

Kinetic salt effects in the reaction of permanganate ions with ferrocyanide ions in concentrated electrolyte solutions

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Received 17 May 1989

The oxidation of ferrocyanide by permanganate ion has been studied in several electrolyte solutions over the concentration range of 0–6 mol dm⁻³. The observed kinetic salt effect may be interpreted as arising as a result of ion–solvent interactions. In the case of magnesium salt, however, another effect, probably that of a local hydrolysis, also contributes to the kinetic salt effect.

Изучено окисление ферроцианида ионами перманганата в нескольких электролитических растворах в пределах концентрации 0–6 моль дм⁻³. Наблюденный кинетический соляной эффект может быть объяснен как результат взаимодействия между ионами и растворителем. Однако, в случаях солей магния дальнейший эффект, вероятно эффект местного гидролиза, тоже способствует кинетическому соляному эффекту.

During the last few years we have been interested in the study of kinetic salt effects in concentrated solutions of electrolytes [1–7]. The most striking feature emerging from such studies has been the linear dependence of $\ln k$ on c (k being the rate constant and c the salt concentration). Also the slopes S (see eqns (2–4)) of $\ln k$ vs. c plots for different salts are linearly correlated with the B (Jones–Dole) viscosity coefficients [8] of the salts. The Jones–Dole coefficient is defined by the equation

$$\eta / \eta_0 = 1 + A\sqrt{c} + Bc$$

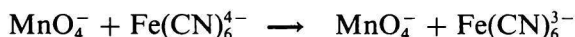
(η being the viscosity of the salt solution of concentration c , η_0 that of solvent and A a positive parameter theoretically computable). B is a measure of ion–solvent interactions [8]. Accordingly, it may be concluded that the kinetic salt effects in concentrated solutions of supporting electrolytes are determined by the salt–solvent interactions. However, two reactions seem to be an exception to this rule: the oxidation of ferrocyanide ions and molybdocyanide ions by

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peroxodisulfate [7, 9]. In these cases, the point for magnesium salts lies off the *S*—*B* correlation line. We have pointed out [7] that such behaviour can be attributed to local hydrolysis effects, with the negative 4- valent ions being protonated and thereby becoming less reactive. In order to confirm this hypothesis, we have undertaken the study of the present system, changing the oxidant and maintaining the reductant, in this case the ferrocyanide ion. Previous studies on this reaction are in Refs. [10, 11]. According to these studies the rate law is

$$v = k [\text{MnO}_4^-][\text{Fe}(\text{CN})_6^{4-}]$$

corresponding to the reaction scheme



Experimental

All the products employed in this study were commercial ones of anal. grade and were used without further purification. For all runs initial concentrations of reagents were $[\text{MnO}_4^-] = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}(\text{CN})_6^{4-}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$.

Concentrations of added salts covered the 1.0 to 6.0 mol dm^{-3} range for LiNO_3 and NaNO_3 and 1.0 to 3.0 mol dm^{-3} range for $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and $\text{Sr}(\text{NO}_3)_2$. As the reaction rate is independent of pH in the range 5—6 [12] this variable was adjusted to ≈ 5.5 . Fresh solutions of permanganate and ferrocyanide were made up for each set of runs. All the solutions were prepared with deionized deoxidized water (conductivity $< 10^{-6} \text{ S cm}^{-1}$).

The kinetics were followed in a Hi-Tech stopped-flow spectrophotometer at $298.2 \pm 0.1 \text{ K}$ and at an observation wavelength of 420 nm. Data were processed using Hi-Tech kinetics software in conjunction with an Apple IIe.

Results and discussion

Second-order rate constants for the oxidation of ferrocyanide by permanganate ions for different added electrolytes are compiled in Table 1. The results indicate the existence of a positive salt effect which is specific in that its magnitude depends upon the nature of the salt. As in previous studies $\ln k$ varies linearly with the concentration of salt. A typical example of this is represented in Fig. 1, which is a plot of $\ln k$ vs. the concentration of LiNO_3 .

These results can be interpreted by taking as a starting basis the following expression [14]

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\neq}} \quad (1)$$

Table 1

Values of $k \cdot 10^{-3}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ at different concentrations of electrolytes at 298.2 K

$c/(\text{mol dm}^{-3})$	LiNO_3	NaNO_3	$\text{Mg}(\text{NO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$\text{Sr}(\text{NO}_3)_2$
0.5			38 ± 3	39 ± 3	57 ± 3
1.0	36 ± 2	54 ± 3	50 ± 4	53 ± 4	71 ± 7
1.5			61 ± 5	62 ± 5	84 ± 6
2.0	43 ± 2	62 ± 7	70 ± 6	73 ± 6	100 ± 9
2.5			80 ± 6	90 ± 7	119 ± 9
3.0	51 ± 4	64 ± 6	92 ± 7	104 ± 8	140 ± 11
4.0	60 ± 8	67 ± 8			
5.0	70 ± 4	70 ± 6			
6.0	84 ± 4	72 ± 5			

