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Complexes of Tri- and Tetra-Protonated Forms of 1,4,8,12-Tetraazacyclopentadecane with Chloride, Nitrate, Iodate, and Sulfate Ions in Aqueous Media: II. Analysis of the Underlying Experimental and Theoretical Assumptions

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Abstract. In a previous paper [1] the complexation behavior of 1,4,8,12-tetraazacyclopentadecane with various anions was studied. This analysis depended on various assumptions involving the accuracy and the interpretation of the experimental data. In this paper these assumptions are examined using pH potentiometry, ^{13}C NMR, and conductometric techniques. The validity of each of the assumptions was confirmed.

Key words. Tetraazacyclopentadecane, macrocyclic polyamine, anion complexation.

1. Introduction

In the previous paper we analyzed the complexation behavior of the tetra- and tri-protonated species of 1,4,8,12-teraazacyclopentadecane (H_4L^{4+} and H_3L^{3+}) with Cl^-, NO_3^-, IO_3^-, and SO_4^{2-} [1]. We found 1 : 1 complexes of H_4L^{4+} with each of these four anions. Both IO_3^- and SO_4^{2-} formed 2 : 1 complexes with the H_4L^{4+} species, but not with the H_3L^{3+} species. These results rely on four crucial assumptions concerning the pH potentiometric data: (1) the measured pH values may be accurately interpreted in terms of $[H^+]$ under the varying conditions of the present experiments; (2) H_2L^{2+} forms no complexes with anions present in the solutions; (3) protonated L species do not form complexes with iodide ions; and (4) protonated L species do not form complexes involving two different types of anions. This paper describes the experimental and calculational procedures used to justify these assumptions.

2. Materials and Experimental Methods

2.1. MATERIALS

All chemicals were reagent grade. We tested KI, KCl, K_2SO_4, KNO_3, $NaIO_3$, and NaCl solutions for the presence of possible trace acidic or basic impurities by a

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procedure in which the pH of the various electrolyte solutions is monitored as very small amounts of HCl or NaOH are added. The solutions were nitrogen-scrubbed and had an ionic strength of 0.5 M. The concentration of impurities did not exceed 0.01 mF in any of the solutions.

1,4,8,12-Tetraazacyclopentadecane samples were obtained from Strem Chemicals Inc. and were used without further purification. Stock solutions of the amine were analyzed by pH potentiometric titration with HCl to the sharp $a = 2$ mol HCl/mol L endpoint. Endpoint volumes were reproducible to better than $\pm 0.5\%$. L buffer solutions were prepared by the addition of suitable amounts of HCl to portions of the L stock solution.

2.2. pH POTENTIOMETRIC MEASUREMENTS

All pH measurements were made with a Beckman Model 71 pH meter equipped with conventional glass and calomel reference electrodes. These measurements were independent of the particular electrode used. The meter was standardized at each temperature with solutions ranging from 1.00 mF to 5.00 mF HCl. The ionic strength of each solution was adjusted to its appropriate value with KCl or NaCl depending upon whether the experiment was to be performed in a potassium or a sodium salt medium.

Particular care was taken to insure thermal and chemical equilibrium. Electrodes were immersed in the solutions for at least $\frac{1}{2}$ hour before each titration and for at least 10 minutes before each pH measurement. The various calibration experiments used in this study are described in more detail in a later section.

2.3. ^{13}C NMR MEASUREMENTS

^{13}C proton decoupled NMR spectra were obtained with a JEOL FX-90Q Nuclear Magnetic Resonance Spectrometer. The concentration of L in each sample solution was ~ 0.03 F L with ionic strength 0.5 M in either KI, KCl, or K_2SO_4. An equimolar KCl and KIO_3 mixture was used to adjust the ionic strength for the iodate complexation studies. The v/v concentration of each solution in D_2O was 10%. L mixtures were titrated with 0.50 F HCl, also 10% in D_2O, in a 10 mm sample tube maintained near 30°C.

Data acquisition typically consisted of 1200 scans, with sweepwidth of 5000 Hz (~ 200 ppm). The spectrometer was calibrated before each experiment by measuring the single carbon resonance for portions of a stock solution containing d_6-DMSO in 10% D_2O in the same sample tube that would later be used for the experimental titration. This resonance line was set to 39.5 ppm (relative to tetramethylsilane) and was used as an external reference.

