

Predominance of Initial-state Properties in Volume Relations for Solvent Exchange Kinetics

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In the exchange of solvent water with $M^{2+}(\text{aq})$ ($M = \text{Mn, Fe, Co, Ni}$) or with $M(\text{NH}_3)_5(\text{OH}_2)^{3+}(\text{aq})$ ($M = \text{Cr, Co, Rh, Ir}$), the partial molar volumes of the transition states display less than one-third of the variability of the partial molar volumes of the initial states as M is varied within each series.

Volumes of activation ΔV^* for aqua exchange between $M(\text{H}_2\text{O})_6^{2+}$ ($M = \text{Mn, Fe, Co, Ni}$) and solvent water show a roughly linear *inverse* correlation with the partial molar volumes \bar{V}^0 of $M^{2+}(\text{aq})$, with slope -1.2 ± 0.2 . Relevant data are collected in Table 1, in which the ΔV^* values refer to various $M(\text{ClO}_4)_2$ concentrations up to about 0.1 mol l^{-1} rather than infinite dilution but can be treated as temperature-independent infinite-dilution values since the concentration dependence of properties of $M^{2+}(\text{aq})$ and the transition state $\{M^{2+}(\text{aq})\}^*$ for aqua-exchange must be almost identical in dilute solution. Thus, the partial molar volume \bar{V}^* of $\{M^{2+}(\text{aq})\}^*$ can be set as equal to $(\Delta V^* + \bar{V}^0)$, ignoring the volume of the incoming water molecule which is common to the series.

Table 1 shows that \bar{V}^* varies over a range of only *ca.* $3 \text{ cm}^3 \text{ mol}^{-1}$ (which is almost negligible, in view of discrepancies between \bar{V}^0 values in the literature²⁻⁶) while \bar{V}^0 and ΔV^* range over $12 \text{ cm}^3 \text{ mol}^{-1}$ in opposite directions. In other words, \bar{V}^* is insensitive to the nature of M , and so *trends in ΔV^* are largely determined by initial-state, rather than transition-state, properties.* The object of the present study was to determine whether this last observation might have any general validity, by comparing ΔV^* for aqua exchange with new \bar{V}^0 data for the rather different series $M(\text{NH}_3)_5(\text{OH}_2)^{3+}$ ($M = \text{Cr, Co, Rh, Ir}$).

Apparent molar volumes ϕ_v of aqueous $[M(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$ were measured with a Sodev 02D vibrating-tube densimeter over the concentration range $0.01\text{--}0.05 \text{ mol l}^{-1}$ (except for $0.008\text{--}0.024 \text{ mol l}^{-1}$ for $M = \text{Ir}$) dictated by solubility and the reliability of the density measurements

($\pm 3 \times 10^{-6} \text{ g cm}^{-3}$). The purity of the anhydrous salts⁷⁻¹⁰ was important,¹¹ and was checked by elemental microanalysis, u.v.-visible spectra, and hydrogen-ion-exchange equivalence.^{7,11} No attempt was made to suppress the expected slight degree of acid dissociation of the aqua-ions in solution, as the volume effect is negligible,¹¹ the volume of ionization of aqua-ions in general being near zero.¹²

No clear systematic variation in ϕ_v with the molar concentration c of $[M(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$ was discernable outside the bounds of the cumulative experimental uncertainty ($\pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$). It is not, however, strictly correct to identify the mean value of ϕ_v with the infinite-dilution value ϕ_v^0 ,^{9,13} since the experimentally accessible concentration range lies above the Debye-Hückel region, and two recent reports^{14,15} serve to emphasize that ϕ_v is likely to decrease significantly as c is reduced below 0.01 mol l^{-1} . Thus, in terms of the Redlich-Meyer equation (1),^{5,16} the near-constancy of ϕ_v results from

$$\phi_v = \phi_v^0 + S_v\sqrt{c} + b_v c \quad (1)$$

opposing trends in the terms with the Debye-Hückel ($S_v = 27.45 \text{ cm}^3 \text{ mol}^{-1.5} 10^{-5}$)⁵ and b_v coefficients. Table 2 summarises the results according to equation (1); the b_v values correspond to broad maxima in ϕ_v in the region $c = 0.02$ to 0.06 mol l^{-1} .

Clearly, for $M(\text{NH}_3)_5(\text{OH}_2)^{3+}(\text{aq})$ just as for $M^{2+}(\text{aq})$, ΔV^* for aqua-exchange is inversely correlated with \bar{V}^0 (slope -0.70) or, perhaps more realistically, with the mean ϕ_v of the perchlorate salts at mid-range of the concentrations at which ϕ_v and ΔV^* were measured (*ca.* 0.02 mol l^{-1} ; slope -0.74). The partial molar volumes \bar{V}^* of the transition states vary less than one-third as rapidly as do \bar{V}^0 for the initial states as M is varied.

