Cryptate Formation in Nonaqueous Solvents: New Aspects in Single-Ion Thermodynamics

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The stability constants (K_s) of cryptate complexes with K^+, Ag^+, and Tl^+ have been determined by potentiometric titration in methanol and in several aprotic, polar solvents at various temperatures. The enthalpies and entropies of complexation have been calculated from the temperature dependence of K_s. By use of the free energies and enthalpies of solvation of the metal ions, the differences between the free energies (enthalpies) of transfer of the cryptate complex and the cryptand in the aprotic solvents with water as reference have been calculated and found to agree to ±0.2 kJ mol^{-1} in free energies and to ±5.4 kJ mol^{-1} in enthalpies. These values offer another method for the estimation of the free energies and enthalpies of solvation of single ions.

Introduction

Macrobicyclic polyethers (cryptands **1–3**) have been syn-
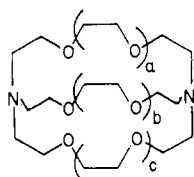
1. $a = 1, b = c = 0$ (2,1,1)
2. $a = b = 1, c = 0$ (2,2,1)
3. $a = b = c = 1$ (2,2,2)

thesized recently by Lehn and co-workers.[2a] These ligands are gaining increasing interest since they form stable complexes (cryptates) with alkali ions. The stability constants are several orders of magnitude larger than the complex formation constants of naturally occurring or synthetic monocyclic ligands with alkali ions.[2,3] In water, the cryptate stability constants and the corresponding thermodynamic properties have been discussed in terms of ion solvation, ligand solvation, and ion–ligand interactions.[4,5]

We have studied the cryptate formation of three different cations (potassium, silver, and thallium) in various polar, aprotic solvents. Using the solvation energy of the cations,[6,7] we have found constant differences between the thermodynamic transfer properties of $Ag(2,2,2)^+$ and $(2,2,2)$ in the aprotic solvents. This allows the prediction of stability constants in polar, aprotic solvents or the calculation of the free energy and enthalpy of transfer of the cations from water to aprotic solvents from simple potentiometric titration of the cations with $(2,2,2)$.

Experimental Section

Cryptands (2,1,1), (2,2,1), and (2,2,2) and $AgNO_3$, KNO_3, and $KClO_4$ were purchased from Merck and used without further purification. $TlClO_4$ was obtained from Tl_2CO_3 and $HClO_4$ by metathesis in water. The precipitated $TlClO_4$ was recrystallized twice and dried under vacuum.

Tetraethylammonium perchlorate (TEAP) (Pfaltz u. Bauer) was recrystallized twice from methanol, washed with ether, and dried under vacuum at 60 °C. Methanol (MeOH) was rectified over magnesium methanolate under an atmosphere of nitrogen. Propylene carbonate (PC), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me$_2$SO) were dried over molecular sieves and distilled under reduced N_2 pressure over a 1-m Vigreux column. Acetonitrile (AN) was purified according to Coetzee's procedure.[8] Hexamethylphosphortriamide (HMPT) was dried over molecular sieves (10 Å) and fractionally distilled from a new batch of 10-Å molecular sieves at 2 torr under nitrogen. The boiling point of the middle portions was 76.8–77.3 °C; the specific conductance κ was 1×10^{-8} Ω^{-1} cm^{-1}. The water content, which was determined by a Karl Fischer titration, was always less than 1×10^{-3} mol kg^{-1}.

Potentiometric experiments were carried out with the equipment shown in Figure 1. The reference electrode used in all titrations was a Ag/Ag$^+$ electrode which was immersed in the same solvent as that under investigation; the two half-cells were separated by a salt bridge containing 0.1 M TEAP in the same solvent.

