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# Reaction Kinetics in a Microemulsion Medium IV. Hexacyanoferrate(III)–Iodide Reaction in Water/Aerosol-OT/Heptane Microemulsion and Mixed Solvents

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The kinetics of the reaction between $[Fe(CN)_6]^{3-}$ and $I^-$ was studied in a W/O microemulsion (Water/AOT/Heptane at different [Water]/[Amphiphile] mole ratios) and in mixed water–organic media (water–formamide, water–ethylene glycol, and water–dioxane). The pseudo-first-order rate constants were observed to radically increase in microemulsion media with a [Water]/[AOT] mole ratio below 6. At a mole ratio of 5.4, the rate constant was found to be about 20-fold greater than that in water. At a constant mole ratio, the rate constant was witnessed to be independent of [AOT]. In all mixed media, the rate decreased with increasing proportion of the nonaqueous solvent. The ionic-strength effect on the reaction did not obey either the modified Brønsted–Bjerrum or Brønsted–Bjerrum–Pitzer relations in the studied nonaqueous media, except for ethylene glycol. This disagreement is very prominent in the studied W/O microemulsion medium at [Water]/[AOT] $\omega=9.1$. The activation parameters for the pseudo-first-order reaction in all of the studied media suggested distinct difference of the microemulsion from other solvents. A reasonable compensation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ i.e., the isokinetic effect, was observed.

Like micelles, microemulsions serve as unique compartmentalized environments for different kinds of reactions; both moderate and high-rate accelerating effects were observed.[1—10] In such media, the interface between the water and oil, possessing widely different physical natures compared to an aqueous or nonaqueous continuum, has power to significantly influence the kinetic process, depending on the locations of the interacting species in the compartment. The enzyme kinetics, mainly of the hydrolytic reaction and substitution and oxidation–reduction reactions, have been studied by different workers in various compartmentalized media viz., reverse micelles, microemulsions, etc.[1—10] The rates have been established to be mainly dependent on the types of micelle and on the compositions of microemulsion, particularly on the [water]/[amphiphile] mole ratio and additives.

Compared to micelles, microemulsions are versatile for the compartment sizes in them, and can be altered at will both in the absence and presence of additives. Although investigations of the reaction kinetics in microemulsion media are a growing trend, the field has so far been only slightly explored with respect to the activation parameters as well as salt and additive effects. Information is important for a fundamental understanding of the reactions in compartmentalized environments where the dielectric constant, solvent structure, electrostatic interaction, ion-exchange phenomena, etc. contribute appreciably to kinetic events.

In a program concerning kinetics in microemulsion media, we studied the inversion of sucrose, the alkaline phosphatase-catalyzed hydrolysis of *p*-nitrophenyl dihydrogen phosphate and the alkaline fading of crystal violet in such media under various conditions.[2,8,9] The kinetics of a similar reaction (oxidation of $[Fe(CN)_6]^{4-}$ by $S_2O_8^{2-}$) in microemulsion media has recently been reported.[3b] In this study, a detailed investigation of the $[Fe(CN)_6]^{3-}$–$I^-$ reaction was made in Water/AOT/Heptane microemulsion media, and a correlative attempt was made to rationalize the results realized under various solvent environments, temperatures, and ionic strengths.

## Experimental

**Materials:** The surfactant Aerosol–OT (AOT) was a (99% pure) product of Sigma Chemicals, USA (a sample used earlier[11]). The heptane, potassium hexacyanoferrate(III) and potassium iodide were A.R. grade products of E. Merck, Germany. The other solvents, dioxane (Dx), formamide (Fa), and ethylene glycol (Eg), were also of A.R. grade products of S.D. Chemicals, India. Their refractive indices and boiling points closely agreed with the literature values, and were used without further purification. Inconsistent kinetic results were obtained with dioxane. Freshly distilled material, however, produced consistent results. The salts NaCl and KCl were Excellar-grade products of BDH, England.

Doubly distilled conductivity water was employed in solution preparation.

**Method:** Spectral measurements were taken in a UV-vis Shimadzu 160A spectrophotometer in 0.5 cm Silica Cuvettes at constant temperature (accuracy±0.2°C) by water circulation through the spectrophotometer cell holder.

**Preparation of Microemulsion:** A solution of the amphiphile

AOT in heptane was prepared. Aqueous solutions of potassium iodide and potassium hexacyanoferrate(III) were separately added to two parts of the AOT–Hp preparation in order to produce one-phase microemulsions on the basis of a phase diagram reported earlier.[12] Mixed solutions of $H_2O$–AOT–Hp were then homogenized for a couple of minutes and clear microemulsion solutions were obtained. The proportions of the $H_2O$/AOT/Hp mixtures were selected to produce the desired [Water]/[AOT] mole ratio in the final solution. These homogenized solutions were isotropic, stable and of low viscosity, having excellent stability.

**Kinetic Measurements:** The speed of the reaction between $[Fe(CN)_6]^{3-}$ and $I^-$ was found to be appreciable. The course of the reaction was followed spectrophotometrically by monitoring the formation of $I_3{}^-$ (at 355 nm) in the reaction. The KI concentration was kept in large excess so as to make the reaction order independent of this component. It was thus made pseudo-first-order with respect to the hexacyanoferrate(III) ion, (discussed in a subsequent section). At 355 nm, both $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ had comparable absorbances, and hence the absorbances contributed by these two species, existing during the reaction, remained the same so that the increase in absorbance was eventually due to the formation of $I_3{}^-$. The measurements were, therefore, taken with $[Fe(CN)_6]^{3-}$ solutions as controls. The concentrations of $I_3{}^-$ at different stages of the reaction were estimated from the extinction coefficients of $I_3{}^-$, separately determined at 355 nm according to Beer's law.

The kinetic runs were conducted in microemulsion media by mixing previously thermostated KI and $K_3[Fe(CN)_6]$ contained solutions and quickly placing the mixture in the spectrophotometric cell. The overall concentrations of the reactants in the microemulsion media were the same. Therefore, along with a decrease in $\omega$, the effective concentration of the reactants in the water pool increased. Besides the microemulsion media, other solvent media used were ethylene glycol, formamide and mixed pairs of Wa–Fa, Wa–Dx, and Wa–Eg. Measurements were also taken in solvents at different ionic strengths. To drive the activation parameters for the reaction, experiments were also performed at fixed solvent compositions at different temperatures in the range 293—308 K. It was considered that the basic physical properties of the solvent media (including the microemulsion structure and composition) remained unaltered in this narrow range of temperature.[3,5] According to an earlier report,[13] the pH of the medium in the range 3.0—7.5 and above has practically no effect on the reaction.

