distance of 2.23 Å.[8] The steric requirements of a methanol molecule allow only four inner-shell-coordinated molecules in equatorial positions. These were positioned so that the vanadium-oxygen bond vector bisects the C-O-H valence angle of each methanol molecule and the equatorial ligands are close-packed to the axially coordinated methanol. Both the ^1H and the ^{13}C ENDOR results indicate that the metal-nucleus distances for equatorially positioned hydroxyl protons and methyl carbon atoms are underestimated by ~0.1 and 0.3 Å, respectively, when compared to X-ray results.[8] This difference is due either to the stronger isotropic hfc of equatorially positioned ligands with the unpaired electron in the metal d_{xy} orbital or to breakdown of the strong-field approximation for the short electron-proton distances involved. This discrepancy represents the greatest error in our present study and is seen for both inner- and outer-sphere equatorial ligands. Therefore, the equatorial vanadium-oxygen bond length was adjusted to 2.04 Å on the basis of the X-ray structure of $VO(H_2O)_4SO_4 \cdot H_2O$[8]. The requirement of the equatorially positioned ligands as closely packed to the axially bound methanol molecule is sufficient to fix the O=V—O angle with equatorial oxygens at 97.9°, in exact agreement with X-ray results.[8] The steric volumes of the four equatorially positioned methanol molecules prevent a binding geometry with all four methyl groups simultaneously in, above, or below the molecular *x*,*y* plane. We, therefore, positioned two methyl groups of trans-coordinated molecules above the plane with the other two positioned below the plane. This conformation permits two equatorial hydroxyl protons to lie exactly in the molecular *x*,*y* plane ($\angle O{=}V\cdots H = 90°$) while the other two lie below the *x*,*y* plane ($\angle O{=}V\cdots H = 115°$). This arrangement is, thus, in agreement with the sets of narrow and broad resonances observed in the ENDOR spectra for two types of equatorially positioned hydroxyl protons.

With the inner coordination shell fixed, we then searched for plausible sites of outer-sphere-bound methanol molecules that could account for the ENDOR data. The axially positioned methanol molecule hydrogen-bonded to the vanadyl oxygen was fixed according to the ENDOR-determined metal-proton distance of its hydroxyl group and the average metal-proton distance to the methyl group. In particular, the vanadium-(hydroxyl) proton distance determined by ENDOR spectroscopy yields a D-H···A distance for hydrogen bonding that is in excellent agreement with expectation. The remaining, outer-sphere-located methanol molecules were positioned according to van der Waals nonbonded constraints imposed by the inner-sphere ligands, steric accommodation of closely packed, outer-sphere molecules, and metal-nucleus distances in reasonable agreement with ENDOR results. These considerations allow plausible binding sites for two symmetry-related, equatorially positioned, outer-sphere methanols and one axially located outer-sphere molecule on the side of the molecular *x*,*y* plane opposite from the vanadyl oxygen. As a result of these modeling constraints, the outer-sphere molecules each have orientations that place their hydroxyl groups according to D-H···A distance and angle into plausible hydrogen-bonding interactions with inner-sphere-located methanol oxygen atoms. These interactions could conceivably stabilize the outer-sphere-bound methanol molecules. The ENDOR results provide direct evidence for outer-sphere-bound solvent molecules also in water-methanol mixtures. Their metal-proton distances indicate that they would be similarly stabilized through hydrogen-bonding interactions.

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Dilatometric Studies on Reaction Volumes for the Formation of Nickel(II) Complexes in Aqueous Solution

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Reaction volumes for the formation of nickel(II) complexes with a monodentate ligand (acetate, OAc^-), bidentate ligands (ethylenediamine, en; glycinate, gly^-; sarcosinate, sar^-), and a tetradentate ligand (ethylenediamine-*N*,*N'*-diacetate, $edda^{2-}$) and reaction volumes for proton dissociation of the conjugate acid of the ligands have been measured dilatometrically at 25.0 °C and $I = 0.10$ mol dm^{-3} ($NaClO_4$) in aqueous solution. ΔV° values (cm^3 mol^{-1}) for complex formation are as follows: 8.0 ± 1.5 ($Ni(OAc)^+$), 11.2 ± 0.2 ($Ni(gly)^+$), 12.0 ± 0.5 ($Ni(gly)_2$), 11.7 ± 0.5 ($Ni(sar)^+$), 9.9 ± 0.8 ($Ni(sar)_2$), 5.2 ± 0.5 ($Ni(en)^{2+}$), 5.6 ± 0.9 ($Ni(en)_2^{2+}$), 28.6 ± 0.2 (Ni(edda)). ΔV° values (cm^3 mol^{-1}) for proton dissociation are as follows: −10.6 ± 0.2 (HOAc), 1.4 ± 0.3 (Hgly), 0.7 ± 0.2 (Hsar), 5.6 ± 0.2 (Hen^+), 12.0 ± 0.1 (H_2en^{2+}), −0.6 ± 0.2 ($Hedda^-$), 4.9 ± 0.3 (H_2edda). The proton dissociation constants of conjugate acids of ligands and the stability constants of the nickel(II) complexes were also determined potentiometrically under the same conditions as for the dilatometric study. We discussed these reaction volumes in terms of electrostriction, contraction of donor atoms in ligands in the first coordination sphere, expansion of complexes by bond elongation due to bound ligands, and "volume chelate effect" resulting from the different packing of multidentate ligands at the metal ion and in the bulk solvent.

Introduction

Recently chemical processes at high pressure have been extensively studied with developments of high-pressure techniques.[1-3] It has been proved that reaction volumes are the most useful for a better understanding of solute-solvent interactions and that the volume profile of chemical processes is very useful in mechanistic consideration.[3-9] One of our purposes is to measure reaction volumes for the formation of a series of metal complexes to provide fundamental data for the complexation in solution and to make possible prediction of the pressure effect on the complexation. For the present study we selected some nickel(II) complexes with ligands having various combination of N and O donors.

