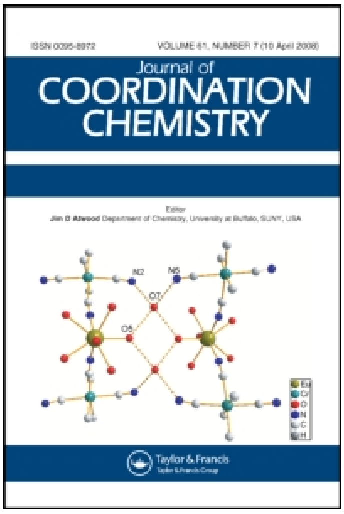

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VOLUME EFFECTS PRODUCED BY THE COORDINATION OF Zn(II) TO POLYFUNCTIONAL ORGANIC ACIDS

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VOLUME EFFECTS PRODUCED BY THE COORDINATION OF Zn(II) TO POLYFUNCTIONAL ORGANIC ACIDS

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To interpret the volume changes, ΔV, produced by the interaction of Zn(II) with proteins the values for the ΔV of coordination of Zn(II) with the specific ligands must be known. This consideration provided the impetus for determining the ΔV for the formation of 1:1 Zn(II): poly-functional acid complexes. The data for monocarboxylates are omitted because the reactions do not go to completion.[1,2] Water and 8.00 M urea were employed as solvents to establish medium effects.

The volume changes were determined with micro-dilatometers[3] which could be read to 0.01 μl. The temperature was 30.0° and maintained to ± 0.001°. The procedure was similar to that employed with Cu(II)[4] except that the final concentration of Zn(II) was 0.020 M and the final ligand concentration was 0.008 or 0.010 M. Other concentrations were employed to establish concentrations and salt effects.[4] The organic acids concentration checked by potentiometric titrations agreed to ± 0.5% with the calculated values. Restandardized acids and bases which agreed to ± 0.2% of manufacturers' specifications were used. Zinc concentration was determined by EDTA titration.[5] Deionized water was re-distilled before use. Most of the reagents were from the same sources used previously.[4] Tartronic acid (98% pure, manufacture specifications) was purchased from Aldrich Chemical Company.

For the systems investigated the following equilibrium must be considered:

$$\mathrm{Zn} + \mathrm{L} \rightleftharpoons \mathrm{ZnL} \qquad K_1 = \frac{(\mathrm{ZnL})}{(\mathrm{Zn})(\mathrm{L})} \qquad (1)$$

$$\mathrm{ZnL} + \mathrm{L} \rightleftharpoons \mathrm{ZnL_2} \qquad K_2 = \frac{(\mathrm{ZnL_2})}{(\mathrm{ZNL})(\mathrm{L})} \qquad (2)$$

$$\mathrm{Zn} + \mathrm{HL} \rightleftharpoons \mathrm{ZnL} + \mathrm{H^+} \qquad K_{H1} = \frac{(\mathrm{ZnL})(\mathrm{H^+})}{(\mathrm{Zn})(\mathrm{HL})} \qquad (3)$$

The experiments were designed to quantitatively produce a 1:1 complex; competitive reactions and higher order complexes are insignificant providing $K_1/K_2 \geqslant 10$ (detailed discussion in reference 4). The value reported as ΔV_c is equivalent to ΔV_1, the volume change for the formation of a 1:1 complex, Eq. (1).

The concentration of reactants was decreased relative to that employed in the previous study with Cu(II)[4] thus diminishing salt effects, precipitate formation, dilution effects and activity coefficient corrections. The influence of this alteration can be inferred from the following: 0.05 M Zn(II) added to 0.025 or to 0.0125 M sodium malonate produced ΔV_c values of 18.6 and 19.4 ml/mole compared to 18.9 and 19.4 ml/mole produced by the corresponding 0.020 M Zn(II) and 0.010 and 0.008 M ligand systems. Similar trends were observed for amino acidates. To achieve quantitative complex formation for a given stoichiometric stability constant the correct ratio and concentration of reactants must be used, e.g., for the protocols employed, the stoichiometric affinity constants must be $\geqslant 3 \times 10^3$ to achieve conversion $\geqslant$95%. When question existed experiments were performed at reactant concentrations ranging from 0.05 M Zn(II):0.0125 M ligand to 0.020 M Zn(II):0.008 M ligand to establish quantitative conversion.

The pH of the system establishes the protonation state of the organic acids and thus their affinity for cations.[6] The affinity of Zn(II) for mono- or dicarboxylic acids is small, resulting in a small volume effect. Since these data could not be evaluated rigorously, they were not reported.