2.4. CONDUCTANCE MEASUREMENTS

Measurements of the electrolytic conductance of L solutions during titration with H_2SO_4 at 25.0 ± 0.1°C was measured with a Leeds and Northrup Model 4959 conductance bridge equipped with a glass dip-type conductance cell.

3. pH Calibration Experiments

The methods used here rely on extremely accurate and precise measurements of pH. For example, some of the complexation experiments with nitrate involved differences of only about 0.03 pH units. In addition, we required *a priori* estimates of the uncertainty in the pH measurements for the nonlinear regression analysis. Consequently, it was important to assess the response of the pH meter under the present experimental conditions.

There are at least two possible sources of error in our measurements of pH. First, the solutions used for standardizing the pH meter were adjusted to the appropriate ionic strength with chloride salts whereas other ionic species were used in the experiments. For example, an HCl, KCl mixture was used to standardize the meter for a complexation study in which the ionic strength of the L solutions was adjusted with KI. Minor changes in specific activity effects or variations in the junction potential at the solution/reference electrode interface might have led to errors in the pH measurements. Therefore, we performed experiments in which we followed the pH of a 0.50 F KI or KCl solution containing 1.00 to 10.0 mF HCl during addition of portions of 0.50 F KCl or KNO_3 solutions made up with the same concentration of HCl. The additions were continued until solution volumes had doubled. In each case the pH values were essentially constant with rms scatter of ± 0.001 pH unit or less.

The iodate complexation studies involved the addition of $NaIO_3$ to L buffers in NaCl media and employed HCl, NaCl for meter calibration. Because the calibrating solution and measurement solutions were similarly constituted, it seemed unnecessary to perform experiments of the type described above. However, it seems noteworthy that the NaCl standardization differed significantly from the KCl standard. That is, pH readings of 1.00 mF HCl in 0.50 F NaCl and 1.00 mF in 0.50 mF KCl differed by approximately 0.03 pH units. At the same time, pK_1 and pK_2 estimates from NaCl experiments essentially matched those from KCl experiments. We ascribe this behavior to the significant difference between the ionic mobilities of Na^+ and K^+ and the consequent difference between the liquid junction potentials at the reference electrode/solution interface.

A second possible source of error in the pH measurements is the existence of nonlinearities in the response of the glass electrode in the mixed electrolyte media of these experiments. A series of calibrating experiments was performed in which 0.50 F KI, KCl, or KNO_3 were added to a 0.50 F KCl solution containing 0.50 mF to 20.0 mF HCl. In each experiment the neutral salt solution was added in about six portions until the volume approximately doubled. The pH varied by about 0.3 units in each experiment. Calculated pH values were based on the known quantity of HCl in each mixture. Calculated and measured values always agreed to within ± 0.003 pH units and the deviations appeared to be randomly scattered. The rms deviations were 0.0015 pH units or less.

Several of the calibration experiments were repeated with solutions with an ionic strength of 0.25 M. The results were essentially identical to those performed at the higher ionic strength.

Finally we performed a series of experiments in which electrodes calibrated with a solution 10.0 mF HCl and 0.50 F KCl were used to measure pH values of a sequence of successively more dilute solutions of HCl in 0.50 F KCl. The concentrations of HCl ranged from 10.0 F to 0.500 F. The response of the electrode was essentially linear with an rms deviation of approximately 0.002 pH units.

We conclude from these calibration experiments that the variations in electrolyte composition in these experiments do not lead to detectable errors in the pH. The experiments also provide the basis for our estimate of the uncertainty of the pH measurements, namely $\sigma = \pm 0.002$ pH units.

4. ^{13}C NMR Experiments

The analysis of our pH potentiometric data relies on the assumption that the H_4L^{4+} and H_3L^{3+} species form anion complexes while the more basic L species do not. The results support this assumption since the fit of the model to the experimental data was always within the expected error of measurement. However, in light of the unexpected complexation behavior of H_3L^{3+}, it seemed prudent to confirm the assumption by means of a different experimental method. We recorded ^{13}C NMR spectra of 4 solutions of L, each containing approximately 0.03 F of the amine in 10% D_2O. These solutions, each of an ionic strength of 0.5 M, contained either KI, KCl, K_2SO_4, or a mixture of 0.25 F KCl and 0.25 F KIO_3. The four spectra were essentially identical, each consisting of six resonances corresponding to the six nonequivalent carbon atoms of the macrocyclic amine.

