Salt and Medium Effects in the Oxidation of Iodide by Hexacyanoferrate(III) †

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The rate of reaction between hexacyanoferrate(III) and iodide ions has been measured in several aqueous concentrated salt solutions and in several isodielectric water–cosolvent mixtures. The results are not in agreement with the predictions of the Olson–Simonson model, but can be rationalized as a consequence of the salt–water and cosolvent–water interactions.

The reaction between hexacyanoferrate(III) ion and iodide ion has been studied by several authors.[1-9] It is first order with respect to $[Fe(CN)_6{}^{3-}]$, second order with respect to $[I^-]$; at low iodide concentration the order with respect to this ion decreases toward one, as in other iodide oxidations. The reaction rate is pH-dependent, but on this point the results of different workers are not in agreement.[6-8]

The most extensive study on the kinetic salt effects in this reaction has been that of Indelli.[5] According to these studies, the reaction rate is increased in a specific way by different salts: for salts with a common anion the sequence of rate constants k is $Na^+ < K^+ < Sr^{2+} \approx Ba^{2+} \approx Ca^{2+} \approx Mg^{2+} \ll La^{3+} \lll Th^{4+}$, and for salts with a common cation $NO_3{}^- < Cl^- < SO_4{}^{2-} < ClO_4{}^-$. These results were interpreted by Indelli as being a consequence of the Olson–Simonson effect.[10] Majid and Howlett [8] have also studied the kinetic salt effect on this reaction. Their results are, in general, in agreement with those of Indelli.

The purpose of this paper is to extend the concentration range of salts utilized as supporting electrolyte, by making a study of the kinetic salt effect in concentrated solutions of salts. We have also studied the kinetics of the reaction in some isodielectric cosolvent–water mixtures, in order to determine the influence on the association of the cation present in the reaction medium with hexacyanoferrate(III) ion in the kinetics of this reaction (the Olson–Simonson effect).

Experimental

Reagents.—The reagents used were all AnalaR grade chemicals from various sources, with the exception of sodium butyrate. This reagent was a Merck p.s. material and was purified by dissolving it in methanol and precipitating it by adding diethyl ether. The water used had a resistance $>5\ M\Omega$ and was obtained by distillation from $KMnO_4$ and by passing distilled water through a mixed-bed ion-exchange column.

Kinetic Data.—Kinetic runs in salt solutions and in water–cosolvent mixtures were carried out in 1-cm silica cells in the thermostatted cell compartment of a Beckman DB-GT spectrophotometer. The temperature in the cell was fixed at 298.0 ± 0.1 K. These runs in solutions containing an excess of iodide ion were followed by monitoring the changes in absorbance at 400 nm at fixed time intervals. At this wavelength both hexacyanoferrate(III) and tri-iodide ions absorb, so that relation (1) is obeyed; A is the total absorbance of the

$$A = \varepsilon(a - x) + \varepsilon'(x/2) \qquad (1)$$

solution, ε the molar absorption coefficient of hexacyanoferrate(III), ε′ that of tri-iodide, a the initial concentration of hexacyanoferrate(III), and $(a - x)$ its concentration at the time of measurement. Table 1 gives the values of ε and ε′ in water and in the water–cosolvent mixtures. (In media containing salts neither ε nor ε′ changed from the values in water.) In the salt-containing solutions the concentrations of reactants were $[KI] = 0.1$ mol dm^{-3} and $[K_3Fe(CN)_6] = 4 \times 10^{-4}$ mol dm^{-3}. In the water–cosolvent mixtures, $[KI] = 0.4$ mol dm^{-3} and $[K_3Fe(CN)_6] = 8 \times 10^{-4}$ mol dm^{-3}. (In the runs with $NaClO_4$, the sodium salts were used at the same concentrations.) The solutions also contained $K_2(H_2edta)$ (edta = ethylenediaminetetra-acetate) in order to prevent the catalysis of some metal ions that could be present as impurities $\{[K_2(H_2edta)] = 5 \times 10^{-4}$ mol dm$^{-3}\}$.

