The Peroxodisulphate–Iodide Reaction. Reactivity and Ionic Association and Solvation in Isodielectric Water–Solvent Mixtures

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The association constants of the potassium peroxodisulphate ion pair ($KS_2O_8^-$) and the reaction rate between peroxodisulphate and iodide ions have been measured in several isodielectric water–solvent mixtures. The sequence of the rate constants does not follow that of the association constants, but agrees qualitatively with the sequences of transition-state solvation energies calculated from excess free energies of mixing. This fact suggests the influence of solvent structure on the reactivity.

The reaction between peroxodisulphate ion and iodide ion has been studied by several authors.[1–9] It is first order with respect to both reactants. Generally, the kinetic salt effects of a variety of added salts of various valency types have been studied.[4] The results of these studies have been interpreted by postulating the formation of ion pairs.[4,10] If the reactants were present as potassium salts, the rate-determining step would involve the participation of the $KS_2O_8^-$ ion pair and I^- as reactive species. However, the existence of the $KS_2O_8^-$ ion pair in solution has never been proved by an independent procedure.

On the other hand, there is some kinetic information on this reaction concerning binary aqueous solvent mixtures.[5–9] According to Amis and Potts,[6] electrostatic influences predominate for this reaction in ethanol–water mixtures. Meretoja,[7] working with methanol–water mixtures, reached the same conclusion. Nevertheless, Howells,[5] when using dextrose solutions, observed that the reaction rate was greater than in water. This indicates that there are instances when some other solvent effects, aside from the electrostatic effect, play an important role.

In our opinion in order to understand the solvent effects in this reaction, the solvent–water interactions should be taken into account. An insight into such interactions can be gained, for a given mixture, from the thermodynamic properties. In fact, several authors [8,11] have tried to correlate kinetic parameters (usually $\Delta G^\ddagger$ or k) with thermodynamic properties; their observations suggest that this correlation exists.

For this reason we report in this paper a study of ionic association and reactivity in several isodielectric water–organic solvent mixtures. We have selected solvent mixtures with different thermodynamic properties with the purpose of ascertaining whether ionic association or water–solvent interactions explain the experimental results.

Experimental

Reagents.—The reagents used were all AnalaR grade chemicals from various sources, and were not purified further. The water used had a resistance >5 MΩ and was obtained by distilling from $KMnO_4$ and passing the distilled water through a mixed-bed ion-exchange column.

Kinetic Data.—Kinetic runs were carried out in 1-cm silica cells in the thermostatted cell compartment of a Perkin-Elmer 554 spectrophotometer. The temperature in the cell was fixed at 298.0 ± 0.1 K. These kinetic runs were made in solutions containing an excess of iodide ions by following the changes in absorbance at fixed time intervals at 400 nm (at this wavelength only tri-iodide ions absorb). Table 1 gives the values of the molar absorption coefficient (ε) in water and in the water–co-solvent mixtures. The concentrations of reactants were [KI] = 0.1 and $[K_2S_2O_8] = 2 \times 10^{-4}$ mol dm^{-3}. 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}).[4,8] In every case we found that the co-solvents were inert in relation to the reactants and products.

Table 1. Viscosity (η), molar absorption coefficient of I_3^- (ε) in KI (0.1 mol dm^{-3}), and observed rate constants for the reaction between $S_2O_8^{2-}$ and I^- in different isodielectric water–co-solvent mixtures

Co-solvent	% (w/w)	$10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}	$10^5 k$/s^{-1}	$10^3\eta$/P
Pure water	—	5.95	41.17	—
Methanol	5.68	6.07	31.75	1.0786
Ethanol	4.39	6.15	33.28	1.0922
t-Butyl alcohol	2.94	6.04	35.30	1.1838
dmf	12.28	6.53	13.05	1.1770
Acetonitrile	6.02	6.14	21.90	0.9627
Glycerol	9.95	6.19	37.33	1.1592
Sucrose	10.75	6.15	43.25	1.2120
Dextrose	10.52	5.63	50.70	1.1610

The results of kinetic runs are collected in Table 1 as pseudo-first-order rate constants (k/s^{-1}). Table 1 also gives the composition of each mixture. This composition was selected in order to have the same macroscopic dielectric constant for all the mixtures. Solvent mixtures were prepared by weight, and the dielectric constant data are from the literature.[12–16]

Viscosity and Density Data.—We have measured the viscosities and densities of the water–co-solvent mixtures. The densities were determined picnometrically and the viscosities from the flow time of solutions in an Ostwald-type viscosimeter. These data are reported in Table 1.

Conductance Measurements.—The conductance measurements were carried out using a Beckman RC18A bridge. The cell, with a constant of 0.491 cm^{-1}, was a Beckman 6J05 conductance cell. The temperature was fixed at 298.15 ± 0.005 K using an oil-bath. The cell containing the solutions was flushed with nitrogen before the measurements. The results are reported in Table 2, which gives the molar concentrations, the equivalent conductances, and the association constants of the $KS_2O_8^-$ ion pair. Owing to the large number of

Table 2. Equivalent conductivity (Λ) and association constants (K) of the $KS_2O_8^-$ ion pair at different molar concentrations (c)

	100% Water		MeOH–water (5.68 : 94.32)		EtOH–water (4.39 : 95.61)	
10^4c/mol dm^{-3}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}
4.00	153.45	11	141.30	150	148.97	153
6.00	151.86	12	138.50	130	145.00	149
8.00	150.48	12	135.70	123	141.70	145
9.00	149.96	11	134.40	122	140.20	145
10.00	149.65	9.0	133.30	119	138.80	144