Experimental Section

Reagents. Nickel(II) perchlorate solution was prepared by the following procedure. Perchloric acid (70%) was added to a nickel(II) chloride solution, and the solution was heated to expel hydrogen chloride.

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(1) Kelm, H., Ed. *High Pressure Chemistry*; Reidel: Boston, MA, 1978.
(2) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: New York, 1981.
(3) van Eldik, R., Ed. *Inorganic High Pressure Chemistry*; Elsevier: New York, 1986.
(4) le Noble, W. J. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 207.
(5) McCabe, J. R.; Grieger, R. A.; Eckert, C. A. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 156.
(6) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.
(7) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2564.
(8) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 3589.
(9) Funahashi, S.; Uchiyama, N.; Ishii, M.; Tanaka, M. *Inorg. Chim. Acta* **1987**, *128*, 169.

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Table I. Acid Dissociation Constants of the Conjugate Acid of Ligands and Reaction Volumes of Proton Dissociation Reaction of Weak Acids

reactions	pK_a	$\Delta V^\circ/\mathrm{cm^3\ mol^{-1}}$
$NH_4^+ \rightleftharpoons H^+ + NH_3$	9.258 ± 0.003[a] (9.29)[b]	6.1 ± 0.1[a] (7.0)[c]
$HOAc \rightleftharpoons OAc^- + H^+$	4.591 ± 0.001 (4.53)[d]	−10.6 ± 0.2 (−11.3)[e]
$Hgly \rightleftharpoons gly^- + H^+$	9.63 ± 0.01 (9.68)[f]	1.4 ± 0.3 (1.9)[g]
$H_2gly^+ \rightleftharpoons Hgly + H^+$	2.37 ± 0.01 (2.33)[f]	
$Hsar \rightleftharpoons sar^- + H^+$	10.012 ± 0.003 (10.01)[h]	0.7 ± 0.2
$H_2sar^+ \rightleftharpoons Hsar + H^+$	2.172 ± 0.001 (2.24)[h]	
$Hen^+ \rightleftharpoons en + H^+$	9.886 ± 0.002 (9.89)[f]	5.6 ± 0.2 (6.7)[i]
$H_2en^{2+} \rightleftharpoons Hen^+ + H^+$	7.104 ± 0.002 (7.10)[f]	12.0 ± 0.1 (12.1)[i]
$Hedda^- \rightleftharpoons edda^{2-} + H^+$	9.769 ± 0.005 (9.62)[j]	−0.6 ± 0.2
$H_2edda \rightleftharpoons Hedda^- + H^+$	6.532 ± 0.001 (6.55)[j]	4.9 ± 0.3

[a] Reference 13. [b] Paoletti, P.; Stern, J. H.; Vacca, A. *J. Phys. Chem.* **1965**, *69*, 3759. [c] Hamann, S. D.; Lim, S. C. *Aust. J. Chem.* **1954**, *7*, 329. [d] Yasuda, M.; Yamasaki, K.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1067. [e] Høiland, H. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1180. [f] Griesser, R.; Sigel, H. *Inorg. Chem.* **1970**, *9*, 1238. [g] Grant, M. W. *J. Chem. Soc., Faraday Trans. 1*, **1973**, *69*, 560. [h] Basolo, F.; Chen, Y. T. *J. Am. Chem. Soc.* **1954**, *76*, 953. [i] Cabani, S.; Mollica, V.; Lepori, L. Lobo, S. T. *J. Phys. Chem.* **1977**, *81*, 987. [j] Degischer, G.; Nancollas, G. H. *Inorg. Chem.* **1970**, *9*, 1259.

After the absence of any chloride ions was confirmed, the solution was cooled and the precipitated nickel(II) perchlorate was recrystallized from water. A nickel(II) perchlorate stock solution involving a small amount of perchloric acid was prepared. The concentration of nickel(II) was determined by a replacement titration with the Cu–TAR–EDTA system.[10] The Gran plot[11] was used for the determination of excess acid. Sodium acetate (NaOAc) of reagent grade was recrystallized from water. Sarcosine (*N*-methylglycine, Hsar) was recrystallized twice from acetone–water. Reagent grade glycine (Hgly), 2-morpholinoethanesulfonic acid (abbreviated as MES, with the acid form written as Hmes), 3-morpholinopropanesulfonic acid (MOPS, Hmops), and ethylenediamine-*N*,*N'*-diacetic acid (EDDA, H_2edda) were recrystallized twice from ethanol–water. Reagent grade ethylenediamine (en) was placed in contact with sodium hydroxide (ca. 10 wt %) overnight. The supernatant was then distilled in vacuum, and the ethylenediamine solution was prepared by dissolving the distillate in CO_2-free water. Tris(ethylenediamine)nickel(II) perchlorate was obtained by the addition of 100 g of ca. 0.5 mol dm^{-3} sodium perchlorate solution to the solution containing 40 g of ethylenediamine and 50 g of nickel(II) nitrate. The purple precipitate was recrystallized from water. The crystals were dried at 100 °C for 1 h in vacuum, and the composition was confirmed as $[Ni(C_2H_8N_2)_3](ClO_4)_2$ by elemental analyses of C, H, N, and Ni. *Caution*! One should be careful when handling the dry complex perchlorate. Explosion may result.

Potentiometry. The acid dissociation constants of the conjugate acid of the ligands and the stability constants of the nickel(II) complexes were determined by potentiometry using a pH meter (Corning, 130) with a glass electrode (Metrohm, EA 109T) and a calomel electrode filled with an NaCl solution (Metrohm, AG 9100). The ionic strength of all the solutions used was kept at I = 0.100 mol dm^{-3}. The liquid junction potential has been taken into account. Titrations were carried out by using a microburet (Metrohm) with a 0.1 mol dm^{-3} sodium hydroxide solution as the titrant at 25 ± 0.1 °C under nitrogen atmosphere. The titration was made at least twice.

