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Thermodynamics of Solvent Extraction of Thallium(*I*)

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The equilibrium molalities of Tl^+ in the system $\{Tl_2SO_4 + Na_2SO_4 + H_2SO_4 + D_2EHMTPA + n\text{-}C_8H_{18} + \text{water}\}$ were measured at ionic strength from 0.1 mol/g in the aqueous phase containing Na_2SO_4 as a supporting electrolyte and at constant initial molality of extractant, in the organic phase at temperatures from 278.15 to 303.15 K. The standard extraction constants K^0 at various temperatures were obtained by extrapolation and polynomial approximation methods. Thermodynamic properties for the extraction process were calculated.

1. Introduction

At present, the production flow of extraction of thallium as Tl^{3+} with di-(2-ethyl-hexyl)-phosphoric acid (D_2EHPA) kerosene solvent has been developed,[1] but it requires the oxidation of Tl^+ to unstable Tl^{3+} with strongly oxidizing bromine water before extraction, and it also has an adverse effect on health and the environment. To find the selective extractant of Tl^+, we have synthesized a new extractant di-(2-ethyl-hexyl-mono-thio)-phosphoric acid ($D_2EHMTPA$), which accomplishes the extraction and back-extraction of Tl^+ in the same sulfuric acid system. The results are satisfactory.[2] But studies on the thermodynamics of solvent extraction of Tl^+ with $D_2EHMTPA$ have never been reported. In this article, the authors measured the concentration of Tl^+ in an aqueous phase at different ionic strengths in high concentration and high acidity. The standard extraction constants K^0 are obtained by the extrapolation and polynomial approximation methods.[3-5] Thermodynamic quantities for the extraction process have been calculated.

The extraction reaction mechanism of Tl^+ with $D_2EHMTPA$ in sulfuric acid medium is a cation exchange process.[2] In the presence of excess extractant, the extraction reaction is:

$$Tl^+\,(aq) + H_2A_2\,(org) = T/HA_2\,(org) + H^+\,(aq) \qquad \text{(Eq 1)}$$

where (aq) and (org) refer to the aqueous and organic phase, respectively, H_2A_2 is the dimer of the extractant ($D_2EHMTPA$), and $TlHA_2$ is the extraction complex. The standard equilibrium constant K^0 is given by:

$$\begin{aligned}\log K^0 &= \log K_M + \log[\gamma\{T/HA_2\}/\gamma\{H_2A_2\}]\\ &\quad + \log[\gamma\{H^+\}/\gamma\{Tl^+\}] \qquad \text{(Eq 2)}\end{aligned}$$

where γ is the activity coefficient in the molality scale, and K_M is the equilibrium concentration product, which is defined as:

$$K_M = [m\{T/HA_2\} \cdot m\{H^+\}]/m\{H_2A_2\}/m\{Tl^+\} \qquad \text{(Eq 3)}$$

where m is the molality.

2. Experimental

The water used was doubly deionized and its conductance was $1.5 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$ (Ω is ohm). The thallium sulfate was of guarantee reagent grade, the sulfuric acid was of analytical reagent (AR) grade (99 mass% pure), and the anhydrous sodium sulfate was of AR grade and was dried for 4 h in an oven at 170 °C before use. According to the method recommended by Levin and Sergeeva,[1] the extractant ($D_2EHMTPA$) was purified; its density was $\rho = 0.9770$ and its index of refraction was $n_D^{20} = 1.4657$. The $n\text{-}C_8H_{16}$ used as a diluent was of AR grade.

All initial solutions to be measured were freshly prepared. The aqueous phase was prepared by dissolving Tl_2SO_4 in an aqueous solution of H_2SO_4 of constant molality. The initial molality of the Tl_2SO_4 was $a = 0.005$ mol kg^{-1}, and the initial molality of the H_2SO_4 was $c = 0.05$ mol kg^{-1}. The supporting electrolyte (Na_2SO_4) was used to adjust the total ionic strength I of the aqueous solution to 0.1 to 2.0 mol kg^{-1}. The organic phase was prepared by dissolving $D_2EHMTPA$ in $n\text{-}C_8H_{16}$, the initial molality of $D_2EHMTPA$ being kept constant ($b = 0.05$ 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 Tl^+ ($m\{Tl^+\}$) in the equilibrium aqueous phase was determined using a WYX-402 atomic absorption spectrophotometer.

