$(\partial x^S(z)/\partial z)^2]$, the probability distribution is

$$P_S[x(z)] = P_0 \exp\left(-\frac{\Phi}{kT}\right) = P_0 \exp\left(-\frac{K}{2\gamma} \int_0^l \left(\frac{\partial x(z)}{\partial z}\right)^2 dz\right) \tag{C.7}$$

This expression for the probability distribution of the macroscopic concentration is in the Landau–Ginzburg or Schlögl form.[31] There is long-range correlation in the system described by the Landau–Ginzburg potential and the two-point covariance function varies as $1/r$; that is, it scales by the volume of the system. This long-range correlation is inherent to the Landau–Ginzburg theory since it describes the slow, macroscopic fluctuations which can only be relaxed by diffusion.

Following the same procedure starting from eq C.2, we can derive the distribution function in Landau–Ginzburg form from the distribution function in terms of excess work for thermal diffusion and viscous flow.

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Activity Coefficients in Electrolyte Mixtures: HCl + ThCl₄ + H₂O for 5–55 °C

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The emf of the cell without liquid junction (A) was used to study the HCl + ThCl₄ + H₂O mixed electrolyte system. The

$$\text{Pt, H}_2(\text{g,1 atm})|\text{HCl}(m_A), \text{ThCl}_4(m_B)|\text{AgCl,Ag} \tag{A}$$

emf was measured for solutions at constant total ionic strengths of 0.006, 0.008, 0.01, 0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 3.0 mol·kg⁻¹ and at temperatures ranging from 5 to 55 °C. The mean activity coefficients of HCl in the mixtures were calculated using the Nernst equation. Two detailed treatments are given of the data for 25 °C. In the first, the Harned equations were fitted to the activity coefficient data using least-squares regression techniques. Results show that the quadratic equation is adequate for the full range of Y_B to 0.9 for $I \leq 2.0$ mol·kg⁻¹ but only for smaller Y_B at $I = 3.0$. Second, an ion-interaction (Pitzer) equation treatment is given in which experimental isopiestic measurements, solubility, and the activity coefficient data are analyzed and the necessary parameters developed for the H⁺–Th⁴⁺–Cl⁻–H₂O system.

I. Introduction

We have been interested in studying aqueous solutions of mixed electrolytes to determine the nature and extent of ion–ion interactions. The electromotive force method has been found to give excellent data for mixtures of hydrochloric acid and metal chloride salts.[1-6] For salts with single charged cations the behavior is simple, with only small differences between the H–M interaction of unlike ions and the average for H–H and M–M interactions.[7] For salts with double charged cations,[2,3,8] these differences are larger and pertain to three-particle interactions (M–Cl–H, etc.), as well as two-particle interactions. Also, where the cation has a multiple electrical charge, an electrostatic term for unsymmetrical mixing arises. This was first identified as a higher order limiting law by Friedman;[9] subsequently, Pitzer[6,10] developed an

expression valid over the full range of concentration. This higher order electrostatic term is small for 2–1 mixing but very substantial for 3–1 mixing, as was noted for the HCl–AlCl$_3$[10] and HCl–LaCl$_3$[1] examples. It is still larger for 4–1 mixing, which makes a study of the system HCl–ThCl$_4$ of particular interest. While Harned and Gancy[11] reported some measurements on this system, a broader study is needed.

In other respects, ThCl$_4$ solutions are more complex than those of LaCl$_3$ or AlCl$_3$ or cases with doubly or singly charged cations. The tendency to hydrolyze is much stronger[12,13] for Th^{4+} than for any of the ions studied previously. While the HCl present in all of the solutions measured in this research is adequate to suppress hydrolysis, this factor must be considered in the broader discussion of literature results. Another potential complexity in the interpretations is the formation of chloride complexes.[14,15]

We have carried out a series of experiments by measuring the emf of the cell (A) without liquid junction. Constant ionic strength

$$\text{Pt, H}_2\text{(g,1 atm)}|\text{HCl}(m_A), \text{ThCl}_4(m_B)|\text{AgCl,Ag} \quad \text{(A)}$$
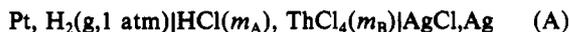
values varied from $I = 0.006$ to $I = 3.0$ mol·kg^{-1}, temperatures ranged from 5 to 55 °C, and ionic strength fractions Y_B of ThCl$_4$ ranged from 0.1 to 0.9. The emf of cell A is governed by the Nernst equation:

$$E = E° - (RT/F) \ln a_{\text{HCl}} \quad (1)$$

$$\ln a_{\text{HCl}} = \ln [\gamma_A{}^2(m_A)(m_A + 4m_B)] \quad (1a)$$

Two treatments of the results are presented. The first follows the method of Harned and co-workers,[16,17] who demonstrated that for many acid salt mixtures the following equation adequately describes the activity coefficient data of the acid as a function of ionic strength.

$$\log \gamma_A = \log \gamma°_A - \alpha_{AB}Y_B - \beta_{AB}Y_B{}^2 \quad (2)$$

Here Y_B is the ionic strength fraction of ThCl$_4$ and is equal to $10m_B/I$ where $I = 10m_B + m_A$. If eq 2 remained valid to $Y_B = 1$, it would give the trace activity coefficient for HCl in ThCl$_4$(aq), but for the present system the possibility of hydrolysis of Th^{4+} must be considered when the concentration of added HCl decreases to zero. Thus, we refrain from tabulating trace activity coefficients and discuss the situation for pure ThCl$_4$(aq) below.

The second treatment is based on the ion-interaction (Pitzer) equations.[6,18] In this approach it is essential to have independent information about the parameters for pure HCl(aq), and these are well-known. It is also desirable to have independent information about pure ThCl$_4$(aq). Isopiestic measurements of Robinson[19] are available. These data are combined with existing data[15] on the solubility of Th(OH)$_4$ at 25 °C to develop the necessary parameters for pure ThCl$_4$(aq) and for, mixing H$^+$–Th^{4+} in the H$^+$–Th^{4+}–Cl$^-$–H$_2$O system.

II. Experimental Section

Thorium tetrachloride, 99.9%, purchased from Alfa Products, was recrystallized from water, dried, and stored before use. Stock solutions were prepared by dissolving the solid and diluting it with double distilled, deionized water. Reagent-graded hydrochloric acid was distilled twice to the azeotropic concentration, keeping the middle third fraction each time. The final azeotropic mixture was diluted to give appropriate stock solutions. Molalities of both the stock solutions were determined gravimetrically with silver chloride and were known to within ±0.02% and ±0.03% for HCl and ThCl$_4$, respectively. Cell solutions were made by direct weighing of the appropriate stock solutions and water. Buoyancy corrections were applied to all apparent masses.

Electrodes were constructed according to procedures given by Bates.[20] The silver–silver chloride electrodes were of the thermal-electrolytic type and were formed by thermal decomposition of well-washed silver oxide on platinum helices at 500 °C. They were then coated with silver chloride by anodization in hydrochloride acid. Bias potentials of the silver–silver chloride electrodes were always less than 0.05 mV. The platinum–hydrogen electrodes were coated with platinum black deposited from a chloroplatinic

acid solution containing a small amount of lead acetate trihydrate. Experimental details of the cell design, the temperature measurement, purification of the hydrogen gas, and other experimental details, have been given in a previous communication from our laboratory.[21] All electromotive force measurements reported were made using a Keithley 191 digital multimeter.

