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Thermodynamics of the System $InCl_3$–HCl–H_2O at 25° C [1]

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A comprehensive equation for the thermodynamic properties of the system $InCl_3$–HCl–H_2O 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 molal 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.

KEY WORDS: aqueous electrolytes; equation of state; indium chloride; Pitzer equation; thermodynamic properties.

1. INTRODUCTION

Aqueous $InCl_3$ differs markedly from other M^{3+}–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.

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By making measurements on the system $InCl_3$–HCl–H_2O, the hydrolysis can be controlled or eliminated. Measurements were made and have been reported recently [1] for the electrochemical cell:

$$\mathrm{Pt, H_2 \mid HCl(m_A), InCl_3(m_B), H_2O \mid AgCl, Ag} \qquad \text{(a)}$$

Published [2, 3] values are available for the cell:

$$\mathrm{In(s) \mid HCl(m_A), InCl_3(m_B), H_2O \mid AgCl, Ag} \qquad \text{(b)}$$

The present paper presents an analysis of all of 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 $0.33\,\mathrm{mol \cdot kg^{-1}}$, the present equation has limitations for some properties outside of this range, but its refinement is straightforward when cell (b) is measured at a higher molality. And the present range is sufficient to show clearly the tendency toward ion association to $InCl^{2+}$.

$$\mathrm{In^{3+} + Cl^- = InCl^{2+}} \qquad \text{(I)}$$

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

$$\mathrm{In^{3+} + 2In(s) = 3In^+} \qquad \text{(II)}$$

Equilibrium constant values [6, 7] reported for the hydrolysis reaction

$$\mathrm{In^{3+} + H_2O = InOH^{2+} + H^+} \qquad \text{(III)}$$

and for the association reaction (I) are considered in the calculations. Conductance data [8] are also considered and are found to be generally consistent with respect both to ion association and to hydrolysis effects.

2. EQUATIONS

The ion-interaction equations for a multisolute system as first proposed in 1974 [4b] and widely used since [5] 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.

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.

$$E_a = E_a^0 - \frac{2RT}{F} \ln \gamma_{HCl} - \frac{RT}{F} \ln[m_H m_{Cl}] \tag{5}$$

$$E_b = E_b^0 - \frac{4RT}{3F} \ln \gamma_{InCl_3} - \frac{RT}{3F} \ln[m_{In} m_{Cl}^3] \tag{6}$$

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, $\beta^{(0)}_{H,Cl}$, $\beta^{(1)}_{H,Cl}$, $C_{H,Cl}$, and E_a^0 were taken from the previous work [1, 4, 5]. The adjustable parameters are $\beta^{(0)}_{In,Cl}$, $\beta^{(1)}_{In,Cl}$, $\beta^{(2)}_{In,Cl}$, ${}^s\theta_{In,H}$, $C_{In,Cl}$, $\Psi_{In,H,Cl}$, and E_b^0.

3. 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}, $m_B = 0.0527$, the tertiary parameters are presumably negligible. Hakomori's estimate of 558 mV for E_b^0 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 dependent factors for $\beta^{(0)}_{In,Cl}$ and ${}^s\theta_{In,H}$ are the same; hence, only the combination $({}^s\theta_{In,H} + \beta^{(0)}_{In,Cl})$ can be obtained. Also, there is so little difference in the composition dependency in Eq. (2) for $\Psi_{H,In,Cl}$ and $C_{In,Cl}$ 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 I.

$$\begin{aligned}
\ln \gamma_{\mathrm{InCl_3}} = \ln \gamma(\mathrm{In}^3, 3\mathrm{Cl}) &= 3f^{\gamma} + \frac{3m_{\mathrm{H}}m_{\mathrm{Cl}}}{I}\,[\exp(-x_1) - g(x_1)]\,\beta^{(1)}_{\mathrm{H,Cl}} \\
&+ \frac{3m_{\mathrm{H}}}{2}\,[\beta^{(0)}_{\mathrm{H,Cl}} + \beta^{(1)}_{\mathrm{H,Cl}}\,g(x_1)] \\
&+ \frac{3m_{\mathrm{H}}}{4}\,(2m_{\mathrm{Cl}} + Z)\,C_{\mathrm{H,Cl}} + \frac{1}{2}\,(3m_{\mathrm{In}} + m_{\mathrm{Cl}})\,\beta^{(0)}_{\mathrm{In,Cl}} \\
&+ \left\{\frac{3m_{\mathrm{In}}m_{\mathrm{Cl}}}{I}\,[\exp(-x_1) - g(x_1)] + \frac{1}{2}\,(3m_{\mathrm{In}} + m_{\mathrm{Cl}})\,g(x_1)\right\}\beta^{(1)}_{\mathrm{In,Cl}} \\
&+ \left\{\frac{3m_{\mathrm{In}}m_{\mathrm{Cl}}}{I}\,[\exp(-x_2) - g(x_2)] + \frac{1}{2}\,(3m_{\mathrm{In}} + m_{\mathrm{Cl}})\,g(x_2)\right\}\beta^{(2)}_{\mathrm{In,Cl}} \\
&+ \frac{1}{4}\,(6m_{\mathrm{In}}m_{\mathrm{Cl}}3Zm_{\mathrm{In}} + Zm_{\mathrm{Cl}})\,C_{\mathrm{In,Cl}} + 3m_{\mathrm{In}}m_{\mathrm{H}}{}^{\mathrm{E}}\theta'_{\mathrm{In,H}} \\
&+ \frac{1}{2}\,m_{\mathrm{H}}({}^{\mathrm{s}}\theta_{\mathrm{In,H}} + {}^{\mathrm{E}}\theta_{\mathrm{In,H}}) + \frac{1}{4}\,m_{\mathrm{H}}(3m_{\mathrm{In}} + m_{\mathrm{Cl}})\,\Psi_{\mathrm{In,H,Cl}} \qquad (3)
\end{aligned}$$

