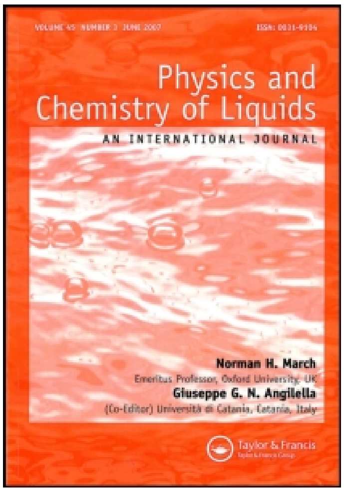

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Thermodynamics of solvent extraction of thallium with diethylhexyl phosphoric acid

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The equilibrium molalities Tl^+ were measured in $\{Tl_2SO_4 + Na_2SO_4 + D_2EHPA + n\text{-}C_8H_{18} + \text{Water}\}$ system at ionic strength from 0.1 to $2.0\,\text{mol kg}^{-1}$ containing Na_2SO_4 as supporting electrolyte in aqueous phase and at constant molality extractant at temperatures from 278.15 K 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; thallium; D_2EHPA

1. Introduction

Nowadays, reclaimation technics of thallium is by extraction of thallium with di-2-ethylhexylphosphoric acid (D_2EHPA) in hydrometallurgy. In this article, D_2EHPA is used as extractant in extracting thallium. The extraction reaction mechanism of extracting Tl^+ with D_2EHPA in sulfuric acid medium is cation exchange process [1–5]. In presence of excessive extractant, the extraction reaction [6] is:

$$Tl^+(aq) + H_2R_2(org) = TlHR_2(org) + H^+(aq), \tag{1}$$

where (aq) and (org) refer to the aqueous and organic phase, respectively, H_2R_2 is the dimer of the extractant (D_2EHPA), and $TlHR_2$ is the extraction complex. The standard equilibrium constant K [0] is given by

$$\log K^0 = \log K_M + \log\left[\frac{\gamma\{TlHR_2\}}{\gamma\{H_2R_2\}}\right] + \log\left[\frac{\gamma\{H^+\}}{\gamma\{Tl^+\}}\right], \tag{2}$$

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

$$K_M = \frac{[m\{TlHR_2\} \cdot m\{H^+\}]}{m\{H_2R_2\}/m\{Tl^+\}}, \tag{3}$$

where m is the molality.

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2. Experimental

The water used was doubly deionised and its conductance was $1.5 \times 10^{-4}\,\Omega^{-1}\,\mathrm{m}^{-1}$. The thallium sulphate was of GR grade, the sulphuric acid was of AR grade (99% mass pure), and the anhydrous sodium sulphate was of AR grade and dried for 4 h in the oven at 170°C before use. According to the method recommended by Levin and Sergeeva [1], the extractant (D_2EHPA) was purified. The n-C_8H_{18} used as 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 $a = 0.001\,\mathrm{mol\,kg^{-1}}$, and the initial molality of the H_2SO_4 was $c = 0.03\,\mathrm{mol\,kg^{-1}}$. The supporting electrolyte (Na_2SO_4) was used to adjust the total ionic strength I of the aqueous solution to 0.1–2.0 $\mathrm{mol\,kg^{-1}}$. The organic phase was prepared by dissolving D_2EHPA in n-C_8H_{18}, the initial molality of D_2EHPA being kept constant ($b = 0.02\,\mathrm{mol\,kg^{-1}}$).

A volume ($10\,\mathrm{cm}^3$) 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 7230 type spectrophotometer [7].

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:

$$m\{\mathrm{TlHR_2}\} = \frac{[2a - m\{\mathrm{Tl}^+\}]}{\rho}, \tag{4}$$

$$m\{\mathrm{H_2R_2}\} = b - \frac{[2a - m\{\mathrm{Tl}^+\}]}{\rho}, \tag{5}$$

where ρ is the density of the organic phase. Substitution of Equations (4), (5) and (10) (see later) in to Equation (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 0.1–2.0 $\mathrm{mol\,kg^{-1}}$ are listed in Table 1, where each value of K_M is the mean of two replicate measurements. From the Table 1, we can see that the values of K_M seesawed with the temperatrue and ionic strengh, so a more in-depth dicussion was absolutely needed.

