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Molar Volumes and Electrostriction Behavior of Dicarboxylate, Disulfonate, Tartrate, and Bis(ethylenediamine)glycinatocobalt(III) Ions in Water

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The ionic partial molar volumes at infinite dilution, V^∞(ion), were determined for several dicarboxylate ions, disulfonate ions, tartrate ions, and $[Co(gly)(en)_2]^{2+}$ (gly=glycinate ion and en=ethylenediamine) from density measurements at 25°C. The values of V^∞(ion) obtained for the divalent anions generally increased with their van der Waals volumes. Significant differences in V^∞(ion) were observed between geometrical isomers with dicarboxylate and disulfonate ions and were attributed to those in both of electrostriction volume and the void space volume around the anions. The former volume was decreased and the latter was increased with increasing distance between two negatively charged groups in the anions. A relatively strong electrostriction behavior of the tartrate ions, compared to the dicarboxylate ions, suggested the presence of an extra electrostriction caused by hydroxyl groups. The electrostriction strength of $[Co(gly)(en)_2]^{2+}$ was significantly large compared to that of $[Ni(en)_3]^{2+}$, rather close to those of $[Cr(en)_3]^{3+}$ and $[Co(en)_3]^{3+}$, and was attributed to the dissymmetrically localized charge distribution in the $[Co(gly)(en)_2]^{2+}$ ion. The effective ionic radii and apparent van der Waals volumes were estimated by using Glueckauf's equation from the ionic partial molar volume and were discussed in comparison with those calculated from the van der Waals increments of atoms.

The ionic partial molar volumes at infinite dilution, V^∞(ion), provide useful information about ion-solvent interactions and the effective volumes of ions in solutions,[1] and are helpful for an estimation of the ion-size parameter in the theoretical equations regarding the activity coefficient and molar conductivity of ions.[2] The partial molar volumes of a series of dicarboxylate ions or disulfonate ions are of interest in connection with how the effective ionic volumes and ion-solvent interactions depend on the configuration and conformation of the ions in aqueous solutions. In the present study we measured the densities of aqueous solutions of sodium, potassium, or bis(ethylenediamine)glycinatocobalt(III) complex salts of the several divalent anions in order to obtain the ionic partial molar volumes at 25 °C. The anions investigated were as follows: oxalate^{2-}, malonate^{2-}, succinate^{2-}, fumarate^{2-}, maleate^{2-}, phthalate^{2-}, 2,6-naphthalenedicarboxylate^{2-} (2,6-NDC^{2-}), (*R*,*R*)-tartrate^{2-}, *meso*-tartrate^{2-}, *o*-benzenedisulfonate^{2-} (*o*-BDS^{2-}), *m*-benzenedisulfonate^{2-} (*m*-BDS^{2-}), 2,6-naphthalenedisulfonate^{2-} (2,6-NDS^{2-}), and 2,7-naphthalenedisulfonate^{2-} (2,7-NDS^{2-}). We discuss the electrostriction volume and the void space (or dead space) around the ion through the effective ionic radius, or the apparent van der Waals volume, estimated from the observed ionic partial molar volume, in connection with the configuration and conformation of the ions in aqueous solutions. The adequacy of using the effective ionic radii for an estimation of the ion-size parameter is also examined.

