

Solute-solute interactions and the kinetics of chemical reactions in aqueous solutions

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Abstract - Kinetics of chemical reactions involving substrates in aqueous solutions are examined from the standpoint of solute \leftrightarrow water, solute \leftrightarrow solute and solute \leftrightarrow cosolvent interactions. The rôle of water \leftrightarrow solute interactions is illustrated by contrasting isobaric and isochoric dependences of rate constants on temperature. The Savage-Wood treatment of group interactions between solutes in aqueous solutions provides a basis for treating the effects of added cosolutes on rate constants. Application of this treatment is illustrated using data describing kinetics of reactions involving organic and inorganic substrates. With increase in the amount of added solute/cosolvent, a better description is in terms of chemical reaction in binary mixed solvents. The dependence of rate constant on solvent composition is discussed in terms of preferential solvation of initial and transition states by either aqueous or non-aqueous components. The Inverse Kirkwood-Buff method offers an interesting approach for exploring these trends in solvent \leftrightarrow solute interaction as a function of solvent composition.

INTRODUCTION

Liquid water is a remarkable substance (1). Both apolar and polar solutes are reasonably soluble in water at ambient temperature and pressure. Water is miscible with other liquids despite often dramatic differences in properties. Water supports chemical reactions involving a vast range of mechanisms and processes. It is not surprising therefore that intense interest centres on the kinetics of chemical reactions in which water and related aqueous systems are used as solvents. The sensitivity of rate constants to composition of aqueous solutions is well established. A striking example concerns the rate constants for alkaline hydrolysis of both organic and inorganic solutes which increase rapidly when DMSO is added, a trend attributed to the marked destabilisation of OH⁻ ions with increase in mole fraction of DMSO in the mixture (2-5). Understanding such trends in kinetic parameters attracts continued interest in understanding the patterns quantitatively (6-8) based on information regarding mechanisms of reaction and the thermodynamic properties of aqueous solutions. In this commentary we review recent developments concerning the kinetics of reactions in aqueous solution and the effects of added solute and cosolvent. Friedman comments (9) on attempts to unite two classical and often separate themes; (i) solute \leftrightarrow water interactions, and (ii) solute \leftrightarrow solute interactions. Here we draw into consideration a third theme, kinetics of reactions in solution.

CHEMICAL REACTIONS IN AQUEOUS SOLUTION

According to Transition State Theory(10-12), a first order rate constant k describing the reaction of substrate- j in an ideal aqueous solution is determined by the difference in standard chemical potentials of initial (IS) and transition (TS) states; equations (1) and (2).

$$k = (k_B T/h) \cdot \exp\{-\Delta^*G^{\circ}(\text{aq})/R.T\} \quad (1)$$

where, at fixed temperature T and pressure p ,

$$\Delta^*G^{\circ}(\text{aq}) = \mu^{\circ}(\text{TS};\text{aq}) - \mu^{\circ}(\text{IS};\text{aq}) \quad (2)$$

Transition State Theory offers a welcome patina of thermodynamic respectability to chemical kinetics. An important contribution to the partial molar properties of IS and TS solutes, including $\mu^{\circ}(\text{TS};\text{aq})$ and $\mu^{\circ}(\text{IS};\text{aq})$, arises from solute \leftrightarrow water interactions. In terms of the model suggested by Gurney (13) each molecule of solute- j is surrounded by a cosphere in which the organisation of water molecules differs from that in the bulk solvent outside the cosphere at the same T and p . The cosphere for some solutes may comprise more than one component sphere (14) but in general terms one can distinguish two classes of solute- j . If