## Results and Discussion

**Reaction Mechanism and Experimental Conditions.** The reaction between $I^-$ and $[Fe(CN)_6]^{3-}$ is an interesting one for which the suggested mechanism[14] is the following, and steps one and two are reversible:[15]

$$K^+ + [Fe(CN)_6]^{3-} \overset{K_1}{\rightleftharpoons} \{K[Fe(CN)_6]\}^{2-} \tag{1}$$

$$I^- + \{K[Fe(CN)_6]\}^{2-} \overset{K_2}{\rightleftharpoons} \{IK[Fe(CN)_6]\}^{3-} \tag{2}$$

$$I^- + \{IK[Fe(CN)_6]\}^{3-} \xrightarrow[\text{rate-determining step}]{} I_2{}^- + \{K[Fe(CN)_6]\}^{3-} \tag{3}$$

$$I_2{}^- + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + I_2 \tag{4}$$

If step (3) is rate-determining, then

$$\text{Rate} = k[I^-][IKFe(CN)_6{}^{3-}]. \tag{5}$$

Replacing $[IKFe(CN)_6{}^{3-}]$ in terms of the concentrations set up by the pre-equilibria (1) and (2),

$$\text{Rate} = kK_1K_2[K^+][Fe(CN)_6{}^{3-}][I^-]^2. \tag{6}$$

At constant $[K^+]$, since

$$\text{Rate} = k'K_1K_2[Fe(CN)_6{}^{3-}][I^-]^2,$$
$$\text{where } k' = k[K^+], \tag{7}$$

the reaction is first-order with respect to hexacyanoferrate(III) and second-order with respect to iodide. We have made the process pseudo-first-order keeping KI in excess and the related kinetics,

$$-\frac{d[Fe(CN)_6{}^{3-}]}{dt} = k_1[Fe(CN)_6{}^{3-}], \tag{8}$$

(where $k_1$ is the pseudo-first-order rate constant $= k'K_1K_2[I^-]^2$) was followed spectrophotometrically by monitoring the rate of production of $I_2$ (in reality $I_3{}^-$) at 355 nm. The results were analyzed in the light of the integrated first-order rate law in the form

$$\ln\frac{a}{a-x} = k_1t. \tag{9}$$

Here, $a$ is the initial concentration of $[Fe(CN)_6]^{3-}$; $x$ was obtained from the relation $x = 2A_t/\varepsilon$, where $A_t$ is the absorbance at time $t$ and $\varepsilon$ is the molar extinction coefficient of $I_3{}^-$ at 355 nm which is 22000 $mol^{-1}\,dm^3$ for W/O microemulsion (practically independent of $\omega$) and 28000 $mol^{-1}\,dm^3\,cm^{-1}$ for water and other aqueous organic media. A family of straight lines in support of Eq. 9 are presented in Fig. 1, their slopes yielding the related rate constants ($k_1$) expressed in $s^{-1}$. The rate constants were obtained within a $\pm 5\%$ error limit.

The third-order rate constant ($k_3$) in the rate law,

$$-\frac{d[Fe(CN)_6{}^{3-}]}{dt} = k_3[Fe(CN)_6{}^{3-}][I^-]^2, \tag{10}$$

$k_3$ ($k'K_1K_2$) can be obtained by dividing $k_1$ by $[I^-]^2$. In accordance with Eq. 6, the reaction was found to be first order with respect to $K^+$ (Fig. 2a), first-order with respect to $[Fe(CN)_6]^{3-}$ (Fig. 1; rate constant, $k_1 = 2.8\times10^{-5}\ s^{-1}$ at $[K^+] = 0.3$ and $[I^-] = 0.28\ mol\,dm^{-3}$ and 298 K) and second-order with respect to $I^-$ (Fig. 2b; rate constant, $k_3 = 3.4\times10^{-4}\ mol^{-2}\,dm^6\,s^{-1}$). To determine the order of the reaction with respect to the $K^+$ ion, kinetic experiments were performed at constant $[K_3Fe(CN)_6]$ and [KI] with varying KCl, the ionic strength being maintained constant by the addition of NaCl; the association of $Na^+$ ion with $[Fe(CN)_6]^{3-}$ was considered to be minor.

The conversion of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ by reacting with $I^-$ was influenced by the $K^+$ ion; the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ self-exchange process also affected it. According to recent reports,[16,17] the $K^+$ ion is also involved in the transition state of the exchange kinetics. The kinetics of the conversion reaction herein reported was, therefore, inclusive of the retarding influence of the exchange process. Although the separation of the latter from the overall kinetic