The stability constants of silver cryptate were determined by simple potentiometric titration of a Ag$^+$ solution with a solution of the cryptand (Cry). The ionic strength was kept constant at $I = 0.1$ M by addition of TEAP. The concentration of the free silver ion was measured with a silver electrode (Metrohm EA 242), potentials being measured with a diode-modulating impedance transformer (Knick, Type 85). If the same experimental procedure is used to titrate a solution containing Ag$^+$ and another cation M$^+$, then the stablity constant for the other cation can be obtained from the measurable concentration of the free silver ion and the known equilibrium constant of the silver complex. The silver electrode in this system only functions as an auxiliary electrode to monitor the competitive complexation reactions of the two cations:

$$Ag^+ + Cry \xrightleftharpoons{K_{Ag}} Ag\,Cry^+ \qquad (1)$$

$$M^+ + Cry \xrightleftharpoons{K_M} M\,Cry^+ \qquad (2)$$
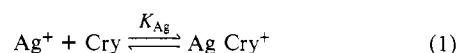
The results were checked by titrating Tl$^+$ (in DMF and Me$_2$SO) and K$^+$ (in AN) directly with cryptand (2,2,2). The detecting electrode for Tl$^+$ was a thallium amalgam electrode; for K$^+$, a potassium-sensitive electrode (Ingold PK-201-K7) was used. The results obtained by the different procedures agreed within experimental error.

All experiments were carried out under an atmosphere of nitrogen. The studies were performed in a temperature range of 20–25 °C.

Results

The complexation of a metal cation (M$^+$) by a cryptand (Cry) in a solvent (S) is given by the equation

$$M^+ + Cry \xrightleftharpoons{K_s} M\,Cry^+$$
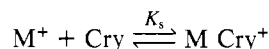
where K_s is the concentration stability constant. Table I lists the values of log K_s and the free energies of complexation (ΔG) of the silver ion with three different cryptands [(2,1,1), (2,2,1), (2,2,2)] in water and various nonaqueous solvents. The corresponding enthalpies of complexation (ΔH) have been calculated by a least-squares fit of log K_s plotted vs. $1/T$ (eq 3) and are also given in Table I. log K_s and the thermodynamic

$$\Delta H = -2.303R\mathrm{d}(\log K_s)/\mathrm{d}(1/T) \qquad (3)$$

parameters ΔG, ΔH, and $T\Delta S$ for the complexation of K$^+$ and Tl$^+$ by cryptand (2,2,2) have been determined as well (Table II).

Discussion

The cations K$^+$, Tl$^+$, and Ag$^+$ have been chosen for the study of complex formation with cryptands to compare three different types of cations. In terms of Pearson's HSAB principle,[9] the potassium ion is a hard cation and the thallium ion is a
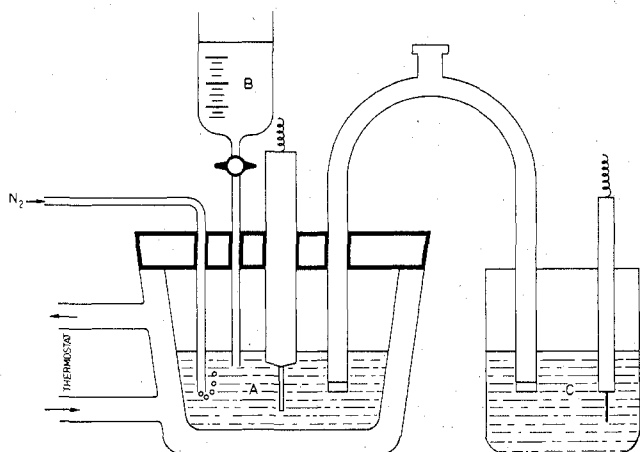
Figure 1. Equipment for potentiometric determination of stability constants of metal ion cryptates: (A) 10^{-3} M AgNO$_3$, 10^{-1} M Et$_4$NClO$_4$; (B) 10^{-2} M cryptand, 10^{-2} M MClO$_4$, 10^{-1} M Et$_4$NClO$_4$; (C) 10^{-2} M AgNO$_3$, 10^{-1} M Et$_4$NClO$_4$).