Table 1. Viscosities (η), molar absorption coefficients of $Fe(CN)_6{}^{3-}$ (ε) and of $I_3{}^-$ in 0.4 mol dm^{-3} KI (ε′), and observed rate constants for the reaction of $Fe(CN)_6{}^{3-}$ with I^- in different isodielectric water–cosolvent mixtures

Cosolvent	% w/w	$10^{-2}\varepsilon$/ dm^3 mol^{-1} cm^{-1}	$10^{-3}\varepsilon'$/ dm^3 mol^{-1} cm^{-1}	10^5k/s^{-1}	$10^2\eta$/P
None		8.73	6.95	10.9	—
dmf	20.59	8.78	7.83	0.55	1.416
Methanol	10.20	8.72	6.98	5.90	1.122
Ethanol	7.90	8.73	7.25	6.82	1.196
Sucrose	18.62	8.63	7.32	13.5	1.425
Dextrose	17.92	8.65	6.74	16.0	1.468

The results of kinetic runs are collected in Table 2 as pseudo-first-order rate constants (s^{-1}) for the salt-containing solutions, and in Table 1 for the water–cosolvent mixtures. Table 1 also contains the composition of the mixtures which were selected so as to give the same dielectric constant ($D = 74$) in each case. The dielectric constant data are from the literature.[11-13]

Viscosity and Density Data.—We measured the viscosities and densities of some salt solutions in order to obtain the Jones–Dole coefficient B [14] of the salts and to determine their type in the Nightingale classification [15] (see Discussion section). The densities were determined picnometrically and the viscosities from the flow time of solutions in an Ostwald-type viscosimeter. The values are reported in Table 3 which also includes the coefficients B. We also measured the viscosities of water–cosolvent mixtures (Table 1).

Conductance Measurements.—The conductance measurements were carried out using a Beckman RC18A bridge. The

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† *Non-S.I. unit employed:* P = 10^{-1} Pa s.

Table 2. Observed rate constants ($10^5 k/s^{-1}$) for the reaction of $Fe(CN)_6^{3-}$ with I^- as a function of the supporting electrolyte concentration

c/mol dm^{-3}	$LiNO_3$	$NaNO_3$	KNO_3	$Ca(NO_3)_2$	$Mg(NO_3)_2$
0.500	—	—	—	3.50	3.60
0.626	—	—	—	3.95	4.65
0.750	—	—	—	4.57	6.03
0.875	—	—	—	5.88	7.87
1.000	1.2	1.4	2.30	6.93	10.5
1.175	—	—	—	8.88	13.7
1.250	—	—	2.53	—	—
1.350	—	—	—	11.4	19.7
1.500	2.00	1.72	2.70	14.2	25.5
1.750	—	—	2.98	20.8	39.7
2.000	3.13	2.33	3.30	—	—
2.250	—	—	3.62	—	—
2.500	—	—	3.85	—	—
2.700	3.95	3.12	4.08	—	—
3.000	7.23	4.25	—	—	—
3.500	11.0	4.95	—	—	—
4.000	15.5	6.07	—	—	—
4.500	20.7	8.18	—	—	—
5.000	29.3	10.3	—	—	—

c/mol dm^{-3}	NaCl	Na_2SO_4	NaH_2PO_4	$NaClO_4$	$Na(O_2CMe)$	NaPr	$NaBu^t$
0.500	—	0.87	—	—	—	—	—
0.750	—	1.3	—	—	—	—	—
1.000	1.5	1.80	1.6	1.6	1.5	1.0	1.1
1.250	—	—	—	2.00	—	—	—
1.350	—	2.82	—	—	—	—	—
1.500	2.72	3.25	2.73	2.48	1.93	1.3	1.4
1.750	—	4.42	—	2.83	—	—	—
2.000	3.97	6.45	4.58	3.73	2.47	1.6	1.80
2.250	—	—	—	4.57	—	—	—
2.350	—	—	—	—	—	—	2.05
2.500	—	—	—	5.17	—	—	—
2.700	5.95	—	10.9	6.02	3.58	2.32	2.68
3.000	8.33	—	14.9	—	4.08	2.78	3.08
3.500	11.3	—	27.7	—	5.12	3.43	—
4.000	14.3	—	47.0	—	6.08	4.22	—

cell, with a constant of 0.491 cm^{-1}, was a Beckman 6J05 conductance cell. The temperature was fixed at 298.150 ± 0.005 K using an oil-bath. The cell containing the solutions was flushed with nitrogen before the measurements. The solutions were stirred during the measurements in order to avoid the drift observed in readings which is probably caused by adsorption at the electrodes.[16,17] The results are reported in Table 4, which gives the molar concentrations, the equivalent conductances, and the approximate association 'constants' of the $KFe(CN)_6^{2-}$ ion pair calculated by the Davies [18] method as modified by James and Monk.[16]

