined in the course of the present investigation complement results obtained earlier on salt effects on reactivity for peroxodisulphate oxidations of complexes in this series.[6]

EXPERIMENTAL

Materials

The iron(II) complexes $[Fe(bipy)_3](ClO_4)_2$[7] and $[Fe(bipy)_2(CN)_2] \cdot 3H_2O$,[8] and the salt $K_2[Fe(bipy)(CN)_4] \cdot 3H_2O$[8] were prepared by published methods. $LiNO_3 \cdot H_2O$ and $Li_2SO_4 \cdot H_2O$ were obtained from Merck, $NaNO_3$ from Fisher, $LiClO_4$, $NaClO_4$ and $Na_2S_2O_8$ from Aldrich, and KNO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ from May and Baker. All these commercial materials were used as received. Solutions were prepared using deionised water. Their pH was measured with a CD 620 pH meter – values ranged from 5.8 ($LiNO_3$) to 7.0 (KNO_3, Li_2SO_4).

Methods

All kinetic measurements were determined using the apparatus described previously;[9] conditions are detailed in the Tables. Activation volumes were evaluated from the dependence $\ln(k_p/k_0) = f(P)$; their uncertainties are ± 1.0 cm^3 mol^{-1}. Rate constants k_0 were measured at a pressure of 25 bar, an »atmospheric« pressure slightly above 1 bar being necessary to prevent leakage from the high pressure cell. EDTA was added to reaction mixtures in order to avoid any catalysis of the reaction by any traces of metal ions.

RESULTS

Rate constants for peroxodisulphate oxidation of the iron complexes are reported in Tables I to IV. Activation volumes derived from these rate con-

TABLE I

Second order rate constants at 25 bar, k_0 / dm³ mol⁻¹ s⁻¹, activation volumes, $\Delta V^\ddagger$ / cm³ mol⁻¹, and ratios of rate constants at high pressure, k_p (pressure, p / kbar) to those at 25 bar for the reaction $[Fe(bipy)_3]^{2+} + S_2O_8^{2-}$ in concentrated electrolyte solutions at 298.2 K. Initial complex concentration 1.25×10^{-4} mol dm⁻³, $\lambda = 526$ nm

Electrolyte	$10^2\ c(Na_2S_2O_8)$	$10^2\ k_0$	p / kbar (k_p / k_0)				$\Delta V^\ddagger$
	mol dm⁻³	dm³ mol⁻¹ s⁻¹					cm³ mol⁻¹
water[a]	0.15	57	0.50 (1.66)	0.75 (2.00)	1.00 (2.37)	1.25 (3.12)	−21.9
water[b]	0.40	53.0	0.60 (1.67) (1.25)	0.80 (1.97) (1.59)	1.00 (2.33) (1.80)	1.25 (2.85) (2.09)	−20.8
6M LiNO₃	1.07	27.8 / 28[c]	0.60 (1.37)	0.95 (1.69)	1.20 (2.00)	1.40 (2.33)	−14.9
2.5M Li₂SO₄	0.50	52.5	0.50 (1.36)	0.75 (1.62)	1.05 (2.04)	1.40 (2.48)	−16.3
6M NaNO₃	5.33	6.77 / 6.9[c]	0.50 (1.35)	0.80 (1.62)	1.00 (1.83)	1.30 (2.27)	−15.5
3M Mg(NO₃)₂	0.67	38.6 / 36[c]	0.55 (1.41)	0.85 (1.70)	1.10 (2.09)	1.45 (2.68)	−16.8

[a]Rate constants and activation volume from Ref. 4; $I = 4.8 \times 10^{-3}$ mol dm⁻³. [b]$I = 12.3 \times 10^{-3}$ mol dm⁻³. [c]Rate constants from Ref. 6.

