

# Thermodynamics of Solvent Extraction of Indium with P507

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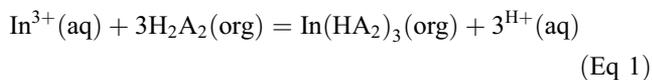
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**At high acidity and high ionic concentration, molalities of  $\text{In}^{3+}$  were measured in aqueous phase containing  $\text{Na}_2\text{SO}_4$  as supporting electrolyte at ionic strength from 0.1 to 2.0 mol/kg and at constant molality extractant at temperatures from 278.15 to 303.15 K in organic phase. The standard extraction constants  $K^0$  at various temperatures were obtained by methods of extrapolation and polynomial approximation. Thermodynamic quantities for the extraction process were calculated.**

**Keywords** extraction, indium, P507, thermodynamics

## 1. Introduction

P507 is an industrial extractant (2-ethylhexyl hydrogen 2-ethylhexylphosphonate) that has been used in separation of rare earth elements, also of indium, from sulfuric acid-sulfate system. The extraction reaction mechanism is a cation exchange process.<sup>[1,2]</sup> In the presence of excessive extractant, the extraction reaction (where P507 is expressed by HA) is:



where (aq) and (org) refer to the aqueous and organic phase, respectively,  $\text{H}_2\text{A}_2$  is the dimer of the extractant P507, and  $\text{In}(\text{HA}_2)_3$  is the extraction complex. The standard equilibrium constant  $K^0$  is given by:

$$\begin{aligned} \log K^0 = & \log m\{\text{In}(\text{HA}_2)_3\} - \log m\{\text{In}^{3+}\} - \log m\{\text{H}_2\text{A}_2\}^3 \\ & - 3pH + \log [\gamma\{\text{In}(\text{HA}_2)_3\} / \gamma\{\text{H}_2\text{A}_2\}] \\ & - \log \gamma\{\text{In}^{3+}\} \end{aligned} \quad (\text{Eq 2})$$

where  $\gamma$  is the activity coefficient in the molality scale, and  $m$  is the molality.

## 2. Experimental

The water used was doubly deionized, and its conductance was  $1.5 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$ . The indium sulfate was of

GR grade, the sulfuric acid was of AR grade (99% mass pure), and the anhydrous sodium sulfate was of AR grade and dried for 4 h in the oven at 170 °C before use. The purity of the extractant (P507) is 99.5%. The  $n\text{-C}_8\text{H}_{16}$  that was used as diluent was of AR grade.

All initial solutions to be measured were freshly prepared. The aqueous phase was prepared by dissolving  $\text{In}_2(\text{SO}_4)_3$  in an aqueous solution of  $\text{H}_2\text{SO}_4$  of constant molality. The initial molality of the  $\text{In}_2(\text{SO}_4)_3$  was  $a = 0.005 \text{ mol/kg}$ , and the initial molality of the  $\text{H}_2\text{SO}_4$  was  $c = 0.05 \text{ mol/kg}$ . The supporting electrolyte ( $\text{Na}_2\text{SO}_4$ ) was used to adjust the total ionic strength  $I$  of the aqueous solution to 0.1 to 2.0 mol/kg. The organic phase was prepared by dissolving P507 in  $n\text{-C}_8\text{H}_{16}$ , the initial molality of P507 being kept constant ( $b = 0.07 \text{ mol/kg}$ ).

A volume ( $10 \text{ cm}^3$ ) of the organic phase was brought into contact with the same volume of aqueous phase in an extraction bottle and the two-phase mixture was shaken mechanically for 15 min. The extraction bottles were kept at different temperatures: 278.15, 283.15, 288.15, 293.15, 298.15, and 303.15 K, within  $\pm 0.05 \text{ K}$ . After standing for 15 min, the two phases were separated and the molality of  $\text{In}^{3+}$  ( $m\{\text{In}^{3+}\}$ ) in the equilibrium aqueous phase was determined using a 7230 type spectrophotometer. The results are listed in Table 1.

The equilibrium molalities ( $m\{i\}$  for the species  $i$ ) in the organic phase were calculated from the initial molalities  $a$ ,  $b$ , and  $m\{\text{In}^{3+}\}$  in the aqueous phase:

$$m\{\text{In}(\text{HA}_2)_3\} = [a - m\{\text{In}^{3+}\} / 2] / \rho \quad (\text{Eq 3})$$

$$m\{\text{H}_2\text{A}_2\} = b - 6 \times (a - m\{\text{In}^{3+}\} / 2) / \rho \quad (\text{Eq 4})$$

where  $\rho$  is the density of the organic phase.

