Relationships between Computed and Experimentally Determined Molecular Volumes and Radii

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Theoretically computed molecular volumes and radii based on overlapping van der Waals spheres have been derived for a wide range of inorganic molecular ions and compared with experimentally determined partial molal volumes and thermochemical radii. The correlations are remarkably good and may be used to estimate with some confidence either the partial molal volumes of ions which have not been experimentally determined or the lattice energies of molecular salts. The accuracy of the calculated partial molar volumes may be sufficient to calculate the molar volumes of activation for transition states.

Recently we have described the calculation of molecular volumes of co-ordination and organometallic ions[1,2] and illustrated their applications to a range of packing and crystallisation problems in the solid state. The molecular volumes and surface areas of molecules and ions are calculated on the assumption that a molecule may be defined as a collection of overlapping van der Waals spheres. This methodology has been particularly widely used in organic chemistry, but little applied to co-ordination and organometallic compounds. The effective radii of the inorganic molecules and ions $[R_{\text{eff}}(V_{\text{m}})]$ are computed from the molecular volumes (V_{m}) on the basis that they are approximately spherical. A computer program which calculates these quantities is available. It is written in C and runs on Apple Macintosh computers.

Gavezzotti[3] has shown that V_{m} could be matched to some properties of simple gases, liquids and solids. He compared his V_{m} values with the covolume, which is the b parameter in the van der Waals equation of state (1). Taking b to be equal

$$(P + aV^{-2})(V - b) = RT \qquad (1)$$

to $4V_{\text{p}}$ where V_{p} is the proper volume of one molecule in collision theory, his results show that, for organic compounds of moderate polarity and not subject to hydrogen-bond formation, $V_{\text{p}}/V_{\text{m}} \approx 0.6$. The ratio for compounds which undergo hydrogen bonding was not only larger but also more variable.

In this paper the effective radii of inorganic molecular ions are compared with two experimentally determined quantities, thermochemical radii and partial molal volumes. These comparisons demonstrate that calculated effective radii correlate well with these experimental quantities, justifying their use as molecular ion size descriptors in the solid-state structural analyses which have been discussed elsewhere.

Comparison with Thermochemical Radii

Kapustinskii[4] has proposed an equation which may be used to estimate the lattice energy of a crystal provided that the thermochemical radii of both the anion (R_{a}) and cation (R_{c}) are known. His equation is based on the observation that if the Madelung constants for a number of structures are divided by the number of ions per formula unit, approximately the same value is obtained for them all. The equation takes the form (2)

Table 1 Thermochemical and effective radii of some inorganic anions

Anion	R_{a}	$R_{\text{eff}}(V)$	Anion	R_{a}	$R_{\text{eff}}(V)$
F^-	1.26	1.30	ClO_4^-	2.40	2.24
$MeCO_2^-$	1.62	2.28	$[CrO_4]^{2-}$	2.56	2.35
Cl^-	1.72	1.77	$[SiF_6]^{2-}$	2.59	2.40
NO_3^-	1.79	2.02	$[PtCl_4]^{2-}$	2.93	2.92
Br^-	1.88	1.95	$[MnCl_6]^{2-}$	3.22	3.21
CN^-	1.91	1.89	$[OsCl_6]^{2-}$	3.24	3.23
I^-	2.10	2.10	$[TeI_6]^{2-}$	3.83	3.87
BF_4^-	2.32	2.09			

$$U = \frac{-1214 v z_+ z_-}{R_{\text{c}} + R_{\text{a}}}\left(1 - \frac{\rho}{R_{\text{c}} + R_{\text{a}}}\right) \qquad (2)$$

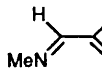
where v is the number of ions per formula unit and z_+ and z_- are the cation and anion charges. The constant ρ characterises the repulsive forces between the electronic shells of ions and has a value of 0.345 Å. If the lattice energy is known (either from experiment or accurate calculation[4,5]) then the equation may be used to calculate the thermochemical radii. By examining salts of alkali metals, where the thermochemical radius of the cation is simply its ionic radius, the thermochemical radii of complex anions may be determined. Similarly, the thermochemical radii of complex cations may be determined by examining halide salts.