Table I. Stability Constants (log K_s), Free Energies ΔG (kJ mol^{-1}), Enthalpies ΔH (kJ mol^{-1}), and Entropies ΔS (J deg^{-1} mol^{-1}) of Ag$^+$ Complexation by Cryptands at 25 °C[a]

Cry	solvent	log K_s	$-\Delta G$	$-\Delta H$	ΔS
(2,1,1)	H$_2$O[b]	11.13	63.6	71.5	−25
(2,1,1)	MeOH[b]	10.61	60.7	102.9	−142
(2,1,1)	DMF	8.62	49.1	98.5	−165
(2,2,1)	H$_2$O[b]	11.82	67.5	51.0	54
(2,2,1)	MeOH[b]	14.64	83.6	80.8	8
(2,2,1)	DMF	12.43	70.9	88.7	−14
(2,2,2)	H$_2$O[c]	9.6	54.8	53.6	5
(2,2,2)	MeOH[b]	12.20	69.7	85.8	−54
(2,2,2)	DMF	10.03	57.2	56.4	−3
(2,2,2)	Me$_2$SO	7.15	40.8	47.8	−24
(2,2,2)	PC	16.29	94.5	99.5	−17
(2,2,2)	AN	8.92	51.0	54.4	−11
(2,2,2)	HMPT	6.3	35.8		

[a] Precision: log K_s, ±0.03; ΔG, ±0.2 kJ mol^{-1}; ΔH, ±3 kJ mol^{-1}; ΔS, ±10 J deg^{-1} mol^{-1}. Only in HMPT is the error three times as large. Abbreviations: MeOH, methanol; DMF, *N*,*N*-dimethylformamide; Me$_2$SO, dimethyl sulfoxide; PC, propylene carbonate; AN, acetonitrile; HMPT, hexamethylphosphortriamide. [b] B. G. Cox, H. Schneider, H. Schulz, and J. Stroka, in preparation. [c] G. Anderegg, *Helv. Chim. Acta*, **58**, 1218 (1975).

Table II. Stability Constants (log K_s), Free Energies ΔG (kJ mol^{-1}), Enthalpies ΔH (kJ mol^{-1}), and Entropies ΔS (J deg^{-1} mol^{-1}) of K$^+$ and Tl$^+$ Complexation by (2,2,2) at 25 °C[a]

ion	solvent	log K_s	$-\Delta G$	$-\Delta H$	ΔS
K$^+$	H$_2$O[b]	5.58	31.8	46.0	48
K$^+$	H$_2$O	5.4[c]	30.1[d]	47.7[d]	59[d]
K$^+$	DMF	7.89	45.0	53.0	−27
K$^+$	Me$_2$SO	6.92	39.5	60.8	−71
K$^+$	PC	11.10	63.2	69.2	−20
K$^+$	AN	10.71	61.1	74.1	−44
Tl$^+$	H$_2$O[b]	6.5	37.0	55.2	−62
Tl$^+$	DMF	7.7	43.9	66.1	−75
Tl$^+$	Me$_2$SO	6.3	35.6		
Tl$^+$	PC	11.78	68.2		
Tl$^+$	HMPT	5.32	30.4		

[a] Precision: log K_s, ±0.04; ΔG, ±0.2 kJ mol^{-1}; ΔH, ±4 kJ mol^{-1}; ΔS, ±15 J deg^{-1} mol^{-1}. Only in HMPT is the error twice as large. For abbreviations see Table I, footnote *a*. [b] G. Anderegg, *Helv. Chim. Acta*, **58**, 1218 (1975). [c] J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975). [d] E. Kauffmann, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **59**, 1099 (1976).

