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Partial Molar Volumes and Refractions of Cobalt(III) Complexes, Part 1: Homologous Series of Hexaaminecobalt(III) Complexes

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Both the partial molar volumes ($V^{\circ}_{\text{solute}}$) and refractions ($R^{\circ}_{\text{solute}}$) of the solute at infinite dilution have been determined for a series of four octahedral N_6-coordinated cobalt(III) species with increasing ligand size (ammonia, ethylenediamine, sepulchrate, and 1,2-diaminocyclohexane). The experimental values for $V^{\circ}_{\text{solute}}$ are consistent with the relative sizes of the ligands but show larger values than those generated by computer modeling as the size of the cation increases. This suggests that the void space of the cation increases with the size of the cation. It is proposed that increasing hydrophobicity of the alkane ligand frameworks contributes to larger volumes.

KEY WORDS: Amine ligands; cobalt(III) complexes; molar volume; partial molar volume; molar refraction.

1. INTRODUCTION

Highly accurate measurements of density and index of refraction for dilute aqueous solutions may be used to determine the partial molar volumes and refraction for the solutes at infinite dilution. It would be instructive to apply this method to highly charged cationic complexes of the same charge and similar composition. A series of homologous octahedral-coordinated cobalt(III) complexes was chosen. The only ligating element for these complexes was nitrogen, but the size of the overall complex ion was systematically increased by using ligands with larger alkane frameworks in proximity to the ligating nitrogen atoms. The ligands ranged from the simple ammonia molecule to bidentate ethylenediamine (en) to the hexadentate

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sepulchrate cage (sep) to the larger bidentate diamine, 1,2-diaminocyclohexane (chxn).[2]

Therefore, a series of dilute aqueous solutions (*ca.* 0.01 mol-L^{-1} maximum) of each of the following compounds: $[Co(NH_3)_6]Cl_3$, $[Co(en)_3]Cl_3$, $[Co(sep)]Cl_3$, and $[Co(chxn)_3]Cl_3$ was prepared. The density and refractive index of each solution were measured. The analogous ethylenediamine complex of chromium(III) was also examined for comparison, since it is similar to the cobalt complex in molar mass. This was done, in part, to determine how sensitive the technique was in estimating the relative sizes of the different complexes and to compare the absolute values of molar volumes to those derived from computational methods.

2. EXPERIMENTAL

2.1. Metal Complexes

The hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$,(1) the tris-ethylenediamine complex, $[Co(en)_3]Cl_3\cdot 3H_2O$,(2) and the sepulchrate complex, $[Co(sep)]Cl_3$(3) were each synthesized according to published procedures. The synthesis of the tris(trans-1,2-diaminocyclohexamine) complex, $[Co(chxn)_3]Cl_3\cdot 3H_2O$, was based upon a literature method which yielded the bromide salt.(4) The conversion to the chloride salt was accomplished by ion-exchange chromatography (done twice) using BioRad AG3-X4A 200–400 mesh chloride form resin. Commercially available $[Cr(en)_3]Cl_3\cdot 2H_2O$ was purchased from Ventron Alpha Products and carbon analysis indicated that it was the dihydrate.

2.2. Solutions

A series of five solutions for each compound studied was prepared using about 10, 25, 40, 50, and 60 mg of the compound in 20 g of water. First, the solid was added to a tared 25-mL Erlenmeyer flask and its exact mass recorded; after retaring, 20 mL of deionized water was added and its mass recorded. The flasks were tightly sealed with stretch film until density and refractive index measurements were made within 2 h after preparation of the solutions.

2.3. Density and Index of Refraction Measurements

Density and refractive index were measured with an Anton Paar DMA 4500 density meter mated to an Anton Paar RXA 170 refractometer through plastic tubing. Samples were drawn using reduced pressure through the two pieces of

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[2] en = 1,2-diaminoethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane, and chxn = trans-1,2-diaminocyclohexane.

apparatus and the measurements of density and refractive index were made simultaneously. The temperature was controlled with Peltier temperature controllers with an uncertainty of 0.03 °C. All measurements were made at 20.00 °C. The uncertainty for the density measurements is 0.00002 g-mL^{-1} and for the refractive index measurements, 0.00005.