TABLE II

Second order rate constants at 25 bar, k_0; activation volumes, $\Delta V^{\ddagger}$; and ratios of rate constants at high pressure, k_p, to k_0; for the reaction $[\text{Fe(bipy)}_2(\text{CN})_2] + \text{S}_2\text{O}_8^{2-}$ in different concentrated electrolytes at 298.2 K. Complex concentration: 2.5×10^{-4} mol dm^{-3} in electrolytes, 1.8×10^{-4} mol dm^{-3} in water; $\lambda = 520$ nm

Electrolyte	$10^3\ c(\text{Na}_2\text{S}_2\text{O}_3)$ mol dm^{-3}	$10^2\ k_0$ dm^3 mol^{-1} s^{-1}	p / kbar (k_p / k_0)				$\Delta V^{\ddagger}$ cm^3 mol^{-1}
water[a]	2.0	12.0	0.34 (1.11)	0.69 (1.23)	1.04 (1.41)		−7.7
water	5.0	10.6	0.50 (1.19)	0.80 (1.32)	1.25 (1.52)	1.40 (1.60)	−8.3
water	2.3	10.0	0.50 (1.14)	0.80 (1.35)	1.00 (1.49)	1.40 (1.66)	−8.5
6M LiNO$_3$	4.0	98.5 / 110[b]	0.50 (1.26)	0.80 (1.46)	1.00 (1.68)	1.30 (1.91)	−12.5
6M LiNO$_3$	2.3	100	0.50 (1.31)	0.80 (1.48)	1.15 (1.78)	1.45 (2.03)	−12.0
4M LiClO$_4$	6.0	62.0	0.50 (1.29)	0.80 (1.56)	1.20 (1.90)	1.50 (2.16)	−12.9
4M NaClO$_4$	5.0	44.6	0.60 (1.23)	0.85 (1.28)	1.00 (1.34)	1.45 (1.61)	−7.9
2.5M KNO$_3$	2.3	21.4 / 21[b]	0.55 (1.18)	0.85 (1.38)	1.10 (1.48)	1.35 (1.59)	−8.7
3M Mg(NO$_3$)$_2$	2.3	151 / 140[b]	0.50 (1.25)	0.80 (1.38)	1.20 (1.60)	1.40 (1.69)	−9.3

[a]Rate constants and activation volume from Ref. 5. [b]Rate constants from Ref. 6.

TABLE III

Second order rate constants at 25 bar, k_0; activation volumes, $\Delta V^{\ddagger}$; and ratios of rate constants at high pressure, k_p, to k_0; for the reaction $[Fe(bipy)(CN)_4]^{2-} + S_2O_8^{2-}$ in different concentrated electrolytes at 298.2 K. Initial complex concentration: 3.2×10^{-4} mol dm^{-3}; $c(Na_2S_2O_8) = 4 \times 10^{-3}$ mol dm^{-3}; $\lambda = 478$ nm

Electrolyte	$10\,k_0$ dm^3 mol^{-1} s^{-1}	p / kbar (k_p/k_0)					$\Delta V^{\ddagger}$ cm^3 mol^{-1}
water	1.65	0.65 (1.11)	0.80 (1.14)	1.15 (1.18)	1.25 (1.21)	1.40 (1.24)	−3.7
6M LiNO$_3$	9.3 10[a]	0.55 (1.14)	0.85 (1.25)	1.05 (1.27)	1.35 (1.32)	1.50 (1.37)	−5.0
4M LiClO$_4$	8.75	0.85 (1.13)	1.05 (1.20)	1.30 (1.24)	1.50 (1.29)		−4.2
2.5M Li$_2$SO$_4$	11.5	0.80 (1.05)	1.10 (1.10)	1.25 (1.09)	1.50 (1.11)		−1.7
6M NaNO$_3$	8.0 7.4[b]	0.60 (1.01)	0.95 (1.03)	1.40 (1.03)	1.50 (1.02)		0.0
6M NaClO$_4$	11.2	0.80 (1.06)	1.00 (1.07)	1.35 (1.11)	1.50 (1.10)		−1.7
2.5M KNO$_3$	4.3 4.0[b]	0.80 (1.04)	1.00 (1.09)	1.25 (1.07)	1.50 (1.12)		−1.8
3M Mg(NO$_3$)$_2$	10.0 9.7[b]	0.80 (1.15)	1.05 (1.16)	1.30 (1.26)	1.50 (1.26)		−3.9

[a]Rate constants and activation volume from Ref. 5. [b]Rate constants from Ref. 6.

