Solubility of Salts of Hexachlororhenate(IV) Ions with Complex Cations in Water and in Water + Alcohol Mixtures: Free Energies of Transfer of the Complex Ions

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It is shown that when the solubilities of two salts of the same valence type with a common anion are known in water and in mixtures of water with a co-solvent, and when the free energies of transfer $\Delta G_t^\ominus$ from water into the mixture are known for one of the cations, $\Delta G_t^\ominus$ for the other cation can be calculated. Solubilities of $\{a,f\text{-}[Co(py)_4Cl_2]\}_2[ReCl_6]$ in the mixtures water + Bu^{t}OH and water + methanol and the solubilities of $\{a,f\text{-}[Co(4Me\text{-}py)_4Cl_2]\}_2[ReCl_6]$ and of $\{a,b\text{-}[Co(SCN)Cl(en)_2]\}_2[ReCl_6]$ in water Bu^{t}OH have been measured at 25.0 °C (py = pyridine, 4Me-py = 4-methylpyridine, en = ethylenediamine). These values have been combined with literature data for the solubility of $Cs_2[ReCl_6]$ and for $\Delta G_t^\ominus(Cs^+)$ in these mixtures to produce values for $\Delta G_t^\ominus$ for the complex cations. $\Delta G_t^\ominus$ Values found for $a,f\text{-}[Co(py)_4Cl_2]^+$ in water + methanol, together with kinetic data for the solvolysis of the cation and with values for $\Delta G_t^\ominus(Cl^-)$ in the same mixtures, have been used to derive values for $\Delta G_t^\ominus$ for the cation in the solvolytic transition state, $[Co(py)_4Cl]^{2+}$. This confirms that the effect of solvation of the cation in the transition state dominates over that of the cation in the initial state.

FOR a salt of the type M_mX_n, where M^{n+} = the cation and X^{m-} = the anion, the free energy of transfer of the salt $\Delta G_t^\ominus(M_mX_n)$ from water into a mixture of water + co-solvent is given by equation (1), where $K_{ip} = (n/m)^n(C_M f_\pm)^{m+n}$ is the solubility ionic product, superscripts w and s indicate water and the mixture respectively, the molar concentration of M^{n+} in a saturated solution is C_M, and $f_\pm$ is the mean ionic activity coefficient for the $n:m$ salt on the molar scale. From (1) and K_{ip}, equation (2) follows, where $\Delta G_t^\ominus(M^{n+})$ and $\Delta G_t^\ominus(X^{m-})$

$$\Delta G_t^\ominus(M_mX_n) = RT\ln K_{ip}^w/K_{ip}^s \qquad (1)$$

$$m\Delta G_t^\ominus(M^{n+}) + n\Delta G_t^\ominus(X^{m-}) = (m+n)RT\ln(C_M^w f_\pm^w/C_M^s f_\pm^s) + A \qquad (2)$$

are on the mole fraction scale and A is a constant for any particular solvent composition for changing from the molar scale to the mole fraction scale. When equation (2) is combined with the analogous equation for another salt of the same type, R_mX_n, for the cation R^{n+} with the same anion X^{m-}, equation (3) follows, where values for $f_\pm$

$$\Delta G_t^\ominus(M^{n+}) - \Delta G_t^\ominus(R^{n+}) = \frac{(m+n)}{m} RT\left\{\ln\left(\frac{C_M^w C_R^s}{C_M^s C_R^w}\right) + \ln\left[\left(\frac{f_\pm^w}{f_\pm^s}\right)_M \left(\frac{f_\pm^s}{f_\pm^w}\right)_R\right]\right\} \qquad (3)$$

can be calculated for each salt at the ionic strengths, I, appropriate to the solubilities, using Davies' equation, (4).[1] Therefore, if the solubilities of two salts with a

$$-\log f_\pm = 0.5\,mn\left(\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.30I\right) \qquad (4)$$

common anion and of the same charge type $n:m$ are determined, the use of equation (3) with the derived values of C_M and C_R together with the values of $f_\pm$ calculated from equation (4) enables values of $\Delta G_t^\ominus(M^{n+})$ to be assigned if the values of $\Delta G_t^\ominus(R^{n+})$ are known.