The system was calibrated using distilled water and air for the density and refractive index at least once every 2 days. All density and refractive index measurements in this study fall within a small range of values because of the low solute concentrations used. The ranges for the density and refractive index are 0.99820–0.99980 g-mL^{-1} and 1.33299–1.33371, respectively. These ranges fall well within the manufacturer's recommendation for the calibration procedure used here.

2.4. Space-Filling Volume Measurements

Calculations of the volumes for the cationic complexes and for chloride were performed using a Silicon Graphics Octane workstation. These semi-empirical methods optimize molecular geometry by energy-minimization routines. All space-filling structures, from which molecular volumes can be estimated, are then constructed by superimposing standard van der Waals radii to each atom.

2.5. Data Treatment

Volumetric studies of aqueous ionic solutions normally report the apparent molar volume of the ionic species as a function of the square root of its molarity or molality(5, 6) in order to account for the change in molar volume of water as predicted by the Debye–Hückel limiting law. The equation used to determine apparent molar volume was originally introduced by Marignac(7) and may be written as

$$\phi_v = \frac{V - n_1 V^{\circ}_{1m}}{n_2} \tag{1}$$

where ϕ_v is the apparent molar volume, V is the total volume, V°_{1m} is the molar volume of pure water, and n_1 and n_2 are the number of moles of water and ionic solute, respectively.

The apparent molar volume (ϕ_v) has been employed since the late nineteenth century for electrolyte solutions. It measures the change in a volume of water caused by the addition of solute, to wit

$$V = n_1 V^{\circ}_{1m} + n_2 \phi_v \tag{2}$$

Masson(8) noted that ϕ_v for electrolyte solutions could be represented by

$$\phi_v = V^{\circ}_{2m} + S\underline{m}_2^{1/2} \tag{3}$$

where S was an empirical parameter, $\underline{m}_2$ is the molality of the solute, and V_2° is the partial molar volume of the solute at infinite dilution. Later, Redlich and Rosenfeld(5) demonstrated the theoretical significance of S by employing the Debye–Hückel theory and later still, Redlich and Meyer(6) added an additional empirical term to account for nonlinearity of ϕ_v with $\underline{m}_2^{1/2}$. Thus,

$$\phi_v = V_{2m}^\circ + S_V \underline{m}_2^{1/2} + b\underline{m}_2 \tag{4}$$

where b is an empirical constant and S_V is a theoretical constant dependent upon ionic type (*e.g.*, 1:1, 1:2, *etc.*). It is more common to use molarity leading to slightly different values for S_V and b. Molality is used here since it is directly proportional to mole ratio that figures prominently in the ensuing discussion.

The uses of this expression for studying dilute electrolyte solutions are threefold:

1. to verify the value of S_V,
2. to determine b for the various binary electrolyte solutes, and
3. to determine V_{2m}°, the partial molar volume of the solute.

The principal purpose of this study is to determine V_2° for a series of related compounds.

For nearly a half-century, volumetric studies of solutions of electrolytes have employed the RRM equation, or modifications of it, to determine the partial molar volume of the solute at infinite dilution (V_{2m}°) using the Debye–Hückel parameter. The apparent molar volume is determined from the density measurements using

$$\phi_v = \frac{1000}{\underline{m}_2}\left(\frac{1}{\rho} - \frac{1}{\rho_1^\circ}\right) + \frac{M_2}{\rho} \tag{5}$$

The densities of the pure solvent and the solution are ρ_1° and ρ, respectively, and M_2 is the solute molar mass. For purposes of this development, the equations are recast in terms of mole ratio ($r = n_2/n_1$). Thus,

$$\phi_v = V_{2m}^\circ + S_V' r^{1/2} + b'r \tag{6}$$

and

$$\phi_v = \frac{M_1}{r}\left(\frac{1}{\rho} - \frac{1}{\rho_1^\circ}\right) + \frac{M_2}{\rho} \tag{7}$$

where

$$S_V = S_V'\left(\frac{M_1}{1000}\right)^{1/2}$$

$$b = b'\left(\frac{M_1}{1000}\right)$$

and M_1 is the solvent molar mass.

