Correlations between the Transfer Thermodynamics of Simple Electrolytes and Structural Parameters with Particular Reference to Steric Hindrance

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Structural studies on Li^+, Na^+, Ca^{2+}, and Ag^+ in aqueous solution by neutron diffraction and computer simulation explain certain trends in the free energies of transfer of these ions from water to mixed aqueous solvents; in particular, the thermodynamic evidence of decreasing steric hindrance to solvation by bulky ligands in the order $Li^+ > Na^+ > Ag^+$ is consistent with the structures of the ion-complexes in aqueous solution.

Neutron diffraction with isotopic substitution, a technique recently developed by Enderby *et al.*,[1] allows the distribution of water molecules around ions in aqueous solution to be determined with unprecedented confidence. Li^+ (6) and Ca^{2+}[1] (10) (Table 1) are close-packed by their (n) co-ordinated water molecules.[1] MD (molecular dynamics) calculations[2] give essentially the same structures, so we can accept their value (6) for Na^+, for which the experimental technique is unsuitable. Ag^+ (4) has the most open structure of these four key ions.[3]

The purpose of this communication is to demonstrate some striking correlations between these results and certain thermodynamic quantities.

The free energies of transfer of H^+, Li^+, Na^+, and Ag^+ chloride from water to certain mixed aqueous solvents in Table 2 are selected from many such values.[4] Although the $\Delta G_t^\circ(MCl)$ are all positive, Feakins and Watson[5] suggested that ΔG_t° for cations is dominated by a negative term, $\Delta G_t^\circ(M^+)_1$, because the organic molecules are stronger Lewis bases than water. For 'hard' cations and ligands, interacting electrostatically, equation (1) applies.

$$\Delta G_t^\circ(M^+)_1 = -N_A \Delta q e z n R^{-1} \qquad (1)$$

The effective charge in the co-ordinating lone-pair orbital changes by $-\Delta q$ on average when the ion is transferred; it

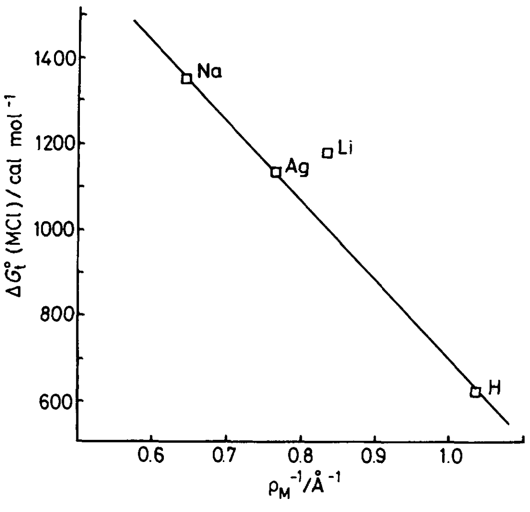

Figure 1. ΔG_t° *vs.* ρ_M^{-1}; water to 30% (w/w) acetone (1 cal = 4.184 J).

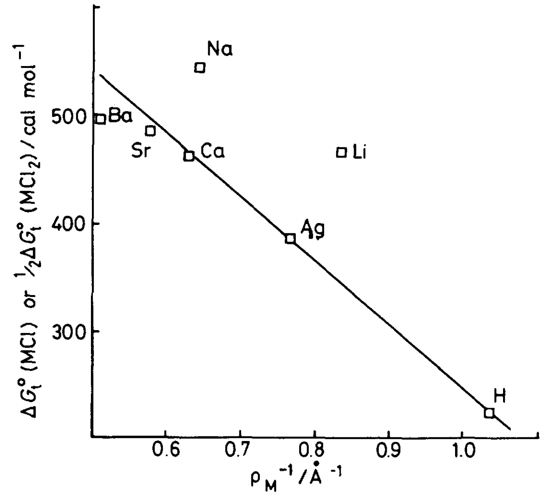

Figure 2. ΔG_t° *vs.* ρ_M^{-1}; water to 10% (w/w) Bu^{t}OH.