Dilatometry. In this work, we used both the Hashitani type[12] cell and a modified type[13] of a dilatometric cell. In order to measure volume changes by a dilatometer, we constructed a high-precision thermostated bath that enabled us to maintain temperature within $\pm 6 \times 10^{-4}$ °C. The temperature was monitored by a quartz thermometer (Hewlett-Packard, Model 2801A). One solution in the lower compartment of a dilatometer was mixed with the other solution in the upper compartment, and the volume change was observed. The ionic strength of both solutions was adjusted to 0.100 mol dm^{-3} with $NaClO_4$. For the calculation of molar volume changes, the measured volume changes were corrected for the contribution attributable to dilution by mixing.[13]

Results

Determination of the Acid Dissociation Constants of Ligands and the Stability Constants of the Nickel(II) Complexes. Although these constants are available in the literature, it is indispensable, in order to obtain reliable data for reaction volume, to redetermine them under our experimental conditions. Plots of $\bar{q}_H$ against −log [H$^+$] are given in Figure s1,[28] where $\bar{q}_H$ is the average number of protons bound to a ligand. Obtained values of the acid dissociation constants are summarized in Table I together with the literature values. Plots of $\bar{n}_L$ vs −log [L] are depicted in Figure s2,[28] where $\bar{n}_L$ is the average number of ligands (L) bound to a nickel(II) ion. Obtained values of the stability constants are listed in Table II together with the literature values.

Volume Change for Neutralization of H$^+$ and OH$^-$. When complexation reactions occur in aqueous media, the reaction between hydrogen ion and hydroxide ion should often take place simultaneously. Therefore, we first measured the reaction volume for the neutralization of $HClO_4$ with NaOH. The obtained value was compared with the available values to check the reliability of the present method in use.

An $HClO_4$ solution in the lower compartment of a dilatometer was mixed with an NaOH solution in the upper compartment and the volume change was observed. The reaction volume for the $H^+ + OH^-$ reaction was determined to be $\Delta V^\circ_{H_2O} = 21.2 \pm 0.1$ cm^3 mol^{-1} at 25.00 °C and $I = 0.100$ mol dm^{-3}. The obtained value agrees well with the literature values (21.17,[14] 20.4,[15] 20.5,[16] and 20.8[13] cm^3 mol^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}).

Reaction Volume for the Proton Dissociation of Weak Acids. We measured the reaction volume for the proton dissociation of the conjugate acid of bases used in the present study. Procedures for the EDDA system are given below as an example. A solution consisting of EDDA, NaOH, MOPS, and MES (the latter two used as buffer) was put in the upper compartment of the dilatometer, while an $HClO_4$ solution was put in the lower compartment. These two solutions under various conditions were mixed (see Table III). Although obtainable by calculation, the concentration of the hydrogen ion was confirmed with a pH meter. In Table IV are given the experimental results obtained in this system. The observed volume change, Δv, is the sum of the contributions from these reactions and can be written as

$$\Delta v = n_{OH}\Delta V^\circ_{OH} + n_{mops}\Delta V^\circ_{mops} + n_{mes}\Delta V^\circ_{mes} + n_{edda}\Delta V^\circ_{edda} + n_{Hedda}\Delta V^\circ_{Hedda} \quad (1)$$

where n_B and ΔV°_B denote the number of moles of the base B produced in the proton dissociation reaction, $HB \rightleftharpoons H^+ + B$ (charges omitted for generalization), and the corresponding reaction volume, respectively. When we dealt with the protonation in some experiments, we retained the same symbols, and then the observed reaction volume should be $-n_B\Delta V^\circ_B$ instead of $n_B\Delta V^\circ_B$. In this case n_B denotes the number of moles of the base B protonated. As is apparent from Table IV, the contribution of MOPS and MES to the volume change is very small. Rearrangement of eq 1 leads to eq 2.

$$[\Delta v - (n_{OH}\Delta V^\circ_{OH} + n_{mops}\Delta V^\circ_{mops} + n_{mes}\Delta V^\circ_{mes})]/n_{edda} = (n_{Hedda}/n_{edda})\Delta V^\circ_{Hedda} + \Delta V^\circ_{edda} \quad (2)$$

Using the known values of ΔV°_{OH}, ΔV°_{mops} (−7.1 ± 0.2 cm^3 mol^{-1}),[13] and ΔV°_{mes}, we plotted the left-hand side of eq 2 vs n_{Hedda}/n_{edda} for several measurements (Figure 1). From the intercept and the slope of the resulting straight line, the reaction volumes were determined to be $\Delta V^\circ_{edda} = -0.6 \pm 0.2$ cm^3 mol^{-1} and $\Delta V^\circ_{Hedda} = 4.9 \pm 0.3$ cm^3 mol^{-1}. All the reaction volumes obtained for the proton dissociation are summarized in Table I.

Reaction Volumes for the Formation of Nickel(II) Complexes. Procedures for the Ni(II)–glycine system are given below as an example. A solution containing nickel(II) perchlorate, perchloric acid, and MES as buffer was put in the lower compartment, while a solution involving glycine and NaOH was placed in the upper compartment. Concentrations of these solutions are shown in Table sI.[28] Changes in the number of moles of species occurring

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(10) Yamada, H.; Maeda, T.; Kojima, I. *Anal. Chim. Acta* **1974**, *72*, 426.
(11) Gran, G. *Analyst (London)* **1952**, *77*, 661.
(12) Uemoto, M.; Hashitani, T. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2333.
(13) Funahashi, S.; Sengoku, K.; Amari, T.; Tanaka, M. *J. Solution Chem.* **1987**, *17*, 109.
(14) Millero, F. J.; Hoff, E. V.; Kahn, L. *J. Solution Chem.* **1972**, *1*, 309.
(15) Hamann, S. D. *J. Phys. Chem.* **1963**, *67*, 2233.
(16) Lown, D. A.; Thirsk, H. R.; Wynne-Jones, L. *Trans. Faraday Soc.* **1968**, *64*, 2073.

