intermetallic distances in both **3** and **4** are, however, inconsistent with such an explanation; therefore, the magnetic properties of these dimers were examined in detail to determine the nature of the metal–metal interaction.

Molar susceptibilities for **3** and **4** were measured between 6 and 300 K on a SQUID susceptometer. Above 100 K the observed magnetism is predominantly due to temperature-independent paramagnetism (TIP), resulting from orbital mixing of the spin-singlet ground states with low-lying (paramagnetic) excited states.[11] Below approximately 50 K the sample magnetization is dominated by traces (<0.25%) of paramagnetic impurities. The experimental data can be accurately simulated by assuming 99.78% purity and a TIP of 8.8×10^{-5} cgsu/mol of Ti for **3** and 99.75% purity and a TIP of 1.68×10^{-4} cgsu/mol of Ti for **4**.[12] EPR spectroscopy establishes that both compounds have normal metal–metal bonds, rather than spin-coupled diradical ground states: except for a small impurity peak at $g = 1.972$, characteristic of magnetically dilute Ti^{3+} ions,[13] the EPR spectra of both **3** and **4** are featureless at both 298 and 77 K.[14]

The mechanism by which **3** is formed, and whether or not it involves the intermediacy of monomeric complexes such as **2** (M = Ti), is not yet known. What is clear, however, is that the formation of dimeric complexes, such as **3**, is greatly preferred over pyramidalized monomers, such as **2**, for the trisilanol ligand used here. The use of smaller transition-metal ions (e.g., V(III), Cr(III), or Fe(III)), which can adopt less pyramidalized coordination geometries with **1**, should favor the formation of **2** and is currently being explored.

Acknowledgment. We thank Professor Christopher Reed (University of Southern California) for his assistance with the magnetic studies and Professor T. Don Tilley (University of California, San Diego) for providing access to an EPR spectrometer. These studies were supported by the National Science Foundation (Grant CHE-8703016) and an NSF-Presidential Young Investigator Award (CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Funds for the purchase of the X-ray diffraction equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: An index for the supplementary material, X-ray crystal data for **3** and **4** including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles and magnetic data for **1**, **3**, and **4** including experimental procedures, tables of SQUID data, a detailed description of the simulation procedure, and plots of experimental and simulated data (33 pages); listings of calculated and observed structure factors (36 pages). Ordering information is given on any current masthead page.

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Articles

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Thermodynamics of Aqueous EDTA Systems: Apparent and Partial Molar Heat Capacities and Volumes of Aqueous Cadmium, Mercury, and Lead EDTA Complexes

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Apparent molar heat capacities and volumes have been measured for $Na_2CdEDTA(aq)$, $Na_2HgEDTA(aq)$, and $Na_2PbEDTA(aq)$. Standard-state partial molar heat capacities $\bar{C}_{p,2}^{\circ}$ and volumes $\bar{V}_2^{\circ}$ have been calculated along with the partial molar properties at 0.1 *m* ionic strength that are needed for various thermodynamic calculations. Equilibrium constants for the exchange reactions of $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ with $Ca^{2+}(aq)$ have been calculated to 250 °C.

Introduction

As part of our research on the thermodynamics of reactions involving aqueous complexes of EDTA (ethylenediaminetetraacetate), we have measured heat capacities and densities of aqueous solutions of $Na_2CdEDTA$, $Na_2HgEDTA$, and $Na_2PbEDTA$.

Aqueous solutions of EDTA are used as sequestering agents in industrial applications that include cleaning boilers, softening boiler and process water, treating oil wells to remove scale minerals, and decontaminating nuclear reactor systems. There are also medicinal uses of EDTA that include treating Alzheimer's disease by complexation of aluminum,[1] treating ulcers,[2] treating periarthritis and similar ailments,[3] and using as agents for increased contrast in NMR body imaging.[4] Specific to the salts studied in this paper is the use of EDTA to remove cadmium, mercury, and lead[5] from the body. EDTA treatment of metal poisoning may introduce risks,[6] but its wide versatility in the complexation

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of many heavy-metal ions (including plutonium[7]) makes it a valuable chemical treatment.[8,9]