Each L mixture was then titrated with a 0.50 F HCl solution that was also made up in 10% D_2O. The chemical shift versus volume data follow a pattern similar to the one illustrated in Figure 1. The downfield direction of all the chemical shift displacements up to $a = 2$ mol HCl/mol L added correspond to carbon atom deshielding. The extent of the displacements vary from one resonance to the next, reflecting differing degrees of interaction with protonated nitrogen sites and probably reflecting conformational and solvation changes in the sequence of protonated L species up to H_2L^{2+}.

Beyond $a = 2$ mol HCl/mol L each of the resonance lines is abruptly displaced in an upfield direction corresponding to carbon atom shielding. This behavior is consistent with anion complexation of the H_3L^{3+} species formed beyond $a = 2$ mol HCl/mol L. One apparent exception is the titration in KI medium where the chemical shifts at $a = 3$ mol HCl/mol L are slightly downfield of those at $a = 2$ mol HCl/mol L. We interpret this result as indicating a smaller extent of anion complexation of H_3L^{3+} in the mixed iodide/chloride medium than in the other solutions. Since, as we shall show later, iodide ions do not form complexes with protonated L species, the observed behavior of chemical shift displacements in the mixed iodide/chloride solution is consistent with formation of a weak H_3LCl^{2+} complex.

Figure 2 compares the chemical shift due to a single carbon atom of L during HCl titration in the various salt media. The ^{13}C NMR spectra of L solutions in KI, KCl, K_2SO_4, or mixed KCl, KIO_3 electrolytes are identical to within ± 0.05 ppm during titration with HCl up to $a = 2$ mol HCl/mol L added. We conclude that the L, HL^+, and H_2L^{2+} species present in these mixtures do not form detectable anion complexes.

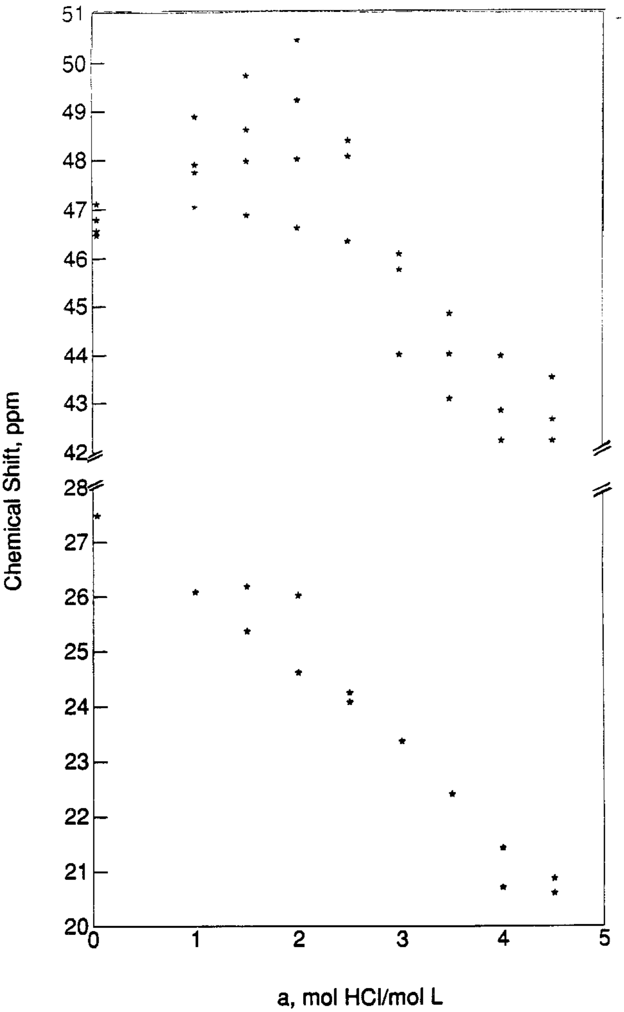

Fig. 1. ^{13}C NMR chemical shifts of 0.05 F L in 0.5 F KCl (10% v/v D_2O) during titration with 0.5 F HCl (10% v/v D_2O). Chemical shifts are in ppm downfield from TMS.

