Influence of Solvation on the Initial and Transition States for Anation Reactions of Transition-metal Complexes in Mixed Aqueous Solvents

By **Cecil F. Wells**, Department of Chemistry, University of Birmingham, Edgbaston, P.O. Box 363, Birmingham B15 2TT

A free-energy cycle has been applied to the rate-determining step in mixed aqueous solvents for the anation of cations having all aquo-ligands or only one aquo-ligand together with a variety of other ligands. Combining rate data with activities of water and calculated values for the equilibrium constants for outer-sphere complexes of the incoming ligand with the cation in the mixture, the relative effects of changes of solvation in the initial and transition states can be assessed. At mole fractions of co-solvent less than those where sharp structural changes occur in the mixture, changes of solvation in either the initial or in the transition state may dominate, depending on the identity of the incoming ligand and of the complex cation; but, in general, at mole fractions of co-solvent higher than those where the sharp changes in solvent structure occur, changes in solvation in the initial state have a dominant effect on the rates.

In water, the substitution of a ligand X^{m-} into an aquo-complex $M^{n+}_{aq.}$ proceeds *via* the rapid formation of an outer-sphere complex followed by a slow loss of water from $M^{n+}_{aq.}$ with X^{m-} occupying the site vacated in the inner sphere,[1] as in (1). The observed second-order rate

$$M^{n+}_{aq.} + X^{m-}_{aq.} \overset{K}{\rightleftharpoons} M^{n+}_{aq.}\cdot X^{m-}_{aq.} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} MX^{(n-m)+}_{aq.} + H_2O \quad (1)$$

constant $k_w = Kk_f$, provided $K[X^{m-}_{aq.}] \ll 1$ and $k_d \ll k_f$. Although, in pure water, $k_f = k_{ex.}$, the rate of exchange of solvent between the inner sphere of M^{n+} and the bulk solvent, in many other pure solvents, $k_f \neq k_{ex.}$: mechanism (1) probably needs some modification in these latter solvents.[2] To investigate the effects of changes in the solvation of M^{n+} on the rate of anation without change in mechanism, it is therefore preferable to use water with varying amounts of added co-solvent, rather than to compare rates in a range of pure solvents.

However, it has been suggested [3] that for M^{n+} and $X^{m-} = NH_3$ in water–methanol the observed increase in rate at low mole fractions, x_2, of methanol is due to the preferential operation of (2) over (1). Although the free

$$M^{n+}MeOH_{aq.} + X^{m-}_{aq.} \overset{K'}{\rightleftharpoons} M^{n+}MeOH\cdot X^{m-}_{aq.} \underset{k_d'}{\overset{k_f'}{\rightleftharpoons}} MX^{(n-m)+}_{aq.} + MeOH \quad (2)$$

energy of transfer, $\Delta G^{\ominus}_t$, of M^{n+} from water into water–methanol [4a] for $M^{n+} = Na^+$ or K^+, is positive and $\Delta G^{\ominus}_t \sim 0$ for Rb^+ and Cs^+ at $x_2 < 0.3$ and compares with the conclusions from n.m.r. experiments [5] that unipositive alkali metals (excluding Li^+) are preferentially solvated by H_2O rather than MeOH, $\Delta G^{\ominus}_t$ for bipositive transition-metal ions shows that they are more stable in water–methanol at $x_2 < 0.3$ than in water.[4a] However, it is unlikely that all this stabilization results from the influence of MeOH on the inner sphere of M^{n+}; [4b,6] it would appear that the *maximum* possible proportion of inner-sphere complex $Ni^{2+}MeOH_{aq.}$ is 10% of the total Ni^{2+} for x_2 *ca.* 0.3,[3] which compares well with the maximum result for $Ni^{2+}(EtOH)_{aq.}$.[6] Moreover, it has been shown using substituted aquo-complexes $ML^{n+}_{aq.}$ in water [7] and other pure solvents,[8] where L is an electron-releasing ligand, that the presence of L increases the rate of loss of a water molecule from $ML^{n+}_{aq.}$. Therefore, the inductive effect of the alkyl group of any alcohol molecule in the inner sphere of M^{n+} might be expected to increase the reactivity of an H_2O molecule in the inner sphere rather than be ejected itself. Further, in mechanism (2) for varying X^{m-} with $|m| = 0$, K will vary little with solvent composition [2] at low x_2 and with K (water)/K (mixture) ~ 1, $k_s/k_w \sim k_{ex.}$ (mixture)/$k_{ex.}$ (water), where k_s is the observed second-order rate constant in the mixture. For mechanism (2) with $|m| = 0$ for the same M^{n+}, $k_{ex.}$ (mixture)/$k_{ex.}$ (water) should be relatively invariant with X^{m-}, resulting in k_s/k_w always varying in the same way with increasing x_2 for a range of X^{m-}. However, contrary to this expectation, for $M^{n+} = Ni^{2+}$ with increasing x_2, k_s/k_w increases [3] for $X^{m-} = NH_3$ and decreases for $X^{m-} =$ 2,2′-bipyridine(bipy) [9] and 1,10-phenanthroline(phen); [10] ring closure for the bidentate ligands has no influence on the rate.[7] In addition, the enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, of activation for $X^{m-} =$ bipy with $M^{n+} = Ni^{2+}$ show [9] extrema in the same region of x_2 where the physical properties of the water–methanol mixture show extrema; [11] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for these reactions also show [12] extrema in water–ethanol and water-t-butyl alcohol in the same composition range where the physical properties of the respective mixtures exhibit extrema.[11] This, together with the above, strongly suggests that it is the structural changes in the bulk solvent mixture responsible for the extrema in the physical properties which largely control the variation of rate with solvent composition in water-rich mixtures, for a rate-determining step involving the loss of a water molecule from the inner sphere of solvated $Ni^{2+}_{aq.}$. Thus, solvation changes in both the inner and outer spheres will cause the rate constant to vary for the loss of water from $Ni^{2+}_{aq.}$. Naturally, at high mole fractions of co-solvent, the reaction will move towards a mechanism of type (2); but this may not occur until $x_2 \sim$ 0.7—0.8.[3,9]

