

Solubilities of Salts and Kinetics of Reactions involving Inorganic Complex Ions in Aqueous Acetone Mixtures

Derivation of Transfer Chemical Potentials for Ions in these Aqueous Mixtures at Ambient Pressure and 298.2 K

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Solubilities of salts, including those formed by complex ions, are reported for aqueous solutions and for solutions in aqueous acetone mixtures. Data from many sources are combined to yield transfer chemical potentials for an extensive range of ions (at 298 K and ambient pressure) based on the TATB assumption, which assumes that transfer chemical potentials for Ph_4As^+ and Ph_4B^- ions are equal. Derived transfer parameters are used in analyses of kinetic data describing substitution, isomerisation and redox reactions. Transfer parameters point towards the importance of ion size, electric charge and hydrophilic/hydrophobic character in determining solvation of ions in binary aqueous mixtures.

The effects of added organic cosolvent on rate constants for reaction in aqueous solution between cations M^{2+} and anions X^- can be understood¹ in terms of the impact of cosolvent on the reference chemical potentials of these ions and of transition states. If the second-order rate constants for a given reaction are $k(\text{aq})$ in aqueous solution and $k(x_2)$ in a solvent mixture (where x_2 is the mole fraction of organic cosolvent), the effect of added solvent is described using the equation

$$\begin{aligned} \Delta(\text{aq} \rightarrow x_2) \Delta^\ddagger G^\ddagger(\text{sln}; T; p; c\text{-scale}) &= \Delta(\text{aq} \rightarrow x_2) \mu_+^\ddagger(\text{sln}; T; p; c\text{-scale}) \\ &\quad - \Delta(\text{aq} \rightarrow x_2) \mu^\ddagger(\text{M}^{2+}; \text{sln}; T; p; c\text{-scale}) \\ &\quad - \Delta(\text{aq} \rightarrow x_2) \mu^\ddagger(\text{X}^-; \text{sln}; T; p; c\text{-scale}) \end{aligned} \quad (1)$$

where

$$\Delta(\text{aq} \rightarrow x_2) \Delta^\ddagger G^\ddagger(\text{sln}; T; p; c\text{-scale}) = RT \ln \{k(\text{aq})/k(x_2)\}. \quad (2)$$

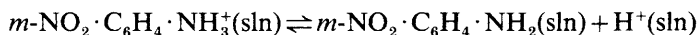
Here we use the concentration scale,² and so the reference state for a given solute j is a solution where $c_j = 1 \text{ mol dm}^{-3}$ and the activity coefficient $y_j = 1.0$; at constant solvent composition, $\lim(c_j \rightarrow 0) y_j = 0$. In this study, the pressure p is ambient and $T = 298.2 \text{ K}$. Eqn (1) and (2) involve transfer chemical potentials for ions describing differences in reference chemical potentials for ions in aqueous solution and in solvent mixtures of mole fraction x_2 . Although transfer chemical potentials for salts are often readily determined using, for example, solubility data, such is not the case for ions.^{3–6} At some stage calculation of transfer parameters for ions requires an extrathermodynamic

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assumption. Granted such an assumption, the transfer chemical potentials for a salt can be separated into contributing transfer parameters for ions. Derived transfer parameters should be self-consistent for a range of ions in a given solvent system and for a given ion across a range of aqueous mixtures. One possible approach uses the Born equation. Despite its lack of success⁷ in accounting for enthalpies of hydration for ions, this equation appears to be enjoying an unwarranted renaissance,⁸ at least for systems at high temperatures and pressures⁹ and for some non-aqueous solvents, *e.g.* liquid ammonia.¹⁰ However, most treatments of transfer parameters for ions in binary aqueous mixtures favour an assumption²⁻⁶ which equates transfer parameters for either Ph_4As^+ and Ph_4B^- ions (the TATB assumption) or Ph_4P^+ and Ph_4B^- ions (the TPTB assumption). Transfer parameters for ions calculated using one of these assumptions are in close agreement with those calculated using the other assumption.¹¹ Certainly one or other of these assumptions forms the basis of recent treatments of the thermodynamic properties of salt solutions.^{6, 11-18}

Further details of the TATB and TPTB assumptions are discussed in ref. (2), where we note evidence for slight differences between solvation parameters for the anion and the two cations. Although most authors currently favour application of the TATB and TPTB assumptions, a striking exception concerns the analysis of transfer parameters and their application to kinetic data discussed by Wells [*e.g.* ref. (19)–(23) together with references cited therein]. However, we have given reasons² for rejecting this approach. We postpone comment on a rejoinder²³ to our criticisms. We will deal with points raised by Wells²³ in a later paper which draws together estimates of transfer parameters for several binary aqueous systems. We do not accept the transfer parameters for ions in aqueous mixtures reported by Lahiri *et al.*²⁴⁻³⁰ It is claimed^{29, 30} that the reported transfer parameters are not based on an extrathermodynamic assumption. This statement is incorrect.³¹ In fact the calculations make an assumption concerning transfer parameters for Fe^{II} and Fe^{III} ions;³¹ for details see ref. (32).

Two extensive compilations of transfer parameters for ions in methanol–water mixtures are based on the TPTB assumption, the data set including simple ions and a large number of inorganic complexes.^{2, 11} Estimates of transfer parameters based on the TPTB (or TATB) assumption are sparse for solutes in acetone–water mixtures. Wells has reported estimates of transfer parameters for this system.^{19, 33} Voshchilova *et al.*³⁴ reported that the transfer chemical potentials of indium(III) cations are zero over the range $0 \leq x(\text{acetone}) \leq 0.27$. Behr *et al.*³⁵ reported transfer parameters for Zn^{II} ions in acetone–water mixtures as measured using electrochemical techniques, the derived parameters depending significantly on the redox system used as reference. Ang³⁶ confirmed the importance of factors other than solvent permittivity in determining transfer parameters by showing that $\text{p}K_{\text{a}}$ for the dissociation of *m*-nitroanilinium cations, *i.e.*



in acetone–water mixtures is strikingly dependent on solvent composition³⁷ (see also the kinetics of acid-catalysed hydrolysis³⁸).