The uncertainty in the values of activity coefficients determined in the study is estimated to be 0.005 or less at low I. This uncertainty depends on the uncertainty in experimental potentials, the consistency of the temperature measurements, error in the values of the molal concentrations of the solutions, poisoning of the hydrogen electrode, and the solubility of the silver–silver chloride electrode, particularly at high ionic strengths.

Experimental potentials were initially determined at 25 °C. The temperature of the cells was then lowered to 15 °C and then to 5 °C. Cell temperatures were then returned to 25 °C and then raised in ascending order to 55 °C, and finally (in some cases) brought back to 25 °C. The cell temperatures were measured and controlled to better than ±0.01 K.

The values of $E°$, the standard potential of the silver–silver chloride electrodes at 5, 15, 25, 35, 45, and 55 °C were 0.23431, 0.32878, 0.22259, 0.21587, 0.20857, and 0.20059 V, respectively. These values were determined following the procedures recommended by Bates et al.[22] and consisted of measurement of the cell of type A containing a solution of HCl of molality 0.01 mol·kg^{-1}.

Experimental potentials were determined for cell A of aqueous mixtures of hydrochloric acid and thorium chloride at constant total ionic strengths of 0.006, 0.008, 0.010, 0.050, 0.10, 0.25, 0.50, 1.0, 2.0, and 3.0 mol·kg^{-1} at ionic strength fractions of 0.1, 0.25, 0.4, 0.5, 0.6, 0.75, and 0.9, and at 5, 15, 25, 35, 45, and 55 °C. All emf measurements have been repeated at the experimental ionic strengths. The deviant data from the smooth plot of log γ_A versus Y_B are rejected.

III. Results and Harned-Equation Calculations

Water vapor makes a significant contribution to the total gas pressure of the cells used in this study. As a result, it was necessary to make corrections to the hydrogen fugacity. The corrections were made by calculating the activity of water for each solution and then calculating the hydrogen fugacity from the computed water activity and the experimental atmospheric pressure. The details of the iterative calculations involved have been described as part of earlier studies from our laboratory.[1,2,21]

The complete array of experimental potentials of cell A corrected to a hydrogen gas pressure of 1 atm are presented in the Appendix in Table IV as a function of the ionic strength fraction of thorium chloride, Y_B. The term Y_B is related to the molality of thorium tetrachloride by $Y_B = 10m_B/I$. An analogous expression for the ionic strength fraction of hydrogen chloride is $Y_A = m_A/I$. The total ionic strength of the mixture I is given by $I = m_A + 10m_B$.

The mean activity coefficient of the acid was calculated by rearranging the Nernst equation to give:

$$-\log \gamma_A = 1/2[(E - E°)/k + \log m_A(m_A + 4m_B)] \quad (3)$$

where $k = (RT/F) \ln 10$ and $E°$ is the standard emf of cell A at the temperature studied.

The values of log γ_A as a function of Y_B in mixed electrolyte systems at constant ionic strength are entered in Table V. Then eq 2, Harned's equation, was employed to express the variation of log γ_A versus Y_B. In eq 2, $\gamma°_A$ is the activity coefficient of pure HCl at an ionic strength equal to the total ionic strength of the mixture, and the terms α_{AB} and β_{AB} are usually referred to as Harned interaction coefficients, which are functions of both the temperature and total ionic strength.

Equation 2 was fitted to the values of $-\log \gamma_A$ calculated from eq 3 for various Y_B and I. By least-squares regression, the Harned coefficients as well as $-\log \gamma°_A$ were determined. The values of α_{AB} and β_{AB}, their standard deviations, and the standard error of the fit of log γ_A are given in Table I for 25 °C with the complete array for other temperatures in the Appendix in Table VI. At all ionic strengths up to 2.0, the agreement is acceptable in various

TABLE I: Harned Coefficients for the System HCl + ThCl$_4$ + H$_2$O at 25 °C

$$\log \gamma_A = \log \gamma^\circ_A - \alpha_{AB} Y_B - \beta_{AB} Y_B^2$$

I	$\log \gamma^\circ_{A\,exp}$	$\log \gamma^\circ_A$ ● $s(\log \gamma^\circ_A)$	α_{AB} ● $s(\alpha_{AB})$	β_{AB} ● $s(\beta_{AB})$	10^4 rmsd
0.006	−0.032 72	−0.031 93 ± 0.0007	−0.0015 ± 0.0042	0.0224 ± 0.0040	9
0.008	−0.036 61	−0.037 34 ± 0.0008	−0.0016 ± 0.0042	0.0325 ± 0.0045	10
0.01	−0.041 84	−0.042 54 ± 0.0009	−0.0071 ± 0.0048	0.0475 ± 0.0052	12
0.05	−0.079 36	−0.081 28 ± 0.0015	−0.0082 ± 0.0080	0.0852 ± 0.0087	19
0.1	−0.099 18	−0.099 35 ± 0.0007	−0.0215 ± 0.0035	0.1145 ± 0.0038	8
0.25	−0.114 90	−0.115 18 ± 0.0010	−0.0024 ± 0.0053	0.1011 ± 0.0057	13
0.5	−0.120 62	−0.120 13 ± 0.0011	0.0224 ± 0.0058	0.0853 ± 0.0062	14
1.0	−0.092 36	−0.091 33 ± 0.0014	0.0413 ± 0.0071	0.0713 ± 0.0077	17
2.0	0.003 89	0.003 78 ± 0.0015	0.0318 ± 0.0080	0.1536 ± 0.0086	19
3.0	0.119 26	0.112 47 ± 0.0077	0.0235 ± 0.0413	0.2970 ± 0.0443	97
3.0[a]	0.119 26	0.117 19 ± 0.0018	0.0883 ± 0.0114	0.1922 ± 0.0150	20

[a] With the omission of the value of $\log \gamma_A$ for Y_B = 0.9.

respects, including the overall root mean square deviation (rmsd). Also, the values of $\log \gamma^\circ_A$ here derived in the third column agree with previous values for pure HCl(aq) in the second column.

For I = 3 the rmsd is unreasonably large. Furthermore, the earlier measurements of Harned and Gancy[11] are in good agreement with the present results. The only reasonable explanation appears to be the formation of one or more complexes which increase in concentration rather suddenly with increase in both I and Y_B and appear to be important only for the final measurement at I = 3, Y_B = 0.9. Values of α and β recalculated without this point are given in Table I for 25 °C and in Table VI for other temperatures. With the omission of the point at Y_B = 0.9, the rmsd has decreased to an acceptable value. Figure 1 shows the curves for $\log \gamma_A$ at I = 3 for each of the calculations. This figure also makes it clear that only the curve calculated without the point at Y_B = 0.9 is satisfactory, and it is typical of the curves for other ionic strengths. The uncertainty shown in Table I for β_{AB} and the difference between the two values of $\log \gamma_A$ suggest that some complex formation remains at Y_B = 0.75. More detailed analysis does not seem justified at this time, however.