5. Dependence of Acidity and Complexation Constants on Ionic Strength

In deriving the set of model equations we assumed that the L species do not form complexes with iodide ions. Recall that KI was used as a background electrolyte in the chloride, nitrate, and sulfate complexation studies. In order to test this assumption, we examined the dependence of pK_1 and pK_2 on ionic strength in order to confirm that iodide ions represent non-complexing anions in solutions of protonated L species.

Values of pK_1 and pK_2 as a function of ionic strength are obtained as by-products of the pH potentiometric experiments. Average values of these constants at 25°C appear in Table 1. Each entry represents the results of several sets of data. Some of

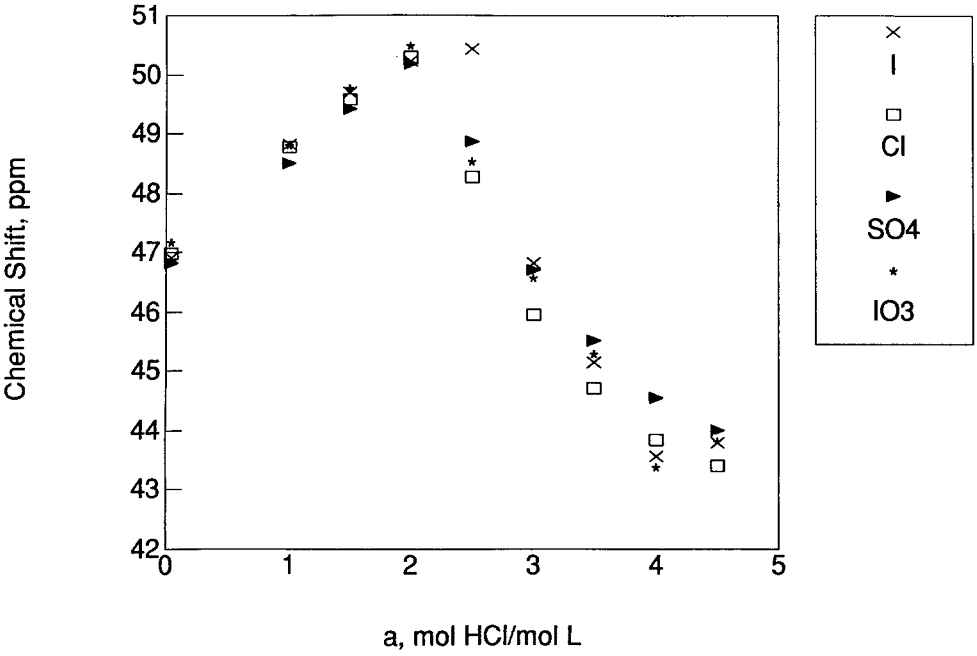

Fig. 2. ^{13}C NMR chemical shifts for the extreme downfield line of L during titrations with HCl. Initial L concentrations were 0.05 F in ionic strength 0.5 M electrolyte media (10% v/v D_2O).

Table I. Ionic strength dependent pK_1 and pK_2 values for H_4L^{4+} at 25 °C.[a]

pK_1	pK_2	I, M
3.331	5.011	0.12
3.482	5.114	0.25
3.582	5.184	0.37
3.648	5.229	0.50

[a] Entries represent average values taken from several experiments. Standard deviations of replicate results were ±0.005 pH units or less.

this data was obtained using different stock solutions of L buffer mixtures. Reproducibility was typically ±0.005 pH units. Individual results were generally within a range of ±0.01 pK units; the greatest variation between replicates was less than 0.03 pK units.

We first note that the entries at an ionic strength $I = 0.5$ M are in approximate agreement with the previously determined estimates of $pK_1 = 3.60$ and $pK_2 = 5.28$ in 0.50 F KNO_3[2]. Appropriate adjustment of the earlier values to take account of the formation of the complexes $H_4L(NO_3)^{3+}$ and $H_3L(NO_3)^{2+}$ leads to $pK_1 = 3.58$

and $pK_2 = 5.22$ compared with the present values of 3.65 and 5.23, respectively. The pK_2 values are in good agreement. The difference in the pK_1s is attributable to experimental uncertainties, and is not significant in this work.