3.1. *Effective ionic strength in the equilibrium aqueous phase*

There were five ionic species (H^+, Na^+, HSO_4^-, SO_4^{2-} and Tl^+) in the equilibrium aqueous phase. There 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 sulphuric acid is

$$\mathrm{HSO_4^-} = \mathrm{H^+} + \mathrm{SO_4^{2-}}.$$

Table 1. Values of log K_M and effective ionic strength I at temperatures in the range 278.15–303.15 K.

T (K)	278.15	283.15	288.15	293.15	298.15	303.15
$I = 0.1$						
I'	0.1374	0.1347	0.1301	0.1718	0.1242	0.1210
log K_M	1.1170	1.4326	1.3711	1.4402	1.2808	1.3155
$I = 0.2$						
I'	0.2483	0.2449	0.2392	0.2860	0.2328	0.2293
log K_M	1.2905	1.4092	1.3969	1.1783	1.3395	1.1973
$I = 0.4$						
I'	0.4497	0.4463	0.4302	0.4852	0.4341	0.4306
log K_M	1.3483	1.5121	1.3124	1.2937	1.3931	1.3711
$I = 0.5$						
I'	0.5489	0.5456	0.5393	0.5819	0.5335	0.5302
log K_M	1.4275	1.385	1.3793	1.5607	1.3395	1.2265
$I = 0.6$						
I'	0.6487	0.6446	0.6383	0.6784	0.6327	0.6295
Log K_M	1.3904	1.3931	1.4066	1.5607	1.4795	1.3246
$I = 0.8$						
I'	0.8458	0.8247	0.8365	0.8712	0.8313	0.8284
log K_M	1.3711	1.4452	1.7218	1.5839	1.4249	1.0576
$I = 1.0$						
I'	1.0440	1.0401	1.0349	1.0645	1.0300	1.0273
log K_M	1.4326	1.5052	1.4066	1.5818	1.4601	1.0576
$I = 1.2$						
I'	1.2424	1.2395	1.2335	1.2586	1.2290	1.2263
log K_M	1.4866	1.6084	1.4936	1.6382	1.3655	1.2265
$I = 1.4$						
I'	1.4409	1.4383	1.4322	1.4537	1.4280	1.4256
log K_M	1.3877	1.4576	1.3931	1.4223	1.3795	0.6808
$I = 1.5$						
I'	1.5404	1.5378	1.5340	1.5514	1.5276	1.5251
log K_M	1.5098	1.3306	1.3483	1.3795	1.3931	1.0174
$I = 1.6$						
I'	1.6399	1.6371	1.6311	1.6492	1.6271	1.6247
log K_M	1.6205	1.4747	1.2968	1.4936	1.4818	1.2121
$I = 1.8$						
I'		1.8361	1.8301	1.8454	1.8263	1.8241
log K_M		1.5167	1.3454	1.4118	1.5029	0.9796
$I = 2.0$						
I'			2.0292	2.0419	2.0257	2.0236
log K_M			1.4576	1.5368	1.3985	0.8228

K_2 is the second dissociation constant:

$$K_2 = \left[m\{\mathrm{H}^+\} \cdot \frac{m_2}{m_1}\right] \cdot \left[\frac{\gamma_2 \cdot \gamma\{\mathrm{H}^+\}}{\gamma_1}\right]. \tag{6}$$

The temperature dependence of K_2 between 0 and 55°C has been given by Pitzer *et al.* as:

$$\ln K_2 = \frac{-14.0321 + 2825.2}{\mathrm{T}}. \tag{7}$$

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

$$m_1 + m_2 = a + c + d, \tag{8}$$

where d is the initial molality of the $\mathrm{Na_2SO_4}$ used as the supporting electrolyte. The values of m_1 and m_2 can be obtained from Equations (6)–(8). The effective ionic strength I in the equilibrium aqueous phase can then be calculated as

$$I = \frac{[m\{\mathrm{Tl}^+\}] + m_1 + 4m_2 + 2d + m\{\mathrm{H}^+\}]}{2}, \tag{9}$$

