Aquation of Tris(5-nitro-1,10-phenanthroline)iron(II) in Binary Aqueous Mixtures; Comparison of Kinetic Parameters for Reaction and Thermodynamic Properties of the Mixtures †

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Rate constants for the aquation of tris(5-nitro-1,10-phenanthroline)iron(II) have been determined in a wide range of binary aqueous mixtures. The results are presented and discussed in terms of correlation diagrams involving the excess molar Gibbs function of mixing for the binary mixtures. The behaviour of this iron(II) complex is compared and contrasted with that of t-butyl chloride. The possible advantages of this mode of treatment of kinetic results are outlined.

THE kinetics of a number of substitution reactions of transition-metal complexes have been investigated in a variety of mixed aqueous solvents.[1,2] Often the object of such studies has been to diagnose the nature of the mechanism from the variation of reactivity with solvent composition, using correlations of rates ‡ with, for example, functions of the bulk dielectric constant or empirical parameters such as Grunwald–Winstein solvent Y values.[4] Less often, attempts are made to interpret reactivity trends in terms of known physical properties of the solvent mixtures. The effect of solvent structure on reactivity has been described and discussed, in terms of viscosities and enthalpies of vaporisation, for reactions of metal(II) cations with 2,2′-bipyridyl;[5] the over-riding importance of viscosity in determining reactivity has been illustrated for reactions of metal(II) cations with pyridine-2-azo-4′-dimethylaniline.[6]

The reasons why the rate constant of a particular reaction in water at a fixed pressure and temperature changes when a co-solvent is added are many and various.[7] Nevertheless an important aspect of any discussion of these phenomena is the way in which the solvent, water, and co-solvent interact. An indication of the magnitude and dependence on composition of such interactions can be gained from the excess molar Gibbs function of mixing, G^E, for the mixture. One of our current interests is to see if such thermodynamic excess functions can be used to correlate reactivity patterns for inorganic substitution reactions.

A reaction which has proved a useful probe for medium effects on reactivities is aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in acidic media [equation (1)].

$$[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+} + 3\mathrm{H}^+ \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq}) + 3[\mathrm{5\text{-}NO_2\text{-}Hphen}]^+ \quad (1)$$

The rate-determining step in this reaction is loss of the first ligand;[8] this ligand loss appears to be dissociative.[9] The first object of the present paper is to extend the range of solvent systems described by reporting reactivity patterns for the co-solvents tetrahydrofuran (thf) and dimethyl sulphoxide (dmso). The second object is to see whether there is a correlation between the activation quantity $\Delta G^{\ddagger}$, as calculated from the observed rate constant using transition-state theory, and the thermodynamic excess function G^E for a wide range of solvent mixtures. We also compare the $\Delta G^{\ddagger}$–G^E pattern for aquation of $[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$ with that for solvolysis of t-butyl chloride, the organic S_N1 paradigm.

EXPERIMENTAL

Reagents.—Solutions containing tris(5-nitro-1,10-phenanthroline)iron(II) were prepared from AnalaR grade ammonium iron(II) sulphate and a slight excess of the ligand (B.D.H.). Organic co-solvents were of the best commercially available grade, redistilled when necessary (t-butyl alcohol and methanol).

Kinetic Runs.—These were made in duplicate or triplicate in 1 cm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Rate constants were computed on a PDP11 machine, using a standard least-mean-squares program.

RESULTS

Kinetics.—Experimentally determined first-order rate constants for the aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in tetrahydrofuran–water and in dimethyl sulphoxide–water mixtures, at 308.2 K, are reported in Tables 1 and 2 respectively. A few kinetic results for the aquation of tris(4,7-dimethyl-1,10-phenanthroline)iron(II) in these mixed solvents are reported in Table 3. First-order rate constants for aquation of $[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$ in a variety of mixed aqueous solvents, in sulphuric acid of concentration 0.54 mol dm^{-3} and at 298.2 K, are collected in Table 4. This Table also shows the calculated difference

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† No reprints available.