Discussion

Figure 1 is a typical plot of log k *vs.* the concentration of salt in the medium; in all cases a linear variation of log k with the salt concentration is observed. If the activity coefficients of the reactants and activated complex (‡) are written as in equation (2) (γ_i = ionic activity coefficient; A = Debye–Hückel constant; z_i = ionic charge; b_i = parameter of interaction among reactants, activated complex, and solvent),[19] Brönsted's formula [20] gives expression (3) (k_0 = rate constant

$$\log \gamma_i = -[(A z_i^2 \sqrt{c})/(1 + \sqrt{c})] + b_i c \qquad (2)$$

$$\log k = \log k_0 + [(5A\sqrt{c})/(1 + \sqrt{c})] + (2b_{I^-} + b_{Fe(CN)_6^{3-}} - b_{\ddagger})c \qquad (3)$$

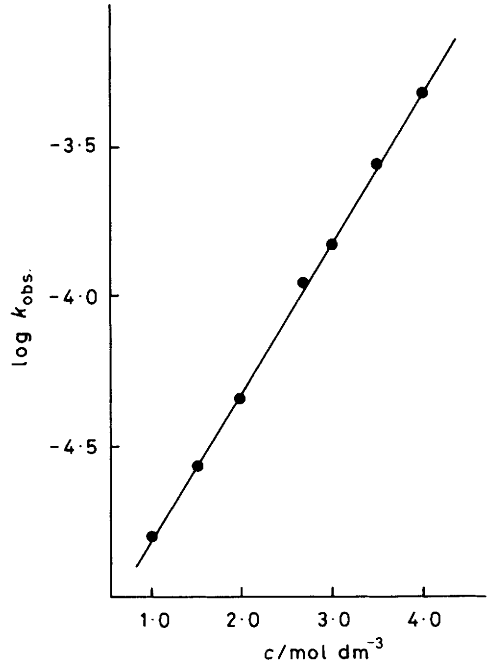

Figure 1. Plot of log $k_{obs.}$ as a function of the concentration of NaH_2PO_4

Table 3. Densities (ρ), relative viscosities (η/η_0), and Jones–Dole coefficients (B) for different salt solutions

	NaH_2PO_4		NaPr		$NaBu^t$	
c/mol dm^{-3}	ρ/kg m^{-3}	η/η_0	ρ/kg m^{-3}	η/η_0	ρ/kg m^{-3}	η/η_0
(*a*) At 298.0 ± 0.1 K						
0.010	998.1	1.004	—	—	—	—
0.025	999.6	1.010	—	—	—	—
0.050	1 001.7	1.019	999.3	1.021	999.3	1.027
0.075	1 004.0	1.030	1 000.4	1.034	1 000.3	1.040
0.100	1 006.1	1.039	1 001.4	1.044	1 001.3	1.052
0.125	1 008.2	1.048	1 002.7	1.055	1 002.3	1.065
0.150	1 010.5	1.059	1 003.6	1.066	1 003.2	1.078
0.175	1 012.6	1.069	1 004.6	1.077	1 004.3	1.091
0.200	1 015.0	1.079	1 005.6	1.088	1 005.3	1.106
B/ dm^3 mol^{-1} ± $t\bar{\sigma}$ *	0.39 ± 0.01		0.46 ± 0.02		0.51 ± 0.02	
(*b*) At 313.0 ± 0.1 K						
0.010	993.3	1.003	—	—	—	—
0.025	994.6	1.008	—	—	—	—
0.050	996.6	1.019	994.3	1.020	994.2	1.023
0.075	998.9	1.027	995.5	1.029	995.2	1.034
0.100	1 001.0	1.038	996.5	1.040	996.3	1.045
0.125	1 003.6	1.049	997.5	1.048	997.1	1.057
0.150	1 005.4	1.058	998.6	1.059	998.3	1.071
0.175	—	—	999.6	1.070	999.2	1.083
0.200	—	—	1 000.6	1.081	1 000.0	1.093
B/ dm^3 mol^{-1} ± $t\bar{\sigma}$ *	0.43 ± 0.03		0.41 ± 0.03		0.48 ± 0.03	

	$Na(O_2CMe)$		$NaClO_4$	
c/mol dm^{-3}	ρ/kg m^{-3}	η/η_0	ρ/kg m^{-3}	η/η_0
0.075	995.4	1.024	998.4	1.004
0.100	996.3	1.032	—	—
0.125	997.4	1.038	1 002.5	1.006
0.150	998.4	1.045	—	—
0.160	998.8	1.048	—	—
0.175	999.4	1.053	1 006.5	1.008
0.250	—	—	1 012.5	1.011
B/ dm^3 mol^{-1} ± $t\bar{\sigma}$ *	0.26 ± 0.03		0.031 ± 0.008	

* t = Student t for a 95% confidence level and $\nu = N - 2$ degrees of freedom; $\bar{\sigma}$ = standard deviation of mean.