Experimental

Materials. Chloride, sulfate, malonate, succinate, fumarate, maleate, phthalate, and *meso*-tartrate of $[Co(gly)(en)_2]^{2+}$ were prepared by a double decomposition between the silver salt of anions and the iodide of the complex obtained according a method described in the literature.[3] The oxalate was prepared similarly from the chloride. These salts[4] were recrystallized twice from a water–ethanol mixture and air-dried at room temperature. The numbers of water of crystallization, $n(H_2O)$, were 1.0, 3.0, 0.1, 2.0, 2.0, 2.0, 3.0, 3.7, and 4.9 for chloride, sulfate, oxalate, malonate, succinate, fumarate, maleate, phthalate, and *meso*-tartrate, respectively. The molar extinction coefficients of these complex salts at λ=488 nm were confirmed to be in agreement with one another by studies using a Hitachi 340 spectrophotometer: their average was 97.7±0.2 $mol^{-1}\ dm^3\,cm^{-1}$. Potassium oxalate (reagent grade), sodium malonate, sodium succinate, sodium fumarate, and sodium maleate (extra pure grade) were obtained from Wako Pure Chemical Industries, Ltd. and used without further purification; $n(H_2O)$ were 1.0, 0.0, 5.8, 0.0, and 0.2, respectively. Sodium (*R*,*R*)-tartrate (reagent grade) and sodium salts of *m*-BDS^{2-}, 2,6-NDS^{2-}, and 2,7-NDS^{2-} (obtained from the same company) were recrystallized twice from water and air-dried; $n(H_2O)$ were 2.0, 1.6, 0.2, and 3.5, respectively. Potassium salts of *o*-BDS^{2-} and 2,6-NDC^{2-} (obtained from Aldrich Chemical Company, Inc.) were similarly purified and dried; $n(H_2O)$ were 1.0 and 0.0, respectively. The determination of $n(H_2O)$ values was carried out by the dehydration at ca. 150 °C under reduced pressure with an Abderhalden dryer and by the Karl-Fischer method with an AQ-5 Aquacounter of Hiranuma Sangyo Co., Ltd.

Measurements. All aqueous solutions were made by weight. The concentrations of solutions were as follows: 0.0008—0.0045 mol dm^{-3} with sodium and potassium salts of the divalent anions and 0.0003—0.0040 mol dm^{-3} with the salts of $[Co(gly)(en)_2]^{3+}$. The density measurements were carried out at 25 °C by using a vibrating-tube SS-D-200 twin-type densimeter of Shibayama Scientific Co., Ltd. with two external measuring cells immersed in a water bath controlled to 25.00±0.01 °C. The apparatus constants were determined by using water and dry air as standard substances. The errors in the density measurements were usually within 2×10^{-6} $g\,cm^{-3}$.

Results and Discussion

The density of a solution, d, can be expressed by the equation:[1]

$$d = d_0 + 10^{-3}\,[M - d_0 V^{\infty}(\text{salt})]\,c - 10^{-3} S_v d_0 c^{3/2} - 10^{-3} b_v d_0 c^2, \qquad (1)$$

where M is the molecular weight of the solute, c is the molar concentration, d_0 is the density of the solvent, V^{∞}(salt) is the partial molar volume of the salt at infinite dilution, S_v and b_v are constants. The values of S_v are theoretically given as 9.706 and 14.944 $\text{cm}^3\text{dm}^{3/2}\text{mol}^{-3/2}$ in water at 25 °C for 2 : 1 or 1 : 2 and 2 : 2 electrolytes, respectively.[1] The values of b_v are usually in the range of −40 to 10 $\text{cm}^3\text{dm}^3\text{mol}^{-2}$.[1] The last term including b_v in Eq. 1 can be neglected in this study, since its values are considered to be smaller than 1×10^{-6} g cm^{-3} for solutions of concentrations below 0.005 mol dm^{-3}. Thus, we can use the following approximate equation:

$$d + 10^{-3} S_v d_0 c^{3/2} = 10^{-3}[M - d_0 V^{\infty}(\text{salt})]\,c + d_0. \qquad (2)$$

This equation indicates a linear relationship between the left side and the concentration. Using Eq. 2, we analyzed the observed densities.[5] The values of V^{∞}(salt) were obtained from the linear slope, $10^{-3}[M - d_0 V^{\infty}(\text{salt})]$, by a least-squares calculation,[8] and are shown in Table 1.[7]

The ionic partial molar volumes of the anions, V^{∞}(anion), were evaluated in the following way, and are shown in Table 1. The V^{∞}(anion) values from sodium or potassium salts were obtained by taking $V^{\infty}(\text{Na}^+)$ and $V^{\infty}(\text{K}^+)$ as −6.6 and 3.6 $\text{cm}^3\text{mol}^{-1}$, respectively.[1] By subtracting these V^{∞}(anion) values from V^{∞}(salt) of the complex salts, the ionic partial molar volumes of $[\text{Co(gly)(en)}_2]^{2+}$ were obtained to be 126.7± 0.6 $\text{cm}^3\text{mol}^{-1}$ (on the average). Subtracting this value from V^{∞}(salt) with each complex salt, we also obtained the V^{∞}(anion) values. Significant differences in V^{∞}(anion) were observed between the geometrical isomers: fumarate^{2-} and maleate^{2-}; *o*-BDS^{2-} and *m*-BDS^{2-}; 2,6-NDS^{2-} and 2,7-NDS^{2-}. The V^{∞}(anion) of an isomer possessing two negatively charged groups (two carboxylato groups or two sulfonato groups) situated more distantly from each other is larger than that of another isomer. We discuss later why such differences arise.