‡ Recent examples can be traced through references cited in ref. 2, for dielectric-constant correlations, and refs. 1—3 for Y-value correlations.

[1] See, for example, 'Inorganic Reaction Mechanisms,' ed. J. Burgess, *Chem. Soc. Specialist Periodical Reports*, 1971, vol. 1, pp. 163—166, 172—173, 201—204; 1972, vol. 2, pp. 150—151, 162—163, 168—169; 1974, vol. 3, pp. 182—184, 201—203, 318—324; C. H. Langford and V. S. Sastri, 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, *M.T.P. Internat. Rev. Sci.*, Butterworths, London, 1971, vol. 9, series 1, ch. 6.

[2] J. Burgess, 'Inorganic Reaction Mechanisms,' ed. A. McAuley, *Chem. Soc. Specialist Periodical Reports*, in the press.

[3] G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688.

[4] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[5] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2190, 2198, 2207.

[6] E. F. Caldin and M. W. Grant, *J.C.S. Faraday I*, 1973, 1648.

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

[8] 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.

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

in Gibbs free energy of activation for the reaction ($\delta_m\Delta G^\ddagger$) in the mixed solvents compared with that in water, and the

TABLE 1

First-order rate constants ($10^3k/s^{-1}$) for aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in tetrahydrofuran–water mixtures at 308.2 K

Acid	$HClO_4$	H_2SO_4	H_3PO_4	HCl	
Concentration/mol dm^{-3}	0.40	0.40	0.40	0.40	0.07
x (thf)					
0.0037		2.21	2.30	2.39	2.19
0.0076		2.09	2.51	2.35	1.98
0.0115		2.09	2.79	2.25	2.09
0.0156		2.21	3.5	2.46	2.69
0.024		2.51	4.1	2.83	3.5
0.033		3.0	5.1	3.7	3.9
0.042		3.2	6.9	4.2	
0.052		4.2	9.5	4.8	5.3
0.074	2.1	5.4	18	6.9	6.7
0.097	2.3	7.6	24	11.7	7.6
0.128	2.8	15.0		19	16
0.20	4.6	25	80	40	28
0.31	6.9			80	
0.47	8.5				

TABLE 2

First-order rate constants ($10^3k/s^{-1}$) for aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in dimethyl sulphoxide–water mixtures at 308.2 K

Acid	$HClO_4$	H_2SO_4	H_3PO_4	HCl	
Concentration/mol dm^{-3}	0.40	0.40	0.40	0.40	0.07
x (dmso)					
0.0043		2.35	2.21	2.48	
0.0087		2.48	2.48	2.67	
0.0132		2.67	2.30	2.58	
0.0178		2.85	2.94	2.71	
0.027		3.1	3.7	2.94	
0.038		3.4	4.2	2.94	3.0
0.048		3.8	6.2	3.6	
0.056		3.9	7.1	4.3	
0.084	2.5	4.8		5.7	4.1
0.112	3.2	5.8		7.8	5.5
0.144	5.0	6.9		11	

TABLE 3

First-order rate constants for aquation of tris(4,7-dimethyl-1,10-phenanthroline)iron(II) in tetrahydrofuran–water and in dimethyl sulphoxide–water mixtures at 308.2 K in H_2SO_4 (0.4 mol dm^{-3})

x (thf) *	$10^5k/s^{-1}$	x (dmso) *	$10^5k/s^{-1}$
0.024	2.9	0.027	8.4
0.074	3.0	0.084	6.9

* The rate constant under comparable conditions in aqueous solution is 10.8×10^{-5} s^{-1}.