Figure 2. Dependence of (a) free energies of Ag(2,2,2)$^+$ formation on free energies of transfer for Ag$^+$ from water and (b) enthalpies of Ag(2,2,2)$^+$ formation on enthalpies of transfer for Ag$^+$ from water at 25 °C.
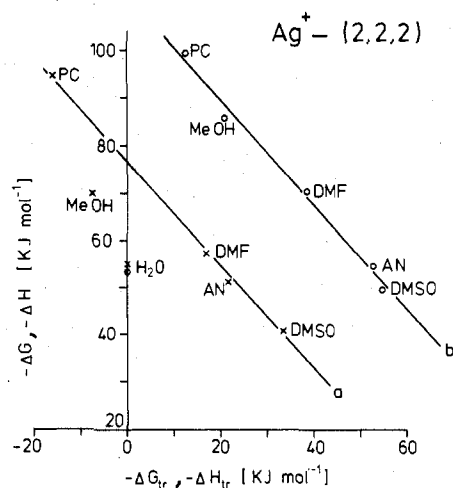
soft cation which interact mainly electrostatically with the oxygen and nitrogen atoms of the cryptands. The silver ion will form partially covalent bonds with the cryptands since this ion is known to form very stable complexes with nitrogen-containing ligands. The stability constants of the Ag$^+$ cryptate complexes are therefore 10^2–10^4 times larger than those of K$^+$ and Tl$^+$. The aprotic solvents used cover a relatively wide range of solvent properties: Me$_2$SO is an aprotic solvent with intermolecular association,[10] while PC is recommended as a reference solvent[11] which shows relatively mild, unspecific interactions with a solute. The magnitude of the stability constants (eq 1) depends on the solvation of the cation, of the cryptand, and of the complex.

The solvation energy of cryptate complexes is made up of two contributions: (1) the electrostatic interaction between the encased cation and the solvent and (2) the solvation of the organic surface of the cryptates. As long as the diameter of the bare ion is comparable with the cavity size of the cryptand, the ion will be shielded from the solvent by a cryptand shell whose thickness considerably reduces the electrostatic, ion–solvent interaction. As for the cryptand (2,2,2), the thickness of the ligand layer has been estimated at 4.1 Å. In general, the second contribution does not change very much from solvent to solvent when compared with the ionic solvation

energy. It is only in water and other protic solvents that a special type of solvation (in water it is the hydration of the second kind[12,13]) may cause deviations from simple behavior.

The solvation energy of the uncharged cryptand will also be much smaller than that of the ions. The free energy ΔG (or enthalpy ΔH) of complexation of Ag$^+$ by (2,2,2) is therefore plotted vs. the free energy (enthalpy) of transfer ΔG_{tr} (ΔH_{tr}) of Ag$^+$ with water as a reference solvent (Figure 2). There is a good linear dependence between ΔG and ΔG_{tr} for aprotic solvents and between ΔH and ΔH_{tr} for all solvents used except water. In the case of K$^+$ the straight lines are displaced but parallel.

When water is used as a reference, the following relationship between the stability constants and free energies of transfer from water (W) to a nonaqueous solvent (S) holds:

$$\Delta G_{tr} = -2.303RT \log [K(S)/K(W)]$$
$$= \Delta G_{tr}(MCry^+) - \Delta G_{tr}(M^+) - \Delta G_{tr}(Cry) \quad (4)$$

The difference between the free energies of transfer of the cryptate and the cryptand is given by eq 5 and the difference

$$\Delta G_{tr}(MCry^+) - \Delta G_{tr}(Cry) = \Delta G_{tr} + \Delta G_{tr}(M^+) \quad (5)$$

between the enthalpies by eq 6. In Table III the free energies

$$\Delta H_{tr}(MCry^+) - \Delta H_{tr}(Cry) = \Delta H_{tr} + \Delta H_{tr}(M^+) \quad (6)$$

Table III. Free Energies and Enthalpies of Transfer from Water to Nonaqueous Solvents at 25 °C[a]