Table II. Stability Constants of Nickel(II) Complexes and Reaction Volumes for Nickel(II) Complexation

reactions	log K_{NiL}	$\Delta V°$/cm^3 mol^{-1}	$\Delta V°_{elec}$[a]/ cm^3 mol^{-1}	$\Delta V°_{elong}$[a]/ cm^3 mol^{-1}	$\Delta\Delta V°$[a]/ cm^3 mol^{-1}
$Ni(H_2O)_6^{2+} + NH_3 \rightleftharpoons Ni(H_2O)_5(NH_3)^{2+} + H_2O$	2.88 ± 0.01[b] (2.8)[c]	−0.2 ± 0.5[b] (−2.3)[d]	0	1.1	−1.3
$Ni(H_2O)_6^{2+} + OAc^- \rightleftharpoons Ni(H_2O)_5(OAc)^+ + H_2O$	0.931 ± 0.006 (1.0)[e]	8.0 ± 1.5	5.2	1.1	1.7
$Ni(H_2O)_6^{2+} + gly^- \rightleftharpoons Ni(H_2O)_4(gly)^+ + 2H_2O$	5.80 ± 0.01 (5.83)[f]	11.2 ± 0.2	5.2	2.1	3.9
$Ni(H_2O)_4(gly)^+ + gly^- \rightleftharpoons Ni(H_2O)_2(gly)_2 + 4H_2O$	4.86 ± 0.01 (4.91)[f]	12.0 ± 0.5 (2.1)[g]	2.5	0.8	8.8
$Ni(H_2O)_6^{2+} + sar^- \rightleftharpoons Ni(H_2O)_4(sar)^+ + 2H_2O$	5.386 ± 0.009 (5.50)[h]	11.7 ± 0.5	5.2	2.1	4.4
$Ni(H_2O)_4(sar)^+ + sar^- \rightleftharpoons Ni(H_2O)_2(sar)_2 + 4H_2O$	4.438 ± 0.009 (4.38)[h]	9.9 ± 0.8	2.5	0.8	6.7
$Ni(H_2O)_6^{2+} + en \rightleftharpoons Ni(H_2O)_4(en)^{2+} + 2H_2O$	7.28 ± 0.02 (7.36)[i]	5.2 ± 0.5	0	2.1	3.1
$Ni(H_2O)_4(en)^{2+} + en \rightleftharpoons Ni(H_2O)_2(en)_2^{2+} + 4H_2O$	6.08 ± 0.02 (6.26)[i]	5.6 ± 0.9	0	0.8	4.8
$Ni(H_2O)_6^{2+} + edda^{2-} \rightleftharpoons Ni(H_2O)_2(edda) + 4H_2O$	13.51 ± 0.05 (13.65)[j]	28.6 ± 0.2	7.6	1.8	19.2

[a] See text. [b] Reference 13. [c] Derr, P. F.; Vosburgh, W. C. *J. Am. Chem. Soc.* **1943**, *65*, 2408. [d] Caldin, E. F.; Grant, M. W.; Hasinoff, B. B. *J. Chem. Soc., Faraday Trans. 1*, **1972**, *68*, 2247. [e] Reference *d* in Table I. [f] Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 2229. [g] Reference *g* in Table I. [h] Reference *h* in Table I. [i] Faraglia, G.; Rossotti, F. J. C.; Rossotti, H. S. *Inorg. Chim. Acta.* **1970**, *4*, 488. [j] Reference *j* in Table I.

Table III. Solutions Used for the EDDA System

		concn of soln, mol dm^{-3}					
		upper compartment (52.46 cm^3)				lower compartment (50.84 cm^3)	
run no.		EDDA	NaOH	MOPS	MES	$HClO_4$	vol change,[a] cm^3 mol^{-1}
1	before mixing	1.969×10^{-2}	4.181×10^{-2}	2.06×10^{-4}	1.90×10^{-4}	2.682×10^{-2}	
	after mixing	9.999×10^{-3}	2.123×10^{-2}	1.05×10^{-4}	9.64×10^{-5}	1.320×10^{-2}	3.108×10^{-3}
		9.999×10^{-3}	2.123×10^{-2}	1.05×10^{-4}	9.64×10^{-5}	0	-1.82×10^{-4}
		0	0	0	0	1.320×10^{-2}	-2.30×10^{-4}
2	before mixing	1.969×10^{-2}	4.181×10^{-2}	2.06×10^{-4}	1.90×10^{-4}	3.755×10^{-2}	
	after mixing	9.999×10^{-3}	2.123×10^{-2}	1.05×10^{-4}	9.64×10^{-5}	1.848×10^{-2}	-4.621×10^{-4}
		9.999×10^{-3}	2.123×10^{-2}	1.05×10^{-4}	9.64×10^{-5}	0	-1.82×10^{-4}
		0	0	0	0	1.848×10^{-2}	3.98×10^{-5}
3	before mixing	1.576×10^{-2}	3.205×10^{-2}	0	1.89×10^{-4}	2.682×10^{-2}	
	after mixing	8.002×10^{-3}	1.628×10^{-2}	0	9.57×10^{-5}	1.320×10^{-2}	-5.767×10^{-4}
		8.002×10^{-3}	1.628×10^{-2}	0	9.57×10^{-5}	0	-5.424×10^{-4}
		0	0	0	0	1.320×10^{-2}	-2.30×10^{-4}

[a] The average value of duplicate runs.