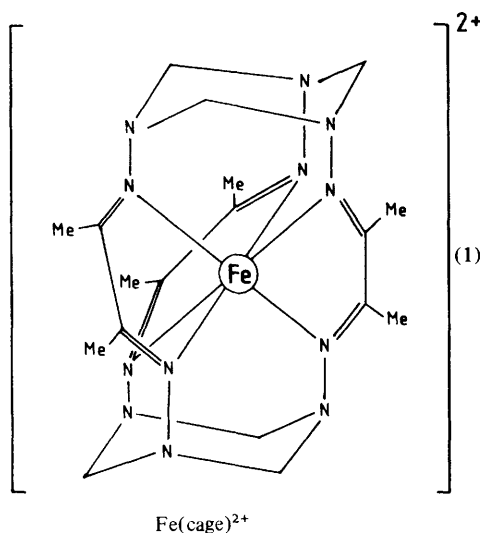
Our programme of research has been aimed at developing extensive and consistent complications of transfer parameters for ions in aqueous mixtures and at applying these data to understanding dependences of rate constants on solvent composition.³⁹ We report here data describing the properties of ions in aqueous acetone mixtures based on the establishment of transfer parameters for Ph_4As^+ and Ph_4B^- ions using appropriate solubility measurements. We use these transfer parameters to establish related transfer parameters for other ions. Application of these properties to understanding trends in reactivities^{2, 39} is discussed for several substitution, isomerisation and redox reactions involving inorganic ions in solution.

Experimental

Materials

Rubidium dichromate, tetraphenylarsonium dichromate and rubidium tetraphenylboronate were prepared by metathetical solution reactions from rubidium chloride, potassium dichromate, tetraphenylarsonium chloride and sodium tetraphenylboronate. The products were recrystallised from water or water-ethanol mixtures as appropriate.

The cobalt(III) and chromium(III) complexes $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$,⁴⁰ $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{ClO}_4$,⁴¹ $[\text{Co}(\text{en})_3]\text{Cl}_3$,⁴² *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ ⁴³ and $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ^{44,45} were prepared by published procedures; the I^- , ClO_4^- and BPh_4^- salts of the $[\text{Co}(\text{en})_3]^{3+}$ cation were precipitated from saturated aqueous solutions of its chloride by the addition of saturated aqueous solutions of the respective sodium salts. The low-spin iron(II)-di-imine complex⁴⁶⁻⁴⁸ (1) [formulae in scheme 1 of ref. (2)] was prepared by the published method and obtained as its perchlorate salt. This was washed with aqueous methanol and dried in a desiccator at ambient temperature. [Perchlorates of low-spin iron(II)-di-imine complexes should not be warmed because they are liable to decompose very rapidly.] The pentacyanoferrate(II) anions $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$, L = piperidine or pyrazine, were prepared⁴⁹ as their sodium salts from $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]$, itself prepared by the action of concentrated aqueous ammonia on sodium nitroprusside.^{50,51}



The purity of the complexes was checked by microanalysis (C, H and N), atomic absorption (Fe) and ultraviolet-visible absorption spectroscopy, as appropriate. In cases where isomeric impurities may have been present, kinetics of either aquation or base hydrolysis were monitored to confirm the linearity of simple first-order kinetic plots for more than three half-lives.

Kinetics and Spectrophotometry

Kinetics of the reaction at 298.2 K were measured by monitoring the dependence on time of absorbances at selected wavelengths in the u.v.-visible region.² Rate constants were calculated using least-squares procedures included in programs for minicomputers linked to the spectrophotometers.²

Solubilities

Solubilities of salts in solutions were measured as described previously.² Concentrations of salts in solution were measured using the absorbances at the characteristic wavelengths reported in the tables that follow.

Results

Solubilities of salts relevant to the calculation of transfer parameters for Ph_4B^- and Ph_4As^+ ions are reported in table 1. Derived transfer parameters are set out in tables 2 and 3. Kinetic data for reactions in acetone–water mixtures are summarised in tables 4–6.

Discussion

Transfer Chemical Potentials

The extremely low solubilities of the two salts $\text{Ph}_4\text{AsBPh}_4$ and Ph_4PBPh_4 in water and in water-rich acetone mixtures block the direct route to the determination of transfer parameters based on the calculation indicated by the equation

$$\begin{aligned} \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{Ph}_4\text{As}^+; \text{sln}) &= \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{Ph}_4\text{B}^-; \text{sln}) \\ &= \frac{1}{2} \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{Ph}_4\text{AsBPh}_4; \text{sln}). \end{aligned} \quad (3)$$

Indirect routes based on solubility data for Ph_4AsX , MBPh_4 and MX salts (where M = cation and X = anion) are possible, although there are difficulties in selecting ions X and M . Preferably all three salts should be sparingly soluble to obviate the need for correcting solubilities with estimated mean activity coefficients. This condition rules out anions such as $\text{X} = \text{Cl}^-$, Br^- and I^- . We examined systems in which $\text{X}^{n-} = \text{ReO}_4^-$, PtBr_6^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. In each case the Ph_4As^+ and K^+ (Rb^+ , Cs^+) salts are sparingly soluble. The per-rhenate salts proved an unattractive choice because the concentration of salts in solutions could not be measured spectrophotometrically⁵² ($\lambda = 200$ and 208 nm for ReO_4^-), these bands being masked by an absorption band from acetone. Concentrations can be monitored spectrophotometrically but indirectly⁵³ through reaction with α -furdioxime. We were apprehensive as to the accuracy of the procedure because ϵ_{max} for the product increases dramatically with increase in the mole fraction of acetone in the solvent mixture. Rather surprisingly the estimated transfer chemical potentials agreed quite closely⁵⁴ with those obtained by the third route examined here. A second possible route involved the hexabromoplatinate(IV) salt but was unsatisfactory because the crystal form of $[\text{Ph}_4\text{As}]_2[\text{PtBr}_6]$ in equilibrium with a saturated aqueous solution differs from that in equilibrium with saturated solutions in acetone-rich aqueous mixtures. Consequently a difference of *ca.* 8 kJ mol^{-1} in transfer parameters for the salt $[\text{Ph}_4\text{As}]_2[\text{PtBr}_6]$ is produced for acetone–water mixtures over the range 20–80 vol %. (A similar observation was recorded⁵⁵ for thallium picrate in its red monoclinic and yellow triclinic forms in methanol–water mixtures.) In the determination of transfer parameters we therefore decided to study the solubilities of dichromates (table 1), the corresponding least soluble alkali-metal salt, $\text{Rb}_2\text{Cr}_2\text{O}_7$, completing the cycle:

$$\begin{aligned} \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{Ph}_4\text{AsBPh}_4) &= \frac{1}{2} \Delta(\text{aq} \rightarrow x_2) \mu^* ([\text{Ph}_4\text{As}]_2[\text{Cr}_2\text{O}_7]) \\ &+ \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{RbBPh}_4) - \frac{1}{2} \Delta(\text{aq} \rightarrow x_2) \mu^* (\text{Rb}_2\text{Cr}_2\text{O}_7). \end{aligned} \quad (4)$$