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

$$m\{T/HA_2\} = [2a - m\{Tl^+\}]/\rho \qquad \text{(Eq 4)}$$

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$$m\{H_2A_2\} = b/2 - [2a - m\{Tl^+\}]/\rho \qquad \text{(Eq 5)}$$

where ρ is the density of the organic phase. The substitution of Eq 4, 5, and 10 (section 3) into Eq 3 yields the values of K_M.

3. Results and Discussion

The values of K_M measured at the various temperatures (in the range 278.15–303.15 K) for several total ionic strengths in the range 0.1 to 2.0 mol kg^{-1} are listed in Table 1, where each value of K_M is the mean of two replicate measurements.

3.1 Effective Ionic Strength in the Equilibrium Aqueous Phase

There were five ionic species (i.e., H^+, Na^+, HSO_4^-, SO_4^{2-} and Tl^+) in the equilibrium aqueous phase. Their molalities and activity coefficients are $m\{H^+\}$, $m\{Na^+\}$, m_1, m_2, and $m\{Tl^+\}$, and $\gamma\{H^+\}$, $\gamma\{Na^+\}$, γ_1, γ_2, and $\gamma\{Tl^+\}$, respectively. The second dissociation of sulfuric acid is:

$$HSO_4^- = H^+ + SO_4^{2-}$$

K_2 is the second dissociation constant:

$$K_2 = [m\{H^+\} \cdot m_2/m_1] \cdot [\gamma_2 \cdot \gamma\{H^+\}/\gamma_1] \qquad \text{(Eq 6)}$$

The temperature dependence of K_2 between 0 and 55 °C has been given by Pitzer[6,7]:

$$\ln K_2 = -14.0321 + 2825.2/T \qquad \text{(Eq 7)}$$

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:

$$m_1 + m_2 = a + c + d \qquad \text{(Eq 8)}$$

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 6 to 8. The effective ionic strength I in the equilibrium aqueous phase can then be calculated as:

$$I = [m\{Tl^+\} + m_1 + 4m_2 + 2d + m\{H^+\}]/2 \qquad \text{(Eq 9)}$$

where

$$m\{H^+\} = (2a - m\{Tl^+\}) - m_1 + 2c \qquad \text{(Eq 10)}$$

The activity coefficients γ_1, γ_2, and $\gamma\{H^+\}$ in Eq 6 can be estimated using the Pitzer equations. According to the theory of Pitzer, the activity coefficients γ_M and γ_X of the

Table 1 Values of $\log K_M$ and effective ionic strength I at temperatures in the range 278.15 to 303.15 K