TABLE IV

Second order rate constants at 25 bar, k_0; activation volumes, $\Delta V^\ddagger$; and ratio of rate constants at high pressure, k_p, to k_0; for reaction $[Fe(CN)_6]^{4-} + S_2O_8^{2-}$ in different concentrated electrolytes at 298.2 K. $c_{compl} = 1 \times 10^{-3}$ mol dm^{-3}, $c_{Na_2S_2O_8} = 1 \times 10^{-2}$ mol dm^{-3}, $\lambda = 420$ nm

Electrolyte	$10^2\,k_0$	p / kbar				$\Delta V^\ddagger$
	dm^3 mol^{-1} s^{-1}	(k_p / k_0)				cm^3 mol^{-1}
water[a]	1.54	0.50 (1.05)	0.75 (1.05)	1.00 (1.02)	1.25 (1.04)	0.0
6M LiNO$_3$	19.9	0.80 (1.00)	1.10 (1.04)	1.25 (1.03)	1.50 (1.01)	0.0
4M LiClO$_4$	17.8	0.80 (1.03)	1.05 (0.98)	1.25 (1.00)	1.50 (1.05)	0.0
2.5M Li$_2$SO$_4$	18.3	0.60 (1.03)	0.90 (1.01)	1.25 (1.01)	1.50 (1.03)	0.0
6M NaNO$_3$	24.0	0.80 (1.00)	1.00 (0.980)	1.20 (0.95)	1.50 (0.98)	0.0
6M NaClO$_4$	50.2	0.80 (0.99)	1.05 (1.00)	1.25 (0.95)	1.45 (0.98)	0.0

[a]Rate constants and activation volume from Ref. 4; $c_{Na_2S_2O_8} = 5 \times 10^{-2}$ mol dm^{-3}.

stants are summarised and compared in Table V. It is difficult to compare the effects of the various electrolytes directly, since their concentrations are widely different – we chose to use the highest practical concentration in each case to maximise their effects.

TABLE V

Summary of activation volumes for peroxodisulphate oxidation of iron(II) complexes, in water and in aqueous salt solutions, at 298.2 K

Added electrolyte	[salt] mol dm^{-3}	$\Delta V^{\ddagger}$ / cm^3 mol^{-1}			
		$[Fe(bipy)_3]^{2+}$	$[Fe(bipy)_2(CN)_2]$	$[Fe(bipy)(CN)_4]^{2-}$	$[Fe(CN)_6]^{4-}$
none		−21.9	−7.7	−3.7	0
none		−20.8	−8.3, −8.5	0	
LiNO$_3$	6.0	−14.9	−12.5, −12.0	−5.0	0
LiClO$_4$	4.0		−12.9	−4.2	0
Li$_2$SO$_4$	2.5	−16.3		−1.7	0
NaNO$_3$	6.0	−15.5		0	0
NaClO$_4$	6.0		−7.9	−1.7	0
KNO$_3$	2.5		−8.7	−1.8	
Mg(NO$_3$)$_2$	3.0	−16.8	−9.3	−3.9	

Wavenumbers for the lowest energy charge-transfer band of the strongly solvatochromic ternary iron-diimine-cyanide complexes in a selection of aqueous electrolyte solutions are listed in Table VI. Solubilities of the uncharged complex in a similar range of media are reported in Table VII.

DISCUSSION

The negative values found for the activation volumes for the peroxodisulphate oxidations of the (2+), uncharged, and (2−) complexes are in agreement with the established bimolecular mechanism for such oxidations, with the activated complexes having an intrinsically smaller volume than the respective reactants. However the large differences between these values, and between them and the expected value of approximately 10 cm^3 mol^{-1} for a simple bimolecular reaction,[3] indicates significant contributions from solvation changes to these observed activation volumes. For the peroxodisulphate oxidations of the (4−) complex hexacyanoferrate(II) the observed activation volumes of zero, within experimental uncertainty, for all added electrolytes indicate that the intrinsic contribution is compensated by an equal and opposite volume increase due to the release of electrostricted solvating water

TABLE VI

Wavenumbers of maximum absorption (ν_{max}) for the lowest energy charge-transfer band of $[Fe(bipy)_2(CN)_2]$ and $[Fe(bipy)(CN)_4]^{2-}$ in aqueous electrolyte solutions