It has been noted that even small errors in densities lead to large uncertainties in ϕ_v at low concentrations, whereas ϕ_v is not greatly affected by errors in concentration.$^{(9)}$ For the overwhelming majority of studies in the literature, the lowest concentrations used are on the order of 0.01 mol-L^{-1} ($r = 2 \times 10^{-4}$ for aqueous solutions). The use of concentrations above 0.01 mol-L^{-1} is problematic for at least two reasons: the limit of applicability of the uncorrected Debye–Hückel equation, from which S_V is determined, is estimated to be about 0.01 mol-L$^{(10)}$ and the extent to which ion pairing occurs increases markedly with concentration, especially for solutions of multivalent ions (see later). Presumably the b term accounts for some of this deviation, though no definitive analysis of this is available in the literature.

It is possible to use the RRM equation in two ways. First is to fit ϕ_v to a quadratic expression in $r^{1/2}$ (or $\underline{m}_2^{1/2}$ or $\underline{M}_2^{1/2}$) and extract V_{2m}°, S_V', and b'. Second is to introduce the accepted value for S_V' and fit $\phi_v - S_V' r^{1/2}$ to a linear regression in r (or $\underline{m}_2$ or $\underline{M}_2$) to determine values of V_{2m}° and b'. It is the latter method that was one of the two methods used in this study to determine V_{2m}°. Since it is most common to use molarity, the function $\phi_v - S_V'' \underline{M}_2^{1/2}$ was fitted to a linear regression in molarity using the accepted value for S_V'' (=27.454 mL-mol$^{-3/2}$-L$^{1/2}$ for 3:1 electrolytes).$^{(11)}$ Because of the relatively large uncertainty in ϕ_v, no reliable values for b'' could be determined. For all systems studied here, the highest concentrations used were about 0.01 mol-L^{-1} because of the limited amounts of the compounds available. This difficulty in determining values for b'' from volumetric studies of solution at low concentration is not unusual. Figure 1 shows $\phi_v - S_V'' \underline{M}_2^{1/2}$ *versus* solute molarity for data obtained by Spedding *et al.*$^{(12)}$ for aqueous solutions of KCl, where S_V'' (=1.868 mL-mol$^{-3/2}$-L$^{1/2}$) is the Debye–Hückel constant for 1:1 electrolytes in terms of molarity.$^{(11)}$ The slope (b'') and the intercept (V_{2m}°) determined by linear regression are 0.0984 mL-L-mol^{-2} and 26.828 mL-mol^{-1}, respectively. However, using just the data from the seven lowest concentration measurements, the largest of which is about 0.01 mol-L^{-1}, one obtains -0.1362 mL-L-mol^{-2} and 26.836 mL-mol^{-1} for b'' and V_{2m}°, respectively. Clearly the determination of V_{2m}° is unaffected by only considering data in the low concentration regime, whereas the determination of b'' becomes unreliable. Moreover, simply averaging the values of $\phi_v - S_V'' \underline{M}_2^{1/2}$ for this low concentration subset gives 26.830 mL-mol^{-1}, a good estimate of V_{2m}°. In fact, Banipal$^{(13)}$ averaged the values of ϕ_v for dilute aqueous sugar solutions in order to estimate values for V_{2m}°.