RESULTS AND DISCUSSION

The Effect of Solvation Changes on the Initial and Transition States.—In order to assess the relative effects of changes in solvation on the initial and transition states of (3), it is necessary to know how close the $M^{n+}\cdots H_2O$

$$\underset{\text{initial state}}{M^{n+}{}_{aq.}\cdot X^{m-}{}_{aq.}} \rightleftharpoons \underset{\text{transition state}}{M^{n+}{}_{aq.}\cdot X^{m-}{}_{aq.}\cdots H_2O} \longrightarrow \underset{\text{final state}}{MX^{(n-m)+}{}_{aq.} + H_2O} \qquad (3)$$

bond in the transition state is to complete rupture. The overall process is clearly of the S_N1/I_d type of reaction; and in pure water the equation of k_f and $k_{ex.}$ suggests that the reaction is really an S_N1/D type with the $M^{n+}\cdots H_2O$ bond virtually completely broken.[1,7] Considerable support is afforded to this from the published data on volumes of activation $\Delta V^{\ddagger}$ for the overall process (1) in pure water, which is a sensitive measure[13] of changes in bonding occurring between the initial and transition states. Values of $\Delta V^{\ddagger}$ for X^{m-} = ammonia,[14] pyridine-2-azo-dimethylaniline,[14] glycine,[15] imidazole,[16] or the murexide ion (mur)[17] with M^{n+} = Ni^{2+}, Co^{2+}, Cu^{2+}, or Zn^{2+} lie in the range 5—12 cm^3 mol^{-1}. For complete loss of a water molecule from the inner sphere of M^{n+} calculated on the basis of changes in electrostriction,[13] $\Delta V^{\ddagger} \sim$ 15 cm^3 mol^{-1}, if the five-co-ordinate $M^{n+}{}_{aq.}$ in the transition state has the same volume as the six-co-ordinate $M^{n+}{}_{aq.}$ in the initial state. With this same assumption, for the transference of a spherical water molecule to a structured area of liquid water[11] using half the O–O distance[18] in ice I as the radius of H_2O, a value of 7 cm^3 mol^{-1} might be expected for $\Delta V^{\ddagger}$. If these are the lower and upper limits expected for the complete loss of an H_2O molecule from the inner sphere of the above $M^{2+}{}_{aq.}$, then $\Delta V^{\ddagger} \sim$ 7—15 cm^3 mol^{-1} compares well with the experimental range 5—12 cm^3 mol^{-1}.

Assuming that the $M^{n+}\cdots H_2O$ bond is sufficiently stretched in the transition state as to be regarded as broken, with no movement as yet of $X^{m-}{}_{aq.}$ from the outer into the inner sphere, a free-energy cycle can be constructed connecting the process initial state→transition state in pure water and in the mixture of water and co-solvent. If $M^{n+}{}_{aq.}H_2O_{aq.}\cdot X^{m-}{}_{aq.}$ and $M^{n+}H_2O_s\cdot X^{m-}{}_s$ are the outer-sphere complexes of six-co-ordinate M^{n+} in the initial state in water and in the mixture respectively, and $M^{n+}{}_{aq.}\cdot X^{m-}{}_{aq.}$ and $M^{n+}{}_s\cdot X^{m-}{}_s$ are the five-co-ordinate outer-sphere complexes of M^{n+} in the transition state in water and the mixed solvent, then the cycle shown in the Scheme can be constructed. The species $H_2O_{aq.}$ and H_2O_s are the expelled water molecules accommodated in the structure of pure water and of the mixed solvent respectively. $\Delta G^{\ddagger}{}_w$ and $\Delta G^{\ddagger}{}_s$ are the free energies of activation in pure water and in the mixture respectively. $\Delta G^{\ominus}{}_t(M^{n+}H_2O\cdot X^{m-})$, $\Delta G^{\ominus}{}_t(M^{n+}{}_{aq.}\cdot X^{m-})$, and $\Delta G^{\ominus}{}_t(H_2O)$ are the free energies of transfer of the outer-sphere complexes of six-co-ordinated M^{n+}, of the outer-sphere complex of five-co-ordinated M^{n+}, and of a water molecule, respectively, between pure water and the mixture.

$$\begin{tikzcd}
M^{n+}H_2O_{aq.}\cdot X^{m-}{}_{aq.} \arrow[r, "\Delta G^{\ddagger}{}_w"] & M^{n+}{}_{aq.}\cdot X^{m-}{}_{aq.} \arrow[r, dash, dashed] \arrow[d, "\Delta G^{\ominus}{}_t(M^{n+}{}_{aq.}\cdot X^{m-})"] & H_2O_{aq.} \arrow[d, "\Delta G^{\ominus}{}_t(H_2O)"] \\
M^{n+}H_2O_s\cdot X^{m-}{}_s \arrow[u, "-\Delta G^{\ominus}{}_t(M^{n+}H_2O\cdot X^{m-})"] \arrow[r, "\Delta G^{\ddagger}{}_s"] & M^{n+}{}_s\cdot X^{m-}{}_s \arrow[r, dash, dashed] & H_2O_s
\end{tikzcd}$$

SCHEME

Equation (4) follows from this cycle. If k_w' and

$$\Delta G^{\ddagger}{}_s = \Delta G^{\ddagger}{}_w - \Delta G^{\ominus}{}_t(M^{n+}H_2O\cdot X^{m-}) + \Delta G^{\ominus}{}_t(M^{n+}{}_{aq.}\cdot X^{m-}) + \Delta G^{\ominus}{}_t(H_2O) \qquad (4)$$

k_s' are the first-order rate constants for the dissociation of an H_2O molecule from the inner co-ordination sphere of $M^{n+}H_2O_{aq.}\cdot X^{m-}$ in water and in the mixed solvent respectively, equation (4) can be rearranged to equation (5). Now, the overall second-order rate constants, k_w and k_s, are related to k_w' and k_s' by equations (6) and (7), where

$$2.303\,RT\log(k_w'/k_s') - \Delta G^{\ddagger}{}_w(H_2O) = \Delta G^{\ominus}{}_t(M^{n+}{}_{aq.}\cdot X^{m-}) - \Delta G^{\ominus}{}_t(M^{n+}H_2O\cdot X^{m-}) \qquad (5)$$

σ_w and σ_s are the statistical factor in water and in the mixed solvent, respectively, to allow for the differing chances of substitution by an H_2O and an X^{m-} in the outer

$$k_w = \sigma_w k_w' K_w \qquad (6)$$

$$k_s = \sigma_s k_s' K_s \qquad (7)$$

sphere,[19] and K_w and K_s are the values of K for the outer-sphere complex in water and in the mixed solvent, respectively. $\Delta G^{\ominus}{}_t(H_2O)$ is given by equation (8),

$$\Delta G^{\ominus}{}_t(H_2O) = G_w - G^{\ominus}{}_w = 2.303\,RT\log a_w \qquad (8)$$

where a_w is the activity of water in the mixture, relative to $a_w = 1.0$ in pure water. Substituting from equations (6)—(8) into (5), equation (9) is obtained. Since $\Delta G^{\ominus}{}_t$

$$2.303\,RT\{\log(k_w/k_s) + \log(\sigma_s/\sigma_w) + \log(K_s/K_w) - \log a_w\} = \Delta G^{\ominus}{}_t(M^{n+}{}_{aq.}\cdot X^{m-}) - \Delta G^{\ominus}{}_t(M^{n+}H_2O\cdot X^{m-}) \qquad (9)$$

(M^{n+}) values in mixtures of water with co-solvents such as alcohols, dioxan, and dimethyl sulphoxide (dmso) (excluding some values for $n = +1$ in H_2O–methanol) are all negative at low x_2 of co-solvent,[4,20] then, if the left-hand side of equation (9) is positive, $\Delta G^\ominus_t(M^{n+}\text{-}H_2O\cdot X^{m-})$ will dominate over $\Delta G^\ominus_t(M^{n+}_{aq.}\cdot X^{m-})$, and *vice versa* if the left-hand side of (9) is negative. Therefore, in their effect on the overall rate a positive value for the l.h.s. of equation (9) indicates that changes of solvation in the initial state dominate and a negative value for the l.h.s. of equation (9) indicates that changes of solvation in the transition state dominate. A similar free-energy cycle and an equation analogous to (9) will apply to the anation of complexes $[ML_5(OH_2)]^{n+}$ where L may be a variety of non-aquo-ligands.

