

Thermodynamics of the System $\text{InCl}_3\text{--HCl--H}_2\text{O}$ at 25 °C

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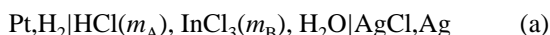
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A comprehensive equation for the thermodynamic properties of the system $\text{InCl}_3\text{--HCl--H}_2\text{O}$ at 25 °C in the ion-interaction (Pitzer) equation form is generated on the basis of a very recent and comprehensive array of electrochemical cell measurements of the HCl activity, together with older published measurements of the activity of InCl_3 in mixtures with 0.02 *m* HCl. Alternate equations with and without explicit consideration of the ion pair InCl_2^+ as a separate species are tested. Excellent agreement is obtained on either formulation between calculated and measured activities, although considerable uncertainty remains concerning the standard potential for the In electrode. Suggestions are made for additional experiments to reduce this uncertainty.

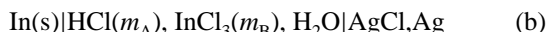
Introduction

Aqueous InCl_3 differs markedly from other $\text{M}^{3+}\text{--Cl}^-$ systems such as AlCl_3 , LaCl_3 , etc., in that In^{3+} has a strong association with Cl^- to InCl_2^+ and a very strong tendency to hydrolyze to InOH^{2+} . Also, if solid indium is present, possibly as an electrode, the reduction reaction forming In^+ must be considered. Thus, the thermodynamics of the In^{3+} , Cl^- , H_2O system is both interesting and challenging.

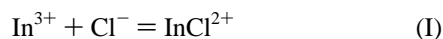
By making measurements on the system $\text{InCl}_3\text{--HCl--H}_2\text{O}$ the hydrolysis can be controlled or eliminated. Measurements were made and have been reported recently¹ for the electrochemical cell



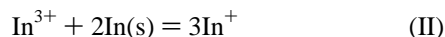
Published^{2,3} values are available for the cell



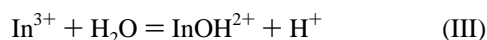
The present paper presents an analysis of all these results in terms of the ion-interaction (Pitzer) equations.^{4,5} Since the data for cell b extend only to an ionic strength of 0.33 mol kg^{-1} , the present equation has limitations for some properties outside of this range, but its refinement is straightforward when cell b is measured at larger molality. And the present range is sufficient to show clearly the tendency toward ion association to InCl_2^+ .



The results for cell b at the lowest molality are examined for possible deviation arising from the reaction



Equilibrium constant values^{6,7} reported for the hydrolysis reaction



and for the association reaction I are considered in the calculations. Conductance data⁸ are also considered and are found to be generally consistent with respect both to ion association and to hydrolysis effects.

Several investigators have studied aqueous $\text{In}_2(\text{SO}_4)_3$.^{9–12} This system is even more complex with more severe hydrolysis and complexation. Indeed, Leitzke and Stoughton¹² conclude that the species InSO_4^+ and $\text{In}(\text{SO}_4)_2^-$ dominate except at extreme dilution. But at high dilution InOH^{2+} will be important. Thus, In^{3+} may never be the dominant species, and little can be learned about its properties from the sulfate studies.

Several structural methods have been applied to aqueous InCl_3 . At high concentration all indicate that the species InCl_2^+ with a symmetrical linear structure is dominant.^{13,14} Our equations are designed to represent this species, but it is not expected to be important at low concentrations.

Equations

The ion-interaction equations for a multisolute system as first proposed in 1974^{4b} and widely used since⁵ are adopted. But the exact form to represent the association to InCl_2^+ must be considered. If the maximum degree of association is moderate, the method^{4c} used for MgSO_4 and other +2 sulfates is simple; hence, it was tested and found to be satisfactory. No separate species is introduced, but a specially designed binary interaction term is added.

The association is so strong, however, that it seemed worthwhile to make an alternate calculation with InCl_2^+ as an explicit species and an equilibrium constant *K* for formation in reaction I. This pattern has been used for the HSO_4^- ion, along with H^+ and SO_4^{2-} in various treatments.^{15,16} For the present system, this introduces ion-interaction terms that can indicate the amount of further association to InCl_2^+ . Thus, the results of this alternate formulation indicate more clearly the actual proportions of In^{3+} , InCl_2^+ , and InCl_2^+ present at various compositions.

Formulation I without InCl_2^+ as a Separate Species. For this calculation, the composition is expressed in terms of the unassociated ionic strength and ionic strength fractions as follows:

$$m_A = m(\text{HCl}) \quad (1\text{a})$$

$$m_B = m(\text{InCl}_3) \quad (1\text{b})$$

$$I = m_A + 6m_B \quad (1\text{c})$$

$$Y_A = m_A/I \quad (1\text{d})$$

$$Y_B = 6m_B/I \quad (1\text{e})$$

The complete equations for $\ln \gamma_{\text{HCl}}$ and $\ln \gamma_{\text{InCl}_3}$ are given in the Appendix as eqs A1 and A2. For formulation I, all terms

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involving the species InCl^{2+} are omitted. The ion molalities in eqs A1 and A2 are given by the simple relationships

$$m_{\text{H}} = m_{\text{A}} = IY_{\text{A}} \quad (2a)$$

$$m_{\text{In}} = m_{\text{B}} = IY_{\text{B}}/6 \quad (2b)$$

$$m_{\text{Cl}} = m_{\text{A}} + 3m_{\text{B}} = I(1 - Y_{\text{B}}/2) \quad (2c)$$

Additional detailed relationships are given in eqs A4–A9. The terms in $\beta_{\text{In,Cl}}^{(0)}$, $\beta_{\text{In,Cl}}^{(1)}$, $\theta_{\text{In,H}}$, $C_{\text{In,Cl}}$, and $\psi_{\text{In,H,Cl}}$ are the usual second- and third-order interaction terms between the indicated ions and need no further comment. The term in $\beta_{\text{In,Cl}}^{(2)}$ is the special term representing approximately the association to InCl^{2+} .

