Analysis of Solvent Effects on the Kinetics of Alkaline Hydrolysis of an Iron(II) Complex using the Kirkwood–Buff Treatment of Preferential Solvation

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Trends in Kirkwood–Buff integral functions for initial and transition states associated with the reaction of $[Fe(phen)_3]^{2+}$ complex cations (phen = phenanthroline) with OH^- anions in water/methyl alcohol mixtures identify the role of preferential solvation in determining the dependence of rate constant on solvent composition.

For the reaction between $[Fe(phen)_3]^{2+}$ (phen = phenanthroline) and OH^- anions in aqueous solution, added methyl alcohol stabilises both transition and initial states {initial state = complex cation + OH^-}.[1] However stabilisation of the transition state is more dramatic and so the rate constant increases.[1] Such a complex pattern is typical of solvent effects in binary aqueous mixtures.[2] These trends can be accounted for in terms of preferential solvation. For reactions in dilute aqueous solutions the dependence of rate constants on composition can be analysed[3,4] in terms of group additivity based on the Savage–Wood model[5] of solute–solute interactions. A quantitative description[6] of preferential solvation for solutes in mixed solvent systems uses the Inverse Kirkwood–Buff treatment[7] of solution phenomena.[8—10] We illustrate the potential which this approach has for understanding trends in kinetic parameters for reactions in solutions.

For two substances α and β in a solution, the Kirkwood–Buff integral function $G_{\alpha\beta}$ is related[8] by equation (1) to the angle-averaged correlation function $g_{\alpha\beta}(R)$. Kirkwood–Buff integral functions offer an insight into the molecular organisation within liquids and solutions. Integral function G_{12} is related to the pair correlation function between molecules of liquid-1 and liquid-2 in a binary mixture at fixed temperature and pressure. For methyl alcohol (2) + water (1) mixtures, the functions G_{12}, G_{11} and G_{22} were calculated[8] using excess molar Gibbs energies of mixing,[11] G_m^E, molar volumes,[12] V_m, and isothermal compressibilities,[13] κ_T, at 298.2 K. The Gibbs energies and volumes were expressed as a function of mole fraction using the Guggenheim–Scatchard equation.[14] The derived parameters were used to calculate the differential $d\mu_2/dx_2$ as a function of x_2, where μ_2 is the chemical potential of methyl alcohol in the mixture with alcohol mole fraction x_2. This differential combined with partial molar volumes yielded the dependence of the three integral functions described above.

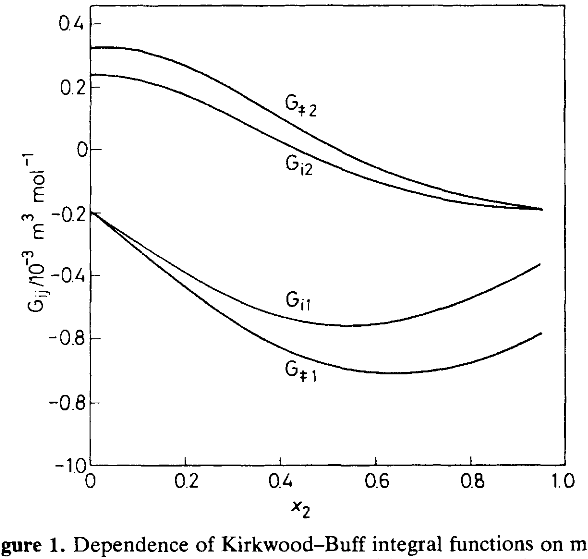

Figure 1. Dependence of Kirkwood–Buff integral functions on mole fraction of methyl alcohol, x_2 in water (1) + methyl alcohol (2) mixtures at 298.2 K. $G_{\neq 1}$ and $G_{\neq 2}$ are integral functions for the transition state; G_{i1} and G_{i2} are corresponding functions for the initial state {initial state = $[Fe(phen)_3]^{2+}$ + OH^-}.