	Bu^tOH–water (2.94 : 97.06)		MeCN–water (6.02 : 93.98)		dmf–water (12.28 : 87.72)	
10^4c/mol dm^{-3}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}
4.00	166.31	133	157.33	154	114.93	19
6.00	162.45	122	153.85	141	113.58	19
8.00	159.49	115	150.20	136	112.39	20
9.00	157.85	114	148.90	135	111.95	18
10.00	156.35	110	147.40	134	111.52	18

	Glycerol–water (9.95 : 90.05)		Sucrose–water (10.75 : 89.25)		Dextrose–water (10.52 : 89.48)	
10^4c/mol dm^{-3}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}	Λ/Ω^{-1} cm^2 equiv.$^{-1}$	K/dm^3 mol^{-1}
4.00	138.24	41	123.79	114	132.88	217
6.00	136.34	40	121.76	100	128.30	217
8.00	134.53	41	120.56	83.3	124.26	217
9.00	133.75	41	119.95	76.9	122.68	217
10.00	133.03	41	119.15	76.9	120.86	217

individual measurements, only mean values of the equivalent conductances are recorded. The association constants have been calculated by the Davies' method as modified by Jenkins and Monk,[17] using a program which computes the fraction of the $KS_2O_8^-$ ion pair. The program has been checked using data for potassium sulphate.[17]

Discussion

The reasons for maintaining a constant value of the dielectric constant are three-fold. (*i*) The long-range interactions between the reactants are therefore approximately the same in the different mixtures. (*ii*) Also, the association constants of the ion pair $KS_2O_8^-$ would be similar in each case. (*iii*) A drastic change in the first solvation shell of the reactants is not probable in passing from water to the water-solvent, because the water is, by far, the most abundant component (see Table 1). For these reasons, the same reactivity should be found in the different media.

However, results do not agree with the above hypothesis. They indicate that the rate constants in these mixtures follow the sequence for the co-solvent, *NN*-dimethylformamide (dmf) < acetonitrile < methanol < ethanol < t-butyl alcohol < glycerol < pure water < sucrose < dextrose, and the association constants K of the $KS_2O_8^-$ ion pair follow the sequence for the co-solvent, pure water < dmf < glycerol < sucrose < t-butyl alcohol < methanol < acetonitrile < ethanol < dextrose.

Reactivity in water cannot be compared with the reactivity in the mixtures. In the former, the association constant is low and therefore should give low reactivity, but the dielectric constant is higher than in the other media, and the encounter between the reactants should be facilitated. If the association factor were the more important of the two, the rate constant in water would be the lowest, and if the coulombic effects were the more important it would be the greatest. In any case, the rate constant sequence does not agree with the association constant sequence.

Of course, the aforementioned reasoning is only valid if it is acknowledged that the first solvation shell of the reactants is not very different in the different media. This is probable because water is the most abundant component and the molar absorption coefficients of the tri-iodide ions, I_3^-, do not change notably in the different media (see Table 1). We conclude that the assumption of ion association does not seem capable of providing a satisfactory interpretation of the experimental results.

On the other hand, several authors[11,18] are currently examining whether reactivities in binary aqueous mixtures can be correlated with excess Gibb's free mixing energies of the respective mixtures. Binary aqueous mixtures can be classified into three groups according to their excess molar thermodynamic functions of mixing.[18–20] These are the 'typically aqueous' (t.a.) mixtures where G^E is positive and is dominated by its entropy component ($|T\Delta S^E| > |\Delta H^E|$), 'typically non-aqueous positive' (t.n.a.p.) mixtures with positive G^E and $|\Delta H^E| > |T\Delta S^E|$, and 'typically non-aqueous negative' (t.n.a.n.) mixtures with negative G^E but again $|\Delta H^E| > |T\Delta S^E|$.

It is useful in this analysis to bear in mind the properties of binary mixtures: methanol, ethanol, t-butyl alcohol, and glycerol with water are t.a.;[19,20] dmf and acetonitrile with water are t.n.a.p.;[21,22] sucrose and dextrose with water are t.n.a.n.[23] It seems, therefore, that our kinetic data cover reactions in the three types of systems, t.a., t.n.a.p., and t.n.a.n.

There is a good relation between $\delta_m\Delta G^‡$ and G^E, where $\delta_m\Delta G^‡ = \Delta G^‡(x_2) - \Delta G^‡\ (x_2 = 0)$ [x_2 = mole fraction of organic solvent, $\Delta G^‡\ (x_2)$ = free energy of activation at the value of x_2]. Reactivity is greater in mixtures with $G^E < 0$ than in water, and the opposite is true for mixtures $G^E > 0$. These results can be rationalised 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 solvation zone of the reactants must pass to the bulk. Bearing in mind that this second zone is a very disordered one, then, according to Caldin and Bennetto, the solvent molecule arrangement (water + co-solvent) in such a zone must be similar to 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 the equation below,[11] where G_{bulk} is the free energy of the bulk, G_{sz} is the free energy of the second solvation zone, G_{ideal} is the free energy of an ideal mixture, and ΔG^{E} is the excess free energy of the mixture.

$$G_{\text{bulk}} - G_{\text{sz}} \cong (G_{\text{ideal}} + \Delta G^{E}) - G_{\text{ideal}} = \Delta G_{E}$$

Therefore, the contribution of this step to the energy of activation will be positive for the mixtures in which $G^{E} > 0$, and negative for those with $G^{E} < 0$. According to this, the rate constants in the t.n.a.n. type mixtures (dextrose–water and sucrose–water) are greater than in water, and lower in the mixtures with $G^{E} > 0$ (methanol–water, ethanol–water, t-butyl alcohol–water, glycerol–water, dmf–water, and acetonitrile–water). So the kinetic effects of non-electrolytes reflect the non-electrolyte–water interactions.

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