Studies on Solvent Extraction of Perrhenate with Trialkylamine by Debye−Hückel and Pitzer Equations[†]

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In the solvent extraction system {$R_3N + NH_4ReO_4 + n\text{-}C_7H_{16} + HCl + H_2O$}, the equilibrium molalities of ReO_4^- were measured at ionic strength from (0.1 to 2.0) $mol\cdot kg^{-1}$ in the aqueous phase containing NH_4Cl as supporting electrolyte in the range of 278.15 K to 303.15 K. The standard extraction constants K^0 at various temperatures were obtained by methods of Debye−Hückel extrapolation and Pitzer polynomial approximation. Thermodynamic properties for the extraction process were calculated.

Introduction

Rhenium is a high melting point metal, which was broadly applied in engine manufacture. One of the key reasons why rhenium is so important today is that it has a rather unique property. Rhenium has no known ductile to brittle transition temperature unlike molybdenum and tungsten even after complete recrystallization annealing. Products from rhenium can be thermally cycled thousands of times with no ill effect. It can be alloyed with tungsten or molybdenum and, near the solubility limits, imparts improved ductility to those materials. High-temperature strength, low friction, ductility, and other rather unique properties make it the material of choice for many critical applications. Solvent extraction is one of the main methods of separation and enrichment of rhenium from non-ferrous metal mine tailings.[1−3] So, it is important to study the extraction system in the theoretical field and industry.

As a continuation of our previous work,[4] in this paper we applied Pitzer's equaiton to the solvent extraction system and discussed the extraction process by the Pitzer electrolyte solution theory. The standard extraction constants K^0 are obtained by methods of Debye−Hückel extrapolation and Pitzer equation polynomial approximation.[5,6]

Trialkylamine (tertiary amine with 8 to 12 subchain carbons which is abbreviated as R_3N, average mole mass 355.8) is one of the most widely used extractants with a lower cost in the separation of rhenium. In the presence of excessive extractant R_3N, the extraction reaction is

$$R_3N(\text{org}) + H^+(\text{aq}) + ReO_4^-(\text{aq}) = H^+\cdot NR_3\cdot ReO_4^-(\text{org}) \tag{1}$$

where (aq) and (org) refer to the aqueous and organic phase, respectively; R_3N is the extractant; and $NR_3\cdot H^+\cdot ReO_4^-$ is the extracted complex. The standard equilibrium constant K^0 is given by

$$\log K^0 = \log[m\{H^+\cdot NR_3\cdot ReO_4^-\}] - \log[m\{H^+\}\cdot m\{ReO_4^-\}\cdot m\{NR_3\}] + \log[\gamma\{H^+\cdot NR_3\cdot ReO_4^-\}] - \log[\gamma\{H^+\}\cdot\gamma\{ReO_4^-\}\cdot\gamma\{NR_3\}] \tag{2}$$

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

Experimental Section

The water used was doubly deionized, and its conductance was 0.15 $mS\cdot m^{-1}$. The ammonium chloride was of AR grade. The n-C_7H_{16} used as diluent was of AR grade (99.5 %). R_3N was purchased from Dalian dyestuff company (99 % mass purity).

All initial solutions to be measured were freshly prepared. The aqueous phase was prepared by dissolving NH_4ReO_4 (99.99 % mass purity) in an aqueous solution of HCl of constant molality. The initial molality of the NH_4ReO_4 was $a = 0.001$ $mol\cdot kg^{-1}$, and the initial molality of the HCl was $c = 0.1$ $mol\cdot kg^{-1}$. The supporting electrolyte (NH_4Cl) was used to adjust the total ionic strength I of the aqueous solution to (0.1 to 2.0) $mol\cdot kg^{-1}$. The organic phase was prepared by dissolving R_3N in n-C_7H_{16}, the initial molality of R_3N being kept constant ($b = 0.02$ $mol\cdot kg^{-1}$).

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 ± 0.05 K. After standing for 15 min, the two phases were separated, and the molality of ReO_4^- ($m\{ReO_4^-\}$) in the equilibrium aqueous phase was determined using a 722 spectrophotometer at $\lambda = 424$ nm with uncertainty of ± 0.001.[7] The data in the thermodynamic extraction equilibrium system did not exist before.