In eqs A5 and A6, ${}^E\theta_{ij}(\text{I})$ and ${}^E\theta'_{ij}(\text{I})$ are the theoretical electrostatic functions for the unsymmetrical mixing^{4d,5} and depend only on the charges of the ions i and j , the total ionic strength, and the solvent properties. The parameter b has its universal value 1.2. The parameter α_1 retains the standard value 2.0 for HCl, of course. For InCl_3 alternate values were tested for α_1 and α_2 . The best fit was obtained for the standard 2.0 for α_1 and 7.0 for α_2 . These last values differ from the 1.4 and 12 selected for the 2–2 electrolytes, but a difference between 3–1 and 2–2 electrolytes is reasonable.

The Nernst equation then represents the relationship between the emf of cell a, E_{a} , and the activity coefficient of HCl in the presence of indium chloride, and between the emf of cell b, E_{b} , and activity coefficient of InCl_3 in the presence of HCl.

$$E_{\text{a}} = E_{\text{a}}^0 - \frac{2RT}{F} \ln \gamma_{\text{HCl}} - \frac{RT}{F} \ln [m_{\text{H}} m_{\text{Cl}}] \quad (3)$$

$$E_{\text{b}} = E_{\text{b}}^0 - \frac{4RT}{3F} \ln \gamma_{\text{InCl}_3} - \frac{RT}{3F} \ln [m_{\text{In}} m_{\text{Cl}}^3] \quad (4)$$

where E_{a}^0 and E_{b}^0 are the standard potentials of cell a and cell b, respectively, with F the Faraday constant.

The parameters for HCl, $\beta_{\text{H,Cl}}^{(0)}$, $\beta_{\text{H,Cl}}^{(1)}$, $C_{\text{H,Cl}}$, and E_{a}^0 , were taken from the previous work.^{1,4,5} The adjustable parameters for formulation I are $\beta_{\text{In,Cl}}^{(0)}$, $\beta_{\text{In,Cl}}^{(1)}$, $\beta_{\text{In,Cl}}^{(2)}$, $\theta_{\text{In,H}}$, $C_{\text{In,Cl}}$, $\psi_{\text{In,H,Cl}}$, and E_{b}^0 .

Formulation II Including InCl^{2+} as an Additional Species. The complete equations now become more complex and involve more parameters, some of which are effectively redundant or may be negligible. Calculations now involve successive cycles of approximation. The ionic strength now varies with the degree of association and is designated I_{a} to distinguish it from the I without association as used in reporting experimental data.¹ All of this is described in the Appendix where samples are given for several test values of the equilibrium constant for reaction I,

$$K = \frac{m_{\text{InCl}}}{m_{\text{In}} m_{\text{Cl}}} \frac{\gamma_{\text{InCl}}}{\gamma_{\text{In}} \gamma_{\text{Cl}}} \quad (5)$$

It was found that K for the best overall fit was very large and that m_{In} was then very small for all experimental compositions. Hence, for the present data base it is a good approximation to set K to infinity, whereupon m_{In} is always zero. Then there is a great simplification and parameter optimization is direct and simple.

Formulation III Approximating Complete Association to InCl^{2+} . Now the InCl_3 becomes a 2–1 electrolyte of $\text{InCl}^{2+} + 2\text{Cl}^-$ with its activity coefficient given by eq A3. Equations A1 and A3 simplify greatly, and the following simple relations apply

$$m_{\text{H}} = m_{\text{A}} = IY_{\text{A}} \quad (6a)$$

$$m_{\text{InCl}} = m_{\text{B}} = IY_{\text{B}}/6 \quad (6b)$$

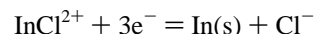
$$m_{\text{Cl}} = m_{\text{A}} + 2m_{\text{B}} = I(1 - 2Y_{\text{B}}/3) \quad (6c)$$

$$I_{\text{a}} = m_{\text{A}} + 3m_{\text{B}} = I(1 - Y_{\text{B}}/2) \quad (6d)$$

The same second- and third-order interaction terms are present, but now they represent interactions of the InCl^{2+} ion with Cl^- and H^+ . The $\beta_{\text{InCl,Cl}}^{(2)}$ term is retained; it represents a further association



The cell a reaction and eq 3 remain unchanged, but note that m_{Cl} is changed: eq 6c instead of eq 2c. Also, the reaction in cell b at the In electrode becomes



Then, instead of eq 4, the cell potential E_{b} is given by

$$E_{\text{b}} = E_{\text{c}}^0 - \frac{RT}{F} \ln \gamma(\text{InCl}^{2+}, 2\text{Cl}^-) - \frac{RT}{3F} \ln [m_{\text{InCl}} m_{\text{Cl}}^2] \quad (7)$$

The new standard potential E_{c}^0 is related to E_{b}^0 by

$$E_{\text{c}}^0 = E_{\text{b}}^0 + (RT/3F) \ln K \quad (8)$$

Experimental Data and Parameter Evaluation

In general, measurements^{2,3} of cell b with the indium electrode are subject to uncertainty from spontaneous reaction of indium metal with water. This was examined carefully by Hampson and Piercy,³ who found that their addition of 0.02 mol kg^{-1} of HCl was adequate to yield good results. Also, their data agree very well with the earlier measurements of Hakomori.² But all of these results are for a single molality of HCl, 0.02 mol kg^{-1} . Thus, it is impossible to evaluate the five binary parameters, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, θ , and E_{b}^0 from their data. At their maximum ionic strength of 0.33 mol kg^{-1} , $m_{\text{B}} = 0.0527$, the tertiary parameters are presumably negligible. Hakomori's estimate of 558 mV for E_{b} is reasonable with an uncertainty of a few millivolts, but nothing further can be determined.

The measurements of Roy et al.¹ for cell a are very extensive and range from 0.05 to 3.5 in I and 0.0 to 0.9 in Y_{B} . Taken alone, they yield values for most parameters. But for cell a the composition dependence of $\beta_{\text{In,Cl}}^{(0)}$ and $\theta_{\text{In,H}}$ is the same; hence, only the combination ($\theta_{\text{In,H}} + \beta_{\text{In,Cl}}^{(0)}$) can be obtained. Also, there is so little difference in the composition dependency in eq A1 for $\psi_{\text{H,In,Cl}}$ and $C_{\text{In,Cl}}$ that their separate evaluation is not possible. And obviously, cell a cannot yield E_{b}^0 .