The solutes studied here are 3:1 electrolytes with cations of considerable size. The simplification of the Debye–Hückel limiting law that leads to direct proportionality between the logarithm of the mean activity coefficient and the square root of ionic strength is based on the assumption that most ionic radii are on the order of 3×10^{-10} m or about 22 mL-mol^{-1} assuming spherical shapes.$^{(10)}$ The estimated volumes of cations studied here based upon space filling models

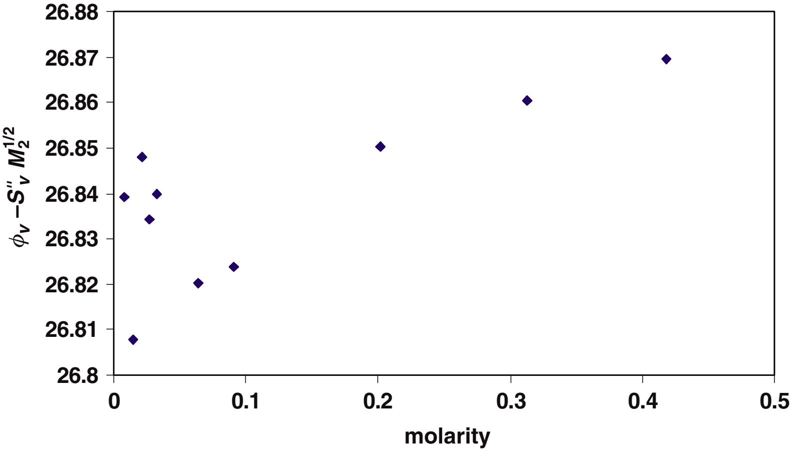

Fig. 1. $\phi_v - S''_V \underline{M}_2^{1/2}$ *versus* molarity for aqueous KCl solutions. Data from Ref. (12).

range from 80 to 240 mL-mol^{-1} (see Table III). This could result in a small though significant change in S_V for these systems. Moreover, there is evidence that b is a function of concentration for multivalent electrolytes.$^{(14)}$

Because of the low concentrations of the solutions studied here and issues discussed above regarding the use of b and S_V, an alternate approach was developed in order to determine V°_{2m} for these compounds based upon methods employed for volumetric studies of nonelectrolyte solutions. The molar volume of a binary

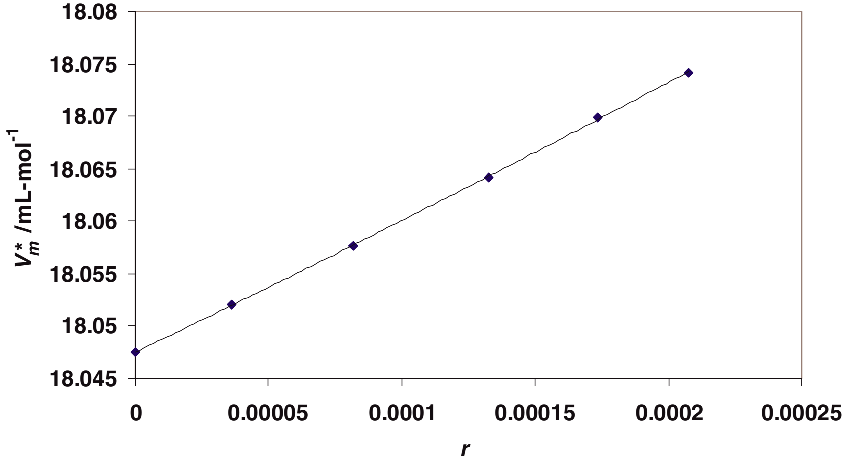

Fig. 2. V_m^* for aqueous $Co(NH_3)_6Cl_3$ solution *versus* its mole ratio.