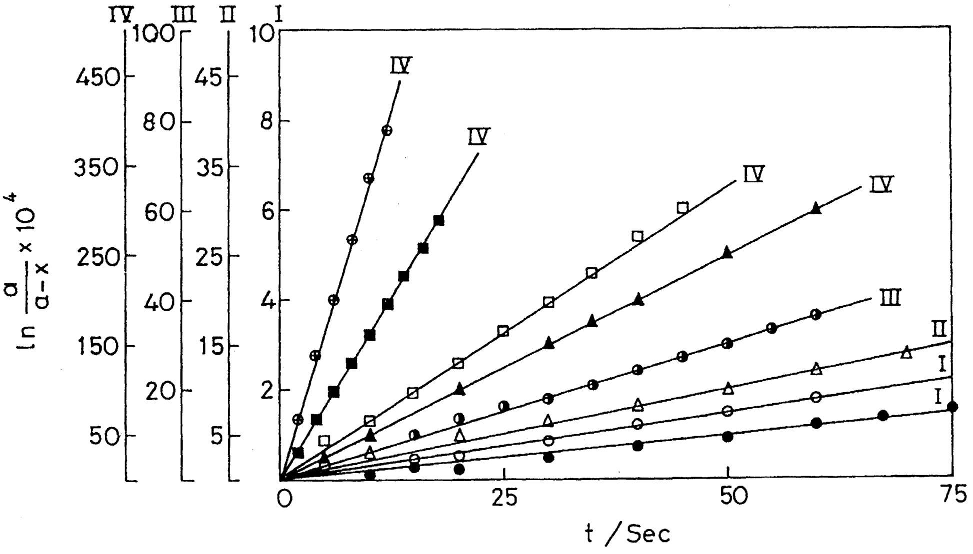

Fig. 1. Polt of $\ln \frac{a}{a-x}$ vs. $t$ for the reaction between $K_3[Fe(CN)_6]$ and KI in different media at 308 K.
●, Eg; ○, Fa; △, Wa; ◑, 50% Dx–$H_2O$; ▲, W/O $\mu_E$ at $\omega$=10.9; □, W/O $\mu_E$ at $\omega$=9.9; ■, W/O $\mu_E$ at $\omega$=6.9; ○, W/O $\mu_E$ at $\omega$=2.8.

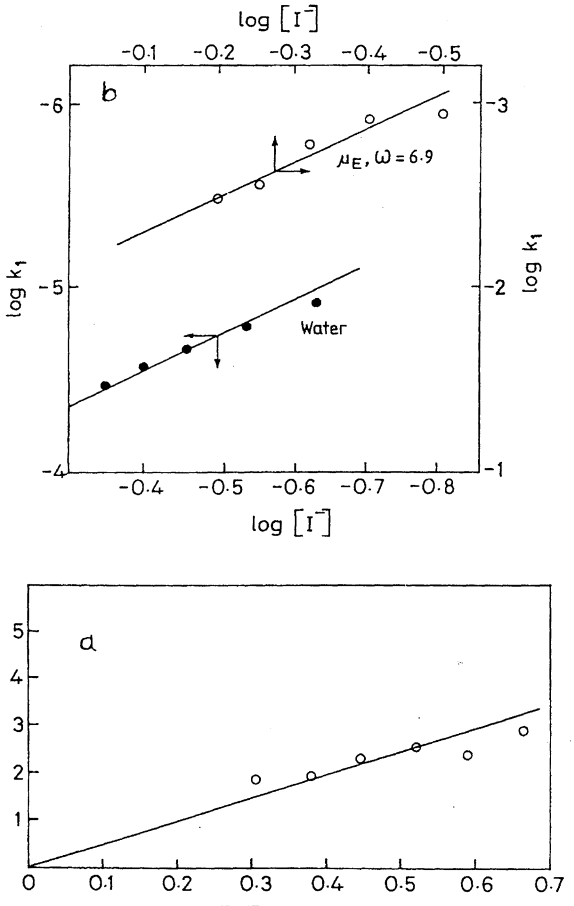

Fig. 2. (a) Plot of $\log k$ vs. $\log [I^-]$ in aqueous (●) and $H_2O/AOT/C_7H_{16}$ microemulsion medium at $\omega$=6.9 (○).
(b) Dependence of $k_3$ on $[K^+]$ in aqueous medium.

process is wanted, it is a proposition of complex origin, and may be dealt with in a future study. According to Tejeda,[18] the pseudo-first-order rate constant ($k_1$) for the same reaction is $10.9 \times 10^{-5}$ $s^{-1}$ at 298 K, $[I^-]$ and $[K^+]$=0.4 mol dm$^{-3}$ and the ionic strength=0.41; we found $8.9 \times 10^{-5}$ $s^{-1}$ under comparable conditions. Similar kinetic routes must also be followed in a microemulsion medium (Fig. 2b).

**Kinetics in Mixed Solvents:** The effects of a mixed ($H_2O$–Eg, etc.) solvent medium on the reaction rate have recently been reported by Burgess et al.[19] The rate constant has been found to decrease with increasing ethylene glycol content in the medium. Table 1 gives the pseudo-first-order rate constants in different water–organic solvent media. The results show that in water–organic solvent media the rate of the pseudo-first-order reaction decreases by 6—10 fold upon going from pure aqueous to nonaqueous environments, irrespective of their types. Figure 3 shows a plot of the logarithm of the rate constants against the reciprocal of the dielectric constant ($D$) of the mixed-solvent media based on

$$\ln k = \ln k_o - \frac{C}{D}, \qquad (11)$$

where $C$ is the characteristic constant for a reaction at a given temperature.[20]

The variation witnessed in Fig. 3 is different in different solvent media. In water–formamide, with increasing $D$ (i.e., with increasing formamide content) the rate constant, decreases whereas in water–ethylene glycol it decreases along with a decrease in $D$ (i.e. with increasing ethylene glycol content). The effect of $D$ in the water–dioxane medium is only moderate with a minimum at $D$=25 at 70% dioxane. At $D$=33, the three mixed water–organic solvent media have comparable effects, which suggests that at other polarity conditions the solvent molecules have specific interactions with the reacting species.[21] A straight-forward correlation of the polarity with the rate constant is absent. The reaction could not be performed in water–dioxane mixtures with dioxane>70% because of a solubility problem. The contri-

Table 1. Pseudo-First Order Rate Constants $k_1$ of $[Fe(CN)_6]^{3-}$ and $I^-$ Reaction in Different Aquo-Organic Solvent Media