'sees' a charge ze ($z = 1$ for Li$^+$, Na$^+$; Na$^+$; 2 for Ca^{2+}) at the centre of the ion at a distance $R = r_i + \delta$. We take $\delta = 0.6$ Å; the choice is not critical. Now equation (2) holds, where b includes $\Delta G_t^\circ(\text{Cl}^-)$ and constant or near-constant terms in $\Delta G_t^\circ(\text{M}^+)$. Since Li$^+$ and Na$^+$ have common n, z, and $R_{\text{Li}} < R_{\text{Na}}$, $\Delta G_t^\circ(\text{LiCl}) < \Delta G_t^\circ(\text{NaCl})$ invariably (Table 2).[4]

$$\Delta G_t^\circ(\text{MCl}) = -N_A \Delta qeznR_M^{-1} + b \qquad (2)$$

Feakins, Lawrence, and Tomkins[6] suggested that Ag$^+$ interacts with 'hard' ligands like a 'hard' alkali-metal ion, but more strongly for a given radius because its nuclear charge is more weakly shielded ($z > 1$). Thus, invariably, $\Delta G_t^\circ(\text{AgCl}) < \Delta G_t^\circ(\text{NaCl})$, Table 2. The short Ag–O distance (Table 1) now confirms the strong interaction. Since the more weakly interacting Na$^+$ has about the same M–O and $n = 6$, the shielding in Ag$^+$, with $n = 4$, must be stereochemically selective as well as weak.

With regard to steric hindrance, replacement of one water ligand in the octahedral aqueous complex of Li$^+$ by Bu^{t}OH for example would result in severe steric strain, raising ΔG_t° above the value expected from equation (2). Ag$^+$, with bigger ligand–ligand separations, and H$^+$, whose solvation is based on H$_3$O$^+$ or SH$^+$ units, should be less vulnerable. Despite different n or z, they can be brought into correspondence with Li$^+$ and Na$^+$ by re-writing equation (2) as equation (3).

$$\Delta G_t^\circ(\text{MCl}) = a\rho_M^{-1} + b \qquad (3)$$

In methanol–water, where least hindrance is expected, we put $\rho_M = R_M$ for Li$^+$ and Na$^+$ and so recover values of ρ_H (0.97 Å) and ρ_{Ag} (1.31 Å) which vary very little (±0.02 Å) over seven transfers up to 80% methanol. These parameters, whose precise significance is unimportant in what follows, reproduce the behaviour of the ions in a remarkable and

Table 1. Structural parameters.[a]

Ion	Pauling radius r_i/Å	Co-ordination number[b] n	M–O/Å	O–O/Å
Li$^+$	0.60	**6**	**1.95**	**2.76**
Ca^{2+}	0.99	**10**	**2.46**	**2.80**[c]
Na$^+$	0.95	6[d]	2.3_5[e]	3.3
Ag$^+$	1.26	**4**	**2.41**	**3.94**
Sr^{2+}	1.13	*10*	*2.5_5*[e]	*2.9*[c]
Ba^{2+}	1.35	*10*	*2.7_5*[e]	*3.1*[c]

[a] Figures in **bold** type are based on experimentally determined neutron diffraction first order difference data. Italicised figures are by analogy only. [b] To nearest whole number. [c] Assuming a bicapped dodecahedron. [d] MD calculations. [e] Taken as r_i + 1.4 Å.

Table 2. Representative free energies of transfer ΔG_t°/cal mol^{-1}, molar standard states.

Water to 20% (w/w)	HCl	LiCl	AgCl	NaCl
Methanol	351	623	710	883
Dioxane	427	631	639	755
Acetone	371	710	696	820
Bu^{t}OH	433	910	764	1089
DMSO	25	282	82[a]	509

[a] The interaction of Ag$^+$ with DMSO involves d$_\pi$–p$_\pi$ interactions (see text).