IV. Ion-Interaction Calculations

While the ion-interaction (Pitzer) equations could be written for the Harned α_{AB} and β_{AB}, it is preferable to fit the ion-interaction parameters to the original emf measurements. Then an equal weight for each measurement is clearly the appropriate basis in a regression and the quality of fit can be judged in relation to the accuracy of the measured quantity. Equation 1 gives the cell potential E in terms of $\ln \gamma_A$, where γ_A is the activity coefficient of HCl and the ion-interaction equation for $\ln \gamma_A$[6,18] in a mixed solution of HCl–ThCl$_4$ is

$$\ln \gamma_A = -A_\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln (1 + bI^{1/2}) \right] +$$

$$I\left(2 - \frac{8}{5}y\right)[\beta^{(0)}_{HCl} + \beta^{(1)}_{HCl}g(\alpha_1 I^{1/2})] + \frac{1}{10}y[\beta^{(0)}_{ThCl} + {}^S\theta_{Th,H} +$$

$$ {}^E\theta_{4,1}(I) + \beta^{(1)}_{ThCl}\exp(-\alpha_1 I^{1/2}) + \beta^{(2)}_{ThCl}\exp(-\alpha_2 I^{1/2})] +$$

$$(1 - y)\left(1 - \frac{3}{5}y\right)\beta^{(1)}_{HCl}g'(\alpha_1 I^{1/2}) + \frac{3}{50}y^2[\beta^{(1)}_{ThCl}g'(\alpha_1 I^{1/2}) +$$

$$\beta^{(2)}_{ThCl}g'(\alpha_2 I^{1/2})]\} + I^2\left\{\left(3 - \frac{13}{5}y\right)\left(1 - \frac{3}{5}y\right)C_{HCl} + \frac{1}{10}y\left[2\left(1 - \right.\right.\right.$$

$$\left.\frac{3}{5}y\right)C_{ThCl} + \left(1 - \frac{4}{5}y\right)\psi_{Th,H,Cl} + (1 - y){}^E\theta'_{4,1}(I)\right]\right\} \quad (4)$$

with

$$g = 2[1 - (1 + x) \exp(-x)]/x^2 \quad (4a)$$

$$g' = -2[1 - (1 + x + x^2/2) \exp(-x)]/x^2 \quad (4b)$$

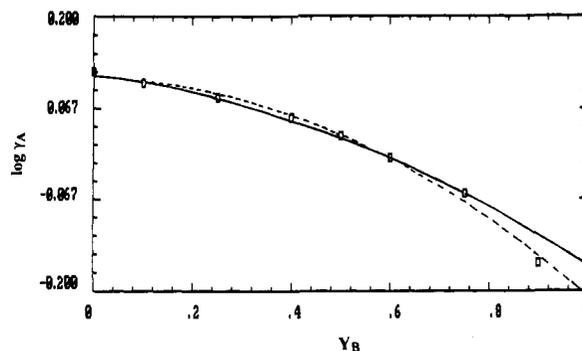Also, $y = Y_B$, the ionic strength fraction of ThCl$_4$. Standard values

Figure 1. Experimental values of $\log \gamma_A$ at I = 3.0 mol·kg^{-1}, rectangles, together with calculated curves based on the fit excluding the point at Y_B = 0.9, solid curve, and on the fit including all points, dashed curve.

TABLE II: Ion-Interaction Equation Parameters

	H,Cl	Th,Cl
$\beta^{(0)}$/kg·mol^{-1}	0.1775	1.092
$\beta^{(1)}$/kg·mol^{-1}	0.2945	13.7
$\beta^{(2)}$/kg·mol^{-1}		−160
C^ϕ/kg^2·mol^{-2}	0.0008	−0.112

$$C_{HCl} = C^\phi_{HCl}/2, \quad C_{ThCl} = C^\phi_{ThCl}/4$$
$${}^S\theta_{Th,H} = 0.60, \quad \psi_{Th,H,Cl} = 0.37$$

are assigned as follows: b = 1.2, α_1 = 2.0, α_2 = 12, all in kg$^{1/2}$·mol$^{-1/2}$. The last value was chosen for 2-2 electrolytes, but the charge product, $|z_+z_-|$, has the same value, 4, for Th^{4+}–Cl$^-$; hence, it is appropriate. A_ϕ is the Debye–Hückel parameter, while ${}^E\theta_{4,1}$ and ${}^E\theta'_{4,1}$ are the theoretical electrostatic functions for mixing of ions of +4 and +1 charges.[1,6,23] The other parameters are discussed below, while their numerical values are given in Table II.

Three types of ion-interaction parameters appear in eq 4. The first type is for H$^+$–Cl$^-$ interaction, and their values are well-known.[6,24] The other types are (a) those for Th^{4+}–Cl$^-$ interactions and (b) those for Th^{4+}–H$^+$ and Th^{4+}–H$^+$–Cl$^-$ interactions. While one might hope to determine all of these from the present measurements, this is not feasible. Only the sum ($\beta^{(0)}_{ThCl}$ + ${}^S\theta_{Th,H}$) can be obtained; also, other parameters are so strongly coupled that their separate determination is impractical.

Felmy et al.[15] measured the solubility of hydrous Th(OH)$_4$ in chloride solutions of controlled H$^+$ concentration and successfully interpreted their results with an ion-interaction equation and Th–Cl parameters based in part on the osmotic coefficient values reported by Robinson[19] for pure ThCl$_4$(aq). This was surprising because general information on the hydrolysis of Th^{4+} suggested significant hydrolysis in the solutions measured by Robinson. More precisely, Felmy et al. assumed a term with a very large negative value, −200 kg·mol^{-1}, for $\beta^{(2)}_{ThCl}$. This implied strong chloride complexation of Th^{4+} to ThCl.$^{3+}$. The Th(OH)$_4$ solubility in Cl$^-$ solutions exceeds that in otherwise comparable ClO$_4^-$ solutions by about

TABLE III: Comparison of MCl_n–HCl–H_2O Systems for Various Charges on M^{n+} at 25 °C

system	θ or $^S\theta$	$^E\theta$ ($I = 1.0$)	ψ	σ/mV
KCl–HCl[7]	-0.009_6			0.20
$BaCl_2$–HCl[3]	0.069	0.145	0.002	0.44
$LaCl_3$–HCl[1]	0.278	0.87	0.009	0.41
$ThCl_4$–HCl	0.60	2.63	0.37	0.64

a factor of 1000, and the term in $\beta^{(2)}$ for Th–Cl yields this difference. There is no indication of significant complexation of Th^{4+} with ClO_4^-. The other three Th–Cl parameters $\beta^{(0)}_{ThCl}$, $\beta^{(1)}_{ThCl}$, and C^{ϕ}_{ThCl} were determined from the osmotic coefficient data.

There are also Th^{4+}–H^+ mixing parameters in eq 4. Some information concerning these was obtained by Felmy and Rai,[25] who developed a general model for Th^{4+}–SO_4^{2-} in the presence

of various other ions including H^+ and Cl^-. Together with other information, they considered literature data for the solubility of $Th(SO_4)_2 \cdot nH_2O$ in HCl(aq) and in H_2SO_4(aq). From these systems they determined a reasonably precise value of 0.60 kg·mol^{-1} for $^S\theta_{Th,H}$ from both chloride and sulfate solutions and a much less well determined value of 0.08 kg^2·mol^{-2} for $\psi_{Th,H,Cl}$ from the chloride system.