For the next stage we have drawn together published estimates of transfer parameters and converted them to a common basis incorporating the TATB assumption; table 2 includes estimates for simple cations and anions. Transfer parameters for various

Table 1. Derivation of transfer chemical potentials for Ph_4As^+ and Ph_4B^- ions from aqueous solutions to acetone–water mixtures from solubility^a measurements ($T = 298 \text{ K}$)

vol % acetone (id)	0	20	40	60	80	90
S	167	124	85.4	36.9	6.6	1.18
$\Delta(\text{salt})$	0	2.2	5.0	11.2	24.0	36.8
			$[\text{Ph}_4\text{As}]_2\text{Cr}_2\text{O}_7^{b,c}$			
S	0.684	2.73	9.37	24.1	30.7	14.5
$\Delta(\text{salt})$	0	-10.3	-19.4	-26.4	-28.3	-22.7
			$\text{RbBPh}_4^{d,e}$			
S	0.054	0.314	2.66	14.7	36.8	42.6
$\Delta(\text{salt})$	0	-8.8	-19.3	-27.8	-32.4	-33.1
$\Delta(\text{TA}^+ = \text{TB}^-)$	0	-7.5	-15.8	-23.3	-29.2	-31.4
$\Delta(\text{Rb}^+)$	0	-1.3	-3.6	-4.5	-3.1	-1.7
$\Delta(\text{Cr}_2\text{O}_7^{2-})$	0	4.7	12.1	20.2	30.2	40.2

^a Solubility $S/\text{mmol dm}^{-3}$; Δ = transfer parameter for salts and ions, e.g. $\Delta(\text{aq} \rightarrow x_2)\mu_j^*(\text{sln}; T; p; c\text{-scale})/\text{kJ mol}^{-1}$ for solute j ; vol % acetone (id) calculated from volumes of liquid components before mixing. ^b from B. Briggs, *Ph.D. Thesis* (University of Leicester, 1986). ^c $\text{Cr}_2\text{O}_7^{2-}$; $\lambda_{\text{max}} = 351 \text{ nm}$. ^d Solubility data in aqueous solution from A. Berne, B. Wajsbrot, P. D. Klahr and O. Popovych, *J. Chem. Eng. Data*, 1983, **28**, 316. ^e Solubility data in aqueous acetone from A. N. Kirgintsev and V. P. Kozitskii, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1968, 1170.

complex ions and oxoanions, based on the TATB assumption have been published elsewhere.⁵⁶ In fact the latter estimates⁵⁶ were based on slightly different estimates for transfer parameters for Ph_4As^+ and BPh_4^- from those quoted above; compared to the precision of transfer parameters the corrections necessary to bring them into line with the estimates in tables 1–3 (3) are negligibly small; i.e. $< 1 \text{ kJ mol}^{-1}$. Table 3 reports solubilities of salts of complexes involved in the kinetic studies and the derivation of transfer chemical potentials for the respective complex ions.

An overall picture of transfer parameters is given in fig. 1–4 for ions in acetone–water mixtures. Data for a selection of inorganic complexes are summarised in fig. 2. The general pattern is similar to that established for transfer parameters for ions in methanol–water mixtures.² Ion size, charge number and, particularly for complex ions, the hydrophilic/hydrophobic character of the groups located on the periphery and exposed to solvent are important factors. Surprisingly, and we would argue² fortuitously, ion transfer parameters for acetone–water solvent system derived by Wells^{19,33} and, using again another method, by Bax and de Ligny⁵⁷ are similar to those calculated using the TATB assumption. As noted above this is not the case for methanol–water systems, where the estimates reported by Wells and by ourselves differ for the reasons discussed previously.² A striking disagreement exists between the estimates reported here and those recently published by Dash *et al.*,⁵⁸ who used an e.m.f. method based on cells with liquid junctions. Not only do the numerical values differ, but so does the form of the dependences of transfer chemical potentials on solvent composition (fig. 3). Kundu and Parker⁵⁹ have reviewed the problems associated with this method and compared the results with transfer chemical potentials obtained using the TATB assumption.

An unexpected feature of the results is the stabilisation of alkali-metal cations in aqueous solution by added acetone even at 90 vol % acetone (mole fraction acetone = 0.8). Evidence from spectroscopic techniques⁶⁰ indicates a strong preference on the part of metal ions in solution for nearest-neighbour solvation by water rather than by acetone. It is, however, possible to understand our results in terms of strong preferential hydration⁶¹ coupled with modest contributions from changes in other parts of the total solvation cosphere⁶² around an ion; e.g. in zone B of the Frank–Wen⁶³ two-sphere

Table 2. Transfer chemical potentials for ions from aqueous solution to acetone–water mixtures calculated from previously published transfer parameters^{a,b} and solubility data

vol % acetone (id)...	20	40	60	80	90
wt % acetone...	16.6	34.6	54.4	76.1	87.7
K ⁺	-1.5	-3.6	-4.5	-3.6	-2.3
Rb ⁺	-1.3	-3.6	-4.5	-3.1	-1.7
Cs ⁺	-1.7	-4.1	-5.1	-3.7	-2.2
Ag ⁺ ^c	-1.0	-4.5	-5.8	-4.6	
Me ₄ N ⁺	-2.4	-5.3	-6.8	-5.8	-4.4
Pr ₄ N ⁺	-4.5	-10.3	-15.6		
Bu ₄ N ⁺	-6.3				
Ph ₄ As ⁺ /Ph ₄ B ⁻	-7.5	-15.8	-23.3	-29.2	-31.4
Cl ⁻	4.5	10.6	16.9	25.3	
Br ⁻	3.9	8.9	14.7	24.7	
I ⁻	2.2	6.6	10.7	15.6	
CN ⁻ ^d	2.4	7.0 ⁱ	11.4 ⁱ	16.5	21.0
NCS ⁻ ^c	1.6	4.9	7.2	12.1	
ClO ₄ ⁻	0.9	2.4	3.3	4.4	6.0
[Sb(OH) ₆] ⁻ ^e		11			
[IrCl ₆] ²⁻ ^f		16.6			
[PtBr ₆] ²⁻	5.0	10.7	17.6	23.0	
[Fe(phen) ₃] ²⁺ ^g	-15.7 ⁱ	-32 ⁱ	-40 ⁱ	-45 ⁱ	
[Co(NH ₃) ₅ (NCS)] ²⁺ ^h	-4.1				
[Cr(ox) ₃] ³⁻ ^j	(15)	(36)			