These correlations permit the prediction of unknown ΔV^* from known \bar{V}^0 or ϕ_v values, *e.g.*, $\Delta V^* = -5, +5$, and $-7 \text{ cm}^3 \text{ mol}^{-1}$ for aqua exchange on $\text{Ru}(\text{NH}_3)_5(\text{OH}_2)^{3+}(\text{aq})$,¹⁸ $\text{Zn}^{2+}(\text{aq})$,² and $\text{Cd}^{2+}(\text{aq})$ ² respectively. If we accept that ΔV^* for solvent exchange is an indicator of mechanism (degree of associative vs. dissociative activation, *etc.*), then the mechanistic predisposition of an aqueous metal complex ion in ligand substitution must reside predominantly in *initial-state* rather than *transition-state* properties. Indeed, the \bar{V}^* values indicate

Table 1. Partial molar volumes \bar{V}^0 (25 °C) and volumes of activation ΔV^* for water exchange of aqueous M^{2+} as perchlorates.

M	$\bar{V}^0/\text{cm}^3 \text{ mol}^{-1}$ ^a	$\Delta V^*/\text{cm}^3 \text{ mol}^{-1}$ ^b	$\bar{V}^*/\text{cm}^3 \text{ mol}^{-1}$ ^{a,c}
Mn	-17.4 ^d	-5.4	-22.8
Fe	-25.3 ^e	3.8	-21.5
Co	-25.4 ^d	6.1	-19.3
Ni	-28.4 ^d	7.2	-21.2

^a Conventional [$\bar{V}^0 = 0$ for $\text{H}^+(\text{aq})$]. ^b Ref. 1. ^c $\bar{V}^* = \bar{V}^0 + \Delta V^*$; concentration dependence of ΔV^* assumed to be negligible. ^d Ref. 2, *via* equation (1); see refs. 3-5 for other salts and extrapolation procedures. ^e Ref. 6.

Table 2. Volume properties of aqueous $[M(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$ in terms of equation (1), and activation volumes for water exchange on $M(\text{NH}_3)_5(\text{OH}_2)^{3+}(\text{aq})$.

M	$\phi_v^0(25 \text{ °C})/\text{cm}^3 \text{ mol}^{-1}$	$b_v(25 \text{ °C})/\text{cm}^3 \text{ mol}^{-2}$	$\phi_v(c = 0.02)/\text{cm}^3 \text{ mol}^{-1}$	\bar{V}^0 of $M(\text{NH}_3)_5(\text{OH}_2)^{3+}(\text{aq})^a/\text{cm}^3 \text{ mol}^{-1}$	$\Delta \bar{V}^*/\text{cm}^3 \text{ mol}^{-1}$	$\bar{V}^*_{\text{a}}/\text{cm}^3 \text{ mol}^{-1}$
Co	203.3 ± 0.3	-59	206.0	70.9	1.2 ± 0.2^b	72.1 ± 0.5
Rh	209.6 ± 0.5	-59	212.3	77.2	-4.1 ± 0.4^c	73.1 ± 0.9
Ir	209.7 ± 0.8	-102	211.5	77.3	-3.2 ± 0.1^d	74.1 ± 0.9
Cr	213.7 ± 0.9	-86	215.8	81.3	-5.8 ± 0.1^e	75.5 ± 1.0
Ru			214.0 ^e			

^a Conventional, relative to $\bar{V}^0(\text{H}^+\text{aq}) = 0$, with $\bar{V}^0(\text{ClO}_4^-) = 44.12 \text{ cm}^3 \text{ mol}^{-1}$ (ref. 5). ^b Ref. 17. ^c Ref. 8. ^d Ref. 9. ^e Estimated from data of ref. 18.

that, contrary to intuition, the transition states of a series of aqua exchange reactions must resemble one another surprisingly closely, regardless of the detailed mechanism.

It seems that a corresponding inverse correlation may exist between the entropies of activation ΔS^* (6, 12, 37, 32 J K⁻¹ mol⁻¹)¹ and ionic partial molar entropies \bar{S}^0 (-74,¹⁹ -107,²⁰ -113,¹⁹ -129¹⁹) for M²⁺(aq) (M = Mn, Fe, Co, Ni), but large discrepancies in the published data obscure the issue [e.g., ΔS^* ranges from -17 to +44 J K⁻¹ mol⁻¹ for Co²⁺(aq),¹ and $\bar{S}^0 = -138¹⁹ or -107²⁰ for Fe²⁺(aq)].$

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