The equilibrium molalities ($m\{i\}$ for the species i) in the organic phase were calculated from the initial molalities a, b, and $m\{ReO_4^-\}$ in the aqueous phase

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Table 1. Values of pH and Effective Ionic Strength I' at Temperatures in the Range (278.15 to 303.15) K[a]

T/K	278.15	283.15	288.15	293.15	298.15	303.15
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.1013	0.0950	0.0896	0.0887	0.0877	0.0863
$m\delta$ $(\cdot 10^{-6})$	0.1614	0.1242	0.1366	0.9685	0.9313	1.987
pH	0.67	0.56	0.56	1.05	1.03	1.06
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.2025	0.1971	0.1904	0.1892	0.1890	0.1876
$m\delta$ $(\cdot 10^{-6})$	0.2856	0.1738	0.2980	0.329	1.043	1.987
pH	0.65	0.58	0.62	1.04	1.02	0.94
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.4041	0.3988	0.3923	0.3908	0.3902	0.3881
$m\delta$ $(\cdot 10^{-6})$	0.5277	0.4843	0.4843	1.875	1.565	2.856
pH	0.68	0.86	0.65	1.03	0.99	0.93
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.5045	0.5015	0.4936	0.4919	0.4910	0.4884
$m\delta$ $(\cdot 10^{-6})$	0.8071	0.5091	0.6954	7.326	2.558	3.725
pH	0.69	0.88	0.70	1.01	0.99	0.92
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.6056	0.6017	0.5962	0.5922	0.5916	0.5888
$m\delta$ $(\cdot 10^{-6})$	1.180	0.6084	0.8071	1.701	2.434	3.415
pH	1.01	0.89	0.76	1.03	1.01	0.87
$I'/\text{mol}\cdot\text{kg}^{-1}$	0.8068	0.8024	0.7978	0.7926	0.7928	0.7891
$m\delta$ $(\cdot 10^{-6})$	1.242	1.055	1.378	1.925	3.601	5.960
pH	1.12	1.07	0.93	0.99	0.97	0.98
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.0085	1.0031	0.9985	0.9937	0.9934	0.9898
$m\delta$ $(\cdot 10^{-6})$	1.304	1.974	1.540	2.285	3.725	4.967
pH	1.10	1.19	0.92	0.97	0.95	0.92
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.2087	1.2041	1.1988	1.1952	1.1941	1.1906
$m\delta$ $(\cdot 10^{-6})$	1.391	2.483	2.260	1.527	2.943	6.022
pH	1.09	1.25	1.06	0.98	0.90	0.88
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.4098	1.4053	1.4007	1.3975	1.3948	1.3913
$m\delta$ $(\cdot 10^{-6})$	1.428	1.987	2.396	3.365	3.688	6.146
pH	1.05	1.10	1.02	0.96	0.92	0.85
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.5112	1.5058	1.5013	1.4979	1.4959	1.4921
$m\delta$ $(\cdot 10^{-6})$	2.049	2.049	2.483	4.371	4.222	7.388
pH	1.15	1.10	1.01	0.90	0.91	0.96
$\log K_m$	4.8880	4.8882	4.8044	4.5580	4.5732	4.3286
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.6153	1.6063	1.6016	1.6009	1.5978	1.5929
$m\delta$ $(\cdot 10^{-6})$	2.608	2.111	2.918	2.434	4.594	6.891
pH	1.16	1.06	1.00	0.89	0.89	0.79
$I'/\text{mol}\cdot\text{kg}^{-1}$	1.8181	1.8079	1.8031	1.8021	1.8003	1.7937
$m\delta$ $(\cdot 10^{-6})$	3.353	2.111	3.464	3.638	5.203	7.388
pH	1.15	0.99	1.02	0.87	0.85	0.82
$I'/\text{mol}\cdot\text{kg}^{-1}$	2.0200	2.0089	2.0037	2.0034	2.0014	1.9955
$m\delta$ $(\cdot 10^{-6})$	3.911	2.856	3.924	3.855	5.290	7.636
pH	1.14	1.10	1.04	0.86	0.83	0.80

[a] $\delta = \text{ReO}_4^-$. Unit of $m\delta$: $\text{mol}\cdot\text{kg}^{-1}$.

$$m\{\text{H}^+\cdot\text{NR}_3\cdot\text{ReO}_4^-\} = [a - m\{\text{ReO}_4^-\}]/\rho \qquad (3)$$

$$m\{\text{NR}_3\} = b - [a - m\{\text{ReO}_4^-\}]/\rho \qquad (4)$$

where ρ is the density of the organic phase.