Values for the solubilities of $Cs_2[ReCl_6]$ have been determined[2] at 25 °C for water and mixtures of water with co-solvents such as methanol and Bu^{t}OH and values for $\Delta G_t^\ominus(Cs^+)$ are available at 25 °C for water + methanol[3] and water + Bu^{t}OH.[4] We record here the determination of the solubilities of the hexachlororhenate(IV) salts of $a,f\text{-}[Co(py)_4Cl_2]^+$, $a,f\text{-}[Co(4Me\text{-}py)_4Cl_2]^+$, and $a,b\text{-}[Co(SCN)Cl(en)_2]^+$ in water + Bu^{t}OH and of $a,f\text{-}[Co(py)_4Cl_2]^+$ in water + methanol and their subsequent use with equations (3) and (4) with $m = 2$ and $n = 1$ (py = pyridine, 4Me-py = 4-methylpyridine, en = ethylenediamine). These derived values for $a,f\text{-}[Co(py)_4Cl_2]^+$ in water + methanol are then combined with kinetic data for the cation's solvolysis and values for $\Delta G_t^\ominus(Cl^-)$ in the same mixtures to evaluate $\Delta G_t^\ominus$ for the cation in the solvolytic transition state.

EXPERIMENTAL

Materials.—The salts $a,f\text{-}[Co(py)_4Cl_2]Cl$ and $a,f\text{-}[Co(4Me\text{-}py)_4Cl_2]Cl$ were prepared by the method of Werner and Feenstra[5] as modified by Elgy and Wells.[6] The salt $a,b\text{-}[Co(SCN)Cl(en)_2][ClO_4]$ was prepared by the procedure described by Werner.[7] Potassium hexachlororhenate(IV) was 99.9% pure from Alfa Products, methanol and potassium chloride were both of AnalaR grade, and Bu^{t}OH was fractionally distilled before use. Water was distilled once in an all-glass still.

Preparation of the Hexachlororhenates(IV).—Samples of the hexachlororhenates(IV) of the above complex ions were prepared starting from the salts quoted above for these cations. Equivalent amounts of the pure salt of the complex cation and of $K_2[ReCl_6]$ were weighed out and each dissolved separately in the minimum amount of distilled water. These solutions were first filtered through Whatman No. 42 paper and then mixed, when the precipitate of the hexachlororhenate(IV) of the complex ion immediately appeared. After separation of this precipitate from the liquid it was dried over silica gel in a vacuum desiccator.

Determination of the Solubility of the Hexachlororhenates(IV).—An excess of the solid hexachlororhenate(IV) of the complex cation was introduced into the solvent maintained at 25.0 ± 0.05 °C using a thermostat. The mixture was continuously stirred and at intervals the solution was decanted into a centrifuge tube and centrifuged for 2 min: this centrifugation was carried out in a fume cupboard where the air temperature was controlled at 25.0 ± 0.1 °C using a Bunsen burner and movement of the front sliding panel. The clear solution was then transferred to a spectrophotometer cell maintained at 25.0 ± 0.05 °C in the thermostatted cell compartment of a Unicam SP6-500 spectrophotometer: as appropriate, the clear solution was diluted before its optical density was measured.

RESULTS AND DISCUSSION

Solubility of $[Co(py)_2Cl_2]_2[ReCl_6]$ *in Water + Methanol.*—The kinetics of the solvolysis of *a,f*-$[Co(py)_4Cl_2]^+$ in water show [6] that the time required for 5% reaction to occur is 26 h at 25 °C. However, the optical densities determined using the above procedure at 233 nm for each solvent mixture with a 10-fold dilution of the clear solution before measurement show that saturation occurs after 80 min and therefore the solvolysis reaction has negligible interference.

If D is the observed optical density for $[Co(py)_4Cl_2]_2[ReCl_6]$, ε_c and C_c are the absorption coefficient and concentration of $[Co(py)_4Cl_2]^+$ respectively, and ε_r is the absorption coefficient of $[ReCl_6]^{2-}$, $C_c = D(\varepsilon_c + 0.5\ \varepsilon_r)^{-1}(\text{path length})^{-1}$. Beer's law was found to be obeyed by $[Co(py)_4Cl_2]Cl$ and by $K_2[ReCl_6]$ for each solvent mixture. If ε_{salt}, $\varepsilon_{K_2[ReCl_6]}$, and ε_{KCl} are the absorption coefficients for $[Co(py)_4Cl_2]Cl$, $K_2[ReCl_6]$, and KCl respectively, at 233 nm, equation (5) follows. Values for ε_{salt} and $\varepsilon_{K_2[ReCl_6]}$ for water and for the solvent mixtures are given in Table 1 for 233 nm. From measurements of the optical densities of 1 mol dm^{-3} KCl in each mixture at 233 nm, values of ε_{KCl} (dm^3 mol^{-1} cm^{-1}) were found to be as follows: pure water, 0.0263; 8.08 wt.%, 0.0345; 16.52 wt.%, 0.0373; 25.33 wt.%, 0.0375; 34.54 wt.%, 0.0335. It is therefore concluded that ε_{KCl} can be neglected in equation (5) for water + methanol.