Statistical adjustment of all parameters in formulation I to fit simultaneously the data from all three sources yields the parameters in Table 1. Table 2 and Figure 1 compare the calculated E_{b} values for cell b with the experimental values. The agreement is good. The large negative value of $\beta^{(2)} = -68.5$ indicates strong association to InCl^{2+} . The value for the standard potential E_{b}^0 is 559.5 mV; it is uncertain in that there is a substantial implied extrapolation of ionic strength from 0.02 to 0. This is discussed below.

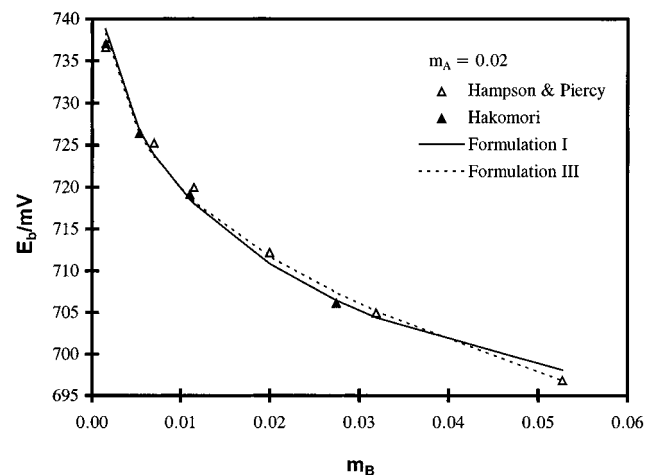
The comparison with the numerous cell a measurements is shown in Figure 2 as calculated curves and experimental points. Also, Table 2 gives the numerical values in the very dilute range. Again, the agreement is good with most deviations less than 1 mV and a maximum deviation of 1.7 mV. Now the redundancy between $\beta_{\text{In,Cl}}^{(0)}$ and $\theta_{\text{H,In}}$ is broken, and the separate values are

TABLE 1: Ion-Interaction Parameters for Formulation I in Eqs A1 and A2

$\beta_{\text{HCl}}^{(0)}/\text{kg mol}^{-1}$	0.1775 ^a	$\beta_{\text{InCl}}^{(0)}/\text{kg mol}^{-1}$	-2.813
$\beta_{\text{InCl}}^{(1)}/\text{kg mol}^{-1}$	0.2945 ^a	$\beta_{\text{InCl}}^{(1)}/\text{kg mol}^{-1}$	9.077
		$\beta_{\text{InCl}}^{(2)}/\text{kg mol}^{-1}$	-68.51
		${}^s\theta_{\text{InH}}/\text{kg mol}^{-1}$	2.150
$C_{\text{HCl}}/\text{kg}^2 \text{ mol}^{-2}$	0.0004 ^a	$C_{\text{InCl}}/\text{kg}^2 \text{ mol}^{-2}$	0.051
		$\psi_{\text{InHCl}}/\text{kg}^2 \text{ mol}^{-2}$	0.094

^a From ref 5.**TABLE 2: Experimental and Calculated Potentials for Formulations I and III**

m_A	m_B	E_{exp} (mV)	formulation I		formulation III	
			E_{cal} (mV)	ΔE (mV)	E_{cal} (mV)	ΔE (mV)
In Electrode, Cell b						
0.02	0.001 50	736.59 ^a	738.79	−2.2	738.20	−1.6
0.02	0.001 515	737.03 ^b	738.70	−1.7	738.11	−1.1
0.02	0.005 332	726.44 ^b	726.72	−0.3	726.32	0.1
0.02	0.006 97	725.23 ^a	723.86	1.4	723.64	1.6
0.02	0.011 04	719.11 ^b	718.56	0.6	718.78	0.3
0.02	0.011 50	719.96 ^a	718.06	1.9	718.33	1.6
0.02	0.020 00	712.19 ^a	710.85	1.3	711.72	0.5
0.02	0.027 44	706.13 ^b	706.47	−0.3	707.40	−1.3
0.02	0.031 90	704.96 ^a	704.38	0.6	705.17	−0.2
0.02	0.052 70	696.82 ^a	698.08	−1.3	696.78	0.0
H ₂ Electrode, Cell a						
0.044 93	0.000 85	390.47 ^c	390.83	−0.4	390.92	−0.4
0.034 97	0.002 50	400.60 ^c	401.58	−1.0	402.00	−1.4
0.030 02	0.003 33	407.01 ^c	407.87	−0.9	408.58	−1.6
0.025 01	0.004 17	414.20 ^c	415.11	−0.9	416.23	−2.0
0.020 26	0.004 96	423.31 ^c	423.11	0.2	424.78	−1.5
0.015 01	0.005 83	433.41 ^c	433.87	−0.5	436.38	−3.0
0.005 02	0.007 50	468.79 ^c	468.48	0.3	473.60	−4.8

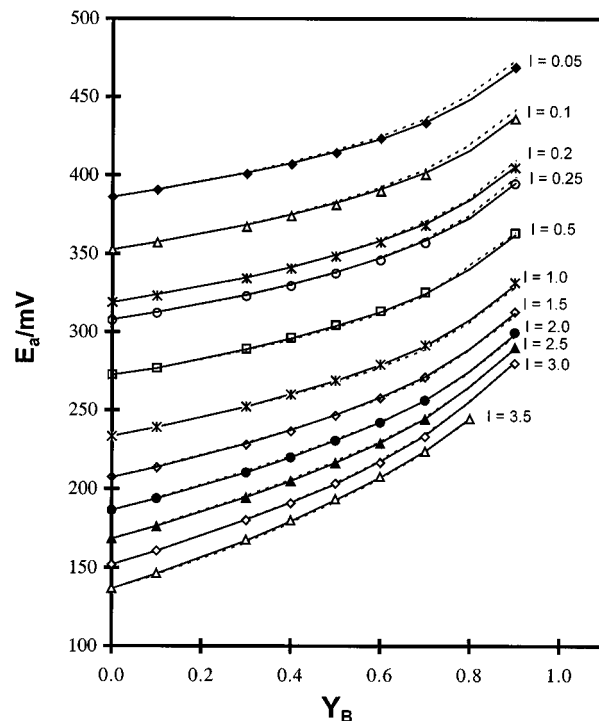
^a Hampson and Piercy.³ ^b Hakomori.² ^c Roy *et al.*¹**Figure 1.** Comparison of the experimental emf values for cell b, symbols, with the calculated curves, continuous and dashed for formulations I and III, respectively. Further details are in Table 2.