Table 1. Partial Molar Volumes, V^{∞}(salt) and V^{∞}(anion), in Water at 25 °C

Salt	(cation)[a]	V^{∞}(salt)	V^{∞}(anion)
		$\text{cm}^3\text{mol}^{-1}$	$\text{cm}^3\text{mol}^{-1}$
Chloride	(M^{2+})	172.2±0.4	23.2[b]
Sulfate	(M^{2+})	152.1±0.6	24.8[b]
Oxalate	(K^{+})	42.6±0.4	$35._4$
	(M^{2+})	161.3±0.4	$34._6$
Malonate	(Na^{+})	35.4±0.4	$48._6$
	(M^{2+})	176.1±0.5	$49._4$
Succinate	(Na^{+})	53.6±0.4	$66._8$
	(M^{2+})	194.4±0.6	$67._7$
Fumarte	(Na^{+})	54.0±0.4	$67._2$
	(M^{2+})	192.8±0.4	$66._1$
Maleate	(Na^{+})	46.8±0.4	$60._0$
	(M^{2+})	187.5±0.5	$60._8$
Phthalate	(M^{3+})	225.0±0.4	$98._3$
2,6-NDC	(K^{+})	146.9±0.5	$139._7$
(*R*,*R*)-Tartrate	(Na^{+})	55.9±0.4	$69._1$
meso-Tartrate	(M^{2+})	194.7±0.5	$68._0$
o-BDS	(K^{+})	127.5±0.5	$120._3$
m-BDS	(Na^{+})	113.7±0.8	$126._9$
2,6-NDS	(Na^{+})	160.9±0.5	$174._1$
2,7-NDS	(Na^{+})	159.3±0.4	$172._5$

a) M^{2+} denotes the $[\text{Co(gly)(en)}_2]^{2+}$ ion. b) Ref. 1.

Glueckauf[8] expressed the partial molar volume of a spherical monoatomic ion by

$$\begin{aligned} V^{\infty}(\text{ion}) &= V^{\infty}(\text{int}) + V^{\infty}(\text{el}) \\ &= 2.52(r+0.55)^3 - 33z_i^2/(r+1.38), \end{aligned} \qquad (3)$$

where r is the crystallographic radius in Å and z_i is the charge number of the ion. V^{∞}(int) is the molar intrinsic volume of an ion involving a void space (or dead space) around it, and V^{∞}(el) is the molar electrostriction volume. Assuming that polyatomic anions are approximately spherical, we applied Eq. 3 in order to estimate radius r, which refers (here) to the effective ionic one (represented as r_{ef}(obsd)). The r_{ef}(obsd) values obtained from V^{∞}(anion) (from their average when plural values are given in Table 1) are shown in Table 2. The differences in V^{∞}(anion) between the geometrical isomers result in those in r_{ef}(obsd). An isomer that shows a greater deviation from the spherical approximation has a larger r_{ef}(obsd) than that of another isomer. According to Eq. 3, this means that the former isomer has a relatively large V^{∞}(int) and a small negative V^{∞}(el), compared to the latter; the V^{∞}(el) values estimated from Eq.3 are shown in Table 3. The differences in V^{∞}(el) between the isomers are slight compared to those in V^{∞}(anion). This indicates that the differences in V^{∞}(anion) can largely be attributed to those in V^{∞}(int). The increase of V^{∞}(int) with a deviation from the spherical shape of the ion is due to that of the effective ionic surface, which results in an increase in the void space volume around the ion.