In our previous investigations[10,11] of EDTA complexes with cations and also in related investigations by others that are cited later, it has been observed that different investigators who have made measurements leading to equilibrium constants have generally obtained results in satisfactory agreement with each other. On the other hand, there is less good agreement between the results of different investigators who have reported enthalpies of complexation reactions, especially when enthalpies have been calculated by way of equilibrium constants at several temperatures and the van't Hoff equation. We attribute most of the uncertainties and possible errors in these ΔH values to the magnification of errors and uncertainties associated with differentiation $[(\mathrm{d}\ \ln K/\mathrm{d}T)_p]$ and to problems connected with the fact that EDTA forms weak complexes with most cations in supporting electrolytes. It therefore follows that ΔC_p values obtained by double differentiation of $K = f(T)$ results or single differentiation of calorimetric $\Delta H = f(T)$ results will have large uncertainties. As previously recognized, the best ΔC_p values are usually obtained by way of direct calorimetric measurements of heat capacities.

Although the complexation equilibria of Cd^{2+}, Hg^{2+}, and Pb^{2+} with EDTA have been investigated extensively near 25 °C, there have been no investigations of these systems at the high temperatures that are important for several applications. One of the purposes of the present research has been to make calorimetric measurements of heat capacities of solutions that will lead to ΔC_p values for the various complexation equilibria, with these ΔC_p values to be used in calculating equilibrium constants and other thermodynamic properties that are applicable to solutions at high temperatures. Because of the way in which we have measured heat capacities, we have also obtained densities of solutions that have led to apparent and partial molar volumes and thence to values of ΔV for these same complexation equilibria. These ΔV values can be used in calculating the pressure dependence of complexation equilibria.

Experimental Section

Water used for all solutions was distilled and then passed through a Milli-Q reagent-grade mixed-bed ion-exchange and activated-carbon system, to yield water with a final resistance of 18 MΩ cm or greater. Standard solutions of NaCl were prepared by mass after drying the salt (Fisher certified, ACS) at 120 °C for several hours.

$Na_2CdEDTA$ (ICN Pharmaceuticals) and $Na_2PbEDTA$ (Tokyo Kasei, certified >99%) were recrystallized twice by a method described previously.[10,11] $Na_2HgEDTA$ was prepared by adding $Hg(NO_3)_2$ (Fisher, ACS) dissolved in dilute $HNO_3(aq)$ to a solution of Na_2H_2EDTA (Fisher certified, ACS) until a slight excess of $Hg(NO_3)_2$ was present. Dilute NaOH was used to raise the pH of the solution slightly after each addition of $Hg(NO_3)_2$. Crystals were precipitated by dilution with ethanol and were then recrystallized twice as for the Cd and Pb EDTA complexes. All salts were dried at 60 °C for 3 days. Stock solutions of the salts were prepared by mass from these dried (but still hydrated) salts. Total water contents of the dried $Na_2CdEDTA$ and $Na_2PbEDTA$ salts were obtained from mass loss on complete dehydration at 150 °C under vacuum, with results that agreed with the amount calculated from elemental analyses of these salts. However, the $Na_2HgEDTA$ salt was found to decompose at 150 °C, and the total water content for this salt was determined solely from the elemental analysis. The empirical formulas of these salts were found to be $Na_2CdEDTA\cdot4.22H_2O$, $Na_2HgEDTA\cdot2.68H_2O$, and $Na_2PbEDTA\cdot1.09H_2O$.

Table I. Results of Calorimetric and Densimetric Measurements at 25.0 °C

m, mol kg^{-1}	V_ϕ, cm^3 mol^{-1}	$C_{p,\phi}$, J K^{-1} mol^{-1}	m, mol kg^{-1}	V_ϕ, cm^3 mol^{-1}	$C_{p,\phi}$, J K^{-1} mol^{-1}
		$Na_2CdEDTA$			
0.2014	169.76	256.4	0.07021	166.13	201.4
0.1641	168.74	239.5	0.04778	164.64	189.4
0.1321	167.63	225.8	0.03001	163.84	177.9
0.1073	166.88	217.9			
		$Na_2HgEDTA$			
0.1881	171.51	341.9	0.06820	169.01	269.7
0.1483	170.71	320.7	0.03973	168.05	260.0
0.1257	170.07	307.0	0.02778	167.65	251.7
0.09848	169.49	289.1			
		$Na_2PbEDTA$			
0.2552	180.62	259.8	0.09009	178.37	207.2
0.2062	180.14	243.8	0.06292	177.45	194.3
0.1703	179.45	230.9	0.03440	177.04	183.9
0.1202	178.88	216.0			

