

PREFERENTIAL SOLVATION IN KINETICS

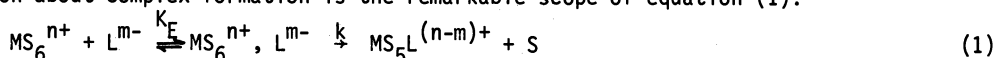
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Abstract - An approach to solvent effects in kinetics of reactions slower than diffusion control is considered based on the partition of the reaction into an encounter equilibrium and a first order rate process for rearrangement of the encounter complex. Solvent effects are partitioned into those relating to encounter equilibria and those relating to the rate process. The distribution of solvent molecules at equilibrium is discussed in terms of NMR derived preferential solvation data and complex formation reactions of various Cr(III) and Ni(II) species are used as specific illustrations.

INTRODUCTION

The purpose of this paper is to attempt a generalized account of solvent effects in kinetics developed from our experience with complex formation reactions in non-aqueous and mixed solvents and strongly influenced by our NMR measurements of "preferential solvation". The first observation about complex formation is the remarkable scope of equation (1).



where MS_6 represents a solvo complex, L a ligand, K_E an equilibrium constant for formation of an outer sphere complex (or encounter species) and k is a first order rate constant.

It has been observed by several authors (see citations in Ref. 1) that it is no surprise to find equation (1) general. Not complex formation but only bimolecularity is required. Any reaction in solution which occurs at overall rates significantly less than diffusion limits allows for the diffusional encounter of the reactants to be treated as a pseudo-equilibrium followed by a slow step which is characterizable by a first order rate constant and amounts to a "unimolecular" rearrangement of the encounter complex. This point has been recognized explicitly in the theory of complex formation, and implicitly in the theory of electron transfer in solution (2).

Solvent effects in kinetics are of two sorts, therefore there are effects on K_E and there are effects on k . Now, since K_E is an encounter equilibrium constant, the theory of effects thereupon is a theory of equilibrium effects.

SOLVENT EFFECTS ON K_E

This is a well studied problem when reactants are ions. It is equivalent in that case to solvent effects on ion pairing. Most theories have been of the "brass ball in a bathtub" sort where the ions are treated as conducting spheres and the solvent is a continuum characterized by one parameter - bulk dielectric constant. This approach has had many successes and some failures. A good example of failure is the rate of change of the rate of formation of the complex of murexide with Ni(II) in dimethylsulfoxide (DMSO) as unreactive CH_3NO_2 is added (Fig. 1). The acceleration caused by CH_3NO_2 cannot be due to change of dielectric constant. Neither can it be explained by competition between DMSO and murexide for an intermediate of reduced coordination number $[Ni(DMSO)_5^{2+}]$ since that requires a plot linear in the reciprocal of DMSO concentration (3). Instead, this is an example of equation (1) where K_E is sensitively dependent upon solvent, probably because the highly polarizable murexide anion is more strongly solvated in bulk by DMSO than CH_3NO_2 .

When a reactant is a solvent molecule, ion pairing is no longer the relevant theory. In this case, knowledge of K_E is equivalent to knowledge of the extent of preferential solvation. The probability that a solvent molecule occupies a reaction site in encounter with a reactive solute will be proportional to the probability that it reacts (hence rate). We use that parameter n/n_0 where n is the number of a particular type of solvent

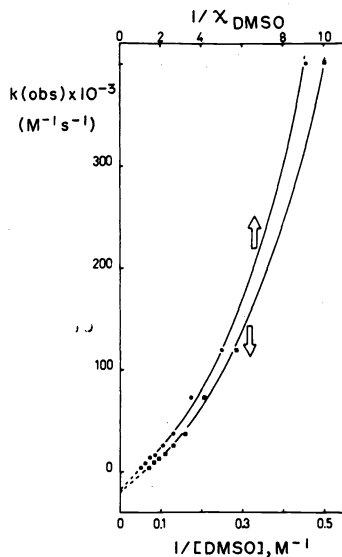


Fig. 1 Plots of rate constants *vs.* reciprocal DMSO contents of the mixed solvents.

