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Thermodynamics of Solvent Extraction of Rhenium with Trioctyl Amine

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The equilibrium molalities of ReO_4^- in the system {TOA + $(NH_4)ReO_4$ + n-C_7H_{16} + HCl + H_2O} were measured at ionic strengths from (0.1 to 2.0) $mol\cdot kg^{-1}$ in an aqueous phase containing NH_4Cl as the supporting electrolyte and at a 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 the methods of Debye−Hückel extrapolation and Pitzer polynomial approximation. Thermodynamic properties for the extraction process were calculated.

Introduction

Rhenium has attracted importance in the chemical industry because of its use as catalyzers and dystectic metals. Solvent extraction is the main method of separation and enrichment of rhenium from mine tailings.[1] Extraction equilibria and thermodynamic properties are the basis of research on extraction processes.[2]

As a continuation of our previous work,[3,4] we have measured the concentration of rhenate in the aqueous phase at different ionic strengths in a hydrochloric acid system. The standard extraction constants K^0 were obtained by methods of extrapolation and polynomial approximation.[5−7] Thermodynamic properties for the extraction process were calculated.

In the presence of an excess of the extractant TOA (trioctyl amine), the reaction for the extraction of rhenate is:

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

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

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

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

Experimental Section

The water used was doubly deionized with a conductivity of $1.5\cdot 10^{-4}\ \Omega^{-1}\cdot m^{-1}$. The HCl was of analytical reagent (AR) grade (99 % mass pure), and the ammonium chloride was of AR grade purity. The n-C_7H_{16} used as the diluent was of AR grade with a density of $\rho = 0.68\cdot 10^3\ kg\cdot m^{-3}$.

All initial solutions to be measured were freshly prepared. The aqueous phase was prepared by dissolving NH_4ReO_4 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 TOA in n-C_7H_{16}, with the initial molality of TOA 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 equilibrated molality of ReO_4^- ($m\{ReO_4^-\}$) in the aqueous phase was determined using a 722 spectrophotometer (Shanghai Jinghua Instrument Co. Ltd.) with an uncertainty of ± 0.001 for three replicate measurements. The results are shown in Table 1 and Figure 1.

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:

$$m\{H^+\cdot NR_3\cdot ReO_4^-\} = [a - m\{ReO_4^-\}]\cdot \rho_W/\rho \tag{3}$$

$$m\{NR_3\} = b - [a - m\{ReO_4^-\}]\cdot \rho_W/\rho \tag{4}$$

where ρ is the density of the organic phase and ρ_w is the density of water.

Results and Discussion

The values of pH measured at the various temperatures (in the range of (278.15 to 303.15) K) for several total ionic strengths in the range (0.1 to 2.0) $mol\cdot kg^{-1}$ are listed in Table 1, where each value of pH is the mean of three replicate measurements with an 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 equilibrated aqueous phase. Their molalities and activity coefficients are $m\{H^+\}$, $m\{NH_4^+\}$, $m\{ReO_4^-\}$, and $m\{Cl^-\}$ and $\gamma\{H^+\}$, $\gamma\{NH_4^+\}$, $\gamma\{ReO_4^-\}$, and $\gamma\{Cl^-\}$, respectively. The effective ionic strength I' in the equilibrated aqueous phase can then be calculated as:

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$$I' = 1/2\sum m_iZ_i^2 = 1/2(m\{\mathrm{ReO_4}^-\} + m\{\mathrm{NH_4}^+\} + m\{\mathrm{Cl}^-\} + m\{\mathrm{H}^+\}) \quad (5)$$

where

$$m\{\mathrm{NH_4}^+\} = m\{\mathrm{NH_4Cl}\} + a \quad (6)$$

$$m\{\mathrm{Cl}^-\} = m\{\mathrm{NH_4Cl}\} + c \quad (7)$$

and the activity of H^+ was obtained from the pH values. The calculated values of I' are listed in Table 1. Then eq 2 could be expressed as:

$$\begin{aligned}\log K^0 &= \log\frac{m[\mathrm{H^+NR_3ReO_4}^-]}{m[\mathrm{ReO_4}^-]\cdot m[\mathrm{NR_3}]} - \log(a[\mathrm{H}^+]) + \\ &\quad \log\frac{\gamma[\mathrm{H^+NR_3ReO_4}^-]}{\gamma[\mathrm{ReO_4}^-]\cdot\gamma[\mathrm{NR_3}]} \\ &= \log K_\mathrm{m} + \mathrm{pH} + \log\frac{\gamma[\mathrm{H^+NR_3ReO_4}^-]}{\gamma[\mathrm{NR_3}]} - \\ &\quad \log\gamma[\mathrm{ReO_4}^-]\end{aligned} \quad (8)$$

and K_m is the equilibrium concentration product, defined as

$$K_\mathrm{m} = m\{\mathrm{H^+\cdot NR_3\cdot ReO_4}^-\}/[m\{\mathrm{ReO_4}^-\}\cdot m\{\mathrm{NR_3}\}] \quad (9)$$