By using the values of the van der Waals increments of atoms, v_0(atom), given by Edward,[9] we calculated the molar van der Waals volumes of the polyatomic anions, which are shown in Table 2 as V_0(calcd).[10] By assuming

$$V_0(\text{calcd}) = 4\pi N_A r_{\text{ef}}(\text{calcd})^3/3,$$

the effective ionic radii, r_{ef}(calcd), were calculated and are shown in Table 2. The r_{ef}(obsd) values are in agreement with those of r_{ef}(calcd) within about 0.1 Å. The apparent molar van der Waals volumes, V_0(app), were estimated from r_{ef}(obsd) by assuming

$$V_0(\text{app}) = 4\pi N_A r_{\text{ef}}(\text{obsd})^3/3$$

Table 2. Effective Ionic Radii, r_{ef}(calcd), and r_{ef}(calcd),and Molar van der Waals Volumes, V_0(app) and V_0(calcd), of the Divalent Anions[a]

Anion		r_{ef}(obsd)	r_{ef}(calcd)	V_0(app)	V_0(calcd)
		Å	Å	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$
Oxalate^{2-}	$(COO^-)_2$	2.46_8	2.41_5	$37._9$	35.5
Malonate^{2-}	$CH_2(COO^-)_2$	2.64_0	2.62_8	$46._4$	45.8
Succinate^{2-}	$(CH_2COO^-)_2$	2.84_4	2.81_1	$58._1$	56.0
Fumarate^{2-}	*trans*-$(CHCOO^-)_2$	2.83_8	2.73_6	$57._6$	51.7
Maleate^{2-}	*cis*-$(CHCOO^-)_2$	2.77_0	2.73_6	$53._6$	51.7
Phthalate^{2-}	*o*-$C_6H_4(COO^-)_2$	3.14_8	3.13_3	$78._7$	77.6
2,6-NDC^{2-}	2,6-$C_{10}H_6(COO^-)_2$	3.49_5	$3.44._9$	$107._7$	103.5
(*R*,*R*)-Tartrate^{2-}	(*R*,*R*)-$(CH(OH)COO^-)_2$	2.86_3	2.95_8	$59._2$	65.3
meso-Tartrate^{2-}	*meso*-$(CH(OH)COO^-)_2$	2.85_2	2.95_8	$58._5$	65.3
o-BDS^{2-}	*o*-$C_6H_4(SO_3^-)_2$	3.33_9	(3.33_9)	$93._8$	(93.9)
m-BDS^{2-}	*m*-$C_6H_4(SO_3^-)_2$	3.39_4	(3.33_9)	$98._6$	(93.9)
2,6-NDS^{2-}	2,6-$C_{10}H_6(SO_3^-)_2$	3.74_6	(3.62_1)	$132._6$	(119.8)
2,7-NDS^{2-}	2,7-$C_{10}H_6(SO_3^-)_2$	3.73_5	(3.62_1)	$131._5$	(119.8)

a) Values in the parentheses were obtained by assuming V_0(calcd)=V_0(app) for *o*-BDS^{2-}.

Table 3. Elecrostriction Volumes, V^∞(el), and Void Space Volumes, V^∞(void), of the Divalent Anions Obtained by Use of Eqs. 3 and 4[a]

Anion	V^∞(el)	V^∞(void)
	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$
Oxalate^{2-}	$-34._3$	$33._8$
Malonate^{2-}	$-32._8$	$36._0$
Succinate^{2-}	$-31._3$	$42._5$
Fumarate^{2-}	$-31._3$	$46._3$
Maleate^{2-}	$-31._8$	$40._5$
Phthalate^{2-}	$-29._2$	$49._9$
2,6-NDC^{2-}	$-27._1$	$63._3$
(*R*,*R*)-Tartrate^{2-}	$-31._1(-39._7)$	$34._9(43._5)$
meso-Tartrate^{2-}	$-31._2(-40._8)$	$33._9(43._5)$
o-BDS^{2-}	$-28._0$	$54._4$
m-BDS^{2-}	$-27._7$	$60._7$
2,6-NDS^{2-}	$-25._8$	$80._1$
2,7-NDS^{2-}	$-25._8$	$78._5$

a) Values in the Parentheses were obtained by assuming Eq. 5.

and are shown in Table 2. Although the V_0(app) is not so much different from that of V_0(calcd), the former is, more or less, larger than the latter in each case of the dicarboxylate and disulfonate ions. The positive deviations of V_0(app) from V_0(calcd) generally increase with increasing distance between two negatively charged groups in the anions, due to the expansion of the void space around the ion (as described above). The negative deviation of V_0(app) from V_0(calcd) for the tartrate ions are attributed to the presence of an extra electrostriction volume caused by the hydroxyl groups (not considered by the second term of Eq. 3, which is expressed as a function of the formal charge). This phenomenon is similar to that observed for neutral compounds containing such hydroxyl groups as glucose.[9]