solute \leftrightarrow water interactions are strong then solute-j is hydrophilic. If solute \leftrightarrow water interactions are weak then solute-j is hydrophobic, water \leftrightarrow water interactions are enhanced (15,16). A key contribution to $\Delta^*G^{\circ}(\text{aq})$ stems from changes in water \leftrightarrow water interactions and water \leftrightarrow solute interactions in the cosphere around solute-j. Unfortunately it is not easy to identify this particular contribution to $\Delta^*G^{\circ}(\text{aq})$ and hence to enthalpies, volumes and entropies of activation. Robertson argued (17,18) that for solvolysis of apolar alkyl halides and related compounds, negative limiting isobaric heat capacities of activation $\Delta^*C_p^{\circ}(\text{aq})$ are a consequence of positive limiting partial molar heat capacities of the initial state; i.e. $C_p^{\circ}(\text{IS};\text{aq}) > 0$ and $C_p^{\circ}(\text{TS};\text{aq}) \approx 0$. Certainly limiting partial molar isobaric heat capacities of apolar solutes in aqueous solutions are positive (19), a consequence of their hydrophobic character. However interpretation of trends in $\Delta^*C_p^{\circ}(\text{aq})$ is not straightforward (18,20).

Another procedure for identifying the solvent contribution is based on suggestions made by Evans and Polanyi (21) concerning isochoric activation parameters. Although definition of isochoric activation parameters has aroused considerable debate (22-25), the original comments (21) remain valid. Evans and Polanyi (21) noted that interpretation of the rôle of solvent in determining the dependence of rate constants on temperature is complicated by the fact that interaction between solute and solvent depends on temperature. They suggested that one way to avoid this problem is to consider this dependence at constant volume. Therefore we combined data describing the pressure and temperature dependence of rate constants for a given reaction with equations (27) describing the dependence of molar volume of water $V^*(1;\text{H}_2\text{O})$ on temperature and pressure. Hence we calculated rate constants at selected temperature but at pressures which correspond to constant $V^*(1;\text{H}_2\text{O})$; i.e. at $V^*(1;\text{H}_2\text{O};298.15 \text{ K}; 101325 \text{ N m}^{-2})$. This isochoric dependence is contrasted with the conventional isobaric dependence of rate constants on temperature. Two examples (28,29) are shown in Figure 1. In reviewing these plots we recall that increases in temperature and pressure disrupt water \leftrightarrow water interactions. Using the Lumry model (30) for liquid water, there is a consequent shift to favour the long-bond dense hydrogen-bonded structure at the expense of the short strong hydrogen-bonded high-volume structure. [At the same time there is an increase in concentration of the potentially reactive free OH groups (31)]. In other words on going from the isobaric to the isochoric plots (Figure 1), water \leftrightarrow water interactions are disrupted in the bulk water although along the isochoric plot the mean water-water distance remains constant.

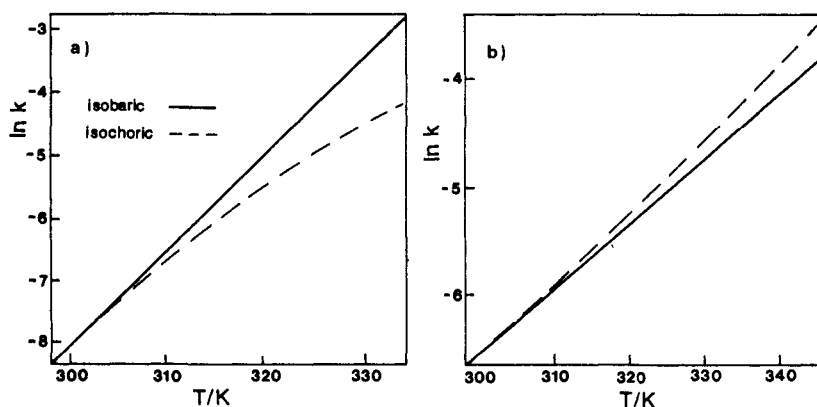


Fig. 1. Comparison of the isothermal(—) and isochoric(-----) dependences of rate constants on temperature for hydrolysis in aqueous solution of (i) $[\text{Fe}(\text{5-Br-phen})_3]^{2+}$, (ii) 1-benzyl-3-phenyl-1,2,4-triazole.