Electrolyte	ν_{max} / cm^{-1}	
	$[Fe(bipy)_2(CN)_2]$	$[Fe(bipy)(CN)_4]^{2-}$
water	19194	20661
2M LiCl	19220	20877
4M LiCl	19268	21053
6M LiCl	19320	21218
8M LiCl	19440	21340
9M LiCl	19460	
10M LiCl		21501
4M LiClO$_4$	19421	21218
4M NaClO$_4$	19301	20921
6M NaClO$_4$	19339	21053
4M NaNO$_3$	19238	20921
4M Li$_2$SO$_4$	19260	20960

TABLE VII

Solubilities of $[Fe(bipy)_2(CN)_2]$ in concentrated electrolyte solutions

Electrolyte	10^4 Solubility / mol dm^{-3}
water	1.82[a]
2M LiNO$_3$	4.07
3M LiNO$_3$	7.30
4M LiNO$_3$	10.2
4M LiClO$_4$	6.30
4M NaClO$_4$	3.19
2.5M KNO$_3$	1.38
3M Mg(NO$_3$)$_2$	1.97

[a]From Ref. 25.

to bulk solvent on transition state formation.[4] We have discussed these intrinsic and solvation contributions earlier,[10] concluding that the size and specific geometry of the diimine ligands play a more important role than simple electrostriction effects. High pressure cyclic voltammetric studies[11,12] of electron transfer for this iron-diimine-cyanide series of complexes[12,13] has given valuable information about volume changes on going from iron(II) to iron(III), and about electrolyte effects thereon. However it should be borne

in mind that precise values and interpretation are, for the three charged members of the series, at the mercy of the need for a single ion assumption. Unfortunately this solvation information is of limited value in discussing our activation volumes, since there is no analogous information on peroxodisulphate reduction. Even were such information available there would still be the difficulty of estimating a contribution from solvating water extruded from the space between the reactants as they approach to the proximity required for electron transfer to take place.

There is a marked trend for the activation volumes for peroxodisulphate oxidation of the iron(II)–diimine–cyanide series of complexes in water from large negative values for hydrophobic $[Fe(bipy)_3]^{2+}$ through intermediate values for ternary complexes to zero for $[Fe(CN)_6]^{4-}$. This trend may be connected with the fact that if electron transfer takes place from the central iron atom the peroxodisulphate anion will be in the limited space between bipyridyl ligands,[14] whereas in oxidation of hexacyanoferrate approach to the iron atom is much less restricted – with intermediate situations for the ternary complexes. In concentrated electrolyte solutions there will be ion-pairing between constituent ions of the added electrolyte and charged reactants. Electrolyte effects on activation volumes can be related to the varying hydrophobicity of the iron complexes. The structural effects of hydrophobic hydration could be reduced by the proximity of ions from the added electrolyte, especially for the hydrophobic $[Fe(bipy)_3]^{2+}$ cation. The change in activation volume on going from hydrophobic $[Fe(bipy)_3]^{2+}$ to hydrophilic $[Fe(CN)_6]^{4-}$ is smaller in the concentrated electrolyte solutions than in water (Tables I to V), with $\Delta V^{\ddagger}$ most affected by the nature of the added electrolyte for the (2+)/(2–) reaction. There is a striking contrast between our activation volume pattern of electrolyte effects decreasing from $[Fe(bipy)_3]^{2+}$ to $[Fe(CN)_6]^{4-}$ and the high pressure cyclic voltammetry results[13] which show the biggest effects for $[Fe(CN)_6]^{4-/3-}$, the smallest for $[Fe(bipy)_3]^{2+/3+}$. Clearly the peroxodisulphate is playing a major role in our redox reactions.

