Salt and Cosolvent Effects on the Sulphite–Hexacyanoferrate(III) Reaction

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The rate of the reaction between sulphite and hexacyanoferrate(III) ions has been measured in several concentrated salt solutions and in several isodielectric water–solvent mixtures. The association constants of the sodium sulphite and the sodium hexacyanoferrate(III) ion pairs have also been measured in these mixtures. The sequence of the association constants is not the same as for the rate constant. The results are explained in terms of solute–solvent interactions.

The reaction between sulphite and hexacyanoferrate(III) ions has been studied by several authors.[1–7] The specific effect of inert cations has been explained on the assumption that the cation may act either as an actual bridge for electron transfer or as a means of allowing the two negatively charged ions to approach close enough for electron transfer through the solvent. Though the association constants of the reactants have not been obtained some evidence appears to support the first possibility.[7] Regarding the anion effects, there was no satisfactory explanation for the experimental results and the specific effects were ascribed to the presence of trace impurities.[3] However, this explanation has been ruled out subsequently.[7] For this reason, the present study is aimed at resolving this controversy. Concentrated salt solutions with a common cation have been used in order to see if a specific anion effect exists. We have also studied the kinetics of this reaction in some isodielectric water–solvent mixtures. We have selected solvent mixtures with different properties to ascertain whether ionic association or water–solvent interactions explain the experimental results.

Experimental

Reagents.—The reagents used were all AnalaR grade chemicals. The water used had a resistance >5 MΩ. Sodium hexacyanoferrate(III) was obtained by passing potassium sulphite through a mixed-bed Lawatit S100 (cationic) cation-exchange column.

The sulphite solutions were maintained at pH 9 and always titrated before use.

Kinetic Data.—Kinetic runs were carried out in 1-cm silica cells in the thermostatted cell compartment of a Perkin-Elmer 554 spectrophotometer by following the changes in absorbance at 420 nm. At this wavelength only the hexacyanoferrate(III) ion absorbs. The molar absorption coefficients of hexacyanoferrate(III) in water and in the water–solvent mixtures are recorded in Table 1. In media containing salts, the value of ε did not change from that in water. In the salt-containing solutions the concentrations of reactants were $[Na_3Fe(CN)_6] = 2 \times 10^{-4}$ and $[Na_2S_2O_3] = 1 \times 10^{-3}$ mol dm^{-3} and in the water–solvent mixtures $[Na_3Fe(CN)_6] = 1 \times 10^{-3}$ and $[Na_2S_2O_3] = 1 \times 10^{-2}$ mol dm^{-3}. The solutions also contained $Na_2(H_2edta)$ (edta = ethylenediamine-*NNN'N'*-tetra-acetate) in order to prevent the catalysis of some metal ions that could be present as impurities,[7] $[Na_2(H_2edta)] = 1 \times 10^{-4}$ mol dm^{-3}.

The results of the kinetic runs are collected in Table 2 for the salt-containing solutions and in Table 1 for the water–solvent mixtures. Table 1 also gives the composition of the mixtures which were selected so as to give the same dielectric constant ($D = 74$) in each case. Solvent mixtures were prepared by weight and the dielectric constant data are from the literature.[8–12] In each case the cosolvents were found to be inert to the reactants and products. Duplicate and triplicate runs were made under all the experimental conditions. The rate constant error was estimated to be less than 2%.

Viscosity, Density, and Conductance Measurements.—The viscosity, density, and conductance measurements were carried out as described previously.[13] The association constants were calculated by the Davies' method as modified by Jenkins and Monk.[14] The association constants of the sodium sulphite ($NaS_2O_3^-$) and the sodium hexacyanoferrate(III) [$NaFe(CN)_6^{2-}$] ion pairs and the viscosities of the mixtures are recorded in Table 1.