Table IV. Moles of Protonated Base in the Determination of Reaction Volume for the Proton Dissociation of EDDA

	run 1[a]	run 2[a]	run 3[a]	$\Delta V°$/cm^3 mol^{-1}
n_{Hedda}	1.34×10^{-4}	9.01×10^{-4}	4.44×10^{-4}	$\Delta V°_{Hedda}$
n_{edda}	9.74×10^{-4}	9.77×10^{-4}	7.49×10^{-4}	$\Delta V°_{edda}$
n_{mops}	4.48×10^{-6}	1.05×10^{-6}		−7.1[b]
n_{mes}	6.04×10^{-7}	7.38×10^{-6}	3.21×10^{-6}	−8.1[c]
n_{OH}	1.70×10^{-4}	1.70×10^{-4}	9.48×10^{-5}	−21.2[c]
$-\log [H^+]$ before mixing	11.011	11.011	10.759	
$-\log [H^+]$ after mixing	7.399	5.694	6.466	

[a] Run number corresponds to that given in Table III. [b] Reference 13. [c] This work.

on mixing are presented in Table sII.[28] We obtained the relationship shown in eq 3, where Δv is the observed volume change

$$[\Delta v - n_{gly}\Delta V°_{gly} - n_{OH}\Delta V°_{OH} - n_{mes}\Delta V°_{mes}]/n_1 = (n_2/n_1)\Delta V°_2 + \Delta V°_1 \quad (3)$$

on mixing, $\Delta V°_1$ and $\Delta V°_2$ are reaction volumes for the stepwise formation of the 1:1 and 1:2 glycinato complexes, respectively, and n_1 and n_2 are the number of moles of the 1:1 and 1:2 complexes produced in the corresponding reactions, respectively. By the use of the obtained values of $\Delta V°_{gly}$, $\Delta V°_{OH}$, and $\Delta V°_{mes}$, $\Delta V°_1$ and $\Delta V°_2$ were estimated from the plots of the left-hand side of eq 3 against n_2/n_1 for several measurements (see Figure 1). We obtained $\Delta V°_1 = 11.2 \pm 0.2$ cm^3 mol^{-1} and $\Delta V°_2 = 12.0 \pm 0.5$ cm^3 mol^{-1}. Obtained values of the reaction volumes for the formation of some nickel(II) complexes are summarized in Table II.

Discussion

Reaction Volumes for the Proton Dissociation of Weak Acids. There are two trends in the reaction volumes obtained in this study: decrease in volume accompanying proton dissociation of carboxylic acids and volume increase for the proton dissociation of ammoniums. Charges produced by proton dissociation of carboxylic acids give rise to the electrostriction on the surrounding solvent, and as a result, contraction of volume should be observed for the whole system. On the other hand, in the case of proton dissociation of the conjugate acid of amines such as NH_3 and en, the reaction volume is positive. Because of an extensive hydrogen bonding around the proton, oxonium forms a large entity and the electrostriction is less pronounced around oxonium than around ammonium. This is in accord with the argument that the volume change on neutralization of proton with hydroxide ions comes

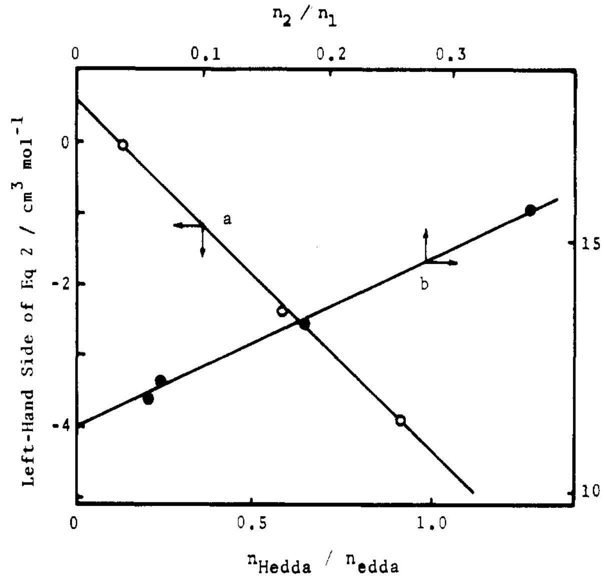
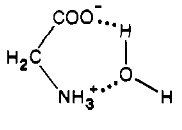


Figure 1. Plots for determination of reaction volumes: (a) plot according to eq 2 (○); (b) plot according to eq 3 (●).

mostly from the release of electrostriction around the OH^- species.[17]

The reaction volume of 5.6 $cm^3\ mol^{-1}$ for proton dissociation of the conjugate acid (Hen^+) of ethylenediamine is close to that of ammonia. However, for the first proton dissociation of the diprotonated species (H_2en^{2+}), it is 12.0 $cm^3\ mol^{-1}$, about twice in magnitude. On the other hand, the volume change of 4.9 $cm^3\ mol^{-1}$ for the proton dissociation of H_2edda is larger than that for $Hedda^-$ (-0.6 ± 0.2 $cm^3\ mol^{-1}$). The diprotonated species of EDDA has the formal charge of zero, but actually it is a zwitterion. In fact it acts as a 2+ species as far as the dissociation of proton on the amine nitrogen is concerned. Moreover ΔV° values for glycine and sarcosine (1.4 ± 0.3 and 0.7 ± 0.2 $cm^3\ mol^{-1}$, respectively) are near to zero as is that of $Hedda^-$ (-0.6 ± 0.2 $cm^3\ mol^{-1}$). This is also attributable to the similar structural feature of these zwitterions in solution.

Studies of NMR in solution support that the nitrogen-protonated glycine associates with water[18]



and that in amino polycarboxylic acids such as EDTA and NTA protons on nitrogen atoms interact with the carboxylate oxygen atoms.[19] The proton dissociation from a zwitterion involves the release of the interaction of carboxylate with ammonium cation and the rupture of the proton–amine bond. Thus this reaction may have dual features of the proton dissociation of carboxylic acid (negative reaction volume) and alkylammonium (positive reaction volume). This may be reflected in the small absolute value of reaction volume for the proton dissociation of zwitterions.