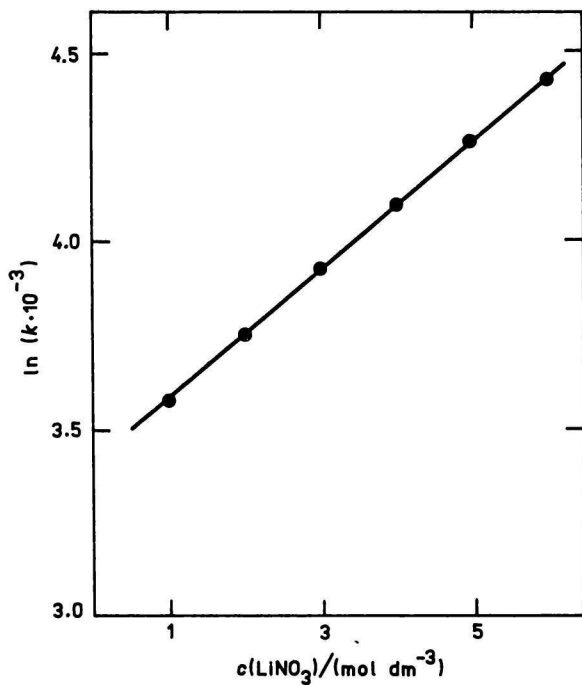


Fig. 1. Plot of $\ln k$ vs. concentration of lithium nitrate for the reaction of $\text{MnO}_4^- + \text{Fe}(\text{CN})_6^{4-}$ at 298.2 K.

in which γ_A and γ_B represent the activity coefficients of the reactants ($\text{Fe}(\text{CN})_6^{4-}$ and MnO_4^-), γ_\ddagger being that for the activated complex. If these coefficients are expressed in the form [15]

$$\ln \gamma_i = \frac{-A' z_i^2 \sqrt{c}}{1 + \sqrt{c}} + bc \quad (2)$$

then with eqn (1), this leads to

$$\ln k = \ln k_0 + \frac{A\sqrt{c}}{1 + \sqrt{c}} + Sc \quad (3)$$

where A' , A , b , S are parameters ($S = b_{\text{Fe}(\text{CN})_6^{4-}} + b_{\text{MnO}_4^-} - b_\ddagger$).

The term $A\sqrt{c}/(1 + \sqrt{c})$, as is well known, represents the coulombic effects of the added salts upon the participants in the reaction. The term Sc accounts for the noncoulombic effects of the salts upon the reactants. The fact $\ln k$ varies linearly with c implies that the *variations* of coulombic interactions, are very small, in concentrated electrolyte solutions, in comparison with the variations of the noncoulombic interactions. Therefore, the cause of the observed salting process is considered to be principally due to these noncoulombic interactions. In our opinion the salt effect has its origin in the hydration of the electrolytes introduced into the system. A decrease in the activity of the solvent occurs as a result of the hydration. From here we can proceed toward the conclusions, by assuming first that eqn (3) can be put in the form

$$\ln k = \ln k'_0 + Sc \quad (4)$$

In this expression k'_0 represents the sum of the “idealized” rate constant at infinite dilution, k_0 , and the coulombic contributions which are approximately constant. The coulombic contributions correspond essentially to the screening of the coulombic interactions between the reactants. As a consequence, k'_0 represents a rate constant, which describes the encounter of the reactant species but in which the repulsive coulombic interactions between the reactants have been eliminated, at least partially. And, moreover, it corresponds to a rate constant in zero concentration of added electrolyte, in which the encounter of reactants is also free of the perturbations duly arising from salting. The values of k'_0 are distinctly different for the different salts (Table 2). These differences can reflect the fact that ionic species reacting in the different media are different ion pairs. In Table 3, the values of S , obtained from the plots of $\log k$ vs. c , are given for each of the salts employed in this study; in Fig. 2 the relationship between S and B , the Jones—Dole parameter, is displayed. The relationship may be described, reasonably, as linear. However, as in previous studies on cyanide complexes oxidation [7, 9], the point for magnesium nitrate also lies off the

Table 2

Values of $k'_0 / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ obtained from eqn (4)

Salt	LiNO ₃	NaNO ₃	Mg(NO ₃) ₂	Ca(NO ₃) ₂	Sr(NO ₃) ₂
$k'_0 \cdot 10^{-3}$	30.8 ± 0.3	57.3 ± 0.4	38 ± 3	34 ± 3	49 ± 1

