Kinetics of Aquation of Tris(5-nitro-1,10-phenanthroline)iron(II) in Acetone–Water and in t-Butyl Alcohol–Water Mixtures: Endostatic Analysis of Activation Parameters †

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Rate constants and derived thermodynamic activation parameters are reported for the aquation of $[Fe(5NO_2\text{-phen})_3]^{2+}$ in acetone–water and in t-butyl alcohol–water mixtures. The data have been analysed to obtain kinetic activation parameters for reaction in corresponding mixtures where the ratio of activities of the two solvent components is constant, *i.e.* under endostatic conditions. A method is described for calculating endostatic activation parameters from kinetic data and molar thermodynamic excess functions for the binary mixture. The results of these calculations are discussed in the light of the known properties and structures of the solvent mixtures. The solvent dependence of the activation Gibbs function, $\Delta G_\alpha^\ddagger$, calculated under endostatic conditions for the aquation of the iron complex, reflects changes in solvent structure more markedly than the conventional activation parameter $\Delta G^\ddagger$ calculated directly from the rate constant using transition-state theory. This trend has been previously reported for the hydrolysis of 2-chloro-2-methylpropane, thereby indicating that the mechanisms of aquation for both reactants are similar, *i.e.* dissociative.

In the aquation of the tris(5-nitro-1,10-phenanthroline)-iron(II) cation in acidic media, equation (1), the rate-determining step is the loss of the first ligand.[1] There is considerable evidence which points to this first step as being dissociative.[2] Aquation rates depend only slightly on acid concentration,[1] but rate constants for this reaction (1) are dependent on the concentration and nature of added salt in aqueous salt solutions,[3] and on the mol fraction, x_2, and nature of the organic co-solvent in binary aqueous mixtures.[4] (We will use the convention where component 1 is water and component 2 is the co-solvent in a binary aqueous mixture.)

$$[Fe(5NO_2\text{-phen})_3]^{2+} + 3\,H^+ \longrightarrow Fe^{2+} + 3[5NO_2\text{-phenH}]^+ \qquad (1)$$

Patterns revealed in plots of kinetic parameters for inorganic reactions against solvent composition for aqueous mixtures[5] prompted an examination of the dependence of the activation Gibbs function, $\Delta G^\ddagger$, on the excess molar Gibbs function of mixing, G^E. The qualitative link discerned for various water-rich solvent mixtures[4] has formed the basis for the quantitative treatment reported in the present paper, where these two quantities, $\Delta G^\ddagger$ for reaction and G^E for the solvent mixture, are brought together.

For a first-order reaction, $\Delta G^\ddagger$, calculated directly from the rate constant using transition-state theory, measures the difference between the standard-state chemical potentials of the reactant, $\mu_3^\ominus$, and transition state, $\mu^\ddagger$ [equation (2)]. The solution standard states

$$\Delta G^\ddagger = \mu^\ddagger - \mu_3^\ominus \qquad (2)$$

can be defined (*cf.* Henry's law) as the hypothetical solution where the mol fraction of the solute and the activity coefficient are unity. Since 1 mol of reactant forms 1 mol of transition state, the analysis is straightforward because if other solution standard states are used the cratic contributions[6] cancel to yield the same numerical value for $\Delta G^\ddagger$, equation (2). (This would not be the case for a

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† No reprints available.

[1] T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 2348; W. W. Brandt and D. K. Gullstrom, *ibid.*, 1952, **74**, 3532.

[2] J. M. Lucie, D. R. Stranks, and J. Burgess, *J.C.S. Dalton*, 1975, 245.

[3] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1974, 1717.

[4] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.

[5] M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55.

[6] R. W. Gurney, 'Ionic Processes in Solution,' McGraw-Hill, New York, 1953.

second-order reaction.[7]) For convenience we adopt as our reference the reaction in water (*i.e.* $x_2 = 0$) and consider the changes in kinetic parameters on going to a mixture where the mol fraction of co-solvent is x_2. Then changes in kinetic activation parameters are indicated by the solvent operator [8], δ_m, as illustrated in equation (3).

$$\delta_m \Delta G^{\ddagger} = \delta_m \mu^{\ddagger} - \delta_m \mu_3^{\ominus} \quad (3)$$

$$\delta_m \Delta G^{\ddagger} = \Delta G^{\ddagger}(x_2) - \Delta G^{\ddagger}(x_2 = 0) \quad (4)$$

Grunwald and Effio[9] suggested that the activation parameters should be compared under conditions where the ratio of the activities of the components of the solvent mixtures are constant, *i.e.* under endostatic conditions. Thus it is possible to calculate, for example, an endostatic activation Gibbs function, $\Delta G_{\alpha}^{\ddagger}$ from $\Delta G^{\ddagger}$ and the excess function G^E for the solvent mixture. In this paper we explore the application of this theory to the kinetics of aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation, equation (1).