We assumed the void space volume, V^∞(void), can be expressed by

$$V^\infty(\text{void}) = V^\infty(\text{int}) - V_0(\text{calcd}), \qquad (4)$$

and showed the values of V^∞(void) in Table 3. Considerably smaller V^∞(void) of the tartrate ions (derivatives of succinate^{2-}) than that of succinate^{2-}, fumarate^{2-}, or maleate^{2-} supports the presence of an extra electrostriction (as described above). The relatively small V^∞(void) of succinate^{2-}, compared to fumarate^{2-}, are consistent with the fact that the succinate ion exists partly in gauche form about two carboxylato groups in aqueous solutions.[11] The slightly small V^∞(void) of *meso*-tartrate^{2-}, compared to (*R*,*R*)-tartrate^{2-}, may be due to the fact that the *meso*-tartrate ion exists predominantly in gauche form.[12] In order to estimate the overall electrostriction volume for the tartrate ions, we assumed the following equation:

$$V^\infty(\text{el}) = V^\infty(\text{ion}) - 2.52[r_{ef}(\text{calcd}) + 0.55]^3, \qquad (5)$$

and obtained the values of $-39._7$ and $-40._8$ $cm^3 mol^{-1}$ for V^∞(el) of (*R*,*R*)-tartrate^{2-} and *meso*-tartrate^{2-}, respectively. These values are more negative than V^∞(el) given in Table 3 and by $-9._3$ and $-10._4$ $cm^3 mol^{-1}$ than $-30._4$ $cm^3 mol^{-1}$ obtained from V^∞(el) in Eq. 3 by putting r_{ef}(calcd) into r. The procedure concerning Eq. 5 is identical to taking the void space volume of the tartrate ions as $43._5$ $cm^3 mol^{-1}$, slightly larger than V^∞(void) of succinate^{2-}. Consequently, the above differences in the volumes correspond to extra electrostriction volumes caused by the hydroxyl groups.

In the same manner as for the divalent anions, we estimated r_{ef}(obsd) and V_0(app) for $[Co(gly)(en)_2]^{2+}$ from its ionic partial molar volume by use of Eq.3. The obtained values are shown in Table 4 and are compared with those estimated for $[Ni(en)_3]^{2+}$, $[Cr(en)_3]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(NH_3)_6]^{3+}$. Although of the ionic partial molar volume of $[Ni(en)_3]^{2+}$ is considerably larger than those of $[Co(en)_3]^{3+}$ and $[Cr(en)_3]^{3+}$, the r_{ef}(obsd) values of these complex ions are very near to one another (within 0.1 Å). This is consistent with that the crystallographic metal-nitrogen bond lengths are not so largely different from one

Table 4. Partial Molar Volumes, V^{∞}(cation), Effective Ionic Radii, r_{ef}(obsd), Apparent Molar van der Waals Volumes, V_0(app), Difference Volumes, V_0(dif), and Crystallographic Metal-Ligand Bond Lengths, r_c(M-N) and r_c(M-O), of the Complex Ions[a]

Complex Ion	V^{∞}(cation)	r_{ef}(obsd)	V_0(app)	V_0(dif)	r_c(M-N)	r_c(M-O)
	$cm^3 mol^{-1}$	Å	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$	Å	Å
$[Co(gly)(en)_2]^{2+}$	$126._7$	3.39_2	$98._4$	$-9._7$	1.96[d]	1.916[e]
$[Ni(en)_3]^{2+}$	160.3[b]	3.64_9	$122._5$	$12._7$	2.11[f]	
$[Cr(en)_3]^{3+}$	123.1[b] 124.5[c]	3.62_3	$120._2$	$10._2$	2.081[g]	
$[Co(en)_3]^{3+}$	119.9[b] 117.6[c]	3.58_8	$116._5$	$6._7$	1.978[h]	
$[Co(NH_3)_6]^{3+}$	55.3[b] 56.3[c]	3.09_6	$74._9$	$12._5$	1.972[h]	

a) The reference values of V^{∞}(cation) were obtained from V^{∞}(salt) of the chlorides by using V^{∞}(anion) given in Table 1; The values of r_{ef}(obsd), V_0(app), and V_0(dif) for $[Cr(en)_3]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(NH_3)_6]^{3+}$ were obtained by using the averaged values of V^{∞}(cation). b) Ref. 19 and the value cited therein. c) Ref. 20. d) An average of the values given by Ref. 21. e) Ref. 21. f) An average of the values given by Ref. 22. g) Ref. 23. h) Ref. 16.

another as shown in Table 4. Such agreement suggests that the V^{∞}(el) in Eq. 3 is a good approximate expression of electrostriction for the tris(en) complexes.