Application of Equation (9).—Throughout, data for k_w and k_s at 25 °C are used. It is unlikely that the statistical factor changes with solvent composition provided x_2 is low, so it is assumed that the ratio $\sigma_s/\sigma_w = 1.0\ a_w = \rho_w/\rho^\ominus_w$, where ρ_w is the partial vapour pressure of water in the mixture and $\rho^\ominus_w$ is the vapour pressure of pure water: values for ρ_w were obtained from the literature for methanol,[21] ethanol,[22] t-butyl alcohol,[23] dioxan,[24] acetone,[25] ethylene glycol,[26] and dmso.[27]

Table of results at 25 °C

M^{n+}	X^{m-}	Largest ligand on M^{n+}	Co-solvent	r(nm)	Ref. for rate data	Added ionic strength (mol dm^{-3})	Dominance of change in solvation
$[Co(NH_3)_5(OH_2)]^{3+}$	Cl^-	OH_2	EtOH	0.421	*a*	0.1	init.
$Ni^{2+}_{aq.}$	bipy	OH_2	EtOH	0.556	12, *b*		init.
$Ni^{2+}_{aq.}$	bipy	OH_2	MeOH	0.556	9		init.
$Ni^{2+}_{aq.}$	bipy	OH_2	Bu^tOH	0.556	12, *b*		init.
$Ni^{2+}_{aq.}$	pada	OH_2	Bu^tOH	0.558	*c*		trans. →init.
$Ni^{2+}_{aq.}$	NH_3	OH_2	MeOH	0.450	3	0.10	trans. →init.
$Ni^{2+}_{aq.}$	phen	OH_2	MeOH	0.556	10	0.05	init.
$Ni^{2+}_{aq.}$	$Hphen^+$	OH_2	MeOH	0.556	10	0.05	trans. →init.
1,6-$[Co(dmg)_2(OH_2)(tmtu)]^+$	tmtu	tmtu	EtOH	1.135	*d*	0.04	init.
1,6-$[Co(dmg)_2(OH_2)(tmtu)]^+$	tmtu	tmtu	Dioxan	1.135	*d*	0.04	init.
1,6-$[Co(dmg)_2(OH_2)(etu)]^+$	etu	etu	Dioxan	1.135	*d*	0.04	trans.
1,6-$[Co(dmg)_2(OH_2)(etu)]^+$	etu	etu	EtOH	1.135	*d*	0.04	trans.
1,6-$[Co(dmg)_2(OH_2)(tu)]^+$	tu	dmg	EtOH	0.925	*e*	0.04	trans. →init.
$[Co(OH_2)(NH_2Et)(en)_2]^{3+}$	Cl^-	NH_2Et	Dioxan	0.705	*f*	0.001	init.
$[Co(OH_2)(NH_2Et)(en)_2]^{3+}$	Cl^-	NH_2Et	Glycol	0.705	*f*	0.001	init.
1,6-$[Rh(dmg)_2(OH_2)(tu)]^+$	Cl^-	dmg	Acetone	0.833	*g*	0.05	trans. →init.
1,6-$[Rh(dmg)_2(OH_2)(tu)]^+$	Cl^-	dmg	EtOH	0.833	*g*	0.05	init.
1,6-$[Rh(dmg)_2(OH_2)(NO_2)]$	Cl^-	OH_2 [h]	Glycol	0.525	*i*	0.05	init.
1,6-$[Rh(dmg)_2(OH_2)(NO_2)]$	Cl^-	OH_2 [h]	EtOH	0.525	*i*	0.05	init.~trans.
$Ni^{2+}_{aq.}$	mur	OH_2	EtOH	0.582	*j*	0.10	trans.
$Ni^{2+}_{aq.}$	mur	OH_2	dmso	0.582	*j*	0.10	trans.
$Ni^{2+}_{aq.}$	mal	OH_2	Dioxan	0.511	*k*	0.10	trans.

The prefix 1,6 in formulae of octahedral complexes indicates that the unidentate ligands are in *trans* positions; init. = initial, trans. = transition state.

[a] G. R. H. Jones, R. C. Edmondson, and J. H. Taylor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1952. [b] J. F. Coetzee, personal communication. [c] E. F. Caldin and P. Godfrey, *J.C.S. Faraday I*, 1974, 2260. [d] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1435. [e] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1576. [f] V. D. Panasyuk and L. G. Reiter, *Russ. J. Inorg. Chem.*, 1966, **11**, 329. [g] G. P. Syrtsova and T. S. Bolgar, *Russ. J. Inorg. Chem.*, 1974, **19**, 856. [h] Since there is no charge on the complex, it is assumed that Cl^- does not remain near negatively charged NO_2^- or dmg; treated *via* equation (14) as ion–dipolar interaction involving Cl^- and H_2O. [i] G. P. Syrtsova and T. S. Bolgar, *Russ. J. Inorg. Chem.*, 1973, **18**, 1140. [j] C. T. Lin and J. L. Bear, *J. Phys. Chem.*, 1971, **75**, 3705. [k] R. A. Howard, D. R. Underdown, and J. L. Bear, *J. Inorg. Nuclear Chem.*, 1977, **39**, 105.

Values for K_w and K_s at low ionic strengths are given by equation (10),[28] where r = the distance from the

$$K = (4\pi N r^3/3\,000)\ e^U \qquad (10)$$

centre of M^{n+} to the centre of X^{m-} in the outer-sphere complex. For an anionic X^{m-}, U is given by (11), where

$$U = |nm|\ e^2/2.303r\boldsymbol{k}TD_s = 24.348\ |nm|/rD_s \qquad (11)$$

D_s is the dielectric constant of the solvent mixture. For a dipolar X^{m-} (*i.e.* $|m| = 0$), U is given by (12), where μ is the dipole moment of X^{m-}. Therefore, at low ionic strengths, for anionic X^{m-}, equation (13) holds and where $|m|$ = zero, we have equation (14). However, some of

$$U = ne\mu/2.303\boldsymbol{k}Tr^2D_s = 5.07 \times 10^{17}\ |n|\ \mu r^{-2}/D_s \qquad (12)$$

$$\log\ (K_s/K_w) = 24.348\ |nm|\ r^{-1}\ (D_s^{-1} - D_w^{-1}) \qquad (13)$$

$$\log\ (K_s/K_w) = 5.07 \times 10^{17}\ |n|\ \mu r^{-2}\ (D_s^{-1} - D_w^{-1}) \qquad (14)$$

the rate data used for anionic X^{m-} were obtained at ionic strengths varying between 0.001 and 0.1 mol dm^{-3}, so the actual K' at ionic strength I was calculated using equation

$$\log\ (K_s'/K_w') = \log\ (K_s/K_w) + 2\log\ ({}_sf_\pm/{}_wf_\pm) + \log\ ({}_wf_c/{}_sf_c) \qquad (15)$$