## 3. Results and Discussion

### 3.1 Effective Ionic Strength in the Equilibrium Aqueous Phase

There were five ionic species ( $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^-$ , and  $\text{In}^{3+}$ ) in the equilibrium aqueous phase. Their molalities

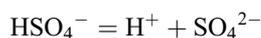
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## Section I: Basic and Applied Research

**Table 1 Values of pH and metallic ion strength at temperatures in the range 278.15 to 303.15 K**

	Temperature (T), K					
	278.15	283.15	288.15	293.15	298.15	303.15
	<i>I</i> = 0.1					
pH	1.65	1.67	1.68	2.01	2.05	2.07
$m_{in} (10^{-5})$	95.40	98.08	90.82	96.22	99.88	104.4
	<i>I</i> = 0.2					
pH	1.57	1.58	1.59	1.89	1.87	1.99
$m_{in} (10^{-5})$	94.08	94.03	86.88	92.46	96.88	102.0
	<i>I</i> = 0.4					
pH	1.53	1.49	1.47	1.69	1.59	1.87
$m_{in} (10^{-5})$	93.24	95.24	81.12	89.12	94.40	97.64
	<i>I</i> = 0.5					
pH	1.48	1.37	1.36	1.58	1.42	1.86
$m_{in} (10^{-5})$	88.80	89.12	79.44	89.62	91.84	95.48
	<i>I</i> = 0.6					
pH	1.42	1.29	1.23	1.50	1.38	1.75
$m_{in} (10^{-5})$	87.24	86.88	78.23	89.68	89.81	90.84
	<i>I</i> = 0.8					
pH	1.35	1.20	1.20	1.38	1.37	1.73
$m_{in} (10^{-5})$	82.26	83.20	76.81	85.44	87.66	90.48
	<i>I</i> = 1.0					
pH	1.27	1.16	1.14	1.31	1.27	1.61
$m_{in} (10^{-5})$	81.60	79.68	76.47	83.41	87.24	88.90
	<i>I</i> = 1.2					
pH	1.19	1.10	1.12	1.28	1.21	1.53
$m_{in} (10^{-5})$	81.12	80.22	75.52	81.43	86.82	89.89
	<i>I</i> = 1.4					
pH	1.21	1.03	1.08	1.20	1.15	1.39
$m_{in} (10^{-5})$	81.64	77.21	75.20	81.82	86.88	87.68
	<i>I</i> = 1.5					
pH	1.13	1.04	1.14	1.14	1.17	1.25
$m_{in} (10^{-5})$	81.12	76.42	74.65	82.48	86.80	87.52
	<i>I</i> = 1.6					
pH		1.01	1.07	1.11	1.11	1.20
$m_{in} (10^{-5})$		76.76	73.74	81.81	86.22	85.11
	<i>I</i> = 1.8					
pH			1.07	1.15	1.09	1.13
$m_{in} (10^{-5})$			73.15	81.12	83.61	84.74
	<i>I</i> = 2.0					
pH			1.03	1.09	1.07	1.19
$m_{in} (10^{-5})$			74.02	80.40	85.24	83.42

and activity coefficients are  $m\{H^+\}$ ,  $m\{Na^+\}$ ,  $m_1$ ,  $m_2$ , and  $m\{In^{3+}\}$ , and  $\gamma\{H^+\}$ ,  $\gamma\{Na^+\}$ ,  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma\{In^{3+}\}$ , respectively. The second dissociation of sulfuric acid is:



$K_2$  is the second dissociation constant:

$$K_2 = [a\{H^+\} \cdot m_2/m_1] \cdot [\gamma_2/\gamma_1] \quad (\text{Eq 5})$$

The temperature dependence of  $K_2$  between 0 and 55 °C has been given by Pitzer et al.<sup>[3]</sup> as:

$$\ln K_2 = -14.0321 + 2825.2/T \quad (\text{Eq 6})$$

Consequently,  $m_1$  and  $m_2$  vary with temperature as well as with the total ionic strength of the solution. In terms of mass equilibrium:

$$m_1 + m_2 = 3a + c + d \quad (\text{Eq 7})$$

where  $d$  is the initial molality of the  $Na_2SO_4$  used as the supporting electrolyte. The values of  $m_1$  and  $m_2$  can be obtained from Eq 5 to 7. The effective ionic strength  $I'$  in the equilibrium aqueous phase can then be calculated as:

$$I' = [m\{In^{3+}\} + m_1 + 4m_2 + 2d + m\{H^+\}]/2 \quad (\text{Eq 8})$$

where

$$m\{H^+\} = 10^{-pH}/\gamma\{H^+\} \quad (\text{Eq 9})$$

The activity coefficients  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma\{H^+\}$  in Eq 5 can be estimated using Pitzer's equations. According to Pitzer's theory, the activity coefficients  $\gamma_M$  and  $\gamma_X$  of the cation M and the anion X in a multicomponent electrolyte solution are given by:<sup>[4]</sup>

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_a (m_a/m^0)(2B_{Ma} + ZC_{Ma}) \\ & + \sum_c (m_c/m^0) \left( 2\Phi_{Mc} + \sum_a (m_a/m^0)\Psi_{Mca} \right) \\ & + \sum_a \sum_{at} (m_a/m^0)(m_{at}/m^0)\Psi_{Maat} \\ & + |Z_M| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca} \end{aligned} \quad (\text{Eq 10})$$

$$\begin{aligned} \ln \gamma_X = & z_X^2 F + \sum_c (m_c/m^0) (2B_{cX} + ZC_{cX}) \\ & + \sum_a (m_a/m^0) \left( 2\Phi_{Ma} + \sum_c (m_c/m^0)\Psi_{McXa} \right) \\ & + \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\Psi_{cc'X} \\ & + |Z_X| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca} \end{aligned} \quad (\text{Eq 11})$$

In estimating  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma\{H^+\}$ , all the mixed parameters are neglected, so that

$$\begin{aligned} \ln \gamma\{H^+\} = & f^r + (m\{Na^+\}/m^0)(m_2/m^0) \left( \beta_{H_2}^{(1)}\gamma_2 + C_{Na_2} \right) \\ & + 2(m_2/m^0)\beta_{H_2}^{(1)} + 2(m_2/m^0)\beta_{H_2}^{(1)}\gamma_1 \\ & + (m\{Na^+\}/m^0)(m_2/m^0)C_{H_2} \end{aligned} \quad (\text{Eq 12})$$

$$\begin{aligned} \ln (\gamma_2/\gamma_1) = & 3f^r + 3(m\{Na^+\}/m^0)(m_2/m^0)\beta_{Na_2}^{(1)}\gamma_2 \\ & + 2(m\{Na^+\}/m^0) \left( \beta_{Na_2}^{(0)} - \beta_{Na_1}^{(1)} \right) \\ & + 2(m\{Na^+\}/m^0)\gamma_1 \left( \beta_{Na_2}^{(1)} - \beta_{Na_1}^{(1)} \right) \\ & + (m\{Na^+\}/m^0)^2 (C_{Na_2} - C_{Na_1}) \\ & + (m\{Na^+\}/m^0)(m_2/m^0)C_{Na_2} \end{aligned} \quad (\text{Eq 13})$$

Using Eq 5 to 13 and the values of Pitzer's parameters at various temperatures, values of the effective ionic strength in the equilibrium aqueous phase were obtained.

### 3.2 Extrapolation to Determine the Value of $K^0$

Because the molalities of the extraction complex and the extractant in the equilibrium organic phase are very small, it can be assumed that  $\gamma\{\ln \text{HA}_2\} \approx \gamma\{\text{H}_2\text{A}_2\} \approx 1$ . If  $\log \gamma\{\text{In}^{3+}\}$  in Eq 2 is expressed by expanded Debye-Hückel equation, the following may be used as a working equation for the extrapolation to determine  $K^0$ :

$$\begin{aligned} \log K' &= \log m\{\text{In}(\text{HA}_2)_3\} - \log m\{\text{In}^{3+}\} \\ &\quad - \log m\{\text{H}_2\text{A}_2\}^3 - 3\text{pH} + 9A(I\rho/c^0)^{1/2} / \\ &\quad \left\{1 + B a^0(I\rho/c^0)^{1/2}\right\} + \log\left(1 + \sum m_i M_w\right) \\ &= \log K^0 + \beta(I/m^0) \end{aligned} \quad (\text{Eq 14})$$

where  $pK'$  is an extrapolation function and can be calculated from the experimental data.  $\rho$  and  $M_w$  are density and molar mass of water.  $a^0$  is the parameter of ion size, and  $\beta$  is an empirical parameter.  $c^0 = 1 \text{ mol m}^{-3}$ ,  $A$  and  $B$  are Debye-Hückel parameters.