well determined. For the third virial parameters C_{InCl} and ψ_{InHCl} , however, the uncertainty remains large since the only measurements from cell b are at very low ionic strength. As seen in Table 1, each of these third-order parameters is small. And if one is removed from the equation and the remaining parameters are optimized, the overall statistical error is not increased significantly. Indeed, a reasonably good fit is obtained without either of these parameters. Thus, the three-particle-interaction parameters involving In^{3+} remain essentially unknown pending measurements on cell b at higher ionic strength.

A similar adjustment of parameters for formulation III (complete association of In^{3+} to InCl_2^+) yields the parameters in Table 3. Table 2 and Figures 1 and 2 include the resulting

TABLE 3: Ion-Interaction Parameters for Formulation III

$\beta_{\text{HCl}}^{(0)}/\text{kg mol}^{-1}$	0.1775 ^a	$\beta_{\text{InCl,Cl}}^{(0)}/\text{kg mol}^{-1}$	-3.480
$\beta_{\text{HCl}}^{(1)}/\text{kg mol}^{-1}$	0.2945 ^a	$\beta_{\text{InCl,Cl}}^{(1)}/\text{kg mol}^{-1}$	16.24
		$\beta_{\text{InCl,Cl}}^{(2)}/\text{kg mol}^{-1}$	-59.32
		${}^s\theta_{\text{InCl,H}}/\text{kg mol}^{-1}$	0.5959
$C_{\text{HCl}}/\text{kg}^2 \text{ mol}^{-2}$	0.0004 ^a	$C_{\text{InCl,Cl}}/\text{kg}^2 \text{ mol}^{-2}$	0.7230
		$\psi_{\text{InH,Cl}}/\text{kg}^2 \text{ mol}^{-2}$	-0.6235

^a From ref 5.**Figure 2.** Experimental (symbols) and the calculated (curves) for the emf of cell a at various ionic strengths, I , and ionic strength fractions of InCl_3 , Y_B , as defined by eqs 1c and 1e.

E_a and E_b values along with those from formulation I and from experiments. The agreement for E_b in Table 2 for formulation III is even better than that for formulation I, although the difference is small. For the full array of H_2 electrode measurements the comparison is shown by the dashed lines in Figure 2, while Table 2 includes values for the dilute range. Again, the agreement is reasonably good, in general, but there are serious deviations for formulation III for the examples with very small $m_A = m(\text{HCl})$. This can be ascribed to the assumption of complete association to InCl_2^+ . The large, negative value of $\beta^{(2)} = -59 \text{ kg mol}^{-1}$ indicates substantial further association of InCl_2^+ to InCl_2^+ , which is in agreement with the structural measurements.^{13,14} As before, the third-order interaction parameters C and ψ are not well determined with the present data base.

Several calculations with formulation II using a range of assumed values of K are described in the Appendix. These yield essentially the same generally good agreements as are shown in Figures 1 and 2 and in Table 2. And they are especially pertinent with respect to the large deviations of formulation III for cell a for very dilute solutions.

Standard Potential for the In Electrode. Table 4 gives the values of E_b^0 and E_c^0 as defined in eqs 4, 7, and 8. Also given are the assumed values of the equilibrium constant for association K . The value $K = 225 \text{ kg mol}^{-1}$ is that selected by Hepler and Hugus⁶ from analysis of the pH measurements of Moeller.⁷

TABLE 4: Standard Potential Values for Cell b from Calculations Based on Different Speciation Models

$K/\text{kg mol}^{-1}$	137 ^a	150	225	265	∞
E_b^0/mV		597.2	598.0	598.3	600.1
E_b^0/mV	559.5	554.3	551.6	550.5	
$E^0(\text{In}^{3+}, \text{In})/\text{mV}$	336.9	331.7	329.0	327.9	

^a Formulation I implies $K = -2\beta^{(2)}$ in the limit at low molality.

Discussion of Results

The most interesting aspect of these results is the nearly equal quality of fit for very different formulations of the equation and for differences in the assumed or implied equilibrium constant for association. That detailed parameters vary is expected, but there are surprisingly large differences in the standard potential E_b^0 for cell b. This indicates that the experimental data base is not broad enough for cell b in the very dilute range that guides the extrapolation to zero ionic strength. At this point, we cannot recommend an accurate value for E_b^0 . Rather, the value for E_b^0 should be taken, along with values for other parameters, for a particular formulation and value of K ; then the predictive calculations will be valid within the range of the present data base.

All of the reported measurements of cell b are for the single H^+ molality of 0.02. This concentration is required for reliable measurements of the In electrode;³ hence, it cannot be decreased. But future measurements at somewhat higher molalities of HCl should reduce the uncertainty in the standard potential. From Table 6 one notes that the maximum deviations for cell a in the dilute range are smallest for the case $K = 150$. Thus, we believe that E_b^0 exceeds 554 mV and is probably within the range between 554 and the 559.5 mV value from formulation I.

This leaves the situation for the standard potential for the $\text{In}^{3+} + 3\text{e}^- = \text{In(s)}$ half-cell essentially unchanged from that of Hakomori² or Hampson and Piercy,³ who gave alternate interpretations of their data yielding E^0 values in or near the same range, 332–337 mV, that corresponds to that given above for E_b^0 .