where

$$m\{\mathrm{H}^+\} = (2a - m\{\mathrm{Tl}^+\}) - m_1 + 2\mathrm{c}. \tag{10}$$

The activity coefficients γ_1, γ_2 and $\gamma\{\mathrm{H}^+\}$ in Equation (6) 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 [8]:

$$\begin{aligned}\ln y_\mathrm{M} = {} & z_\mathrm{M}^2 F + \sum_a \left(\frac{m_a}{m^0}\right)(2B_\mathrm{M}a + ZC_\mathrm{M}a) + \sum_c \left(\frac{m_c}{m^0}\right)(2\Phi_{\mathrm{M}c} + \sum_a \left(\frac{m_a}{m^0}\right)\psi_{\mathrm{M}ca} \\ & + \sum_a \sum_{a'} \left(\frac{m_a}{m^0}\right)\left(\frac{m_a'}{m^0}\right)\psi'_{\mathrm{M}aa} + |Z_\mathrm{M}| \sum_c \sum_a \left(\frac{m_c}{m^0}\right)\left(\frac{m_a}{m^0}\right) C_{ca},\end{aligned} \tag{11}$$

$$\begin{aligned}\ln \gamma_x = {} & z\mathrm{x}^2 F + \sum_c \left(\frac{m_c}{m^0}\right)(2B_{c\mathrm{X}} + ZC_{c\mathrm{X}}) + \sum_a \left(\frac{m_a}{m^0}\right)\left(2\Phi_{\mathrm{M}a} + \sum_c \left(\frac{m_c}{m^0}\right)\psi_{c\mathrm{X}a}\right) \\ & + \sum_c \sum_{c'} \left(\frac{m_c}{m^0}\right)\left(\frac{m_{c'}}{m^0}\right)\psi_{cc'\mathrm{X}} + |Z_\mathrm{X}| \sum_c \sum_a \left(\frac{m_c}{m^0}\right)\left(\frac{m_a}{m^0}\right) C_{ca},\end{aligned} \tag{12}$$

where

$$\begin{aligned}F = f & + \sum_a \sum_c \left(\frac{m_a}{m^0}\right)\left(\frac{m_c}{m^0}\right) B'_{ca} + \sum_c \sum_{c'} \left(\frac{m_c}{m^0}\right)\left(\frac{m_{c'}}{m^0}\right)\Phi'_{cc'} \\ & \sum_a \sum_{a'} \left(\frac{m_a}{m^0}\right)\left(\frac{m_{a'}}{m^0}\right)\Phi'_{aa'},\end{aligned} \tag{13}$$

$$f = -A_p\left[\frac{(I/m^0)^{1/2}}{1 + 1.2(I/m^0)^{1/2}}\right] + \left(\frac{2}{1.2}\right)\ln\left[1 + 1.2\left(\frac{I}{m^0}\right)^{1/2}\right], \tag{14}$$

$$Z = \sum_c \left(\frac{m_c}{m^0}\right)|Z_c| = \sum_a \left(\frac{m_a}{m^0}\right)|Z_a|, \tag{15}$$

$$C_{ij}^{P} = \frac{C_{ij}^{P}}{2(|z_i z_j|)^{1/2}}, \tag{16}$$

where the subscripts '*c*' and '*a*' represent cations and anions, respectively, z is the charge of the ion ($m^0 = 1\,\mathrm{mol\,kg^{-1}}$), A_P is the Debye–Huckel coefficient of the osmotic function (this is given by Bradley and Pitzer [9,10] 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 [11];

$$B_{ca} = \beta_{cs}^{(0)} + \beta_{ca}^{(1)} y_1, \tag{17}$$

$$B'_{ca} = \beta_{ca}^{(1)} y_2, \tag{18}$$

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

$$y_1 = \frac{2[1 - (1 + \alpha\{I/m^0\}^{1/2})]\exp(-\alpha\{I/m^0\}^{1/2})}{(\alpha^2\{I/m^0\})}, \tag{19}$$

$$y_2 = \frac{2[-1 + (1 + \alpha\{I/m^0\}^{1/2} + \alpha^2\{I/m^0\}^{1/2}/2)] \times \exp(-\alpha\{I/m^0\}^{1/2})}{(\alpha^2\{I/m^0\}^{1/2})}. \tag{20}$$