$$A = 1.8246 \times 10^6 / (DT)^{3/2} \quad (\text{Eq 15})$$

$$B = 50.29 / (DT)^{1/2} \quad (\text{Eq 16})$$

In the equations,  $D$  and  $T$ , respectively, represent the inductivity of water and thermodynamic temperature of the system. Using a least-squares method, a linear regression of  $pK'$  versus  $(I/m^0)$  yielded values of  $pK^0$  (D-H), where (D-H) denotes the application of extrapolation. All the  $pK^0$  together with the standard deviations are given in Table 2.

### 3.3 Polynomial Approximation to Determine $K^0$

On the basis of Pitzer's electrolyte-solution theory, a second method of polynomial approximation for determining  $\log K^0$  was proposed. In the extrapolation of seeking  $K^0$ , the least standard deviation is not the only criterion for selecting an ionic size parameter; therefore, we have obtained  $K^0$  by application of polynomial approximation of Pitzer's theory. When evaluating  $\gamma\{\text{In}^{3+}\}$  in the aqueous phase with Pitzer's equation:

$$\begin{aligned} \ln \gamma\{\text{In}^{3+}\} &= 9f^r + 2/3I\left(\beta_{\text{In}2}^{(0)} + 2\Phi_{\text{Na,In}}\right) + 2/3Iy_1\beta_{\text{In}2}^{(1)} \\ &\quad + 2/9I^2(2C_{\text{In}2} + \psi) + 2/9I^2y_2\beta_{\text{Na}2}^{(1)} \\ &\quad + 2/3I^2C_{\text{Na}2} \end{aligned} \quad (\text{Eq 17})$$

Only the interactions of  $\text{In}^{3+}$  with each ion of the  $\text{Na}_2\text{SO}_4$  supporting electrolyte are considered, and all other interactions are neglected. As before,  $\beta_{\text{Na}2}^{(1)}$  and  $C_{\text{Na}2}$  are obtained through references, so the last two terms in Eq 17 are known.  $\Phi_{\text{Na,In}}$  represents the anisomeric hybrid parameter of  $\text{In}^{3+}$  and  $\text{Na}^+$ . According to Pitzer's theory,<sup>[5,6]</sup>  $\Phi_{\text{Na,In}}$  may be taken as the summation of the following two terms:

$$\Phi_{\text{Na,In}} = Q_{ij} + {}^E Q_{ij} \cdot (I) \quad (\text{Eq 18})$$

where  $Q_{ij}$  is a mixed parameter arising from interionic short-range forces, which are assumed to be independent of ionic strength.  ${}^E Q_{ij}(I)$  reflects unsymmetric-mixed long long-range static electrification parameter among different valent state ions, and is called a high-order static term that could be calculated by corresponding terms of group integral theory after neglecting short-range forces.

$${}^E Q_{ij} = (z_i z_j / 4I) \cdot [J(X_{ij}) - 1/2J(X_{ii}) - 1/2J(X_{jj})] \quad (\text{Eq 19})$$

where

$$X_{ij} = 6z_i z_j A_P I^{1/2} \quad (\text{Eq 20})$$

$$J(X_{ij}) = 1/4(X_{ij}) - 1 + X_{ij}^{-1}(1 - e^{-q})y^2 dy \quad (\text{Eq 21})$$

with  $y = \kappa\tau$ , and

$$q = -(X_{ij}/y)e^{-y} \quad (\text{Eq 22})$$

where  $\tau$  is interionic distance,  $\kappa$  is Debye-Hückel parameter. The working equation of the polynomial approximation is:

$$\begin{aligned} \log K' &= \log m\{\text{In}(\text{HA}_2)_3\} - \log m\{\text{In}^{3+}\} \\ &\quad - \log m\{\text{H}_2\text{A}_2\}^3 - 3\text{pH} \\ &\quad - \left[9f^r - I^2(2\beta_{\text{Na}2}^{(1)}y_2 + 2C_{\text{Na}2}/3) + (2/3)I^E Q_{\text{InNa}}\right] \\ &= \log K^0 + (2/3)I\left(\beta_{\text{In}2}^{(0)} + Q_{\text{InNa}}\right) \\ &\quad + (2/3)Iy_1\beta_{\text{In}2}^{(1)}/\ln 10 + (2/9)I^2(2C_{\text{In}2} + \psi_{\text{InNa}2}) \end{aligned} \quad (\text{Eq 23})$$

