Thermodynamics of Solvent Extraction of Rhenium(VII) with N1923

Da-wei Fang, Xue-jun Gu, Ying Xiong, Shuang Yue, and Shu-liang Zang

At temperatures from 278.15 to 303.15 K, equilibrium molalities of ReO_4^- were measured in the aqueous phase containing NH_4Cl as supporting electrolyte at ionic strength from 0.1 to 2.0 $mol \cdot kg^{-1}$ and at constant initial molality of extractant. The standard extraction constants K^0 at various temperatures were obtained by methods of Pitzer's theory. Thermodynamic properties for the extraction process were calculated.

List of Symbols	
a, c, i, j, n	parameter in Pitzer's equation
M, X	cation and anion in a multicomponent electrolyte solution
A_P	Debye-Hückel coefficient of the osmotic function
A_i	parameter in Eq 19
M	molality

1. Introduction

Rhenium is one of the rarest elements in nature. Moreover, it occurs in a scattered form, and methods for its separation in a form of metal or compounds are complicated and costly. These facts result in a high price of rhenium and its compounds, and also in limited practical applications of this element.[1] Solvent extraction is one of the main methods of separation and enrichment of rhenium from nonferrous metals mine tailings. Thermodynamic extraction equilibrium constant and thermodynamic parameters are the basis of research on extraction process techniques and best design.[2]

In this paper, we measured concentration of rheniumate in aqueous phase at different ionic strength in hydrochloric acid system. The standard extraction constants K^0 are obtained by methods of extrapolation and polynomial approximation.[3] Thermodynamic properties for the extraction process are calculated.

In the presence of excessive extractant N1923 (one kind of primary amine), the structure is given in Fig. 1. The extraction reaction is[4]:

$$RNH_2(org) + H^+(aq) + ReO_4^-(aq) = RNH_3ReO_4(org) \quad (Eq~1)$$
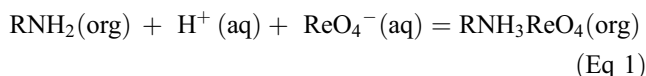
where (aq) and (org) refer to the aqueous and organic phase, respectively, RNH_2 is the extractant N1923, and RNH_3ReO_4

is the extraction complex. The standard equilibrium constant K^0 is given by

$$
\begin{aligned}
\log K^0 = {} & \log[m\{RNH_3ReO_4\}] \\
& - \log[m\{H^+\} \cdot m\{ReO_4^-\} \cdot m\{RNH_2\}] \\
& + \log[\gamma\{RNH_3ReO_4\}] \\
& - \log[\gamma\{H^+\} \cdot \gamma\{ReO_4^-\} \cdot \gamma\{RNH_2\}] \quad (Eq~2)
\end{aligned}
$$

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

2. Experimental

The water used was doubly deionized and its conductivity was $1.5 \times 10^{-4} \Omega^{-1}~m^{-1}$ (Ω is ohm). The ammonium chloride was of AR grade. The n-C_7H_{16} used as diluent was of AR grade.

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 $\sigma = 0.001~mol \cdot kg^{-1}$, 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 0.1-2.0 $mol \cdot kg^{-1}$. The organic phase was prepared by dissolving N1923 in n-C_7H_{16}, the initial molality of N1923 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

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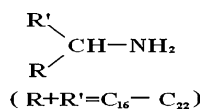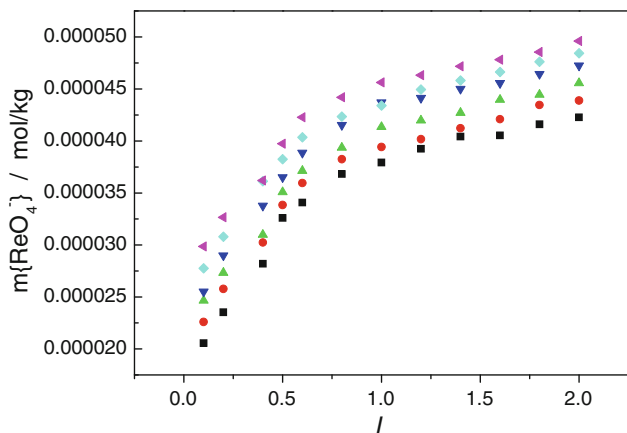
Fig. 1 Structure of N1923