(15) where $f_\pm$ is the mean activity coefficient for M^{n+} and X^{m-} and f_c is the activity coefficient for the outer-sphere complex. Using the Davies relation,[29] $-\log f_\pm = 0.50\ z_+z_-[\sqrt{I}/(1 + \sqrt{I}) - 0.20\ I]$, for activity coefficient, where I = ionic strength, (15) becomes (16), where z = $(n - m)$ is the overall ionic charge on the outer-sphere complex. Values for D_s were interpolated from the values in the literature for the following co-solvents: methanol,[30,31a] ethanol,[30,31b,c,32] t-butyl alcohol,[33,34] dioxan,[35] acetone,[32,36] ethylene glycol,[30] and dmso.[37]

$$\log\ (K_s'/K_w') = \log\ (K_s/K_w) + 345[\sqrt{I}/(1 + \sqrt{I}) - 0.2\,I](D_s^{-\frac{3}{2}} - D_w^{-\frac{3}{2}})(z^2 - 2|nm|) \qquad (16)$$

To determine values for r, it is first necessary to assess the relative sizes of the ligands attached to the metal atom using the bond lengths and angles available:[38] it is always assumed that the largest ligand on the metal atom is interposed between M^{n+} and X^{m-}. Thermochemical radii[39] were used for $Ni^{2+}_{aq.}$ and $[Co(NH_3)_5(OH_2)]^{3+}$ {represented by $[Co(NH_3)_6]^{3+}$} and the crystallographic radii[39] for Co^{3+} and Rh^{3+} in the other complexes and for $X^{m-} = Cl^-$. Crystallographic data[40] for bipy were used to calculate the dimensions of pyridine when X^{m-} = bipy and phen, whereas spectroscopic data[41] were used for pyridine in pyridine-2-azo-*p*-dimethylaniline (pada). Although pada chelates across the pyridine N and an azo N,[42] it is not known which is attached first; but it is established[43] that, as with bipy and phen,[7] ring closure does not interfere with the substitution kinetics. The dimensions of *p*-benzoquinone[38] were used to assess *r* for X^{m-} = murexide ion. Van der Waals radii[39] were used as required to complete the values for *r*. The Table shows the largest ligand attached to each M^{n+}, together with the value found for *r*. Dipole moments used[44] were (C m × 10^{30}) 4.90 for NH_3, 6.17 for H_2O, 7.31 for pyridine (in bipy, phen, and pada), and 16.31 for thiourea (tu): the value of 16.34 × 10^{-30} C m for *sym*-diethylthiourea[45] was used for both ethylenethiourea (etu) and tetramethylthiourea (tmtu).

The Table contains a complete list of the complexes to which the cycle has been applied, together with the identity of the added co-solvent and the source of the kinetic data. When additions of salt were made to achieve a higher constant ionic strength, this latter value is indicated. If the values of rate constant have been quoted at 25 °C, these are used directly: otherwise values for the rate constants at 25 °C were calculated from the transition-state parameters. The results of the application of equation (9) with all corrections necessary are shown in Figures 1—4 classified according to the identity of the co-solvent.

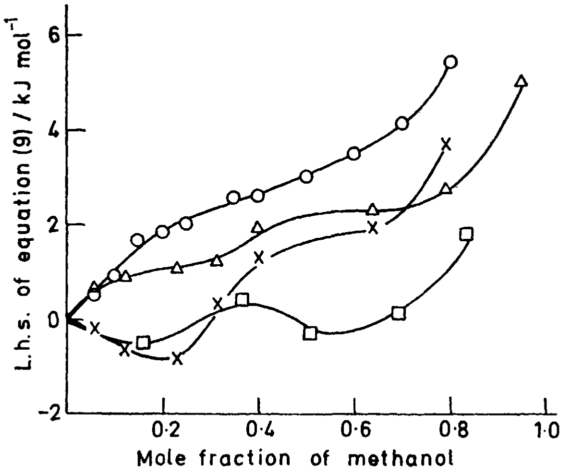

FIGURE 1 Values for the l.h.s. of equation (9) at 25 °C in water–methanol mixtures for the substitution in $Ni^{2+}_{aq.}$ by the following ligands: bipy (○); ammonia (□); phen (△); and the 1,10-phenanthrolinium cation (×)

A glance at these figures shows that, in general, positive values of the l.h.s. of equation (9) are obtained, suggesting that usually changes in solvation of the initial state have a dominant effect on the rate. This contrasts with aquation reactions,[46] where, usually, changes in solvation of the transition state have a dominant effect on the rate.

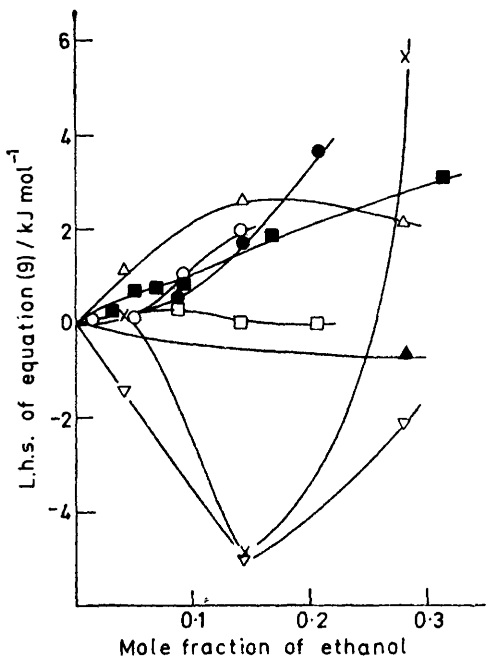

FIGURE 2 Values for the l.h.s. of equation (9) at 25 °C in water–ethanol mixtures for substitution in the following complexes by the ligands stated: $[Co(NH_3)_5(OH_2)]^{3+}$ by Cl^- (○); $Ni^{2+}_{aq.}$ by bipy (■); 1,6-$[Co(dmg)_2(OH_2)(tmtu)]^+$ by tmtu (△); 1,6-$[Co(dmg)_2(OH_2)(tu)]^+$ by tu (×); 1,6-$[Co(dmg)_2(OH_2)(etu)]^+$ by etu (▽); 1,6-$[Rh(dmg)_2(OH_2)(tu)]^+$ by Cl^- (●); 1,6-$[Rh(dmg)_2(OH_2)(NO_2)]$ by Cl^- (□); $Ni^{2+}_{aq.}$ by the murexide anion (▲)