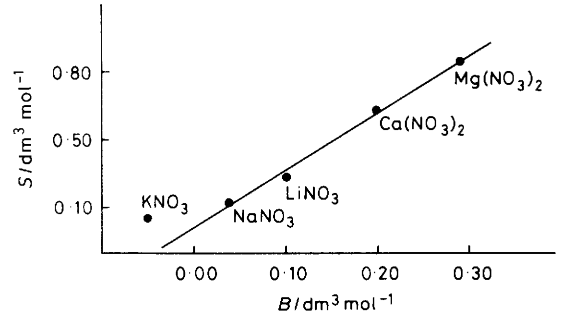

Figure 2. Plot of the slopes S of plots of log $k_{obs.}$ *vs.* c as function of the Jones–Dole coefficient B for salts of a common anion (NO_3^-)

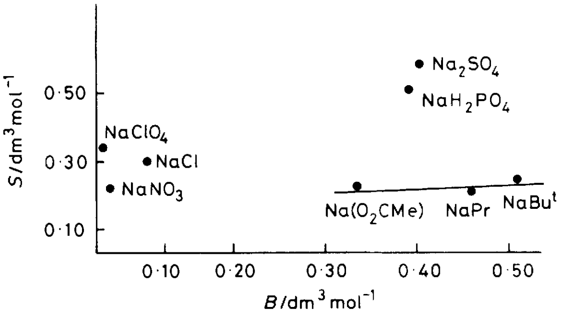

Figure 3. Plot of the slopes S as function of the coefficient B for salts of a common cation (Na^+)

for $\gamma_i = 1$). The linear form of the log k *vs.* c plots suggests that the third term on the right-hand side of expression (3) is much greater than the second one, the slope, $S = 2\,b_{I^-} + b_{Fe(CN)_6^{3-}} - b_{\ddagger}$, being a constant for a given salt (Table 5).

Figure 2 is a plot of S *vs.* the Jones–Dole coefficient B for several salts with a common anion (NO_3^-), and Figure 3 shows the same plot for salts with a common cation (Na^+). With reference to Figure 2, it can be seen that the kinetic salt effect of a salt (as measured by S) is proportional to its B coefficient, which, as is known, is a measure of the ion–solvent interactions.[21] According to this, it must be concluded that, in the concentration range studied, the kinetic salt effect of a salt is proportional to its interaction with the solvent.

Table 4. Equivalent conductances (Λ) and association constants (*K*) of the ion pair $KFe(CN)_6^{2-}$ at different molar concentrations (*c*)

	100% Water		Ethanol–water (7.9 : 92.1)		dmf–water (20.6 : 79.4)	
10^4c/mol dm^{-3}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}
1.00	166.67	5.2	137.49	42	98.31	32
1.50	165.50	3.6	134.92	39	96.75	29
2.00	164.65	—	133.13	36	95.30	27
2.50	163.56	2.3	131.19	34	94.19	25
3.00	162.72	2.0	129.58	33	93.35	24

	Dextrose–water (17.9 : 82.1)		Sucrose–water (18.6 : 81.4)		Methanol–water (10.2 : 89.8)	
10^4c/mol dm^{-3}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	$10^{-1}K$/ dm^3 mol^{-1}
1.00	—	—	—	—	142.20	59
1.50	109.46	55	105.06	51	138.52	56
2.00	107.57	51	103.41	46	135.54	55
2.50	105.44	52	102.16	42	133.24	43
3.00	104.28	49	101.21	39	130.90	53

Table 5. Values of the slopes (*S*) of plots of log $k_{obs.}$ *vs.* *c*/mol dm^{-3} for different salts