| Solvent | Wa–Fa; | $T$=308 K | Wa–Eg; | $T$=298 K | Wa–Dx; | $T$=298 K |
|---|---|---|---|---|---|---|
| (vol%) | $D^{a)}$ | $(k_1 \times 10^5/s^{-1}$ | $D^{b)}$ | $(k_1 \times 10^5/s^{-1})$ | $D^{c)}$ | $(k_1 \times 10^5/s^{-1})$ |
| 0 | 78.5 | $3.6 \pm 0.1$ | 78.5 | $2.8 \pm 0.1$ | 78.5 | $1.8 \pm 0.10$ |
| 5 | 80 | $4.5 \pm 0.2$ | 75 | $1.6 \pm 0.1$ | 60 | $1.4 \pm 0.10$ |
| 10 | 83.7 | $4.2 \pm 0.1$ | 74 | $2.6 \pm 0.1$ | 52 | $1.2 \pm 0.05$ |
| 20 | 87 | $4.1 \pm 0.2$ | 71 | $1.1 \pm 0.05$ | 46 | $0.8 \pm 0.05$ |
| 30 | 89 | $2.9 \pm 0.1$ | 68 | $0.9 \pm 0.05$ | 43 | $1.0 \pm 0.05$ |
| 35 | — | — | — | — | 40 | $1.0 \pm 0.05$ |
| 40 | 90 | $2.5 \pm 0.1$ | 65 | $0.8 \pm 0.02$ | 36 | $0.5 \pm 0.05$ |
| 50 | 91 | $2.3 \pm 0.1$ | 62 | $0.8 \pm 0.04$ | 32 | $1.0 \pm 0.10$ |
| 65 | — | — | — | — | 27 | $1.4 \pm 0.05$ |
| 70 | 108.5 | $1.4 \pm 0.1$ | 53 | $0.4 \pm 0.05$ | 25 | $2.1 \pm 0.05$ |
| 85 | 112 | $0.7 \pm 0.05$ | 43 | $0.2 \pm 0.04$ | | |
| 100 | 109 | $0.6 \pm 0.05$ | 32 | $0.15 \pm 0.02$ | | |

a) Ref. 35, b) Ref. 36, c) Ref. 37.

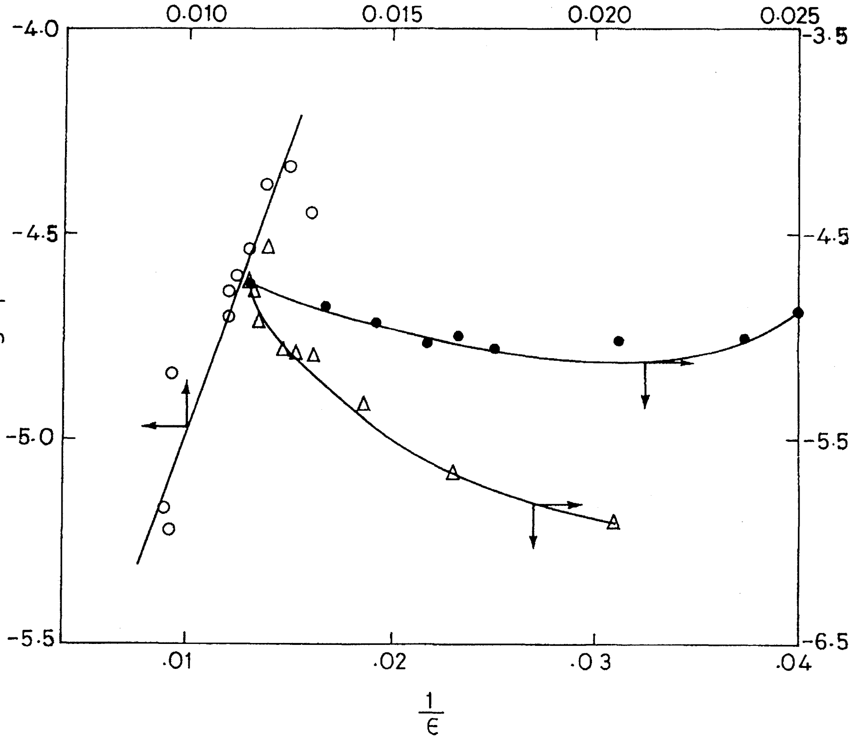

Fig. 3. Plot of $\log k_1$ vs. $D^{-1}$ for different water–organic media. ○, Fa–$H_2O$; △, Eg–$H_2O$; ●, Dx–$H_2O$.

bution of ion association in a mixed water–dioxane medium for the reacting species is considered to be minor based on a report of Tejeda,[22] who obtained very low concentrations of ion pairs in different mixed-solvent media.

**Kinetics in Microemulsion Media:** The kinetics of the reaction in a micellar solution of [AOT]>ten-times its CMC (2 mmol dm$^{-3}$ at 298 K) is slightly different. At [AOT]=5.3 mmol dm$^{-3}$ and $\mu$=0.31 mol dm$^{-3}$, $k_1$=4.6×10$^{-5}$ s$^{-1}$ at 298 K and at [AOT]=20 mmol dm$^{-3}$ and $\mu$=0.33 mol dm$^{-3}$, $k_1$=5×10$^{-5}$ s$^{-1}$. Without AOT the values of $k_1$ are 3.3×10$^{-5}$ s$^{-1}$ and 4.5×10$^{-5}$ s$^{-1}$, respectively, under the same two experimental conditions. The reaction rates in microemulsion media, on the other hand, are significantly different (Table 2). The rate constants in pure water and in W/O microemulsion media tend to become comparable at higher $\omega$; however, an onward decrease in $\omega$ up to 2.8 (keeping the overall concentrations of the reactants as constant) increases the rate constant. The reaction could not be performed in a microemulsion at $\omega > 13$ due to solubility reasons. In the table the superscripts 'all' and 'pool' represent calculations based on the concentrations of the reacting species in the overall medium and waterpool of the microemulsion, respectively. A relevant discussion concerning this matter may be found elsewhere,[21] particularly in connection with enzyme kinetics in a microemulsion medium.[8] The results reveal that on the lower side of $\omega$ the increase in $k_1$ is significant. Ionic reactions in microemulsion media seldom evidence such a striking variation in the reaction rate. However, a high degree