system (V_m) may be written as

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} = x_1 V_{1m} + x_2 V_{2m} \tag{8}$$

where x_1 and x_2 are the mole fractions, and V_{1m} and V_{2m} are the partial molar volumes of solvent and solute, respectively. Division by x_1 gives a new function, V_m^* such that

$$V_m^* = \frac{M_1 + r M_2}{\rho} = V_{1m} + r V_{2m} \tag{9}$$

The slope and intercept determined at each concentration give V_{2m} and V_{1m} which, in the limit of infinite dilution, give V_{2m}° and V_{1m}°. Substitution of Eq. (1) into

$$V = n_1 V_{1m} + n_2 V_{2m}$$

gives

$$\phi_V = V_{2m} + \frac{1}{r}(V_{1m} - V_{1m}^\circ) \tag{10}$$

Substitution of Eq. (9) into Eq. (10) gives

$$V_m^* = V_1^\circ + r\phi_v \tag{11}$$

Finally, substitution of the RRM equation yields

$$V_m^* = V_1^\circ + r V_{2m}^\circ r + S_V' r^{3/2} + b' r^2 \tag{12}$$

This result implies that $(V_m^* - V_1^\circ - S_V' r^{3/2})/r$ is equivalent to $\phi_V - S_V' r^{1/2}$ and a linear regression of either term with respect to r gives V_{2m}° (intercept) and b' (slope). This has been verified using data from this study. Thus, V_m^* may be used to determine V_{2m}° and b' in the same way as ϕ_v. However, if the use of b' and S_V' is problematic for reasons discussed above, another approach has been shown to be reliable. In this approach V_m^* is fit to a polynomial regression in r from which the slope at infinite dilution is V_{2m}°, see Eq. (9). This method has two advantages in determining partial molar volumes. First, it uses no theoretical parameters and second, it provides a way for determining V_{2m} as a function of concentration should that be of interest. Table II reports the coefficients determined using a quadratic polynomial regression of V_m^* *versus* r. In Table III the values of V_{2m}° are reported for all systems studied here using both the RRM equation and the method described above with a quadratic polynomial regression. The differences in V_{2m}° between the two methods range from 0.3 to 4.3% with three of the five systems exhibiting differences of less than 0.6%.

The partial molar refractions of the ionic solutes are obtained in a similar fashion using

$$R_m^* = R_{1m} + rR_{2m} \tag{13}$$

where

$$R_m^* = V_m^* f$$

and

$$f = \frac{n_D^2 - 1}{n_D^2 + 2}$$

R_{2m} is the partial molar refraction of the ionic solute, n_D is the refractive index of the solution measured at the Na D line and f is the solution's Lorentz–Lorenz function. R_m^* is normally more linear than V_m^* as a function of mole ratio(15) and reliable R_{2m}° values were determined using simple linear regressions.

3. EFFECT OF ION PAIRING

The error in the reported partial molar properties at infinite dilution may be assessed by considering all solute species in solution for a 3:1 electrolyte. Here only the formation of 1:1 ion pairs is considered and all others are ignored since their concentrations have been shown to be negligible.(16) Let

n_1 : moles of premixed water added

n_2 : moles of premixed solute added

and

$$n_{\text{cation}} = n_2 - \alpha n_2 = \text{moles of free cation present} \tag{14}$$

$$n_{\text{anion}} = 3n_2 - \alpha n_2 = \text{moles of free anion present} \tag{15}$$

where, α is the degree of association of ion pairs.

The total number of moles in solution, n, is

$$n = n_1 + n_2(4 - \alpha) \tag{16}$$

Using molar volume as an example, the following expression is obtained

$$V_m = \frac{1}{n}(n_1 V_{1m} + n_{\text{cation}} V_{\text{cation}} + n_{\text{anion}} V_{\text{anion}} + n_2 \alpha V_{\text{pair}}) \tag{17}$$

Substitution of Eq. (14) into Eq. (16) yields

$$V_m = \frac{1}{n}[n_1 V_{1m} + n_2\{(V_{\text{cation}} + 3V_{\text{anion}}) + \alpha(V_{\text{pair}} - V_{\text{cation}} - V_{\text{anion}})\}] \tag{18}$$

where

$$V_{\text{cation}} + 3V_{\text{anion}} = V_{2m} \tag{19}$$

which is the fully dissociated molar volume of the solute ignoring electrostriction effects. Using Eq. (9), the relationship becomes

$$V_m^* = V_{1m} + \frac{x_2}{x_1}[V_{2m} + \alpha(V_{\text{pair}} - V_{\text{cation}} - V_{\text{anion}})] \tag{20}$$

