

Thermodynamics of Solvent Extraction of Indium with EHEHPA

Da-Wei Fang, Xing-Zhi Liu, Jia-Zhen Yang, Ying Xiong, and Shu-Liang Zang

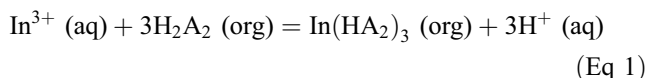
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Molalities of In^{3+} were measured at ionic strength from 0.1 to 2.0 $\text{mol}\cdot\text{kg}^{-1}$ in aqueous phase containing Na_2SO_4 as supporting electrolyte and at constant molality extractant at temperatures from 278.15 to 303.15 K in organic 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 EHEHPA, extraction, indium, thermodynamics

1. Introduction

EHEHPA (2-ethylhexyl hydrogen 2-ethylhexylphosphonate) is a kind of industrial extractant in the separation of rare earth elements from sulphuric acid-sulphate system. The extraction reaction mechanism is cation exchange process.^[1, 2] With excess extractant, the extraction reaction (where EHEHPA is expressed by HA) is:



where (aq) and (org) refer to the aqueous and organic phase, respectively, H_2A_2 is the dimer of the extractant (diethylhexylmonothiophosphoric acid), and $\text{In}(\text{HA}_2)_3$ is the extraction complex. The standard equilibrium constant K^0 is given by

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

where γ is the activity coefficient in the molality scale, m is the molality.

2. Experimental

Doubly deionized water was used with conductance of $1.5 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$. Indium sulphate was GR grade, sulphuric acid AR grade (99% mass pure), and oven-dried

(4 h at 170 °C) anhydrous sodium sulphate of AR grade. The purity of extractant (EHEHPA) is 99.5%, and AR grade $n\text{-C}_8\text{H}_{16}$ was used as diluent.

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 H_2SO_4 of constant molality. The initial molality of the $\text{In}_2(\text{SO}_4)_3$ was $a = 0.001 \text{ mol kg}^{-1}$, and the initial molality of the H_2SO_4 was $c = 0.03 \text{ mol kg}^{-1}$. The supporting electrolyte (Na_2SO_4) was used to adjust the total ionic strength I of the aqueous solution to 0.10–2.0 mol kg^{-1} . The organic phase was prepared by dissolving EHEHPA in $n\text{-C}_8\text{H}_{16}$, the initial molality of EHEHPA being kept constant ($b = 0.02 \text{ mol kg}^{-1}$).

A volume (10 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 ± 0.1 K. After standing for 15 min the two phases were separated and the molality of In^{3+} ($m\{\text{In}^{3+}\}$) in the equilibrium aqueous phase was determined using a 7230 type spectrophotometer.

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 ρ is the density of the organic phase.

3. Results and Discussion

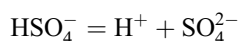
3.1 Effective Ionic Strength in the Equilibrium Aqueous Phase

There were five ionic species (H^+ , Na^+ , HSO_4^- , SO_4^{2-} and In^{3+}) in the equilibrium aqueous phase. The molalities and activity coefficients are $m\{\text{H}^+\}$, $m\{\text{Na}^+\}$, m_1 , m_2 and $m\{\text{In}^{3+}\}$, and $\gamma\{\text{H}^+\}$, $\gamma\{\text{Na}^+\}$, γ_1 , γ_2 and $\gamma\{\text{In}^{3+}\}$, where m_1 and m_2 and γ_1 , γ_2 are the molalities of $\text{HSO}_4^- + \text{SO}_4^{2-}$ and

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activity coefficients of respectively. The second dissociation of sulphuric acid is



K_2 is the second dissociation constant:

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

The temperature dependence of K_2 between 0 and 55 °C has been given by Pitzer et al.^[3] 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 a , c , and d are the initial molalities in the aqueous phase respectively of $\text{In}(\text{HA}_2)_3$, H_2SO_4 and Na_2SO_4 with the latter being 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

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

where

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

The activity coefficients γ_1 , γ_2 and $\gamma\{\text{H}^+\}$ in Eq 5 can be estimated using Pitzer's equations. According to Pitzer's theory, the activity coefficients γ_M and γ_X of the cation M and the anion X in a multicomponent electrolyte solution are given by^[4]:

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

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

In estimating γ_1 , γ_2 and $\gamma\{\text{H}^+\}$, all the mixed parameters are neglected, so that

$$\begin{aligned} \ln \gamma\{\text{H}^+\} = & f^r + (m\{\text{Na}^+\}/m^0)(m_2/m^0)(\beta_{\text{H}_2}^{(1)}\gamma_2 + C_{\text{Na}_2}) \\ & + 2(m_2/m^0)\beta_{\text{H}_2}^{(1)} + 2(m_2/m^0)\beta_{\text{H}_2}^{(1)}\gamma_1 \\ & + (m\{\text{Na}^+\}/m^0)(m_2/m^0)C_{\text{H}_2} \end{aligned} \quad (\text{Eq 12})$$

$$\begin{aligned} \ln(\gamma_2/\gamma_1) = & 3f^r + 3(m\{\text{Na}^+\}/m^0)(m_2/m^0)\beta_{\text{Na}_2}^{(1)}\gamma_2 \\ & + 2(m\{\text{Na}^+\}/m^0)(\beta_{\text{Na}_2}^{(0)} - \beta_{\text{Na}_1}^{(1)}) \\ & + 2(m\{\text{Na}^+\}/m^0)\gamma_1(\beta_{\text{Na}_2}^{(1)} - \beta_{\text{Na}_1}^{(1)}) \\ & + (m\{\text{Na}^+\}/m^0)^2(C_{\text{Na}_2} - C_{\text{Na}_1}) \\ & + (m\{\text{Na}^+\}/m^0)(m_2/m^0)C_{\text{Na}_2} \end{aligned} \quad (\text{Eq 13})$$

Using Eq 5-13 and the values of Pitzer's parameters at various temperatures, values of the effective ionic strength in the equilibrium aqueous phase were obtained. Values of pH and \ln molalities are shown in Table 1 for various ionic strengths through the range $0.1 \leq I \leq 2.0$ at temperatures through range $278.15 \leq T/K \leq 303.15$.

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 $\gamma\{\text{InHA}_2\} \approx \gamma\{\text{H}_2\text{A}_2\} \approx 1$. If $\log \gamma\{\text{In}^{3+}\}$ in Eq 2 is expressed by expanded the Debye-Hückel equation, the following may be used as a working equation for the extrapolation to determine K^0 :

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

where $\text{p}K'$ is an extrapolation function that can be calculated from the experimental data. ρ and M_w are density and molar mass of water. a^0 is the parameter of ion size, and β is an empirical parameter. $c^0 = 1 \text{ mol} \cdot \text{m}^3$, 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 equation, D and T are respectively representing inductivity of water and thermodynamics temperature of the system. Using a least-squares method, a linear regression of $\text{p}K'$ versus (I'/m^0) yielded values of $\text{p}K^0(\text{D-H})$ where (D-H) denotes the application of extrapolation. All these $\text{p}K^0$ 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 to select an ionic size parameter; therefore, we have obtained K^0 by application of a polynomial approximation of Pitzer's theory. When expressing $\gamma\{\text{In}^{3+}\}$ in the aqueous phase with Pitzer's equation, interaction of In^{3+} with each ion of supporting electrolyte Na_2SO_4 is the only interaction

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

T/K	278.15	283.15	288.15	293.15	298.15	303.15
H $m_{\text{In}}(10^{-5})$			$I = 0.1$			
	1.49	1.53	1.55	1.57	1.59	1.61
pH $m_{\text{In}}(10^{-5})$	1.630	1.630	1.646	1.990	2.035	1.975
			$I = 0.2$			
	1.57	1.63	1.66	1.69	1.71	1.74
pH $m_{\text{In}}(10^{-5})$	1.555	1.522	1.540	1.800	1.855	1.830
			$I = 0.4$			
	1.66	1.73	1.77	1.81	1.85	1.89
pH $m_{\text{In}}(10^{-5})$	1.395	1.450	1.412	1.590	1.540	1.630
			$I = 0.5$			
	1.69	1.77	1.81	1.85	1.89	1.93
pH $m_{\text{In}}(10^{-5})$	1.532	1.322	1.280	1.485	1.470	1.485
			$I = 0.6$			
	1.71	1.79	1.84	1.88	1.92	1.96
pH $m_{\text{In}}(10^{-5})$	1.305	1.315	1.230	1.370	1.350	1.585
			$I = 0.8$			
	1.75	1.84	1.88	1.92	1.97	2.01
pH $m_{\text{In}}(10^{-5})$	1.405	1.215	1.175	1.344	1.322	1.357
			$I = 1.0$			
	1.78	1.87	1.91	1.96	2.00	2.05
pH $m_{\text{In}}(10^{-5})$	1.232	1.175	1.008	1.300	1.245	1.300
			$I = 1.2$			
	1.80	1.89	1.94	1.98	2.03	2.08
pH $m_{\text{In}}(10^{-5})$	1.055	1.077	0.960	1.232	1.225	1.262
			$I = 1.4$			
	1.82	1.91	1.96	2.00	2.05	2.10
pH $m_{\text{In}}(10^{-5})$	1.024	1.050	0.970	1.160	1.145	1.155
			$I = 1.5$			
	1.82	1.92	1.97	2.01	2.06	2.11
pH $m_{\text{In}}(10^{-5})$	1.075	1.032	1.005	1.133	1.160	1.120
			$I = 1.6$			
	1.83	1.92	1.97	2.02	2.07	2.12
pH $m_{\text{In}}(10^{-5})$	1.005	0.960	0.920	1.150	1.155	1.160
			$I = 1.8$			
		1.94	1.99	2.04	2.09	2.13
pH $m_{\text{In}}(10^{-5})$		0.990	0.955	1.120	1.160	1.125
			$I = 2.0$			
			2.00	2.05	2.10	2.15
			0.905	1.095	1.095	1.175