While values were available from Felmy et al.[15] and Felmy and Rai[25] for all remaining parameters in eq 4, it was not expected that satisfactory agreement would be obtained without any further adjustment. Rather, various options were explored in which some parameters were retained and others were readjusted to fit satisfactorily all available data. The final values are listed in Table II. The value of $^S\theta_{Th,H}$ is that from Felmy and Rai,[25] while those for $\beta^{(0)}_{ThCl}$, $\beta^{(1)}_{ThCl}$, and C^{ϕ}_{ThCl} were determined from the osmotic coefficient values by a recalculation with minor refinements. Then

TABLE IV: Emf of Cell A for HCl + $ThCl_4$ + H_2O from 5 to 55 °C

Y_B	$I = 0.006$	$I = 0.008$	$I = 0.01$	$I = 0.05$	$I = 0.1$	$I = 0.25$	$I = 0.5$	$I = 1.0$	$I = 2.0$	$I = 3.0$
					5 °C					
0.00	0.48285	0.46978	0.45965	0.38653	0.35520	0.31300	0.27992	0.24282	0.19793	0.16455
0.10	0.48675	0.47380	0.46367	0.39071	0.35934	0.31703	0.28403	0.24731	0.20230	0.16995
0.25	0.49374	0.48060	0.47097	0.39780	0.36628	0.32407	0.29165	0.25492	0.21018	0.17846
0.40	0.50198	0.48889	0.47903	0.40644	0.37497	0.33313	0.30078	0.26422	0.22044	0.18939
0.50	0.50853	0.49527	0.48586	0.41338	0.38199	0.34041	0.30841	0.27124	0.22811	0.19771
0.60	0.51642	0.50325	0.49346	0.42158	0.39071	0.34873	0.31703	0.28022	0.23754	0.20846
0.75	0.53184	0.51880	0.50929	0.43825	0.40748	0.36577	0.33408	0.29694	0.25637	0.22939
0.90	0.55867	0.54614	0.53667	0.46643	0.43649	0.39465	0.36258	0.32596	0.28639	0.26417
					15 °C					
0.00	0.48642	0.47273	0.46224	0.38663	0.35414	0.31054	0.27657	0.23850	0.19246	0.15847
0.10	0.49048	0.47693	0.46643	0.39081	0.35843	0.31472	0.28079	0.24316	0.19711	0.16389
0.25	0.49779	0.48406	0.47401	0.39819	0.36574	0.32216	0.28883	0.25097	0.20539	0.17298
0.40	0.50630	0.49271	0.48239	0.40730	0.37486	0.33145	0.29825	0.26099	0.21622	0.18457
0.50	0.15381	0.49937	0.48949	0.41455	0.38222	0.33917	0.30635	0.26833	0.22409	0.19361
0.60	0.52125	0.50760	0.49739	0.42312	0.39105	0.34790	0.31524	0.27786	0.23412	0.20502
0.75	0.53722	0.52370	0.51384	0.44051	0.40863	0.36573	0.33316	0.29520	0.25358	0.22657
0.90	0.56487	0.55201	0.54224	0.46975	0.43876	0.39561	0.36263	0.32505	0.28493	0.26339
					25 °C					
0.00	0.48934	0.47502	0.46417	0.38591	0.35264	0.30742	0.27248	0.23352	0.18651	0.15203
0.10	0.49353	0.47946	0.46854	0.39069	0.35684	0.31180	0.27703	0.23817	0.19141	0.15813
0.25	0.50110	0.48686	0.47641	0.39829	0.36443	0.31969	0.28534	0.24658	0.20010	0.16807
0.40	0.50994	0.49594	0.48510	0.40734	0.37398	0.32940	0.29500	0.25709	0.21132	0.17999
0.50	0.51699	0.50271	0.49246	0.41506	0.38180	0.33744	0.30340	0.26467	0.21957	0.19009
0.60	0.52542	0.51129	0.50067	0.42403	0.39083	0.34640	0.31275	0.27454	0.23024	0.20157
0.75	0.54201	0.52797	0.51774	0.44222	0.40938	0.36494	0.33130	0.29271	0.25081	0.22396
0.90	0.57057	0.55724	0.54717	0.47250	0.44048	0.39606	0.36281	0.32434	0.28354	0.26428
					35 °C					
0.00	0.49172	0.47715	0.46586	0.38503	0.35055	0.30421	0.26820	0.22832	0.18038	0.14510
0.10	0.49607	0.48161	0.47031	0.38948	0.35500	0.38073	0.27304	0.23304	0.18532	0.15146
0.25	0.50397	0.48921	0.47838	0.39775	0.36266	0.31693	0.28143	0.24193	0.19460	0.16133
0.40	0.51313	0.49857	0.48727	0.40746	0.37248	0.32693	0.29176	0.25284	0.20625	0.17491
0.50	0.52051	0.50570	0.49508	0.41507	0.38070	0.33545	0.30038	0.26117	0.21507	0.18486
0.60	0.52915	0.51453	0.50353	0.42443	0.39046	0.34484	0.31033	0.27117	0.22612	0.19795
0.75	0.54639	0.53184	0.52125	0.44283	0.40926	0.36402	0.32937	0.29016	0.24745	0.22304
0.90	0.57597	0.56209	0.55171	0.47455	0.44148	0.39618	0.36106	0.32233	0.28120	0.26455
					45 °C					
0.00	0.49357	0.47841	0.46672	0.38337	0.34782	0.30022	0.26315	0.22240	0.17348	0.13791
0.10	0.49815	0.48302	0.47147	0.38796	0.35253	0.30489	0.26816	0.22725	0.17889	0.14444
0.25	0.50621	0.49089	0.47980	0.39655	0.36074	0.31340	0.27711	0.23651	0.18852	0.15523
0.40	0.51573	0.50062	0.48881	0.40670	0.37075	0.32389	0.28765	0.24803	0.20070	0.16925
0.50	0.52329	0.50799	0.49707	0.41476	0.37919	0.33274	0.29675	0.25648	0.21008	0.18058
0.60	0.53222	0.51712	0.50578	0.42451	0.38942	0.34236	0.30668	0.26690	0.22184	0.19455
0.75	0.55004	0.53505	0.52415	0.44380	0.41011	0.36229	0.32667	0.28689	0.24367	0.22152
0.90	0.58067	0.56624	0.55564	0.47669	0.44231	0.39563	0.35954	0.32003	0.27868	0.26438
					55 °C					
0.00	0.49484	0.47922	0.46704	0.38128	0.34461	0.29571	0.25770	0.21594	0.16625	0.13035
0.10	0.49955	0.48400	0.47202	0.38603	0.34936	0.30061	0.26290	0.22138	0.17158	0.13693
0.25	0.50795	0.49202	0.48049	0.39462	0.35782	0.30940	0.27224	0.23094	0.18185	0.14837
0.40	0.51775	0.50208	0.48993	0.40529	0.36836	0.32059	0.28323	0.24300	0.19465	0.16540
0.50	0.52555	0.50974	0.49861	0.41377	0.37707	0.39266	0.29255	0.25171	0.20432	0.17569
0.60	0.53491	0.51913	0.50751	0.42416	0.38785	0.33951	0.30293	0.26277	0.21604	0.19010
0.75	0.55325	0.53763	0.52655	0.44406	0.40905	0.36041	0.32377	0.28361	0.23952	0.21885
0.90	0.58480	0.56990	0.55909	0.47791	0.44319	0.39481	0.35762	0.31856	0.27613	0.26228