Fig. 2 Molalities of $\{ReO_4^-\}$ at different temperatures ($\blacksquare$ 278.15 K; $\bullet$ 283.15 K; $\blacktriangle$ 288.15 K; $\blacktriangledown$ 293.15 K; $\blacklozenge$ 298.15 K; $\blacktriangleleft$ 303.15 K)

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 type spectrophotometer,[5] and the results were shown in Fig. 2.

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:

$$m\{R_3NHReO_4\} = [\sigma - m\{ReO_4^-\}]/\rho \qquad (Eq\ 3)$$

$$m\{R_3N\} = b - [\sigma - m\{ReO_4^-\}]/\rho \qquad (Eq\ 4)$$

where ρ is the density of the organic phase.

3. Results and Discussion

The values of pH 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 mol·kg^{-1} are listed in Table 1, where each value of pH is the mean of three replicate measurements.

There were four ionic species (H$^+$, NH$_4^+$, ReO$_4^-$, and Cl$^-$) in the equilibrium 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 equilibrium aqueous phase can then be calculated as:

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

The calculated values of I' are listed in Table 1. Because the molalities of the extraction complex and the extractant in the equilibrium organic phase are very small, in Debye-Hückel theory it can be assumed that $\gamma\{H^+ \cdot NR_3 \cdot ReO_4^-\}/\gamma\{NR_3\} \approx 1$. The Eq 2 could be expressed as:

$$\log K^0 = \log[m\{RNH_3ReO_4\}]$$
$$- \log[m\{H^+\} \cdot m\{ReO_4^-\} \cdot m\{RNH_2\}]$$
$$- \log[\gamma\{H^+\} \cdot \gamma\{ReO_4^-\}] \qquad (Eq\ 6)$$

The activity coefficients $\gamma\{H^+\}$ and $\gamma\{ReO_4^-\}$ in Eq 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 Pitzer[6]:

$$\ln\gamma_M = z_M^2 F + \sum_a (m_a/m^0)(2B_{Ma} + ZC_{Ma})$$
$$+ \sum_c (m_c/m^0)\left(2\Phi_{Mc} + \sum_a (m_a/m^0)\psi_{Mca}\right)$$
$$+ \sum_a \sum_{a'} (m_a/m^0)(m_{a'}/m^0)\psi_{Maa'}$$
$$+ |Z_M| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca} \qquad (Eq\ 7)$$

$$\ln\gamma_X = z_X^2 F + \sum_c (m_c/m^0)(2B_{cX} + ZC_{cX})$$
$$+ \sum_a (m_a/m^0)\left(2\Phi_{Ma} + \sum_c (m_c/m^0)\psi_{cXa}\right)$$
$$+ \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\psi_{cc'X}$$
$$+ |Z_X| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca} \qquad (Eq\ 8)$$

where

$$F = f^r + \sum_a \sum_c (m_a/m^0)(m_c/m^0)B'_{ca}$$
$$+ \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\Phi'_{cc'}$$
$$+ \sum_a \sum_{a'} (m_a/m^0)(m_{a'}/m^0)\Phi'_{aa'} \qquad (Eq\ 9)$$

$$f^r = -A_P\left[(I/m^0)^{1/2}/\left[1 + 1.2(I/m^0)^{1/2}\right] + (2/1.2)\ln\left[1 + 1.2(I/m^0)^{1/2}\right]\right] \qquad (Eq\ 10)$$