Table 2. $\omega$ Dependent Rate Constants $k_1$, $k_3^{\text{pool}}$, and $k_3^{\text{all}}$ of $[\text{Fe(CN)}_6]^{3-}$–$\text{I}^-$ Reaction in $H_2O/AOT/C_7H_{16}$ Microemulsion Media at Overall 0.3 mol dm$^{-3}$ AOT. $[\text{I}^-]_{\text{overall}}=0.0265$ mol dm$^{-3}$; $[\text{Fe(CN)}_6]^{3-}_{\text{overall}}=5.72\times10^{-4}$ mol dm$^{-3}$

| $\omega$ | $[\text{I}^-]^{\text{pool}}$ mol dm$^{-3}$ | $[\text{Fe(CN)}_6]^{3-\ \text{pool}}$ mol dm$^{-3}$ | $k_1\times10^5$ s$^{-1}$ | $k_3^{\text{pool}}\times10^3$ mol$^{-2}$ dm$^6$ s$^{-1}$ | $k_3^{\text{all}}$ mol$^{-2}$ dm$^6$ s$^{-1}$ |
|---|---|---|---|---|---|
| $T$=298 K | | | | | |
| 2.9 | 0.78 | 0.0170 | 206 ± 10 | 3.4 ± 0.2 | 2.90 ± 0.2 |
| 3.8 | 0.57 | 0.0124 | 230 ± 10 | 7.0 ± 0.3 | 3.28 ± 0.2 |
| 5.0 | 0.43 | 0.0094 | 100 ± 5 (100 ± 5) | 5.3 ± 0.2 (5.3 ± 0.2) | 1.42 ± 0.1 (1.42 ± 0.1) |
| 5.4 | 0.41 | 0.0088 | 105 ± 5 | 6.3 ± 0.3 | 1.50 ± 0.08 |
| 5.9 | 0.37 | 0.0080 | 27.4 ± 1 (30 ± 1) | 1.96 ± 1 (2.0 ± 0.1) | 0.39 ± 0.02 (0.4 ± 0.02) |
| 9.1 | 0.24 | 0.0050 | 8.3 ± 0.2 | 1.45 ± 0.02 | 0.12 ± 0.01 |
| 10.9 | 0.20 | 0.0043 | 4.25 ± 0.2 | 0.97 ± 0.40 | 0.056 ± 0.01 |
| (Aq) | 0.28 | 0.0072 | 2.8 ± 0.1 | 0.34 ± 0.02 | |
| $T$=308 K | | | | | |
| 2.8 | 0.78 | 0.0170 | 315 ± 16 | 5.2 ± 0.3 | 4.5 ± 0.2 |
| 3.8 | 0.57 | 0.0124 | 300 ± 15 | 9.2 ± 0.4 | 4.3 ± 0.2 |
| 5.4 | 0.41 | 0.0088 | 270 ± 20 | 16.0 ± 1.0 | 3.8 ± 0.1 |
| 6.9 | 0.32 | 0.0069 | 32 ± 2 | 3.2 ± 0.2 | 0.46 ± 0.05 |
| 8.9 | 0.24 | 0.0053 | 20 ± 1 | 3.3 ± 0.2 | 0.28 ± 0.04 |
| 9.9 | 0.22 | 0.0048 | 6.9 ± 0.3 | 1.8 ± 0.1 | 0.1 ± 0.02 |
| 10.9 | 0.20 | 0.0043 | 4.9 ± 0.3 | 1.2 ± 0.1 | 0.07 ± 0.01 |
| 13.0 | 0.16 | 0.0036 | 4.5 ± 0.3 | 1.65± 0.1 | 0.064± 0.01 |
| (Aq) | 0.36 | 0.0072 | 3.6 ± 0.2 | 0.44± 0.02 | — |

The values within bracket are the rate constants at overall 0.4 mol dm$^{-3}$ AOT.

of reaction turnover has been found in enzyme catalysis.[6,7] The dielectric constant (already discussed) cannot alone account for such a large increase in the rate. The increase in the rate constant with decreasing $\omega$ may be combined effects of increasing the ionic strength in the water pool (arising from an increased effective concentration of the reactants) and its altered polarity.[21] An altered pH in the water pool has no effect in the present case,[13] as stated earlier. A detailed discussion is presented in the next section. The rate constants at different [AOT] were found to be the same at a fixed $\omega$. Therefore, at a fixed water pool size, the reaction is independent of their number density, and an inter-particle interaction hardly affects the process. The $I_2$ formed in the reaction remained in the water pool as $I_3{}^-$; also, partitioning of $[\text{Fe(CN)}_6]^{3-}$ between water and heptane did not occur. The reaction sphere was the confined interior of the microcompartments. The $k_1$ and $k_3$ with reference to the overall solution and microemulsion water pool at various $\omega$ are presented in Table 2. The experimented $[\text{I}^-]$ and $[\text{Fe(CN)}_6]^{3-}$ in the microaqueous pool are also presented therein. The significant enhancement of $k_1$ at low values of $\omega$ was observed.

**Effect of the Ionic Strength:** The effect of the ionic strength ($\mu$) on ionic reactions generally follows a modified Brønsted–Bjerrum relation for high $\mu$ values,

$$\log k = \log k_\text{o} + 1.018\, Z_\text{A} Z_\text{B}\sqrt{\mu}/(1+\sqrt{\mu}), \tag{12}$$

where $k$ and $k_\text{o}$ are the rate constants of the reaction in an aqueous medium at ionic strength $\mu$ and at a hypothetical zero ionic strength, respectively; $Z_\text{A}$ and $Z_\text{B}$ are the charges on the two reacting species which form a complex in the activated state. Since in the present reaction the reacting species are $\{\text{IK[Fe(CN)}_6]\}^{3-}$ and $\text{I}^-$, $Z_\text{A}Z_\text{B}$=+3. The rate constants should increase with $\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ thus producing a slope of 3.05 in an aqueous medium.

The experimentally obtained slope in an aqueous medium was 3.4. Introducing a dielectric-constant correction, the slopes in formamide, ethylene glycol and 50% (v/v) water–dioxane media should be 1.8, 5.4, and 10.4, respectively. The experimental results when processed (Fig. 4a) yielded slopes (Table 3) at variance with the expected values, except for ethylene glycol, where agreement was fair. The salt effects on the same reaction studied by Tejeda et al.[18] in an aqueous medium when treated in terms of Eq. 12 also produced slopes in the range 3.9 and 4.2 for 1 : 1 and 2 : 1 electrolytes, respectively. The modified BB Eq. 12 is not exactly obeyed. Recently, Tejeda[22] considered a convenient ionic strength-dependent rate-constant equation of the presently studied reaction in the following form based on the propositions of Bronsted–Bjerrum and Pitzer:[23]

$$\ln k = \ln k_\text{o} + \Delta Z^2 A_\Phi \left[\frac{\sqrt{\mu}}{1+1.2\sqrt{\mu}} + \frac{2}{1.2}\ln\left(1+1.2\sqrt{\mu}\right)\right]$$