Both pK_1 and pK_2 are significantly dependent on the ionic strength of the solution. pK_1 and pK_2 vary by about 0.32 and 0.22 pK units, respectively, between $I = 0.12$ M and 0.50 M. This variation might be due to changes in ionic species activity coefficients, or to complexation with the iodide ions used to make up the ionic strength. (We exclude the possibility of interactions of the protonated L species with potassium or sodium ions.)

The 'concentration' pK values in Table I are conditional constants; their values pertain to concentrated solutions where the ionic activity coefficients differ significantly from unity. These constants, which we denote here by pK_1^{I} and pK_2^{I}, are related to the thermodynamic pK^0 values by

$$pK_1^{\mathrm{I}} = pK_1^0 + \log \gamma_{\mathrm{H}}^{\mathrm{I}} - \log(\gamma_4/\gamma_2)^{\mathrm{I}} \qquad (1)$$

and

$$pK_2^{\mathrm{I}} = pK_2^0 + \log \gamma_{\mathrm{H}}^{\mathrm{I}} - \log(\gamma_3/\gamma_2)^{\mathrm{I}} \qquad (1a)$$

where γ_{H} is the ionic activity coefficient of H^+ in the concentrated electrolyte of ionic strength I and γ_n is the ionic activity coefficient of the species n^+.

In principle, these equations determine the complexation behavior of L species with iodide ions. pK values for L are determined for a set of solutions of KI of differing concentrations and thus, ionic strengths. Values of the γs are then obtained at each ionic strength. If the resulting values of pK^0 vary systematically with ionic strength, we can conclude that iodide complexes with L; if there is no variation, no appreciable complexation occurs.

Unfortunately, we cannot calculate theoretically ionic activity coefficients for highly charged L species at the relatively high ionic strengths employed here. In previous work [3], we obtained the following empirical formulas, which we called correlations, for γ_4/γ_3 and γ_3/γ_2 at an ionic strength I in terms of their values at a 'standard' ionic strength 0.22 M:

$$\log(\gamma_4/\gamma_3)^{\mathrm{I}} - \log(\gamma_4/\gamma_3)^{0.22} = \Delta \log(\gamma_4/\gamma_3) = 0.962 - 3.46 I^{1/2} + 375 I - 1.591 I^{3/2} \qquad (2)$$

and

$$\log(\gamma_3/\gamma_2)^{\mathrm{I}} - \log(\gamma_3/\gamma_2)^{0.22} = \Delta \log(\gamma_3/\gamma_2) = 0.924 - 4.11 I^{1/2} + 6.11 I - 3.31 I^{3/2} \qquad (2a)$$

These correlations were derived from pH potentiometric measurements with buffer mixtures of a model compound, tetrakis(aminomethyl)methane, with I varying from 0.11 to 0.44 M. Previous work indicates that pK values of this compound are independent of the nature of the electrolyte medium for a variety of 1 : 1 electrolytes [4]. We concluded that the model compound does not form anion complexes, and that the ionic strength dependence of its pK values reflect activity coefficient variations alone. These correlation equations have been successfully employed in describing the behavior of 4^+, 3^+, and 2^+ hexacyclen species.

We now recast the equations for pK_1^{I} and pK_2^{I} into the form:

$$pK_1^{*} = pK_1^{\mathrm{I}} - \Delta \log \gamma_{\mathrm{H}} + \Delta \log(\gamma_4/\gamma_3) \qquad (3)$$

Table II. Ionic strength dependence of H_4L^{4+} acidity constants at 25 °C.

pK_{a1}	I	$\Delta \log \gamma_4/\gamma_3$	$-\Delta \log \gamma_H$	pK_1^{*a}
3.331	0.12	0.147	−0.012	3.47[b]
3.482	0.25	−0.029	0.002	3.46
3.582	0.37	−0.111	0.011	3.48
pK_{a2}	I	$\Delta \log \gamma_3/\gamma_2$	$-\Delta \log \gamma_H$	pK_2^*
5.011	0.12	0.096	−0.011	5.10[b]
5.114	0.25	−0.017	0.002	5.10
5.184	0.37	−0.060	0.011	5.13

[a] pK_1^* and pK_2^* are values adjusted to $I = 0.22$ M. Their values represent the sum of entries in the first, third, and fourth columns.
[b] Uncertainties estimated at ±0.03 pK units.