The thermochemical radii of Kapustinskii have been extended by Jenkins and Thakur[6] who compiled data for 104 anions and four cations. A selection of their anions incorporating a range of geometries and volumes are listed in Table 1 along with their calculated effective radii. In order to compare the calculated molecular volume with the corresponding thermochemical radii, R_{eff} is plotted against R_{a} in Fig. 1. The two parameters correlate well with a correlation coefficient of 0.95. Only $MeCO_2^-$ deviates significantly from the line of best fit, but this cannot easily be assigned to shape effects as other prolate ions do not show the same deviation. This suggests that the assigned radius may be in error. Overall, the good correlation suggests that molecular volumes and surface areas will correlate well with the lattice energies of molecular salts. Furthermore, these results suggest that it should be possible to calculate with some degree of accuracy the lattice energies of molecular salts with large cations and anions from their computed effective radii. An extensive compilation of molecular volumes has been given in previous papers.[1,2,7]

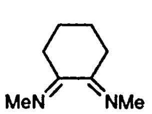
Table 2 Partial molal volumes of ions[a] in water at room temperature and their calculated intrinsic volumes (both in cm^3 mol^{-1})

Ion	V^∞	V^0	Ref.	Ion	V^∞	V^0	Ref.
NH_4^+	18	32	9	$[Zr(ox)_4]^{4-}$	130	208	20
NO_3^-	29	43	9	$[Co(NH_3)_2(NO_2)_4]^-$	130	144	19
ClO_4^-	44	55	9, 11	NEt_4^+	149	148	9
BF_4^-	44	47	9	$[PtCl_6]^{2-}$	150	137	9
$[Cr(NH_3)_5(OH_2)]^{3+}$	71	127	12–14	$[FeL^1{}_3]^{2+}$	160	243	22
$[Co(NH_3)_6]^{3+}$	72	126	12, 15–17	$[Mn(edta)]^{2-}$	162	208	23
$[Rh(NH_3)_6]^{3+}$	79	134	18	$[Ni(edta)]^{2-}$	165	206	23
$[Co(NH_3)_5(NO_2)]^{2+}$	83	130	19	$[Co(edta)]^{2-}$	168	208	23
$[Cr(NH_3)_6]^{3+}$	85	130	12, 15	$[Fe(edta)]^-$	171	209	23
NMe_4^+	90	94	9	$[NMe_3(C_{10}H_{21})]^+$	235	222	24
$[Cr(NH_3)_5Cl]^{2+}$	92	131	12, 13	NBu_4^+	276	252	9
$[Cr(NH_3)_5Br]^{2+}$	101	138	12	BPh_4^-	278	280	9
$[Co(NH_3)_4(NO_2)_2]^+$	104	134	19	$AsPh_4^+$	301	288	9
$[Cr(NH_3)_5I]^{2+}$	106	143	12	$[Fe(bipy)_3]^{2+}$	370	368	25
$[Cr(NH_3)_5(NCS)]^{2+}$	112	148	12	$[FeL^2{}_3]^{2+}$	400	368	22
$[Fe(CN)_6]^{3-}$	120	148	9	$[Fe(phen)_3]^{2+}$	410	408	25
$[Cr(ox)_3]^{3-}$	122	160	20	$[Bu_3N(CH_2)_8NBu_3]^{2+}$	523	477	9
$[Co(en)_3]^{3+}$	126[b]	177	16, 21	$[FeL^3{}_3]^{2+}$	600	666	22

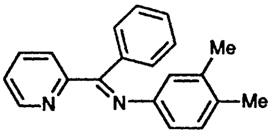
[a] Abbreviations: bipy = 2,2′-bipyridyl; edta = ethylenediaminetetraacetate; en = ethane-1,2-diamine; ox = oxalate; phen = 1,10-phenanthroline. [b] Mean of a number of rather scattered values.