TABLE V: Log γ_A Values for HCl + ThCl$_4$ + H$_2$O from 5 to 55 °C

Y_B	$I = 0.006$	$I = 0.008$	$I = 0.01$	$I = 0.05$	$I = 0.1$	$I = 0.25$	$I = 0.5$	$I = 1.0$	$I = 2.0$	$I = 3.0$
					5 °C					
0.00	-0.02988	-0.03640	-0.04150	-0.07802	-0.09527	-0.11081	-0.11218	-0.07709	0.02857	0.15492
0.10	-0.02842	-0.03656	-0.04163	-0.07965	-0.09627	-0.11101	-0.11293	-0.08133	0.02527	0.14227
0.25	-0.02898	-0.03664	-0.04367	-0.08244	-0.09783	-0.11334	-0.12066	-0.08900	0.01531	0.12667
0.40	-0.03066	-0.03932	-0.04688	-0.08805	-0.10466	-0.12273	-0.13073	-0.10133	-0.00513	0.10027
0.50	-0.03289	-0.04004	-0.04766	-0.09335	-0.10999	-0.13127	-0.14234	-0.10666	-0.01709	0.08227
0.60	-0.03622	-0.04356	-0.05158	-0.09973	-0.12018	-0.13874	-0.15267	-0.12007	-0.03473	0.05227
0.75	-0.04016	-0.05079	-0.06043	-0.11600	-0.13800	-0.15807	-0.17201	-0.13654	-0.07007	-0.00173
0.90	-0.04536	-0.05900	-0.07070	-0.13330	-0.16334	-0.18233	-0.19287	-0.16168	-0.10493	-0.07930
					15 °C					
0.00	-0.03128	-0.03651	-0.04166	-0.07945	-0.09636	-0.11300	-0.11694	-0.08502	0.01662	0.13773
0.10	-0.03005	-0.03700	-0.04203	-0.07970	-0.09736	-0.11320	-0.11733	-0.08935	0.01219	0.12667
0.25	-0.03120	-0.03780	-0.04428	-0.08285	-0.10000	-0.11680	-0.12633	-0.09633	0.00127	0.10867
0.40	-0.03261	-0.04100	-0.04769	-0.08981	-0.10788	-0.12533	-0.13600	-0.11200	-0.02093	0.07989
0.50	-0.03566	-0.04220	-0.04867	-0.09567	-0.11400	-0.13547	-0.14940	-0.11800	-0.03233	0.05827
0.60	-0.03820	-0.04536	-0.05283	-0.10266	-0.12235	-0.14387	-0.15940	-0.13334	-0.05213	0.02587
0.75	-0.04205	-0.05248	-0.06211	-0.12000	-0.14199	-0.16474	-0.18100	-0.15000	-0.08710	-0.02693
0.90	-0.04594	-0.06064	-0.07272	-0.13770	-0.16799	-0.18873	-0.20133	-0.17333	-0.12413	-0.11153
					25 °C					
0.00	-0.03272	-0.03661	-0.04184	-0.07936	-0.09918	-0.11490	-0.12062	-0.09236	0.00389	0.11926
0.10	-0.03140	-0.03792	-0.04243	-0.08343	-0.09839	-0.11559	-0.12261	-0.09514	-0.00127	0.10400
0.25	-0.03255	-0.03898	-0.04488	-0.08629	-0.10108	-0.12089	-0.13158	-0.10497	-0.01317	0.08144
0.40	-0.03433	-0.04324	-0.04849	-0.09009	-0.10986	-0.13022	-0.14051	-0.12127	-0.03556	0.05334
0.50	-0.03681	-0.04341	-0.04967	-0.09781	-0.11775	-0.14075	-0.15404	-0.12779	-0.04776	0.02534
0.60	-0.03992	-0.04705	-0.05408	-0.10585	-0.12613	-0.14857	-0.16531	-0.14335	-0.07012	-0.00426
0.75	-0.04438	-0.05439	-0.06381	-0.12466	-0.14796	-0.17021	-0.18696	-0.16203	-0.10866	-0.05785
0.90	-0.04787	-0.06237	-0.07473	-0.14261	-0.17297	-0.19588	-0.20933	-0.18635	-0.14823	-0.16116
					35 °C					
0.00	-0.03399	-0.03980	-0.04436	-0.08235	-0.10139	-0.12033	-0.12688	-0.10180	-0.01078	0.10159
0.10	-0.03280	-0.03999	-0.04447	-0.08240	-0.10133	-0.12100	-0.12999	-0.10400	-0.01493	0.08587
0.25	-0.03461	-0.04060	-0.04636	-0.08867	-0.10266	-0.12660	-0.13734	-0.11533	-0.02933	0.06667
0.40	-0.03652	-0.04472	-0.04920	-0.09534	-0.11100	-0.13567	-0.14914	-0.13267	-0.05213	0.02827
0.50	-0.03976	-0.04600	-0.05200	-0.10000	-0.12000	-0.14794	-0.16214	-0.14254	-0.06677	0.00427
0.60	-0.04236	-0.04936	-0.05620	-0.10866	-0.13100	-0.15674	-0.17571	-0.15634	-0.08933	-0.03533
0.75	-0.04751	-0.05724	-0.06652	-0.12435	-0.15067	-0.17860	-0.19633	-0.17667	-0.12843	-0.10493
0.90	-0.05158	-0.06516	-0.07780	-0.14579	-0.17667	-0.20423	-0.21806	-0.20200	-0.16733	-0.20693
					45 °C					
0.00	-0.03600	-0.04088	-0.04517	-0.08395	-0.10346	-0.12436	-0.13173	-0.10999	-0.02354	0.08211
0.10	-0.03556	-0.04116	-0.04652	-0.08405	-0.10433	-0.12500	-0.13497	-0.11200	-0.03018	0.06667
0.25	-0.03664	-0.04196	-0.04843	-0.09067	-0.10800	-0.13100	-0.14454	-0.12400	-0.04493	0.04267
0.40	-0.03900	-0.04661	-0.04992	-0.09840	-0.11533	-0.14140	-0.15535	-0.14334	-0.06893	0.00427
0.50	-0.04178	-0.04796	-0.05434	-0.10466	-0.12400	-0.15407	-0.16993	-0.15200	-0.08572	-0.02813
0.60	-0.04440	-0.05141	-0.05836	-0.11400	-0.13621	-0.16227	-0.18087	-0.16667	-0.11109	-0.07133
0.75	-0.04982	-0.05980	-0.06928	-0.13200	-0.16600	-0.18513	-0.20406	-0.18999	-0.14868	-0.14933
0.90	-0.05450	-0.06738	-0.08091	-0.15451	-0.18354	-0.21186	-0.22706	-0.21466	-0.18893	-0.25133
					55 °C					
0.00	-0.03781	-0.04276	-0.04614	-0.86534	-0.10597	-0.12843	-0.13755	-0.11789 ·	-0.03732	0.06226
0.10	-0.03716	-0.04324	-0.04806	-0.08676	-0.10600	-0.12968	-0.14098	-0.12319	-0.04202	0.04807
0.25	-0.03890	-0.04332	-0.04910	-0.09133	-0.10966	-0.13580	-0.15147	-0.13534	-0.05933	0.02167
0.40	-0.04124	-0.04808	-0.05166	-0.10053	-0.11866	-0.14900	-0.16313	-0.15601	-0.08513	-0.02653
0.50	-0.04400	-0.04988	-0.05729	-0.10813	-0.12733	-0.16120	-0.17720	-0.16467	-0.10193	-0.05813
0.60	-0.04780	-0.05320	-0.06073	-0.12000	-0.14134	-0.16893	-0.18920	-0.18167	-0.12414	-0.10133
0.75	-0.05284	-0.06156	-0.07233	-0.13800	-0.17000	-0.19440	-0.21406	-0.20666	-0.16913	-0.18653
0.90	-0.05724	-0.06996	-0.08441	-0.15999	-0.19467	-0.22124	-0.23666	-0.23733	-0.21317	-0.28253

$\beta^{(2)}_{ThCl}$ and $\psi_{Th,H,Cl}$ were determined by regression of the E values at 25 °C of Table A1.