Discussion

As can be seen in Table 2 the results for the salt-containing solutions clearly indicate the existence of a specific anion effect. In previous studies on the kinetic salt effects in this reaction[7] a linear dependence of the rate constants on the concentration of the alkali-metal cation was observed. This first-order dependence was explained by considering that the metal ion had participated in the transfer of electrons between the reacting species. The relatively negative values of the activation entropy seemed to support this conclusion.[7] However, plots of the k values in Table 2 against salt concentration are curved. This behaviour could be explained by taking into account that in concentrated salt solutions, besides the bridge effect of the alkali-metal ion, a primary salt effect exists. Such an effect has, at least, two components: one derived from the coulombic interactions and another from the 'salting effect', that is, the ionic hydration produces a smaller effective concentration of solvent. When concentrated salt solutions are used, the second effect becomes more important[15] because under these conditions there is almost no change in the coulombic interactions when the salt concentration is changed.[16] According to the above reasoning a linear dependence of log k with the salt concentration is expected.[17] However, our experimental results lead to equation (1) which has as a limiting case the observed behaviour in

$$k = k_1 c\, 10^{\alpha c} \qquad (1)$$

diluted salt solutions.[7] The term $10^{\alpha c}$ accounts for the 'salting effect' of the electrolyte and it can be eliminated in the studies with diluted salt solutions. It is possible mathematically to manipulate equation (1) to yield the expression (2). This

$$\log(k/c) = \log k_1 + \alpha c \qquad (2)$$

Table 1. Viscosity (η/P), molar absorption coefficient of $Fe(CN)_6^{3-}$ ion (ε/dm³ mol⁻¹ cm⁻¹), observed rate constants (*k*/dm³ mol⁻¹ min⁻¹), and association constants (*K*) of the $NaS_2O_3^-$ and $NaFe(CN)_6^{2-}$ ion pairs in different isodielectric water–solvent mixtures (T = 298 K)

Solvent	% w/w	$10^2\eta$	$10^{-3}\varepsilon$	k	$K_{NaS_2O_3^-}$	$K_{NaFe(CN)_6^{2-}}$
Pure water			1.02	1.29	20	30
Methanol	10.20	1.122	1.03	0.70	22	118
Ethanol	7.89	1.196	1.02	0.60	28	172
t-Butyl alcohol	5.29	0.989	1.03	1.01	33	106
Glycerol	21.90	1.541	1.02	0.81	38	190
dmf	20.59	1.416	1.04	0.32	32	105
Acetonitrile	10.76	0.984	1.03	0.72	17	95
Dextrose	17.92	1.468	1.02	1.09	58	460
Sucrose	18.62	1.425	1.02	1.45	46	352
Sucrose	32.74		1.03	1.30		
Sucrose	44.89		1.03	1.09		
Sucrose	50.50		1.04	1.05		
Sucrose	60.47		1.04	0.82		

Table 2. Rate constants *k* (dm³ mol⁻¹ min⁻¹) at different salt concentrations (T = 298 K)

c/mol dm⁻³	$NaClO_4$	NaCl	$NaNO_3$
1.0	12	11	11
1.5	25	20	17
2.0	39	31	26
2.5	59	47	42
3.0	86	68	60
3.5	148	102	76
4.0	191	144	102

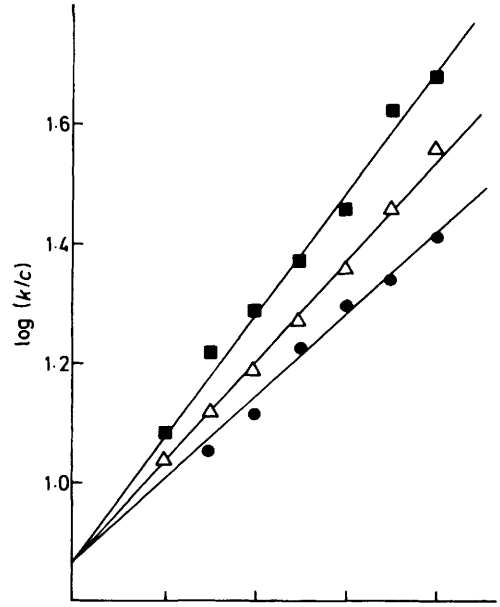

Figure. Plots of log (*k*/*c*) against *c*: (■) $NaClO_4$, (△) NaCl, (●) $NaNO_3$