TABLE 1

Mean rate constants, k, for the aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation in acetone–water mixtures, mol fraction x_2 of acetone, in the presence of 0.054 mol dm^{-3} H_2SO_4

x_2	$10^3k/s^{-1}$ at 298.15	304.65	308.16	314.15 K
0	0.63	1.94	3.7	8.8
0.007	0.64	1.96	3.8	9.1
0.048	0.66	2.12	3.9	10.1
0.078	0.69	2.42	4.6	11.5
0.110	0.82	2.78	5.5	12.6
0.140	0.95	3.3	6.8	14.6
0.160	1.19	3.5	7.2	16.1
0.20	1.59	4.4	8.4	17.8
0.28	2.15	6.0	10.6	23.2

EXPERIMENTAL

Reagents.—Solutions containing the tris(5-nitro-1,10-phenanthroline)iron(II) cation were prepared from AnalaR grade ammonium iron(II) sulphate and a slight excess of the ligand (B.D.H.). The co-solvent acetone was redistilled, and mixtures were prepared using distilled water.

Kinetic Runs.—Solutions were placed in 10 mm stoppered silica cells, held in the thermostatted compartment of a Unicam SP 800A recording spectrophotometer. Runs were carried out in duplicate or triplicate. The absorbance at 526 nm was measured at predetermined time intervals, the output signal from the spectrophotometer being fed to a data logging unit (Solartron A220 DVM and A295 drive unit) and recorded (Facit punch) on punched tape. Using a manual entry unit on the data logger, various key quantities were also entered on each data tape, including time interval, number of cells, and a terminating control number. These quantities were important in the computer analysis of the kinetic data. The reactions were monitored for two or more half-lives.

ANALYSIS OF KINETIC DATA

Rate Constants.—Rate constants for reaction (1) in acetone–water mixtures were calculated using the non-linear least-squares method described by Moore.[10] The measured absorbance, A_t, at time t is a function of the initial value A_0 when $t = 0$, the infinity value, A_∞, when $t = \infty$, and the rate constant k; $A_t = f(A_0, A_\infty, k)_t$. Starting from estimated values for these three unknowns, the data were fitted to the first-order rate equation to obtain a set of improved values. The cycle was repeated continually until the differences between input and output values of A_0, A_∞, and k were negligibly small. In the present example, this usually required five or less cycles. This analytical procedure was built into a program (ALGOL) for an ICL 4130 computer, absorbance data and control parameters being read from the paper tape.

Activation Parameters.—The dependence of rate constant on temperature, T, at fixed pressure and x_2 was analysed to obtain the activation Gibbs function, $\Delta G^{\ddagger}$, activation enthalpy, $\Delta H^{\ddagger}$, and activation entropy, $\Delta S^{\ddagger}$, as defined by

$$k = (\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta G^{\ddagger}/RT) \quad (5)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (6)$$

equations (5) and (6) where $\boldsymbol{k}$ and $\boldsymbol{h}$ are Boltzmann and Planck's constants respectively. These activation para-