$$\varepsilon_c + 0.5\ \varepsilon_r = \varepsilon_{salt} + 0.5\ \varepsilon_{K_2[ReCl_6]} - \varepsilon_{KCl} \qquad (5)$$

TABLE 1

Absorption coefficients (dm^3 mol^{-1} cm^{-1}) at 233 nm in water + methanol at 25 °C

Wt. % methanol	$[Co(py)_4Cl_2]Cl$ $10^{-4}\ \varepsilon$	$K_2[ReCl_6]$ $10^{-3}\ \varepsilon$
0.00	3.20	1.07
8.08	3.10	1.06
16.52	3.12	1.10
25.33	3.18	1.08
34.54	3.25	1.06

Table 2 gives values of C_c for saturated solutions with varying solvent composition at 25 °C calculated as described above. Values for the free energy of transfer of Cs$^+$, $\Delta G_t^{\ominus}(Cs^+)$, were interpolated from the data [3] obtained using the values of $\Delta G_t^{\ominus}(CsCl)$ of Feakins and Voice.[8] Values of $\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}$ were then obtained using these data in equation (3) together with the values of C_c in Table 2, the values of [Cs$^+$] in saturated solutions of $Cs_2[ReCl_6]$ at 25 °C, and values for $f_{\pm}$ calculated from equation (4) for the appropriate ionic strengths in the saturated solutions. These values for $\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}$ are given in Table 2: the contribution of the term in $f_{\pm}$ in equation (3) to these free energies of transfer is always small, never exceeding 1.6%.

TABLE 2

Water + methanol at 25 °C: C_c values for saturated solutions of $[Co(py)_4Cl_2]_2[ReCl_6]$ and free energies of transfer

Wt. % methanol	10^3 C_c/mol dm^{-3}	$\Delta G_t^{\ominus}$-$\{[Co(py)_4Cl_2]^+\}$/ kJ mol^{-1}	$\Delta G_t^{\ominus}$-$\{[Co(py)_4Cl]^{2+}\}$/ kJ mol^{-1}
0.00	0.417		
8.08	0.66	−11.1	−12.5
16.52	0.82	−13.5	−16.0
25.33	1.12	−15.8	−20.4
34.54	1.60	−19.0	−25.5

Solubility of $[Co(py)_4Cl_2]_2[ReCl_6]$ *in Water +* Bu^{t}OH.—Saturation of a series of mixtures of water + Bu^{t}OH by $[Co(py)_4Cl_2]_2[ReCl_6]$ was found to occur after 80 min and therefore interference from solvolysis can be neglected. The salts $[Co(py)_4Cl_2]Cl$ and $K_2[ReCl_6]$ at 25 °C were found to obey Beer's law at 233 nm and Table 3 contains mean values for ε_{salt} and $\varepsilon_{K_2[ReCl_6]}$ at 233 nm. Values of ε_{KCl} (dm^3 mol^{-1} cm^{-1}) for 1 mol dm^{-3} KCl in the various mixtures are as follows: 8.06 wt.%, 0.019; 16.48 wt.%, 0.037; 25.27 wt.%, 0.047; 34.47 wt.%, 0.104. Values of C_c for saturated solutions calculated as described above are given in Table 4, together with the values of $\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}$ for transfer from water into water + Bu^{t}OH derived using equation (3), interpolated values [4] of $\Delta G_t^{\ominus}(Cs^+)$, the values [2] of [Cs$^+$] in saturated solutions of $Cs_2[ReCl_6]$ in water + Bu^{t}OH at 25 °C, and values of $f_{\pm}$ calculated from equation (4). Again the contribution of the term in $f_{\pm}$ in equation (3) to $\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}$ never exceeds 1.6%.