Formulation I without explicit speciation was adequate to fit the present data base and gave a clear indication of strong association to InCl^{2+} , but it gave no clear information about the second step of association to InCl_2^+ . Formulation II is superior in providing information about speciation, although there is considerable variation of $\beta^{(2)}$ with the choice of K . While

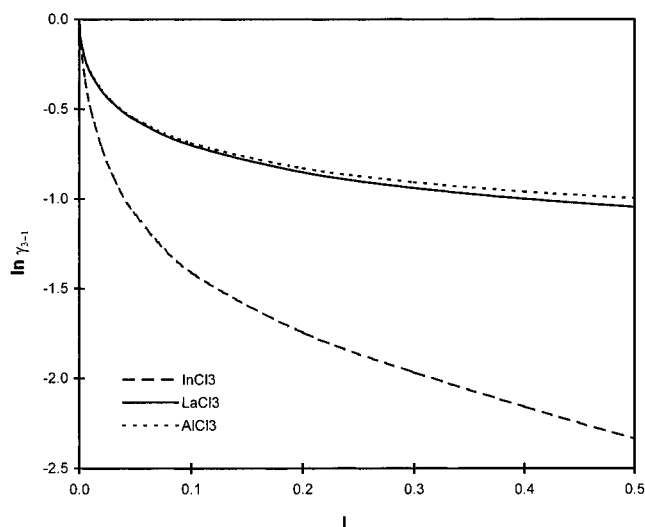


Figure 3. Comparison of the activity coefficients of InCl_3 and those of $\text{LaCl}_3(\text{aq})$ and $\text{AlCl}_3(\text{aq})$. The activity coefficients were calculated from eq A2 with $m_{\text{InCl}} = 0$ and ion-interaction parameters in formulation I.

formulation I may continue to be useful for empirical representation when additional measurements are available, calculations by formulation II will be of greater interest in relation to structural and other information.

Also, it will be very difficult to determine accurately a property of In^{3+} because it becomes or remains a very minor species along most paths of dilution. Thus, in the absence of added H^+ , hydrolysis occurs, and InOH^{2+} is the dominant ion instead of In^{3+} . In the present system, the H^+ is accompanied by Cl^- , and then the InCl^{2+} dominates over In^{3+} . A possibility that merits consideration is the system $\text{InCl}_3\text{--HClO}_4\text{--H}_2\text{O}$. It involves an additional ion, as compared to the present system, but it seems likely that the tendency of $\text{In}^{3+} + \text{ClO}_4^-$ to associate is much less than for Cl^- . But with some Cl^- present, the same two cells could be used for measurements.

The emf values in Table 2 were examined for any deviation at very small $m(\text{In}^{3+})$, indicating reaction II with In(s) forming In^+ . The ΔE values at $m_B = 0.0015$ are in that direction but do not exceed experimental uncertainty; hence, $m(\text{In}^+)$ must be very small or zero.

Figure 3 compares the activity coefficient of InCl_3 , as

TABLE 5: Ion-Interaction Parameters in Eqs A1, A2, and A3 for Three Formulations

	formulation I	formulation II			formulation III
		$K = 150$	$K = 225$	$K = 265$	
$\beta_{\text{In,Cl}}^{(0)}/\text{kg mol}^{-1}$	-2.813	0.9 ^a	0.9 ^a	0.9 ^a	
$\beta_{\text{In,Cl}}^{(1)}/\text{kg mol}^{-1}$	9.077	8.4 ^a	8.4 ^a	8.4 ^a	
$\beta_{\text{In,Cl}}^{(2)}/\text{kg mol}^{-1}$	-68.51				
${}^s\theta_{\text{In,H}}/\text{kg mol}^{-1}$	2.150	0 ^b	0 ^b	0 ^b	
${}^s\theta_{\text{In,InCl}}/\text{kg mol}^{-1}$		0 ^b	0 ^b	0 ^b	
$C_{\text{In,Cl}}/\text{kg}^2 \text{mol}^{-2}$	0.051	0 ^b	0 ^b	0 ^b	
$\psi_{\text{In,H,Cl}}/\text{kg}^2 \text{mol}^{-2}$	0.094	0 ^b	0 ^b	0 ^b	
$\psi_{\text{In,InCl,Cl}}/\text{kg}^2 \text{mol}^{-2}$		0 ^b	0 ^b	0 ^b	
$\beta_{\text{InCl,Cl}}^{(0)}/\text{kg mol}^{-1}$		-4.014	-3.868	-3.819	-3.480
$\beta_{\text{InCl,Cl}}^{(1)}/\text{kg mol}^{-1}$		19.41	18.54	18.25	16.24
$\beta_{\text{InCl,Cl}}^{(2)}/\text{kg mol}^{-1}$		-71.19	-67.95	-66.86	-59.32
${}^s\theta_{\text{InCl,H}}/\text{kg mol}^{-1}$		0.6243	0.6159	0.6131	0.5959
$C_{\text{InCl,Cl}}/\text{kg}^2 \text{mol}^{-2}$		0.8815	0.8384	0.8238	0.7230
$\psi_{\text{InCl,H,Cl}}/\text{kg}^2 \text{mol}^{-2}$		-0.8081	-0.7603	-0.7442	-0.6325
$\beta_{\text{H,Cl}}^{(0)}/\text{kg mol}^{-1}$	0.1775 ^c	0.1775 ^c	0.1775 ^c	0.1775 ^c	0.1775 ^c
$\beta_{\text{H,Cl}}^{(1)}/\text{kg mol}^{-1}$	0.2945 ^c	0.2945 ^c	0.2945 ^c	0.2945 ^c	0.2945 ^c
$C_{\text{H,Cl}}/\text{kg}^2 \text{mol}^{-2}$	0.0004 ^c	0.0004 ^c	0.0004 ^c	0.0004 ^c	0.0004 ^c
$\alpha_1/\text{kg}^{1/2} \text{mol}^{-1/2}$	2.0	2.0	2.0	2.0	2.0
$\alpha_2/\text{kg}^{1/2} \text{mol}^{-1/2}$	7.0	6.0	6.0	6.0	6.0

^a Taken from ref 5 as the average values for 3–1 electrolytes. ^b Set to be zero since m_{In} is very small. ^c Taken from ref 5.