Initially, all emf values were included, but it was noted that the deviation from experiment was much larger, 6.4 mV, for the value at $I = 3.0$, $Y_B = 0.9$ than for any other measurement. This is consistent with the result from the Harned treatment where that point was divergent. With the omission of this one value in the final calculation, the maximum deviation of any point at $I = 3.0$ was reduced to 1.6 mV. The largest deviation elsewhere was 2.3 mV with an average deviation for the entire array of 79 values of 0.6 mV. This deviation exceeds the presumed inaccuracy of the measurements but is only a little larger than the observed deviations of similar measurements for simpler systems (see below); hence, we regard it as satisfactory agreement for this unusually complex example.

The final value determined from the new measurements for

$\beta^{(2)}_{ThCl}$ of -160 kg·mol^{-1} deviates somewhat from the previous value of -200, but the agreement with the solubility of Th(OH)$_4$ remains satisfactory, as is apparent from Figure 2. Similarly, the change in $\psi_{Th,H,Cl}$ does not cause serious disagreement for the solubility of Th(SO$_4$)$_2$·nH$_2$O in HCl(aq).

The representation of an extensive array of several types of quantitative data with an ion-interaction treatment where complexation appears only through a single $\beta^{(2)}$ term is impressive. It remains, however, to discuss the cause of the deviation at $I = 3.0$, $Y_B = 0.9$. Here the observed emf is higher than that calculated, which indicates a lower than expected activity of HCl (see eq 1). We believe that this decrease in HCl activity must arise from chloride complexation effects in addition to that implied by the $\beta^{(2)}$ term which concerns the species ThCl^{+3}. If this additional complexation appears suddenly at high I, it must involve a large number of chloride ions. Thus, ThCl$_6^{2-}$ is a prime can-