Solubility of $[Co(4Me\text{-}py)_4Cl_2]_2[ReCl_6]$ *in Water +* Bu^{t}OH.—The kinetics of the solvolysis of the ion $[Co(4Me\text{-}py)_4Cl_2]^+$ in water [9] show that 5% reaction occurs in 1.4 h at 25 °C, but it was found that saturation of a range of water + Bu^{t}OH mixtures with $[Co(4Me\text{-}py)_4Cl_2]_2$-

TABLE 3

Absorption coefficients (dm^3 mol^{-1} cm^{-1}) in water + Bu^{t}OH at 25 °C

Wt. % Bu^{t}OH	$K_2[ReCl_6]$ $10^{-3}\ \varepsilon$ [a]	$[Co(py)_4Cl_2]Cl$ $10^{-4}\ \varepsilon$ [a]	$[Co(4Me\text{-}py)_4Cl_2]Cl$ $10^{-4}\ \varepsilon$ [a]	$[Co(SCN)Cl(en)_2][ClO_4]$ $10^{-2}\ \varepsilon$ [b]
0.00	1.07	3.20	4.06	1.47
8.06	1.06	3.27	4.02	1.47
16.48	1.16	3.12	4.03	1.47
25.27	1.16	3.09	3.93	1.49
34.47	1.13	3.03	3.90	1.48

[a] Wavelength = 233 nm. [b] Wavelength = 490 nm.

TABLE 4

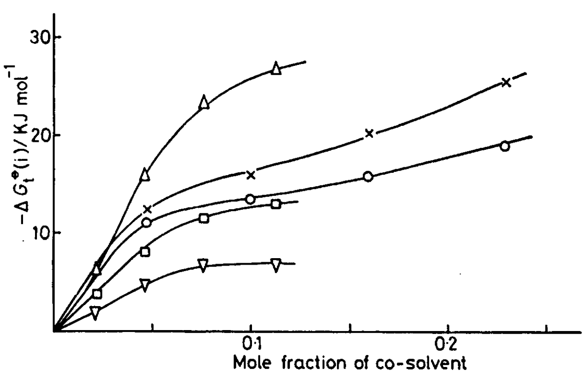
Water + $\mathrm{Bu^tOH}$ at 25 °C: saturated concentrations, C_{sat} (10^4 mol dm^{-3}) for cations i in $[\mathrm{ReCl_6}]^{2-}$ salts and free energies of transfer (kJ mol^{-1}) from water

Wt. %	i = $[\mathrm{Co(py)_4Cl_2}]^+$		i = $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$		i = $[\mathrm{Co(SCN)Cl(en)_2}]^+$	
$\mathrm{Bu^tOH}$	C_{sat}	$\Delta G_t^\ominus(\mathrm{i})$	C_{sat}	$\Delta G_t^\ominus(\mathrm{i})$	C_{sat}	$\Delta G_t^\ominus(\mathrm{i})$
0.00	4.17		0.138		10.73	
8.06	4.80	−3.64	0.238	−6.1	7.67	−1.93
16.48	5.37	−8.0	0.745	−15.9	5.51	−4.70
25.27	7.57	−11.5	2.17	−23.4	5.12	−6.7
34.47	9.27	−13.2	3.13	−26.7	3.91	−6.7

$[\mathrm{ReCl_6}]$ is complete within 80 min. Beer's law was found to be obeyed by $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]\mathrm{Cl}$ in these mixtures at 233 nm. Using these values of $\varepsilon_{\mathrm{salt}}$ (Table 3) together with $\varepsilon_{\mathrm{K_2[ReCl_6]}}$ and $\varepsilon_{\mathrm{KCl}}$ in the same mixtures, values of C_c for $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$ in saturated solutions (allowing 80 min for saturation) of the hexachlororhenate(IV) in water + $\mathrm{Bu^tOH}$ are obtained (Table 4). The values of $\Delta G_t^\ominus\{[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+\}$ (Table 4) for the transfer from water into water + $\mathrm{Bu^tOH}$ were calculated from these values of C_c, the values [2] of $[\mathrm{Cs^+}]$ in saturated solutions of $\mathrm{Cs_2[ReCl_6]}$, the interpolated values [4] of $\Delta G_t^\ominus(\mathrm{Cs^+})$, and $f_\pm$ at the appropriate ionic strengths. In this case, the contribution of the term in $f_\pm$ in equation (3) to $\Delta G_t^\ominus\{[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+\}$ never exceeds 1%.