The latter constraint conforms as far as possible to the conditions suggested by Evans and Polanyi. Aquation of the iron(II) complex requires an extension of the Fe-N bonds, the hydrophobic phen ligands being pushed out into the solvent. Hence the transition state is more hydrophobic than the initial state. In terms of the arguments discussed by Shinoda (32,33) and others (34), this enhancement of water \leftrightarrow water interactions stabilises the transition state. The transition state formed in the solvolysis of benzyl chloride in aqueous solution is more hydrophilic than the initial state. So on going from isobaric to isochoric conditions, the rate constant falls for the iron(II) complex but increases for benzyl chloride. The later trend is also followed (24) by data (24) describing the hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole. Hence we conclude that the mechanism of reaction involves an increase in hydrophilic character (i.e. an increase in solute \leftrightarrow water interaction) on activation.

KINETICS IN DILUTE AQUEOUS SOLUTIONS

The task of interpreting kinetic data describing a given reaction in aqueous solution is rarely straightforward even where parameters describing temperature and pressure dependences are available. For this reason a new variable is introduced, the dependences of kinetic parameters being examined as a function of molality of added solute. The starting hypothesis asserts that comparison of the effects of different solutes on kinetic parameters reveals important details of the activation process. For solute-*j* in aqueous solution containing added solute-*i*, activity coefficient γ_j describes the impact of solute-solute interactions on the chemical potential of solute-*j*, and in general terms, the thermodynamic properties of aqueous solutions. An important contribution to the strength and type of solute-solute interactions emerges from the overlap of cospheres associated with solute molecules. Friedman and Krishnan (35) identified two extremes. In one case the organisation in the cospheres are incompatible leading to destabilisation with $\gamma_j > 1.0$. In the other case the organisation are compatible leading to, in the case of hydrophobic interaction, $\gamma_j < 1.0$, and mutual stabilisation by hydrophobic bonding. Even where the solute molecules are ions, this cosphere contribution is important. For example, salt effects (36) on the rate constant of hydrolysis of phenyl dichloroacetate (Figure 2) follows a pattern which resembles the classic pattern (37,38) produced by the mean ionic coefficients for salts.

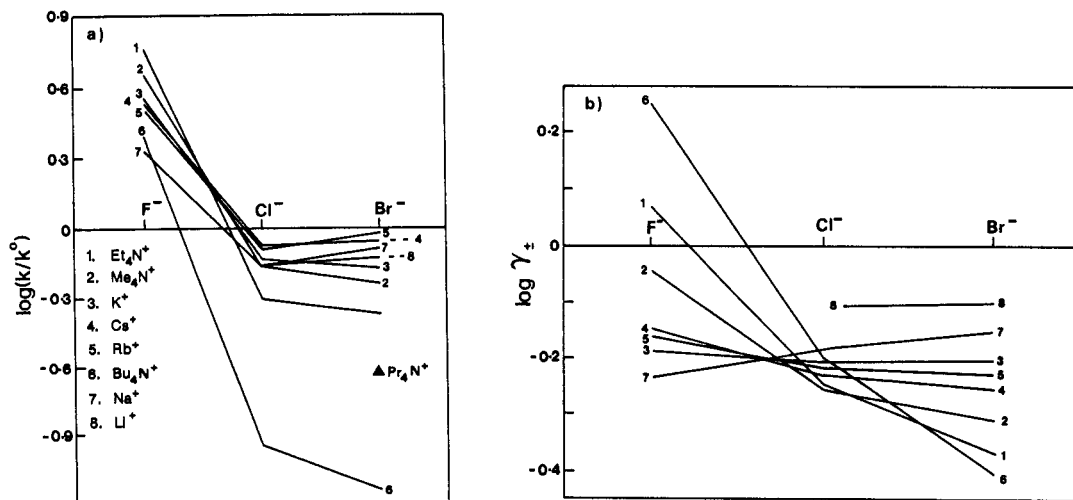


Fig. 2. Dependence on salt (0.9 mol dm^{-3}) at 298.2 K of (a) rate constant for hydrolysis of phenyl dichloroacetate, and (b) mean ionic activity coefficient (redrawn from reference 38).

Interpretation of kinetic data for reactions in aqueous solution requires understanding the impact of cosphere overlap on both initial and transition states. Figure 3 shows, in diagrammatic form, how the rate constant for these reactions depends on the nature of added solute as a result of changes in chemical potentials of initial and transition states brought about by the contrasting effects of IS and TS on the organisation of water in their cospheres.