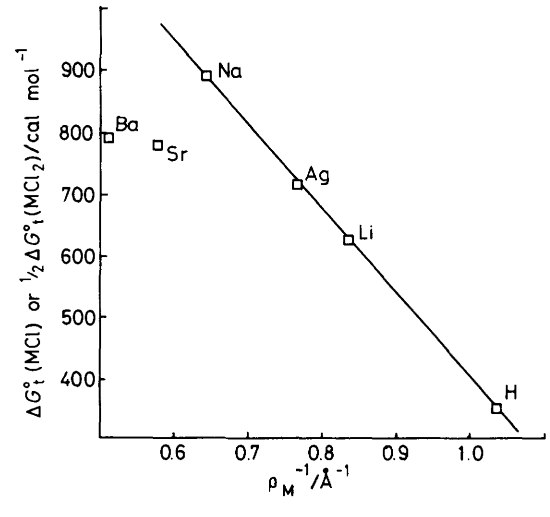

Figure 3. ΔG_t° *vs.* ρ_M^{-1}; water to 20% (w/w) MeOH.

revealing way. For transfers to seven dioxane–water and acetone–water mixtures, up to 60% acetone, $\Delta G_{\mathrm{t}}^{\circ}$ is accurately linear in ρ_{M}^{-1} for the chlorides of H^+, Ag^+, and Na^+, but the $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{LiCl})$ now lie higher, markedly so for acetone–water (*e.g.* Figure 1); the solvation of Li^+ by dioxane and acetone is hindered. For five transfers in Bu^{t}OH – water, up to 50% Bu^{t}OH, the points for Li^+ and Na^+ now both lie above the Ag^+–H^+ line (Figure 2) showing that the solvation of Na^+ by Bu^{t}OH is also hindered. This susceptibility to steric hindrance, decreasing in the order $Li^+ > Na^+ > Ag^+$, is completely consistent with the increase in the O—O distances of their complexes (Table 1). Table 2 shows the value of Ag^+ as an unhindered marker; $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{LiCl})$ shifts to higher values relative to $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{AgCl})$ in the expected order MeOH < dioxane < acetone < Bu^{t}OH.

The dimethyl sulphoxide (DMSO)–water system presents two anomalies. Additional stabilisation of Ag^+ results from d_{π}–p_{π} interaction with the organic ligand.[7] However for four transfers up to 60% DMSO the $\Delta G_{\mathrm{t}}^{\circ}$ for Li^+, Na^+, and H^+ chlorides are accurately linear in ρ_{M}^{-1}, denoting no steric hindrance of Li^+ or Na^+. Again, the donation of the p-electrons of oxygen into acceptor d-orbitals on sulphur may favour an sp lone-pair donor orbital and a linear M–O–S configuration which keeps the methyl groups clear of adjacent ligands.

For alkaline-earth chlorides, equation (2) takes the form of equation (4). Since (Table 1) $n(M^{2+}) > n(M^+)$, we predict $\frac{1}{2}\Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl_2}) < \Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl})$ for M^{2+}, M^+ of the same radius. In 10% methanol–water (Figure 3) the $\frac{1}{2}\Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl_2})$ lie well below $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl})$ as $f(\rho_{\mathrm{M}}^{-1})$. In the same plot for 20% Bu^{t}OH–water (Figure 2) the Ag^+–H^+ line now defines unhindered behaviour. This graph again shows the predictive value of the structural information. If the solvation of Li^+ is

$$\tfrac{1}{2}\Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl_2}) = -N_{\mathrm{A}}\Delta qenR_{\mathrm{M}}^{-1} + b \qquad (4)$$

hindered, that of Ca^{2+}, with identical O–O, must also be; if Na^+ is hindered so too will be Ca^{2+}, Sr^{2+} and Ba^{2+}. The $\frac{1}{2}\Delta G_{\mathrm{t}}^{\circ}(\mathrm{MCl_2})$ are thus displaced upwards, lying on, or only slightly below, the Ag^+–H^+ line.

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