Solubility of $[\mathrm{Co(SCN)Cl(en)_2}]_2[\mathrm{ReCl_6}]$ *in Water* + $\mathrm{Bu^tOH}$.—The kinetics of the solvolysis of *a,b*-$[\mathrm{Co(SCN)Cl(en)_2}]^+$ in water show [10] that 5% reaction at 25 °C occurs in 80 min, but it was found that saturation of the water + $\mathrm{Bu^tOH}$ mixtures occurs within 60 min for $[\mathrm{Co(SCN)Cl(en)_2}]_2[\mathrm{ReCl_6}]$. The salt $[\mathrm{Co(SCN)Cl(en)_2}][\mathrm{ClO_4}]$ was found to obey Beer's law in the range of solvent compositions at 490 nm and the mean values of $\varepsilon_{\mathrm{salt}}$ are given in Table 3. As $\varepsilon_{\mathrm{K_2[ReCl_6]}}$ in pure water and in 34.47 wt.% $\mathrm{Bu^tOH}$ was found to be zero at 490 nm, and assuming $\varepsilon_{\mathrm{K[ClO_4]}}$ = zero at 490 nm, values of C_c for $[\mathrm{Co(SCN)Cl(en)_2}]^+$ for saturated solutions of $[\mathrm{Co(SCN)Cl(en)_2}]_2[\mathrm{ReCl_6}]$ can be calculated as described above using equation (5) with $\varepsilon_{\mathrm{K[ClO_4]}}$ replacing $\varepsilon_{\mathrm{KCl}}$ and and $\varepsilon_{\mathrm{K_2[ReCl_6]}} = \varepsilon_{\mathrm{K[ClO_4]}}$ = zero, with D determined after 60 min equilibration between solid and liquid phases. Values of C_c for these saturated solutions are given in Table 4, together with the values of $\Delta G_t^\ominus\{[\mathrm{Co(SCN)Cl(en)_2}]^+\}$ calculated from equation (3), the values of $[\mathrm{Cs^+}]$ in saturated solutions of $\mathrm{Cs_2[ReCl_6]}$ in water + $\mathrm{Bu^tOH}$,[2] the interpolated values [4] of $\Delta G_t^\ominus(\mathrm{Cs^+})$, and the values of $f_\pm$ calculated for the appropriate ionic strengths. The term in $f_\pm$ in equation (3) never contributes more than 0.5% to $\Delta G_t^\ominus\{[\mathrm{Co(SCN)Cl(en)_2}]^+\}$.

Free Energies of Transfer of Complex Ions.—The Figure shows that the free energies of transfer of complex ions are negative for all solvent compositions investigated, as usually found for cations in water + alcohol mixtures of the same composition range.[3,4,11] The one exception to this latter rule is the case of unipositive ions in water + methanol, where $\Delta G_t^\ominus$ is around zero, sometimes slightly positive and sometimes slightly negative,[3] and it is therefore of great interest to find such large negative values for $\Delta G_t^\ominus\{[\mathrm{Co(py)_4Cl_2}]^+\}$ in water + methanol. These large negative values must arise from the presence of the pyridine ligands, which present their ' hydrocarbon ' ends for the principal contact area between the complex cation and the solvent, and the well known structure-forming capacity of organic groups in aqueous solutions.[12] This latter effect usually results in large negative values for $\Delta G_t^\ominus(\mathrm{i})$ when organic groups are present in species i: [11] examples are the large negative values found [11] for tetra-alkylammonium cations, tetraphenylammonium cations, and tetraphenylborate anions, the latter deviating markedly from the large positive values usually found for purely inorganic anions.[11] In this respect, the effect of methyl substitution in the pyridine ligands is interesting: in water + $\mathrm{Bu^tOH}$, $\Delta G_t^\ominus(\mathrm{i})$ for i = $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$ is much more negative than that for i = $[\mathrm{Co(py)_4Cl_2}]^+$, showing the structure-forming effect of the peripheral, 4-substituted methyl groups in contact with the solvent. This stabilizing effect of large organic ligands in mixed solvents is also shown in the comparison of the smaller negative values of $\Delta G_t^\ominus(\mathrm{i})$ in water + $\mathrm{Bu^tOH}$ for i = $[\mathrm{Co(SCN)Cl(en)_2}]^+$, with only two organic ligands which are not particularly prominent, with the larger negative $\Delta G_t^\ominus(\mathrm{i})$ in water + $\mathrm{Bu^tOH}$ for i = $[\mathrm{Co(py)_4Cl_2}]^+$ and i = $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$, where the organic ligands are large and dominate the cation–solvent contacts. Since $\mathrm{Bu^tOH}$ induces more structure formation in aqueous solution at a lower concentration than found with methanol as a co-solvent,[13] it is interesting to find in the Figure that $[\mathrm{Co(py)_4Cl_2}]^+$,