Results and Discussion

The values of pH measured at the various temperatures (in the range (278.15 to 303.15) K) for several total ionic strengths in the range (0.1 to 2.0) $\text{mol}\cdot\text{kg}^{-1}$ are listed in Table 1, where each value of pH is the mean of three replicate measurements with uncertainty of ± 0.01.

Extrapolation to Determine the Value of K^0. There were four ionic species (H^+, NH_4^+, ReO_4^-, and Cl^-) in the equilibrium aqueous phase. Their molalities and activity coefficients are $m\{\text{H}^+\}$, $m\{\text{NH}_4^+\}$, $m\{\text{ReO}_4^-\}$, and $m\{\text{Cl}^-\}$ and $\gamma\{\text{H}^+\}$, $\gamma\{\text{NH}_4^+\}$, $\gamma\{\text{ReO}_4^-\}$, and $\gamma\{\text{Cl}^-\}$, respectively. The effective ionic strength I' in the equilibrium aqueous phase can then be calculated as

$$I' = 1/2\sum m_i Z_i^2 \qquad (5)$$

The calculated values of I' are listed in Table 1. Then eq 2 could be expressed as

$$\log K^0 = \log K_m + \text{pH} + \log[\gamma\{\text{H}^+\cdot\text{NR}_3\cdot\text{ReO}_4^-\}] - \log[\gamma\{\text{NR}_3\}] - \log\gamma[\text{ReO}_4^-] \qquad (6)$$

and K_m is the equilibrium concentration product, defined as

$$K_m = m\{\text{H}^+\cdot\text{NR}_3\cdot\text{ReO}_4^-\}/[m\{\text{ReO}_4^-\}\cdot m\{\text{NR}_3\}] \qquad (7)$$

Because the molalities of the extraction complex and the extractant in the equilibrium organic phase are very small, it can be assumed that $\gamma\{\text{H}^+\cdot\text{NR}_3\cdot\text{ReO}_4^-\}/\gamma\{\text{NR}_3\} \approx 1$. As $\gamma\{\text{ReO}_4^-\}$ in the equilibrium aqueous phase might be proportional to the effective ionic strength, it can be expressed by the extended Debye–Hückel equation, and the working equation to determine K^0 by extrapolation is

Table 2. Values of log K^0 over the Temperature Range 278.15 K to 303.15 K Obtained Using the Two Methods

T/K	log K^0(D−H)	a^0/A	log K^0(P)	$\beta^{(0)}_{NH_4\cdot ReO_4}$	$y_1\beta^{(1)}_{NH_4ReO_4}$	$1/2\cdot ZC_{NH_4ReO_4}$
303.15	6.4308	0.9	4.4472	−150.73	−5.9945	431.86
298.15	6.5790	0.9	4.7581	−72.534	−7.0394	207.80
293.15	6.5914	0.7	4.6679	696.77	−3.8351	−2001.2
288.15	6.6376	0.8	5.3461	−239.80	−7.9186	687.48
283.15	6.7331	0.9	5.4965	−1743.1	−8.2667	5002.3
278.15	6.8082	0.8	5.2749	−160.03	−6.7637	458.27

$$\log K' = \log K_m + \mathrm{pH} + \frac{A\sqrt{I'\rho}}{1 + Ba^0\sqrt{I'\rho}} = \log K^0 + bI' \tag{8}$$

where log K' is an extrapolation function, which can be calculated from experimental results; a^0 is the ion-size parameter; b is an empirical parameter; and A and B are the Debye−Hückel parameters. Using a least-squares method, a linear regression of log K' vs I' yielded values of log K^0. These are given in Table 2 as log K^0(D−H) together with the standard deviations.