Coordination of Zn(II) to dicarboxylates differs in several respects from Cu(II),[4] namely: (i) the values for the stoichiometric stability constants are smaller.[1,2] (ii) the volume changes are smaller and (iii) the values of ΔV_c varied with structure whereas with Cu(II)

TABLE I

Volume changes resulting from Zn(II) complexing with carboxylates

					H_2O		8 M Urea	
Ligand (sodium salt)	Conc (M)	pH equilibrium	pK	Log K[a]	ΔV_{exp} (μl)	ΔV (ml/mole)	ΔV_{exp} (μl)	ΔV_c (ml/mole)
oxalate	0.008	5.5	1.23(1)[b]	4.8(1)[b]	2.20	27.5 (0.13)[c]	1.63	20.4 (0.32)[c]
	0.010	5.5	4.19(2)	2.7(2)	2.67	26.7 (0.37)	2.01	20.1 (0.29)
malonate	0.008	6.5	2.83(1)	3.8(1)	1.55	19.4 (0.12)	1.23	15.4 (0.28)
	0.010	6.6	5.69(2)	2.1(2)	1.89	18.9 (0.14)	1.51	15.1 (0.34)
malate	0.008	6.0	3.40(1)	–[d]	1.67	20.9 (0.28)	1.42	17.7 (0.31)
	0.010	6.1	5.11(2)	–	2.05	20.5 (0.12)	1.75	17.5 (0.26)
tartrate	0.008	5.5	2.98(1)	3.3(1)	1.93	24.1 (0.45)	1.54	19.3 (0.29)
	0.010	5.5	4.34(2)	1.8(2)	2.39	23.9 (0.21)	1.87	18.7 (0.08)

[a] The logarithm of the stoichiometric stability constants for the formation of the 1:1 and 1:2 zinc complexes.

[b] Reference 7.

[c] The values in brackets are the standard deviations calculated from at least five data points. Whenever the standard deviations were $\geqslant 0.25$, eight or more data points were determined.

[d] The value for the stoichiometric affinity constant for malate is not available; however, the agreement of the data for the 0.05 and 0.02 M Zn(II) systems indicate that the affinity constant is $\geqslant 10^3$. This thesis is supported by inspection of the logarithms of the affinity constants for the di- and monoprotonated forms of malic acid which are 1.66 and 2.93, respectively.[2] The values of the affinity constants for this type of coordination process increase with an increase of the negative charge.[6]

TABLE II
Volume changes resulting from Zn(II) interacting with ligands incorporating nitrogen donor atoms[a]

					H_2O	
Ligand (sodium salt)	Conc (M)	pH equilibrium	pK[b]	Log K[b]	ΔV_{exp} (μl)	ΔV_C (ml/mole)
glycinate	0.008	6.9	2.35(1)	5.4(1)	1.00	12.5 (0.33)
	0.010	7.0	9.78(2)	4.4(2)	1.27	12.7 (0.08)
alaninate	0.008	7.1	2.35(1)	5.0(1)	1.08	13.5 (0.14)
	0.010	7.1	9.87(2)	4.2(2)	1.28	12.8 (0.28)
valinate	0.008	7.0	2.29(1)	4.4(1)	1.14	14.3 (0.41)
	0.010	7.1	9.72(2)	3.8(2)	1.41	14.1 (0.15)
leucinate	0.008	7.1	2.33(1)	–	1.14	14.3 (0.31)
	0.010	7.2	9.75(2)	–	1.45	14.5 (0.45)
serinate	0.008	6.9	2.19(1)	4.9(1)	1.13	14.1 (0.32)
	0.010	6.9	9.21(2)	4.4(2)	1.43	14.3 (0.13)
ethanolamine[c]	0.008	6.7	9.50	3.7(1)	0.34	4.3 (0.24)
	0.010	6.5	–	2.3(2)	0.41	4.1 (0.05)

[a] Format similar to Table I.

[b] Reference 16.