Comparison of free energies of transfer of complex ions i from water into water + co-solvent mixtures at 25 °C, i and co-solvents as follows: i = $[\mathrm{Co(py)_4Cl_2}]^+$ with methanol (○); i = $[\mathrm{Co(py)_4Cl_2}]^+$ with $\mathrm{Bu^tOH}$ (□); i = $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$ with $\mathrm{Bu^tOH}$ (△); i = $[\mathrm{Co(SCN)Cl(en)_2}]^+$ with $\mathrm{Bu^tOH}$ (▽); i = $[\mathrm{Co(py)_4Cl}]^{2+}$ in transition state with methanol (×)

with its contact with solvent largely through the ' hydrocarbon ' end of the organic ligands, is more stabilized at lower concentrations of co-solvent in water + Bu^tOH than in water + methanol.

In discussing the S_N1 type solvolyses of inorganic complexes involving considerable extension of the metal–halide ion bond in the transition state,[14] and in particular the solvolysis of $[Co(py)_4Cl_2]^+$ in water + methanol,[6] a free-energy cycle was constructed relating the free energy of activation $\Delta G^\ddagger$ for the process initial state→transition state in pure water (subscript w) to that in the mixed solvent (subscript s) *via* the free energies of transfer of the various species involved.

$$\begin{tikzcd}
{[Co(py)_4Cl_2]^+_w} \arrow[r, "\Delta G_w^\ddagger"] & {[Co(py)_4Cl]^{2+}_w} \arrow[d, "\Delta G_t^{\ominus}\{[Co(py)_4Cl]^{2+}\}"'] & {+\ Cl^-_w} \arrow[d, "\Delta G_t^{\ominus}(Cl^-)"] \\
{[Co(py)_4Cl_2]^+_s} \arrow[u, "-\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}"] \arrow[r, "\Delta G_s^\ddagger"] & {[Co(py)_4Cl]^{2+}_s} & {+\ Cl^-_s}
\end{tikzcd}$$

Equation (6) can be deduced [6,14] from this cycle, and values for the left-hand side (l.h.s.) can be calculated [6,14] from values for the first-order rate constants found for

$$2.303\ RT \log \frac{k_w}{k_s} - \Delta G_t^{\ominus}(Cl^-) = \Delta G_t^{\ominus}\{[Co(py)_4Cl]^{2+}\} - \Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\} \quad (6)$$

the solvolysis and the free energy of transfer of the halide ion.[3,4,11] The solvolysis of $[Co(py)_4Cl_2]^+$ in water + methanol was found [6] to conform with the general conclusion [14] for similar complexes in water + co-solvent mixtures using a range of co-solvents, that changes in solvation, and particularly of solvent structure, have a dominant effect on the complex in the transition state, $[Co(py)_4Cl]^{2+}$. Now that individual values are available for $\Delta G_t^{\ominus}\{[Co(py)_4Cl_2]^+\}$ in water + methanol in Table 2, values of $\Delta G_t^{\ominus}$ for $[Co(py)_4Cl]^{2+}$ in the transition state may be calculated using the available values [6] for the l.h.s. of equation (6) at 25 °C and are given in Table 2. These values are also included in the Figure which shows that the stabilization of the complex in the mixture relative to pure water increases as the ratio organic ligand : chloride ion in the inner co-ordination shell increases. This result is as expected with the organic ligands having a structure-forming effect on water [13] and the chloride ion having a structure-breaking effect.