Table 3

Jones—Dole coefficients and values of S for each salt

Salt	LiNO ₃	NaNO ₃	Mg(NO ₃) ₂	Ca(NO ₃) ₂	Sr(NO ₃) ₂
$B \cdot 10^3 / (\text{dm}^3 \text{mol}^{-1})$	101	40	293	193	173
$S \cdot 10^3 / (\text{dm}^3 \text{mol}^{-1})$	166 ± 3	39 ± 1	296 ± 35	376 ± 51	354 ± 15

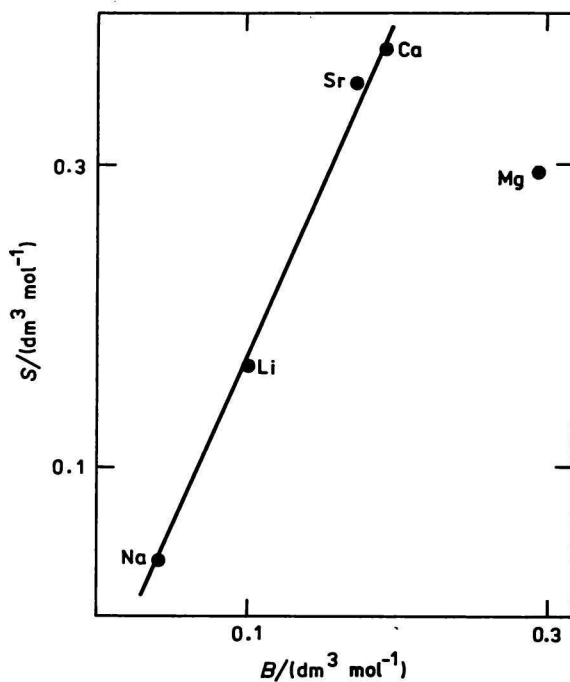


Fig. 2. Plot of S (eqn (4)) vs. Jones—Dole coefficients B for the reaction of $\text{MnO}_4^- + \text{Fe}(\text{CN})_6^{4-}$ in various salts.

correlation, confirming our previous hypothesis that the cyanide complexes, but not the oxidant, are responsible for this effect. As we pointed out in the introduction a local hydrolysis of the ferrocyanide seems to be a reasonable explanation. Indeed, Fig. 3 shows a good correlation of S for this reaction and the ferrocyanide oxidation by peroxodisulfate. Thus, Mg^{2+} has very similar effects on both reactions.

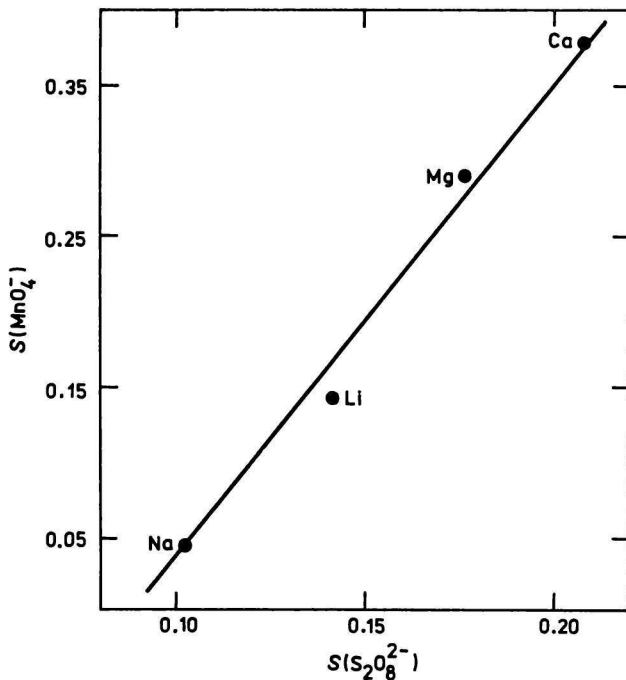


Fig. 3. Correlations between slopes S for peroxodisulfate and permanganate oxidations of ferrocyanide.

The positive salt effect indicates that the ions affect reactivity by reducing the activation barrier, but it is not possible to be specific without separating the observed trends in rate constants into initial and transition state components. As the reaction in question involves, probably, ion pairs, it is difficult to see how medium effects on the initial state could be established, let alone medium effects on the transition state. Nonetheless it is reasonable to suggest that the positive salt effects operating on slope S arise from a greater destabilization of the initial state in comparison with the transition state on adding high concentrations of salt, the ions thereby making water less available for solvating the reactants and

transition states. The relative availability of water molecules for solvating the reactants and transition states has recently been discussed in relation to B viscosity coefficient [16]. These results were interpreted in terms of enhanced ion—solvent interactions in the transition state for viscous flow. Greater ion—water interaction, with added ions in our system, implies less transition state destabilization, as suggested above.

Acknowledgements. The authors acknowledge the financial support of the CAYCIT (PN, PB85-0375).

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