Polynomial Approximation to Determine K^0. Equation 2 could be expressed as

$$\log K^0 = \log[m\{H^+\cdot NR_3\cdot ReO_4{}^-\}] - \log[m\{H^+\}\cdot m\{ReO_4{}^-\}\cdot m\{NR_3\}] - \log[\gamma\{H^+\}\cdot\gamma\{ReO_4{}^-\}] \tag{9}$$

The activity coefficients $\gamma\{H^+\}$ and $\gamma\{ReO_4{}^-\}$ in eq 9 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]

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

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

where

$$\begin{aligned}F = {} & f^r + \sum_a\sum_c (m_a/m^0)(m_c/m^0)B'_{ca} + \sum_c\sum_{c'} (m_c/m^0)(m_{c'}/m^0)\Phi'_{cc'} \\ & + \sum_a\sum_{a'} (m_a/m^0)(m_{a'}/m^0)\Phi'_{aa'}\end{aligned} \tag{12}$$

$$f^r = -A_P[(I/m^0)^{1/2}/[1 + 1.2(I/m^0)^{1/2}] + (2/1.2)\ln[1 + 1.2(I/m^0)^{1/2}] \tag{13}$$

$$Z = \sum_c (m_c/m^0)|Z_c| = \sum_a (m_a/m^0)|Z_a| \tag{14}$$

$$C^P_{ij} = C^P_{ij}/2(|z_iz_j|)^{1/2} \tag{15}$$

where the subscripts "c" and "a" represent cations and anions, respectively; z is the charge of the ion ($m^0 = 1\ \mathrm{mol\cdot kg^{-1}}$); A_P is the Debye−Hückel 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]

$$B_{ca} = \beta^{(0)}_{cs} + \beta^{(1)}_{ca}y_1 \tag{16}$$

$$B_{ca'} = \beta^{(1)}_{ca}y_2 \tag{17}$$

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

$$y_1 = 2[1 - (1 + \alpha\{I/m^0\}^{1/2})\exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}) \tag{18}$$

$$y_2 = 2[-1 + (1 + \alpha\{I/m^0\}^{1/2} + \alpha^2\{I/m^0\}/2)\cdot\exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}^2) \tag{19}$$

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 Tl^+, H^+, and the ions of the supporting electrolyte; (3) following the advice of Pitzer and Mayorga,[12,13] ψ_{Mca} is considered to be independent of ionic strength. In estimating $\gamma\{ReO_4{}^-\}$ and $\gamma\{H^+\}$, all the mixed parameters (Φ_{ij}, Φ_{ij}', andΨ_{ijk}) are neglected, so that the pertinent combination of activity coefficients may be written as

$$\begin{aligned}\ln \gamma_{\mathrm{MX}} = {} & |z_{\mathrm{M}}z_{\mathrm{X}}|F + (v_{\mathrm{M}}/v)\sum_{\mathrm{a}} m_{\mathrm{a}}\cdot[2B_{\mathrm{Ma}} + ZC_{\mathrm{Ma}} + \\ & 2(v_{\mathrm{X}}/v)\Phi_{\mathrm{Xa}}] + (v_{\mathrm{X}}/v)\sum_{\mathrm{c}} m_{\mathrm{c}}[2B_{\mathrm{Cx}} + ZC_{\mathrm{Cx}} \\ & + 2(v_{\mathrm{M}}/v)\Phi_{\mathrm{Mc}}] + \sum_{\mathrm{c}}\sum_{\mathrm{a}} m_{\mathrm{c}}\mathrm{m}_{\mathrm{a}}v^{-1}\cdot \\ & [2v_{\mathrm{M}}Z_{\mathrm{M}}C_{\mathrm{Ca}} + v_{\mathrm{M}}\psi_{\mathrm{Mca}} + v_{\mathrm{X}}\psi_{\mathrm{CaX}}] \\ & + \sum_{\mathrm{c<c'}}\sum m_{\mathrm{c}}m_{\mathrm{c'}}(v_{\mathrm{X}}/v)\psi_{\mathrm{cc'X}} + \sum_{\mathrm{a<a'}}\sum m_{\mathrm{a}}m_{\mathrm{a'}}\cdot \\ & (v_{\mathrm{M}}/v)\psi_{\mathrm{Ma'}} + 2\sum_{n} m_{n}(v_{\mathrm{M}}\lambda_{nm} + v_{\mathrm{X}}\lambda_{n\mathrm{X}})/v\end{aligned} \tag{20}$$