TABLE 6: Experimental and Calculated Potentials for Formulation II Examples

m_A	m_B	$K = 150$		$K = 225$		$K = 265$	
		m_{in}	ΔE (mV)	m_{in}	ΔE (mV)	m_{in}	ΔE (mV)
In Electrode, Cell b							
0.02	0.001 50	0.000 23	-1.8	0.000 17	-1.7	0.000 15	-1.7
0.02	0.001 515	0.000 23	-1.2	0.000 17	-1.2	0.000 15	-1.2
0.02	0.005 332	0.000 57	0.2	0.000 42	0.2	0.000 37	0.2
0.02	0.006 970	0.000 65	1.7	0.000 48	1.7	0.000 42	1.7
0.02	0.011 04	0.000 74	0.4	0.000 54	0.4	0.000 47	0.4
0.02	0.011 50	0.000 74	1.7	0.000 54	1.7	0.000 48	1.7
0.02	0.020 00	0.000 72	0.4	0.000 53	0.4	0.000 46	0.4
0.02	0.027 44	0.000 64	-1.4	0.000 47	-1.4	0.000 42	-1.3
0.02	0.031 90	0.000 59	-0.3	0.000 44	-0.3	0.000 39	-0.3
0.02	0.052 70	0.000 42	0.1	0.000 32	0.1	0.000 28	0.1
H ₂ Electrode, Cell a							
0.044 93	0.000 85	0.000 04	-0.5	0.000 03	-0.5	0.000 03	-0.5
0.034 98	0.002 50	0.000 17	-1.5	0.000 12	-1.4	0.000 11	-1.4
0.030 02	0.003 33	0.000 26	-1.6	0.000 19	-1.6	0.000 17	-1.6
0.025 01	0.004 17	0.000 38	-2.0	0.000 28	-2.0	0.000 25	-2.0
0.020 26	0.004 96	0.000 54	-1.2	0.000 40	-1.3	0.000 35	-1.3
0.015 01	0.005 83	0.000 78	-2.4	0.000 58	-2.6	0.000 51	-2.6
0.005 02	0.007 50	0.001 53	-2.6	0.001 16	-3.1	0.001 03	-3.3

calculated in formulation I without hydrolysis, with curves for AlCl₃ and LaCl₃. Curves for most other 3-1 chlorides^{5,18} are intermediate between those two or are very close. The large decrease caused by association to InCl₂⁺ is apparent.

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Appendix

For the HCl(A)-InCl₃(B)-H₂O system, when In³⁺, InCl₂⁺, H⁺, and Cl⁻ are considered to be present at the equilibrium, the activity coefficients of HCl and InCl₃ can be expressed as

$$\begin{aligned} \ln \gamma_{HCl} = \ln \gamma(H^+, Cl^-) = f^\gamma + \frac{m_H m_{Cl}}{I_a} [\exp(-x_1) - \\ g(x_1)] \beta_{H,Cl}^{(1)} + (m_H + m_{Cl}) [\beta_{H,Cl}^{(0)} + \beta_{H,Cl}^{(1)} g(x_1)] + \left(m_H m_{Cl} + \right. \\ \left. \frac{Z}{2} m_H + \frac{Z}{2} m_{Cl} \right) C_{H,Cl} + m_{In} \beta_{In,Cl}^{(0)} + \left\{ \frac{m_{In} m_{Cl}}{I_a} [\exp(-x_1) - \right. \\ \left. g(x_1)] + m_{In} g(x_1) \right\} \beta_{In,Cl}^{(1)} + \left\{ \frac{m_{In} m_{Cl}}{I_a} [\exp(-x_2) - g(x_2)] + \right. \\ \left. m_{In} g(x_2) \right\} \beta_{In,Cl}^{(2)} + m_{InCl} \beta_{InCl,Cl}^{(0)} + \left\{ \frac{m_{InCl} m_{Cl}}{I_a} [\exp(-x_1) - \right. \\ \left. g(x_1)] + m_{InCl} g(x_1) \right\} \beta_{InCl,Cl}^{(1)} + \left\{ \frac{m_{InCl} m_{Cl}}{I_a} [\exp(-x_2) - \right. \\ \left. g(x_2)] + m_{InCl} g(x_2) \right\} \beta_{InCl,Cl}^{(2)} + m_{In} m_{InCl} {}^E \theta'_{In,InCl} + \\ m_{In} m_H {}^E \theta'_{In,H} + m_{InCl} m_H {}^E \theta'_{InCl,H} + m_{In} ({}^s \theta_{In,H} + {}^E \theta_{In,H}) + \\ m_{InCl} ({}^s \theta_{InCl,H} + {}^E \theta_{InCl,H} + {}^E \theta_{InCl,H}) + \left(m_{Cl} + \frac{Z}{2} \right) m_{In} C_{In,Cl} + \\ \left(m_{Cl} + \frac{Z}{2} \right) m_{InCl} C_{InCl,Cl} + \frac{1}{2} m_{In} (m_H + m_{Cl}) \psi_{In,H,Cl} + \\ \frac{1}{2} m_{InCl} (m_H + m_{Cl}) \psi_{InCl,H,Cl} + \frac{1}{2} m_{In} m_{InCl} \psi_{In,InCl,Cl} \quad (A1) \end{aligned}$$