Here the subscripts Na2 and In2 respectively represent the interactions of  $\text{Na}^+\text{-SO}_4^-$  and  $\text{In}^{3+}\text{-SO}_4^-$ .  $\log K^0$  could be calculated from the experimental data and literature values. According to the working equation, values of  $\log K^0(P)$  were obtained at selected temperatures by polynomial approximations on a computer; these are listed in Table 2. It is evident from Table 2 that the value of  $\log K^0(p)$  is similar to that of  $\log K^0$  (D-H), which shows the consistency of the two methods.

**Table 2 Values of  $\log K^0$  over the temperature range 278.15 to 303.15 K obtained using the two methods and the standard deviation(s)**

Temperature (T), K	$\log K^0$ (D-H)	$S \times 10^{-2}$	$\log K^0$ (P)	$S \times 10^{-2}$
278.15	6.658	4.4	7.033	4.3
283.15	6.539	4.2	6.915	3.8
288.15	6.427	4.0	6.850	3.5
293.15	6.315	3.9	6.732	3.2
298.15	6.406	3.7	6.595	3.0
303.15	6.325	5.5	6.559	3.6

**Table 3** The standard molar thermodynamic quantities for the extraction process in the temperature range 278.15 to 303.15 K

Temperature (T), K	$\Delta_r G_m^0$ , kJ/mol	$\Delta_r H_m^0$ , kJ/mol	$\Delta_r S_m^0$ , J/K mol	$\Delta_r C_{p,m}^0$ , J/K mol
303.15	-162.66	-140.72	78.87	203
298.15	-163.07	-139.70	82.53	207
293.15	-163.49	-138.66	86.18	210
288.15	-163.93	-137.60	89.83	214
283.15	-164.39	-136.52	93.48	218
278.15	-164.86	-135.42	97.13	221

### 3.4 Thermodynamic Quantities for the Extraction Process

The values of  $\log K^0$  obtained at different temperatures were fitted to:

$$\log K^0 = (A_1 + A_2/T + A_3T) \quad (\text{Eq 24})$$

The values of parameters  $A_i$  were obtained:  $A_1 = -1.494$ ,  $A_2 = 2.03 \times 10^3$  and  $A_3 = 4.39 \times 10^{-3}$  with a standard deviation of  $s = 0.0289$ .

The standard molar thermodynamic quantities  $\Delta_r G_m^0$ ,  $\Delta_r H_m^0$ ,  $\Delta_r S_m^0$ ,  $\Delta_r C_{p,m}^0$  for the extraction process are simply related to the parameters in Eq 24:

$$\Delta_r G_m^0 = -(R \ln 10)(A_1 T + A_2 + A_3 T^2) \quad (\text{Eq 25})$$

$$\Delta_r H_m^0 = (R \ln 10)(A_3 T^2 - A_2) \quad (\text{Eq 26})$$

$$\Delta_r S_m^0 = (R \ln 10)(A_1 + 2A_3 T) \quad (\text{Eq 27})$$

$$\Delta_r C_{p,m}^0 = (R \ln 10)(2A_3 T) \quad (\text{Eq 28})$$

where  $R$  is the gas constant. The thermodynamic quantities calculated from Eq 25 to 28 are listed in Table 3.

## 4. Conclusion

The negative experimental association Gibbs free energy  $\Delta G_m^0 < 0$  means that the reaction can occur spontaneously

under the conditions of constant temperature and pressure. As is well known, Gibbs energy includes two factors, that is  $\Delta G_m^0 = \Delta H_m^0 - T \cdot \Delta S_m^0$ . In the reaction,  $\Delta H_m^0 < T \cdot \Delta S_m^0$  leads one to conclude that the entropy is the dominant thermodynamic factor.<sup>[7-9]</sup>

## Acknowledgment

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