TABLE 4

First-order rate constants for aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in mixed aqueous solvents; $[H_2SO_4] = 0.54$ mol dm^{-3}, 298.2 K. $\delta_m\Delta G^\ddagger$ Is the difference between the Gibbs free energy of activation for this cation in the solvent mixture stated and that in aqueous solution; G^E is the Gibbs free energy of mixing for each solvent mixture

Methanol

x_2	0.064	0.100	0.139	0.182	0.23
$10^4k/s^{-1}$	5.4	6.2	7.8	9.7	11.4
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−250	−600	−1 170	−1 710	−2 110
G^E/J mol^{-1}	150	211	262	303	335

TABLE 4 (*Continued*)

Ethanol

x_2	0.033	0.045	0.101	0.170
$10^4k/s^{-1}$	5.4	6.0	7.8	13
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−260	−520	−1 170	−2 440
G^E/J mol^{-1}	107	144	307	479

t-Butyl alcohol

x_2	0.064	0.075	0.087	0.112
$10^4k/s^{-1}$	7.8	8.4	9.9	12
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−1 200	−1 350	−1 770	−2 240
G^E/J mol^{-1}	364	415	466	571

Ethylene glycol

x_2	0.023	0.047	0.094
$10^4k/s^{-1}$	4.9	5.0	5.4
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−0.04	−0.08	−0.25
G^E/J mol^{-1}	−50	−110	−197
x_2	0.139	0.151	0.22
$10^4k/s^{-1}$	5.4	5.6	5.8
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−0.25	−0.34	−0.42
G^E/J mol^{-1}	−260	−288	−371

Glycerol

x_2	0.017	0.036	0.058
$10^4k/s^{-1}$	4.7	4.5	4.3
$\delta_m\Delta G^\ddagger$/J mol^{-1}	+90	+180	+300
G^E/J mol^{-1}	−47	−95	−150

Tetrahydrofuran

x_2	0.033	0.052	0.074
$10^4k/s^{-1}$	6.3	8.4	11
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−650	−1 400	−2 000
G^E/J mol^{-1}	222	341	466

Dioxan

x_2	0.015	0.023	0.031
$10^4k/s^{-1}$	5.3	6.5	7.2
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−210	−720	−970
G^E/J mol^{-1}	77	111	142

Acetone

x_2	0.075
$10^4k/s^{-1}$	7.3
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−1 000
G^E/J mol^{-1}	236

Acetonitrile *

x_2	0.013	0.026	0.040	0.054
$10^4k/s^{-1}$	4.9	5.0	5.4	5.6
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−20	−70	−260	−350
G^E/J mol^{-1}	70	137	206	272
x_2	0.086	0.122	0.160	
$10^4k/s^{-1}$	6.5	7.5	9.8	
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−720	−1 070	−1 730	
G^E/J mol^{-1}	415	561	701	

Dimethyl sulphoxide

x_2	0.018	0.027	0.038
$10^4k/s^{-1}$	5.6	5.9	6.3
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−330	−480	−640
G^E/J mol^{-1}	−133	−201	−270
x_2	0.060	0.084	0.112
$10^4k/s^{-1}$	7.4	7.7	8.6
$\delta_m\Delta G^\ddagger$/J mol^{-1}	−1 040	−1 140	−1 410
G^E/J mol^{-1}	−411	−555	−697

Hydrogen peroxide

x_2	0.020	0.040	0.061	0.082
$10^4k/s^{-1}$	4.73	4.63	4.28	4.13
$\delta_m\Delta G^\ddagger$/J mol^{-1}	+70	+120	+320	+410
G^E/J mol^{-1}	−66	−130	−191	−251
x_2	0.127	0.175	0.225	
$10^4k/s^{-1}$	3.87	3.60	3.15	
$\delta_m\Delta G^\ddagger$/J mol^{-1}	+570	+750	+1 070	
G^E/J mol^{-1}	−361	−463	−550	

* These results refer to $[H_2SO_4] = 0.50$ mol dm^{-3} and have been taken from ref. 33.

excess Gibbs free energy of mixing (G^{E}) for each solvent mixture.

