Solvent effects upon reactions between ions: hexacyanoferrate(II)-peroxodisulphate and sulphite-hexacyanoferrate(III)

Amalia Rodríguez, Carmen Carmona, Ernestina Muñoz and Francisco Sánchez*
Departamento de Química Física, Universidad de Sevilla, Profesor García Gonzalez s/n 41012 Sevilla, Spain
John Burgess
Department of Chemistry, University of Leicester, Leicester, UK

Summary
Different approaches to the interpretation of solvent effects on reactions between ionic reactants are analysed, taking as a basis the kinetic data corresponding to the sulphite-hexacyanoferrate(III) and peroxodisulphate-hexacyanoferrate(II) oxidations. It is concluded that the approach based on the use of solvent parameters is the more promising, although knowledge of the transfer chemical potentials of the reactants may also be useful in the interpretation of kinetic behaviour.

Introduction
Over the years, different approaches have been used to examine solvent effects on reactions between ionic reactants. The simplest possible description is to treat the reactants as conductor spheres inside a continuum dielectric characterized by a static dielectric constant, \( D \). The electrostatic part of the free energy of activation depends on the solvent through the macroscopic dielectric constant and a linear variation of the logarithm of the rate constant with \( D^{-1} \) is predicted by this model. The slope of this plot is positive or negative depending on the reactants having the opposite or the same sign respectively.

A different approach is concerned with transfer chemical potentials (Gibbs free energy of transfer, \( G_{tr} \)) of ions from a reference solvent to other solvents (or solvent mixtures). One of the uses of these parameters is the analysis of reactivity trends with changing solvent composition into initial state (I) and transition state (\( \neq \)) components. Thus, for the process:

\[
A + B \rightarrow \neq \rightarrow \text{products}
\]

the changes in the free energy of activation can be written as:

\[
\delta \Delta G^* = \delta G^*_{A} - \delta G^*_{I}
\]

and the reactivity trends on changing solvent composition can be interpreted on the basis of the stabilization/destabilization of the reactants and transition states respectively.

Finally, in the third approach, rate constants are correlated with a parameter characteristic of the solvent such as its ionizing power, acidity/basicity and so on. These kinds of linear correlations, which can be extended to multiple linear ones, allow the importance of the different factors controlling reactivity to be determined.

The purpose of this work is to carry out an analysis of the above mentioned approaches taking as a basis the kinetic data corresponding to the sulphite-hexacyanoferrate(III) and peroxodisulphate-hexacyanoferrate(II) oxidations in water-cosolvent mixtures. For previous studies on these reactions see references 4 and 5 and others therein.

Experimental
Reagents
All the reagents were Analar grade chemicals and were used without further purification. The water employed had a resistivity > 6.10⁸ Ωm. The pH of the sulphite solutions was maintained at a value of nine and these solutions were always titrated before use.

Kinetic data
Kinetic runs were carried out in 1-cm silica cells in the thermostated cell compartment of a Perkin-Elmer 554 spectrophotometer at 298.2 ± 0.2 K. The H₂O-cosolvent mixtures were prepared by weight. The dielectric constant data at 298.2 K are from literature. In each case the cosolvent was found to be inert in relation to the reactants and products. The solutions also contained K₂H₂edta in order to prevent the catalysis of any metal ions that might be present as impurities ([K₂H₂edta] = 5.10⁻⁴ mol dm⁻³). Duplicate and triplicate runs were made under all the experimental conditions. The rate constant error is estimated to be around 2%. of the reaction between sulphite and hexacyanoferrate(III) ions was made in solutions containing an excess of sulphite ions following the change in absorbance at 420 nm at fixed time intervals (at this wavelength only hexacyanoferrate(III) absorbs). The concentrations of reactants were Na₃Fe(CN)₆ = 10⁻³ mol dm⁻³ and Na₂SO₃ = 10⁻² mol dm⁻³ respectively. The rate constants were evaluated by Guggenheim’s method.

The peroxodisulphate-hexacyanoferrate(II) reaction was carried out in solutions containing an excess of hexacyanoferrate(II) ions by following the change in absorbance at 420 nm. The concentrations of the reactants were K₄Fe(CN)₆ = 3 x 10⁻² mol dm⁻³ and K₂S₂O₈ = 7.5 x 10⁻⁴ mol dm⁻³ respectively. The rate constants were evaluated from linear plots of the function \( -\ln(A_t - A_s) \) versus time. \( A_s \) and \( A_t \) are the absorbance at the end of the reaction and time \( t \) respectively.

Solubilities
The values of the standard transfer chemical potentials were calculated from solubilities, at 298.2 K, in water and

* Author to whom all correspondence should be directed.
in the water-cosolvent mixtures. The solubilities were determined after obtaining equilibrium between the solid phase and its solution. Due to sulphite instability, we made the assumption that the general trends on solubilities of this ion and sulphate ion should be kept the same. Thus solubilities of sulphate ion instead of sulphite ion have been measured. The concentrations of the salts in the different water-cosolvent mixtures were estimated: iodometrically (8) \((K_2S_2O_8)\), turbidimetrically (9) \((K_2SO_4)\) and spectrophotometrically \([K_4Fe(CN)_6 \varepsilon = 1810 \text{ at } 290 \text{ nm}]^{(10)}\), \([\text{Co(NH}_3)_6\text{Fe(CN)}_6 \varepsilon = 1030 \text{ at } 420 \text{ nm}]^{(11)}\). The solubilities of \(\text{Co(NH}_3)_6\text{Pi}^3\), \(\text{KPi}\), \(\text{KPh}_4\text{B}\) and \(\text{Ph}_4\text{AsPi}\) were also measured. The preparation and characterization of these compounds were made using literature sources \((12-15)\).