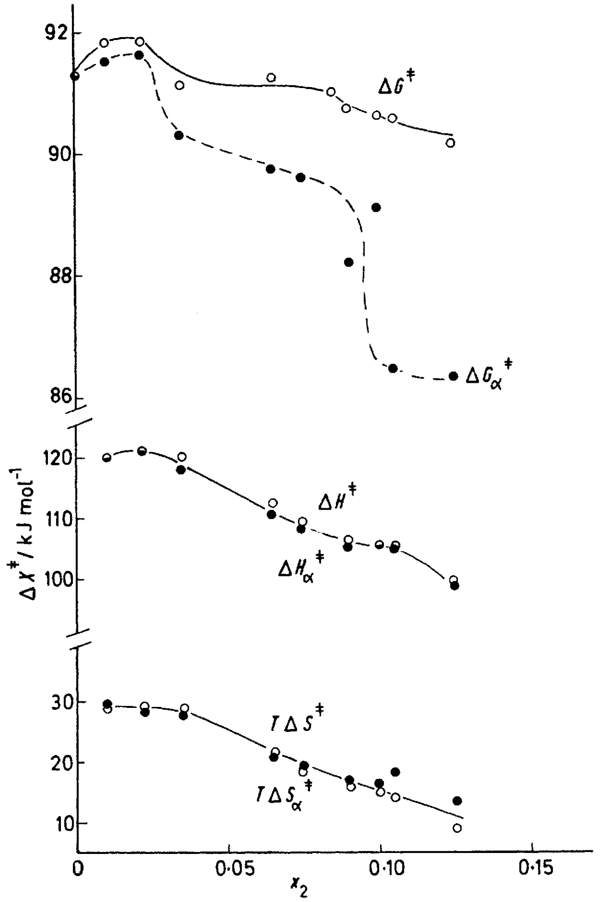

FIGURE 1 Comparison of conventional (○) and endostatic activation parameters (●) for aquation at 298.2 K as a function of the mol fraction of t-butyl alcohol

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[7] E. A. Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 607.

[8] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963.

[9] E. Grunwald and A. Effio, *J. Amer. Chem. Soc.*, 1974, **96**, 423.

[10] P. Moore, *J.C.S. Faraday I*, 1972, 1890.

TABLE 2

Kinetic activation parameters and related endostatic quantities (all in kJ mol^{-1}) for the aquation of $[\mathrm{Fe}(5\mathrm{NO}_2\text{-phen})_2]^{2+}$ in two binary aqueous mixtures at 298.15 K in the presence of 0.054 mol dm^{-3} H_2SO_4

Mol fraction, x_2	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$T\Delta S^{\ddagger}$	$\Delta G_{\alpha}^{\ddagger}$	$\Delta H_{\alpha}^{\ddagger}$	$T\Delta S_{\alpha}^{\ddagger}$
0	92.0	120.9	28.9	92.0	120.9	28.9
t-Butyl alcohol–water mixtures *						
0.01	91.84	120.5	28.6	91.52	120.0	28.5
0.022	91.88	121.3	29.4	91.69	120.9	29.2
0.035	91.12	120.1	29.0	90.63	118.3	28.2
0.065	91.24	112.5	21.3	89.76	110.9	21.1
0.075	91.00	109.2	18.2	89.60	108.5	18.9
0.09	90.75	106.5	15.7	88.20	105.1	16.9
0.10	90.60	105.5	14.9	89.14	105.5	16.4
0.105	90.60	105.0	14.4	86.48	105.2	18.7
0.125	90.16	99.2	9.0	86.31	99.4	13.1
Acetone–water mixtures						
0.01	91.21	122.6 ± 1.1	31.4	91.06	122.0	30.1
0.05	90.97	121.9 ± 2.8	30.0	90.08	115.8	25.7
0.08	90.59	116.6 ± 2.4	26.0	89.19	106.6	17.4
0.11	90.21	115.5 ± 1.9	25.3	88.86	105.2	16.3
0.14	89.87	113.5 ± 1.1	23.6	88.50	102.2	13.7
0.16	89.63	112.0 ± 2.8	22.4	88.17	93.8	5.6
0.20	89.02	108.2 ± 4	18.2	87.07	93.4	6.3
0.28	88.20	102.0 ± 3.2	13.8			

* Rate constants taken from ref. 12.

meters were calculated using the Clarke–Glew method,[11] a computer program (ALGOL) being used to obtain these quantities at 298.15 K.

RESULTS

Mean values for the rate constant for reaction (1) in acetone–water mixtures of various compositions are reported in Table 1. The rate constants are the averages of three or more runs, the value being reproducible to within 3%. When acetone was first added to a solution in water, the rate constant remained almost unaffected until $x_2 \geqslant 0.1$ when it increased more rapidly. This behaviour is similar to that observed when t-butyl alcohol is added.[12] The activation parameters [equations (5) and (6)] are summarised in Table 2 and Figures 1 and 2, these values being calculated from the individual rate constants rather than the averaged values given in Table 1.