Variables	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
I′ = 1.8						
I	…	…	1.872	1.864	1.858	1.852
$Tl^+(\times 10^{-5})$	…	…	10.00	12.80	16.70	20.10
$\log K_M$	…	…	1.863	1.676	1.542	1.413
I′ = 2.0						
I	…	…	2.071	2.064	2.057	2.052
$Tl^+(\times 10^{-5})$	…	…	10.40	12.80	16.70	20.15
$\log K_M$	…	…	1.840	1.702	1.537	1.406
I′ = 0.1						
I	0.149	0.144	0.138	0.132	0.129	0.125
$Tl^+(\times 10^{-5})$	6.10	9.65	13.35	17.10	26.90	32.00
$\log K_M$	2.373	2.152	1.990	1.790	1.635	1.569
I′ = 0.2						
I	0.280	0.272	0.265	0.259	0.253	0.247
$Tl^+(\times 10^{-5})$	6.00	8.00	12.25	16.35	23.50	25.50
$\log K_M$	2.317	2.164	1.947	1.789	1.595	1.530
I′ = 0.4						
I	0.492	0.483	0.476	0.468	0.436	0.455
$Tl^+(\times 10^{-5})$	5.90	7.50	11.30	15.60	18.40	25.50
$\log K_M$	2.270	1.131	1.914	1.733	1.462	1.436
I′ = 0.5						
I	0.592	0.584	0.576	0.569	0.562	0.556
$Tl^+(\times 10^{-5})$	5.90	7.50	11.30	13.90	19.35	24.50
$\log K_M$	2.254	2.131	1.894	1.763	1.575	1.428
I′ = 0.6						
I	0.692	0.684	0.676	0.669	0.662	0.656
$Tl^+(\times 10^{-5})$	5.35	6.90	9.90	14.85	19.35	22.40
$\log K_M$	2.285	2.136	1.937	1.716	1.557	1.450
I′ = 0.8						
I	0.891	0.883	0.875	0.867	0.861	0.855
$Tl^+(\times 10^{-5})$	5.55	7.50	10.25	13.70	17.85	22.00
$\log K_M$	2.250	2.078	1.899	1.728	1.567	1.430
I′ = 1.0						
I	1.091	1.082	1.074	1.067	1.060	1.054
$Tl^+(\times 10^{-5})$	5.90	7.50	10.00	13.35	17.50	21.40
$\log K_M$	2.210	2.064	1.894	1.723	1.558	1.424
I′ = 1.2						
I	1.290	1.281	1.273	1.266	1.259	1.253
$Tl^+(\times 10^{-5})$	5.90	7.25	10.00	13.35	17.50	20.80
$\log K_M$	2.201	2.069	1.883	1.723	1.545	1.423
I′ = 1.4						
I	1.489	1.481	1.472	1.465	1.459	1.453
$Tl^+(\times 10^{-5})$	5.90	7.50	10.25	13.35	17.15	20.45
$\log K_M$	2.194	2.046	1.864	1.711	1.545	1.421
I′ = 1.5						
I	1.589	1.580	1.572	1.565	1.558	1.553
$Tl^+(\times 10^{-5})$	5.90	7.50	10.25	13.30	16.35	20.10
$\log K_M$	2.191	2.042	1.860	1.702	1.562	1.424
I′ = 1.6						
I	1.645	1.680	1.672	1.665	1.658	1.653
$Tl^+(\times 10^{-5})$	5.90	7.50	9.90	13.90	16.35	18.50
$\log K_M$	2.060	2.040	1.872	1.700	1.558	1.420

cation M and the anion X in a multicomponent electrolyte solution are given by[6]:

$$\ln\gamma_{\mathrm{M}} = \mathrm{z_M}^2F + \sum_a (m_{\mathrm{a}}/m^0)\,(2B_{\mathrm{Ma}} + ZC_{\mathrm{Ma}}) + \sum_c (m_{\mathrm{c}}/m^0) \left(2\Phi_{\mathrm{Mc}} + \sum_a (m_{\mathrm{a}}/m^0)\,\psi_{\mathrm{Mca}}\right) + \sum_a \sum_{a'} (m_{\mathrm{a}}/m^0) (m_{\mathrm{a'}}/m^0)\,\psi_{\mathrm{Maa'}} + |\mathrm{Z_M}| \sum_c \sum_a (m_{\mathrm{c}}/m^0)\,(m_{\mathrm{a}}/m^0)\,C_{\mathrm{ca}} \qquad \text{(Eq 11)}$$

$$\ln\gamma_{\mathrm{X}} = \mathrm{z_X}^2F + \sum_c (m_{\mathrm{c}}/m^0)\,(2B_{\mathrm{CX}} + ZC_{\mathrm{cX}}) + \sum_a (m_{\mathrm{a}}/m^0) \left(2\Phi_{\mathrm{Ma}} + \sum_c (m_{\mathrm{c}}/m^0)\,\psi_{\mathrm{cXa}}\right) + \sum_c \sum_{c'} (m_{\mathrm{c}}/m^0) (m_{\mathrm{c'}}/m^0)\,\psi_{\mathrm{cc'X}} + |\mathrm{Z_X}| \sum_c \sum_a (m_{\mathrm{c}}/m^0)\,(m_{\mathrm{a}}/m^0)\,C_{\mathrm{ca}} \qquad \text{(Eq 12)}$$

where

$$F = f^{\gamma} + \sum_a \sum_c (m_{\mathrm{a}}/m^0)\,(m_{\mathrm{c}}/m^0)B'_{\mathrm{ca}} + \sum_c \sum_{c'} (m_{\mathrm{c'}}/m^0)\,(m_{\mathrm{c'}}/m^0)\,\Phi'_{\mathrm{cc'}} + \sum_a \sum_{a'} (m_{\mathrm{a}}/m^0)\,(m_{\mathrm{a'}}/m^0)\,\Phi'_{\mathrm{aa'}} \qquad \text{(Eq 13)}$$