The ionic partial molar volume of $[Co(gly)(en)_2]^{2+}$ is significantly smaller than that of $[Ni(en)_3]^{2+}$, rather close to those of $[Cr(en)_3]^{3+}$ and $[Co(en)_3]^{2+}$, the value of r_{ef}(obsd) is considerably smaller than those of the tris(en) complex ions. Accordingly, the value of V_0(app) of $[Co(gly)(en)_2]^{2+}$ becomes smaller by 24 $cm^3 mol^{-1}$ than that of $[Ni(en)_3]^{2+}$. This difference in V_0(app) is too large to be explained by their molar van der Waals volumes. That is, an extra electrostriction is considered to be present in the case of $[Co(gly)(en)_2]^{2+}$. If the effective ionic radius of $[Co(gly)(en)_2]^{2+}$ can be approximated to be 3.59 Å (obtained for r_{ef}(obsd) of $[Co(en)_3]^{3+}$) the value of V^{∞}(el) is estimated to be −52 $cm^3 mol^{-1}$ by using Eq. 5; the values of V^{∞}(el) for $[Ni(en)_3]^{2+}$, $[Cr(en)_3]^{3+}$, and $[Co(en)_3]^{3+}$ are calculated to be −26, −59, and −60 $cm^3 mol^{-1}$, respectively. This means that the V^{∞}(el) value of $[Co(gly)(en)_2]^{2+}$, though a divalent ion, is close to that of $[Cr(en)_3]^{3+}$ or $[Co(en)_3]^{3+}$ rather than $[Ni(en)_3]^{2+}$. The such strong electrostriction is considered to be related to the dissymmetrically localized charge distribution in the $[Co(gly)(en)_2]^{2+}$ ion: the negative charge is on the carboxylato group of glycinato ligand and the positive charge is on the amino groups of ethylenediamine and glycinato ligands. If the $[Co(gly)(en)_2]^{2+}$ ion is regarded as being a dipolar ion (such as an ion pair formed between a trivalent cation and a monovalent anion), we can understand that the ion-solvent interaction of $[Co(gly)(en)_2]^{2+}$ is similar to that of $[Cr(en)_3]^{3+}$ or $[Co(en)_3]^{3+}$ rather than $[Ni(en)_3]^{2+}$. Such a strong interaction of $[Co(gly)(en)_2]^{2+}$ with the solvent is supported by its relatively large Stokes radius, 3.73 Å,[13] compared to 3.13 Å for $[Ni(en)_3]^{2+}$; the former value is in good agreement with 3.73 Å for $[Cr(en)_3]^{3+}$ and 3.72 Å for $[Co(en)_3]^{3+}$.[14]

By using the van der Waals increments of atoms,[9] the molar van der Waals volumes of free ligands can be calculated to be 41.7, 38.6, and 13.7 $cm^3 mol^{-1}$ for ethylenediamine, glycinate ion, and ammonia, respectively.[15] However, the total volume of ligands constituting the complex ion exceeds the V_0(app) value in each case. This disagreement is due to a neglect of the effective charges on the ligands. It has been known that the central metal atom is largely neutralized by the donation of electrons from the ligating atoms, according to Pauling's electroneutrality rule and the formal charge of the complex ions is largely distributed on the ligand atoms.[16] Thus, assuming the ionicity of each metal-ligand bond to be about 50%, we obtained 36.6, 34.9, and 10.4 $cm^3 mol^{-1}$ for the molar van der Waals volumes of ethylenediamine, glycinato, and ammine ligands coordinated to the metal atoms, respectively.[17] In Table 4, we show the volume differences, V_0(dif), obtained by subtracting the total volume of the ligands from V_0(app). The negative V_0(dif) for $[Co(gly)(en)_2]^{2+}$ is due to the extra electrostriction described above. The V_0(dif) values for the tris(en) complex ions are $6._7$ to $12._7$ $cm^3 mol^{-1}$, somewhat larger than 4.9 $cm^3 mol^{-1}$ for a sphere estimated from 1.25 Å for the metallic bond radii of Cr, Co, and Ni.[18] Such results are thought to be satisfactory, considering that the calculation process involves various assumptions.