All runs whose rate constants are given in Tables 1—4 went to completion. The relatively high concentrations of acid used were dictated by the reluctance of aquation of $[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$ to go to completion in some relatively organic-rich mixtures under weakly acidic conditions. It is for this reason that the range of mole fractions examined for dimethyl sulphoxide–water mixtures is relatively short; under the stated conditions of acid concentration and temperature, the aquation does not go to completion at mole fractions of dmso above *ca.* 0.15. The absence of results in perchloric acid media in water-rich mixtures (Tables 1 and 2) is an unavoidable consequence of the low solubility of the perchlorate of $[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$ in such solvent mixtures. The absence of results in aqueous t-butyl alcohol in mole fractions of t-butyl alcohol of *ca.* 0.03 arises from the immiscibility of the appropriate reaction mixtures at 298.2 K.

Analysis of Thermodynamic Properties.—The molar excess Gibbs function of mixing for a binary liquid mixture expresses the extent to which the molar Gibbs function of mixing at a given temperature, pressure, and mole fraction differs from that of the corresponding ideal liquid mixture. The dependence of G^{E} on mole fraction can be calculated from vapour-pressure data.[10] Because the mole fractions at which G^{E} (or related vapour-pressure data) has been determined do not correspond to the mole fractions at which kinetic data have been obtained, a method of interpolation for the requisite G^{E} values was required. We used the Guggenheim–Scatchard equation [11,12] (2) in which the dependence of G^{E} on x_2 is expressed in a general algebraic

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

form, where x_1 is the mole fraction of water in the binary aqueous mixture. The coefficients A_1—A_n were calculated by fitting G^{E} values to equation (2) using a least-squares technique [13] in an ALGOL program for an ICL 4130 computer. In each case the best fit was taken to correspond to the equation when the standard deviation was a minimum. In practice this depended on the number of data points and their accuracy. From the coefficients so calculated, values of G^{E} at other mole fractions would be readily calculated using a simple basic program for a PDP11 computer. The sources of the G^{E} data are outlined as follows. (*i*) Ethylene glycol–water. Trimble and Potts [14] expressed the dependence of vapour pressure on temperature for a fixed composition using a simple empirical equation. This equation was used to calculate the vapour pressures at 298 K, which were then used to calculate G^{E} values using a simplified version of the Barker method [13] (*i.e.* assuming the vapour to be an ideal gas). G^{E} Data were fitted to equation (2) using three coefficients; G^{E} is negative over the whole composition range, $0 < x_2 < 1.0$. (*ii*) t-Butyl alcohol–water. G^{E} Values [15] at 299 K were fitted to equation (2) using five coefficients; G^{E} is positive over the range $0 < x_2 < 1.0$. (*iii*) Methanol–water. G^{E} Values were obtained from the data given by Morcom,[16] who reported values at 308 K. The data were fitted to equation (2) using four coefficients, G^{E} being negative over the range $0 < x_2 < 1.0$. It was estimated that the corresponding G^{E} values at 298 K are only slightly different and that any difference does not affect the argument given below. (*iv*) Ethanol–water. Linderstrøm-Lang and Vaslow [17] reported G^{E} values for this mixture at 298 K and at low mole fractions of alcohol. Their data were combined with G^{E} values calculated from the vapour-pressure data reported by Dobson; [18] G^{E} is positive over the range $0 < x_2 < 1.0$ and the dependence was fitted using six coefficients in equation (2). (*v*) Dimethyl sulphoxide–water. G^{E} Values were taken from a table given by Kenttämaa and Lindberg,[19] these values being 'smoothed' from vapour-pressure data; G^{E} is negative over the range $0 < x_2 < 1.0$ and the data were fitted using three coefficients in equation (2). (*vi*) Tetrahydrofuran–water. G^{E} Values were taken from the compilation given by Treiner *et al.*; [20] G^{E} is positive over the range, $0 < x_2 < 1.0$ and the data were fitted using nine coefficients. (*vii*) Acetonitrile–water. G^{E} Values were calculated from vapour-pressure data reported by Vierk; [21] G^{E} is positive over the range $0 < x_2 < 1.0$ and the data were fitted using five coefficients. (*viii*) Acetone–water. G^{E} Values were calculated from liquid–vapour-equilibrium data reported by Taylor [22] using Barker's method; [13] G^{E} is positive over the whole range, the data being fitted using seven coefficients in equation (2). (*ix*) Dioxan–water. G^{E} Values were calculated from the data given by Vierk [21] (see also ref. 23); G^{E} is positive over the whole range, the data being fitted using seven coefficients in equation (2). (*x*) Hydrogen peroxide–water. The dependence of G^{E} on x_2 has been examined for this mixture by Scatchard *et al.*,[24] Maass and Giguère,[25] and Giguère *et al.*[26] The G^{E} values, taken from ref. 27, are negative at 348 K; they were fitted to four coefficients in equation (2). (*xi*) Glycerol–water. G^{E} Values, calculated [28] from the activity data reported by Scatchard *et al.*,[29] are negative over the whole range, being fitted to equation (2) using two coefficients.