$$f^{\gamma} = -A_{\mathrm{P}}[(I/m^0)^{1/2}/[1 + 1.2(I/m^0)^{1/2}] + (2/1.2)\ln[1 + 1.2(I/m^0)^{1/2}] \qquad \text{(Eq 14)}$$

$$\mathrm{Z} = \sum_c (m_{\mathrm{c}}/m^0)\,|\mathrm{Z_c}| = \sum_a (m_{\mathrm{a}}/m^0)\,|\mathrm{Z_a}| \qquad \text{(Eq 15)}$$

$$C^{\mathrm{P}}_{\mathrm{ij}} = C^{\mathrm{P}}_{\mathrm{ij}}/2(|\mathrm{z_iz_j}|)^{1/2} \qquad \text{(Eq 16)}$$

and the subscripts c and a represent cations and anions, respectively, z is the charge of the ion ($m^0 = 1$ mol kg^{-1}), A_{P} is the Debye-Huckel coefficient of the osmotic function (this is given by Pitzer[7] and Bradley and Pitzer[8] for a wide range of temperatures and pressures), B_{ca} and C_{ca} are the second and third virial coefficients for the electrolyte, B'_{ca} is the first derivative of B_{ca} with respect to I/m^0, Φ_{ij} is the second virial coefficient representing the difference between the averaged interactions between unlike ions with charges of the same sign and between like ions, Φ'_{ij} is the derivative of Φ_{ij} with respect to I/m^0, and is the third virial coefficient similarly defined but for three ions with charges not all of the same sign. According to Pitzer and Kim,[9]

$$B_{\mathrm{ca}} = \beta^{(0)}_{\mathrm{cs}} + \beta^{(1)}_{\mathrm{ca}}\,y_1 \qquad \text{(Eq 17)}$$

$$B'_{\mathrm{ca}} = \beta^{(1)}_{\mathrm{ca}}\,y_2 \qquad \text{(Eq 18)}$$

where $\beta^{(0)}_{\mathrm{ca}}$ and $\beta^{(1)}_{\mathrm{ca}}$ are characteristic parameters of the electrolyte, and y_1 and y_2 are defined as:

$$y_1 = 2[1 - (1 + \alpha\{I/m^0\}^{1/2})\exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}) \qquad \text{(Eq 19)}$$

$$y_2 = 2[-1 + (1 + \alpha\{I/m^0\}^{1/2} + \alpha^2\{I/m^0\}/2) \times \exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}^2) \qquad \text{(Eq 20)}$$

The values of the Pitzer parameters for $NaHSO_4$ are not given in the literature, but according to Pitzer et al.,[10] the parameters for $NaClO_4$ may be used. In estimating γ_1, γ_2, and $\gamma\{H^+\}$, all of the mixed parameters (i.e., Φ_{ij}, Φ'_{ij}, and ω_{ijk}) are neglected, so that:

$$\ln\gamma\{\mathrm{H}^+\} = f^{\gamma} + (m\{\mathrm{Na}^+\}/m^0)(m_2/m^0)(\beta^{(1)}_{\mathrm{H2}}\,\mathrm{y}_3 + C_{\mathrm{Na2}}) + 2(m_2/m^0)\beta^{(0)}_{\mathrm{H2}} + 2(m_2/m^0)\,\beta^{(1)}_{\mathrm{H2}}y_1 + 2\,(m\{\mathrm{Na}^+\}/m^0)(m_2/m^0)C_{\mathrm{H2}} \qquad \text{(Eq 21)}$$

$$\ln(\gamma_2/\gamma_1) = 3f^{\gamma} + 3(m\{\mathrm{Na}^+\}/m^0)(m_2/m^0)\,\beta^{(1)}_{\mathrm{Na2}}\,y_a + 2(m\{\mathrm{Na}^+\}/m^0)(\beta^{(0)}_{\mathrm{Na2}} - \beta^{(0)}_{\mathrm{Na1}}) + 2(m\{\mathrm{Na}^+\}/m^0)y_1(\beta^{(1)}_{\mathrm{Na2}} - \beta^{(1)}_{\mathrm{Na1}}) + (m\{\mathrm{Na}^+\}/m^0)^2\,(C_{\mathrm{Na2}} - C_{\mathrm{Na1}}) + (m\{\mathrm{Na}^+\}/m^0)(m_2/m^0)C_{\mathrm{Na2}}) \qquad \text{(Eq 22)}$$

Using Eq 8 to 22 and the values of the Pitzer parameters at various temperatures, the values of the effective ionic strength in the equilibrium aqueous phase were obtained by an iterative calculation done on a VAX computer with a convergence criterion on Eq 6. The results are listed in Table 1.