Reaction Volumes for the Complex Formation. For a reaction in which a metal ion $M(H_2O)_6^{2+}$, reacting with a monodentate A^{a-}, gives rise to a complex $MA(H_2O)_5^{2-a}$ with a water molecule set free from the metal ion, the reaction volume is determined by the following factors:

(a) The first factor is release of the electrostriction around $M(H_2O)_6^{2+}$ and A^{a-} by charge neutralization ($\Delta V^\circ_{\text{elec}}$). This effect is the most important when we are dealing with charged ligands. It is absent for neutral ligands, although the electrostriction should be more or less different around $M(H_2O)_6^{2+}$ and $MA(H_2O)_5^{2-a}$ even for noncharged ligand A. We regard the difference as small for neutral ligands.

(b) The second factor is contraction of the donor atoms in ligand A and solvent H_2O bound to the metal ion. The molar volume of a water molecule is said to be about 15 $cm^3\ mol^{-1}$ in the coordination sphere of a divalent metal ion. However this effect is compensatory for A and H_2O, as is evident from a very small reaction volume (-0.2 $cm^3\ mol^{-1}$) for the formation of the nickel monoammine.

(c) The third factor is expansion of $MA(H_2O)_5^{2-a}$ by the elongation of the $M-OH_2$ bond. This is due to the electron donation from the bound ligand A to the metal ion.

We estimated the contribution of electrostriction ($\Delta V^\circ_{\text{elec}}$) to reaction volumes by using the modified Drude–Nernst equation[20,21]

$$\bar{V}_{\text{elec}} = -\frac{Nz^2e^2}{2(r + \Delta r)}\frac{1}{\epsilon^2}\left(\frac{\partial \epsilon}{\partial P}\right)_T \tag{4}$$

with the following values: $r_{Ni} = 69$ pm, $r_O = 140$ pm, $\Delta r = 239$ pm,[21] and $(1/\epsilon^2)(\partial\epsilon/\partial P)_{T=298.3} = 6.01 \times 10^{-7}\ bar^{-1}$.[22] Calculated $\Delta V^\circ_{\text{elec}}$ values are tabulated in Table II.

According to X-ray diffraction studies on aqueous solutions of nickel(II) complexes,[23-25] the bonds between the nickel(II) atom and the oxygen atoms of the coordinated water molecules are elongated by coordination of ethylenediamine or glycinate to the nickel(II) ion. This is the result of the electron donation from amine(s) and/or carboxylate(s) bonded to the nickel(II) ion. Assuming proportionality between the number of amine nitrogen (or carboxylate oxygen) and the degree of the bond elongation, we estimated that the bonds between nickel and oxygen atoms of coordinated water molecules are elongated by ca. 1.5 pm for $Ni(H_2O)_5(NH_3)^{2+}$, by ca. 3 pm for $Ni(H_2O)_4(en)^{2+}$, $Ni(H_2O)_4(gly)^+$, and $Ni(H_2O)_4(sar)^+$, and by ca. 6 pm for $Ni(H_2O)_2(en)_2^{2+}$, $Ni(H_2O)_2(gly)_2$, $Ni(H_2O)_2(sar)_2$, and $Ni(H_2O)_2(edda)$. The volume increments arising from the bond elongation due to the donation from the bound amine(s) and/or carboxylate(s) ($\Delta V^\circ_{\text{elong}}$) were estimated[26] and listed in Table II.

In the last column in Table II, $\Delta\Delta V^\circ$ values defined by $\Delta\Delta V^\circ = \Delta V^\circ - (\Delta V^\circ_{\text{elec}} + \Delta V^\circ_{\text{elong}})$ are given. For monodentate ligands such as ammonia and acetate, the $\Delta\Delta V^\circ$ value reflects the difference of contraction of water and ligand molecules in the first coordination sphere of the nickel ion ($\Delta V^\circ_{\text{cont}}$). Actually $|\Delta\Delta V^\circ| = |\Delta V^\circ_{\text{cont}}| < 2$ for these monodentate ligands: contraction of donor atoms in these ligands on the metal ion is indeed largely compensatory. The contraction of ammonia is more pronounced than that of water molecule on the metal ion, while the acetate ion is less contracted than H_2O on the nickel ion.

Obviously $\Delta\Delta V^\circ$ values involve the reaction volume resulting from the contraction of coordinated ligands for chelating ligands too. In the case of the glycinato complex, for instance, $\Delta V^\circ_{\text{cont}}$ for the amine coordination may be approximated as $\Delta\Delta V^\circ$ for ammonia (-1.3 $cm^3\ mol^{-1}$) and $\Delta V^\circ_{\text{cont}}$ for the carboxylate coordination as $\Delta\Delta V^\circ$ for acetate ($+1.7$ $cm^3\ mol^{-1}$). Therefore $\Delta V^\circ_{\text{cont}}$ for the glycinate coordination may be given by the sum of the two: $1.7 - 1.3 = 0.4$ $cm^3\ mol^{-1}$. Similarly for the coordination of the other amino acetates, $\Delta V^\circ_{\text{cont}}$ should not exceed 1 $cm^3\ mol^{-1}$. Actually $\Delta\Delta V^\circ$ values for the complexation with amino acetates ranges from 3.9 to 8.8 $cm^3\ mol^{-1}$. For the ethylenediamine complexation also, smaller but definite figures for $\Delta\Delta V^\circ$ are observed. These additional reaction volumes should come from chelation. This may be due to the different packing of the coordinated multidentate ligands on the metal ion as compared with the packing of the noncoordinated ligands. ($\Delta\Delta V^\circ - \Delta V^\circ_{\text{cont}}$) for multidentate ligands may be regarded as a measure of the "volume chelate effect". The volume chelate effect for the second chelation is larger than that for the first chelation.