DISCUSSION

There have already been several investigations of the kinetics of aquation of $[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$, equation (1), in mixed aqueous solvents. Organic co-solvents used

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[10] See, for example, J. S. Rowlinson, 'Liquids and Liquid Mixtures,' 2nd edn., Butterworths, London, 1969.

[11] E. A. Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 151.

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[17] C. U. Linderstrøm-Lang and F. Vaslow, *J. Phys. Chem.*, 1968, **72**, 2645.

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[20] C. Treiner, J. F. Bocquet, and M. Chemla, *J. Chim. phys.*, 1973, 72.

[21] A. L. Vierk, *Z. anorg. Chem.*, 1950, **261**, 283.

[22] A. E. Taylor, *J. Phys. Chem.*, 1900, **4**, 355.

[23] G. N. Malcolm, J. S. Rowlinson, and A. Davis, *Trans. Faraday Soc.*, 1957, **53**, 921.

[24] G. Scatchard, L. B. Ticknor, J. R. Goates, and E. R. McCartney, *J. Amer. Chem. Soc.*, 1952, **74**, 3721.

[25] O. Maass and P. A. Giguère, *Canad. J. Res.*, 1940, **B18**, 181.

[26] P. A. Giguère, O. Knop, and M. Falk, *Canad. J. Chem.*, 1958, **36**, 883.

[27] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, 'Hydrogen Peroxide,' Reinhold, New York, 1955, p. 246.

[28] M. Dupree, unpublished work.

[29] G. Scatchard, W. J. Hamer, and S. E. Wood, *J. Amer. Chem. Soc.*, 1938, **60**, 3061.

have included ethanol,[30] t-butyl alcohol,[31] dioxan,[32] acetonitrile,[33] and formic acid.[30] Detailed patterns of the variation of reactivity with solvent composition have been established for the co-solvents t-butyl alcohol[31] and acetonitrile.[33] Detailed patterns for the dependence of aquation rate constant on solvent composition for tetrahydrofuran–water and for dimethyl sulphoxide–water solvent mixtures are shown in Figure 1. Rate constants are sensitive to the nature and concentration of the acid added as well as to the composition of the solvent. The patterns for the co-solvents thf and dmso, including the few results for the analogous $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$ complex, are similar to those reported earlier for t-butyl alcohol and acetonitrile. This range of co-solvents embraces the three groups, t.a., t.n.a.p., and t.n.a.n., of the following classification of binary aqueous mixtures according to their thermodynamic characteristics of mixing. The established similarity of reactivity patterns permits us to proceed to a more detailed analysis of kinetic results in a variety of mixed aqueous solvents. But we must obviously ensure that we compare only results obtained under comparable conditions of nature and concentration of acid, preferably sulphuric acid at as low a concentration as is consistent with reaction (1) going to completion.