$$Z = \sum_c (m_c/m^0)|Z_c| = \sum_a (m_a/m^0)|Z_a| \qquad (Eq\ 11)$$

Table 1 Values of pH, molalities of ReO_4^- 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'	0.092	0.096	0.103	0.114	0.126	0.138
$ReO_4^-(\times 10^{-5})$	2.055	2.260	2.465	2.552	2.775	2.986
pH	1.31	1.26	1.19	1.09	1.00	0.93
$I = 0.2$						
I'	0.192	0.196	0.203	0.212	0.226	0.237
$ReO_4^-(\times 10^{-4})$	2.353	2.577	2.732	2.899	3.079	3.266
pH	1.35	1.30	1.22	1.14	1.04	0.97
$I = 0.4$						
I'	0.390	0.393	0.403	0.406	0.416	0.437
$ReO_4^-(\times 10^{-4})$	2.819	3.024	3.098	3.377	3.613	3.620
pH	1.42	1.37	1.26	1.23	1.15	1.01
$I = 0.5$						
I'	0.483	0.488	0.494	0.502	0.511	0.522
$ReO_4^-(\times 10^{-4})$	3.259	3.384	3.508	3.651	3.824	3.973
pH	1.54	1.46	1.37	1.29	1.20	1.12
$I' = 0.6$						
I'	0.583	0.586	0.592	0.597	0.607	0.613
$ReO_4^-(\times 10^{-4})$	3.408	3.595	3.713	3.887	4.036	4.228
pH	1.56	1.51	1.41	1.35	1.25	1.20
$I = 0.8$						
I'	0.782	0.784	0.791	0.794	0.805	0.810
$ReO_4^-(\times 10^{-4})$	3.682	3.824	3.936	4.153	4.234	4.420
pH	1.60	1.55	1.45	1.41	1.29	1.24
$I = 1.0$						
I'	0.981	0.984	0.989	0.991	1.005	1.007
$ReO_4^-(\times 10^{-4})$	3.793	3.942	4.135	4.371	4.340	4.563
pH	1.62	1.56	1.49	1.46	1.30	1.28
$I = 1.2$						
I'	1.181	1.185	1.190	1.192	1.202	1.209
$ReO_4^-(\times 10^{-4})$	3.924	4.017	4.197	4.414	4.495	4.632
pH	1.63	1.56	1.49	1.46	1.34	1.28
$I = 1.4$						
I'	1.381	1.385	1.390	1.392	1.401	1.408
$ReO_4^-(\times 10^{-6})$	4.042	4.122	4.271	4.501	4.582	4.718
pH	1.64	1.57	1.49	1.47	1.36	1.30
$I = 1.6$						
I'	1.582	1.585	1.580	1.592	1.600	1.608
$ReO_4^-(\times 10^{-6})$	4.054	4.209	4.396	4.557	4.663	4.781
pH	1.64	1.58	1.52	1.48	1.38	1.31
$I = 1.8$						
I'	1.782	1.784	1. 789	1.791	1.798	1.805
$ReO_4^-(\times 10^{-6})$	4.160	4.346	4.445	4.644	4.762	4.855
pH	1.65	1.61	1.52	1.50	1.41	1.34
$I = 2.0$						
I'	1.981	1.984	1.987	1.990	1.996	2.001
$ReO_4^-(\times 10^{-6})$	4.228	4.389	4.557	4.725	4.843	4.961
pH	1.66	1.61	1.56	1.52	1.44	1.39

$$C_{ij}^P = C_{ij}^P / 2 \left(|z_i z_j| \right)^{1/2} \qquad \text{(Eq 12)}$$

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[7,8] 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]

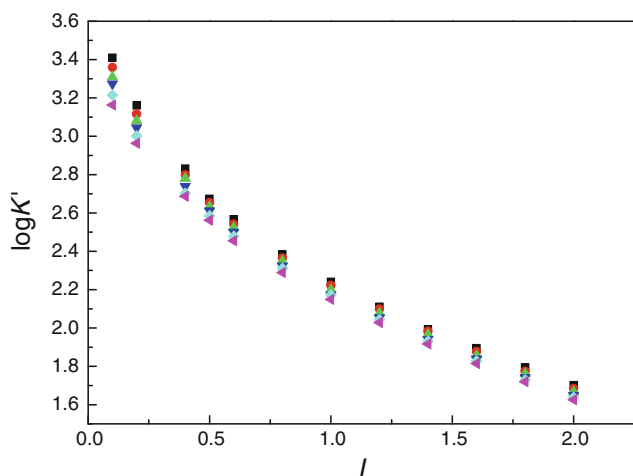$$B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} y_1 \qquad (Eq\ 13)$$