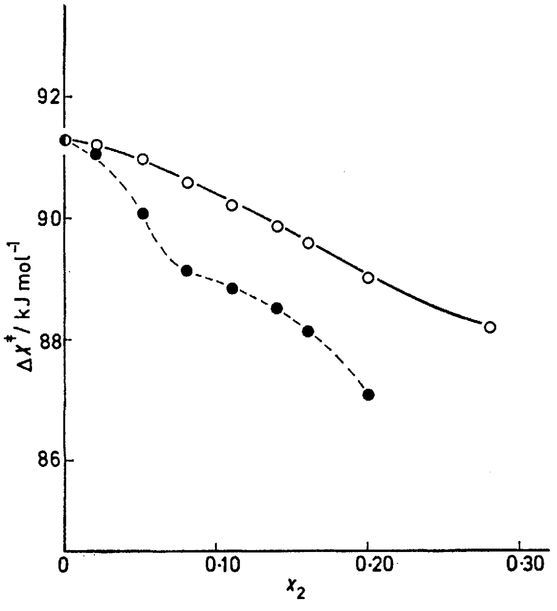

FIGURE 2 Comparison of conventional (○) and endostatic activation Gibbs function (●), $\Delta G^{\ddagger}$ and $\Delta G_{\alpha}^{\ddagger}$, at 298.2 K as a function of mol fraction of acetone

Analysis for Endostatic Quantities.—Having obtained the set of thermodynamic activation parameters given by equations (5) and (6), we now proceeded to calculate a related set of activation parameters for reaction under endostatic conditions. We identify this set by the subscript α, *e.g.* $\Delta G_{\alpha}^{\ddagger}$.

Definitions. In a binary liquid mixture, components 1 and 2, the activity of each component is equal to the product of its mole fraction and the rational activity coefficient, *i.e.* $a_1 = x_1 f_1$ and $a_2 = x_2 f_2$. For a system comprising a solute, component 3, in this mixture, the term endostatic indicates that the thermodynamic partial molar properties of the solute are defined such that the ratio ($\alpha = a_1 : a_2$) is held constant. For example, the (conventional) chemical potential of this solute is defined by $(\partial G/\partial n_3)_{n_1, n_2, T, P}$ where G is the total Gibbs function for the system. The endostatic chemical potential is defined with an additional constraint, *i.e.* $(\partial G/\partial n_3)_{\alpha,(n_1+n_2), T, P}$. Using the later definition the quantities $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ can be related [9] to the endostatic activation parameters, $\Delta G_{\alpha}^{\ddagger}$ and $\Delta H_{\alpha}^{\ddagger}$ respectively, using equations (7)—(9) [*cf.* equation (6)]. Similarly the change

$$\Delta G_{\alpha}^{\ddagger} = \Delta G^{\ddagger} - (\ln\alpha)(\mathrm{d}\Delta G^{\ddagger}/\mathrm{d}x_1)/(\mathrm{d}\ \ln\ \alpha/\mathrm{d}x_1) \qquad (7)$$

$$\Delta H_{\alpha}^{\ddagger} = \Delta H^{\ddagger} - (H_1^{\mathrm{E}} - H_2^{\mathrm{E}})(\mathrm{d}\Delta G^{\ddagger}/\mathrm{d}x_1)/(RT\ \mathrm{d}\ \ln\ \alpha/\mathrm{d}x_1) \qquad (8)$$

$$\Delta G_{\alpha}^{\ddagger} = \Delta H_{\alpha}^{\ddagger} - T\Delta S_{\alpha}^{\ddagger} \qquad (9)$$

in $\Delta G_{\alpha}^{\ddagger}$ on going from a solution in water to a solution in an aqueous mixture is given by $\delta_{\mathrm{m}}\Delta G_{\alpha}^{\ddagger}$. In equation (8), H_1^{E} and H_2^{E} are the relative partial enthalpies of the two solvent components of the mixture. For example, $H_1^{\mathrm{E}} = H_1 - H_1^{\bullet}$ where $H_1^{\bullet}$ is the partial molar enthalpy of component 1 in the mixture and H_1^{*} is the molar enthalpy of the pure component at the same temperature and pressure.

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[11] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

[12] J. Burgess, *J. Chem. Soc. (A)*, 1968, 1085.

[13] E. A. Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 151; G. Scatchard, *Chem. Rev.*, 1849, **44**, 7.