Heat capacities of all solutions were measured at 25.00 ± 0.01 °C with a Picker flow microcalorimeter.[12] The specific heat capacity of water was taken from Kell[13] and had the value 4.1793 J K^{-1} g^{-1}. Small corrections ($f = 1.006$) to the raw heat capacity data were made to allow for small heat losses in the calorimeter, as described by Desnoyers et al.[14] Densities of all solutions were measured relative to water at 25.00 ± 0.01 °C with a Sodev 03D vibrating-tube densimeter,[15] which was calibrated with water and standard NaCl solutions. The density of water at 25 °C was taken from Kell[16] and had the value 0.997 047 g cm^{-3}. The densities of the standard NaCl solutions were obtained from the results of Picker et al.[15] Temperature control for the densimeter and calorimeter was achieved with separate Sodev CT-L circulating baths (constant to ±0.001 °C). Temperatures of the baths were monitored with thermistors that had been calibrated against a Hewlett-Packard 2804A quartz thermometer.

Results

It is convenient to express results of our heat capacity and density measurements as apparent molar properties defined by

$$Y_\phi = (Y_{\mathrm{sol}} - n_1 Y_1^\circ)/n_2 \qquad (1)$$

in which Y_{sol} is the extensive property (heat capacity or volume) of a specified quantity of solution, Y_1° is the property (heat capacity or volume) of 1 mol of water, and n_1 and n_2 are the amounts (moles) of water and of solute in the specified quantity of solution. This equation written specifically for the calculation of apparent molar volumes and heat capacities has the forms

$$V_\phi = [(1000 + mM)/d - 1000/d_1^\circ]/m \qquad (2)$$

$$C_{p,\phi} = [c_p(1000 + mM) - 1000c_{p,1}^\circ]/m \qquad (3)$$

Here M is the molality of the solution, M is the molar mass of the solute, d_1° and $c_{p,1}^\circ$ are the density and specific heat capacity of pure water, and d and c_p are the density and specific heat capacity of the solution. The $C_{p,\phi}$ and V_ϕ results are listed in Table I.

The stability constants for the aqueous cadmium, mercury, and lead EDTA complexes are sufficiently large that we can regard these solutions as 2:1 electrolytes of the type $2Na^+(aq) + M(EDTA)^{2-}(aq)$.

A useful representation of apparent molar properties to moderate ionic strengths is the extended Debye–Hückel equation

$$Y_\phi = Y_\phi^\circ + A_Y\omega^{3/2}m^{1/2} + B_Y\omega m \qquad (4)$$

in which B_Y is an adjustable parameter and Y_ϕ° is the value of Y_ϕ at infinite dilution. The valence factor (ω) is related to the molality (m), charge (z_i), and molal ionic strength (I) by

$$I = \tfrac{1}{2}\sum m_i z_i^2 = \omega m \qquad (5)$$

The values of the limiting-law slopes (A_Y)[17] were taken from

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Table II. Standard-State (Infinite Dilution) Partial Molar Heat Capacities, Volumes, and $B_{Y\omega}$ Parameters at 25.0 °C[a]

solute	$C_{p,\phi}°$, J K^{-1} mol^{-1}	$B_{C\omega}$, J kg K^{-1} mol^{-2}	$V_{\phi}°$, cm^3 mol^{-1}	$B_{V\omega}$, cm^3 kg mol^{-2}
$Na_2CdEDTA$	143.3 ± 1.2	172.7 ± 9.7	161.60 ± 0.04	19.06 ± 0.34
$Na_2HgEDTA$	200.7 ± 1.1	361.3 ± 8.4	165.82 ± 0.12	7.423 ± 0.99
$Na_2PbEDTA$	148.0 ± 1.4	82.35 ± 11	175.08 ± 0.12	2.654 ± 0.76

[a] The ± values are the standard deviations associated with the fit of eq 4 to our experimental results. Total uncertainties (calorimetric, densimetric, chemicals, and extrapolations) are about ±6 J K^{-1} mol^{-1} and ±0.6 cm^3 mol^{-1}.