equation implies that, if the original assertions are correct, plots of log (*k*/*c*) against *c* should yield a straight line. Such a plot is shown in the Figure and it is indeed linear. Using the above plot, the following k_1 and α values can be computed: k_1 = 7.54, $\alpha_{ClO_4^-}$ = 0.200, α_{Cl^-} = 0.170, and $\alpha_{NO_3^-}$ = 0.135. It is also interesting to note that, as expected,[7] the intercept of these plots is the same whichever salt is considered but the slopes are different depending on the 'salting effect' exerted by the salt. Therefore, it can be concluded that in the range of salt concentrations used by the authors a specific effect of the anions is observed and this may be explained on the basis of the 'salting effect' of the electrolyte.

However, this 'salting effect' on the reactants cannot be the decisive factor in diluted solutions. In these solutions the association of the reactants with the cation of the salt or the changes in water structure caused by the salts could be important.[17,18] For this reason we have studied the reactivity in water–cosolvent mixtures.[19,20] We have selected mixtures with different structural properties, but with the same dielectric constants. Owing to the high water content of the mixtures, a drastic change in the first solvation shell of the reactants is not likely in passing from pure water to the mixtures. It could also be expected that the association constants of the $NaS_2O_3^-$ and $NaFe(CN)_6^{2-}$ ion pairs would be similar in each case. However, this latter hypothesis must be confirmed because bulk dielectric constants do not reflect the microscopic behaviour of solutions. For this reason we have measured the association constants of the reactants with the cation (Na^+) present in the reaction medium. In fact, as shown in Table 1, the association constants are not the same in the different mixtures, in spite of their isodielectric properties. Also, it can be seen in Table 1 that the association constant sequence does not agree with the rate constant sequence. Therefore, the assumption of ionic association alone does not provide a satisfactory interpretation of the experimental results.

In our opinion, structural properties of the mixtures, as defined by ΔG^E values, are also important in relation to the reactivity pattern. Our mixtures are of different types, as mentioned before. Mixtures of methanol, ethanol, t-butyl alcohol, and glycerol with water are typically aqueous (t.a.; $\Delta G^E > 0$, $|T\Delta S^E| > |\Delta H^E|$).[21,22] The water–dmf (dmf = dimethylformamide) and water–acetonitrile mixtures are typically non-aqueous positive (t.n.a.p.; $\Delta G^E > 0$, $|T\Delta S^E| < |\Delta H^E|$).[23,24] Finally, sugar–water mixtures are typically non-aqueous negative (t.n.a.n.; $\Delta G^E < 0$, $|T\Delta S^E| < \Delta H^E|$).[25] A survey of Table 1 indicates that reactivity in t.n.a.n. is higher than in t.a. and t.n.a.p. This behaviour has also been observed for similar reactions;[13,17] however, for these reactions the rate constants in t.n.a.n. mixtures, with $\Delta G^E < 0$, were greater than in water. In the present case this happens in the sucrose–water mixture but not in the glucose–water mixture. This could be explained in the following way. Working with t.a. and t.n.a.p. mixtures, both dielectric constant and structural effects produce the same behaviour, that is, a rate constant decrease from the value in water. However, when t.n.a.n. mixtures are used, while the dielectric constant decrease acts against the rate constant increase, the other effect favours the rate constant increase. The dominant influence, of course, is dependent on the charge product of the reactants, and for a given dielectric constant and charge product, on the value of ΔG^E of the mixture. When the charge product is low (2 or 3 in previously studied cases[13,17]) rate constants in t.n.a.n. mixtures are always greater than in water. When the charge product is 6, as in the present reactions, only in some t.n.a.n. (those with more negative ΔG^E) is the rate constant greater than in water. This could explain why in the sucrose–water mixture the rate constant is greater than in water and the opposite is true in glucose–water. It is to be expected that a more marked decrease in the dielectric constant of the sucrose–water mixture will bring about a decrease in rate because of the negative influence of diminishing the dielectric constant. In order to confirm the aforementioned idea, the dielectric constant of the sucrose–water mixture has been decreased. As was expected, the rate constant values decrease below the value in water (see Table 1), that is, the dielectric constant decrease becomes the dominant factor.

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