^a Transfer parameter = $\Delta(\text{aq} \rightarrow x_2)\mu^*(\text{sln}; 298.15 \text{ K}; p; c\text{-scale}/\text{kJ mol}^{-1})$; estimates recalculated using TATB assumption unless otherwise indicated). ^b vol % (id) indicates composition prepared by mixing volumes of water and acetone. ^c C. Barraque, J. Vedel and B. Tremillon, *Bull. Soc. Chim. Fr.*, 1968, 3421. ^d Calculated from KCN solubilities; M. J. Blandamer, J. Burgess and A. J. Duffield, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1. ^e Calculated from Na[Sb(OH)₆] solubilities; M. J. Blandamer, J. Burgess and R. D. Peacock *J. Chem. Soc., Dalton Trans.*, 1974, 1084. ^f Calculated from solubilities of K₂IrCl₆; ref. (95). ^g Derived from solubilities and transfer chemical potentials; ref. (87). ^h Calculated from solubilities for [Co(NH₃)₅(NCS)]ClO₄, reported by V. Holba, J. Benko, O. Grancicova and O. Vollarova, *Trans. Met. Chem.*, 1985, **10**, 84. ⁱ Interpolated from data in ref. (87). ^j Approximate values (solubility and anion charge are high) from solubilities of K₃[Cr(ox)₃]·3H₂O; ref. (39).

Table 3. Transfer chemical potentials for two complex ions from aqueous solution to acetone–water mixtures^a

vol % acetone (id)...	0	20	40
[Co(NH ₃) ₅ (ONO)]Cl ₂ ; λ = 483 nm			
A _{ss} ^b	1.57	0.92	0.42
Δ(salt)	0	4.0	9.8
Δ(cation)	0	-5.0	-11.4
<i>cis</i> -[Cr(en) ₂ Cl ₂]Cl; λ = 520 nm			
S	0.30	0.24	0.22
Δ(salt)	0	1.1	1.5
Δ(cation)	0	-3.4	-9.1

^a For definitions of symbols see footnotes to table 1. ^b A_{ss} = absorbance of saturated solution.

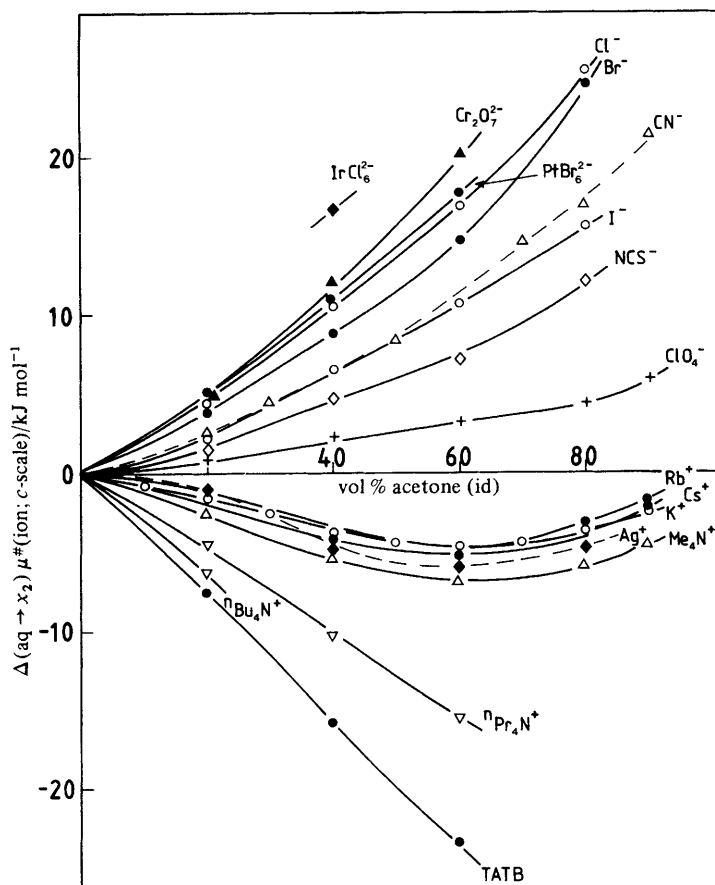


Fig. 1. Transfer chemical potentials for simple ions from aqueous solutions to acetone–water mixtures at 298.15 K; transfer parameters for ion j is $\Delta(\text{aq} \rightarrow x_2) \mu_j^\#(\text{sln}; 298.15 \text{ K}; p; \text{c-scale})$ and solvent composition is expressed in vol % (id).

model.^{64,65} It is perhaps unfortunate that the set of TATB-based transfer chemical potentials does not include data for 2+ and 3+ metal ions. However, estimates are available of transfer parameters for Zn^{2+} and In^{3+} ions based on assumptions generally believed to be consistent with the TATB assumption. Estimates³⁵ for Zn^{2+} are based on the $[\text{Cr}(\text{biphenyl})_2]^{0/+}$ assumption, those for In^{3+} ions being based³⁴ on the assumption that transfer chemical potentials for ET_4N^+ and picrate ions are equal. Derived transfer parameters for K^+ , Zn^{2+} and In^{3+} ions (fig. 4) show a destabilisation of Zn^{2+} and In^{3+} ions in acetone-rich mixtures. Lewandowski reports⁶⁶ the same trends in e.m.f.-based transfer chemical potentials for Cu^{2+} ions. The overall trends prompt the suggestion that K^+ ions may well be destabilised when the mole fraction of acetone exceeds 0.8. Consequently the pattern is similar to that observed, for example, in the case of cyanide ions in methanol–water mixtures.² Strongly hydrophilic ions retain their primary hydration shells up to quite high mole fractions of organic cosolvents⁶⁷ but are greatly destabilised as the water content tends to zero.