Table III. Partial Molar Properties at I = 0.10 [0.033 m $Na_2M(EDTA)$] at 25.0 °C

solute	$\bar{C}_{p,2}^{\dagger}$, J K^{-1} mol^{-1}	$\bar{V}_2^{\dagger}$, cm^3 mol^{-1}
$Na_2CdEDTA$	201.46	165.54
$Na_2HgEDTA$	271.42	168.98
$Na_2PbEDTA$	200.09	177.92

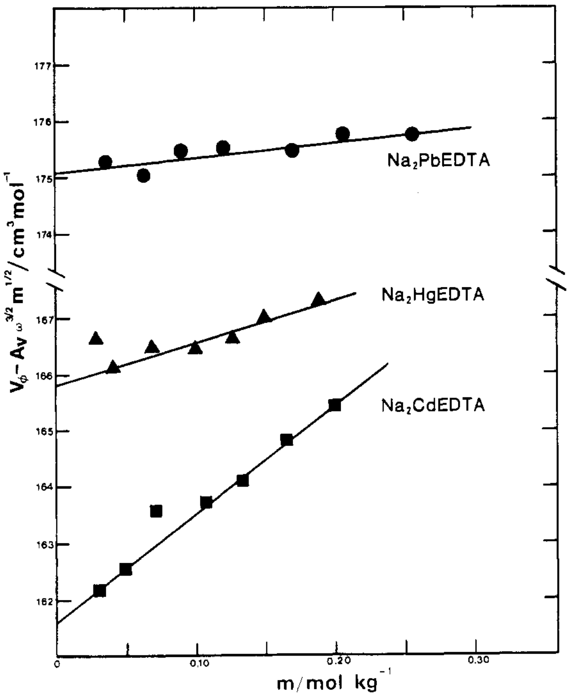

Figure 1. Apparent molar volumes minus the Debye–Hückel limiting slopes ($A_V\omega^{3/2}m^{1/2}$) for $Na_2CdEDTA$(aq), $Na_2HgEDTA$(aq), and $Na_2PbEDTA$(aq). Lines are least-squares fits of eq 4.

Ananthaswamy and Atkinson:[18] $A_V = 1.8743$ cm^3 kg$^{1/2}$ mol$^{-3/2}$ and $A_C = 32.783$ J K^{-1} kg$^{1/2}$ mol$^{-3/2}$ at 25 °C.

We have fitted eq 4 to our experimental results ($C_{p,\phi}$, V_ϕ, and corresponding molalities in Table I) and have obtained the values of $C_{p,\phi}°$, B_C, $V_\phi°$, and B_V that are listed in Table II. Figures 1 and 2 show graphs of $Y_\phi - A_Y\omega^{3/2}m^{1/2}$ against m as suggested by eq 4. Note that the values of the apparent molar properties at infinite dilution ($C_{p,\phi}°$ and $V_\phi°$) are equal to the corresponding standard-state partial molar quantities that we represent by $\bar{C}_{p,2}°$ and $\bar{V}_2°$. The values of $\bar{C}_{p,2}°$ and $\bar{V}_2°$ that we have obtained can be used to obtain values of $\Delta C_p°$ and $\Delta V°$ (conventional standard state based on properties of solutes at infinite dilution) for reactions involving the corresponding EDTA complexes.

Many previous investigations of EDTA complexes have been carried out with solutions maintained at constant ionic strength (often 0.1 m or 0.1 M) with an "inert" supporting electrolyte. To make the best use of our results in combination with those from these earlier investigations, we have calculated partial molar properties at ionic strength 0.1 m from our apparent molar properties and eq 4 by way of the equation