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

T/k	a^0	$\log K^0(\text{D-H})$	$S \times 10^{-2}$	$\log K^0(\text{P})$	$s \times 10^{-2}$
278.15	5.5	6.777	2.7	7.071	3.1
283.15	4.9	6.687	2.4	6.954	3.8
288.15	4.9	6.607	2.3	6.889	3.4
293.15	4.5	6.477	2.2	6.712	3.2
298.15	4.2	6.434	2.0	6.635	2.9
303.15	3.9	6.369	3.0	6.599	3.5

$\log K^0$ (D-H) represent evaluation via the Debye-Huckel approach and $\log K^0$ (P) represent evaluations via Pitzer's theory

considered, and others are neglected. According to the equation:

$$\ln \gamma \{ \text{In}^{3+} \} = 9f^r + 2/3I(\beta_{\text{In}_2}^{(0)} + 2\Phi_{\text{Na,In}}) + 2/3Iy_1\beta_{\text{In}_2}^{(1)} + 2/9I^2(2C_{\text{In}_2} + \psi) + 2/9I^2y_2(\beta_{\text{Na}_2}^{(1)} + 2/3I^2C_{\text{Na}_2}) \quad (\text{Eq 17})$$

As before, $\beta_{\text{Na}_2}^{(1)}$ and C_{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 In^{3+} and Na^+ . According to Pitzer's theory,^[5, 6] $\Phi_{\text{Na,In}}$ may be taken as summation of the following two terms:

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

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

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

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

$$y = \kappa \tau$$

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

where τ is interionic distance, κ is the Debye-Hückel parameter. The working equation for polynomial approximation is:

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

where subscripts Na^2 and In^2 respectively express the interaction of $\text{Na}^+ \text{-SO}_4^{2-}$ and $\text{In}^{3+} \text{-SO}_4^{2-}$. $\log K^0$ can then be calculated from the experimental data with literature values. According to the working equation, $\log K^0(\text{P})$ is obtained by polynomial approximation with a computer, and are listed in Table 2. It is evident from Table 2 that the values of $\log K^0(\text{p})$ are similar to those of $\log K^0(\text{D-H})$, which shows the consistency of the two methods which supports the credibility of the data.

3.4 Thermodynamic Quantities for the Extraction Process

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

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

The values of parameters A_i were obtained: $A_1 = -22.47$, $A_2 = 4.92 \times 10^3$ and $A_3 = 4.16 \times 10^{-2}$ with a standard deviation of $s = 0.0204$.

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:

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

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

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

T/K	$\Delta_r G_m^0$, kJ mol^{-1}	$\Delta_r H_m^0$, kJ mol^{-1}	$\Delta_r S_m^0$, J (Kmol)^{-1}	$\Delta_r C_{p,m}^0$, J (Kmol)^{-1}
303.15	-156.90	-141.50	55.35	1923
298.15	-157.26	-131.80	89.92	1957
293.15	-157.80	-121.92	124.50	1992
288.15	-158.51	-111.87	159.07	2027
283.15	-159.39	-101.65	193.64	2061
278.15	-160.04	-91.26	228.22	2096

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

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

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 us to conclude that the entropy is the dominant thermodynamic factor.^[7-9]

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