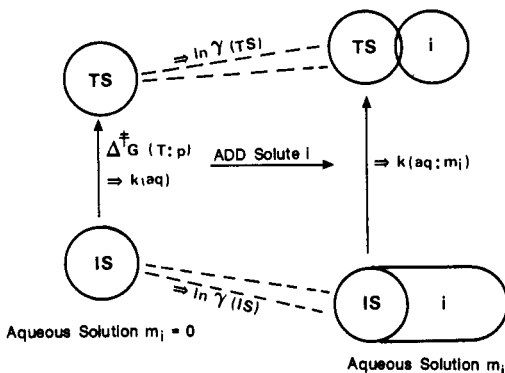


Fig. 3. Effect of cosphere overlap involving added solute-*i* and both initial and transition states leading, in the case shown, to stabilisation of initial state and destabilisation of transition state, and hence a decrease in rate constant.

These ideas are placed on a quantitative footing (39-42) at least for dilute solutions by expressing the activity coefficients in terms of pairwise interaction parameters. In an aqueous solution containing trace amounts of solute- j in the presence of solute- i , molality m_i , trace activity coefficient γ_j linear in m_j and proportional to g_{ij} , a pairwise Gibbs interaction energy parameter (39). One application (44) of this approach considers the kinetics of hydrolysis of *p*-methoxyphenyl dichloroacetate in which the chemical reaction incorporates N water molecules into the substrate on proceeding to the transition state; see also reference (45). Hence equation (3) describes the effect of adding urea (symbol U), molality m_U on the rate constant.

$$\ln\{k(m_U)/k(m_U=0)\} = \ln\gamma(\text{IS}) - \ln\gamma(\text{TS}) - N \cdot \phi \cdot M_1 \cdot m_U \quad (3)$$

Here ϕ is the practical osmotic coefficient, M_1 is the molar mass of water such that k is the first order rate constant for ester hydrolysis.

Hence,

$$\ln\{k(m_U)/k(m_U=0)\} = [2/R.T.(m^0)^2] \cdot [g(U \leftrightarrow \text{IS}) - g(U \leftrightarrow \text{TS})] \cdot m_U - N \cdot \phi \cdot M_1 \cdot m_U \quad (4)$$

An interesting development based on equation (4) uses the Savage-Wood additivity principle (46). Pairwise solute \leftrightarrow solute Gibbs energy interaction parameters are expressed in terms of pairwise group interaction parameters. Hence for two solutes P and Q in aqueous solution,

$$g(P \leftrightarrow Q) = \sum(i=1; i=k) \sum(j=1; j=l) n_i(P) \cdot n_j(Q) \cdot G(i \leftrightarrow j) - M_1 \cdot R.T/2 \quad (5)$$

Here $n_i(P)$ is the number of groups- i in molecule P and $n_j(Q)$, the number of groups- j in molecule Q where $G(i \leftrightarrow j)$ are group interaction parameters. Wood (46,47) and Lilley (48) offer general rules which show how the molecular formula for a given molecule P can be written in terms of contributing groups. Barone (49) and Somsen (50) have explored further aspects of the additivity principle. Wood (47) summarise estimates of group interaction parameters [SWAG(51)] based on equilibrium thermodynamic properties of solutions. These treatments are applied to both initial and transition states. In the case of added urea, the rate constant for ester hydrolysis using $N = 2$, equation (4) is given by equation (6).

$$\ln\{k(m_U)/k(m_U=0)\} = [2/R.T.(m^0)^2] \cdot [-4.5 \cdot G(\text{CONH} \leftrightarrow \text{OH}^{\text{TS}})] \cdot m_U - 2 \cdot \phi \cdot M_1 \cdot m_U \quad (6)$$

Here $G(\text{CONH} \leftrightarrow \text{OH}^{\text{TS}})$ refers to pairwise interaction involving CONH groups in urea and OH groups exposed to the solvent by the transition state. Figure 4 shows how agreement between experiment and theory emerges when $G(\text{CONH} \leftrightarrow \text{OH}^{\text{TS}})$ is set at -20 J kg^{-1} .