$$\bar{Y} = Y_\phi + I(\partial Y_\phi/\partial I) \tag{6}$$

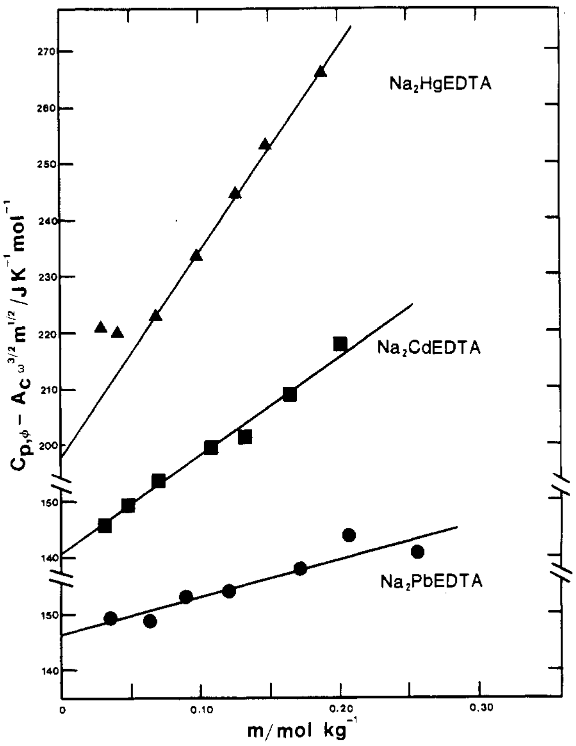

Figure 2. Apparent molar heat capacities minus the Debye–Hückel limiting slopes ($A_C\omega^{3/2}m^{1/2}$) for $Na_2CdEDTA$(aq), $Na_2HgEDTA$(aq), and $Na_2PbEDTA$(aq). Lines are least-squares fits of eq 4.

Table IV. Conventional Partial Molar Properties for Ions at I = 0 (°) and I = 0.1 (†)[a]

ion	$\bar{C}_{p,2}°$, J K^{-1} mol^{-1}	$\bar{C}_{p,2}^{\dagger}$, J K^{-1} mol^{-1}	$\bar{V}_2°$, cm^3 mol^{-1}	$\bar{V}_2^{\dagger}$, cm^3 mol^{-1}
H^+	0	0	0	0
Na^+	42.8	46.2	-1.21	-1.08
Cl^-	-127.2	-113.7	17.89	18.55
ClO_4^-	-25.5	-9.9	43.99	44.64
Ca^{2+}	-25.8	-19.5	-17.2	-16.0
Cd^{2+}	-6.4	-4.1	-14.2	-13.6
Hg^{2+}	-16.3	-3.4	-14.1	-13.2
Pb^{2+}	-56.0	-46.6	-17.7	-16.9
H_2EDTA^{2-}	83.2	129.4	156.73	159.11
$CaEDTA^{2-}$	95.4	143.2	158.51	161.08
$CdEDTA^{2-}$	57.7	109.1	164.02	167.70
$HgEDTA^{2-}$	115.1	179.0	168.24	171.14
$PbEDTA^{2-}$	62.4	107.7	177.50	180.08

[a] Values for $CdEDTA^{2-}$, $HgEDTA^{2-}$, and $PbEDTA^{2-}$ are from this work, while sources for the other ions are discussed in the text.

Results of these calculations are given in Table III.

Subsequent calculations in this paper require partial molar properties for $Na_2CdEDTA$, $Na_2HgEDTA$, and $Na_2PbEDTA$ listed in Table III as well as values for several other species. It is convenient to do all of these calculations with conventional standard-state properties for ions based on $Y_\phi°(H^+, aq) \equiv 0$. Table IV lists these conventional standard-state partial molar volumes and heat capacities (I = 0 and I = 0.1 m) for all of the ions of present interest. We have denoted the thermodynamic quantities that pertain to an ionic strength of 0.1 m (or M) by a superscript †. Values for the volumes and heat capacities of $CdEDTA^{2-}$(aq),

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[18] Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* **1984**, *29*, 81.

Table V. Selected Thermodynamic Properties at $I = 0.1$ for Heavy Metal Ion Reactions with $H_2EDTA^{2-}(aq)$ as $M^{2+}(aq) + H_2EDTA^{2-}(aq) = 2H^+(aq) + M(EDTA)^{2-}(aq)$[a]

$M^{2+}(aq)$	$\log K^\dagger$	$\Delta H^\dagger$, kJ mol^{-1}	$\Delta S^\dagger$, J K^{-1} mol^{-1}	$\Delta \bar{C}_p{}^\dagger$, J K^{-1} mol^{-1}	$\Delta \bar{V}^\dagger$, cm^3 mol^{-1}
Ca^{2+}	−5.78	15.3	−59.4	33.3	18.0
Cd^{2+}	−0.03	3.0	9.5	−16.2	22.2
Hg^{2+}	5.11	−36.6	−24.9	53.0	25.2
Pb^{2+}	1.49	−11.8	−11.1	24.9	37.9

[a] The values listed above for Ca^{2+} came from Table IV. Other values are discussed in the text.