TABLE VI: Harned Coefficients for the System $HCl + ThCl_4 + H_2O$

$$\log \gamma_A = \log \gamma^\circ{}_A - \alpha_{AB}Y_B - \beta_{AB}Y_B{}^2$$

I	$\log \gamma^\circ{}_{A\,exp}$	$\log \gamma^\circ{}_A \pm s(\log \gamma^\circ{}_A)$	$\alpha_{AB} \pm s(\alpha_{AB})$	$\beta_{AB} \pm s(\beta_{AB})$	10^4 rmsd
		5 °C			
0.006	−0.029 88	−0.029 89 ± 0.0005	−0.0068 ± 0.0026	0.0279 ± 0.0029	6
0.008	−0.036 40	−0.036 94 ± 0.0006	−0.0013 ± 0.0025	0.0409 ± 0.0032	7
0.01	−0.041 50	−0.042 10 ± 0.0009	−0.0095 ± 0.0047	0.0452 ± 0.0051	11
0.05	−0.078 02	−0.078 99 ± 0.0008	−0.0089 ± 0.0043	0.0766 ± 0.0047	10
0.1	−0.095 27	−0.096 63 ± 0.0011	−0.0262 ± 0.0054	0.1103 ± 0.0059	13
0.25	−0.110 81	−0.110 95 ± 0.0008	−0.0128 ± 0.0040	0.1018 ± 0.0088	10
0.5	−0.112 18	−0.111 01 ± 0.0010	0.0211 ± 0.0052	0.0788 ± 0.0056	12
1.0	−0.077 09	−0.077 81 ± 0.0013	0.0242 ± 0.0069	0.0753 ± 0.0075	16
2.0	0.028 57	0.029 01 ± 0.0014	0.0251 ± 0.0070	0.1388 ± 0.0076	17
3.0	0.154 92	0.149 47 ± 0.0044	0.0029 ± 0.0228	0.2702 ± 0.0248	55
3.0[a]	0.154 92	0.151 70 ± 0.0030	0.0379 ± 0.0191	0.2183 ± 0.0250	35
		15 °C			
0.006	−0.031 28	−0.030 55 ± 0.0006	−0.0014 ± 0.0033	0.0212 ± 0.0036	8
0.008	−0.036 51	−0.036 95 ± 0.0005	−0.0064 ± 0.0052	0.0361 ± 0.0028	6
0.01	−0.041 66	−0.042 31 ± 0.0009	−0.0083 ± 0.0047	0.0461 ± 0.0052	11
0.05	−0.079 45	−0.079 64 ± 0.0006	−0.0082 ± 0.0031	0.0810 ± 0.0034	7
0.1	−0.096 36	−0.097 60 ± 0.0012	−0.0212 ± 0.0063	0.1089 ± 0.0068	15
0.25	−0.113 00	−0.112 99 ± 0.0006	−0.0098 ± 0.0003	0.1045 ± 0.0034	7
0.5	−0.116 94	−0.115 45 ± 0.0015	0.0244 ± 0.0077	0.0808 ± 0.0083	18
1.0	−0.085 02	−0.084 75 ± 0.0001	0.0359 ± 0.0075	0.0695 ± 0.0081	18
2.0	0.016 62	0.016 89 ± 0.0014	0.0332 ± 0.0071	0.1381 ± 0.0077	17
3.0	0.137 73	0.133 44 ± 0.0043	0.0139 ± 0.0225	0.1401 ± 0.0244	54
3.0[a]	0.137 73	0.136 00 ± 0.0017	0.0509 ± 0.0108	0.2206 ± 0.0014	19
		25 °C			
0.006	−0.032 72	−0.031 93 ± 0.0007	−0.0015 ± 0.0042	0.0224 ± 0.0040	9
0.008	−0.036 61	−0.037 34 ± 0.0008	−0.0016 ± 0.0042	0.0325 ± 0.0045	10
0.01	−0.041 84	−0.042 54 ± 0.0009	−0.0071 ± 0.0048	0.0475 ± 0.0052	12
0.05	−0.079 36	−0.081 28 ± 0.0015	−0.0082 ± 0.0080	0.0852 ± 0.0087	19
0.1	−0.099 18	−0.099 35 ± 0.0007	−0.0215 ± 0.0035	0.1145 ± 0.0038	8
0.25	−0.114 90	−0.115 18 ± 0.0010	−0.0024 ± 0.0053	0.1011 ± 0.0057	13
0.5	−0.120 62	−0.120 13 ± 0.0011	0.0224 ± 0.0058	0.0853 ± 0.0062	14
1.0	−0.092 36	−0.091 33 ± 0.0014	0.0413 ± 0.0071	0.0713 ± 0.0078	17
2.0	0.003 89	0.003 78 ± 0.0015	0.0318 ± 0.0080	0.1536 ± 0.0086	19
3.0	0.119 26	0.112 47 ± 0.0077	0.0235 ± 0.0413	0.2970 ± 0.0443	97
3.0[a]	0.119 26	0.117 19 ± 0.0018	0.0883 ± 0.0114	0.1922 ± 0.0150	20
		35 °C			
0.006	−0.033 99	−0.033 19 ± 0.0007	0.0010 ± 0.0035	0.0225 ± 0.0038	8
0.008	−0.039 80	−0.039 96 ± 0.0005	−0.0055 ± 0.0028	0.0373 ± 0.0030	7
0.01	−0.044 36	−0.044 90 ± 0.0006	−0.0116 ± 0.0032	0.0532 ± 0.0034	8
0.05	−0.082 35	−0.082 74 ± 0.0011	−0.0038 ± 0.0058	0.0808 ± 0.0062	14
0.1	−0.101 39	−0.101 82 ± 0.0025	−0.0110 ± 0.0132	0.1125 ± 0.0141	31
0.25	−0.120 33	−0.120 13 ± 0.0008	−0.0000 ± 0.0043	0.1039 ± 0.0005	10
0.5	−0.126 88	−0.125 98 ± 0.0015	0.0304 ± 0.0075	0.0819 ± 0.0082	18
1.0	−0.101 80	−0.100 10 ± 0.0013	0.0496 ± 0.0066	0.0709 ± 0.0071	16
2.0	−0.010 78	−0.009 86 ± 0.0014	0.0439 ± 0.0075	0.1476 ± 0.0081	18
3.0	0.101 59	0.095 52 ± 0.0053	0.0141 ± 0.0274	0.3504 ± 0.0297	66
3.0[a]	0.101 59	0.098 33 ± 0.0033	0.0545 ± 0.0207	0.2852 ± 0.0271	38
		45 °C			
0.006	−0.036 00	−0.035 58 ± 0.0004	−0.0004 ± 0.0023	0.0244 ± 0.0025	5
0.008	−0.040 88	−0.040 93 ± 0.0006	−0.0030 ± 0.0032	0.0362 ± 0.0035	8
0.01	−0.045 17	−0.046 24 ± 0.0009	−0.0112 ± 0.0045	0.0550 ± 0.0048	11
0.05	−0.083 95	−0.084 12 ± 0.0009	−0.0012 ± 0.0044	0.0875 ± 0.0048	11
0.1	−0.103 46	−0.104 20 ± 0.0006	−0.0178 ± 0.0032	0.1180 ± 0.0035	8
0.25	−0.124 36	−0.124 01 ± 0.0010	−0.0030 ± 0.0053	0.1050 ± 0.0058	13
0.5	−0.131 73	−0.131 13 ± 0.0012	0.0330 ± 0.0063	0.0832 ± 0.0068	15
1.0	−0.109 99	−0.108 03 ± 0.0016	0.0529 ± 0.0084	0.0738 ± 0.0091	20
2.0	−0.023 54	−0.022 80 ± 0.0015	0.0587 ± 0.0077	0.1419 ± 0.0083	18
3.0	0.082 21	0.077 47 ± 0.0033	0.0334 ± 0.0172	0.3647 ± 0.0187	41
3.0[a]	0.082 11	0.079 04 ± 0.0025	0.0560 ± 0.0163	0.3284 ± 0.0211	30
		55 °C			
0.006	−0.037 81	−0.037 17 ± 0.0007	0.0023 ± 0.0034	0.0232 ± 0.0037	8
0.008	−0.042 76	−0.042 93 ± 0.0006	−0.0028 ± 0.0030	0.0394 ± 0.0033	7
0.01	−0.046 14	−0.047 19 ± 0.0008	−0.0094 ± 0.0043	0.0563 ± 0.0047	10
0.05	−0.086 53	−0.085 97 ± 0.0007	−0.0014 ± 0.0038	0.0890 ± 0.0041	9
0.1	−0.105 97	−0.106 62 ± 0.0013	−0.0233 ± 0.0069	0.1324 ± 0.0073	16
0.25	−0.128 43	−0.128 00 ± 0.0013	−0.0093 ± 0.0068	0.1048 ± 0.0074	16
0.5	−0.137 55	−0.136 86 ± 0.0013	0.0371 ± 0.0066	0.0838 ± 0.0072	16
1.0	−0.117 89	−0.117 44 ± 0.0014	0.0544 ± 0.0072	0.0871 ± 0.0078	17
2.0	−0.037 32	−0.036 42 ± 0.0016	0.0527 ± 0.0080	0.1610 ± 0.0087	19
3.0	0.062 26	0.060 66 ± 0.0051	0.0827 ± 0.0266	0.3295 ± 0.0289	64
3.0[a]	0.062 26	0.060 66 ± 0.0027	0.0737 ± 0.0171	0.3375 ± 0.0224	32

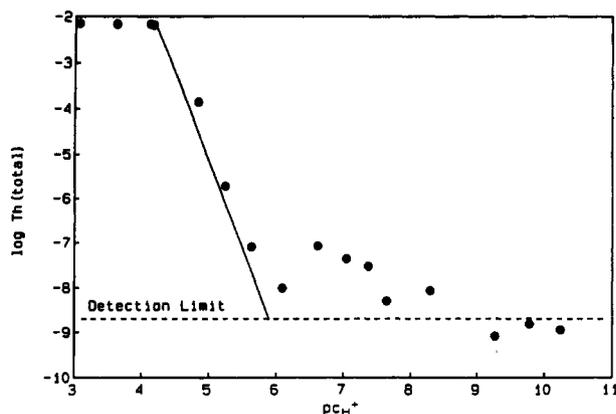[a] With the omission of the value of $\log\gamma_A$ for $Y_B = 0.9$.

Figure 2. Solubility of amorphous $Th(OH)_4$ in 0.6 m NaCl with experimental data given by points and calculated data given by a solid line. Diagrams for 1.2 and 3.0 m NaCl are similar.

didate; it is known in solids such as K_2ThCl_6, but there is little independent evidence of its occurrence in solution. The aqueous species $ThCl_4$ has been reported,[14] however. The conversion of about 13% of the thorium to $ThCl_6^{2-}$ would account for the deviation in emf at $I = 3$, $Y_B = 0.9$. If $ThCl_4$ were the species formed, about 20% conversion would be needed. Also, there is information[26] about $Th_2(OH)_2Cl_2^{4+}$, but such hydrolyzed species would not explain the present results since their formation would produce additional H^+ and increase, not decrease, the activity of HCl.