and

$$pK_2^* = pK_2^I - \Delta \log \gamma_H + \Delta \log(\gamma_3/\gamma_2) \tag{4}$$

where pK_1^* and pK_2^* are the conditional acidity constants at $I = 0.22$ M and pK^I is the conditional constant at some other ionic strength. $\Delta \log(\gamma_3/\gamma_3)$ and $\Delta \log(\gamma_3/\gamma_2)$ are obtained from the empirical correlation formulas. Values for $\Delta \log \gamma_H$, defined as $\log \gamma_H$ (at ionic strength I) $- \log \gamma_H$ (at $I = 0.22$ M) are obtained from an extended form of the Debye–Hückel equation, taking å, the ion size parameter, as 0.9 nm. Calculated pK_1^* and pK_2^* values are listed in Table II. In view of the uncertainties of approximately ±0.03 pK units in these values (based on uncertainties of ±0.01 in pK) and ±2% in both γ_H and activity coefficient ratios γ_4/γ_3 and γ_3/γ_2, the pK^* values are essentially constant and independent of both the ionic strength and the iodide concentration. This behavior indicates that none of the protonated L species present in these solutions forms appreciable concentrations of iodide complexes.

The correlation formulas are empirical and as such rely on a number of assumptions whose validity are difficult to establish. To provide further support for our conclusions we consider the dismutation reaction.

$$H_3L^{3+} + H_3LCl^{2+} = H_4LCl^{3+} + H_2L^{2+} \tag{5}$$

whose thermodynamic equilibrium constant is

$$K^0 = \frac{[H_2L^{2+}][H_4LCl^{3+}]\gamma_2\gamma_3}{[H_3L^{3+}][H_3LCl^{3+}]\gamma_2'\gamma_3'} = K\frac{\gamma_2\gamma_3}{\gamma_2'\gamma_3'} \tag{6}$$

where γ_2, γ_3, γ_2', and γ_3' are ionic activity coefficients of H_2L^{2+}, H_4LCl^{3+}, H_3LCl^{2+}, and H_3L^{3+}, respectively, and K is the concentration product equilibrium constant for reaction (13). Because H_2L^{2+} and H_3LCl^{2+} are similar in constitution and charge, we assume that $\gamma_2 = \gamma_2'$ and $\gamma_3 = \gamma_3'$. Consequently, K is essentially equal to K^0, the thermodynamic equilibrium constant, and should be independent of the ionic strength and iodide concentration. However, if iodide did complex with

H_2L^{2+} and H_3L^{3+}, the value of K or K^0 would vary systematically with the ionic strength or iodide concentration (assuming different concentrations of the complexes).

Values of K are readily calculated from existing equilibrium constant data using

$$\log K = pK_1 + \log K_{4Cl} = pK_2 - \log K_{3Cl} \tag{7}$$

The results of these calculations together with values of K derived from iodate complexation constants are listed in Table III. We also need some estimate of the uncertainties in each value. While precise estimates are difficult to derive, we find that even optimistic error bounds of ±0.01 pK units in acidity constants and ±3% error bounds in complexation constants lead to log K uncertainties of ±0.04, which is larger than the observed variation in log K. Consequently, we conclude that protonated L species do not significantly interact with iodide ions and that the equilibrium constants listed in Table I of the previous paper are the formation constants of solvated H_4L^{4+} and H_3L^{3+} species with various anions. Similarly, the acidity constants in Table III are acid dissociation constants for solvated species uncomplicated by complexation interactions.

6. Mixed Complex Formation

We now consider the possible formation of mixed complexes $H_4LCl(IO_3)^{2+}$ and $H_4LCl(SO_4)^{+}$. In the complexation studies involving iodate, Cl^- as NaCl, was employed as the background electrolyte. Analysis of the model indicates that the formation of $H_4LCl(IO_3)^{2+}$ cannot be distinguished from that of $H_4L(IO_3)_2^{2+}$ by experiments made at constant ionic strength. This is a consequence of the fact that the ionic strength is approximately equal to $[Cl^-] + [IO_3^-]$, and that both $[Cl^-]$ and $[IO_3^-]$ are much larger than the analytical concentration of L.