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 $\gamma\{\mathrm{T}l\mathrm{HA_2}\} \approx \gamma\{\mathrm{H_2A_2}\} \approx 1$. As $\gamma\{\mathrm{H}^+\}/\gamma\{\mathrm{T}l^+\}$ in the equilibrium aqueous phase might be proportional to the effective ionic strength, the following may be used as a working equation for the extrapolation to determine K^0:

$$\log K_{\mathrm{M}} = \log K^0 + \Delta b(I/m^0) \qquad \text{(Eq 23)}$$

where $\log K_{\mathrm{M}}$ can be calculated from the experimental data, Δb is an empirical parameter, and $m^0 = 1$ mol kg^{-1}. Using a least-squares method, a linear regression of $\log K_{\mathrm{M}}$ versus (I/m^0) yielded values of $\log K^0$. These are given in Table 2 as $\log K^0$(D-H) together with the standard deviations of the fit of Eq 23.

3.3 Polynomial Approximation To Determine K^0

On the basis of the Pitzer electrolyte-solution theory, a second method for determining $\log K^0$ was proposed by Liu et al.[2] In using the Pitzer equations to determine K^0, it is assumed that: (a) the effective ionic strength is regarded as

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)

T, K	$\log K^0$ (D-H)	$s_K \times 10^2$	$S_f \times 10^2$	$\log K^0$ (P)	$s_K \times 10^2$	$s_f \times 10^2$
303.15	1.505	1.8	3.4	1.694	2.6	1.2
298.15	1.612	1.0	1.8	1.767	3.4	1.5
293.15	1.769	1.2	1.8	1.844	7.3	1.9
288.15	1.961	1.0	1.8	2.044	3.3	1.4
283.15	2.171	0.8	1.3	2.131	3.9	1.3
278.15	2.350	1.4	2.2	2.459	5.5	1.6

Table 3 The standard molar thermodynamic properties for the extraction process in the temperature range 278.15 to 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)$^{-1}$	$\Delta_r C_{pm}{}^0$, J (Kmol)$^{-1}$
303.15	−8.66	−43.89	−116	991
298.15	−9.29	−48.81	−133	975
293.15	−9.99	−53.64	−149	958
288.15	−10.78	−58.39	−165	942
283.15	−11.64	−63.06	−182	925
278.15	−12.59	−67.65	−198	909

Table 4 $\log K^0$ and thermodynamic properties of the extraction reaction

Variables	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
$\log K^0$	2.350	2.171	1.961	1.769	1.612	1.505
$\Delta_r G^0_M$, kJ mol^{-1}	−12.59	−11.64	−10.78	−9.99	−9.29	−8.66

the total ionic strength in the aqueous phase; (b) interactions between ions can be regarded as those among Tl^+, H^+, and the ions of the supporting electrolyte; (c) following the advice of Pitzer and Mayorga,[11] ψ_{TlNa_2} is considered to be independent of ionic strength. According to Pitzer and Kim,[9] the pertinent combination of activity coefficients for M^{zM+} and N^{zN-} may be written as:

$$\begin{aligned} z_N \ln\gamma_M - z_M \ln\gamma_N = {} & z_M z_N (z_M - z_N) F + \sum_a (m_a/m^0) \\ & \times [2z_N B_{Ma} - 2z_M B_{Na} + Z(z_N C_{Ma} - z_M C_{Na})] \\ & + 2 \sum_c (m_0/m^0)\, (z_N \Phi_{Mc} - z_M \Phi_{Nc}) \\ & + \sum_c \sum_a (m_c/m^0)\, (m_a/m^0) (z_N \psi_{Mca} - z_M \psi_{Nca}) \\ & + \sum_a \sum_{a'} (m_a/m^0)\, (m_a/m^0)\, z_N \psi_{Naa'} - z_M \psi_{Naa'}) \end{aligned} \tag{Eq 24}$$