$$\text{or}\quad \ln k = \ln k_\text{o} + \Delta Z^2 A_\Phi X, \tag{13}$$

where, $k$, $k_\text{o}$, and $\mu$ have the same significance as given before, $X$ represents the third bracketed terms,

$$\Delta Z^2 = (Z_\text{A}+Z_\text{B})^2 - (Z_\text{A}^2 + Z_\text{B}^2),$$

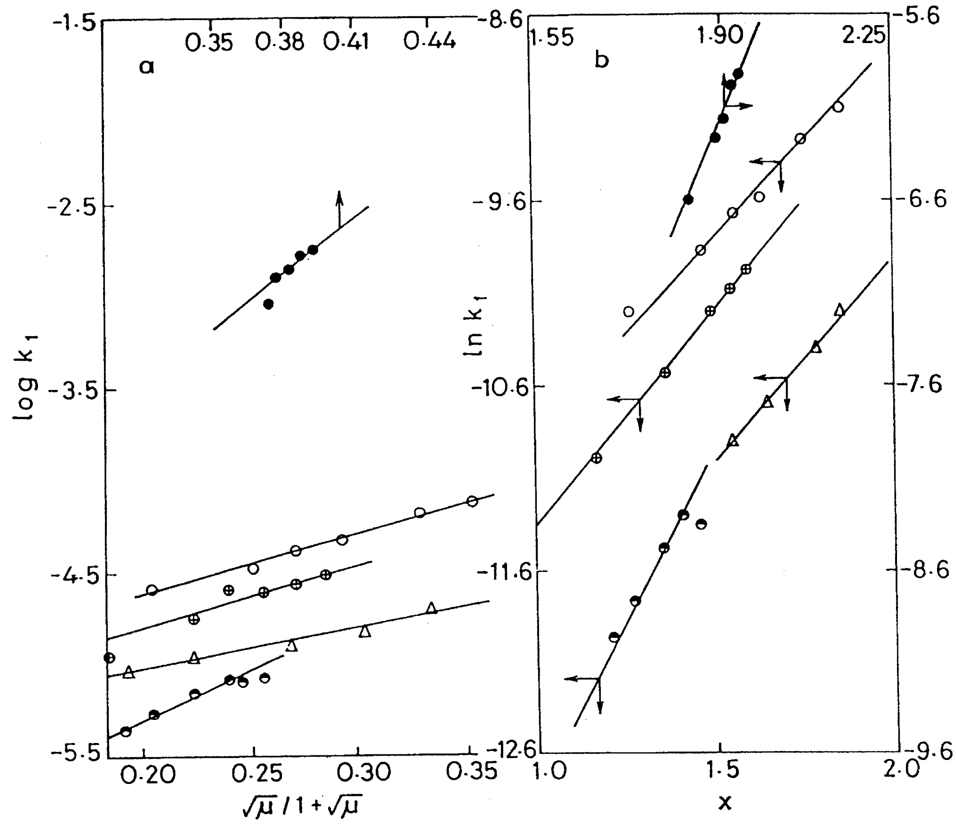

Fig. 4. (a) Plot of log ($k_1$) vs. $\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ according to Eq. 12.
(b) Plot of ln $k_1$ vs. $X$ according to Eq. 13. ○, $H_2O$; ◑, $\mu_E$ at $\omega$=9.1; ⊕, Fa; △, 50% Dx–$H_2O$ (v/v); ◓, Eg.

Table 3. Modified Brønsted–Bjerrum (MBB) and Brønsted–Bjerrum–Pitzer (BBP) Slopes for $[Fe(CN)_6]^{3-}$ and $I^-$ Reaction in Different Media at 298 K

| Solvent | Modified BB Slope | | BBP Slope | | $\Delta Z^2$ | Log $k_o$ | |
|---|---|---|---|---|---|---|---|
| | Obsd | Calcd | Obsd | Calcd | | MBB | BBP |
| Water | 3.4 | 3.0 | 2.2 | 2.2 | 6.0 | −5.4 | −5.3 |
| Formamide | 3.6 | 1.8 | 2.2 | 1.3 | 10.0 | −6.0 | −5.9 |
| Ethylene glycol | 5.0 | 5.4 | 3.6 | 3.2 | 6.4 | −6.2 | −6.3 |
| 50% Water–dioxane (v/v) | 3.1 | 10.4 | 2.5 | 8.0 | 2.0 | −5.8 | −5.9 |
| Microemulsion ($\omega$=9.1) | 9.2 | 4.3 | 6.6 | 3.2 | 12.0 | −5.8 | −5.9 |

a) Wt% composition $H_2O/AOT/C_7H_{16}$ (13.3/36.8/49.9) at $\omega$=9.1. b) $k_o$ is the hypothetical rate constant at zero ionic strength.

and $A_\Phi=\frac{A}{3}$. '$A$' relates the density of the medium ($\rho$) to its dielectric constant ($D$) and the absolute temperature ($T$) given in