L^1



L^2



L^3

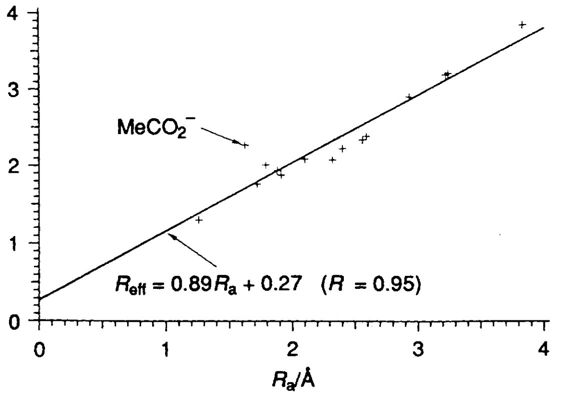


Fig. 1 Plot of effective radius *versus* thermochemical radii for the ions in Table 1

Comparison with Partial Molal Volumes

Another experimentally determined quantity to which the effective radii may be compared is the partial molal volume of an ion.[8] This technique has been applied to a much larger range of ions than the thermochemical radii and is based on the observation that the volume of a solvent changes when an electrolyte is added to it. In order to minimise the ion–solvent interactions these experiments must be carried out at very low concentrations. Measuring very small changes in volume is difficult and so partial molal volumes (φ_m) are determined by accurate density measurements[9] from equation (3) where m is

$$\varphi_m = \frac{1000}{mdd_m}(d_m - d) + \frac{M}{d} \qquad (3)$$

the molality of the electrolyte, d the density of the solvent, d_m the density of the solution and M the molecular weight of the electrolyte. By measuring this quantity at several different small molalities, the limiting value at infinite solution (V^∞) can be determined from a plot of φ_m *versus* $m^{\frac{1}{2}}$. Glueckauf[10] has shown that the aqueous partial molal volumes in absence of any electronic effects (the intrinsic volume V^0) is given by expression (4) where r_0 is the crystallographic radius (in Å) of the ion. The

$$V^0 = 2.52(r_0 + 0.55)^3 \qquad (4)$$

increment of 0.55 Å arises from the open structure of water, *i.e.* the water molecules are not arranged tightly around the ion. By substituting r_{reff} for r_0 in equation (4), r_{eff} may be compared to the partial molal volumes. In Table 2 the calculated partial molal volumes and intrinsic volumes of 34 inorganic ions are proposed.

The partial molal volumes in Table 2 are based on the widely used assumption that the partial molal volume of H^+ is zero. This is probably close to reality since most estimates for the absolute value cluster around $V^\infty(H^+) = -5$ cm^3 mol^{-1}. It is interesting that the proposed method of estimation gives partial molal volumes differing by only 8 cm^3 mol^{-1} for the tetraphenylarsonium and tetraphenylborate ions, *i.e.* their values are accurately estimated to within likely uncertainties in the experimentally determined values, whereas on the $V^\infty(H^+) = 0$ assumption their partial molal volumes differ by more than 20 cm^3 mol^{-1}. This result is of some significance because a large body of data on single-ion solvation properties is based on the assumption that the partial molal volumes of $[AsPh_4]^+$ and $[BPh_4]^-$ are equal.

The volume parameters in Table 2 are plotted in Fig. 2. The correlation coefficient of 0.98 indicates that there is a good relationship between partial molal volumes and intrinsic volumes. The slope of the graph, which is very close to unity, suggests that the intrinsic volume calculated by equation (4) accounts for most of the partial molal volume of the ions.

The intercept of −25 cm^3 mol^{-1}, however, suggests that the size of the ion is not the only factor determining the partial molal volumes. The other factor involved is termed the electrostriction volume and causes the partial molal volume to be smaller than the intrinsic volume. This reduction in the apparent volume is caused by interactions between the charges