$HgEDTA^{2-}(aq)$, and $PbEDTa^{2-}(aq)$ were calculated from the results listed in Table II and values for $Na^+(aq)$ listed in Table IV. Values for the cationic species in Table IV were derived from perchlorate results when possible[19,20] and also from other salts.[10,12,14,15,21-24]

Equilibrium constants for the complexation reactions of $H_2EDTA^{2-}(aq)$ with $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ as well as the corresponding enthalpy and entropy changes for these reactions are required in calculations that follow. We have selected equilibrium constants from Martell and Smith[25] at 0.1 M for the complexation reactions of $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ with $EDTA^{4-}(aq)$, which we represent by

$$M^{2+}(aq) + EDTA^{4-}(aq) = M(EDTA)^{2-}(aq) \qquad (7)$$

We have also calculated values for the equilibrium constants associated with the complexation reactions of $H_2EDTA^{2-}(aq)$ with $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ from the data listed by Anderegg[26] for the ionization of $H_2EDTA^{2-}(aq)$ and values from Martell and Smith[25] cited earlier. Reactions of this type are described by

$$M^{2+}(aq) + H_2EDTA^{2-}(aq) = M(EDTA)^{2-}(aq) + 2H^+(aq) \qquad (8)$$

We have calculated $\Delta H^\dagger$ values associated with reaction 8 for $M^{2+}(aq) = Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ from combinations and averages of the available calorimetric data for reactions represented by eq 7 and the enthalpies of ionization of $H_2EDTA^{2-}(aq)$ from Vasil'ev et al.[27]

We have selected enthalpies for reactions of type 7 from Izatt et al.[28] For $Cd^{2+}(aq)$ complexation we have calculated $\Delta H^\dagger = -39.3 \pm 2$ kJ mol^{-1} as an average of results at 25[29-32] and 20 °C,[33,34] after correction of the 20 °C values to 25 °C with our heat capacity values, and the estimated heat capacity change for the ionization of $H_2EDTA^{2-}(aq)$ from Vasil'ev et al.[27] Similar calculations involving $Hg^{2+}(aq)$[30,32,33,35] and $Pb^{2+}(aq)$[29,31-34] have led to the values $\Delta H^\dagger = -77.6 \pm 2$ and -57.6 ± 1 kJ mol^{-1}, respectively. We have combined these values with enthalpies of ionization for $H_2EDTA^{2-}(aq)$ from Vasil'ev et al.[27] to obtain the values listed in Table V. We have also calculated the entropy changes associated with reactions represented by eq 8 with the relationship $-RT \ln K^\dagger = \Delta H^\dagger - T\Delta S^\dagger$ and have listed these results in Table V. The $\Delta C_p{}^\dagger$ and $\Delta V^\dagger$ values listed in Table V were calculated from the results given in Table IV.

Table VI. Calculated Equilibrium Constants for the Reaction $M^{2+}(aq) + CaEDTA^{2-}(aq) = M(EDTA)^{2-}(aq) + Ca^{2+}(aq)$

t, °C	$\log K^\dagger$ Cd^{2+}	$\log K^\dagger$ Hg^{2+}	$\log K^\dagger$ Pb^{2+}
0	5.94	11.73	7.70
20	5.79	11.05	7.35
25	5.75	10.89	7.27
37	5.66	10.54	7.09
50	5.58	10.19	6.90
75	5.41	9.60	6.58
100	5.26	9.09	6.31
125	5.11	8.65	6.06
150	4.97	8.26	5.84
175	4.84	7.92	5.65
200	4.71	7.62	5.47
250	4.48	7.11	5.03

Equilibrium Calculations

As discussed previously, there are data available for the equilibrium constants and enthalpies associated with complexation of $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ with $EDTA^{4-}(aq)$ at or near 25 °C. These data can be used to calculate equilibrium constants over ranges of temperature by using the van't Hoff equation and the Kirchoff equation:

$$(\partial \ln K/\partial T)_p = \Delta H^\circ/RT^2 \qquad (9)$$

$$(\partial \Delta H^\circ/\partial T)_p = \Delta C_p{}^\circ \qquad (10)$$

Partial molar volumes can be used to calculate equilibrium constants at elevated pressures by way of the equation

$$(\partial \ln K/\partial p)_T = -\Delta V^\circ/RT \qquad (11)$$

Combination and integration of eq 9–11 with ΔC_p and ΔV taken to be independent of temperature and pressure leads to

$$\ln K_T{}^\dagger = \ln K_{298}{}^\dagger - (\Delta H_{298}{}^\dagger/R)[(1/T) - (1/298.15)] + (\Delta C_p{}^\dagger/R)[\ln (T/298.15) + (298.15/T) - 1] - (\Delta V^\dagger/RT)(p - 1) \qquad (12)$$

Equation 12 is expected[36,37] to be accurate over wide ranges of temperature and pressure for isocoulombic (same number and charge types of ions on both sides of reaction equation) reactions.