The modest stabilisation of alkali-metal ions in aqueous solutions when small amounts of acetone are added could be an artefact of the TATB assumption. This assumption may be in error^{68–74} by several percent because the solvation by a common

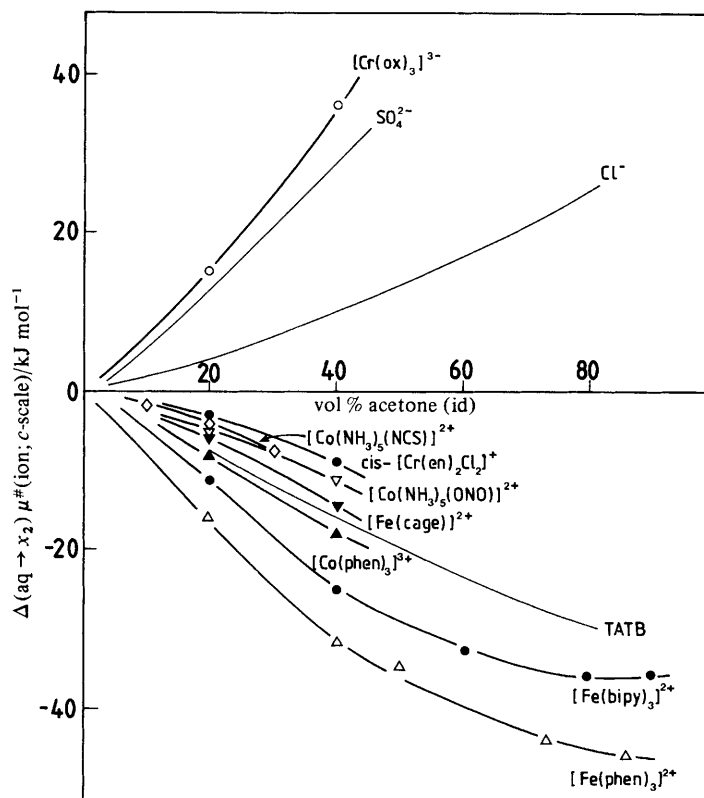


Fig. 2. Transfer chemical potentials for various cobalt, iron and chromium complex ions from aqueous solutions to acetone–water mixtures; data for Cl^- and SO_4^{2-} ions and TATB ions are included for comparison; see caption to fig. 1 for definition of terms.

solvent differs for cations and anions. However, if we make a correction following the suggestion by Kim,^{13,68–70} we find a slight increase in the stabilisation. Nevertheless, a change in estimated transfer chemical potential of one ion has a knock-on effect with respect to estimates of transfer chemical potentials for other ions. An example makes the point. For a mixture containing 60 vol % acetone, we may set the transfer chemical potential for K^+ ions equal to 1 kJ mol^{-1} ; consequently the transfer chemical potential for Cl^- ions is 9 kJ mol^{-1} , which is not unreasonable. However, for ClO_4^- ions the associated transfer parameter would be -2 kJ mol^{-1} , and so the question changes to one of understanding the stabilisation of certain anions rather than cations.

Kinetics of Chemical Reactions

Aquation of Cobalt(III) and Chromium(III) Complexes

Added acetone reduces rate constants describing the equation of halogenocobalt(III) complexes.^{75,76} These trends are analysed in table 4 in terms of the effects of added acetone on initial and transition states for aquation of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

At 298 K and ambient pressure, the rate constant^{77,78} for aquation of *cis*- $[\text{Cr}(\text{en})\text{Cl}_2]^+$ is $3.3 \times 10^{-4} \text{ s}^{-1}$, which decreases (determined⁷⁹ spectrophotometrically) to 2.9×10^{-4} and $2.6 \times 10^{-4} \text{ s}^{-1}$ when 20 and 40 vol % acetone, respectively, is added. The

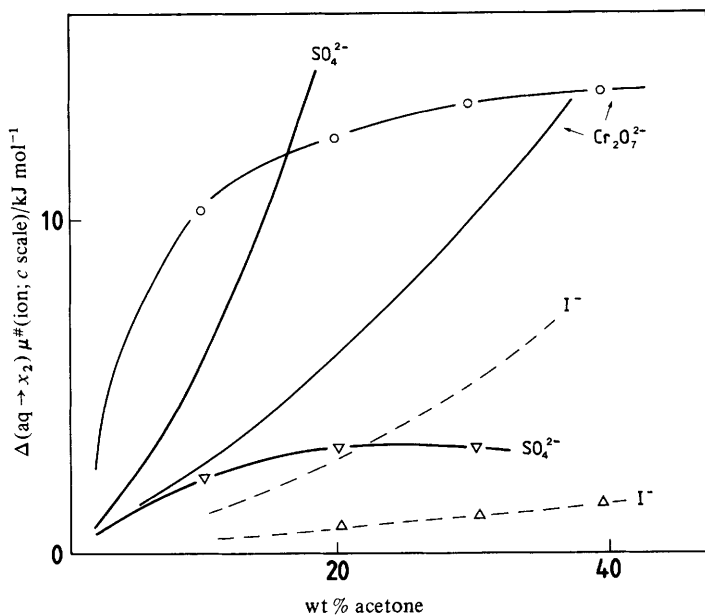


Fig. 3. Comparison of transfer chemical potentials for selected anions calculated using the TATB extrathermodynamic assumption (broken line) and taken from ref. (58); see caption to fig. 1 for definition of terms except that here solvent composition is expressed in weight % acetone.

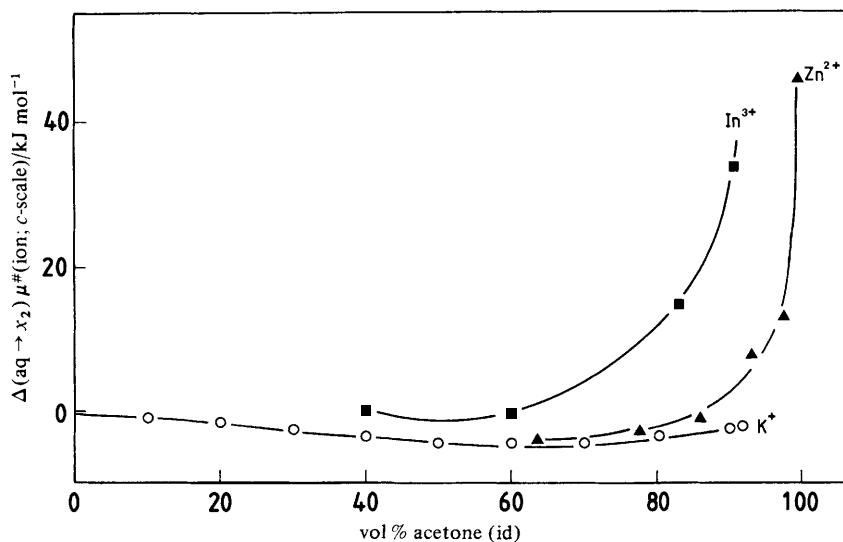


Fig. 4. Transfer chemical potentials for K^+ , Zn^{2+} and In^{3+} ions from aqueous solutions to acetone–water mixtures at 298.15 K; see caption to fig. 1 for definition of terms and the assumptions involved.