$$\begin{aligned} \ln \gamma_{InCl_3} = \ln \gamma(In^{3+}, 3Cl^-) = 3f^\gamma + \frac{3m_H m_{Cl}}{I_a} [\exp(-x_1) - \\ g(x_1)] \beta_{H,Cl}^{(1)} + \frac{3m_H}{2} [\beta_{H,Cl}^{(0)} + \beta_{H,Cl}^{(1)} g(x_1)] + \frac{3m_H}{4} (2m_{Cl} + \\ Z) C_{H,Cl} + \frac{1}{2} (3m_{In} + m_{Cl}) \beta_{In,Cl}^{(0)} + \left\{ \frac{3m_{In} m_{Cl}}{I_a} [\exp(-x_1) - \right. \\ \left. g(x_1)] + \frac{1}{2} (3m_{In} + m_{Cl}) g(x_1) \right\} \beta_{In,Cl}^{(1)} + \left\{ \frac{3m_{In} m_{Cl}}{I_a} [\exp(-x_2) - \right. \\ \left. g(x_2)] + \frac{1}{2} (3m_{In} + m_{Cl}) g(x_2) \right\} \beta_{In,Cl}^{(2)} + \frac{3}{2} m_{InCl} \beta_{InCl,Cl}^{(0)} + \\ \left\{ \frac{3m_{InCl} m_{Cl}}{I_a} [\exp(-x_1) - g(x_1)] + \frac{3}{2} m_{InCl} g(x_1) \right\} \beta_{InCl,Cl}^{(1)} + \\ \left\{ \frac{3m_{InCl} m_{Cl}}{I_a} [\exp(-x_2) - g(x_2)] + \frac{3}{2} m_{InCl} g(x_2) \right\} \beta_{InCl,Cl}^{(2)} + \\ 3m_{In} m_{InCl} {}^E \theta'_{In,InCl} + 3m_{In} m_H {}^E \theta'_{In,H} + 3m_{InCl} m_H {}^E \theta'_{InCl,H} + \\ \frac{1}{2} m_H ({}^s \theta_{In,H} + {}^E \theta_{In,H}) + \frac{1}{2} m_{InCl} ({}^s \theta_{In,InCl} + {}^E \theta_{In,InCl}) + \\ \frac{1}{4} (6m_{In} m_{Cl} + 3Zm_{In} + Zm_{Cl}) C_{In,Cl} + \frac{1}{4} (6m_{InCl} m_{Cl} + \\ 3Zm_{InCl}) C_{InCl,Cl} + \frac{1}{4} m_H (3m_{In} + m_{Cl}) \psi_{In,H,Cl} + \\ \frac{3}{4} m_{InCl} m_H \psi_{InCl,H,Cl} + \frac{1}{4} m_{InCl} (3m_{In} + m_{Cl}) \psi_{In,InCl,Cl} \quad (A2) \end{aligned}$$

$$\begin{aligned} \ln \gamma(InCl^{2+}, 2Cl^-) = 2f^\gamma + \frac{2m_H m_{Cl}}{I_a} [\exp(-x_1) - \\ g(x_1)] \beta_{H,Cl}^{(1)} + \frac{4m_H}{3} [\beta_{H,Cl}^{(0)} + \beta_{H,Cl}^{(1)} g(x_1)] + \frac{2m_H}{3} (2m_{Cl} + \\ Z) C_{H,Cl} + \frac{4}{3} m_{In} \beta_{In,Cl}^{(0)} + \left\{ \frac{2m_{In} m_{Cl}}{I_a} [\exp(-x_1) - g(x_1)] + \right. \\ \left. \frac{4}{3} m_{In} g(x_1) \right\} \beta_{In,Cl}^{(1)} + \left\{ \frac{2m_{In} m_{Cl}}{I_a} [\exp(-x_2) - g(x_2)] + \right. \\ \left. \frac{4}{3} m_{In} g(x_2) \right\} \beta_{In,Cl}^{(2)} + \frac{2}{3} (2m_{InCl} + m_{Cl}) \beta_{InCl,Cl}^{(0)} + \\ \left\{ \frac{2m_{InCl} m_{Cl}}{I_a} [\exp(-x_1) - g(x_1)] + \frac{2}{3} (2m_{InCl} + \right. \\ \left. m_{Cl}) g(x_1) \right\} \beta_{InCl,Cl}^{(1)} + \left\{ \frac{2m_{InCl} m_{Cl}}{I_a} [\exp(-x_2) - g(x_2)] + \right. \\ \left. \frac{2}{3} (2m_{InCl} + m_{Cl}) g(x_2) \right\} \beta_{InCl,Cl}^{(2)} + 2m_{In} m_{InCl} {}^E \theta'_{In,InCl} + \\ 2m_{In} m_H {}^E \theta'_{In,H} + 2m_{InCl} m_H {}^E \theta'_{InCl,H} + \frac{2}{3} m_{In} ({}^s \theta_{In,InCl} + \\ {}^E \theta_{In,InCl}) + \frac{2}{3} m_H ({}^s \theta_{InCl,H} + {}^E \theta_{InCl,H}) + \frac{2}{3} m_{In} (2m_{Cl} + \\ Z) C_{In,Cl} + \frac{1}{3} (4m_{InCl} m_{Cl} + 2Zm_{InCl} + Zm_{Cl}) C_{InCl,Cl} + \\ \frac{2}{3} m_{In} m_H \psi_{In,H,Cl} + \frac{1}{3} m_H (2m_{InCl} + m_{Cl}) \psi_{InCl,H,Cl} + \\ \frac{1}{3} m_{In} (2m_{InCl} + m_{Cl}) \psi_{In,InCl,Cl} \quad (A3) \end{aligned}$$

where $\gamma(In^{3+}, 3Cl^-)$ and $\gamma(InCl^{2+}, 2Cl^-)$ are the activity coefficients of InCl₃ when it is treated as a 3-1 and a 2-1 electrolyte, respectively, and

$$f^\gamma = -A_\Phi \left[\frac{I_a^{1/2}}{1 + bI_a^{1/2}} + \frac{2}{b} \ln(1 + bI_a^{1/2}) \right] \quad (A4)$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I_a) \quad (\text{A5})$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I_a) \quad (\text{A6})$$

$$g(x) = \frac{2}{x^2} [1 - (1+x)\exp(-x)] \quad (\text{A7})$$

$$x_1 = \alpha_1 I_a^{1/2}, \quad x_2 = \alpha_2 I_a^{1/2} \quad (\text{A8})$$

$$Z = \sum_i |z_i| m_i = 3m_{\text{In}} + 2m_{\text{InCl}} + m_{\text{H}} + m_{\text{Cl}} \quad (\text{A9})$$

The ionic strength after association is given by

$$I_a = \frac{1}{2} \sum_i z_i^2 m_i = \frac{1}{2} (9m_{\text{In}} + 4m_{\text{InCl}} + m_{\text{H}} + m_{\text{Cl}}) \quad (\text{A10})$$

For cell a, the electrode potential can be expressed as

$$E_a = E_a^0 - \frac{2RT}{F} \ln \gamma_{\text{HCl}} - \frac{RT}{F} \ln(m_{\text{H}} m_{\text{Cl}}) \quad (3)$$