Then, substitution of eq 20 into eq 9 yields a working equation

$$\begin{aligned}\log K' = {} & \log K_m - \log m\{\mathrm{H}^+\} - \ln[\gamma\{\mathrm{H}^+\}\cdot \\ & \gamma\{\mathrm{ReO_4}^-\}]/\ln 10 \\ = {} & \log K^0 + 2/\ln 10\cdot m_{\mathrm{NH_4}}\beta^{(0)}_{\mathrm{NH_4\cdot ReO_4}} + 2/\ln 10\cdot \\ & y_1 m_{\mathrm{NH_4}}\beta^{(1)}_{\mathrm{NH_4ReO_4}} + 2/\ln 10\cdot Zm_{\mathrm{NH_4}}C_{\mathrm{NH_4ReO_4}}\end{aligned} \tag{21}$$

Using a least-squares method, regression of the extrapolation function (log K') calculated from the experimental results against $\beta^{(0)}_{\mathrm{NH_4\cdot ReO_4}}$, $y_1\beta^{(1)}_{\mathrm{NH_4ReO_4}}$, and $1/2\cdot ZC_{\mathrm{NH_4ReO4}}$ yielded the values of log K^0 which are here denoted by log K^0(P) and are given in Table 2.

From Table 2, we could see that the log K^0(D−H) stepwisely increased with the decrease of temperature, but the log K^0(P) showed no orderliness. Also, the a^0 in the Debye−Hückel equation changed from (0.7 to 0.9) A, which denotes the constant of the parameter, but the parameters of the Pitzer equation showed a large variety. So, we can confirm that the Debye−Hückel equation is more suitable for this extraction system.

Thermodynamic Properties for the Extraction Process. The values of log K^0 obtained at various temperatures obtained were fitted to the following equation.[14−16]

$$\log K^0 = (A_1 + A_2/T + A_3T) \tag{22}$$

The values of parameters A_i are: $A_1 = 15.74$, $A_2 = -745.5$, and $A_3 = -0.02252$.

The standard molar thermodynamic properties $\Delta_{\mathrm{r}}G^0_{\mathrm{m}}$, $\Delta_{\mathrm{r}}H^0_{\mathrm{m}}$, $\Delta_{\mathrm{r}}S^0_{\mathrm{m}}$, and $\Delta_{\mathrm{r}}C^0_{P,\mathrm{m}}$ for the extraction process are simply related to the parameters in eq 22

$$\Delta_{\mathrm{r}}G^0_{\mathrm{m}} = -(R\ln 10)(A_1T + A_2 + A_3T^2) \tag{23}$$

$$\Delta_{\mathrm{r}}H^0_{\mathrm{m}} = (R\ln 10)(A_3T^2 - A_2) \tag{24}$$

$$\Delta_{\mathrm{r}}S^0_{\mathrm{m}} = (R\ln 10)(A_1 + 2A_3T) \tag{25}$$

$$\Delta_{\mathrm{r}}C^0_{P,\mathrm{m}} = (R\ln 10)(2A_3T) \tag{26}$$

where R is the gas constant. The thermodynamic quantities calculated from eqs 23 to 26 are listed in Table 3.