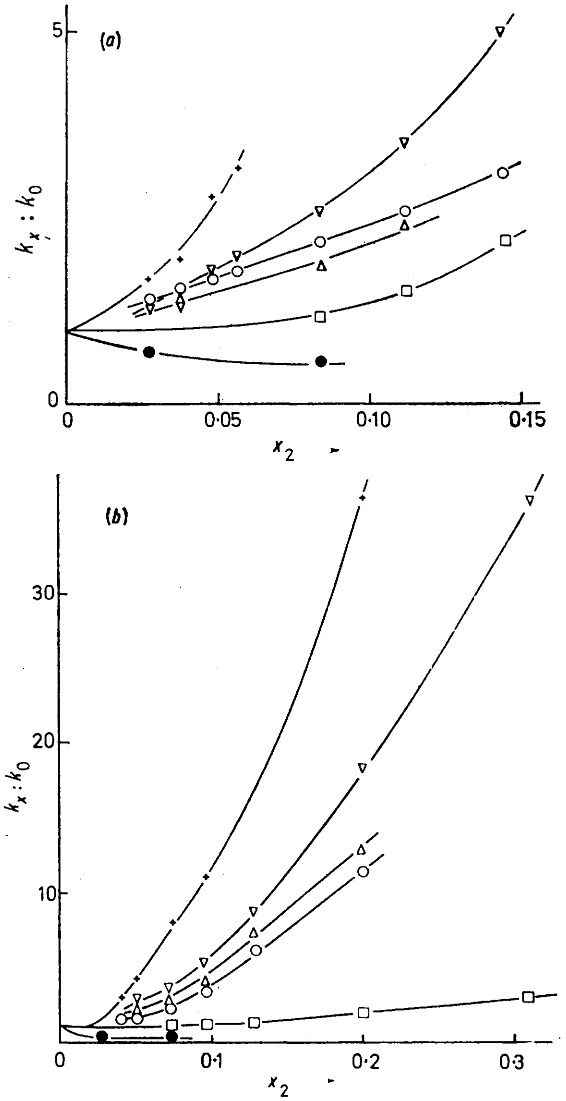

FIGURE 1 Ratios ($k_x : k_0$) of first-order rate constants for aquation of substituted tris(1,10-phenanthroline)iron(II) cations in binary aqueous mixtures (k_x = rate constant for reaction in aqueous mixture where the co-solvent mole fraction is x_2, and k_0 = rate constant for reaction in water *i.e.* where $x_2 = 0$) at 308.2 K (open symbols for the $5\text{-}NO_2phen$ complex, filled circles for the $4,7\text{-}Me_2phen$ complex). (*a*), Dimethyl sulphoxide–water; (*b*), tetrahydrofuran–water. (+), 0.40 mol dm^{-3} H_3PO_3; (▽), 0.40 mol dm^{-3} HCl; (△), 0.07 mol dm^{-3} HCl; (○) and (●), 0.40 mol dm^{-3} H_2SO_4; (□), 0.04 mol dm^{-3} $HClO_4$

Some time ago we noticed a similarity between plots of $\delta_m\Delta G^\ddagger$ [equation (3)] against x_2 for the aquation of

$$\delta_m\Delta G^\ddagger = \Delta G^\ddagger(x_2) - \Delta G^\ddagger(x_2 = 0) \qquad (3)$$

$[Fe(5\text{-}NO_2phen)_3]^{2+}$ and plots of G^E against x_2 for the respective solvent mixtures. At that time, our observations were limited to a few aqueous mixtures. Hence we embarked on our present investigation in which we have obtained more kinetic results for different types of aqueous mixtures, all at the same sulphuric acid concentrations and temperature. Because the basis of our approach is novel, we summarise briefly the background to the subject.