The molar excess Gibbs function of mixing for a binary liquid mixture is related to its composition by equation (10).

$$G^{\mathrm{E}} = RT \ln (x_1 \ln f_1 + x_2 \ln f_2) \qquad (10)$$

Differentiation of equation (10) with respect to x_1 and the Gibbs—Duhem relation yield [8] an expression, equation (11), for ln α, *cf.* equation (7). Differentiation of equation (11)

$$\ln \alpha = (1/RT)\{(\mathrm{d}G^{\mathrm{E}}/\mathrm{d}x_1) + \ln [x_1/(1 - x_1)]\} \qquad (11)$$

with respect to x_1 yields (12), which is an expression for a term common to both equations (7) and (8).

$$\mathrm{d} \ln \alpha/\mathrm{d}x_1 = (1/RT)[(\mathrm{d}^2G^{\mathrm{E}}/\mathrm{d}x_1^2) + (1/x_1x_2)] \qquad (12)$$

Properties of solvent mixtures. The dependence of G^{E} on x_2 for a binary liquid mixture can be represented by the Guggenheim–Scatchard [13] expression (13). Thus values

$$G^{\mathrm{E}} = x_1(1 - x_1) \sum_{i=1}^{n} A_i(1 - 2x_1)^{i-1} \qquad (13)$$

of G^{E} for a given binary mixture were fitted to equation (13) using a least-squares method.[4] The number of coefficients, n, was increased until the standard deviation between calculated and input values of G^{E} was a minimum. The computer program (ALGOL) provided the required coefficients, *i.e.* $A_1, A_2, A_3 \ldots A_n$. Using these coefficients, it is possible to calculate the quantities ln α and d ln α/dx_1 as required in equations (11) and (12) respectively. Thus with reference to equation (11), it follows from (13) that $\mathrm{d}G^{\mathrm{E}}/\mathrm{d}x_1$ can be calculated from these A coefficients as shown by equation (14). In the same way $\mathrm{d}^2G^{\mathrm{E}}/\mathrm{d}x_1^2$ can be calculated from

$$\mathrm{d}G^{\mathrm{E}}/\mathrm{d}x_1 = \left[\sum_{i=1}^{n} A_i(1 - 2x_1)^i\right] - \left[x_1(1 - x_1) \sum_{i=1}^{n} 2A_1(i - 1)(1 - 2x_1)^{i-2}\right] \qquad (14)$$

these coefficients using equation (15). If instead of G^{E} data, the dependences of the molar enthalpies of mixing on mol

$$\mathrm{d}^2G^{\mathrm{E}}/\mathrm{d}x_1^2 = \left[4x_1(1 - x_1) \sum_{i=1}^{n} A_i(i - 1)(i - 2)(1 - 2x_1)^{i-3}\right] - 2\left\{\left[\sum_{i=1}^{n} A_i i(1 - 2x_1)^{i-1}\right] + \left[\sum_{i=1}^{n} A_i(i - 1)(1 - 2x_1)^{i-1}\right]\right\} \qquad (15)$$

fraction are fitted to equation (13), the calculated intercepts of the tangent to the curve at x_1 on the $x_1 = 0$ and $x_2 = 0$ axes yield the relative molar enthalpies, $H_2 - H_2^{\bullet}$ and $H_1 - H_1^{\bullet}$ respectively [*cf.* equation (8)]. The gradient of this tangent is given by the analogue of equation (14).

The remaining term in both equations (7) and (8), *i.e.* $\mathrm{d}\Delta G^{\ddagger}/\mathrm{d}x_1$, was obtained by first fitting the dependence of $\Delta G^{\ddagger}$ on x_1 to a running polynomial, equation (16), through successive groups of three data points, i = 1—3. Then $\mathrm{d}\Delta G^{\ddagger}/\mathrm{d}x_1$ was

$$\Delta G^{\dagger}(i) = ax_1^2(i) + bx_1(i) + c \qquad (16)$$

calculated from the coefficients a and b at the middle point (i = 2). This series of calculations was completed using a small computer program (ALGOL).

Calculation. In the final stage of the analysis, the separate pieces of information were brought together in another small program. Here the input parameters were $\Delta G^{\ddagger}$ (or $\Delta H^{\ddagger}$) at various mol fractions of co-solvent, the n coefficients defined by equation (13), and the gradient $\mathrm{d}\Delta G^{\ddagger}/\mathrm{d}x_1$ [*cf.* equation (16)]. The output consisted of the various quantities such as ln α [*cf.* equation (11)] and the required endostatic activation parameters.