Table 4. Analysis of kinetic data for reactions in acetone–water mixtures; dependences of activation, initial state and transition state parameters^a on solvent composition

vol % acetone (id)...	0	10	20	30	40
	reaction; aqutation of [Co(en) ₂ Cl ₂] ⁺				
$k_1/10^{-5} \text{ s}^{-1}$	4.00	3.11	2.50	1.9	1.5 ^b
$\Delta^{\ddagger}G$	0	0.6	1.2	1.9	2.4
$\Delta\mu\{[\text{Co}(\text{en})_2\text{Cl}_2]^+\}$	0		-2.7		-7.1
$\Delta\mu(\neq)$	0		-1.5		-4.7
	reaction; aqutation of [Cr(en) ₂ Cl ₂] ⁺				
$k_1/10^{-4} \text{ s}^{-1}$	3.3		2.9		2.6
$\Delta^{\ddagger}G$	0		0.3		0.6
$\Delta\mu\{[\text{Cr}(\text{en})_2\text{Cl}_2]^+\}$	0		-3.4		-9.1
$\Delta\mu(\neq)$	0		-3.1		-8.5
	reaction; linkage isomerisation of [Co(NH ₃) ₅ (ONO)] ²⁺ → [Co(NH ₃) ₅ (NO ₂)] ²⁺				
$k_1/10^{-4} \text{ s}^{-1}$	3.8		3.4		2.5
$\Delta^{\ddagger}G$	0		0.3		1.0
$\Delta\mu\{[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}\}$	0		-5.0		-11.4
$\Delta\mu(\neq)$	0		-4.7		-10.4
	redox reaction; Co(en) ₂ (cysteinato) ⁺ + S ₂ O ₈ ^{c,d}				
$\Delta^{\ddagger}G$	3.8		1.2		1.8
$\Delta\mu\{[\text{Co}(\text{en})_2\text{cysteinato}]^+\}$	0		-0.8		-2.6
$\Delta\mu(\text{S}_{2\text{O}_8})^{2-}$	0		-5.2		-13.9
$\Delta\mu(\text{initial state})$	0		4.4		-11.3
$\Delta\mu(\neq)$	0		5.6		13.1
	redox reaction; [IrCl ₆] ²⁻ + I ⁻				
$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	324				7.0
$\Delta^{\ddagger}G$	0				9.5
$\Delta\mu([\text{IrCl}_6]^{2-})$	0				16.5
$\Delta\mu(\text{I}^-)$	0				6.6
$\Delta\mu(\text{initial state})$	0				23.2
$\Delta\mu(\neq)$	0				32.7
	redox reaction; [Fe(cage)] ²⁺ + S ₂ O ₈ ²⁻				
$k_2/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	6.4		2.0		0.6
$\Delta^{\ddagger}G$	0		2.9		5.9
$\Delta\mu\{[\text{Fe}(\text{cage})]^{2+}\}$	0		-6.0		-13.5
$\Delta\mu([\text{S}_2\text{O}_8]^{2-})$	0		5.2		13.9
$\Delta\mu(\text{initial state})$	0		-0.8		0.4
$\Delta\mu(\neq)$	0		2.1		6.3

^a Activation; $\Delta^{\ddagger}G = \Delta(\text{aq} \rightarrow x_2) \Delta^{\ddagger}G^*(\text{sln}; 298.15 \text{ K}; p)/\text{kJ mol}^{-1}$. Ion transfer; $\Delta\mu(\text{ion}) = \Delta(\text{aq} \rightarrow x_2) \mu^*(\text{sln}; 298.15 \text{ K}; p)/\text{kJ mol}^{-1}$. Transition-state transfer:

$$\Delta\mu(\neq) = \Delta(\text{aq} \rightarrow x_2) \mu_{\ddagger}^*(\text{sln}; 298.15 \text{ K}; p)/\text{kJ mol}^{-1}.$$

^b Interpolated. ^c Interpolated parameters at 20 and 40 vol %; $k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 50.5$. ^d See note (h) of table 2.

results of a comparable initial-state–transition-state analysis are set out in table 4 and illustrated in fig. 5.

In each case the modest decrease in rate constant with added acetone stems from a slightly greater stabilisation of the initial state than that of the transition state. This trend is a consequence of charge separation on going from initial to transition state, a less important consideration in the case of chromium(III) chloride aqutation, where there is probably significant associative character to the aqutation reaction.

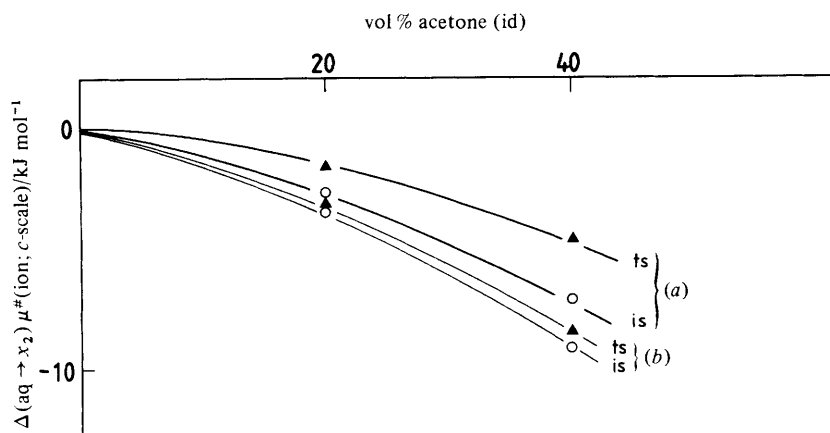


Fig. 5. Dependence on solvent composition of the chemical potentials for initial (○) and transition (▲) states in the aquation of (a) *trans*-[Co(en)₂Cl₂]⁺ and (b) *cis*-[Cr(en)₂Cl₂]⁺ ions in acetone–water mixtures.

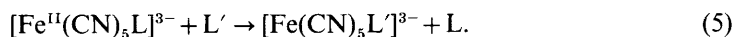
Table 5. Kinetics of reaction between pentacyanoferrate(II) complexes and cyanide ions in aqueous acetone mixtures

vol % acetone (id)	$k_{\text{lim}}/10^{-4} \text{ s}^{-1}$	
	[Fe(CN) ₅ pip] ³⁻ ^a	[Fe(CN) ₅ pz] ³⁻ ^b
0	53 ^b	4.2
20	77	4.2
40	89	4.4
60	—	4.2

^a Ref (9), 293 K. ^b Ref. (9), 298 K. ^c (62, 70 and 88) × 10⁻⁴ s⁻¹, respectively, at 298 K [N. E. Katz, P. J. Aymomino, M. P. Blesa and J. A. Olabe, *Inorg. Chem.*, 1978, **17**, 556; E. C. Pedrosa, J. A. Salas, M. Katz and N. E. Katz, *J. Coord. Chem.*, 1983, **12**, 145; and see ref. (82)]. ^d With *N*-methylpyrazinium cation; H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.