Most applications of EDTA involve the use of Na_2H_2EDTA adjusted to a pH value specific to each application. We have therefore chosen to write the equations for reactions of various metal ions with $H_2EDTA^{2-}(aq)$ as in eq 8. Our previous measurements of the heat capacity and volume for $H_2EDTA^{2-}(aq)$[10] facilitate such calculations.

Medicinal and many other uses of EDTA that require limitation of the harsh sequestering ability of the uncomplexed salt use the calcium or zinc complex. We have therefore chosen to write

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equations for the exchange reactions with $CaEDTA^{2-}(aq)$

$$M^{2+}(aq) + CaEDTA^{2-}(aq) = M(EDTA)^{2-}(aq) + Ca^{2+}(aq) \quad (13)$$

Because the reactions represented by eq 13 are isocoulombic, we have a favorable case for extrapolation to high temperatures and/or pressures. Equilibrium data for these exchange reactions permit useful comparisons of the stabilities of the $M(EDTA)^{2-}(aq)$ ions relative to that of $CaEDTA^{2-}(aq)$. We have calculated equilibrium constants from the data listed in Table V using eq 12. We have used water saturation pressures above 100 °C as listed by Haar et al.[38] The results of these calculations are given in Table VI.

Discussion

In our earlier studies[10,11] we plotted the residual heat capacity against residual volume after subtraction of the Born (electrostriction) terms. It was found that all of the metal ion–EDTA complexes were packed into small groupings consistent with their coordination numbers and the effects of ligand field stabilization.[10] The residual or nonelectrostriction component is a large factor in determining the thermodynamic properties of such ions. Here we attempt to make some generalizations concerning these properties.

Spectroscopic studies[39] have shown that the structures of many aqueous EDTA complexes are similar to those in the solid state. Aqueous EDTA complexes of many cations do not have the most common six-coordinate geometry of solid-state EDTA complexes. Instead, one carboxylate of an EDTA molecule is detached from the metal ion, which usually results in coordination by a molecule of water. The resulting "quinquedentate" structure is common among many EDTA complexes. We attribute many of the differences in the thermodynamic properties of EDTA complex ions to the relative distribution of quinquedentate and hexadentate structures.[10,40] Our measured standard-state volumes (present work and ref 10 and 11) for the complexes of EDTA with divalent Cd, Hg, Mn, Co, Ni, Cu, Zn, and Sr are all consistent with the suggestion that these complexes are mixtures of quinquedentate and hexadentate structures. This is supported by spectra for several of these complexes in solution.[41]

The fact that our measured volume of the lead EDTA complex is significantly larger than those for the above-mentioned ions is not simply due to the "large" size of Pb^{2+} since the radius of this ion is about 0.1 Å less than the radius of Ba^{2+} (and the volume of the complex ion is about 13 $cm^3\ mol^{-1}$ larger[11]). It has been suggested[39] that the nonbonding s electrons of Pb^{2+} may influence the stereochemistry of this ion in solution. The observed eight-coordinate structure in the solid state[42] is attributed to the formation of dimeric lead–EDTA units in which the seventh coordination site involves a water molecule and the eighth involves a neighboring EDTA molecule. This result along with our present results suggests that the lead ion associated with EDTA prefers a large coordination number involving EDTA and two water molecules, which leads to a substantially larger total partial molar volume than that of other complexes, including those known to form seven-coordinate structures.[10,40]

The standard-state heat capacities are all influenced by the same factors as the standard-state volumes, with additional contributions from relaxation effects due to the change in the distribution of structures with changes in temperature, as discussed by Ots.[43] It is evident that the standard-state volumes and heat capacities are not sensitive to direct size–charge effects of the metal cation but rather to induced structural and coordinational changes of the EDTA molecule.

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Registry No. $Na_2CdEDTA$, 35803-35-1; $Na_2HgEDTA$, 14689-27-1; $Na_2PbEDTA$, 21135-97-7; Cd, 7440-43-9; Hg, 7439-97-6; Pb, 7439-92-1; Ca, 7440-70-2.

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