[c] Reference 2.

there was only a minor dependence. Of the available dicarboxylates only four had stoichiometric affinity constants sufficiently high to warrant study, Table I. Coordination of Zn(II) to oxalate, forming a five-member chelate, produced a ΔV_c of 27.5 ml/mole at 0.008 M ligand concentration.[7] With malonate, Zn(II) forms a six-member ring yielding a ΔV_c of 19.4 ml/mole. The influence of structure is illustrated by reference to the aliphatic C–4 dicarboxylates: succinate, fumarate and maleate. None of these compounds were characterized by formation constants sufficiently large to drive Eq. (1) to completion. The factors responsible for the larger volume effect produced by oxalate relative to that of malonate are tenuous. Entropic considerations are of secondary importance because the entropy change for these systems are equal, 28 Gibbs/mole.[8] One assumes that the formation of a Zn(II):oxalate complex results in a greater release of electrostricted water than that produced by the corresponding Zn(II):malonate system.

The incorporation of a hydroxyl group in juxtaposition to a coordinating carboxylate group promotes increased volume effects. The values for ΔV_c for the mono- and dihydroxy derivatives of succinate, malate and tartrate, are 20.9 and 24.1 ml/mole respectively. A similar volume increment was observed for tartronate compared to malonate; the formation of a Zn(II):tartronate complex produced a volume change of 21.9 ml/mole for the 0.05 M Zn:0.0125 M ligand system.[9] Thus the presence of a hydroxyl radical adjacent to a coordinating carboxylate increases the magnitude of the volume effect by more than two ml/mole. The volume increase due to the presence of a hydroxyl radical is caused by the release of electrostricted water from this group upon coordination.

The coordination of Zn(II) to α-amino acidates results in volume increases which are determined primarily by the carboxylate radical and to a smaller extent by the amine groups. The aliphatic radical influences the volume effects in a secondary manner. There is a small monotonic increase of the volume parameter as the molecular weight increases from glycinate to valinate, i.e., the values increase from 12.5 to 14.3 ml/mole, Table II. Valinate and leucinate produce equivalent volume changes. The incorporation of a hydroxyl group engenders only a small change in the volume parameter, i.e., the ΔV_c for serinate:Zn(II) complex is about 0.8 ml/mole larger than that of its parent compound, alaninate. Thus the role of the hydroxyl group in amino acidates must differ from that observed in the carboxylate coordination processes.

The substitution of 8 M urea for water attenuated the volume effects for the zinc:carboxylate systems by 20.5 per cent, standard deviation of 4.0 per cent, Table I. This is similar to the effect of urea on Cu(II) coordination processes[4] and the protonation of carboxylates;[10,11] this suggests that similar principles are operational. Namely, this solute causes a reduction of the activity of water and an increase of the dielectric constant of the medium. The latter factor is responsible for the reduction of the electrostrictive capacity of the ionic reactants by diminishing the electrostatic force fields in accord with the Drude-Nernst equation[2] (see references four and eleven for discussion). Coordination studies involving amino acidates in 8 M urea were not performed because of the possible conversion of urea to isocyanate at the elevated pH required for reaction thereby introducing the possibility of a carbamylation reaction with the amine radical of the amino acidate.[3]

An estimate of the contribution of nitrogen donor atoms to volume effects were made from studies involving ethanolamine and imidazole. Volume changes of 4.1 and 4.3 ml/mole were determined for the reaction of 0.020 M Zn(II) with 0.010 and 0.008 M ethanolamine. Precipitation occurs, however the error introduced is considered as being small because steady state volume is reached three minutes after mixing yet precipitation continues as a function of time. The reaction of 0.020 M Zn(II) with imidazole gave volume changes of 3.8 and 3.6 ml/mole for 0.010 and 0.008 M imidazole, respectively. The value for ΔV_1 was not calculated because the experimental volume effects were the resultant of the formation of several complexes; this occurs because of overlapping values of the affinity constants; 2.5, 2.3, 2.3 and 2.0.[15]

It is apparent that the volume effects produced by Zn(II) coordination processes differs substantially from that of the corresponding Cu(II) systems which is to be expected in view of the disparity of these two cations. The dependence of volume effects on the structure of the reacting dicarboxylate compound is a statement of the dependence of this parameter on the free energy of complex formation. When the interaction energies are relatively low the displacement of water of electrostriction is less than for systems characterized by larger bonding energies. Support for this hypothesis is provided by reference to the amino acidates, Table II; these systems are characterized by large affinity constants, consequently the influence of associated structural features is relatively small. On the other hand, the coordination of Zn(II) to nitrogen donor atoms produces larger volume changes than that observed with the corresponding Cu(II) systems; in the absence of configurational changes this indicates a greater displacement of electrostricted water. The rationale underlying this phenomenon requires additional investigation. One conclusion of this study is that it is difficult to predict volume effects from one system to another; experimental evidence is necessary to provide this information.

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