Because the molalities of the extraction complex and the extractant in the equilibrium organic phase are small, in Debye–Hückel theory it can be assumed that $\gamma\{\mathrm{H^+\cdot NR_3\cdot ReO_4}^-\}/\gamma\{\mathrm{NR_3}\} \approx 1$. As $\gamma\{\mathrm{ReO_4}^-\}$ in the equilibrated 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

$$\log K' = \log K_\mathrm{m} + \mathrm{pH} + A(I'\rho/c^0)^{1/2}/\{1 + Ba^0(I\rho/c^0)^{1/2}\} = \log K^0 + \mathrm{b}I' \quad (10)$$

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, A and B are the Debye–Hückel parameters, and $c^0 = 1\ \mathrm{mol\cdot dm^3}$. Using a least-squares method, a linear regression of $\log K'$ versus I' yielded values of $\log K^0$. These are given in Table 2 as $\log K^0$(D-H) (see Figure 2).

Using the smallest slope is more rational than the smallest standard deviation in the linear regression. In the extrapolation, several possible values of the ion-size parameter a^0 were used, and the best value of a^0 was chosen. The extrapolated lines with the smallest slope are almost parallel with the I'. On the basis of this method, the most suitable values of a^0 at different temperatures were chosen and are shown in Table 2.

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

$$\log K^0 = \log[m\{\mathrm{H^+\cdot NR_3\cdot ReO_4}^-\}] - \log[m\{\mathrm{H}^+\}\cdot m\{\mathrm{ReO_4}^-\}\cdot m\{\mathrm{NR_3}\}] - \log[\gamma\{\mathrm{H}^+\}\cdot\gamma\{\mathrm{ReO_4}^-\}] \quad (11)$$

Table 1. Values of pH, $m\{\mathrm{ReO_4}^-\}$, and Effective Ionic Strength I at Temperatures in the Range (278.15 to 303.15) K

T/K	278.15	283.15	288.15	293.15	298.15	303.15
$I = 0.1$						
I'	0.124	0.081	0.085	0.079	0.078	0.092
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	0.06209	0.7450	0.9934	2.670	3.725	4.718
pH	1.01	1.50	1.42	1.54	1.60	1.32
$I = 0.2$						
I'	0.223	0.182	0.189	0.184	0.184	0.186
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	0.1242	0.9340	1.242	2.794	4.222	7.326
pH	1.05	1.52	1.39	1.47	1.52	1.44
$I = 0.4$						
I'	0.383	0.379	0.385	0.394	0.399	0.399
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	0.5588	1.490	2.359	3.166	4.594	8.444
pH	1.52	1.61	1.50	1.36	1.32	1.31
$I = 0.5$						
I'	0.481	0.493	0.486	0.491	0.499	0.513
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	1.118	1.055	2.421	3.787	5.215	7.947
pH	1.59	1.39	1.49	1.42	1.33	1.19
$I = 0.6$						
I'	0.582	0.585	0.586	0.596	0.602	0.611
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	1.490	1.552	3.104	3.601	6.333	8.878
pH	1.58	1.52	1.51	1.36	1.32	1.22
$I = 0.8$						
I'	0.782	0.779	0.785	0.793	0.808	0.833
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	1.987	2.421	4.160	4.905	6.705	8.506
pH	1.59	1.66	1.53	1.42	1.27	1.08
$I = 1.0$						
I'	0.976	0.981	0.985	1.000	1.018	1.024
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.608	2.794	4.160	5.277	6.519	10.74
pH	1.73	1.62	1.55	1.35	1.20	1.15
$I = 1.2$						
I'	1.173	1.185	1.185	1.198	1.211	1.243
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.173	2.918	4.036	5.960	8.381	9.375
pH	1.83	1.57	1.56	1.38	1.27	1.05
$I = 1.4$						
I'	1.376	1.386	1.385	1.393	1.413	1.421
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.235	3.415	5.588	7.699	9.437	13.66
pH	1.76	1.56	1.58	1.46	1.26	1.19
$I = 1.5$						
I'	1.476	1.484	1.484	1.503	1.515	1.519
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.421	3.911	6.022	6.333	10.49	14.53
pH	1.78	1.59	1. 60	1.34	1.24	1.21
$I = 1.6$						
I'	1.576	1.587	1.582	1.605	1.626	1.655
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.297	3.539	6.581	6.581	9.685	11.67
pH	1.76	1.54	1.63	1.33	1.17	1.01
$I = 1.8$						
I'	1.776	1.790	1. 782	1.801	1.820	1.830
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	2.794	3.849	8.195	8.381	10.86	15.46
pH	1.77	1.51	1.65	1.38	1.22	1.15
$I = 2.0$						
I'	1.977	1.986	1.981	1.999	1.992	2.062
$\mathrm{ReO_4}^-(\cdot 10^{-6})$	3.291	4.408	9.002	9.127	11.42	11.30
pH	1.75	1.57	1.67	1.40	1.20	0.99