The reaction volumes for the formation of nickel complexes with ethylenediamine-*N,N'*-diacetate ($edda^{2-}$), *N*-(2-hydroxyethyl)-ethylenediamine-*N,N',N'*-triacetate ($hedta^{3-}$) and ethylenediamine-*N,N,N',N'*-tetraacetate ($edta^{4-}$) are calculated with the values in Table II.

To calculate $\Delta V^\circ(Ni(edda))$ we considered the coordination of two glycinate ions to the nickel ion. Then the term $[\Delta\Delta V^\circ(Ni(en)^{2+}) - 2\Delta\Delta V^\circ(Ni(NH_3)^{2+})]$ is added to take into account the volume chelate effect by ethylenediamine: $\Delta V^\circ(Ni(edda)) = \Delta V^\circ(Ni(gly)^+) + \Delta V^\circ(Ni(gly)_2) + \Delta\Delta V^\circ(Ni(en)^{2+}) - 2\Delta\Delta V^\circ(Ni(NH_3)^{2+}) = 11.2 + 12.0 + 3.1 + 2.6 = 28.9$ $cm^3\ mol^{-1}$.

To calculate $\Delta V^\circ(Ni(hedta))$ from the known value of $\Delta V^\circ(Ni(edda))$, the term $[\Delta\Delta V^\circ(Ni(gly)^+) - \Delta\Delta V^\circ(Ni(NH_3)^{2+})]$ is added to take into account the volume chelate effect due to the chelate ring formation by a carboxylate side arm: $\Delta V^\circ(Ni(hedta)^-) = \Delta V^\circ(Ni(edda)) + \Delta\Delta V^\circ(Ni(gly)^+) - \Delta\Delta V^\circ(Ni(NH_3)^{2+}) - \Delta V^\circ_{\text{elong}}(Ni(edda)) + \Delta V^\circ_{\text{elong}}(Ni(hedta)^-) = 28.6$

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(17) Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 971.

(18) Leipert, T. K.; Noggle, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 269.

(19) Chapman, D.; Lloyd, D. R.; Prince, R. H. *J. Chem. Soc.* **1963**, 3645.

(20) Drude, P.; Nernst, W. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1894**, *15*, 79.

(21) Swaddle, T. W.; Mak, M. K. S. *Can. J. Chem.* **1983**, *61*, 473.

(22) Srinivasan, K. R.; Kay, R. L. *J. Chem. Phys.* **1974**, *60*, 3645.

(23) Ohtaki, H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1976**, *43*, 701.

(24) Fujita, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 455.

(25) Ozutsumi, K.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3635.

(26) If 344 pm is accepted as the radius of the spherical $Ni(H_2O)_6^{2+}$ complex, the increase in volume of the sphere for 1.5, 3, and 6 pm bond elongation is 1.4, 3.2, and 5.5 $cm^3\ mol^{-1}$, respectively. If we take into account only the elongation of the bond between nickel and oxygen atom of coordinated water molecules, the volume increment ($\Delta V^\circ_{\text{elong}}/cm^3\ mol^{-1}$) is expected to be $1.4 \times (5/6)$ for $Ni(H_2O)_5(NH_3)^{2+}$ and $Ni(H_2O)_5(OAc)^+$, $3.2 \times (4/6)$ for $Ni(H_2O)_4(gly)^+$, $Ni(H_2O)_4(sar)^+$, and $Ni(H_2O)_4(en)^{2+}$, $(5.5 - 3.2) \times (2/6)$ for $Ni(H_2O)_2(gly)_2$, $Ni(H_2O)_2(sar)_2$, and $Ni(H_2O)_2(en)_2^{2+}$, and $5.47 \times (2/6)$ for $Ni(H_2O)_2(edda)$.

+ 3.9 + 1.3 − 1.8 + 1.1 = 33.1 cm^3 mol^{-1}. The term [$\Delta V^\circ_{\mathrm{elong}}$(Ni(hedta)$^-$) − $\Delta V^\circ_{\mathrm{elong}}$(Ni(edda))] should be added as a correction term for the electron donation from the third carboxylate coordinated in Ni(hedta)$^-$. The electrostriction for this case may be considered by the following reaction, in which we have one uninegative anion on both sides: Ni(edda) + OAc$^-$ $\rightleftharpoons$ Ni(edda)(OAc)$^-$. Therefore we neglected the contribution of electrostriction, which may be regarded as small.

From ΔV°(Ni(edda)) we calculated ΔV°(Ni(edta)$^{2-}$) as follows: ΔV°(Ni(edta)$^{2-}$) = ΔV°(Ni(edda)) + 2$\Delta\Delta V^\circ$(Ni(gly)$^+$) − 2$\Delta\Delta V^\circ$(Ni(NH$_3$)$^{2+}$) − $\Delta V^\circ_{\mathrm{elong}}$(Ni(edda)) + $\Delta V^\circ_{\mathrm{elong}}$(Ni(edta)$^{2-}$) + $\Delta V^\circ_{\mathrm{elec}}$(Ni(edda)(OAc)$_2^{2-}$) = 28.6 + 7.8 + 2.6 − 1.8 + 0 + 3.2 = 40.4 cm^3 mol^{-1}. We took into account the contribution of electrostriction from the following reaction (the last term): Ni(edda) + 2OAc$^-$ $\rightleftharpoons$ Ni(edda)(OAc)$_2^{2-}$.

Yoshitani has recently reported 33.7 and 44.4 cm^3 mol^{-1} as reaction volumes for the formation of Ni(hedta)$^-$ and Ni(edta)$^{2-}$, respectively.[27] The calculated reaction volumes for the formation of Ni(edda) and Ni(hedta)$^-$ compare very favorably with the experimental values. The experimental value for Ni(edta)$^{2-}$ is a little too high as compared with the calculated value.