Substitution at Pentacyanoferrates(II)

Generally substitution reactions of the type



which occur by a *D*-mechanism, show remarkably small solvent effects on reactivity in binary aqueous solvent media.⁸⁰ However, this small solvent effect on reactivity seems to arise from large but almost equal solvent effects on both initial and transition states.⁸¹ Medium effects on rate constants are again small for reactions in solvents comprising acetone–water mixtures (table 5); they are more marked for hydrophobic pip than for hydrophilic pz as leaving groups.⁸²

There can be little doubt that here two large solvent effects on initial and transition states approximately cancel. We have not carried out an analysis of solvent effects on initial and transition states for these reactions. The reasons can be traced to problems associated with the calculation of solvent effects on the initial state in view of the high solubility of Fe(CN)₅L³⁻ salts and the 3- charge on the anion. (Ion-pairing is likely to be more extensive on adding acetone than methyl alcohol to the aqueous solution.)

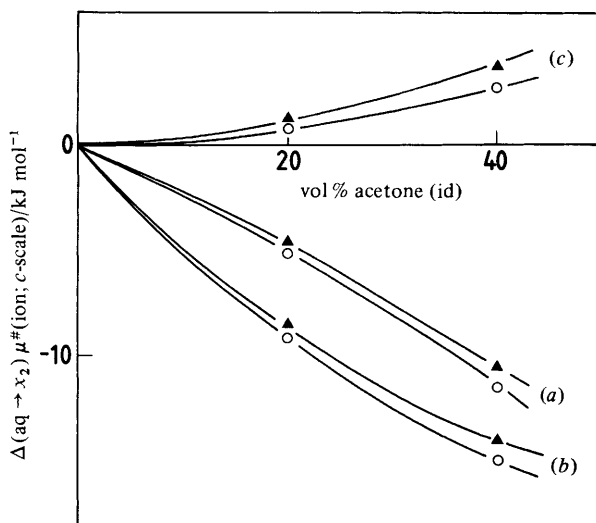
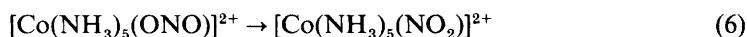


Fig. 6. Dependence on solvent composition of the chemical potentials for initial (○) and transition states (▲) in the isomerisation of $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ ions in acetone–water mixtures; comparison of dependences using chemical potentials of ions calculated using (a) the TATB assumption, (b) the parameters reported by Wells [*cf.* ref. (20)] and (c) an assumption which sets transfer parameters for K^+ = transfer parameters for Cl^- ions.

Earlier we obtained reasonable consistency for the transfer chemical potential, $\Delta(\text{aq} \rightarrow x_2)\mu^\#[\text{Fe}(\text{CN})_5(4\text{CNpy})^{3-}]$ derived from solubility measurements on its sodium salt, which is in fact too soluble for this purpose, and on its $[\text{Cr}(\text{en})_3]^{3+}$ salt, where ion-pairing must again be significant (*cf.* $z_+z_- = -9$) even at the relatively low concentrations involved. Subsequent work on thallium(I) salts of pentacyanoferrate(II) anions of this type suggests⁸³ that our agreement based on the data for Na^+ and $[\text{Cr}(\text{en})_3]^{3+}$ salts may have been fortuitous.

Isomerisation and Racemisation

The rate constant for intramolecular⁸⁴ nitrito–nitro linkage isomerisation in the reaction



is $3.8 \times 10^{-4} \text{ s}^{-1}$ in aqueous solution. We have now determined rate constants of 3.4×10^{-4} and 2.5×10^{-4} in 20 and 40 vol % acetone, respectively. The initial-state–transition-state analysis of this reactivity trend is set out in table 4; the pattern is very similar to that for aquation of the chlorocobalt(III) and chlorochromium(III) complexes analysed above. Fig. 6 shows how closely the results of an initial-state–transition-state analysis using the TATB assumption parallel those based on the Wells transfer parameters. It also shows how a more classical assumption (*i.e.* based on similar sized and isoelectronic species) which sets $\Delta(\text{aq} \rightarrow x_2)\mu^\#(\text{K}^+) = \Delta(\text{aq} \rightarrow x_2)\mu^\#(\text{Cl}^-)$ leads to a very different interpretation. Whereas both the TATB assumption and the Wells treatment lead to a picture of slightly less stabilisation of the transition state than that of the initial state, the classical assumption leads to a picture of slightly greater destabilisation of the transition state than that for the initial state. We have presented elsewhere³⁹ our initial-state–transition-state analysis of reactivity trends for racemisation of the $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ ions. Whether the mechanism is of the one-end-off type or, as recently suggested⁸⁵ for $[\text{Co}(\text{ox})_3]^{3-}$, a twist mechanism with bond extension

on forming the transition state,⁸⁶ greater ligand–solvent interactions in the expanded transition state lead to a slightly greater change in transfer chemical potentials for the respective transition states. In these cases the conclusions are independent of the assumption used to calculate transfer chemical potentials for ions, as the effects of added acetone on initial and transition states are so large compared with its effect on the activation barrier. In the case of $[\text{Cr}(\text{ox})_3]^{3-}$ racemisation, interaction of the hydrophilic oxalate ligand with the solvent leads to slightly greater destabilisation of the transition state by added acetone. The same explanation can be applied to the nitrito \rightarrow nitro isomerisation, although this time the slightly more unfavourable interaction of the hydrophilic NO_2 ligand in the transition state results in the transfer chemical potential of the transition state being less negative rather than more positive than that of the initial state.