Table 3. Standard Molar Thermodynamic Properties for the Extraction Process in the Temperature Range (278.15 to 303.15) K

T	$\Delta_{\mathrm{r}}G^0_{\mathrm{m}}$	$\Delta_{\mathrm{r}}H^0_{\mathrm{m}}$	$\Delta_{\mathrm{r}}S^0_{\mathrm{m}}$	$\Delta_{\mathrm{r}}C^0_{P,\mathrm{m}}$
K	kJ·mol^{-1}	kJ·mol^{-1}	J·(K·mol)$^{-1}$	J·(K·mol)$^{-1}$
303.15	−37.5	−25.4	39.9	−261.5
298.15	−37.3	−24.1	44.3	−257.2
293.15	−37.0	−22.8	48.6	−252.8
288.15	−36.7	−21.5	52.9	−248.5
283.15	−36.5	−20.3	57.2	−244.2
278.15	−36.2	−19.1	61.5	−239.9

Conclusions

The extractant has a satisfactory extraction effect at various temperatures of the experiment. $\Delta_{\mathrm{r}}G^0$ and K^0 increase with a decrease of experimental temperatures, which indicates low temperature benefits extraction. The negative experimental association Gibbs energy, $\Delta G^0_{\mathrm{m}} < 0$, means that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure, and the enthalpy is the dominant thermodynamic factor.[12−14]

Literature Cited

(1) Zhou, L.-Z.; Chen, S.-C. *Separation and metallurgy of rare and scattered metals [M]*; Metallurgy industry Press: Beijing, 2008; Vol. 11 (in Chinese).
(2) Lan, X.; Liang, S.; Song, Y. Recovery of rhenium from molybdenite calcine by a resin-in-pulp process. *Hydrometallurgy China* **2006**, *82*, 133–136.
(3) Cao, Z. F.; Zhong, H.; Qiu, Z. H. Solvent extraction of rhenium from molybdenum in alkaline solution. *Hydrometallurgy* **2009**, 153–157.
(4) Lou, Z. N.; Xiong, Y.; Fang, D. W.; Shan, W. J.; Liu, X. Z. Thermodynamics of Solvent Extraction of Rhenium With N235. *J. Liaoning Univ.* **2009**, *2*, 108–111 (in Chinese).
(5) Song, K.-Y.; Yang, J.-Z.; Song, Y.-L.; Wang, X.-P. Studies on the thermodynamics of the solvent extraction of metals I. {Copper(II) + sodium perchlorate + 8-hydroxyquinoline + trichloromethane}. *J. Chem. Thermodyn.* **1990**, *22*, 695–707.
(6) Liu, X.-Z.; Yang, J.-Z.; Song, Y.-L.; Kang, Y.-H. Thermodynamics of solvent extraction of metal 2: $In_2(SO_4)_3 + Na_2SO_4 + D_2EHMTPA + n\text{-}C_8H_{18} + H_2O$. *Acta Chim. Sin.* **1992**, *50*, 789–795 (in Chinese).
(7) Maqinke, Z.: *Spectrophotometer determination of elements*; Geologic Publishing Company: Beijing, 1983.
(8) Pitzer, K. S. An interaction approach: theory and data correlation. In *Activity Coefficients in Electrolyte solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Roton, FL, 1991.
(9) Pitze, K. S. In *Activity coefficients in electrolyte solutions*; Pytkowicz, R. M., Ed.; CRC Press: FL, 1979; p 157.
(10) Bradley, D. J.; Pitzer, K. S. Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hueckel parameters to 350.degree.C and 1 kbar. *J. Phys. Chem.* **1979**, *83*, 1599.
(11) Pitzer, K. S.; Kim, J. Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701.
(12) Pitzer, K. S.; Roy, R. N.; Silvester, L. F. Thermodynamics of electrolytes. 7. Sulfuric acid. *J. Am. Chem. Soc.* **1977**, *99*, 4930.
(13) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **1973**, *77*, 2300.
(14) Yang, J.-Z.; Song, P.-S.; Wang, D.-B. Thermodynamic study of aqueous borates III. The standard association constant of the ion pair $Li^+B(OH)_4^-$. *J. Chem. Thermodyn.* **1997**, *29*, 1343–1351.
(15) Yang, J.-Z.; Sun, B.; Song, P.-S. Thermodynamics of ionic association 1: The standard association constant of the ion pair $Li^+B(OH)_4^-$. *Thermochim. Acta* **2000**, *352*, 69–74.
(16) Yang, J.-Z.; Zhang, R.-B.; Xue, H.; Tian, P. Thermodynamics of the ion pair $[GaCl]^{2+}$ at temperatures from 278.15 K to 318.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 401–407.

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