and

$$V_{\text{pair}} - (V_{\text{cation}} + V_{\text{anion}}) = \Delta V \tag{21}$$

It is reasonable to assume that

$$V_{2m}^{\circ} \gg \Delta V \tag{22}$$

Conductometric studies(16) indicate that at the concentrations employed in this study, α ranges from 25 to 65%. Even though, it can be concluded that the error in estimating the volume of the dissociated complex (V_{2m}°) using the limiting slope method is small given the small size of ΔV and the decreasing value of α as the concentration of solute decreases.

4. RESULTS AND DISCUSSION

Figures 2 and 3 show V_m^* and R_m^* *versus* the mole ratio for aqueous $[Co(NH_3)_6]Cl_3$ solutions at 20.0 °C, respectively. The limiting slopes give the partial molar values of the solute at infinite dilution (V_{2m}° and R_{2m}°). The volumetric and refractometric data for $[Co(en)_3]Cl_3$, $[Co(sep)]Cl_3$, $[Co(chxn)_3]Cl_3$ and $[Cr(en)_3]Cl_3$ exhibit similar behavior. Table I shows the density and refractive index data for each of the complexes studied. The mole ratios refer to the moles of anhydrous solute per mole of water. Table II gives the coefficients for the polynomial regressions for V_m^* as described in Section 2.5.

4.1. Partial Molar Volume

Table III shows the volumes for complex cations computed as described in Methods and the measured partial molar volume of the solutes. Also included are the V_{2m}° values determined for the intercept of $\phi_v - S_V'' \underline{M}_2^{1/2}$ *versus* molarity. The difference between the measured partial molar volume of $[Co(NH_3)_6]Cl_3$ at infinite dilution from the "V_m^*" method and the volume of the cation calculated using the "space-filling" methodology described in Methods is 41.3 mL-mol^{-1}. The crystal ionic volume of chloride as calculated from the average of crystal radii(17) is 14.9 mL-mol^{-1} or 44.7 mL-(3 mol)$^{-1}$. Thus the experimental and computed values agree to within 3.4 mL-mol^{-1}. However, this is not the case for the other systems with organic moieties. As the ligands increase in size (from en to

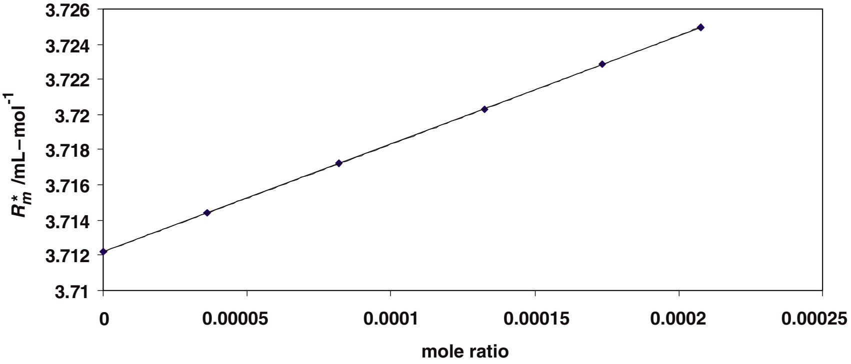

Fig. 3. R_m^* for aqueous $Co(NH_3)_6Cl_3$ solution *versus* its mole ratio.