However, a more detailed look at Figures 1—4 shows that there are a few significant deviations from the above conclusion. In water–methanol (Figure 1), for X^{m-} =

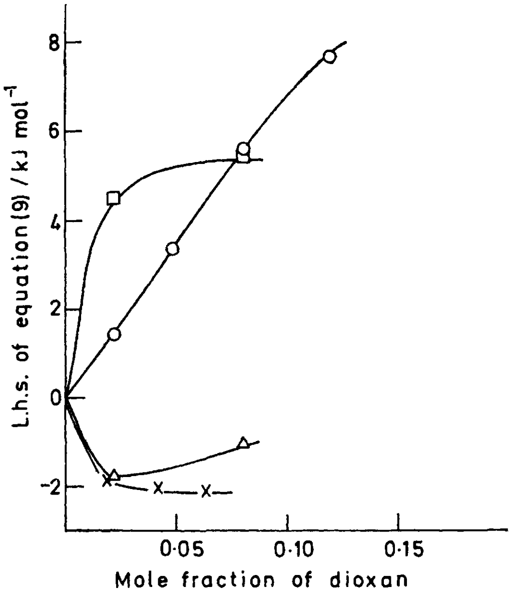

FIGURE 3 Values of the l.h.s. of equation (9) at 25 °C in water–dioxan mixtures for substitution in the following complexes by the ligands stated: $[Co(OH_2)(NH_2Et)(en)_2]^{3+}$ by Cl^- (○); 1,6-$[Co(dmg)_2(OH_2)(tmtu)]^+$ by tmtu (□); 1,6-$[Co(dmg)_2(OH_2)(etu)]^+$ by etu (△); $Ni^{2+}_{aq.}$ by $(malonate)^{2-}$ (×)

NH_3 and $M^{n+} = Ni^{2+}_{aq.}$, the l.h.s. of (9) hovers about zero showing perhaps equal influence of solvation on the initial and transition states; it seems likely that a similar situation exists for X^{m-} = the phenanthrolinium cation at low mole fractions of co-solvent. In water–ethanol (Figure 2), changes in solvation of the transition state dominate for X^{m-} = tu and etu and M^{n+} = a complex cobalt(III) cation containing X^{m-} already substituted, at least for $x_2 \leqslant 0.25$; for $X^{m-} = Cl^-$ with the neutral complex of Rh^{III} and X^{m-} = mur with $Ni^{2+}_{aq.}$, there is almost an equal effect of solvation on the initial and transition states. For water–t-butyl alcohol, Figure 4 suggests that for $x_2 < 0.04$ and X^{m-} = pada with $Ni^{2+}_{aq.}$ changes in solvation in the transition state may dominate before switching to a strong dominance of solvation changes in the initial state for $x_2 > 0.04$. With dioxan as co-solvent, etu with the complex of Co^{III} already containing etu (as found also in water–ethanol), and malonate (mal) with $Ni^{2+}_{aq.}$, show that changes in solvation in the transition state dominate at low x_2. In water–dmso, the murexide ion with $Ni^{2+}_{aq.}$ shows about equal effects operating in the initial and transition states, and in water–acetone Cl^- with the rhodium(III) complex shows a domination of solvation changes in the transition state for $x_2 < 0.06$.

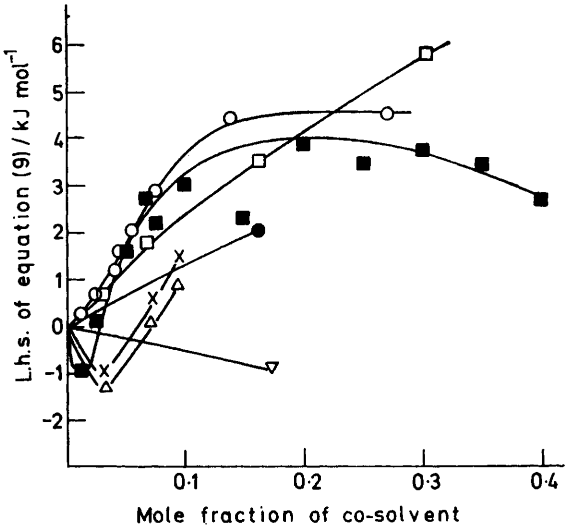

FIGURE 4 Values of the l.h.s. of equation (9) at 25 °C in water–co-solvent mixtures. For Bu^tOH as co-solvent and substitution of $Ni^{2+}_{aq.}$ by bipy (○) and pada (■). For dmso as co-solvent and substitution of $Ni^{2+}_{aq.}$ by the murexide anion (▽). For ethylene glycol as co-solvent and substitution of the following complexes by chloride anions: 1,6-$[Rh(dmg)_2(OH_2)(NO_2)]$ (●); $[Co(OH_2)(NH_2Et)(en)_2]^{3+}$ (□). For acetone as co-solvent and substitution of 1,6-$[Rh(dmg)_2(OH_2)(tu)]^+$ by Cl^- using the vapour pressure data for water of Taylor (△) and of Beare, McVicar, and Ferguson (×)

These changes in sign of the l.h.s. of equation (9) over the values of x_2 quoted above correlate quite well with the regions where sharp changes in solvent structure occur in these mixtures.[4,11,20] At compositions with x_2 less than the mole fraction where these changes in the structure occur, changes in solvation in either the initial or transition state may dominate; but, at compositions where x_2 is greater than the mole fractions where these sharp changes in solvent structure occur, changes in solvation of the initial state appear to have a dominant effect on the rates.

Finally, it is perhaps pertinent to enquire whether any of the assumptions made in the above analysis or any of the quantities used have errors sufficiently large to invalidate the above conclusions. We can examine the relative importance of the terms used in equation (9) and their effects on the all important sign of the two sides.

The analysis on the right-hand side depends on $\Delta G^{\ominus}_t(M^{n+})$ being, in general, negative. Values of $\Delta G^{\ominus}_t$ for individual ions used here are derived from values for $\Delta G^{\ominus}_t(H^+)$ calculated by the author.[4,20] This latter quantity comprises an electrostatic term, $\Delta G^{\ominus}_t(H^+)_e$, calculated from the application of the Born equation to the transfer of the tetrahedral species $H_3O^+(OH_2)_4$, and a non-electrostatic term, $[\overset{+}{R}OH_2] \times \Delta G^{\ominus}_t(\overset{+}{R}OH_2)$, where $\overset{+}{R}OH_2$ represents those of the species $H_3O^+(OH_2)_4$ in which the co-solvent induces a change in the mixed solvent: $\Delta G^{\ominus}_t(\overset{+}{R}OH_2)$ is given by equation (17) where

$$\Delta G^{\ominus}_t(\overset{+}{R}OH_2) = -RT\ln K'' \qquad (17)$$

K'' is the thermodynamic equilibrium constant for (18) with $x \geqslant 5$. If $H^+(OH_2)_{x\ solv.}$; = P and $H^+[(OH_2)_{x-1}(ROH)]_{solv.} = \overset{+}{R}OH_2$, $K_c = [\overset{+}{R}OH_2]/[P][ROH]$ and $F_c = f_{\overset{+}{R}OH_2} f_{H_2O}/f_P f_{ROH}$ (where the activity coefficient $f \longrightarrow 1$ as [ion] $\longrightarrow 0$ and [co-solvent] $\longrightarrow 0$), $K'' = K_c[H_2O]F_c$:

$$H^+(OH_2)_{x\ solv.} + ROH_{solv.} \overset{K''}{\rightleftharpoons} H^+[(OH_2)_{x-1}(ROH)]_{solv.} + H_2O_{solv.} \qquad (18)$$

values for $K_cF_c^{-1}$ are derived experimentally from the spectrophotometric examination of *p*-nitroaniline in the mixtures.[4,20,47] Values for $\Delta G^{\ominus}_t(X^-)$ are then derived from $\Delta G^{\ominus}_t(HX)$ using these values of $\Delta G^{\ominus}_t(H^+)$, and then values for $\Delta G^{\ominus}_t(M^{n+})$ can be derived from $\Delta G^{\ominus}_t(MX_n)$ and the values for $\Delta G^{\ominus}_t(X^-)$.[4,20] It is noteworthy, that other methods used for the separation of $\Delta G^{\ominus}_t(MX_n)$ into values of $\Delta G^{\ominus}_t$ for individual ions,[48] which depend on assumptions quite different from the above, also produce $\Delta G^{\ominus}_t(M^{n+})$ which are in general negative, although values for $\Delta G^{\ominus}_t(M^{n+})$ for any particular M^{n+} differ numerically among the methods used for the separation.[48] The method used here for producing values of $\Delta G^{\ominus}_t$ for individual ions is really only valid [4,20] for x_2 values up to approximately 0.30: hence, all other assumptions concerned with the application of equation (9) have to be assessed critically for the region x_2 = 0—0.30.

On the left-hand side of equation (9), the importance of the term in log a_w relative to that in log (k_w/k_s) varies considerably, not only from one system to another but with solvent composition for any particular system. However, although sometimes numerically the two terms are added and sometimes subtracted, it is rare for the log a_w term to induce a change in sign of the term in $\log(k_w/k_s)$: this only happens at one or two solvent compositions for $Ni^{2+}_{aq.}$ with NH_3 and with the phenanthrolinium cation in water–methanol and for *trans*-$[Co(dmg)_2$-

$(OH_2)(tu)]^+$ (dmg = dimethylglyoximate) with thiourea in water–ethanol. The term in log (K_s/K_w) rarely exceeds 10—20% of the combined term in log (k_w/k_s) and log a_w and is frequently <10% of this combined term. The only examples where this term changes the sign of the combined term are $Ni^{2+}_{aq.}$ with the murexide ion in water–ethanol, $Ni^{2+}_{aq.}$ with NH_3 in water–methanol, and $[Co(NH_3)_5(OH_2)]^{3+}$ with Cl^- in water–ethanol. The corrections to this term in log (K_s/K_w) for ionic strength by equation (16), where required, are only very small and never influence this sign of the l.h.s. of equation (9). Nevertheless, the validity of assumption that only coulombic effects *via* the Born equation appear in the calculation of log (K_s/K_w) should be explored, as solvational changes are known to contribute [4,20] considerably to values for $\Delta G^{\ominus}_t$ for individual ions. In the calculation of log (K_s/K_w) we are dealing only with the formation of outer-sphere complexes, and values for log K_s for these determined from conductivity measurements in mixtures of water and co-solvent, provided in general $K_s > 10$,[49–51] frequently vary linearly with D_s^{-1}, as required by this assumption: values of $K_s < 10$ produced by the computer analysis of conductivity data can be very unreliable.[49–51] Examples of such linear plots are found for the following outer-sphere complexes in mixtures of water with the co-solvent indicated: $[NEt_4]$-[pic] (pic = picrate),[52] $Mn[SO_4]$ (at least over a fair range of [MeOH]),[53] and M(*m*-bzds) (bzds = benzenedisulphonate) [53,54] where M = Ca^{2+}, Sr^{2+}, and Mn^{2+} (over a reasonable range of [MeOH]) with methanol; KBr and RBr where R = NMe_4^+, NEt_4^+, NPr_4^+, and NBu_4^+ with ethanol;[55] NaCl, $Na[ClO_3]$, $Na[ClO_4]$, and $Li[ClO_4]$ with Bu^tOH;[56] $Mn[SO_4]$,[57] $PbCl^+$,[58] $La[Fe(CN)_6]$,[59] and Mn(*m*-bzds) [60] with ethylene glycol; $Mn[SO_4]$,[61] Mn(*m*-bzds),[61] and $La[Fe(CN)_6]$ [59] with acetone; $Mn[SO_4]$,[62] Mn(*m*-bzds),[62] $Na[NO_3]$,[63] $Tl[NO_3]$,[64] KCl,[65] CsI,[65] NaCl at 50 °C,[66] NaCl at 25 °C (nearly linear),[67] $Na[BrO_3]$,[68] $[NBu^n_4]I$,[68] $[NBu^n_4]Br$,[68] $[NEt_4][ClO_4]$,[51] $[NEt_4]Br$,[51,69] $La[Fe(CN)_6]$,[59] K(bzs) (bzs = benzenesulphonate),[70] K(*p*-bzds),[70] LiCl,[71] and the following nearly linear, TlCl,[72] $K[NO_3]$,[73] $Ag[NO_3]$,[73] RbI [74] with dioxan; $K[IO_3]$ with glycerol (nearly linear, contrary to the plot shown in the ref.);[75] KI with dmso (with some deviations).[50] It seems reasonably safe to conclude, therefore, that, in the formation of outer-sphere complexes in these aqueous mixtures as in equation (1), structural effects only have a minimal influence, at least on differences in ln K_s: the assumption of the dependence of log (K_s/K_w) only on coulombic effects appears to be justified, especially in a relatively narrow region like x_2 = 0—0.30.