Results and discussion

Rate constants for the two reactions are given in Tables 1 and 2, respectively.

At this point, the following fact should be realized: because of the experimental requirements, the reactions have been studied at different ionic strengths. As an ionic strength increase gives rise to a rate constant increase for reactions between ions of the same sign, if we wish to compare the results of the two reactions, the \(k\) values must be corrected. Thus we will examine the results after extracting a standard allowance for the long-range Debye–Huckel interactions \((16)\) according to the following equation:

\[
\log k = \log k_0 + 2 \frac{1.814 \times 10^6}{(D T)^{1/2}} \frac{Z_A Z_B}{1 + \frac{1}{1 + (D T)^{1/2}}} \tag{3}
\]

where \(k\) is the actual rate constant, \(D\) is the macroscopic dielectric constant and the other symbols have their usual meaning. The values of \(k_0\) have been tabulated in Tables 3 and 4 respectively as \(\delta \Delta G^\circ_{r=0}\) where \(\delta \Delta G^\circ_{r=0} = \Delta G^\circ_{t=0} \text{(water-cosolvent)} - \Delta G^\circ_{t=0} \text{(water)}\).

The standard transfer chemical potentials for all the salts were calculated using Equation 4

\[
\delta \mu_{\text{r}}(\text{salt}) = nRT \ln \left[ \frac{S(w) \pm (w) / S(x) \pm (x)}{1} \right] \tag{4}
\]

where \(S(w)\) and \(S(x)\) are the solubilities in water and in the solvent mixtures respectively. Usually \(\delta \mu_{\text{r}}(\text{salt})\) are calculated on the assumption that the ratio of the mean activity coefficients in water and in the aqueous solvent mixtures is in all cases a unity \((17,18)\). However, we have calculated these ratios by means of Equation 5 and their values have been considered in Equation 4.

\[
\log \gamma_\pm = \frac{1.826 \times 10^6}{(D T)^{1/2}} \frac{Z_A Z_B}{1 + \frac{1}{1 + (D T)^{1/2}}} \tag{5}
\]

The estimation of transfer chemical potentials for ions has been made using the extrathermodynamic assumption \(\delta \Delta G^\circ_{r}(\text{Ph}_4\text{As}^+)) = \delta \Delta G^\circ_{r}(\text{BiPh}_4^+)\) \((19,20)\). The values corresponding to the reactants are given in Tables 5 and 6. Also \(\delta \Delta G^\circ_{r}\) and \(\delta \Delta G^\circ_{r}\) are included in the Tables.

As expected, the general trends of \(\delta \Delta G^\circ_{r}\) on changing composition show a decrease of reactivity on decreasing the macroscopic dielectric constant of the medium. Although this reactivity decrease is in agreement with the predictions of the simplest approach discussed in the introduction, the results of the present experiments cannot be unequivocally explained by application of this model. The \(\delta \Delta G^\circ_{r}\) versus \(D^{-1}\) dependence although approximately linear in some mixtures, shows different slopes in the different media, that is, \(\delta \Delta G^\circ_{r}\) values depend on the solvent for a fixed dielectric constant showing the existence of specific solvent effects (Figures 1 and 2). These results are not in fact surprising because this theory characterizes the solvent by the macroscopic dielectric constant and, therefore, it does not account for

Table 1. Observed rate constants (\(k\)) in H\(_2\)O-cosolvent mixtures, at 298.2 K, for the reaction between sulphite and hexacyanoferrate(III) ions.

| D  | 10\(^3k\)/M\(^{-1}\) s\(^{-1}\) |
|----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|    | H\(_2\)O | MeOH | t-BuOH | EtglyOH | GlyOH | Dextrose | Sucrose |
| 78.5 | 16.8 | 12.5 | 15.8 | 9.40 | 14.8 | 17.6 | 17.6 |
| 76  | 9.33 | 14.8 | 13.7 | 5.02 | 12.1 | 18.9 | 18.5 |
| 74  | 6.17 | 14.1 | 13.7 | 5.02 | 8.69 | 21.8 | 17.0 |
| 70  | 4.30 | 14.1 | 2.63 | 6.33 | 19.5 | 15.4 |
| 64  | 3.89 | 14.4 | 1.92 | 5.13 | 18.4 | 14.8 |
| 60  | 2.88 | 17.7 | 1.30 | 3.49 | 16.4 | 13.3 |

Table 2. Observed rate constants (\(k\)) in H\(_2\)O-cosolvent mixtures, at 298.2 K, for the reaction between peroxodisulphate and hexacyanoferrate(II) ions.

| D  | 10\(^3k\)/M\(^{-1}\) s\(^{-1}\) |
|----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|    | H\(_2\)O | MeOH | t-BuOH | EtglyOH | GlyOH | Dextrose | Sucrose |
| 78.5 | 5.15 | 6.62 | 5.99 | 5.45 | 4.81 | 5.37 | 5.97 |
| 76  | 8.17 | 6.67 | 4.54 | 3.07 | 5.52 | 6.50 |
| 74  | 11.8 | 9.28 | 3.17 | 1.50 | 6.07 | 4.51 |
| 70  | 19.5 | 12.0 | 2.14 | 1.40 | 5.75 | 3.03 |
| 64  | 13.7 | 1.76 | 1.18 | 5.07 | 2.22 |
| 60  | 17.0 | 1.62 | 1.07 | 3.63 | 1.27 |