Salt	S/dm^3 mol^{-1} $\pm t\sigma$
KNO_3	0.15 ± 0.01
$NaNO_3$	0.21 ± 0.02
$LiNO_3$	0.34 ± 0.02
$Ca(NO_3)_2$	0.62 ± 0.01
$Mg(NO_3)_2$	0.84 ± 0.02
NaCl	0.30 ± 0.04
$NaClO_4$	0.34 ± 0.03
Na_2SO_4	0.57 ± 0.02
NaH_2PO_4	0.50 ± 0.02
$Na(O_2CMe)$	0.22 ± 0.01
NaPr	0.21 ± 0.01
$NaBu^t$	0.24 ± 0.03

Table 6. Values of the ion-pair concentration in several water–cosolvent mixtures

Solvent	$10^4[KFe(CN)_6^{2-}]$/ mol dm^{-3}
100% Water	0.7
Ethanol–water (7.9 : 92.1)	4.0
dmf–water (20.6 : 79.4)	3.4
Dextrose–water (17.9 : 82.1)	4.8
Methanol–water (10.2 : 89.8)	5.0
Sucrose–water (18.6 : 81.4)	4.3

The correlation of *S* and *B* for the salts with a common cation is not so good as the corresponding one for the salts with a common anion. This could be explained by the fact that the different anions in Figure 3 belong to different types in the Nightingale classification of ionic hydration.[15] Thus, Cl^-, NO_3^-, and ClO_4^- ions belong to group 3, $H_2PO_4^-$ and SO_4^{2-} to group 2, and O_2CMe^-, Pr^-, and Bu^{t-} to group 4. (In fact, all the cations in Figure 2 belong to the same type, with the exception of K^+ which deviates from the correlation.) It can be concluded that, in the concentration range studied, the kinetic salt effect is exerted fundamentally through the solvent. Because *B* is sensitive to the structural change induced by the ions in the solvent,[22] this interaction through the solvent must be due not only to a loss of hydration of the reactants (destabilizing) when the electrolyte becomes hydrated, but also to a structural effect. In fact, the dehydration effect is of little importance in dilute solutions, but in these solutions the structural effect could be present (an overlap of the Gurney cosphere of the reactants and salts). This structural effect could be the origin of the negative salt effect of tetra-alkylammonium ions observed in this and other reactions.[23] A negative salt effect in a reaction between ions of the same sign cannot be explained by an Olson–Simonson effect, nor can the fact (see Table 5) that the differences in the effects of anions are of the same order, and sometimes greater, than those of cations.

Our results on the kinetics in the water–cosolvent mixtures are not in agreement with those expected from an Olson–Simonson effect. The sequence of the rate constant *k* in these mixtures is dimethylformamide (dmf)–water $\ll$ methanol–water < ethanol–water < water < sucrose–water < dextrose–water, and the sequence of the association constants *K* of the $KFe(CN)_6^{2-}$ ion pair is water $\ll$ dmf–water < ethanol–water $\approx$ sucrose–water < dextrose–water $\approx$ methanol–water. In fact, the concentrations of ion pairs in the mixtures must be nearly the same: these concentrations, calculated from the association constants, are given in Table 6. It can be seen that the quotient of the ion-pair concentrations in dextrose–water and dmf-water is 1.4 and the quotient of the corresponding rate constants is 29.2.

The results obtained in water–cosolvent mixtures can be rationalized by taking the model of Caldin and Bennetto[24] as a basis: in the process of forming an ' encounter complex ' from the reactants, some of the solvent molecules in the second zone of solvation of the reactants[25,26] must pass to the bulk. Bearing in mind that this second zone is a very disordered one, according to Caldin and Bennetto the arrangement of solvent molecules (water + cosolvent) in such a zone will not be very different from that corresponding to an ideal mixture. This implies that the change in free energy accompanying the process solvent in the second zone ⟶ solvent in the bulk can be approximated as in equation (4) (free energies: G_{bulk},

$$G_{bulk} - G_{sz} \approx (G_{ideal} + \Delta G^E) - G_{ideal} = \Delta G^E \quad (4)$$

of the bulk; G_{sz}, the second zone of solvation; G_{ideal}, of an ideal mixture; ΔG^E = excess free energy of the mixture). Therefore, the contribution of this step to the energy of activation will be positive for mixtures in which $\Delta G^E > 0$ and negative for those where $\Delta G^E < 0$. According to this, the rate constants will be greater in the second type of mixtures (dextrose–water and sucrose–water) than in water, and lower in mixtures where $\Delta G^{E} > 0$ (ethanol–water, methanol–water, and dmf–water). So, the kinetic effects of non-electrolytes reflect the water–non-electrolyte interactions, as do the kinetic salt effects.

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