M^+	solvent	ΔG_{tr} (M^+)[b]	ΔH_{tr} (M^+)[b]	$\Delta\Delta G_{tr}$[d]	$\Delta\Delta H_{tr}$[e]
Ag^+	MeOH	7.5	−20.9	−7.4	−53.1
Ag^+	DMF	−17.2	−38.5	−19.6	−41.3
Ag^+	Me$_2$SO	−33.5	−54.8	−19.5	−49.0
Ag^+	PC	15.9	−12.6	−23.8	−58.5
Ag^+	AN	−21.8	−52.7	−18.0	−53.5
K^+	DMF	−9.6	−39.3	−22.8	−46.3
K^+	Me$_2$SO	−12.1	−34.7	−19.8	−49.5
K^+	PC	5.9	−20.9	−25.5	−44.1
K^+	AN	7.9	−22.6	−21.4	−50.7
Tl^+	DMF	−11.7[c]		−18.6	
Tl^+	Me$_2$SO	−25.1[c]		−23.7	
Tl^+	PC	8.4		−22.8	

[a] ΔG_{tr} and ΔH_{tr} in kJ mol^{-1}. For abbreviations see Table I, footnote *a*. [b] B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974). [c] B. G. Cox, *Annu. Rep. Prog. Chem., Sect. A*, **70**, 249 (1973). [d] $\Delta\Delta G_{tr} = \Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$. [e] $\Delta\Delta H_{tr} = \Delta H_{tr}(M(2,2,2)^+) - \Delta H_{tr}(2,2,2)$.

and enthalpies of transfer from water to nonaqueous solvents for Ag^+, K^+, and Tl^+ are listed together with $\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$ from eq 5 and $\Delta H_{tr}(M(2,2,2)^+) - \Delta H_{tr}(2,2,2)$ from eq 6. The difference between the transfer free energies of the cryptate and the cryptand is constant within ±2.5 kJ mol^{-1} for all aprotic solvents and cations. This means that the difference between the transfer free energies of the cryptate and the cryptand is nearly zero on the transfer from one aprotic solvent to another. This result is in agreement with free energies of transfer for $M(2,2,2)^+$ calculated from the Born equation which is at most 2.7 kJ mol^{-1} (HMPT). The maximum difference in the Born free energies of transfer is 2.5 kJ mol^{-1} between PC and HMPT. Also $\Delta H_{tr}(M(2,2,2)^+) - \Delta H_{tr}(2,2,2)$ is zero within accuracy on transfer between polar aprotic solvents. For $M^+ = K^+$, Ag^+, and Tl^+ eq 7 and 8 hold.

$$\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2) = -21.4 \pm 2.5 \text{ kJ mol}^{-1} \quad (7)$$

$$\Delta H_{tr}(M(2,2,2)^+) - \Delta H_{tr}(2,2,2) = -49.1 \pm 5.4 \text{ kJ mol}^{-1} \quad (8)$$

The standard deviations have been calculated from the results in Table III neglecting the experimental error quoted for each individual system, which was estimated to be larger.

These data have been used to calculate the free energies and enthalpies of transfer of Tl^+ from water to HMPT. The value of $\Delta G_{tr}(Tl^+) = -28.0 \pm 2.5$ kJ mol^{-1} is in agreement with that estimated from thallium-205 NMR, $\Delta G_{tr}(Tl^+) = 25$ kJ mol^{-1}.[14]

In Table IV the differences between the transfer free energies of Ag^+ cryptates and cryptands and the corresponding enthalpy data have been compared for all three cryptands in the same solvent. The thermodynamic properties do not show a simple trend on changing cryptands and the constant enthalpy data of Ag^+ in methanol may be fortuitous. Furthermore, Ag^+ fits best in the cavity of $(2,2,2)$, but in complexes with $(2,2,1)$ and $(2,1,1)$ direct contact between the solvent and the only partially encased ion will be possible.

The free energy and enthalpy differences in eq 5 and 6 contain contributions from the uncharged cryptand which should be obtainable without any extrathermodynamic assumptions. Since at the present time no experimental data are available in the literature, two extreme cases may be discussed when dividing the differences (5) and (6) into individual quantities:

(a) $\Delta G_{tr}(MCry^+) = \Delta G_{tr}(Cry)$ $\Delta H_{tr}(MCry^+) = \Delta H_{tr}(Cry)$