$$f^{\gamma} = -A_{\Phi}\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] \qquad (4a)$$

$$g(x) = \frac{2}{x^2}\,[1 - (1 + x)\exp(-x)] \qquad (4b)$$

$$x_1 = \alpha_1 I^{1/2}, \qquad x_2 = \alpha_2 I^{1/2} \qquad (4c)$$

$$m_{\mathrm{H}} = m_{\mathrm{A}} = IY_{\mathrm{A}}, \qquad m_{\mathrm{In}} = m_{\mathrm{B}} = IY_{\mathrm{B}}/6 \qquad (4d)$$

$$m_{\mathrm{Cl}} = m_{\mathrm{A}} + 3m_{\mathrm{B}} = I(1 - Y_{\mathrm{B}}/2) \qquad (4e)$$

$$Z = 3m_{\mathrm{In}} + m_{\mathrm{H}} + m_{\mathrm{Cl}} = I(2 - Y_{\mathrm{B}}) \qquad (4f)$$

The terms in $\beta^{(0)}_{\mathrm{In,Cl}}$, $\beta^{(1)}_{\mathrm{In,Cl}}$, ${}^{\mathrm{s}}\theta_{\mathrm{In,Cl}}$, $C_{\mathrm{In,Cl}}$, and $\Psi_{\mathrm{In,H,Cl}}$ are the usual second- and third-order interaction terms between the indicated ions and need no further comment. The term in $\beta^{(2)}_{\mathrm{In,Cl}}$ is the special term representing approximately the partial association to InCl^{2+}.

In Eqs. (2) and (3), ${}^{\mathrm{E}}\theta_{ij}(\mathrm{I})$ and ${}^{\mathrm{E}}\theta'_{ij}(\mathrm{I})$ 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. For $\mathrm{InCl_3}$ 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.

$$E_{\rm a}=E_{\rm a}^{0}-\frac{2RT}{F}\ln\gamma_{\rm HCl}-\frac{RT}{F}\ln[m_{\rm H}m_{\rm Cl}] \tag{5}$$

$$E_{\rm b}=E_{\rm b}^{0}-\frac{4RT}{3F}\ln\gamma_{\rm InCl_3}-\frac{RT}{3F}\ln[m_{\rm In}m_{\rm Cl}^{3}] \tag{6}$$

where $E_{\rm a}^0$ and $E_{\rm b}^0$ are the standard potentials of cell (a) and cell (b), respectively, with F -the Faraday constant.

The parameters for HCl, $\beta^{(0)}_{\rm H,Cl}$, $\beta^{(1)}_{\rm H,Cl}$, $C_{\rm H,Cl}$, and $E_{\rm a}^0$ were taken from the previous work [1, 4, 5]. The adjustable parameters are $\beta^{(0)}_{\rm In,Cl}$, $\beta^{(1)}_{\rm In,Cl}$, $\beta^{(2)}_{\rm In,Cl}$, ${}^{s}\theta_{\rm In,H}$, $C_{\rm In,Cl}$, $\Psi_{\rm In,H,Cl}$, and $E_{\rm b}^0$.

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Statistical adjustment of all parameters in Formulation I to fit simultaneously the data from all three sources yields the parameters in Table I.

Table I. Ion-Interaction Parameters for Formulation I in Eqs. (2) and (3)

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

^{a} From Ref. 5.

Figure 1 compares 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^0_b is 559.5 mV; it is uncertain in that there is a substantial implied extrapolation of ionic strength from 0.02 to zero. This is discussed below.