The two complexes can be distinguished by comparing complexation constants obtained at different ionic strengths and chloride concentrations. This procedure is

Table III. Ionic strength dependence of the equilibrium constant for the reactions $H_3L^{3+} + H_3LCl^{2+} = H_4LCl^{3+} + H_2L^{2+}$ and $H_3L^{3+} + H_3L(IO_3)^{2+} = H_4L(IO_3)^{3+} + H_2L^{2+}$.

Reaction: $H_3L^{3+} + H_3LCl^{2+} = H_4LCl^{3+} + H_2L^{2+}$					
Ionic Strength, M	pK_1	log K_{4Cl}	pK_2	log K_{3Cl}	log K[a]
0.12	3.331	0.56	5.011	0.03	−1.15
0.25	3.482	0.40	5.114	−0.05	−1.18
0.37	3.582	0.31	5.184	−0.10	−1.19
0.50	3.648	0.28	5.229	−0.14	−1.16
Reaction: $H_3L^{3+} + H_3L(IO_3)^{2+} = H_4L(IO_3)^{3+} + H_2L^{2+}$					
0.25	3.482	1.59	5.114	0.63	−0.67[a]
0.50	3.648	1.46	5.229	0.56	−0.68

[a] log K values calculated using Equation 7.

nontrivial because the ionic activity coefficients vary with the ionic strength. In the present case, we can estimate this variation by examining the complexation reaction $H_3L^{3+} + IO_3^- = H_3L(IO_3)^{2+}$ and its conditional equilibrium constants at $I = 0.25$ M and $I = 0.50$ M.

The conditional constants differ from the thermodynamic constants by a factor of $\gamma_3\gamma_{IO3}/\gamma_{2+}$ where γ_3 and γ_{2+} are ionic activity coefficients of 3+ and 2+ L species. Data given in Table I indicates that this ratio decreases by a factor of (4.24/3.66 =) 1.16 when the ionic strength increases from 0.25 M to 0.50 M. Conditional equilibrium constants for the stepwise complexation reaction $H_4L(IO_3)^{3+} + IO_3^- = H_4L(IO_3)_2^{2+}$ also differ from the thermodynamic value by an activity coefficient factor $\gamma_3\gamma_{IO3}/\gamma_2$. By assuming similar activity coefficient behavior for like constituted L species ($H_4L(IO_3)^{3+}$ and H_3L^{3+}, for example) we can estimate the activity coefficient variation for the stepwise ternary complexation. In other words, we adjust the observed ionic strength 0.25 M ternary complexation reaction to ionic strength 0.50 M using activity coefficients from a different L complexation reaction.

Using Table I of the previous paper, the stepwise formation constant at $I = 0.25$ M is found to be 4.18. Adjusted to $I = 0.50$ M, this value is 3.6, compared with the observed value of 3.5. Thus, after adjustment for activity effects, the stepwise complexation constant for the ternary complex of iodate with L appears to be independent of the ionic strength and, more significantly, independent of the chloride ion concentration. On the other hand, formation of a mixed complex via the reaction $H_4L(IO_3)^{3+} + Cl^- = H_4LCl(IO_3)^{2+}$ would result in a significant increase of the adjusted complexation constant between $I = 0.25$ M and $I = 0.50$ M. We conclude that the stoichiometry of the ternary iodate/L complex is 1 L : 2 IO_3.

The chloride-sulfate complex can be excluded because the set of model equations which do not include the $H_4LCl(SO_4)^+$ complex provide an excellent fit to the data. Sulphate complexation studies employed H_4L^{4+}/H_3L^{3+} buffers in which the molar ratio of chloride to tetraprotonated L species was about 6:1. The corresponding ratio in the H_3L^{3+}/H_2L^{2+} buffer was about 4:1. The total chloride concentrations of the buffer mixtures varied significantly ($\approx 30\%$) as the sulfate was added. Unlike the situation in the iodate studies, the chloride concentration is not large compared with the H_4L^{4+} concentration, nor is it linearly related to the sulfate concentration. The presence of a mixed $H_4LCl(SO_4)^+$ complex in these solutions would significantly alter the pH vs composition data and would be reflected in unacceptably large χ^2 values. Since χ^2 was not large, we conclude that any possible mixed chloride-sulfate complexes can be ignored.

7. Conductometric Titrations

We performed a number of conductometric titrations of dilute L solutions with a variety of acids in order to gain additional information about the stoichiometry of complexes of various anions with L. The titration of a 0.010 F L solution with 0.10 F H_2SO_4 let to a particularly interesting result. The conductometric curve for this titration is shown in Figure 3.