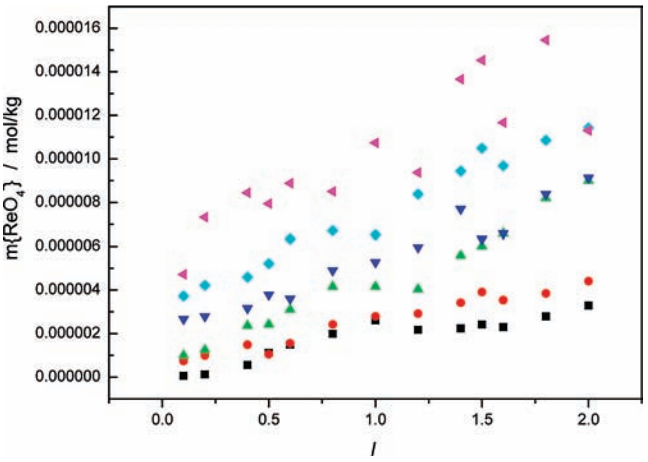

Figure 1. Molalities of $\{\mathrm{ReO_4}^-\}$ at different temperatures. (■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ◆, 298.15 K; left-pointing triangle, 303.15 K).

The activity coefficients $\gamma\{H^+\}$ and $\gamma\{ReO_4^-\}$ in eq 11 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]

$$\ln \gamma_M = z_M^2 F + \sum_a (m_a/m^0)(2B_{Ma} + ZC_{Ma}) + \sum_c (m_c/m^0)(2\Phi_{Mc} + \sum_a (m_a/m^0)\psi_{Mca}) + \sum_a \sum_{a'} (m_a/m^0)(m_{a'}/m^0)\psi_{Maa'} + |Z_M| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca} \qquad (12)$$

$$\ln \gamma_X = z_X^2 F + \sum_c (m_c/m^0)(2B_{CX} + ZC_{cX}) + \sum_a (m_a/m^0)(2\Phi_{Ma} + \sum_c (m_c/m^0)\psi_{cXa}) + \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\psi_{cc'X} + |Z_M| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca}$$

where

$$F = f^r + \sum_a \sum_c (m_a/m^0)(m_c/m^0)B'_{ca} + \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\Phi'_{cc'} + \sum_a \sum_{a'} (m_a/m^0)(m_{a'}/m^0)\Phi'_{aa'} \qquad (14)$$

$$f^r = -A_P[(I/m^0)^{1/2}/[1 + 1.2(I/m^0)^{1/2}] + (2/1.2)\ln[1 + 1.2(I/m^0)^{1/2}] \qquad (15)$$

$$Z = \sum_c (m_c/m^0)|Z_c| = \sum_a (m_a/m^0)|Z_a| \qquad (16)$$

$$C_{ij}^P = C_{ij}^P/2(|z_i z_j|)^{1/2} \qquad (17)$$

where 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–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, and 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 of not all the same sign. According to Pitzer and Kim,[11]

$$B_{ca} = \beta_{cs}^{(0)} + \beta_{ca}^{(1)} y_1 \qquad (18)$$

$$B'_{ca} = \beta_{ca}^{(1)} y_2 \qquad (19)$$

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

$$y_1 = 2[1 - (1 + \alpha\{I/m^0\}^{1/2}) \exp(-\alpha\{I/m^0\}^{1/2})/(\alpha^2\{I/m^0\}) \qquad (20)$$

$$y_2 = 2[-1 + (1 + \alpha\{I/m^0\}^{1/2} + \alpha^2\{I/m^0\}/2) \exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}^2) \qquad (21)$$