The values of Pitzer's parameters for $\mathrm{NaHSO_4}$ are not given in the literature, but according to Pitzer *et al.* [12], the parameters for $\mathrm{NaClO_4}$ may be used. In estimating γ_1, γ_2 and $\gamma\{\mathrm{H^+}\}$, all the mixed parameters (Φ_{ij}, Φ'_{ij} and ψ_{ijk}) are neglected, so that

$$\begin{aligned}\ln\gamma\{\mathrm{H^+}\} = {} & f + \left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right)\left(\frac{m_2}{m^0}\right)\left(\beta_{\mathrm{H2}}^{(1)} y_3 + C_{\mathrm{Na2}}\right) + 2\left(\frac{m_2}{m^0}\right)\beta_{\mathrm{H2}}^{(0)} + 2\left(\frac{m_2}{m^0}\right)\beta_{\mathrm{H2}}^{(1)} y_1 \\ & + 2\left(\frac{m\{Na^+\}}{m^0}\right)\left(\frac{m_2}{m^0}\right)C_{\mathrm{H2}},\end{aligned} \tag{21}$$

$$\begin{aligned}\ln\left(\frac{\gamma_2}{\gamma_1}\right) = {} & 3f + 3\left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right)\left(\frac{m_2}{m^0}\right)\beta_{\mathrm{Na2}}^{(1)} y_a + 2\left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right)\left(\beta_{\mathrm{Na2}}^{(0)} - \beta_{\mathrm{Na1}}^{(0)}\right) \\ & + 2\left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right) y_1 \left(\beta_{\mathrm{Na2}}^{(0)} - \beta_{\mathrm{Na1}}^{(0)}\right) + \left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right)^2 (C_{\mathrm{Na2}} - C_{\mathrm{Na}i}) \\ & + \left(\frac{m\{\mathrm{Na^+}\}}{m^0}\right)\left(\frac{m_2}{m^0}\right)C_{\mathrm{Na2}}\Big).\end{aligned} \tag{22}$$

Using Equations (8)–(22) and the values of Pitzer's parameters at various temperatures, 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 Equation (6). The results are listed in Table 1.

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

T (K)	log K^0 (D-H)	s × 10^2	log K^0 (P)	s × 10^2
303.15	1.043	1.54	1.069	2.79
298.15	1.175	1.53	1.231	2.76
293.15	1.391	1.04	1.414	1.87
288.15	1.562	1.16	1.638	2.09
283.15	1.691	1.15	1.729	2.05
278.15	1.900	1.64	1.996	2.69

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 $\gamma\{\mathrm{TlHA_2}\} \approx \gamma\{\mathrm{H_2A_2}\} \approx 1$. As $\gamma\{\mathrm{H^+}\}/\gamma\{\mathrm{Tl^+}\}$ 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:

$$\log K_\mathrm{M} = \log K^0 + \Delta b\left(\frac{I}{m^0}\right), \tag{23}$$

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

3.3. *Polynomial approximation to determine K^0*

On the basis of Pitzer's electrolyte-solution theory, a second method for determining log K^0 was proposed by Song *et al.* [2]. In using Pitzer's equations to determine K^0 it is assumed that: (1) the effective ionic strength is regarded as the total ionic strength in the aqueous phase; (2) interactions between ions can be regarded as those between $\mathrm{Tl^+}$, $\mathrm{H^+}$ and the ions of the supporting electrolyte; (3) following the advice of Pitzer and Mayorga [13] $\psi_{\mathrm{TlNa_2}}$ is considered to be independent of ionic strength. According to Pitzer and Kim [11] the pertinent combination of activity coefficients for $\mathrm{M}^{z\mathrm{M}+}$ and $\mathrm{N}^{z\mathrm{N}-}$ may be written as