$$A=(1.3287\times10^5\rho)/(DT)^{3/2}. \tag{14}$$

In water, water–ethanol and water–butanol ($\mu$=0.1—0.9 mol dm$^{-3}$) Tejeda[22)] obtained slope values of 2.3, and 3.6 and 3.5, respectively, which correspond to $\Delta Z^2$ ca. 6. Since the complex reaction is thus involved with an univalent and tervalent ion in the rate-determining step (cf. Eq. 3), $\Delta Z^2=[4^2-(1^2+3^2)]=6$. In this regard, the Brønsted–DHLL equation was found by Tejeda[19)] to be less satisfactory. The slopes obtained by plotting ln $k_1$ vs. $X$ (Fig. 4b) in this study are given in column three of Table 3; the slope in the aqueous medium is 2.2 for $\mu$ in the range 0.3—1.0 mol dm$^{-3}$, which corresponds to $\Delta Z^2$ ca. 6.0. Using the medium dielectric constants, the values of $\Delta Z^2$ obtained for formamide, ethylene glycol and 50% (v/v) $H_2O$–Dx were 10.0, 5.4, and 2.0, respectively. These values are convincingly lower for $H_2O$–Dx and higher for formamide; ethylene glycol behaves as expected. A fundamental difference between an aqueous and nonaqueous solvent media influencing the reaction is envisaged. In a microemulsion medium at $\omega$=9.1, the slopes obtained for Eqs. 12 and 13 were 9.2 and 6.6 respectively. In this treatment $\mu$ in the water pool was estimated on the basis of 10% dissociation[24)] of AOT and complete ionization of other electrolytes. Taking the dielectric constant of the water pool to be 61, as reported earlier,[8)] the value of $\Delta Z^2$ obtained from the slope was 12.0. The reaction between an univalent ion ($I^-$) and a tervalent ion $\{IK[Fe(CN)_6]\}^{3-}$ in the rate-determining step in the microemulsion medium is not straightforwardly related to $\mu$ neither according to the modified BB equation nor the BBP relation; the findings with formamide and 50% water–Dx (v/v) media are similar. It is interesting to note that the water–ethanol and water–1-butanol media in Tejeda's work[22] yielded $\Delta Z^2$ ca. 6, the $\Delta Z^2$ realized in ethylene glycol in this study is 6.4, whereas for the $H_2O$–Dx medium it is 2.0 and for formamide it is 10.0. Hydroxylic solvents appear to obey the BB and BBP relations.

In the present context, a concise account of composition-dependent kinetics of different reactions in microemulsion formed with AOT is worthwhile. For the studied persulphate iodide,[3,5] crystal violet (CV)–NaOH,[5,9,10] viologen radical cations–quinones[25] and *p*-nitrophenyl phosphate (PNPP)–alkaline phosphatase (AP) and other enzyme reactions,[26] the rates were observed to essentially depend on the $[H_2O]/[AOT]$ ratio or $\omega$. The rate of the $I^-$–$S_2O_8{}^{2-}$ reaction was found to be inversely proportional to $\omega$; similar kinetic behaviors have been reported by Moya et al.[3] and Izquierdo et al.[5] for a CV–NaOH reaction with decane as oil. In a $H_2O$/AOT/isooctane W/O microemulsion at constant $\omega$, the pseudo first-order rate of the CV–NaOH reaction has been reported[9] to decline with increasing [AOT], whereas the second-order rate marginally increases. The waterless microemulsion, ethylene glycol/AOT/isooctane, caused a greater rate enhancement compared to that of aqueous preparations, along with a trend for a rate increase with decreasing $\omega$. Although the pseudo first-order rate of the same reaction[10] exhibited a maximum at $\omega=10$ with isooctane as the oil, the second-order rate was maximized at $\omega=10$ and beyond. In a very recent study[27] in $H_2O$/AOT/cinnamic alcohol, the pseudo first-order rate constant for the CV–NaOH reaction was found to pass through a maximum at $\omega=10$; however, the second-order rate constant remained practically nonvariant. In O/W preparations, the pseudo first-order rate constant for the said reaction was maximized at [Cinnamic Alcohol]/[AOT], $\omega'=2$, whereas the second-order rate constant increased with $\omega'$. The PNPP–AP[8] and other enzyme reactions[27] in W/O microemulsions with different oils have generally exhibited maxima in rate at characteristic $\omega$ values. The salt effects on the CV–NaOH reaction rates in aqueous microemulsion media show trends that are different from that in an aqueous medium.[9,10] The effect in ethylene glycol/AOT/isooctane is more different than that of an aqueous microemulsion environment. The above-discussed results suggest an oil- and $\omega$-dependent reaction rate. The results of the present study advocate the characteristic behaviors of the dynamics of a typical oxidation–reduction reaction in a W/O microemulsion medium.

**Activation Energetics of the Reaction:** An evaluation of the activation parameters of the kinetic process in a microemulsion requires a determination of the rate constants at different temperatures. The temperature effect on the structural properties of a microemulsion is important in this regard. Toprakciaglu[28] found a minor temperature effect on the W/O microemulsion stabilized by AOT, whereas from SANS (small-angle neutron scattering) measurements, Rouivere et al.[29] observed a 20% decrease in AOT-stabilized droplets of $D_2O$ in decane for a temperature increase of 23 °C. Based on time-resolved fluoresence probing, Lang et al.[30] reported a 25—35% decrease in the radius for a temperature rise of 35 °C. A reduction in the droplet size has also been pointed out by Bisal et al.[31] based on conductivity measurements. Thus, the temperature-influenced altered structure of a microemulsion is expected to offer an additional effect on the kinetic process. The temperature variation in the present study was 16 °C, which is fairly low to cause any appreciable structural change in the microemulsion. Good linear plots according to the Arrhenius equation have therefore been realized. There have been recent instances where the activation parameters could be determined for reactions in microemulsion media by the temperature variation method.[3,5]

The activation parameters for the reaction derived from the Arrhenius and Eyring equations are presented in Table 4. An Arrhenius plot $\ln k_1$ vs. $T^{-1}$ is shown in Fig. 5. The activation energies are higher in nonaqueous media than in water. They are strikingly low in a microemulsion medium, and decrease along with a decrease in $\omega$. This corroborates with the rate-accelerating effects in a microemulsion with decreasing $\omega$. The enthalpies of activation ($\Delta H^\ddagger$) consequently have the same trends as $E_a$. The $\Delta G^\ddagger$ values are reasonable lower in a microemulsion medium. The entropy of activation is, on the other hand, high. The aqueous medium and aqueous-pooled microemulsion have negative entropies; the value increases with decreasing pool size. Formamide and ethylene glycol give intermediate negative values; the water–Dx medium is strikingly different. The usually observed rule of $\Delta S^\ddagger = -42\ Z_A Z_B$ approximately holds for many ionic

Table 4. Activation Parameters for the Reaction Between $[Fe(CN)_6]^{3-}$ and $I^-$ at 298 K

| Solvent | $E_a$/kJ mol$^{-1}$ | $\Delta H^\ddagger$/kJ mol$^{-1}$ | $\Delta S^\ddagger$/J mol$^{-1}$ K$^{-1}$ | $\Delta G^\ddagger$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Water | $38 \pm 2$ | $33 \pm 2$ | $-218 \pm 7$ | $98 \pm 4$ |
| Formamide | $56 \pm 3$ | $51 \pm 3$ | $-175 \pm 7$ | $103 \pm 5$ |
| Ethylene glycol | $56 \pm 3$ | $51 \pm 2$ | $-181 \pm 10$ | $105 \pm 5$ |
| Water-dioxane 50% (v/v) | $92 \pm 4$ | $87 \pm 3$ | $-40 \pm 2$ | $88 \pm 4$ |
| Microemulsion ($\omega$=10.9)[a] | $27 \pm 1$ | $22 \pm 1$ | $-228 \pm 10$ | $90 \pm 4$ |
| Microemulsion ($\omega$=3.8)[a] | $15.6 \pm 1$ | $10.6 \pm 1$ | $-239 \pm 10$ | $82 \pm 3$ |

a) Wt% composition $H_2O$/AOT/$C_7H_{16}$ (15.9/36.5/47.6) at $\omega$=10.9 and (5.7/37.8/56.5) at $\omega$=3.8.