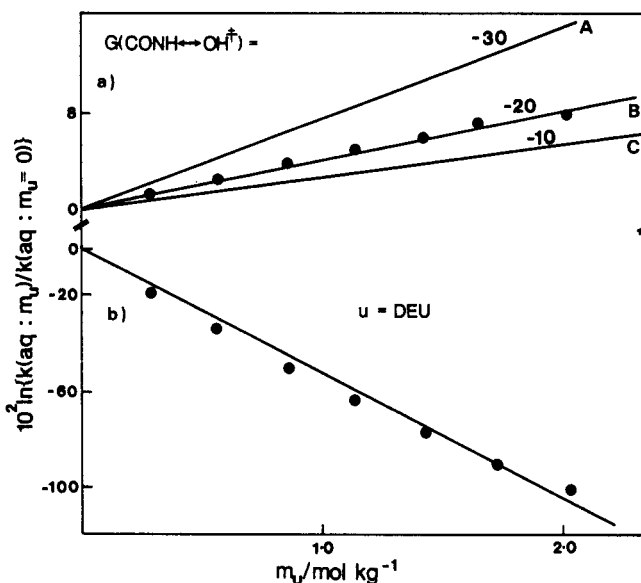


Fig. 4. Dependence of rate constant for hydrolysis of phenyl dichloroacetate in aqueous solution containing (a) urea and (b) diethylurea.

To account for the effect of added dimethylurea on the rate constant for ester hydrolysis, an additional pairwise group interaction parameter is required, namely $G(\text{CH}_2 \leftrightarrow \text{OH}^{\text{TS}})$ equal to 45 J kg^{-1} . Using these two group interaction parameters we can account for the dependence of rate constants on molality of added diethylurea; Figure 4.

This approach is not confined to organic substrates. For example, data (52) describing rate constants for aquation of $[\text{Fe}(\text{5-NO}_2\text{-phen})_3]^{2+}$ cation produce plots of $\ln(k)$ against

$m(\text{ROH})$ which show constant increments with increase in the number of hydrophobic methylene groups consistent with an increase in hydrophobic interaction between iron(II) complex and alkyl groups of ROH on activation. Recently we have examined the effects of added mono- and polyhydric alcohols on kinetic parameters for hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole in aqueous solutions (53). The group additivity principle is successful for monohydric and vicinal diols. In fact the patterns are sufficiently well established to use the effects of added solutes on rate constants as a method of probing mechanisms of reaction(54). However several polyhydric alcohols produce changes in rate constants which do not conform to the predicted pattern (53) because the additivity principle takes no account of stereochemical aspects of solute \leftrightarrow water and solute \leftrightarrow solute interactions (55,56).

KINETICS OF REACTION IN AQUEOUS MIXTURES

With increase in molality of added solute [cf. equation (7)] so description of the dependence of rate constant on composition breaks down if the analysis is based on pairwise interactions between solutes in aqueous solutions. A better approach treats the solvent as a binary mixture and the initial and transition states as solutes. Hence in an aqueous mixture mole fraction x_2 of cosolvent, at fixed T and p

$$\Delta^*G(\text{sln};x_2) = \mu^0(\text{TS};\text{sln};x_2) - \mu^0(\text{IS};\text{sln};x_2) \quad (7)$$

The reference is usually aqueous solution (i.e. $x_2 = 0$) leading to the dependence of $\Delta^*G^0(\text{sln};x_2)$ on x_2 expressed in terms of transfer parameters for initial and transition states.

$$\Delta(\text{aq} \rightarrow x_2)\Delta^*G^0(\text{sln}) = \Delta(\text{aq} \rightarrow x_2)\mu^0(\text{TS};\text{sln}) - \Delta(\text{aq} \rightarrow x_2)\mu^0(\text{IS};\text{sln}) \quad (8)$$

The dependence of $\Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{sln})$ for solute-j on mole fraction composition of the mixture reflects the competing influences of water \leftrightarrow solute-j and cosolvent \leftrightarrow solute-j interactions. The intensity of these interactions also depends on the strength of water \leftrightarrow cosolvent interactions in the liquid mixture. The task of interpreting kinetic data has three related parts;

- (i) calculation of transfer parameters,
- (ii) analysis of the properties of the liquid mixture, and
- (iii) linking information gained by tasks (i) and (ii) with the concept of preferential solvation/hydration.