The electrode potential for cell b can be expressed either for the In^{3+}/In pair as

$$E_b = E_b^0 - \frac{4RT}{3F} \ln \gamma(\text{In}^{3+}, 3\text{Cl}^-) - \frac{RT}{3F} \ln(m_{\text{In}} m_{\text{Cl}}^3) \quad (4)$$

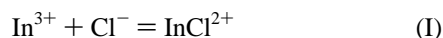
or for the $\text{InCl}^{2+}/\text{In}$ pair as

$$E_b = E_c^0 - \frac{RT}{F} \ln \gamma(\text{InCl}^{2+}, 2\text{Cl}^-) - \frac{RT}{3F} \ln(m_{\text{InCl}} m_{\text{Cl}}^2) \quad (7)$$

The two standard potentials, E_b^0 and E_c^0 , are related by the association equilibrium constant as

$$E_c^0 = E_b^0 + (RT/3F) \ln K \quad (8)$$

Three cases were considered in data regression as discussed in the main text. Details of the treatment for formulation I (complete dissociation of InCl_3 into In^{3+} and Cl^-) and formulation III (complete association of In^{3+} and Cl^- to InCl^{2+}) have been described. For the case of partial association of In^{3+} and Cl^- (formulation II), the molalities of species in the solution (except H^+) are controlled by the association reaction



Molalities of In^{3+} , InCl^{2+} and H^+ can be written in terms of m_A , m_B , and the molality of Cl^- , m_{Cl} .

$$m_{\text{In}} = m_{\text{Cl}} - m_A - 2m_B \quad (\text{A11a})$$

$$m_{\text{InCl}} = m_A + 3m_B - m_{\text{Cl}} \quad (\text{A11b})$$

$$m_{\text{H}} = m_A \quad (\text{A11c})$$

The equilibration constant for reaction I is given by

$$K = \frac{m_{\text{InCl}} \gamma_{\text{InCl}}}{m_{\text{In}} m_{\text{Cl}} \gamma_{\text{In}} \gamma_{\text{Cl}}} \quad (5)$$

The molality of m_{Cl} can be obtained by solving the quadratic equation from substitution of eq A11 into eq 5:

$$m_{\text{Cl}} = \{[K(m_A + 2m_B) - \gamma_{\text{InCl}}/\gamma_{\text{In}}\gamma_{\text{Cl}}] + ([K(m_A + 2m_B) - \gamma_{\text{InCl}}/\gamma_{\text{In}}\gamma_{\text{Cl}}]^2 + 4K(\gamma_{\text{InCl}}/\gamma_{\text{In}}\gamma_{\text{Cl}})(m_A + 3m_B))^{1/2}\}/2K \quad (\text{A12})$$

where the activity coefficient factor, $\gamma_{\text{InCl}}/\gamma_{\text{In}}\gamma_{\text{Cl}}$, can be obtained

from eqs A2 and A3 as

$$\ln \frac{\gamma_{\text{InCl}}}{\gamma_{\text{In}}\gamma_{\text{Cl}}} = 3 \ln \gamma(\text{InCl}^{2+}, 2\text{Cl}^-) - 4 \ln \gamma(\text{In}^{3+}, 3\text{Cl}^-) \quad (\text{A13})$$

An iterative procedure was used in the determination of the ion-interaction parameters and the ionic speciation of solutions. The iterative procedure included the following steps. First, an initial value of m_{Cl} was set for each of the experimental data points, and the m_{In} , m_{InCl} , and m_{H} values were obtained from eq A11. Second, a linear least-squares fitting routine was used to optimize the ion-interaction parameters, together with the E^0 value for cell b, based on the emf data and the initial molalities of the ionic species. Third, the ion-interaction parameters obtained from the second step were used to yield a new value of $\gamma_{\text{InCl}}/\gamma_{\text{In}}\gamma_{\text{Cl}}$ and a new set of equilibrium molalities of species. These new values of molalities were then used in the next round of optimization of ion-interaction parameters. Convergence is finally reached for both the equilibrium molalities of species and the ion-interaction parameters. The adjustable parameters in formulation II are $\beta_{\text{InCl,Cl}}^{(0)}$, $\beta_{\text{InCl,Cl}}^{(1)}$, $\beta_{\text{InCl,Cl}}^{(2)}$, $\theta_{\text{InCl,H}}$, $\psi_{\text{InCl,H,Cl}}$, $C_{\text{InCl,Cl}}$, and $E_c^{(0)}$. Since the molality of In^{3+} is always very small, it seemed appropriate to assign zero values to the mixing and third-order parameters involving $m_{\text{In}^{3+}}$: $\theta_{\text{In,H}}$, $\theta_{\text{In,InCl}}$, $C_{\text{In,Cl}}$, $\psi_{\text{In,InCl,Cl}}$, and $\psi_{\text{In,H,Cl}}$, all of which would be expected to be small. The second-order parameters $\beta^{(0)}$ and $\beta^{(1)}$ have similar values near 0.9 and 8.4 for all nonassociating 3–1 chlorides;^{5,18} hence, these values were assigned to $\beta_{\text{In,Cl}}^{(0)}$ and $\beta_{\text{In,Cl}}^{(1)}$. The parameter $\beta_{\text{In,Cl}}^{(2)}$ would represent association to InCl^{2+} , but this is represented as an explicit association reaction in formulation II; hence, $\beta_{\text{In,Cl}}^{(2)}$ was eliminated. Alternate values for the exponents α_1 and α_2 were tested. The standard value 2.0 for α_1 was satisfactory; 6.0 was slightly better than adjacent integers for α_2 and was adopted.

Ion-interaction parameters obtained from calculations with formulations I, III, and II with several assumed K values are listed in Table 5. Formulation I gives better agreement for the H_2 electrode data while formulations II and III are better for the In electrode data, but the differences are not very large. Among the formulation II and III equations, the overall deviations for both sets of data decrease with increase in K , although there is an opposite trend for the very dilute range for E_a in Table 6. But the differences in overall deviations are very small, and the primary conclusion is that the present data base does not provide a basis for a clear choice of K or between the different formulations.

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