It is useful in this analysis to bear in mind the properties of two classic binary mixtures: (*a*) acetone–chloroform; and (*b*) methanol–carbon tetrachloride. In case (*a*), G^E is negative[34] over the whole composition range and this behaviour can be attributed to intercomponent hydrogen bonding between acetone and chloroform which is more intense than the acetone–acetone and chloroform–chloroform interactions. In contrast, G^E for system (*b*) is positive because methanol–methanol hydrogen-bonding interactions are stronger than intercomponent interactions. It is also noteworthy that in both cases the sign and magnitude of G^E are determined to a major extent by the sign and magnitude of the molar excess enthalpy, H^E. Indeed for non-aqueous systems, it is a general rule that $|H^E| > |TS^E|$ where T is the temperature and S^E is the molar excess entropy of mixing. Aqueous mixtures can be classified using these ideas as guidelines.[35]

Typically aqueous (t.a.) mixtures are characterised by positive G^E values where the size and magnitude of G^E is determined by TS^E rather than H^E, *i.e.* $|TS^E| > |H^E|$. Indeed, the importance of entropy quantities is a characteristic of aqueous systems. Examples of co-solvents in t.a. mixtures are methanol, ethanol, t-butyl alcohol, dioxan, and thf. Typically non-aqueous (t.n.a.)

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[30] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.

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

[32] J. Burgess, F. M. Mekhail, and E. R. Gardner, *J.C.S. Dalton*, 1973, 1335.

[33] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.

[34] J. S. Rowlinson, 'Liquids and Liquid Mixtures,' 2nd edn., Butterworths, London, 1969.

[35] F. Franks in 'Hydrogen-bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 31.

mixtures are characterised by $|H^E| > |TS^E|$, but G^E can be either positive (t.n.a.p.) or negative (t.n.a.n.). For example, acetonitrile–water is a t.n.a.p. system but hydrogen peroxide–water and dimethyl sulphoxide–water are examples of t.n.a.n. systems.

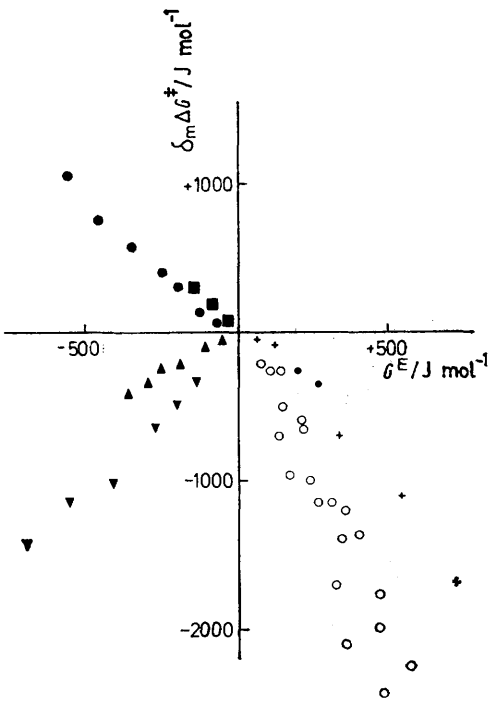

FIGURE 2 Relation between $\delta_m\Delta G^\ddagger$ and G^E for aquation of tris(5-nitro-1,10-phenanthroline)iron(II). T.a. mixtures are represented by open circles, (○), t.n.a.p. mixtures by crosses (+) and t.n.a.n. mixtures by solid symbols [(●), hydrogen peroxide; (■), glycerol; (▲), glycol; (▼), dimethyl sulphoxide]