The markedly negative $\Delta V^{\ddagger}$ values for the $[Fe(bipy)_3]^{2+}/S_2O_8^{2-}$ reaction presumably arise from the resultant of the decrease of intrinsic volume and in electrostriction on going from the initial to the transition state – in this reaction there is charge cancellation on forming the transition state. The hydration of the constituent ions of the electrolytes introduced into the system causes a decrease in water activity[15] and thus could lead to solvation changes, particularly of the initial state. Gibbs solvation energies are in the order $\Delta G(Li^+) > \Delta G(Na^+) > \Delta G(K^+)$;[16] the extent of hydration depends on the charge/radius ratio. Solvation of $S_2O_8^{2-}$ is probably reduced in the presence of added electrolyte, to an extent depending on its nature and concentration. The decreasingly negative $\Delta V^{\ddagger}$ on going from water to concentrated electrolyte solution presumably arises from the fact that in the presence of added electrolyte the $S_2O_8^{2-}$ will need to lose less electrostricted water on entering

the transition state than when the reaction takes place in water alone. This is probably the reason why the (2+)/(2−) reaction has a rather smaller negative $\Delta V^{\ddagger}$ in the presence of added electrolyte than in its absence. In contrast, addition of lithium salts to the (0)/(2−) reaction leads to increasingly negative $\Delta V^{\ddagger}$ values. Table II shows that even for the uncharged complex $[Fe(bipy)_2(CN)_2]$ $\Delta V^{\ddagger}$ values depend significantly on the nature and concentration of the added electrolyte, particularly on its cation. The study of electrolyte effects on band energies of electronic transitions could help in rationalising the specific electrolyte effects on reactivity, with solvatochromic shifts (so-called halochromism),[17] indicating the possibility of the existence of specific interactions in the vicinity of the solute. For symmetric complexes such as $[Fe(bipy)_3]^{2+}$ or $[Fe(CN)_6]^{4-}$ it appears that the electrolyte affects the ground and excited states to a similar extent, so that the positions of the charge-transfer absorption bands remain essentially constant – a similar observation has been made for the symmetrical $[Cr(NCS)_6]^{3-}$ anion in concentrated electrolyte solutions.[18] Ternary complexes such as $[Fe(bipy)_2(CN)_2]$ and $[Fe(bipy)(CN)_4]^{2-}$ do show marked solvatochromic behaviour[19] and can be used as probes in our present investigation. The wavenumbers of maximum absorption for their charge-transfer bands are given in Table VI. The first and second bands for $[Fe(bipy)(CN)_4]^{2-}$, at around 20660 and 27500 cm^{-1} respectively, may be assigned to electron excitation from the two highest occupied π-m.o.s of coordinated 2,2'-bipyridyl to a vacant antibonding m.o. involving an $e_g{}^*$ orbital mainly localised on the central iron atom. The third band ($v \sim 33500$ cm^{-1}) may be assigned to π-π^* excitation in the 2,2'-bipyridyl ligands; it corresponds to the first band for free 2,2'-bipyridyl. The spectrum of $[Fe(bipy)_2(CN)_2]$ is similar, but the first band is split into a peak at 19194 cm^{-1} and a shoulder at 25590 cm^{-1}. This split (Davydov split) is caused by delocalization of excitation π-HOMO-$e_g{}^*$ on both bipy ligands; there is also a hint of a Davydov split in the second band.[20] Table VI shows that the maximum of the first absorption band depends significantly on the nature and concentration of the electrolyte, especially of its cation. When the complex is dissolved in the electrolyte solution, the lone pair of the terminal nitrogen of the cyanide ligand can interact with the cation of the electrolyte. The electronic shift resulting from this interaction affects the π-bonding between the iron and the cyanide, but weakens that between iron and bipy. The hypsochromic shift produced in the electrolyte solution for the cyano-complexes (Table VI) can be explained as a consequence of electrolyte cation interaction at the cyanide nitrogen. The positive charge introduced by the cation to the cyanide nitrogen atom would be expected to increase the energy required for the excitation of electrons into participation with the π-electron system of the aromatic ligands. Similar solvatochromic behaviour was observed for $[Fe(phen)_2(CN)_2]$ as a consequence of protonation at the cyanide nitrogen atoms both in water[21] and in organic solvents;[22] complexation by Hg^{2+} at the