molecules in encounter with a solute in a mixed solvent and n_0 is the corresponding number in the neat solvent. Reactions for which no solvent effects other than the participation of a solvent molecule as one partner of a bimolecular reaction (e.g. as the nucleophile in a nucleophilic substitution) will show rates proportional to n/n_0 . An example is found in the reaction of $\text{Cr}(\text{NCS})_6^{3-}$ with water in water- CH_3CN mixtures (4). CH_3CN is solvolytically unreactive and Fig. 2a shows solvolysis rate as a function of the NMR determined n/n_0 for water. Fig. 2b shows that the complex is preferentially solvated by CH_3CN . Comparison of

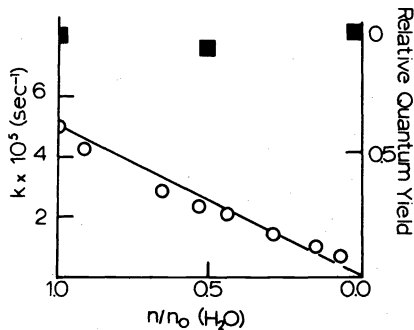


Fig. 2a. The rate of hydrolysis of $\text{Cr}(\text{NCS})_6^{3-}$ thermally (open circles) and photochemical quantum yields (closed circles) as a function of the composition of the solvation shell.

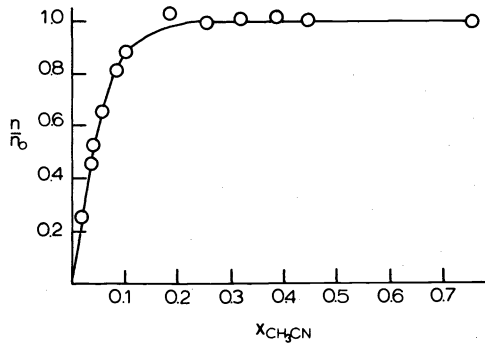


Fig. 2b. The preferential solvation curve for $\text{Cr}(\text{NCS})_6^{3-}$ in CH_3CN - H_2O mixtures as derived from nmr. n/n_0 represents the fraction of solvation shell (or outer sphere) sites occupied by CH_3CN .

Fig. 2a and 2b shows the value of a preferential solvation study in this case.

There is also an important point to be made about the origin of preferential solvation in this case. Figure 3 shows a relative activity curve for CH_3CN and H_2O in binary

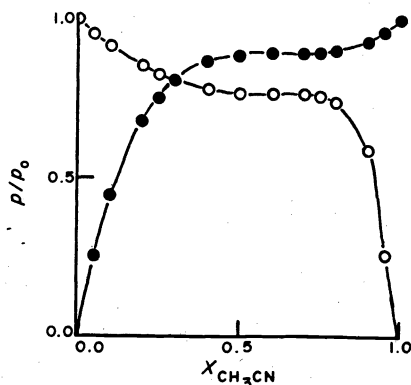


Fig. 3. Partial vapor pressure relative to the vapor pressure over the pure solvent as a function of mole fraction of CH_3CN : open circles water; closed circles, CH_3CN . The data were obtained at 20° .

mixtures. Comparing Fig. 3 and Fig. 2b, it is clear that there is a very close relation between three quantities: (1.) the activity of H_2O in bulk binary mixtures, (2.) the probability that water occupies solvation sites, and (3.) reaction rate. The transfer of water from bulk solvent to the solvation sphere of the complex depends primarily on the bulk solvent behaviour. Here, Covington *et al.*'s (5) coordination model of preferential solvation (which is basically quite sound) has erred seriously. To assume that activity coefficients for a component in the solvation shell and in bulk are approximately the same is the least likely of several alternate approximations. This is because the behaviour of a solvent molecule in bulk is determined by interaction with other solvent molecules (solvent structure), whereas in the solvation shell of an ionic solute, the orientation forced by extremely high field gradients overrides solvent-solvent interactions.

In the case shown in Fig. 2a, it is clear that all sites in the solvation shell around the complex are equivalent. Preferential solvation in this case can be treated by an adsorption model (6), assuming solvent molecules in the solvation shell interact strongly with the solute and negligibly with each other (i.e. activity coefficients of unity for both solvation shell components and a standard state corresponding to the solvation shell in the pure solvent when the solvation number is n_0). Then the coordination model is superior if sites are inequivalent as did arise in the study of DMSO exchange with $Cr(DMSO)_6^{3+}$ in $DMSO-CH_3NO_2$ mixtures by Langford, Scharfe, and Jackson (7).