Lastly, there is the assumption that the ligand in the outer sphere exchanges only with a water molecule in the inner sphere. There are two aspects to this: first, in the water–co-solvent mixture do the co-solvent molecules penetrate into the inner sphere to any significant extent; and secondly, do any co-solvent molecules which succeed in doing this subsequently exchange with the ligand in the outer sphere? Although the answer to the second of these is the important one, it depends partially on the extent to which the first occurs. In the absence of any tendency of the co-solvent to exchange with the ligand, the first effect will be contained within the solvational change covered by equations of the same type as (18) and therefore contained within $\Delta G^{\ominus}_t(M^{n+})$: consequently, in the absence of any direct evidence for co-solvent–ligand exchange, a small extent of penetration of co-solvent into the inner sphere suggests that the co-solvent–ligand exchange can be neglected. The extent of this penetration of the co-solvent into the inner sphere may be judged from the relative preference which cations show for H_2O molecules or co-solvent molecules, as indicated by cation n.m.r. measurements or by p.m.r. measurements. Direct evidence for the co-solvent–ligand exchange may be obtained from the application of relaxation techniques and particularly from the number of relaxation processes seen within any particular system. The earlier discussion for the simple alcohols, based on the small extent of penetration of the co-solvent into the inner sphere, suggests that co-solvent–ligand exchange can be neglected with these co-solvents for x_2 = 0—0.30: this is supported by ultrasonic experiments with $Mn[SO_4]$ in water–methanol,[76] where Mn^{2+} shows a preference for H_2O in its inner sphere. For dioxan, a few ^{23}Na n.m.r. measurements suggest a preference for dioxan in the inner sphere,[5] but p.m.r. measurements for mixtures containing Co^{2+} or Al^{3+} suggest a preference for water: [77,78] this latter view is supported by ultrasonic investigations with Mn^{2+}.[76] Likewise, p.m.r. measurements suggest a preference for water over acetone in the inner sphere of Al^{3+}.[78] With ethylene glycol as co-solvent, a rough analysis of the $^{133}Cs^+$ n.m.r. results of Richards and co-workers [79] using the relationship of Covington *et al.*[5] suggests a strong preference for water in the inner sphere: moreover, kinetic observations using ultrasonics on mixtures containing $Zn[SO_4]$ show that only a water molecule in the inner sphere of Zn^{2+} is exchanged for SO_4^{2-} at $x_2 \leqslant 0.25$.[80] N.m.r. measurements with $^7Li^+$ and $^{133}Cs^+$ in water–dimethyl sulphoxide suggest [81] about equal preference for H_2O and dmso, but when the results of Briggs and Hinton [82] using $^{205}Tl^+$ are analysed roughly using the relationship of Covington *et al.*[5] they suggest a strong preference for dmso: this latter view is supported by the p.m.r. results for Ni^{2+} and Co^{2+},[78] and preference is found for dmso at $x_2 > 0.2$ for Ag^+ [83] and Al^{3+} [79] and for Be^{2+} in water-rich conditions changing with Be^{2+} to preference for H_2O in dmso-rich conditions.[84] Moreover, pressure-jump experiments with $Be[SO_4]$ in water–dmso show [85] other relaxations in addition to that derived from the exchange of SO_4^{2-} with an H_2O in complexes $[Be(OH_2)_{4-y}(dmso)_y]^{2+}$: that assigned to exchange of SO_4^{2-} with dmso in $[Be(OH_2)_3(dmso)]^{2+}$ is observed at $x_2 \geqslant 0.10$. Consequently, although it seems safe to conclude that, as for simple alcohols, based on the small degree of penetration of the co-solvent into the inner sphere, when dioxan, ethylene glycol, or acetone are the co-solvent, the exchange of the ligand with a co-solvent molecule in the inner sphere can also be neglected, this may not be the case for cations in water–dmso. However, this latter stricture only applies to one system in the Table, and even here only rates at $x_2 < 0.18$ are used. In general, if only on statistical grounds, any deviation from this conclusion will be more likely to occur with cations where only H_2O is present in the inner sphere of the original complex, like $Ni^{2+}{}_{aq.}$, rather than, as with most examples in the Table, with complexes where only one H_2O group is present in the inner sphere. Finally, it is noteworthy that $SO_4{}^{2-}$ shows[85] only one relaxation involving exchange with H_2O in the inner sphere of all the complexes $[Be(OH_2)_{4-y}(dmso)_y]^{2+}$ for $y = 0$—4, supporting the view above that the main effect of dmso molecules in this case is contained within the solvation effects as represented by an equation of the same type as (18).

[9/1034 *Received*, 2nd *July*, 1979]

REFERENCES

[1] M. Eigen and R. G. Williams, *Adv. Chem. Ser.*, 1965, **49**, 55.

[2] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2191; *J. Solution Chem.*, 1973, **2**, 217.

[3] W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1971, **93**, 4379; F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 1496.

[4] C. F. Wells, (*a*) *J.C.S. Faraday I*, 1973, 984; (*b*) *J.C.S. Faraday Discuss.*, 1977, **64**, 248.

[5] A. K. Covington, K. E. Newman, and T. H. Lilley, *J.C.S. Faraday I*, 1973, 973; A. K. Covington and K. E. Newman, *Adv. Chem. Ser.*, 1976, **155**, 153.

[6] R. F. Pasternack and R. A. Plane, *Inorg. Chem.*, 1965, **4**, 1176.

[7] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

[8] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1976, **15**, 400; J. F. Coetzee and D. M. Gilles, *ibid.*, p. 405.

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

[10] M. L. Sanduja and W. MacF. Smith, *Canad. J. Chem.*, 1969, **47**, 3773.

[11] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[12] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[13] D. R. Stranks, *Pure Appl. Chem.*, 1974, **38**, 303.

[14] E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *J.C.S. Faraday I*, 1972, 2267.

[15] M. W. Grant, *J.C.S. Faraday I*, 1973, 560.

[16] A. D. Yu, M. D. Waissbluth, and R. A. Grieger, *Rev. Sci. Instr.*, 1973, **44**, 1390.

[17] A. Jost, *Ber. Bunsengesellschaft Phys. Chem.*, 1975, **79**, 850.

[18] D. Eisenberg and W. Kauzmann, ' The Structure and Properties of Water,' Oxford University Press, 1969, ch. 3.

[19] J. Neely and R. Connick, *J. Amer. Chem. Soc.*, 1970, **92**, 3476.

[20] C. F. Wells, *J.C.S. Faraday I*, 1974, 694; 1975, 1868; 1976, 601; 1978, 636, 1569; *J.C.S. Faraday Discuss.*, 1977, **64**, 248; *Adv. Chem. Ser.*, 1979, **177**, 53; and unpublished work.

[21] J. A. V. Butler, D. W. Thomson, and W. H. Maclemnan, *J. Chem. Soc.*, 1933, 674.

[22] H. J. E. Dobson, *J. Chem. Soc.*, 1925, **127**, 2866; R. Shaw and J. A. V. Butler, *Proc. Roy. Soc.*, 1930, **A129**, 519.

[23] J. Kenttämaa, E. Tommila, and M. Martti, *Ann. Acad. Sci. Fennicae*, 1959, No. 93; A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1962, 1608.

[24] A.-L. Vierk, *Z. anorg. Chem.*, 1950, **261**, 283; A. L. Bacarella, A. Finch, and E. Grunwald, *J. Phys. Chem.*, 1956, **60**, 573.

[25] A. E. Taylor, *J. Phys. Chem.*, 1900, **4**, 355, 676; W. G. Beare, G. A. McVicar, and J. B. Ferguson, *ibid.*, 1930, **34**, 1310.

[26] H. M. Trimble and W. Potts, *Ind. and Eng. Chem.*, 1935, **27**, 66.

[27] J. J. Lindberg and J. Kenttämaa, *Suomen Kem.*, 1960, **B33**, 98.

[28] J. E. Prue, ' Ionic Equilibria,' Pergamon, Oxford, 1966, ch. 11.