for $\ln[\gamma\{H^+\}/\gamma\{Tl^+\}]$, Eq 24 may be reduced to:

$$\begin{aligned} \ln[\gamma\{H^+\}/\gamma\{Tl^+\}] = {} & 2(m_2/m^0)(B_{H2} - B_{Tl2}) + (m_2/m^0)(m_{Na}/m^0) \\ & (C_{H2} - C_{Tl2}) + 2(m_{Na}/m^0)(\Phi_{HNa} - \Phi_{TlNa}) \\ & + (m_{Na}/m^0)(m_2/m^0)(\psi_{HNa2} - \psi_{TlNa2}) \end{aligned} \tag{Eq 25}$$

Then, the substitution of Eq 25 into Eq 2 yields a working equation:

$$\begin{aligned} \log K' = {} & \log K_M + [2(m_2/m^0)(\beta^{(0)}_{H2} + \beta^{(1)}_{H2} y_1 + (m_{Na} m^0) C_{H2}) \\ & + 2(m_{Na}/m^0)\Phi_{NaH}]/\ln 10 \\ = {} & \log K^0 + 2(m_2/m^0)(\beta^{(0)}_{Tl2} + \Phi_{TlNa})/\ln 10 \\ & + 2(m_2/m^0) y_1 \beta^{(1)}_{Tl2}/\ln 10 (m_2/m^0)(m_{Na}/m^0) \\ & \times (\psi_{TlNa} + 2C_{Na_2} - \psi_{HNa_2})/\ln 10 \end{aligned} \tag{Eq 26}$$

Using a least-squares method, the regression of the extrapolation function ($\log K'$) calculated from the experimental results against $2(m_2/m^0)/\ln 10$, $2(m_2/m^0)y_1/\ln 10$, and $(m_2/m^0)(m_{Na}/m^0)/\ln 10$ yielded a value of $\log K^0$, which is here denoted by $\log K^0$(p) and is given 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).

3.4 Thermodynamic Properties for the Extraction Process

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

$$\log K^0 = (A_1 + A_2/T + A_3 T) \tag{Eq 27}$$

The values of parameters A_i are: $A_1 = -57.84$, $A_2 = 10{,}140.5$, and $A_3 = 0.0854$ with a standard deviation of $s = 0.039$.

The standard molar thermodynamic properties $\Delta_r G^0_M$, $\Delta_r H^0_M$, $\Delta_r S^0_M$, $\Delta_r C^0_{P,M}$ for the extraction process are simply related to the parameters in Eq 27:

$$\Delta_r G^0_M = -(R \ln 10)(A_1 T + A_2 + A_3 T^2) \tag{Eq 28}$$

$$\Delta_r H^0_M = (R \ln 10)(A_3 T^2 - A_2) \tag{Eq 29}$$

$$\Delta_r S^0_M = (R \ln 10)(A_1 + 2A_3 T) \tag{Eq 30}$$

$$\Delta_r C^0_{P,M} = (R \ln 10)(2A_3 T) \tag{Eq 31}$$

where R is the gas constant. The thermodynamic quantities calculated from Eq 28 to 31 are listed in Table 3.

4. Conclusions

- The extractant has a satisfactory extraction effect at various temperatures of the experiment. $\Delta_r G^0$ and K^0 increase with decreases in experimental temperatures, which indicates that low temperature benefits extraction.

- The negative experimental association of Gibbs energy, $\Delta G^0_M < 0$, means that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure. As is well known, the association of Gibbs energy includes two factors, that is $\Delta G^0_M = \Delta H^0_M - T \cdot \Delta S^0_M$ In the association reaction, $\Delta H^0_M > T \cdot \Delta S^0_M$ leads us to conclude that the enthalpy is the dominant thermodynamic factor.[12-14]
- The standard extraction constants K^0 at various temperatures were obtained by methods of extrapolation and polynomial approximation. The thermodynamic properties for the extraction process were calculated (Table 4).

The experimental results could establish a good foundation for optimization design in industrial production.

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