Aquation and Reaction with Hydroxide ions of Iron(II) Complexes

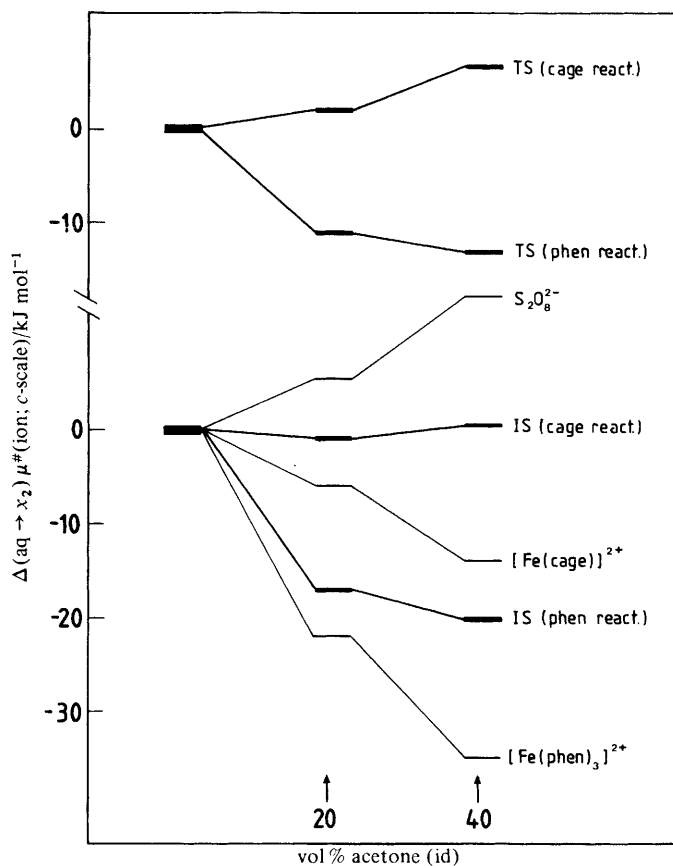
The dependence of rate constants for aquation of $[\text{Fe}(\text{phen})_3]^{2+}$ complex cations on solvent composition for acetone-rich water mixtures has been reported and discussed by van Meter and Neumann.⁸⁷ The small change in rate constant represents the balance between large stabilisations of both the complex and transition state on transfer from aqueous solutions to solutions in aqueous acetone mixtures. Some years ago we reported rate constants for base hydrolysis of $[\text{Fe}(\text{phen})_3]^{2+}$ cations in acetone–water mixtures.⁸⁸ We use these results at the end of the Discussion section, where we compare the results of an initial-state–transition-state analysis for this reaction in various mixed aqueous media.

Redox Reactions

Rate constants for these reactions show a dependence on relative permittivities of solvents, which was earlier suggested as a general principle,^{89,90} later as a central feature of the Marcus–Hush theory for electron transfer by the outer-sphere mechanism^{91–93} and recently a key assumption in the derivation of rate constants for electron-transfer within mixed-valence bridged dinuclear complexes.⁹⁴ However, the expected dependence is often not found for redox reactions between charged ions in aqueous media. For the latter systems, the work term associated with the bringing together of substrates to form the precursor complex prior to electron transfer often dominates the overall energetics of reaction. In such systems initial-state–transition-state analysis often reveals the importance of solvation or desolvation in determining reactivity trends.³⁹ This has already been illustrated⁹⁵ for a few redox reactions in acetone–water mixtures, including oxidation of iodide by hexachloroiridate(IV) and peroxodisulphate oxidation of the cystein complex⁹⁶ $[\text{Co}(\text{cyst}(\text{en})_2)^+]$ and⁸⁴ of $[\text{Fe}(\text{phen})_3]^{2+}$. The conclusions reached earlier⁹⁵ are still valid, as the small differences between TATB-based transfer chemical potentials and the Wells estimates do not affect the deductions. Thus in the reaction between IrCl_6^{2-} and I^- ions the transition state ($[\text{I}\cdots\text{IrCl}_6]^{+3-}$) is markedly more destabilised than the initial state on increasing the acetone content of the solvent. This situation is entirely parallel to that for reactions in aqueous methanol.² In the reaction between $[\text{Co}(\text{cyst}(\text{en})_2)^+]$ and $\text{S}_2\text{O}_8^{2-}$ ions, initial-state and transition-state solvation effects are small and comparable, since peroxodisulphate destabilisation and $[\text{Co}(\text{cyst}(\text{en})_2)^+]$ stabilisation on addition of acetone are compensatory. In the reaction between $[\text{Fe}(\text{phen})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ ions, both initial and transition states are stabilised owing to the strongly hydrophobic character of the phenanthroline ligand. It is of interest to compare the kinetics of the peroxodisulphate oxidation of $[\text{Fe}(\text{phen})_3]^{2+}$ with those of the much less hydrophobic complex $[\text{Fe}(\text{cage})]^{2+}$. Kinetic data for the reaction between $[\text{Fe}(\text{phen})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ ions in aqueous solution containing 0, 10 and 40 vol %

Table 6. Kinetics of reaction between $[\text{Fe}(\text{cage})]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ in acetone–water mixtures at 298 K

$[\text{S}_2\text{O}_8^{2-}]/\text{mmol dm}^{-3}$	6.7	13.3	20.0	26.7	33.3	
	$k(\text{obs})/10^{-4} \text{ s}^{-1}$					k_2^a
aq	0.6	1.1	1.5	1.9	2.3	6.4
20 vol % (id)	2.0	3.4	4.0	5.5	7.0	2.0
40 vol % (id)	4.3		15.1		23.2	0.6

^a Units of k_2 are $10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.**Fig. 7.** Comparison of the effects of added acetone on initial and transition states for reaction in aqueous acetone between $\text{S}_2\text{O}_8^{2-}$ ions and (a) $[\text{Fe}(\text{phen})_3]^{2+}$, and (b) $[\text{Fe}(\text{cage})]^{2+}$ cations; IS indicates combined effects of added acetone on iron(II) complex and $\text{S}_2\text{O}_8^{2-}$ anions.

acetone are given in table 6. The initial-state–transition-state analysis of the observed reactivity trend is included at the foot of table 4. The results of the analysis for this and the reaction between $[\text{Fe}(\text{phen})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ ions are compared in fig 7.

For the reaction between $[\text{Fe}(\text{phen})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ ions, the initial state and transition state are both considerably stabilised, with the initial state the more affected. For the reaction between $[\text{Fe}(\text{cage})]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ ions, the lower hydrophobicity of the iron complex results in the initial state being hardly affected by increasing acetone content,

while the transition state is markedly destabilised. The hydrophobic phenanthroline ligand dominates in the former reaction, the hydrophilic peroxodisulphate ion in the latter.

These results form a fairly complete picture of the properties of ions and medium effects on reactivities of inorganic complexes in aqueous acetone mixtures. In a subsequent paper we draw together results for several solvent systems in order to compare and contrast the effects of different cosolvents on ions in aqueous solutions.

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