In using Pitzer's equations to determine K^0, the following is assumed: (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 among ReO_4^-, H^+, and the ions of the supporting electrolyte; and (3) following the advice of Pitzer and Mayorga,[12,13] $\psi_{Mca'}$ is considered to be independent of ionic strength. In estimating $\gamma\{ReO_4^-\}$ and $\gamma\{H^+\}$, all of the mixed parameters (Φ_{ij}, Φ'_{ij}, and Ψ_{ijk}) are neglected so that the pertinent combination of activity coefficients may be written as

$$\ln \gamma_{MX} = |z_M z_X|F + (\upsilon_M/\upsilon)\sum_a m_a[2B_{Ma} + ZC_{Ma} + 2(\upsilon_X/\upsilon)\Phi_{Xa}] + (\upsilon_X/\upsilon)\sum_c m_c[2B_{Cx} + ZC_{Cx} + 2(\upsilon_M/\upsilon)\Phi_{Mc}] + \sum_c \sum_a m_c m_a \upsilon^{-1}[2\upsilon_M Z_M C_{Ca} + \upsilon_M \psi_{Mca} + \upsilon_X \psi_{CaX}] + \sum_{c<c'} \sum m_c m_{c'}(\upsilon_X/\upsilon)\psi_{cc'X} + \sum_{a<a'} \sum m_a m_{a'}(\upsilon_M/\upsilon)\psi_{Maa'}2 + \sum_n m_n(\upsilon_M \lambda_{nm} + \upsilon_X \lambda_{nX})/\upsilon \qquad (22)$$

Then, substitution of eq 22 into eq 11 yields a working equation

$$\begin{aligned}\log K' &= \log K_m - \log m\{H^+\} - \ln[\gamma\{H^+\}\cdot\gamma\{ReO_4^-\}]\cdot \gamma\{ReO_4^-\}]/\ln 10 \\ &= \log K^0 + 2/\ln 10\cdot m_{NH_4}\beta^{(0)}_{NH_4\cdot ReO_4} + 2/\ln 10\cdot y_1 m_{NH_4}\beta^{(1)}_{NH_4ReO_4} + 2/\ln 10\cdot Zm_{NH_4}C_{NH_4ReO_4}\end{aligned} \qquad (23)$$

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

In Table 2, it is shown that the correlation coefficient of the Debye–Hückel equation regressions were not satisfied owing to the determination of a^0, but the standard deviation and correlation coefficient of Pitzer equation were both reasonable. So we thought the log K^0 by Pitzer equation are the final results.

Thermodynamic Properties for the Extraction Process. The values of log K^0 obtained at various temperatures obtained by Pitzer's equation were fitted to the following equation (see Figure 3).[14−16]

$$\log K^0 = (A_1 + A_2/T + A_3/T) \qquad (24)$$

The values of parameters A_i are: $A_1 = -631.01 \pm 1.26$, $A_2 = 95164 \pm 182$, and $A_3 = 1.0598 \pm 0.0022$ with a standard deviation of $s = 0.189$.

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

T/K	log K^0(D-H)	a^0/A	R	s	log K^0(P)	R	s	$\beta^{(0)}_{NH_4\cdot ReO_4}$	$y_1\beta^{(1)}_{NH_4ReO_4}$	$1/2\cdot ZC_{NH_4ReO_4}$
303.15	6.6087	1.90	−0.063	0.016	4.0377	0.993	0.057	233.42315	−5.60259	−1082.14163
298.15	6.7889	1.60	−0.038	0.031	4.2155	0.999	0.023	202.60796	−4.95949	−940.16723
293.15	6.8335	1.80	0.370	0.015	4.3570	0.998	0.029	−193.07156	−4.25313	892.23843
288.15	7.0731	1.60	0.021	0.043	4.7637	0.996	0.056	112.87538	−6.49685	−524.31732
283.15	7.2173	1.50	−0.096	0.022	4.9162	0.995	0.060	94.285	−5.96502	−438.31245
278.15	7.4211	1.30	−0.008	0.159	5.9344	0.990	0.107	−7.38883	−14.7927	37.62043