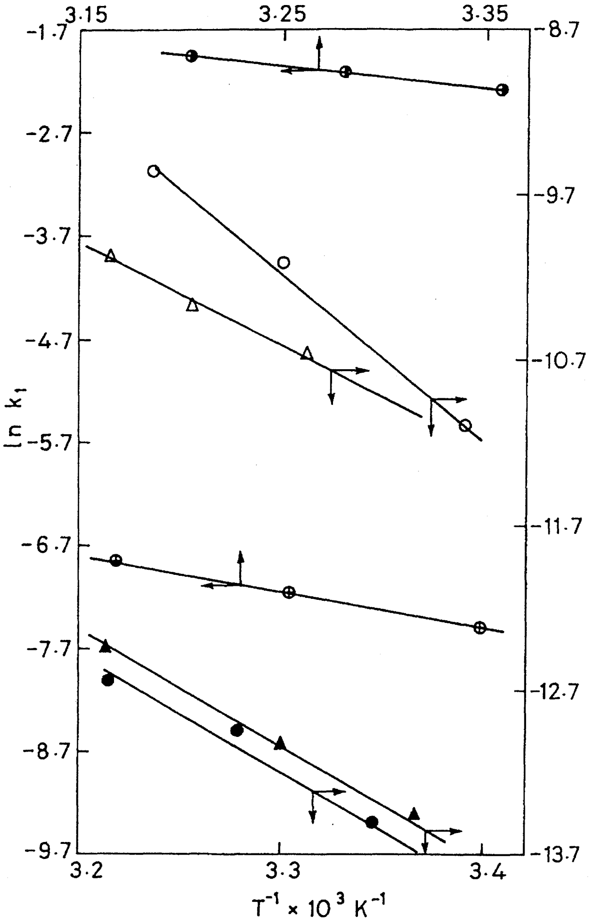

Fig. 5. Dependence of $\ln k_1$ on $T^{-1}$ in different solvent media, ○, 50% (v/v) Dx–$H_2O$; △, $H_2O$; ▲, Eg; ●, Fa; ⊕, W/O $\mu_E$ with $\omega=10.9$; ◑, W/O $\mu_E$ ($\omega=3.8$).

reaction in aqueous medium,[32] but does not hold for the studied reaction in either an aqueous medium or an aqueous pool of microemulsion.

The aqueous and W/O microemulsion media are comparable in respect to entropy. The lower enthalpy in the latter environment was adjusted by lowering of $\Delta S^{\ddagger}$. The magnitude of the negative entropy is comparable with that of an enzyme-catalyzed reaction in a microemulsion medium,[8] but greater than in the $I^-+S_2O_8^{2-}$ reaction.[3] On the whole, polar media end up with large negative entropies, which for the moderately polar ($D=34.4$) but weakly structured $H_2O$–Dx (50% v/v) medium is significantly less negative. In aqueous and W/O microemulsion media, the reaction in the rate-limiting step is entropy controlled ($T\Delta S^{\ddagger}>\Delta H^{\ddagger}$), which reverses in a $H_2O$–Dx environment ($T\Delta S^{\ddagger}<\Delta H^{\ddagger}$); in formamide and ethylene glycol media, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ offer comparable contributions. A reasonable effect of compensation[33,34] between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is depicted in Fig. 6, having a compensation temperature of 320 K vis-a-vis the experimental temperature of 298 K. The microemulsion at $\omega=3.8$ has shown a deviation.

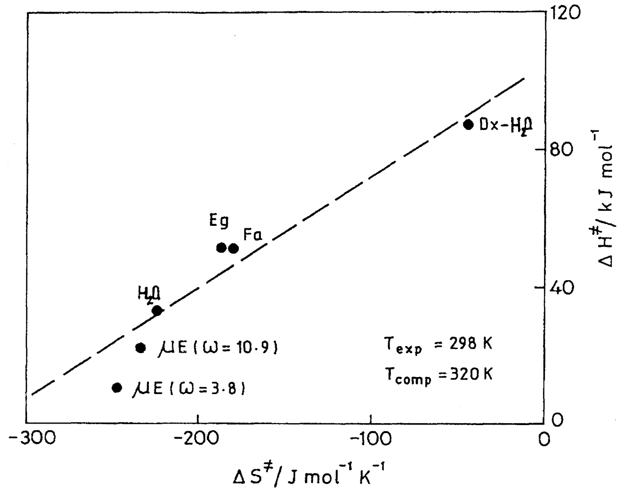

Fig. 6. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ correlation for the $[Fe(CN)_6]^{3-}$ and $I^-$ reaction in different media.

## Conclusions

1) The micro water pool in water/AOT/heptane microemulsion at a [water]/[AOT] mole ratio less than 6 is significantly effective for oxidation reduction between $[Fe(CN)_6]^{3-}$ and $I^-$.

2) The mixed aqueous non-aqueous solvent studied has shown specificities in influencing the reaction.

3) In describing the effect of the ionic strength on the course of the reaction the modified Brønsted–Bjerrum and the Brønsted–Bjerrum–Pitzer equations are comparable; they are obeyed in hydroxylic solvents viz., water and ethylene glycol.

4) The distinct difference in the activation parameters in a microemulsion medium from other nonaqueous solvent media supports the special role of compartmentalization in influencing the oxidation–reduction reaction.

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