sep to chxn), the difference between the measured partial molar volumes and the computed cationic volumes increases. The values for the partial molar volumes at infinite dilution for the solutes are normally rationalized as resulting from contributions from the intrinsic molar volume of the nonhydrated solute molecule (V_2^{int}) and the volumetric effects caused by solvent–solute interactions, commonly referred to as the void volume (V_2^{void}).(18) Thus,

$$V_{2m}^{\circ} = V_2^{\mathrm{int}} + V_2^{\mathrm{void}}$$

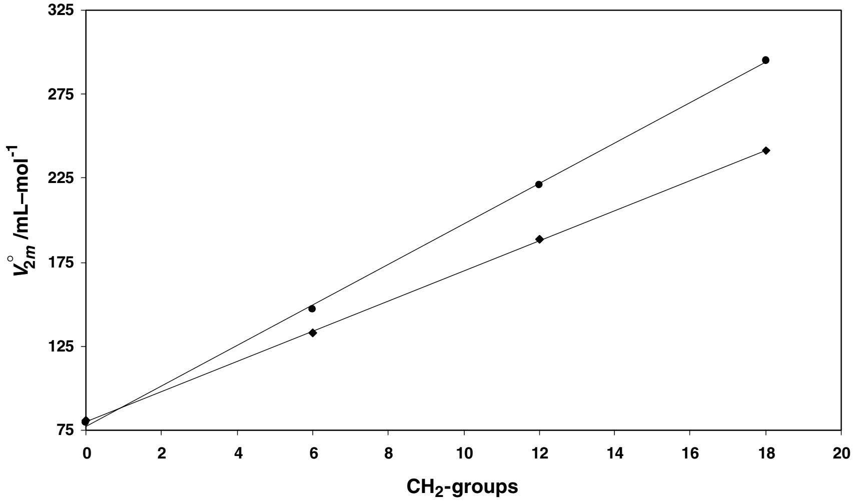

Fig. 4. Observed (●) and computed (◆) V_{2m}° values for Co(III) complexes *versus* number of CH_2-groups in the complexes. (This is explained in the text.)

Table I. Density and Index of Refraction for Solutions of Mole Ratio, r (20.00 °C)

r ($\times 10^4$)	ρ (g-mL^{-1})	n_D	r ($\times 10^4$)	ρ (g-mL^{-1})	n_D
$[Co(NH_3)_6]Cl_3$			$[Co(en)_3]Cl_3$		
0	0.99820	1.33299	0	0.99820	1.33299
0.3598	0.99848	1.33312	0.2913	0.99844	1.33311
0.8157	0.99985	1.33328	0.6062	0.99870	1.33324
1.324	0.99924	1.33345	0.8923	0.99899	1.33338
1.736	0.99953	1.33359	1.116	0.99919	1.33348
2.076	0.99980	1.33371	1.411	0.99941	1.33359
$[Co(sep)]Cl_3$			$[Co(chxn)_3]Cl_3$		
0	0.99820	1.33299	0	0.99820	1.33299
0.2046	0.99841	1.33315	0.1630	0.99835	1.33309
0.4938	0.99870	1.33329	0.3816	0.99858	1.33322
0.7864	0.99899	1.33343	0.6354	0.99882	1.33336
0.9945	0.99920	1.33355	0.8020	0.99898	1.33347
1.196	0.99938	1.33365	0.9761	0.99918	1.33360
$[Cr(NH_3)_6]Cl_3$					
0	0.99820	1.33299			
0.2670	0.99841	1.33316			
0.5923	0.99866	1.33327			
1.003	0.99903	1.33345			
1.233	0.99918	1.33353			
1.437	0.99939	1.33365			

The molar volumes computed by molecular modeling account for the intrinsic volume only. It seems reasonable to expect that V_2^{void} increases with increasing size of the ligands and perhaps because of the increasing hydrophobicity of the ligands.$^{(19)}$ The addition of more $—CH_2—$ links to the frameworks of the complex ions increases the "organic" nature of the molecule and therefore the hydrophobicity of the ligands increases substantially. The linear relationships shown in Fig. 4 for both computed and measured molar volumes suggest that the number of methylene groups plays a key role in determining the volume of the complexes.