The comparison with the numerous cell (a) measurements is shown in Fig. 2 as calculated curves and experimental points. Again, the agreement

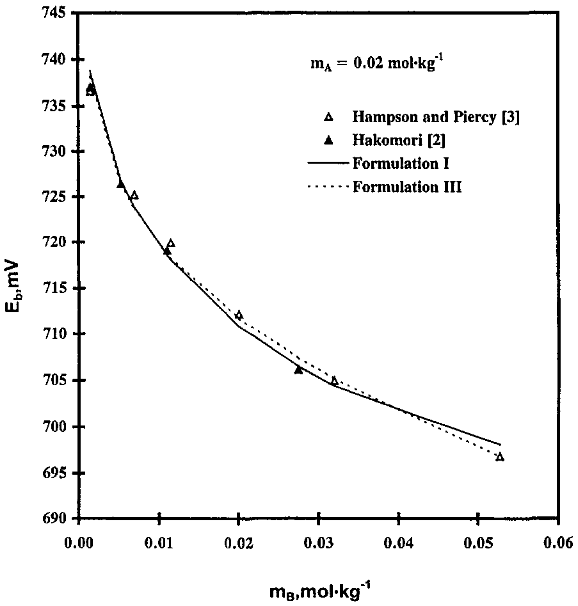

Fig. 1. Comparison of the experimental EMF values for cell (b) (symbols) with the calculated curves for Formulations I (solid curve) and III (dashed curve), respectively.

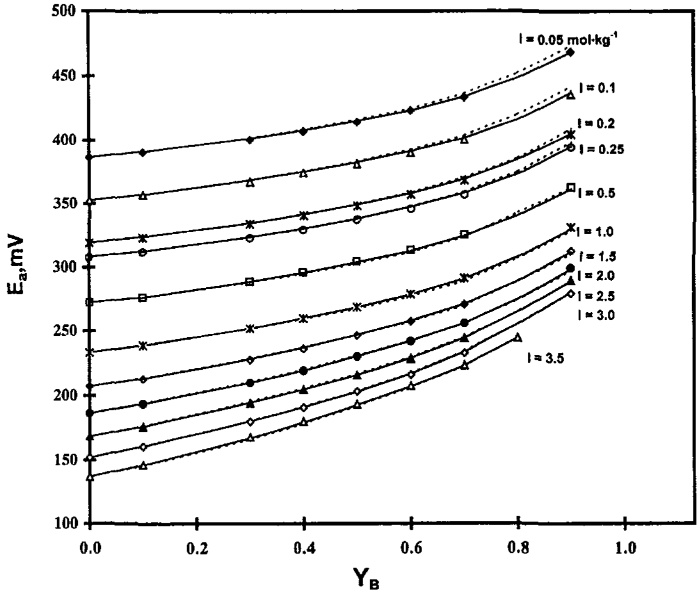

Fig. 2. Experimental (symbols) and calculated (curves) EMF values for cell (a) at various ionic strengths, I, and ionic strength fractions of $InCl_3$, Y_B.

is good with most deviations less than 1 mV and a maximum deviation of 1.7 mV. Now the redundancy between $\beta^{(0)}_{In,Cl}$ and ${}^{s}\theta_{H,In}$ is broken and the separate values are well determined, because the composition-dependent factors are different for $\beta^{(0)}_{In,Cl}$ and for ${}^{S}\theta_{In,H}$ in Eq. (3). For the third virial parameters $C_{In,Cl}$ and $\Psi_{In,H,Cl}$. However, the uncertainty remains large since the only measurements from cell (b) are at very low ionic strength. As shown in Table I, 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 a higher ionic strength.

From the large, negative value of $\beta^{(2)}$ it is clear that the association in reaction (I) is so great that alternate calculations should be made in which $InCl^{2+}$ is recognized as an additional species. The equations now become much more complex and a full description cannot be included here. Such calculations have been made (Formulation II) and will be reported elsewhere [11] in detail. It is interesting to note here the results for the extreme case of complete association to $InCl^{2+}$, Formulation III. These are shown as the dashed curves in Figs. 1 and 2. The agreement in Fig. 1 for cell (b) (In electrode) is even better than for Formulation I, while the agreement in Fig. 2 for cell (a) (H_2 electrode) is not quite as good. But the agreement is good for both extreme cases and, as expected, also for any large but finite value of the association constant.

The standard potential for cell (b) for Formulation I is 559.5 mV, which yields 336.9 mV for the In/In^{3+} electrode. While these values are reasonable, the uncertainty is large. Formulation II treatments with finite association constants yield values lower by several mV. One can only conclude at this point that the cell (b) potential is in the range 550 to 560 mV.

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