For a given solute-j in a solvent formed from a binary liquid mixture, water (1) + methyl alcohol (2), the corresponding Kirkwood–Buff quantities are the integral functions G_{j1} and G_{j2}, where G_{j1} expresses the affinity[8] of solute-j for solvent-1 in its cosphere. The difference $G_{j1} - G_{j2}$ describes the preference of solute-j for solvent-1 over solvent-2. Thus, G_{j1} is given[10] by equation (2). $V_j^\infty(x_2)$ is the limiting partial molar volume of solute-j in the solvent mixture. Further,[10] equation (3) gives $G_{j1} + G_{j2}$. Here $[d\mu_j^\circ/dx_2]$ characterises the dependence of the transfer chemical potential for solute-j on mole fraction composition of the solvent mixtures. Transfer parameters for the iron(II) complex cation $[Fe(phen)_3]^{2+}$ were calculated from solubility data[15] for thiocyanate salts using the tetraphenylarsonium tetraphenylboron (TATB) assumption which assumes[1] that the transfer parameters for Ph_4As^+ and Ph_4B^- ions are equal. We calculated transfer parameters for the overall initial state $\Delta(aq \rightarrow x_2)\ \mu^\circ$ (complex cation + OH^- anion) by combining the transfer parameters for the cation and hydroxide ions.[1] Combination of these data with the dependence of rate constants for alkaline hydrolysis yielded transfer parameters for the transition state, TS; *i.e.*, $\Delta(aq \rightarrow x_2)\mu^\circ(TS)$, is calculated by subtracting the transfer parameters from the initial state from the kinetic Gibbs energies of activation. The dependence of $\Delta(aq \rightarrow x_2)\ \mu^\circ$ (complex cation + OH^-) and $\Delta(aq \rightarrow x_2)\ \mu^\circ$ (TS) on x_2 were fitted to a polynomial in mole fraction x_2 in order to calculate the derivative $[d\mu_j^\circ/dx_2]$ at selected mole fractions. Estimates of $V_j^\infty(x_2)$ for both initial and transition states were obtained from the dependence on x_2 of partial molar volumes for iron(II) complexes in these mixtures.[16]

$$G_{\alpha\beta} = \int_0^\infty [g_{\alpha\beta}(R) - 1].4\pi R^2.dR \qquad (1)$$

$$G_{j1} = x_2.(V_2/V_m).[G_{j1} + G_{j2}] + k_T.R.T + V_j^\infty(x_2) \qquad (2)$$

$$G_{j1} + G_{j2} = [(d\mu_j^\circ/dx_2).V_m].[R.T + x_2.(1-x_2).d^2G_m^F/dx_2^2] \qquad (3)$$

In Figure 1, we show the dependence of the integral functions for the transition state $G_{\neq 1}$ and $G_{\neq 2}$ and for the initial state, G_{i1} and G_{i2} where subscript-i refers to a composite property for the iron(II) complex and hydroxide ion.

For the initial state, the curves show preferential solvation of the initial state by methyl alcohol over water; *i.e.* $G_{i2} - G_{i1}$ is >0, decreasing with increase in mole fraction of methyl alcohol in the solvent. The closing of the gap at high x_2 reflects the strong preferential solvation of OH^- ions by water. But

G_{i2} exceeds G_{i1}, indicating the dominant role of the hydrophobic complex. In this reaction, the overall hydrophobic character of the transition state exceeds that of the initial state in that the Fe–N bonds stretch, forcing the phen groups further into the solvent and the OH^- ion is 'buried' into the complex cations. The integral functions show that $G_{\neq 2} - G_{\neq 1}$ is > 0, indicating an even stronger preferential solvation of the hydrophobic transition state by alcohol,[17,18] over that by water. The contribution from the preferential solvation of OH^- by water at high x_2 is, as intuitively expected, accordingly less dramatic.

These calculations point out an interesting link extending from kinetics, through equilibrium thermodynamic properties of solutions and liquid mixtures, to statistical thermodynamic treatments of liquid systems. Further application of these calculations to analysis of kinetic data for both inorganic and organic substrates will be reported elsewhere.

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