Table II. Coefficients for Quadratic Regression of V_m^* *versus* Mole Ratio (r) [$V_m^* = ar^2 + br + c$]

Compound	a	b	c
$[Co(NH_3)_6]Cl_3$	31,713	122.24	18.048
$[Co(en)_3]Cl_3$	−2,570.8	189.97	18.048
$[Co(sep)]Cl_3$	72,413	263.99	18.048
$[Co(chxn)_3]Cl_3$	−102,073	337.82	18.047
$[Cr(en)_3]Cl_3$	−70,153	200.40	18.047

Table III. Measured and Calculated Partial Molar Volumes and Refractions (mL-mol^{-1})

Compound	$(V_2^\circ)^a$	$(V_2^\circ)^b$	$(V_2^\circ)^c$	Difference^d	$(R_2^\circ)^e$	R^f	Difference^g
$[Co(NH_3)_6]Cl_3$	122.2	124.9	80.9	41.3	61.4	32.8	28.6
$[Co(en)_3]Cl_3$	190.0	198.3	132.8	57.2	82.3	54.5	27.8
$[Co(sep)]Cl_3$	264.0	265.5	189.0	75.0	110.4	87.8	22.6
$[Co(chxn)_3]Cl_3$	337.8	339.9	241.3	96.5	129.2	105.3	23.9
$[Cr(en)_3]Cl_3$	200.4	198.3	134.7	55.6	83.3	54.5	28.8

[a] Calculated from V_m^* fit to a quadratic expression in r.

[b] Calculated from RRM equation.

[c] Computed from the space-filling model.

[d] Equations (1)–(3).

[e] Calculated from R_m^* fit linearly to r.

[f] The molar refraction of the ligands computed from the contributions of their constituent atoms or groups of atoms.

[g] Equations (5)–(6).

The computed molar volumes of the cationic complexes are compared to the measured partial molar volumes of the compounds at infinite dilution minus three times the van der Waals volume of chloride. As the number of CH_2-linkages increases from 0 to 18, the difference between the values increases due to the increasing hydrophobicity of the ligands. The slopes of the measured and computed molar volumes are 12.01 and 8.96 mL-(methylene group)$^{-1}$, respectively. This feature may also be seen in the comparison between the measured and computed molar volumes for a series of neat straight chain hydrocarbons. Plots of molar volume *versus* the number of carbon atoms are extremely linear giving slopes of 15.98 and 11.02 mL-$(CH_2)^{-1}$ for the measured and computed values, respectively.[3] Takaizumi *et al.* have estimated the molar volume of the methylene group to be 16 mL from their volumetric study of a cobalt(III) rotaxane complex.(21) A similar study by Franks and Desnoyers for alcohols yielded 15.9 mL-$(CH_2)^{-1}$,(22) while Biondi estimated the van der Waal's value for the methylene group to be 10.23 mL.(23)

Complex ions of the same charge and ligand composition should display comparable molar volumes. This analysis is supported by the result with the $[Cr(en)_3]^{3+}$ species, which has a molar mass very similar to that of the cobalt complex and carries the same charge (see Table III).

4.2. Partial Molar Refraction

Table III gives the partial molar refractions at infinite dilution for all complexes studied. Also listed are the molar refractions of the ligands calculated using

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[3] Observed molar volumes calculated from densities taken from Ref. (20) and computed volumes determined by the methods described in Section 2.4.

the tabulated atomic constitutive data developed by Vogel.(24) Presumably, the difference between the measured and calculated values provides the partial molar refraction for MCl_3, where $M = Co^{3+}$, Cr^{3+}. The average difference between R°_{2m} and the calculated molar refraction of the ligands is 25.7 ± 3.0 mL-mol^{-1} for the cobalt complexes.

5. CONCLUSIONS

The experimental V°_{2m} values give an accurate value of the volume of the compounds in aqueous solution as compared to the values generated by computational methods. The V°_{2m} results follow the expected trend for increasing ligand size and are highly correlated with the number of methylene groups in the ligands. This technique may offer a relatively facile method for estimating relative values of V°_{2m} for complex ions used in chemical reactions, *e.g.*, electron-transfer cross-reactions and therefore it may be of some interest to transition metal chemists. In principle, the method can be extended to nonaqueous solutions of complex ions or neutral complexes.

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