Transfer parameters for sparingly soluble neutral solutes and salts are conveniently calculated using solubility data (6,7). We have discussed the problems associated with calculating transfer parameters for ions (8,57). For the most part we have used the TATB/TPTB assumption (57-60) in which the transfer parameters for Ph_4As^+ and Ph_4B^- ions (and, Ph_4P^+) ions are assumed equal. This assumption is probably valid to better than 10% of a given derived transfer parameter. Consequently it is possible to estimate in many cases transfer parameter for initial states involved in reactions between iron(II) complex cations and hydroxide ions in a range of binary aqueous mixtures. Combination with kinetic data leads to reaction profiles for the alkaline hydrolysis of these ions, showing the dependence on x_2 of $\Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{sln})$ for $j = \text{TS}, \text{OH}^-$ and iron(II) complex cation. Data for two systems are summarised in Figure (5) where the cosolvents are methanol (57), ethanol (60) and propanone (59,61).

The dependence on vol % of organic cosolvent for a given rate constant is the result of a complex dependences of initial and transition state chemical potentials. Moreover these dependences reflect an underlying competition between solute and each solvent component; i.e. preferential solvation. In order to understand these aspects of kinetics we need to examine the patterns in rather more detail.

With reference to binary aqueous mixtures, the classification given by Franks (61) is based on the excess molar thermodynamic properties of mixing at 298.2 K and ambient pressure (62). Thus ethyl alcohol, methyl alcohol and propanone form Typically Aqueous mixtures because $G_m^E > 0$ and $|T.S_m^E| > |H_m^E|$. However DMSO + water mixtures for which $G_m^E < 0$ are Typically Non-aqueous because $|H_m^E| > |T.S_m^E|$. The aim is to link this information with the kinetic data discussed above and hence to probe the interactions between both IS and TS with the components of the liquid mixture. Consequently considerable interest has been shown in Inverse Kirkwood-Buff calculations (63) along the lines discussed by Ben-Naim (64-66), Hall (67) and recently by Newman (68). Thus Newman has shown how these calculations yield integral functions G_{j1} and G_{j2} for solute-j in water(1) + cosolvent(2) mixtures. The treatment has been applied by Newman and Covington (69) to analyse nmr data describing preferential solvation of ions in aqueous mixtures.

The function G_{j1} expresses the 'affinity' of solute-j for solvent-1 and hence the difference $G_{j1}-G_{j2}$ records the preference of solute-j for solvent-1 over solvent-2 in its cosphere. Information about the mixture is required including G_m^E , volumetric and compressibility data. Careful statistical analysis is also demanded because the calculation requires first and second differentials of thermodynamic properties (70). For the solute-j, transfer parameters are required together with information concerning partial molar volumes. This information is not always available. Fortunately we have sufficient information on iron(II) complexes in terms of both transfer parameters and density data (71) to undertake these calculations