[29] C. W. Davies, *J. Chem. Soc.*, 1938, 2093; ' Ionic Association,' Butterworths, London, 1962, ch. 3.

[30] G. Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

[31] (*a*) A. R. Martin and A. C. Brown, *Trans. Faraday Soc.*, 1938, **34**, 742; (*b*) J. Wyman, *J. Amer. Chem. Soc.*, 1931, **53**, 3292; (*c*) J. L. Hall and H. O. Phillips, *Proc. W. Va. Acad. Sci.*, 1954, **26**, 26.

[32] W. Graffunder and E. Heymann, *Z. Physik*, 1932, **72**, 744.

[33] A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1962, 1608.

[34] T. L. Broadwater and R. L. Kay, *J. Phys. Chem.*, 1970, **74**, 3802.

[35] F. E. Critchfield, *J. Amer. Chem. Soc.*, 1953, **75**, 1991.

[36] P. S. Albright, *J. Amer. Chem. Soc.*, 1937, **59**, 2098.

[37] J. J. Lindberg and J. Kenttämaa, *Suomen Kem.*, 1960, **B33**, 104.

[38] ' Interatomic Distances,' *Special Publ.*, The Chemical Society, London, 1958, no. 11; 1965, no. 18.

[39] M. C. Ball and A. H. Norbury, ' Physical Data for Inorganic Chemists,' Longmans, London, 1974, pp. 133—146.

[40] L. L. Merritt and E. D. Schroeder, *Acta Cryst.*, 1956, **9**, 801.

[41] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectroscopy*, 1958, **2**, 301.

[42] I. M. Kotz and W. C. Loh Ming, *J. Amer. Chem. Soc.*, 1953, **75**, 4159.

[43] R. G. Wilkins, *Inorg. Chem.*, 1964, **3**, 520; M. A. Cobb and D. N. Hague, *J.C.S. Faraday I*, 1972, 932.

[44] ' Handbook of Physics and Chemistry,' 53rd edn., CRC Press Inc., Cleveland, 1972—73, pp. E63—66.

[45] E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 1933, 87.

[46] C. F. Wells, *J.C.S. Faraday I*, 1977, 1851.

[47] C. F. Wells, *Trans. Faraday Soc.*, 1965, **61**, 2194; 1966, **62**, 2815; 1967, **63**, 147; C. F. Wells and C. Barnes, *ibid.*, 1970, **66**, 1154; C. F. Wells, *J.C.S. Faraday I*, 1972, 993; *J. Phys. Chem.*, 1973, **77**, 1994, 1997.

[48] R. G. Bates, in ' Hydrogen-Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, pp. 49—86; O. Popovych, *Crit. Rev. Anal. Chem.*, 1970, **1**, 73; B. G. Cox, R. Natarajan, and W. E. Waghorne, *J.C.S. Faraday I*, 1979, 1780.

[49] C. F. Mattina and R. M. Fuoss, *J. Phys. Chem.*, 1975, **79**, 1604.

[50] A. D'Aprano, J. Komiyama, and R. M. Fuoss, *J. Solution Chem.*, 1976, **5**, 279.

[51] M. Tissier and G. Douhéret, *J. Solution Chem.*, 1978, **1**, 87.

[52] F. Accascina, A. D'Aprano, and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1959, **81**, 1058.

[53] C. J. Hallada and G. Atkinson, *J. Amer. Chem. Soc.*, 1961, **83**, 3759.

[54] H. Tsubota and G. Atkinson, *J. Amer. Chem. Soc.*, 1965, **87**, 164.

[55] R. L. Kay and T. L. Broadwater, *J. Solution Chem.*, 1976, **5**, 57.

[56] F. Accascina, R. De Lisi, and M. Goffredi, *Electrochim. Acta*, 1970, **15**, 1209; 1971, **16**, 101.

[57] S. Petrucci, P. Hemmes, and M. Battistini, *J. Amer. Chem. Soc.*, 1967, **89**, 5552.

[58] J. C. James, *J. Amer. Chem. Soc.*, 1949, **71**, 3243.

[59] J. C. James, *J. Chem. Soc.*, 1950, 1094.

[60] P. Hemmes and S. Petrucci, *J. Amer. Chem. Soc.*, 1969, **91**, 275.

[61] G. Atkinson and S. Petrucci, *J. Amer. Chem. Soc.*, 1964, **86**, 7.

[62] G. Atkinson and C. J. Hallada, *J. Amer. Chem. Soc.*, 1962, **84**, 721.

[63] M. V. Ramana-Murti and R. C. Yadav, *Electrochim. Acta*, 1972, **17**, 643.

[64] A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, 1968, **72**, 4710.

[65] J. E. Lind and R. M. Fuoss, *J. Phys. Chem.*, 1961, **65**, 999.

[66] T. H. Leong and L. A. Dunn, *J. Phys. Chem.*, 1972, **26**, 2294.

[67] R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, 1963, **67**, 911.

[68] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1957, **79**, 3304.

[69] N. G. Foster and E. S. Amis, *Z. phys. Chem.*, 1965, **7**, 360.

[70] B. R. Staples and G. Atkinson, *J. Phys. Chem.*, 1967, **71**, 667.

[71] T. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, 1964, **68**, 971.

[72] A. D'Aprano and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1969, **91**, 279.

[73] I. D. McKenzie and R. M. Fuoss, *J. Phys. Chem.*, 1969, **73**, 1501.

[74] T. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, 1964, **68**, 974.

[75] H. Sadek, A. M. Hafez, and F. Y. Khalil, *Electrochim. Acta*, 1969, **14**, 1089.

[76] G. Atkinson and S. K. Tor, *J. Phys. Chem.*, 1965, **69**, 128.

[77] L. S. Frankel, T. R. Stengle, and C. N. Langford, *Canad. J. Chem.*, 1968, **46**, 3183.

[78] S. Thomas and W. L. Reynolds, *Inorg. Chem.*, 1970, **9**, 78.

[79] J. D. Halliday, R. E. Richards, and R. R. Sharp, *Proc. Roy. Soc.*, 1969, **313**, 45.

[80] F. Fittipaldi and S. Petrucci, *J. Phys. Chem.*, 1967, **71**, 3411.

[81] A. K. Covington, I. R. Lantzke, and J. M. Thain, *J.C.S. Faraday I*, 1974, 1869; A. K. Covington and J. M. Thain, *ibid.*, p. 1879.

[82] R. N. Briggs and J. F. Hinton, *J. Solution Chem.*, 1978, **7**, 1.

[83] A. Clauson, A. A. El-Harakany, and H. Schneider, *Ber. Bunsengesellschaft Phys. Chem.*, 1973, **77**, 994; H. Schneider, *Electrochim. Acta*, 1976, **21**, 711.

[84] H. H. Füldner, D. H. Devia, and H. Strehlow, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 499.

[85] D. H. Devia and H. Strehlow, *Ber. Bunsengesellschaft Phys. Chem.*, 1979, **83**, 627.