In conclusion the following four factors are important in the consideration of the reaction volume for the formation of metal complexes: electrostriction, contraction of donor atoms in the first coordination sphere, expansion of metal complexes by the elongation of the bond M–OH$_2$ due to bound amine(s) and/or carboxylate(s), and the volume chelate effect.

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Supplementary Material Available: Plots of $\bar{q}_{\mathrm{H}}$ against −log [H$^+$] (Figure s1), plots of $\bar{n}_{\mathrm{L}}$ vs −log [L] (Figure s2), compositions of solutions used for the Ni(II)–glycine system (Table sI), and moles of species in reactions occurring by mixing in the Ni(II)–glycine system (Table sII) (9 pages). Ordering information is given on any current masthead page.

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(27) Yoshitani, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1646.
(28) See paragraph at end of paper regarding supplementary material.

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Synthesis and Characterization of Mixed Niobium–Vanadium Phosphates

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From solutions containing several percentage molar ratios V/(V + Nb), mixed niobyl–vanadyl phosphates were obtained. The mixed phosphate with maximum vanadium content was 21%. From analysis by EDX-SEM, DTA, IR spectra, X-ray diffraction, and diffuse-reflectance spectra, it was established that the mixed phosphates are solid solutions.

Introduction

Compounds with the formula MOAO$_4$ (M = V, Nb, Ta; A = P, As) constitute an isomorphic series that has two types of crystal forms: one tetragonal and the other orthorhombic. X-ray diffraction studies have established the structure of tetragonal forms MOPO$_4$[1-3] and MOAsO$_4$,[4,5] which consist of chains of corner-shared [MO$_6$] octahedra running parallel to the *c* axis. In the *ab* plane, each [MO$_6$] octahedron shares corners with four [AO$_4$] tetrahedra, which link the octahedral chains to produce a three-dimensional lattice. The layers of these compounds along the *c* axis are linked by the trans oxygen vertices of the octahedra. However, the M atoms are not centered within the octahedra but displaced along the *c* axis so that it can establish two M–O linkages; one is short, which corresponds to a M=O bond; the other is longer, a simple M—O linkage and therefore weaker.

Hydrates of some of these compounds are known, and their formation may be explained by breaking of the long M–O linkages of the respective anhydrous forms and subsequent substitution of the O of the adjacent layer by a water molecule in the sixth coordination position of the metal. Hydrates of this kind are reported for VOPO$_4$,[6,7] VOAsO$_4$,[4] NbOPO$_4$,[8] and NbOAsO$_4$,[5] which have a variable number of water molecules and present a tetragonal structure similar to that of their respective anhydrous forms.

It is interesting that this type of compound may undergo intercalation reactions in which the matrix of the original product is preserved throughout. Two types of intercalation reactions have been described: (1) those in which alcohols,[9,10] amines,[10,11] or amides[12] enter the interlamellar space to coordinate with the metal atom, either by direct means or through a water molecule, and (2) those in which the laminar charge produced by the reaction of vanadium(V) to vanadium(IV) is compensated by the intercalation of inorganic[13] or organic[14] cations.

However, vanadyl phosphates and arsenates have a poor hydrolytic stability, which leads to the solid being partially dissolved[13,14] especially during redox intercalation reactions in aqueous media. To circumvent this, solvents like acetone[14] or aqueous alcoholic mixtures[13] are used. On the other hand, although aqueous suspensions of the niobyl phosphates and arsenates have great stability, they have an important limitation because niobium itself is highly stable in the (V) oxidation state and cannot undergo the type of redox topotactic intercalation reactions induced by moderate reducing agents.

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(1) Jordan, B.; Calvo, C. *Can. J. Chem.* **1973**, *51*, 2621-2625.
(2) Longo, J. M.; Kierkegaard, P. *Acta Chem. Scand.* **1966**, *20*, 72-78.
(3) Longo, J. M.; Pierce, J. W.; Kafalas, J. A. *Mater. Res. Bull.* **1971**, *6*, 1157-1166.
(4) Chernorukov, N. G.; Egorov, N. P.; Korshunov, I. A. *Zh. Neorg. Khim.* **1978**, *23*, 2672-2675; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 1479-1481.
(5) Chernorukov, N. G.; Egorov, N. P.; Korshunov, I. A. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1979**, *15*, 335-338.
(6) Bordes, E.; Courtine, P.; Pannetier, G. *Ann. Chim.* (*Paris*) **1973**, *8*, 105-113.
(7) Ladwig, G. *Z. Anorg. Allg. Chem.* **1965**, *338*, 266-278.
(8) Chernorukov, N. G.; Egorov, N. P.; Mochalova, I. R. *Zh. Neorg. Khim.* **1978**, *23*, 2931-2934; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 1627-1629.
(9) Benes, L.; Votinsky, J.; Kalousova, J.; Klikorka, J. *Inorg. Chim. Acta* **1986**, *114*, 47-50.
(10) Beneke, K.; Lagaly, G. *Inorg. Chem.* **1983**, *22*, 1503-1507.
(11) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. *Inorg. Chem.* **1982**, *21*, 3820-3825.
(12) Martínez-Lara, M.; Moreno-Real, L.; Jimênez-Lôpez, A.; Bruque-Gâmez, S. Rodríguez-García, A. *Mater. Res. Bull.* **1986**, *21*, 13-22.
(13) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782-1787.
(14) Martínez-Lara, M.; Jimênez Lôpez, A.; Moreno-Real, L.; Bruque, S.; Casal, B.; Ruiz-Hitzky, E. *Mater. Res. Bull.* **1985**, *20*, 549-555.

0020-1669/88/1327-3372$01.50/0