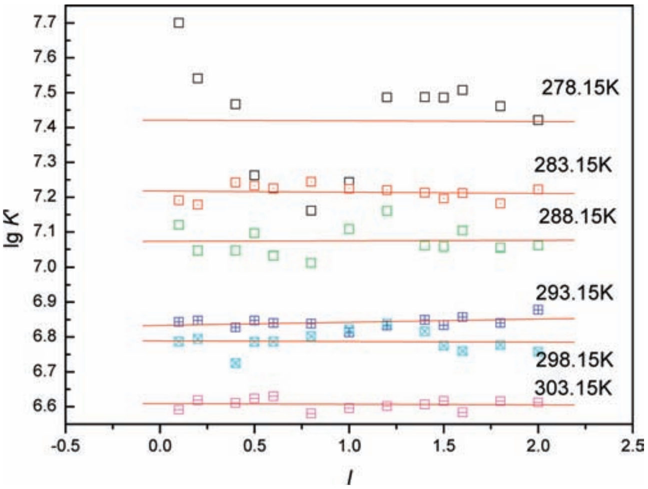

Figure 2. log *K*′ at various *I* by the Debye−Hückel method (black square, 278.15 K; red square, 283.15 K; green square, 288.15 K; dark blue square, 293.15 K; light blue square, 298.15 K; pink square, 303.15 K).

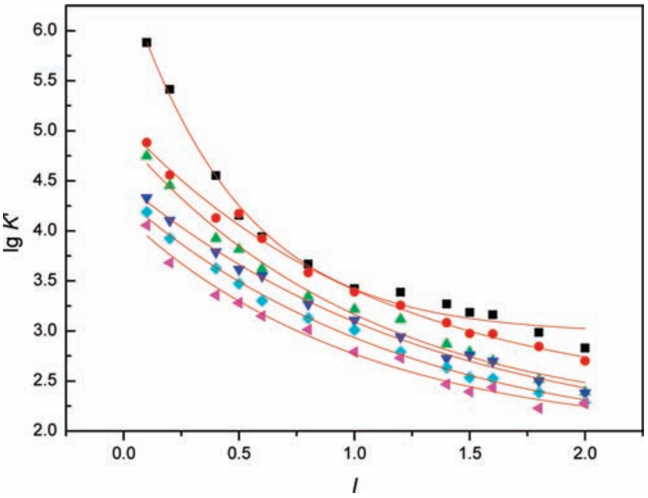

Figure 3. log *K*′ at various *I* by Pitzer method (■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ◆, 298.15 K; left-pointing triangle, 303.15 K).

The standard molar thermodynamic properties $\Delta_rG_M{}^0$, $\Delta_rH_M{}^0$, $\Delta_rS_M{}^0$, and $\Delta_rC_{P,M}{}^0$ for the extraction process are simply related to the parameters in eq 24:

$$\Delta_rG_M{}^0 = -(R\ln 10)(A_1T + A_2 + A_3T^2) \tag{25}$$

$$\Delta_rH_M{}^0 = (R\ln 10)(A_3T^2 - A_2) \tag{26}$$

$$\Delta_rS_M{}^0 = (R\ln 10)(A_1 + 2A_3T) \tag{27}$$

$$\Delta_rC_{P,M}{}^0 = (R\ln 10)(2A_3T) \tag{28}$$

where *R* is the gas constant. The thermodynamic quantities calculated from eqs 25 to 28 are listed in Table 3. It is shown that the Gibbs energy, the enthalpy, and the entropy decrease with an increase of temperature, while the thermal capacity increases. It indicates the benefit of a low temperature extraction reaction. The reaction will be spontaneous above a temperature of 298.15 K.

Conclusions

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

T	$\Delta_rG_M{}^0$	$\Delta_rH_M{}^0$	$\Delta_rS_M{}^0$	$\Delta_rC_{P,M}{}^0$
K	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot(K\cdot mol)^{-1}$	$J\cdot(K\cdot mol)^{-1}$
303.15	−24.28	42.73	221	12301
298.15	−23.68	−18.27	18.2	12098
293.15	−24.10	−78.25	−185	11895
288.15	−25.53	−137.2	−388	11692
283.15	−27.98	−195.2	−590	11489
278.15	−31.44	−252.1	−793	11286

The extractant has a high efficiency of extraction at various temperatures in the experiment because the extraction efficiency is almost 99 %, calculated from the data in Table 1 using eqs 3 and 4, which also indicates that the extraction reaction progresses to completion. Furthermore, molalities of $ReO_4{}^-$ in the aqueous phase are lower at lower temperatures and lower ionic strengths, which indicates that the extraction action has its best effect in these conditions. Δ_rG^0 and K^0 increase with a decrease of temperature, which indicates the benefits of low temperature extraction. The negative Gibbs energy, $\Delta G_M{}^0 < 0$, indicates that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure. The enthalpy is the dominant thermodynamic factor.

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