Table IV. Differences in the Free Energies and Enthalpies of Transfer from Water to Nonaqueous Solvents between Ag^+ Cryptates and Cryptands at 25 °C[a]

solvent	Cry	$\Delta\Delta G_{tr}$[b]	$\Delta\Delta H_{tr}$[c]
MeOH	(2,1,1)	10.4	−52.3
MeOH	(2,2,1)	−8.6	−50.7
MeOH	(2,2,2)	−7.4	−53.1
DMF	(2,1,1)	−2.7	−65.5
DMF	(2,2,1)	−20.6	−76.2
DMF	(2,2,2)	−19.6	−41.3

[a] ΔG_{tr} and ΔH_{tr} in kJ mol^{-1}. [b] $\Delta\Delta G_{tr} = \Delta G_{tr}(AgCry^+) - \Delta G_{tr}(Cry)$. [c] $\Delta\Delta H_{tr} = \Delta H_{tr}(AgCry^+) - \Delta H_{tr}(Cry)$.

These equations resemble the extrathermodynamic assumptions of the type

$$\Delta G_{tr}(\text{ferrocene}) = \Delta G_{tr}(\text{ferrocinium}(1+))$$

or the large cation–large anion couples.[6,15] Difficulties may arise from the possibility that the oxygen and nitrogen atoms of the cryptand come into contact with the solvent while they are directed toward the cation in the cavity.

(b) $\Delta G_{tr}(MCry^+) = 0$ $\Delta H_{tr}(MCry^+) = 0$

This assumption is suggested by the chemical shift of $^7Li^+$,[16] $^{23}Na^+$,[17] $^{133}Cs^+$,[18] and $^{205}Tl^+$ cryptates.[19] The chemical shift is independent of the solvent as long as the cationic diameter and the cavity size are of similar magnitude. Since the chemical shift of diamagnetic species depends mainly on the nearest-neighbor interactions, this observation means that M^+ is within the cavity and is separated from the solvent by a ligand layer. Although this does not imply the free energies and enthalpies are zero, the contribution of cryptate solvation is only small, as mentioned before. Further support is given by the experiments of Delpuech and Villermaux,[20] who found, from vapor-phase analysis, that the free energy of transfer of $Na(2,2,2)^+Cl^-$ is equal to that of Cl^- in water–methanol mixtures. Further experiments are in preparation to enable distinction between cases (a) and (b).

This report shows that $\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$ and also the corresponding enthalpy difference are constant between water and several aprotic solvents for Ag^+, K^+, and Tl^+. This enables cationic free energies and enthalpies of transfer between water and aprotic solvents to be determined by complexometric titration with $(2,2,2)$ using a silver electrode. Although this method is less general than the well-known "extrathermodynamic" models of ferrocene/ferrocinium,[21] bis(diphenyl)chromium(I/0),[22] or the large cation–large anion assumption,[6,15,23] the experimental ease—comparable with that in experiments using the negligible liquid junction assumption[24]—may favor its use.

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Thermodynamics of the Zinc Bicarbonate Ion Pair

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Zinc(II) is shown to form a mono complex with bicarbonate in dilute aqueous solution. Values of the log of the equilibrium constant for the reaction $Zn^{2+}_{aq} + HCO_3^- \rightleftharpoons ZnHCO_3^+_{aq}$ are 1.42, 1.40, 1.47, 1.57, and 1.63 at temperatures 10, 25, 40, 55, and 70 °C.

Introduction

Recent work by Bauman et al.,[1] Almon,[2] and Siebert[3] on $CaHCO_3^+$ and $MgHCO_3^+$ ion pairs has confirmed the existence of these complexes in dilute aqueous solutions over a temperature range of 10–90 °C. Zinc bicarbonate was selected for study to gain insight into the effects of electronegativity and polarizability on metal bicarbonate interactions. Zinc is more polarizable than calcium or magnesium and has a greater electronegativity. Its ionic radius lies between that of Ca^{2+} and Mg^{2+}.