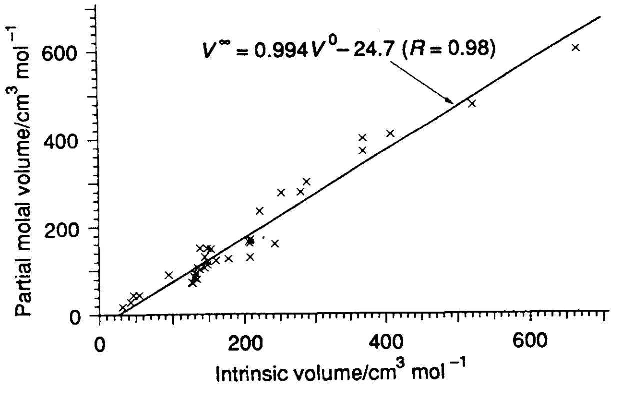


Fig. 2 Plot of partial molal volume *versus* intrinsic volume for the ions in Table 2

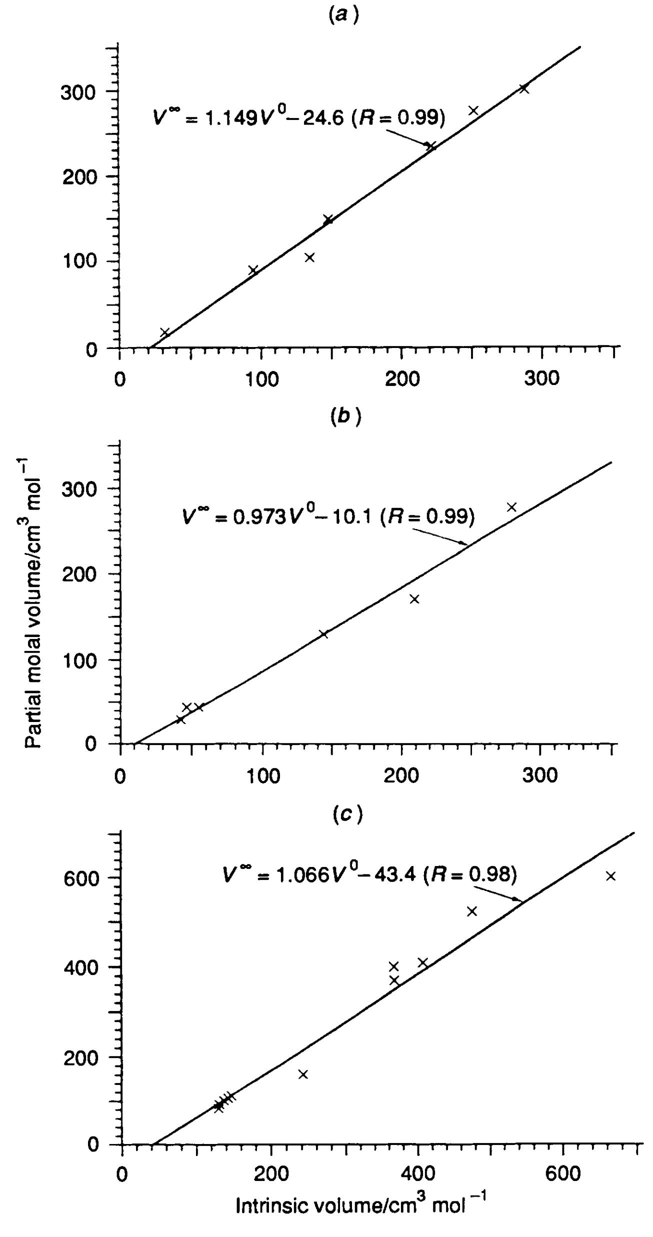
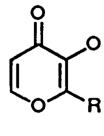
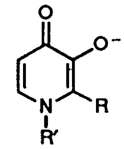