Application. Kinetic data for aquation of the iron complex, equation (1), in water–t-butyl alcohol and –acetone mixtures were combined with the thermodynamic properties for these two mixtures, obtained from the literature. The set of data given by Kenttamaa *et al* [14] was used for t-butyl alcohol–mixtures. The parameters obtained by Blandamer and Waddington [15] in their analysis of vapour-pressure [16] and enthalpy-of-mixing data[17] were used for acetone–water mixtures [see also ref. 18]. The calculated dependences of $\Delta G_{\alpha}^{\ddagger}$, $\Delta H_{\alpha}^{\ddagger}$, and $T\Delta S_{\alpha}^{\ddagger}$ on mol fraction are summarised in Figures 1 and 2.

DISCUSSION

The endostatic treatment of kinetic data is attractive because it combines two sets of data which, at least intuitively,[4] ought to be linked together quantatively, *i.e.* thermodynamic activation parameters and thermodynamic properties of the solvent mixture. However, the calculations do require reliable and self-consistent data. For example, the calculation of $\mathrm{d} \ln \alpha/\mathrm{d}x_1$ [*cf.* equation (12)] requires the second differential of the expression for G^{E} [equation (13)], thereby placing a heavy burden on the reliability of the G^{E} data. Indeed this second differential cannot be calculated with absolute confidence from published G^{E} data in all cases. Nevertheless some tests can be applied for thermodynamic consistency.[19] For example,[9] if $\mathrm{d} \ln (f_1/f_2)/\mathrm{d}x_1$ is negative then $\mathrm{d} \ln \alpha/\mathrm{d}x_1$ must be positive. Grunwald and Effio report [9] that this test fails for the data [14] used here for the t-butyl alcohol–water mixtures, although we observed that this criterion is satisfied for the water-rich mixtures over the range for which we have kinetic data.

Previously we suggested [3] that as the Fe–N bond breaks in the primary dissociative step of the aquation reaction (1) so more of the hydrophobic aromatic ring is exposed to the solvent. In these terms the transition state is more hydrophobic than the initial state. However, this feature of the reaction should only be of importance in aqueous systems containing sufficient water for the latter to comprise its characteristic three-dimensional hydrogen-bonded organisation. It might be anticipated therefore that as co-solvent is gradually added the nature of the mixture changes from being water-structure based to one where this structure is no longer extant and the plot of $\Delta G^{\ddagger}$ against x_2 ought to reflect this change.

There is now good evidence [20] from a wide range of

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[20] M. J. Blandamer in ' Water—A Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1973, vol. 2, ch. 9.

properties, spectroscopic, thermodynamic, and kinetic, that, near some mol fraction characteristic of the co-solvent, a change often occurs from a mixture in which the water structure is enhanced by the co-solvent to a structure-broken system. For example this change occurs near $x_2 = 0.04$ for t-butyl alcohol mixtures and near $x_2 = 0.06$ for acetone mixtures at *ca.* 298 K. Such features are shown by the typically aqueous (t.a.) class of co-solvents.[4,21] When x_2 exceeds these mole fractions, the properties of the mixture are indicative of extensive correlation between concentration fluctuations,[20] which in a limit can lead to phase separation at a lower critical solution temperature. This tendency is most marked at another mol fraction characteristic of the co-solvent, *e.g.* $x_2 = 0.5$ for acetone mixtures. Again as x_2 increases so this tendency diminishes and the properties of the mixture resemble those expected for a conventional mixture of two polar liquids.

Despite the dramatic changes in properties and structures of these aqueous mixtures in the water-rich range, $\Delta G^{\ddagger}$ usually changes gradually as x_2 increases.[22] This behaviour stems from a compensation [22–24] between changes in the solvent dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[25] It is therefore of some significance that the solvent dependence of $\Delta G_{\alpha}^{\ddagger}$ (*i.e.* $\delta_m \Delta G_{\alpha}^{\ddagger}$) provides some clear indication of the changes in mixture organisation near the mol fraction discussed above. In particular, the pattern observed for $\delta_m \Delta G_{\alpha}^{\ddagger}$ in the t-butyl alcohol–water mixtures shows in a striking way the importance of changes in the solvent structure in the $x_2 \simeq 0.04$ and $\simeq 0.1$ regions. Thus the endostatic quantity $\Delta G_{\alpha}^{\ddagger}$ is more sensitive to solvent than $\Delta G^{\ddagger}$ for the aquation of the iron complex [equation (1)] and for the aquation of t-butyl chloride.[9] Since the latter reaction is dissociative, the similarity of pattern is in agreement with the proposal that the aquation of the iron complex occurs by a dissociative mechanism.

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