It must also be recognized that the solutions of $ThCl_4(aq)$ used in the isopiestic measurements would have contained the chloride complexes discussed above. Their effect on the activity of water and on the osmotic coefficient would be less specific than on the activity coefficient. Hydrolysis may not be negligible in the absence of added HCl. Also, the precision of the osmotic data is lower than that of the emf measurements. Thus, while there is an approximation involved in using the parameters $\beta^{(0)}_{ThCl}$, $\beta^{(1)}_{ThCl}$, and C^ϕ_{ThCl} calculated from the osmotic data without consideration of these higher complexes in our general equation, this is acceptable until more complete and precise data become available. We also note that parameters are known for several 4–1 electrolytes[6] such as $Na_4P_2O_7$ and $K_4Fe(CN)_6$, where there is no indication of comparable complications, and the values are similar to those for $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ in Table II for $ThCl_4$. Thus, we conclude that the Th^{4+}–Cl^- parameters in Table II are plausible and that the entire set of parameters represents an impressive array of experimental data.

V. Discussion

It is interesting to compare the ion-interaction treatments for MCl_n–HCl–H_2O systems for various cation charges. Table III presents this information for $ThCl_4$–HCl–H_2O and for typical cases for single, double, and triple charges. Included is the value at ionic strength 1 mol·kg^{-1} of the higher order function for unsymmetrical mixing $^E\theta$. This quantity is zero, of course, for 1–1 mixing; it has an inverse trend with change in I for other cases. The rapid increase in $^E\theta$ with cation charge is apparent. Indeed, for 2–1 mixing the $^E\theta$ function is only marginally significant, and it is often omitted. But for 3–1 mixing the $^E\theta$ term is required for a good fit in the dilute range,[1,10] and it is even about three times larger for the 4–1 case. The triple interaction M–H–Cl term $\psi_{M,H,Cl}$ is negligible for the 1–1 and 2–1 examples and remains small for the 3–1 case. For Th^{4+}, however, one must consider that the $\beta^{(2)}$ term was introduced (it is absent for the other cases) and that it constitutes an approximate description of $ThCl^{3+}$ complex formation. With this complication for the Th–Cl interaction, it is not surprising that ψ is larger for the $ThCl_4$ system, but a more detailed interpretation is not apparent.

The standard deviations of fit, σ, to the experimental emf values increase only moderately with cation charge. In view of the much more rapid increase in various parameters, some increase in σ is expected since the theory is not exact. Thus, we regard the fit to 0.6 mV as quite satisfactory, even without special consideration of the complications of further complexation of Th^{4+} ions. Although the parameters of Table II represent the data for $ThCl_4$–HCl–H_2O satisfactorily, caution should be exercised in detailed interpretations of these parameters. The complete redundancy of $^S\theta$ and $\beta^{(0)}_{ThCl}$ was noted above, as was the rather strong partial coupling of other parameters and the approximate nature of the parameters for pure $ThCl_4$.

Accurate measurements of the activity of H_2O for the $ThCl_4$–HCl–H_2O system over a range of composition with sufficient HCl to suppress hydrolysis would provide very valuable information. It would eliminate the $^S\theta$–$\beta^{(0)}_{ThCl}$ redundancy and reduce other ambiguities. The volatility of HCl would be a complication for isopiestic measurements, but it could probably be dealt with. Additional information such as this is required to fully describe the properties of unhydrolyzed $ThCl_4(aq)$ as well as of the ternary $ThCl_4$–HCl–H_2O.

Appendix

Table IV gives the complete array of measured emf values at 5, 15, 25, 35, 45, and 55 °C, at various ionic strengths from 0.006 to 3.0, and at ionic strength fractions of $ThCl_4$ from 0.0 to 0.90. Table V gives the full array of values of log γ_A derived from the emf values from eq 1. Table VI gives the Harned parameters for all temperatures; those for 25 °C were given in Table I and fully described in the text.

Registry No. Hydrochloric acid, 7647-01-0; thorium tetrachloride, 10026-08-1.

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Kinetics of "Extraction" of Copper(II) by Micelle-Solubilized Complexing Agents of Varying Hydrophilic Lipophilic Balance. 1. Stopped-Flow Study

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Micellar particles can solubilize lipophilic extractants similarly to the organic phase in classical biphasic extraction. A series of 6-(alkylamino)methyl-2-(hydroxymethyl)pyridines (C_nNHMePy with n = 1, 4, 8, 10, 12, 14, and 16), good complexing agents for copper(II), has been used in this work to investigate the role of hydrophobic interactions on the kinetics of complexation in micellar media. Apparent rate constants for complex formation (k_f^{app}) and dissociation (k_d^{app}) obtained from stopped-flow experiments are reported in different micellar systems (CTAB, SDS, and $C_{12}EO_6$), showing important variations with the value of n. These results which mainly concerned the protonated form of the extractant molecules (pH 3.5) have permitted precise determination of the role played by the electrostatic interactions. k_f^{app} is found to decrease more than 20 times in CTAB and about 10 times in $C_{12}EO_6$ for n changing from 1 to 16. The influence of copper(II) and surfactant concentrations on the observed rate constants is interpreted in terms of partition coefficients which have been independently determined from dialysis experiments. The reaction is found to be insensitive to surfactant concentration for n = 1, 4, and 8 in CTAB and only for n = 1 and 4 for $C_{12}EO_6$. The activation parameters are determined for n = 4 and 14 in water, in CTAB, and in $C_{12}EO_6$. The effect of the addition of alcohol and oil to form different o/w microemulsions is finally reported.

Introduction

The usefulness of organized systems, such as micelles and microemulsions, in metal extraction processes has been amply demonstrated in the recent literature,[1-24] where a constantly growing number of papers can be observed in this field. The present paper and the following one in this issue will be concerned with an important aspect of the potentialities of these systems, namely, their ability to play the part of the organic phase in a classical solvent extraction process. Indeed, the hydrophobic core of the micellar particles can solubilize hydrophobic extractants, and in this respect the micellar pseudophase can act similarly to the organic phase in a classical biphasic extraction. Recent data have shown that although micellar solutions are purely isotropic, phase separation is not a real problem since it can be achieved by means of ultrafiltration techniques.[24]

The latter observation is very important as it substantiates the efforts that have been done in the past few years in one of our laboratories to demonstrate the interest of using micelles and microemulsions as model extraction systems.[7,8] From a fundamental point of view, micellar media are very attractive because their microheterogeneous structure guarantees a perfect tran-

sparency to light. This property has invaluable advantages for physicochemical studies, especially for kinetic and mechanistic studies resting on optical methods. On the other hand, from an applied point of view, it becomes thinkable of achieving metal ion extraction in media which are up to 99% aqueous, which, viewed from the environmental side, is also quite attractive.

The aim of the present series of papers was two-fold. First, we wanted to investigate the role of the hydrophilic/hydrophobic character of the complexing molecules on the kinetics of complexation of metal ions in micellar media. A series of 6-(alkylamino)methyl-2-(hydroxymethyl)pyridines, which are good complexing agents for copper(II),[25,26] has been used for this purpose, varying their hydrophilic lipophilic balance (HLB) from very hydrophilic to very hydrophobic. Our second objective was to better understand the role of the interfacial kinetics, which constitutes a much debated question in the current literature.[27-34] As far as micellar systems are concerned this refers to the microscopic interface separating the micellar pseudophase and the bulk aqueous phase, which can be assumed to mimic in some way macroscopic liquid–liquid interfaces. Different approaches of this complicated problem will be considered.

The part eventually contributed by interfacial processes to the overall complexation kinetics is expected to be affected by changing the HLB of the complexing molecule and also by varying the nature of the surfactant so as to change the sign of the electric charges borne by the micelles. Both points will be examined in