SOLVENT EFFECTS ON k

We must now consider solvent effects on the aspect of reaction that is not subject to equilibrium modeling - the genuine solvent kinetic effects which operate on the rate of rearrangement of an encounter complex to give products. This question can be divided into three parts.

First, a solvent may be simply a reactant (nucleophile in nucleophilic substitution, electron donor or acceptor in a redox process). We will then be interested in comparison of rates for one reactive solvent to another at low and constant n/n_0 for the reactive solvent (so that the energetic role of solvents may be compared) where bulk medium and non-reacting solvation shell molecules are held constant. The reactions of $Cr(NCS)_6^{3-}$ represent a simple case. Reference 4 pointed out that H_2O , alcohols, and pyridine all reacted at similar rates at constant n/n_0 , suggesting a dissociative interchange pathway for these nucleophilic substitutions. (However, we do see a sharp contrast between the above 3 solvents and CH_3CN and CH_3NO_2 which are extremely unreactive in interchange. This indicates that a dissociative transition state involving Cr , SCN^- , and CH_3CN has a "transmission coefficient of nearly unity in the direction of binding SCN^- .)

Second, a solvent molecule in the solvation shell may stabilize or destabilize a transition state by interaction with the solute (e.g. the first sphere ligands of the solute complex) without itself being a species involved in what Ingold once characterized as "covalence change". This secondary sort of solvent effect is commonly smaller than the first. Thus, if a ligand substitution reaction uses, for example, one water molecule as a reactant and another (or others) for hydrogen bonding to ligands not directly involved in the substitution, the rate of the reaction will depend upon n/n_0 for water. But, in this case, the effect of removal of the reactant water molecule is much more profound than depriving the transition state of the subsidiary waters. The dependence on n/n_0 will be non-integral as shown in Fig. 4 for the reaction of $transCr(NH_3)_2(NCS)_4^-$ with H_2O in H_2O-CH_3CN mixtures (8). Here the more rapid decline of solvolysis rate than n/n_0 as CH_3CN replaces water shows that in addition to the role of water as a reactant, it is also needed to stabilize the transition state in another, quantitatively less significant, way. This is associated with a significant isotope effect when NH_3 is replaced by ND_3 in the complex but not when D_2O replaces H_2O in the solvent. In a dissociative substitution, loss of a ligand sigma bond to SCN^- in the transition state is associated with stronger sigma bonds to $-NH_3$ ligands. Thus, the ammine protons become more acidic and act as stronger hydrogen bond donors than in the ground state. (An even more striking example of more than one solvent molecule being important to a transition state is shown in Fig. 5.) This is again a phenomenon dependent mainly on hydrogen bonding (9).

Third, (finally), changes in the bulk properties of the solvent beyond the contact solvation shell (solvent molecules not in encounter with solute) may influence reaction rates. These long range effects will be primarily associated with changes (fluctuations) in solvent polarization. Non-electrostatic effects may be expected to be small. The trick is to isolate these effects from the two classes of solvent effects discussed above. (Discussions in the literature have not usually related to clear experimental separations (10).)

We have collected literature for solvent exchange reactions of metal complexes and extended the limited class of studies for the situation that the exchange involves at least