In their recent discussion of the solvation of initial and transition states of inorganic reactions, Blandamer and Burgess [15] critically examined the operation of equation (6) in mixed aqueous solvents. The conclusion drawn [14] from the application of equation (6) to the S_N1-type solvolysis of a wide range of inorganic complexes in water-rich conditions was that the dominance of solvation effects, which usually occurs in the transition state, depends upon the fact [3,4,11] that $\Delta G_t^{\ominus}(i)$ when i is a bipositive metal ion is more negative than $\Delta G_t^{\ominus}(i)$ when i is a unipositive metal ion. Blandamer and Burgess suggested that the errors in these single-ion values [3,4,11] for $\Delta G_t^{\ominus}$ are cumulative, but for two ions A^{2+} and B^+, the analogy of the right-hand side of equation (6) can be represented as equation (7). The first three terms on the

$$\Delta G_t^{\ominus}(A^{2+}) - \Delta G_t^{\ominus}(B^+) = \Delta G_t^{\ominus}(AX_2) - \Delta G_t^{\ominus}(BX) - \Delta G_t^{\ominus}(HX) + \Delta G_t^{\ominus}(H^+) \quad (7)$$

right-hand side of equation (7) are obtainable from direct experimental measurement, leaving only one single-ion value, $\Delta G_t^{\ominus}(H^+)$, which is calculated without reference to any other single-ion value for $\Delta G_t^{\ominus}$.[3,4,11] For example, for water + methanol,[3] when the experimental values for $\Delta G_t^{\ominus}(AX_2)$ and $\Delta G_t^{\ominus}(BX)$, where X^- is Cl^-, are inserted into equation (7), using pairs of aquo-cations $A^{2+}_{aq.}$ and $B^+_{aq.}$ of approximately the same size (*e.g.* Sr^{2+} and K^+, Ba^{2+} and Rb^+, Zn^{2+} and Li^+, Cd^{2+} and Na^+), together with the experimental values for $\Delta G_t^{\ominus}(HCl)$, the value of $\Delta G_t^{\ominus}(AX_2) - \Delta G_t^{\ominus}(BX) - \Delta G_t^{\ominus}(HX)$ is always positive, whereas the calculated [3] $\Delta G_t^{\ominus}(H^+)$ always has a larger negative value. This approach confirms that $-\Delta G_t^{\ominus}(A^{2+}) > -\Delta G_t^{\ominus}(B^+)$ for metal cations, as concluded from single-ion values for $\Delta G_t^{\ominus}$ in general for water + co-solvent mixtures.[3,4,11] Our method for calculating $\Delta G_t^{\ominus}(H^+)$ involves adding $\Delta G_t^{\ominus}$ for the solvent sorting in the solvated proton incurred in the transfer (calculated from an experimental equilibrium constant) to the coulombic contribution to $\Delta G_t^{\ominus}$, derived from the transfer of the aquo-proton between different dielectric media.[3,4,11] Earlier methods of deriving the non-coulombic contribution to $\Delta G_t^{\ominus}$, such as calculation of $\Delta G_t^{\ominus}$ for ions from $\Delta G_t^{\ominus}$ for the transfer of a neutral species of the same size,[16] or extrapolation of $\Delta G_t^{\ominus}(HX)$ to the situation where X^- has infinite size,[17] produce values for $\Delta G_t^{\ominus}(H^+)$ which are more negative than ours,[3,4,11] thereby accentuating $-\Delta G_t^{\ominus}(A^{2+}) > -\Delta G_t^{\ominus}(B^+)$ when substituted into equation (7). Our single-ion values for $\Delta G_t^{\ominus}(i)$ where i is a cation compare well with the conclusions on solvent sorting derived from cation n.m.r. measurements where there is overlap. The cations Na^+, Rb^+, and Cs^+ all have [3] positive values of $\Delta G_t^{\ominus}(i)$ in water + methanol in water-rich conditions where cation n.m.r. shows a preference for immediate solvation by water molecules; [18] $\Delta G_t^{\ominus}(Cs^+)$ in water + dmso (dimethyl sulphoxide) has negative values in water-rich conditions [19] consistent with the small preference for dmso molecules shown by ^{133}Cs n.m.r.[18] The reason why the conclusion [14] from the application of equation (6) to the S_N1-type solvolyses of organic halides differs from the earlier assignment [20] of a solvation effect solely dominating the initial state lies in the limitation imposed on the earlier study by using only ΔH values. Our discussion uses ΔG values,[14] which produces an overall result, showing that solvation sometimes dominates in the transition state and sometimes in the initial state for organic halides.

[1/200 *Received, 9th February,* 1981]

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