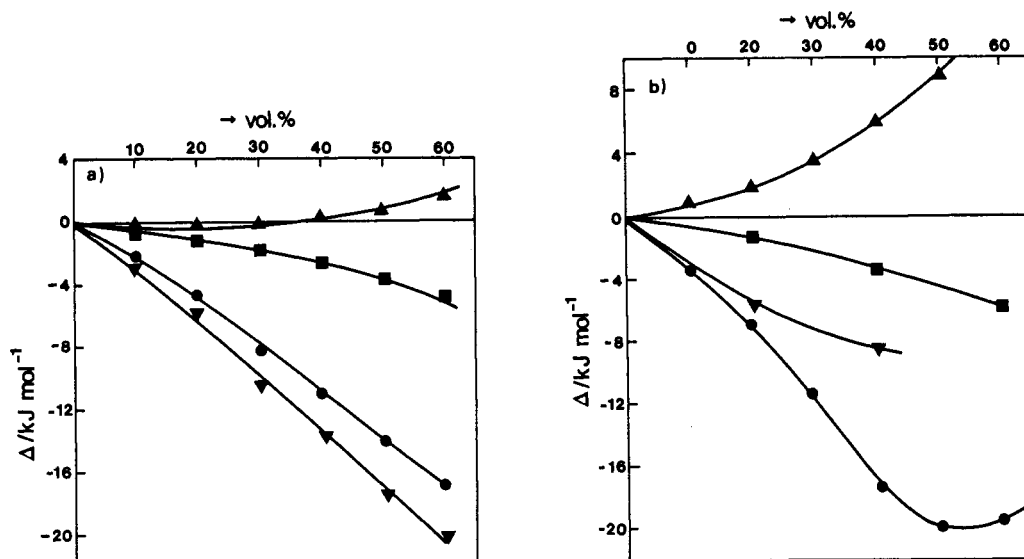


Fig. 5. Alkaline hydrolysis of iron(II) complex cation $[\text{Fe}(\text{phen})_3]^{2+}$ in binary aqueous mixtures showing dependence on vol% of organic solvent of standard chemical potentials of initial state, $\Delta(\text{aq}+x_2)\mu^0\{[\text{Fe}(\text{phen})_3]^{2+};\text{sln}\}$, [●], hydroxide ions $\Delta(\text{aq}+x_2)\mu^0(\text{OH}^-;\text{sln})$, [▲], and transition state $\Delta(\text{aq}+x_2)\mu^0(\text{IS};\text{sln})$ [▼], together with that for the activation Gibbs energy, $\Delta(\text{aq}+x_2)\Delta^\ddagger G^0(\text{sln})$ [■]; (A) methanol, (B) ethanol.

(72). In Figure (6) we compare G_{j_1} and G_{j_2} for the initial state ($= [\text{Fe}(\text{phen})_3]^{2+} + \text{OH}^-$) and corresponding transition state for alkaline hydrolysis in water(1) + methanol(2) mixtures.

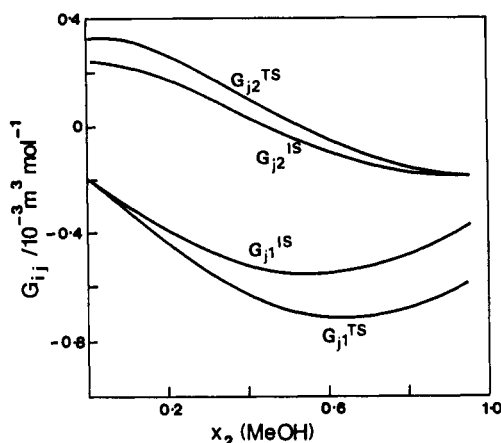


Fig. 6. Inverse Kirkwood Buff Integral functions describing preferential solvation of initial state $\{= [\text{Fe}(\text{phen})_3]^{2+} + \text{OH}^-\}$, $G_{j_1}^{\text{IS}}$ and $G_{j_2}^{\text{IS}}$, and transition state $G_{j_1}^{\text{TS}}$ and $G_{j_2}^{\text{TS}}$ for the alkaline hydrolysis of $[\text{Fe}(\text{phen})_3]^{2+}$ complex in methyl alcohol(2) + water(1) mixtures; cf. Figure 5.

The mechanism of this reaction requires that the Fe-N bonds stretch and OH^- ions burrow into the complex. The dominant functions for both IS and TS are G_{j_2} but at high x_2 the increase in G_{j_1} for the IS is attributed to preferential solvation of OH^- ions by water. This effect is less dramatic for TS because the OH^- ions are less exposed to the solvent.

DISCUSSION

The task of understanding the rôle of solvents in kinetics of chemical reactions has occupied the attention of chemists for many years. Understanding this rôle has obvious economic, ecological and biological importance. We have shown that considerable progress has been made. Statistical thermodynamic treatments and equilibrium properties of solutions are used to probe interactions involving initial and transition states in reactions. We have shown how these treatments are applied to kinetic data describing reactions involving organic and inorganic substrates. The next stage requires extension of these ideas to consideration of enthalpies, volumes and entropies of activation.

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