In parallel with our earlier studies, chloride was selected as the common anion for the determinations. Zinc chloride complexing has been studied by a number of people with differing results.[4-10] The data are summarized by Libus and Tialowska.[10] Our experiments were designed to fall outside the range of $ZnCl_x^{2-x}$ complexing. The mean activity coefficients for zinc chloride solutions[11] are virtually identical with those found for calcium chloride up to an ionic strength of 0.6. The single ion activity coefficients calculated for Zn^{2+} from the MacInnes assumption using the mean salt method agree to within 1% with those calculated from the Debye–Hückel equation using an a_0 value of 6 Å over a range of ionic strength from 0 to 0.9. This value is suggested by Klotz and Rosenberg.[22]

The hydrolysis of Zn^{2+} to form various OH^- complexes has been studied by a number of authors.[12-15] The results of their measurements applied to a 0.1 M zinc chloride solution at pH 5.5 (the midpoint of our working range) indicate that less than 0.5% of the total Zn^{2+} ion is complexed with hydroxide ion.

One difficulty in the study of $ZnHCO_3^+$ as compared with $CaHCO_3^+$ or $MgHCO_3^+$ is the threat of zinc carbonate (Smithsonite) precipitation; $pK_{sp} = 10.27$.[16] Smithsonite is 2 orders of magnitude less soluble than calcite ($pK_{sp} = 8.34$) and 6 orders less soluble than $MgCO_3$ ($pK_{sp} = 4.52$), and solutions were often supersaturated with respect to zinc carbonate precipitation by a considerable amount. However, precipitation does not occur rapidly at room temperature and aqueous solutions can maintain supersaturation for long periods of time. In contrast, the equilibrium between the free ions and the zinc bicarbonate ion pair appears to be very rapid; i.e., a solution reaches a stable pH within a few minutes after an addition of HCO_3^- or Zn^{2+} is made. A paper by Taketatsu[17]

reported that the precipitate formed by the addition of $KHCO_3$ or K_2CO_3 to a solution containing Zn^{2+} ion could be partially redissolved by shaking; the fraction of the zinc which can be redissolved was observed to increase with increasing concentrations of carbonate or bicarbonate. These observations strongly suggest that some soluble carbonate and/or bicarbonate complexes of zinc exist, but no attempt has been made to characterize these complexes or determine equilibrium constants governing their formation.

In order to evaluate the equilibrium constant for the reaction

$$Zn^{2+} + HCO_3^- \rightleftharpoons ZnHCO_3^+ \qquad (1)$$

one must be able to evaluate the activities of the three reacting species. This can be done by utilizing the acid–base properties of HCO_3^- and determining its activity from pH measurements as described by Siebert and Hostetler.[3]

The investigation depended on measurements of changes in pH as alternate additions of $KHCO_3$ and $ZnCl_2$ solutions were made to a solution containing these species in equilibrium with an atmosphere of CO_2 at constant partial pressure. A slow stream of CO_2 was bubbled through the solution to maintain a constant P_{CO_2} and also provide for stirring. The equations which define the system are

$$m(ZnHCO_3^+) = m(K^+) + m(H^+) - m(HCO_3^-) \qquad (2)$$

and

$$m(Zn^{2+}) = m(Zn^{2+}_T) - m(ZnHCO_3^+) \qquad (3)$$

from mass balance, and since

$$K_1 = a_1(HCO_3^-)a_1(H^+)/a_1(H_2CO_3) = \\ a_2(HCO_3^-)a_2(H^+)/a_2(H_2CO_3) \qquad (4)$$

if $a(H_2CO_3) = K_0 P_{CO_2}$ it is assumed to remain constant over the entire experiment.

$$a_2(HCO_3^-) = a_1(H^+)a_1(HCO_3^-)/a_2(H^+) \qquad (5)$$

Finally

$$K_f = \frac{a_1(ZnHCO_3^+)}{a_1(Zn^{2+})a_1(HCO_3^-)} = \frac{a_2(ZnHCO_3^+)}{a_2(Zn^{2+})a_2(HCO_3^-)} \qquad (6)$$

The subscripts 1 and 2 refer to the molalities or activities in