It is seen therefore that our kinetic data cover reactions in the three types of systems, t.a., t.n.a.n., and t.n.a.p. Figure 2 is a plot of all our comparable kinetic results for aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$ against the respective G^E values for the solvent mixtures. What is most striking about this Figure is that all the results for solvent mixtures containing t.a. co-solvents (of which we have used eight) fall into one narrow sector. In other words there is a marked correlation between $\delta_m\Delta G^\ddagger$ and G^E for this reaction in such solvent mixtures. Further, the plot of $\delta_m\Delta G^\ddagger$ against G^E for acetonitrile–water solvent mixtures (t.n.a.p.) lies close to the t.a. results. The situation with regard to t.n.a.n. mixtures is not clear. It could be argued that glycerol- and hydrogen peroxide–water mixtures can be included in the t.a.–t.n.a.p. correlation simply by extending the correlation line back through the origin. We would prefer to postpone speculation on the results in t.n.a.n. mixtures until we have examined kinetic patterns for other inorganic reactions, in order to see whether the pattern for these t.n.a.n. solvents is universal. Our conclusions apply to water-rich solvents. The refusal of the title reaction to proceed to completion in co-solvent-rich mixtures prevents us from defining how extensively our correlation holds in such mixtures.

In view of the similarity of mechanism between the aquation of this iron(II) complex and solvolysis of t-butyl chloride, it is interesting to compare Figure 2 with an analogous plot for the latter reaction. Kinetic data for this solvolysis are available for binary aqueous mixtures containing methanol,[36,37] ethanol,[36,38] t-butyl alcohol,[38] thf,[39] dioxan,[36,38] acetone,[36,40] acetonitrile,[39] dmso,[41] ethylene glycol,[42] glycol,[42] and hydrogen peroxide [43] as co-solvent. We have calculated $\delta_m\Delta G^\ddagger$ values from these rate constants, and G^E values as described above; the results are plotted in Figure 3. There are certain features common to Figures 2 and 3. For solvolysis of t-butyl chloride, the same clustering of points for t.a. mixtures in one narrow sector is observed and again the results for the t.n.a.p. mixtures containing acetonitrile are close to these. However, whereas the points for aquation of the iron(II) complex for t.a. and t.n.a.p. mixtures fall in the negative $\delta_m\Delta G^\ddagger$–positive G^E quadrant, those for solvolysis of t-butyl chloride in t.a. and t.n.a.p. mixtures all fall in the positive $\delta_m\Delta G^\ddagger$–positive G^E quadrant. This difference is attributed to the different natures of the respective leaving groups. As the 5-NO_2phen departs from the iron, exposure of more of the hydrophobic periphery of this ligand renders the transition state more hydrophobic than the initial state.[44] In contrast, the hydrophilic nature of the chloride ion renders the transition state for the reaction

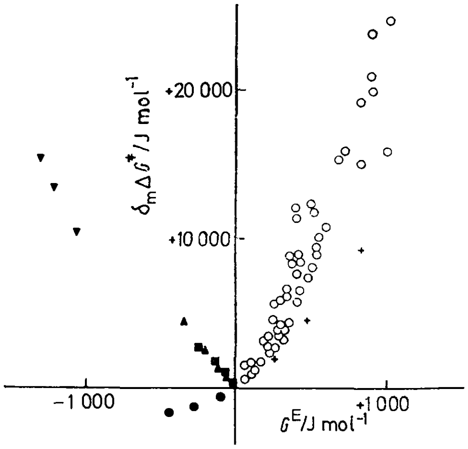

FIGURE 3 Relation between $\delta_m\Delta G^\ddagger$ and G^M for the solvolysis of t-butyl chloride; symbols as in Figure 2

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of t-butyl chloride more hydrophilic than the initial state. The situation for the t.n.a.n. mixtures is more complicated (*cf.* previous paragraph).

Correlation diagrams of the type depicted in Figures 2 and 3 provide a convenient and informative summary of experimental information. They are, we believe, potentially important since they are based on two quantities both of which reflect intercomponent interactions, and both of which can be directly determined. We feel that analyses of this type should provide a slightly less empirical approach to the diagnosis of reaction mechanisms from solvent effects on reactivities. Related correlation diagrams for enthalpies and for entropies (*i.e.* for $\delta_m\Delta H^\ddagger - H^E$ and for $T\delta_m\Delta S^\ddagger - TS^E$) may also prove valuable, when the availability of a greater body of appropriate kinetic data for both organic and inorganic reactions permits their construction.

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