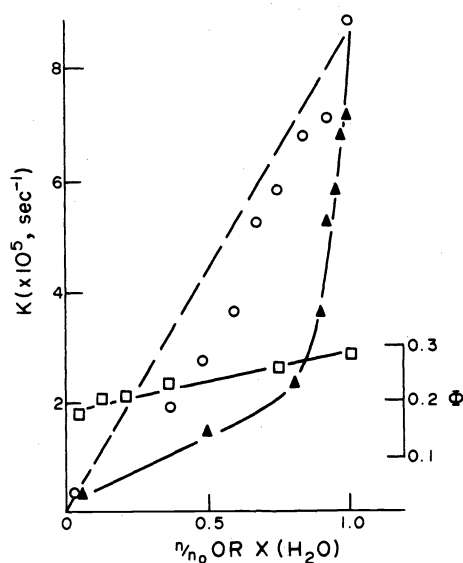


Fig. 4. Correlations of reactivity of *trans*- $\text{Cr}(\text{NH}_3)_2(\text{NCS})_4^-$ with solvent composition. Triangles show the rate constants for thermal solvolysis plotted against the mole fraction of water in the CH_3CN -water mixtures. Circles show these thermal rate constants replotted against the value of n/n_0 for water. The dashed line indicates the ideal behavior for a reaction involving a 1:1 encounter between the complex and a molecule of the reactive solvent, water. Squares show the dependence of the quantum yield for photo-solvolysis on the value of n/n_0 for water. (The quantum yield scale is on the right hand axis.)

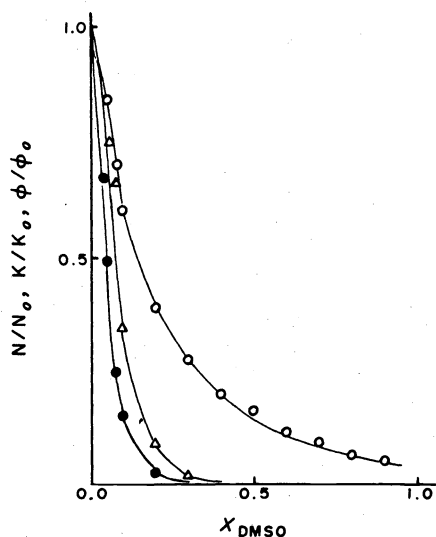


Fig. 5. Relative thermal rates (\bullet) and quantum yields (Δ) for racemization of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ in DMSO - H_2O , and n/n_0 for water (\circ) vs. mole fraction of DMSO ; $T = 25^\circ$.

constant leaving ligand, entering ligand, and non-substituted ligands (11). That is, we have considered variation of solvent properties holding the reaction itself constant (a minimum requirement - we are not confident that encounter complexes were constant). An example is shown in Table 1 where dimethylformamide (DMF) exchange with $\text{Ni}(\text{DMF})_6^{2+}$ is reported as a function of added electrolyte. The electrolyte effect on activation enthalpy is (as in other examples (11)) unmeasurable up to $> 1 \text{ m LiClO}_4$. This is a salt concentration where there are no more than enough bulk DMF molecules to fill primary solvation shells of Li^+ and ClO_4^- . Arguments (10) based on DMF structure are clearly limited. We do see small changes in rate constants (not activation enthalpies) in the concentrated electrolytes. The effect is exactly the one expected if anions occupy encounter sites, blocking some of those sites to access by solvent. Clearly, the observed rate constant for solvent exchange must be pro-

TABLE 1. DMF exchange at Ni(II) ion (n.m.r. line-broadening studies)

Nuclear magnetic resonance probe	[Ni ²⁺] (M)	Anion	Added electrolyte	ΔH^* (kcal mol ⁻¹)	k_{ex} (25 °C) (s ⁻¹)
¹⁷ O	0.01-0.1	ClO ₄ ⁻	Nil	9.4	7.7×10^3
¹ H	0.01-0.04	ClO ₄ ⁻	Nil	15.0	3.8×10^3
	0.01-0.04	ClO ₄ ⁻	Nil	10	3.7×10^3
	0.0334	ClO ₄ ⁻	Nil	12.7 ± 0.5	5.1×10^3
	0.0259	ClO ₄ ⁻	0.528 M n-Bu ₄ NClO ₄	13.6 ± 0.5	3.2×10^3
	0.0232	ClO ₄ ⁻	1.077 M LiClO ₄	13.0 ± 0.5	2.7×10^3

portional to the number of encounter sites occupied by solvent molecules.

As to electrostatic effects from the bulk, the effects are also probably smaller than would be derived from consideration of bulk dielectric constant. The fluctuation of solvent polarization related to passage through the transition state may commonly be associated with a time scale too short for orientational polarization and depend only on optical polarization. An elegant and practical theory of such effects has now been developed for a wide range of reactions by Levich, Dogonadze, and their collaborators (2,12).

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