cyanide-nitrogen has an analogous effect.[23] The shift of the band position increases for 4M electrolytes $NaClO_4 < LiClO_4$ both for the dicyano and the tetracyano complexes (Table VI). It corresponds to solubility trends for $[Fe(bipy)_2(CN)_2]$, where soly.$(NaClO_4) <<$ soly.$(LiClO_4)$ (Table VII). These observations indicate stronger interaction of Li^+ than of Na^+ with the lone pair of the terminal nitrogen of the coordinated cyanide. These cations are probably partly or fully desolvated. Besides the $S_2O_8^{2-}$ (positive) contribution to $\Delta V^{\ddagger}$, the negative contribution to $\Delta V^{\ddagger}$ values in $LiClO_4$ (4M) and $LiNO_3$ (6M) (Table II) presumably arises from the fact that the $[Fe(bipy)_2(CN)_2],Li^+$ associated species needs to lose Li^+ (or rather partly hydrated Li^+) on entering the transition state. This is probably why in the presence of lithium salts the (0)/(2–) reaction has a higher $\Delta V^{\ddagger}$ than the corresponding reaction in water. The assumption that the function of the added electrolyte's cation is simply to lower the coulombic repulsion in the transition state for (2–)/(2–) and (4–)/(2–) reactions cannot be the explanation since the same effect should be observed in the (0)/(2–) reaction of the uncharged complex, for which the Debye-Hückel and electrostatic work should in principle be non-existent. According to Swaddle $\Delta V^{\ddagger}$ is determined in large part by solvent compressibility. Solvent in the solvation shell of ions is compressed by electrostriction and thus less compressible than bulk solvent. There is thus local loss of solvent compressibility near the solute.[24] The effect of pressure on reaction rate constants decreases with increasing number of cyanide ligands. For the (4–)/(2–) reaction, *i.e.* oxidation of $[Fe(CN)_6]^{4-}$, no significant effect of pressure on rate constant was detected, either in water or in concentratred electrolyte solutions. Decreasingly negative $\Delta V^{\ddagger}$ values are observed in the series of cyano-complexes as the number of cyanide ligands increases, with concomitant increase in local loss of solvent compressibility adjacent to the iron complex. The results show that the $\Delta V^{\ddagger}$ values depend significantly on the nature and concentration of the electrolyte, particularly on the cation involved.

To digress briefly from kinetics and activation volumes, the solubilities reported in Table VII considerably extend knowledge of salt effects on the solubility of $[Fe(bipy)_2(CN)_2]$.* Earlier work[25] established the pattern of effects of several alkali metal and tetraalkylammonium bromides and chlorides on the solubility of this uncharged complex; the Table VII results are complementary in that they provide information on the effects of salts of

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* It is not worthwhile at the moment to extend this study to the other complexes in the iron(II)–2,2'-bipyridyl–cyanide series since the other three members are charged – there is currently no satisfactory method of dissecting salt solubilities into single ion contributions. Moreover such salts of $[Fe(bipy)_3]^{2+}$ as the perchlorate, nitroprusside, and hexachlororhenate are too sparingly soluble, the sulphate, nitrate, and halides too freely soluble, for convenient measurement and satisfactory thermodynamic analysis, respectively; alkali metal salts of $[Fe(bipy)(CN)_4]^{2-}$ are also too freely soluble.