Glueckauf's equation (Eq. 3) is valid as a standard expression for the partial molar volume of the ions examined in this study, and is useful for an estimation of their effective ionic radii; the values of r_{ef}(obsd) usually obtained are in agreement with those of r_{ef}(calcd) within about 0.1 Å, though for $[Co(gly)(en)_2]^{2+}$ the former is smaller by about 0.2 Å than the latter. This means that Eq. 3 can be satisfactorily used for an estimation of the ion-size parameter in the theoretical equations of the activity coefficient and molar conductivity of ions.

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4) The $[Co(gly)(en)_2]^{2+}$ ion has been known to be a stable and inert complex in aqueous solutions under usual conditions.[3,21)]

5) The tables of the observed densities (d) are deposited as Document No. 8832 at the Office of the Editor of Bull. Chem. Soc. Jpn.

6) The least squares calculation was carried out, including the density of water (d_0=0.997047 g cm^{-3} at 25.0 °C).

7) The effect of hydrolysis of the dicarboxylate ions on V^∞(anion) can be neglected for the following reason. Considering the hydrolysis, the V^∞(anion) can be approximately expressed by:

$$V^\infty(\text{anion}) = V^\infty(A^{2-}) + \alpha[V^\infty(HA^-) + V^\infty(OH^-) - V^\infty(A^{2-}) - V^\infty(H_2O)],$$

where A^{2-} is the divalent anion, HA^- is the monoprotonated anion, and α is the fraction of HA^-. The second term in the right side does not exceed 0.1 cm^3 mol^{-1} since the sum of the values in the brackets is presumed to be 3.2 to 9.5 cm^3 mol^{-1} from the $V^\infty(OH^-)$ and $V^\infty(H_2O)$ values[1)] and the difference between $V^\infty(HA^-)$ and $V^\infty(A^{2-})$ estimated by Eq. 3 and the value of α is considered to be smaller than 0.01 under present conditions from the protonation constants of the dicarboxylate ions.[24)]

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10) The values of v_0(atom) in Å^3 used are as follows: 5.6 and 8.1 for the sp^3 and sp^2 carbon atoms, respectively; 5.7, 5.3, and 7.2 for the hydrogen atoms attached to aliphatic and aromatic carbon atoms and oxygen atom, respectively; 6.2, 11.3, and 10.1 for the oxygen atoms, [-O-], [=O] and [-O$^-$], respectively.[9)] By using these v_0(atom), the molar van der Waals volume of [-COO$^-$] was estimated to be 17.8 cm^{3}mol^{-1}. That of [-SO$_3{}^-$] were taken as 26.0 cm^3 mol^{-1} on the assumption of V_0(calcd)=V_0(app) for o-BDS^{2-} by considering that the V_0(calcd) and V_0(app) values of phthalate^{2-} were close to each other as shown in Table 2, since we had no available v_0(atom) data for the sulfur and oxygen atoms of this group.[9)]

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14) Calculated from the ionic molar conductivities given by the literatures: Ref. 25 for $[Ni(en)_3]^{2+}$; Ref. 26 for $[Cr(en)_3]^{3+}$ and $[Co(en)_3]^{3+}$.

15) The values of v_0(atom) for the nitrogen and hydrogen atoms of amino group were taken to be 7.2 and 5.2 Å^3, respectively.[9)]

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17) The values of v_0(atom) for the nitrogen and hydrogen atoms of amino group and the ligating oxygen atom of carboxylato group were assumed to be 5.9, 3.8, and 8.2 Å^3, respectively. These values are the middle ones between those of 7.2, 5.2, and 10.1 Å^3 for the corresponding atoms in free ligands given in Refs. 10 and 15 and those of 4.6, 2.3, and 6.2 Å^3 for the atoms in the ligands of 100% covalent metal-ligand bonding.[9)]

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