$$\begin{aligned} z_\mathrm{N}\ln\gamma_\mathrm{M} - z_\mathrm{M}\ln\gamma_\mathrm{N} = {} & z_\mathrm{M}z_\mathrm{N}(z_\mathrm{M}-z_\mathrm{N})F \\ & + \sum_c \left(\frac{m_a}{m^0}\right) \times [z_\mathrm{N}B_{\mathrm{M}a} - z_\mathrm{M}B_{\mathrm{N}a} + Z(z_\mathrm{N}C_{\mathrm{M}a} - z_\mathrm{M}C_{\mathrm{N}a})] \\ & + 2\sum_c\sum_a \left(\frac{m_0}{m^0}\right)(z_\mathrm{N}\Phi_{\mathrm{M}c} - z_\mathrm{M}\Phi_{\mathrm{N}c}) \\ & + \sum_c\sum_a \left(\frac{m_c}{m^0}\right)\left(\frac{m_a}{m^0}\right)(z_\mathrm{N}\psi_{\mathrm{M}ca} - z_\mathrm{M}\psi_{\mathrm{N}ca}) \\ & + \sum_a\sum_{a'} \left(\frac{m_a}{m^0}\right)\left(\frac{m_a}{m^0}\right) z_\mathrm{N}\psi_{\mathrm{N}aa'} - z_\mathrm{M}\psi_{\mathrm{N}aa'}, \end{aligned} \tag{24}$$

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

$$\ln\left[\frac{\gamma\{H^+\}}{\gamma\{Tl^+\}}\right] = 2\left(\frac{m_2}{m^0}\right)(B_{H2} - B_{Tl2}) + \left(\frac{m_2}{m^0}\right)\left(\frac{m_{Na}}{m^0}\right)(C_{H2} - C_{Tl2}) + 2\left(\frac{m_{Na}}{m^0}\right)(\Phi_{HNa} - \Phi_{TlNa}) + \left(\frac{m_{Na}}{m^0}\right)\left(\frac{m_2}{m^0}\right)(\psi_{HNa2} - \psi_{TlNa2}). \tag{25}$$

Then, substitution of Equation (25) into Equation (2) yields a working equation

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

Using a least-squares method, 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 $\log K^0(\mathrm{p})$ and is given in Table 2. It is evident from Table 2 that the value of $\log K^0(\mathrm{p})$ is similar to that of $\log K^0(\mathrm{D\text{-}H})$.

3.4. *Thermodynamic quantities for the extraction process*

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

$$\log K^0 = \left(\frac{A_1 + A_2}{\mathrm{T} + A_3\mathrm{T}}\right). \tag{27}$$

The values of parameters A_i were obtained: $A_1 = 14.73$, $A_2 = -478.44$ and $A_3 = 0.0040$ with a standard deviation of $s = 0.0028$.

The standard molar thermodynamic quantities $\Delta_r G^0_m$, $\Delta_r H^0_m$, $\Delta_r S^0_m$, $\Delta_r H^0_m$, $\Delta_r C^0_{P,m}$ for the extraction process are simply related to the parameters in Equation (27):

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

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

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

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

where R is the gas constant. The thermodynamic quantities calculated from Equations (28)–(31) are listed in Table 3.

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

T(k)	$\Delta_r G_m^0$ (kJmol^{-1})	$\Delta_r H_m^0$ (kJmol^{-1})	$\Delta_r S_m^0$ (kJmol^{-1}))	$\Delta_r C_{Pm}^0$ (kJmol^{-1})
303.15	−5.98	−61.19	−182.13	−464
298.15	−6.87	−58.89	−174.48	−456
293.15	−7.72	−56.63	−166.82	−448
288.15	−8.54	−54.40	−159.17	−441
283.15	−9.31	−52.21	−151.51	−433
278.15	−10.05	−50.07	−143.86	−425

4. Conclusion

The negative experimental association Gibbs free energy $\Delta_r G_m^0 < 0$ means that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure. As is well known, association Gibbs energy includes two factors, that is $\Delta_r G_m^0 = \Delta_r H_m^0 - T \cdot \Delta_r S_m^0$. In the association reaction, $\Delta_r H_m^0$, and $\Delta_r S_m^0 < 0$, which leads us to conclude that the enthalpy is the dominant thermodynamic factor [14–16].

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