two oxoanions. However it is not a straightforward matter to compare the two sets of results, since the Table VII values refer to much higher electrolyte concentrations than the earlier work. A qualitative comparison is provided in Figure 1, where the bold symbols and lines indicate experimental results and ranges, the thin lines are simply to aid comparisons. The oxoanions clearly have a markedly different effect from the halides, just as the alkali metal cations have a markedly different effect from the organic cations. Both for anions and cations increasing hydrophilicity leads to a general anti-clockwise rotation. The earlier report discussed the solubility pattern in terms of Setchenow coefficients,[26] permitting comparisons with other inorganic and several organic solutes.[27] We do not feel that such a treatment can be justified here, as it is exceedingly unlikely that the linear dependence of logarithms of solubilities on concentration assumed in the derivation of Setchenow coefficients will be obeyed at such high electrolyte concentrations as those of Table VII – indeed the curvature of the tetraalkylammonium bromide plots in Figure 1 provides due warning.
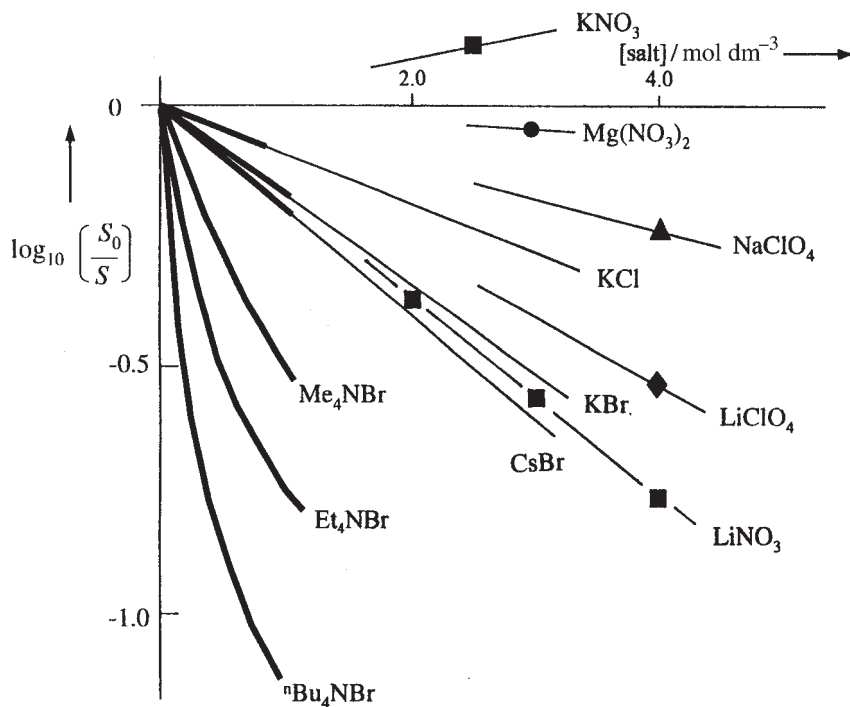

Figure 1. Dependence of logarithms of ratios of $Fe(bipy)_2(CN)_2$ solubility in water to solubilities in salt solutions, $\log_{10}(S_0/S)$, on salt concentration. The thick lines in the region of low salt concentration in each case represent the best smooth curve through a number of points (see Ref. 25).

To return to kinetics, we summarise our conclusions regarding the observed patterns of electrolyte effects on $\Delta V^{\ddagger}$ values, suggesting that there are three contributing factors:

– High concentrations of added electrolyte lead to relative desolvation of reactants and transition states.

– Interaction of cyanide ligands with partially or wholly desolvated cations from the added electrolyte.

– Differences in solvent compressibility between bulk and solvating water.

If information on electrostriction effects on solvation changes consequent on reduction of peroxodisulphate become available, then it may prove possible to combine this with the data on the series of iron(II)/(III)-diimine-cyanide complexes and our results on activation volumes to provide a detailed and revealing picture of intrinsic and solvation contributions to this series of redox reactions.

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SAŽETAK

Aktivacijski volumeni u reakciji oksidacije niskospinskog željeza(II) s peroksodisulfatom u vodenim otopinama soli

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Dani su aktivacijski volumeni za oksidaciju peroksodisulfatom za četiri kompleksa Fe^{2+}-2,2'-bipiridincianidnog niza tj. $[Fe(bpy)_3]^{2+}$, $[Fe(bpy)_2(CN)_2]$, $[Fe(bpy)(CN)_4]^{2-}$, i $[Fe(CN)_6]^{4-}$, u vodenim otopinama nitrata, sulfata i perklorata Li^+, Na^+, K^+ odnosno Mg^{2+}, koje su sadržavale sve do 6 mol dm^{-3} dodane soli. Ustanovljena je i prodiskutirana ovisnost aktivacijskih volumena o prirodi i koncentraciji dodane soli kao i o prirodi kompleksa željeza(II). Dodatne informacije relevantne za hidrataciju kompleksnih substrata na početku oksidacije peroksodisulfatom dobivene su iz solvatokromije (halokromije) $[Fe(bpy)_2(CN)_2]$ i $[Fe(bpy)(CN)_4]^{2-}$ i iz topljivosti $[Fe(bpy)_2(CN)_2]$ u nekima od elektrolitnih otopina koje su upotrijebljene u kinetičkim studijama pod visokim tlakom.