The initial rising portion of the curve corresponds to stepwise protonation of L to form HL^+ and H_2L^{2+}. The essentially linear increase of volume-corrected conductance, $(V + v)/RV$, where R is the resistance, V is the initial solution volume,

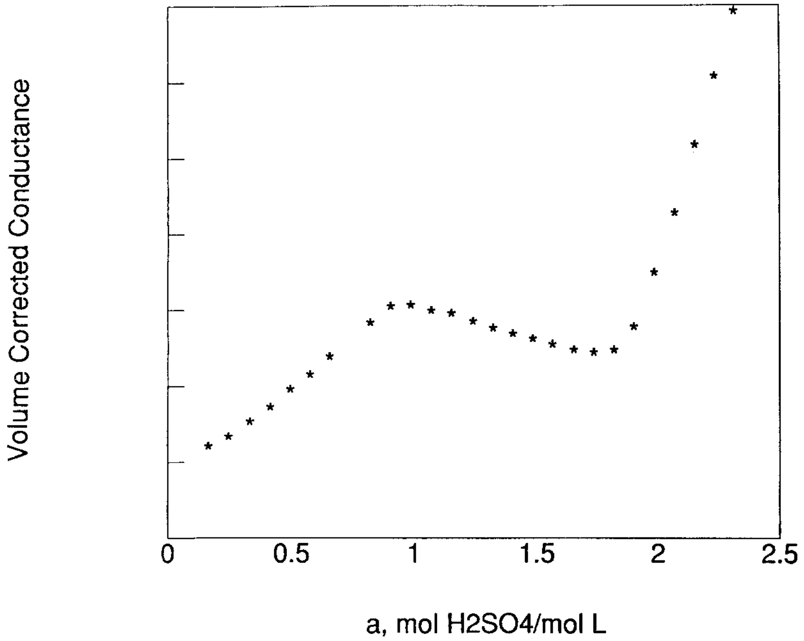

Fig. 3. Conductometric titration of 25 mL of 0.010 F L with 0.100 F H_2SO_4 reagent at 25 °C.

and v is the volume of added titrant, is consistent with the protonation reaction where neither L, HL^+, nor H_2L^{2+} form sulfate complexes. It is worth noting that conductometric titrations of L solutions with HNO_3 and HCl behave identically in this region of the curve and confirm that the L, HL^+, and H_2L^{2+} species do not form complexes with these ions.

As expected, a local maximum in the curve occurs at $a = 1.0$ mol H_2SO_4/mol L; while a local minimum appears near $a = 2.0$ mol H_2SO_4/mol L. The middle region of the curve corresponds to the reaction $H_2SO_4 + H_2L^{2+} = H_4L(SO_4)^{2+}$. The final steeply rising portion of the curve is due to excess H_2SO_4. There is no evidence of the formation of an H_3L^{3+} species.

In order to understand this behavior we examine the reaction $2H_3L^{3+} + SO_4^{2-} = H_2L^{2+} + H_4L(SO_4)^{2+}$. The equilibrium constant for this reaction is

$$K = \frac{\gamma_{SO_4}\gamma_3^2}{\gamma_2^2} K^0 = \frac{[H_2L^{2+}][H_4L(SO_4)^{2+}]}{[H_3L^{3+}]^2[SO_4^{2-}]} \tag{8}$$

where K^0 is the thermodynamic value for the constant. In terms of constants to be listed in the Tables, $K = K_1 K_{4SO4}/K_2$. The value of K at 25 °C and $I = 0.50$ M is about 2.4, indicating that while dilute solutions of H_3L^{3+} and sulfate contain small amounts of H_2L^{2+} and $H_4L(SO_4)^{2+}$, H_3L^{3+} is the dominant solution species. However, the activity coefficient terms in the equilibrium constant expression are strongly dependent on ionic strength; the ratio $\gamma_3^2\gamma_{SO4}/\gamma_2^2$ increases rapidly with decreasing ionic strength. Apparently, the value of the activity coefficient ratio at the low ionic strength prevailing during the second portion of the experiment

(~0.04 M) is more than two orders of magnitude larger than its value at ionic strength 0.50 M solutions, accounting for the unusual behavior.

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