Fig. 3 Plots of partial molal volume *versus* intrinsic volume for (*a*) 1+ cations, (*b*) 1– anions and (*c*) 2+ cations

on the ions and the permanent dipoles of the water molecules, which locally break down the structure of the water allowing closer water–ion contacts than would be allowed between a neutral molecule and water.[10] In fact the partial molal volumes of very small ions are negative (*e.g.* Na^+, –1.21; Pr^{3+}, –42.53; OH^-, –4.04 $cm^3\ mol^{-1}$) implying that the electrostriction term dominates the intrinsic volume for these ions.[22] Thus the degree of this electrostriction will depend on the ionic charge. In Fig. 3 the partial molal volumes are plotted against the intrinsic volumes for the 1+, 1– and 2+ ions respectively. The slopes for all three of these plots are near unity but the intercepts vary greatly. The intercepts for the 1+ and 1– ions are –24 and –10 $cm^3\ mol^{-1}$, the absolute values of which are quite a lot less than the value of –38 $cm^3\ mol^{-1}$ for the 2+ ions, as expected. All are less than V^∞ for the lanthanide(3+) ions. It would be very useful to have a series of partial molar volumes for uncharged inorganic complexes in order to avoid single-ion assumptions and minimise electrostriction effects. Unfortunately they are inconveniently insoluble in water {for example $[Co(NH_3)_3(NO_2)_3]$ and in the iron series $[Fe(diimine)_2(CN)_2]$} or aquate too quickly {*e.g.* $[Co(NH_3)_3Cl_3]$}. Metal(III) complexes of pyrone and pyridinone ligands, *e.g.* aluminium, gallium and iridium, tris(ligand) complexes of **I** and **II** are moderately soluble and may well provide a useful series in this respect, particularly as the R′ group in **II** may be varied from H up to n-C_6H_{13} and substituted phenyl groups.



I



II

The electrostriction term is not expected to be constant for increasing ion size. In fact as the size of the ion increases the electrostriction term decreases. This effect can be clearly seen in Table 2 where the difference between the partial molal volume and intrinsic volume decreases as the size of the ion increases for a given ionic charge. Note that the largest ions (>278 $cm^3\ mol^{-1}$) have partial molal values greater than the intrinsic volumes. Assuming that these large ions have little electrostriction what could be the cause of this discrepancy? The most likely explanation is that there are many indentations in the surface of these larger ions which are not large enough to accommodate water ions but the volume of which is excluded from the intrinsic volume because of the method of volume calculation. This effect could probably be avoided by calculating r_{eff} from the solvent accessible volume,[26] a quantity which is much harder to calculate than the molecular volume. The largest ion studied, $[FeL^3{}_3]^{2+}$, has an intrinsic volume much greater than its partial molal volume. This discrepancy has been noted previously,[22] using a much simpler method of approximating the intrinsic volume, but has yet to be explained.

In this work the effective radius has been used to calculate intrinsic volumes of some ions in water. These volumes have been compared to partial molal volumes and show the expected trends in terms of both the size and charges of the ions. More quantitative results such as the exact effects of size and charge on the electrostriction volume which are not fully understood[27] will need a much larger sample set, but the qualitative agreement further demonstrates that the effective radius is a good description of molecular ion size.

It is anticipated that the approach detailed in this paper for estimating partial molar volumes may be extended from ground-state complexes to transition states of reactions involving complexes. A large body of kinetic data is available for inorganic substitution and electron-transfer reactions. The discussion of the role of solvation changes in going from the initial to the transition state in determining reactivity trends would be facilitated by a greater insight into the transition-state solvation. This would be particularly valuable in the aquation of chlorocobalt(III) complexes and the base hydrolysis of iron(II) diimine complexes where $\Delta V^{\ddagger}$(solvation) dominates over $\Delta V^{\ddagger}$(intrinsic) [recalling that $\Delta V^{\ddagger}_{\text{obs}} = \Delta V^{\ddagger}$(intrinsic) + $\Delta V^{\ddagger}$(solvation)]. It would also be valuable in situations such as the intramolecular electron transfer within binuclear species, *e.g.* cobalt(III) pentacyanopyrazineferrate(II), where it is impossible to establish initial-state solvation due to the rapidity of the reaction. Specifically the estimation of solvation contributions to experimentally determined activation volumes would be considerably aided by the possibility of calculating partial molar volumes of transition states to compare with those of the initial states (measured and/or calculated). Indeed this information coupled with measured or estimated partial molar volumes of the respective product would provide a detailed picture of the activation profile to complement overall volume profiles established from kinetic measurements.

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