$$B'_{ca} = \beta_{ca}^{(1)} y_2 \qquad (Eq\ 14)$$

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

$$y_1 = 2\left[1 - \left(1 + \alpha\{I/m^0\}^{1/2}\right)\exp\left(-\alpha\{I/m^0\}^{1/2}\right)\right]/ \left(\alpha^2\{I/m^0\}\right) \qquad (Eq\ 15)$$

$$y_2 = 2\left[-1 + \left(1 + \alpha\{I/m^0\}^{1/2} + \alpha^2\{I/m^0\}/2\right)\right.$$
$$\left.\times\exp\left(-\alpha\{I/m^0\}^{1/2}\right)\right]/\left(\alpha^2\{I/m^0\}^2\right) \qquad (Eq\ 16)$$

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,[10,11] 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}, and ψ_{ijk}) are neglected, so that the pertinent combination of activity coefficients may be written as

$$\ln\gamma_{MX} = |z_M z_X|F + (v_M/v)\sum_a m_a$$
$$\times [2B_{Ma} + ZC_{Ma} + 2(v_X/v)\Phi_{Xa}]$$
$$+ (v_X/v)\sum_c m_c[2B_{Cx} + ZC_{Cx} + 2(v_M/v)\Phi_{Mc}]$$
$$+ \sum_c\sum_a m_c m_a v^{-1}[2v_M Z_M C_{Ca} + v_M\Psi_{Mca} + v_X\psi_{CaX}]$$
$$+ \sum_{c<c'}\sum m_c m_{c'}(v_X/v)\psi_{cc'X}$$
$$+ \sum_{a<a'}\sum m_a m_{a'}(v_M/v)\psi_{Maa'}$$
$$+ 2\sum_n m_n(v_M\lambda_{nm} + v_X\lambda_{nX})/v \qquad (Eq\ 17)$$

Then, substitution of Eq 17 into Eq 6, yields a working equation

$$\log K' = \log K_m - \log m\{H^+\} - \ln[\gamma\{H^+\}\cdot\gamma\{ReO_4^-\}]/\ln 10$$
$$= \log K^0 + 2/\ln 10\cdot m_{NH_4}\beta_{NH_4\cdot ReO_4}^{(0)}$$
$$+ 2/\ln 10\cdot y_1 m_{NH_4}\beta_{NH_4 ReO_4}^{(1)}$$
$$+ 2/\ln 10\cdot Zm_{NH_4}C_{NH_4 ReO_4} \qquad (Eq\ 18)$$

Using a least-squares method, regression of the extrapolation function ($\log K'$) calculated from the experimental results against $\beta_{NH_4\cdot ReO_4}^{(0)}$, y_1 $\beta_{NH_4 ReO_4}^{(1)}$, and $\frac{1}{2}\cdot ZC_{NH_4\cdot ReO_4}$, in Fig. 3, yielded the value of $\log K^0$ which are here denoted by $\log K^0(P)$ and are given in Table 2.

3.1 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.[12-14]

$$\log K^0 = (A_1 + A_2/T + A_3 T) \qquad (Eq\ 19)$$

Fig. 3 $\log K'$ at various I by Pitzer's method (■ 278.15 K; ● 283.15 K; ▲ 288.15 K; ▼ 293.15 K; ◆ 298.15 K; ◀ 303.15 K)

Table 2 The standard molar thermodynamic properties for the extraction process in the temperature range 278.15-303.15 K

T, K	$\log K^0$, P	$\Delta_r G_m^0$, 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	3.1783	−18.44	−19.35	-3.03	−271
298.15	3.2272	−18.44	−18.01	1.43	−266
293.15	3.2884	−18.42	−16.69	5.90	−262
288.15	3.328	−18.38	−15.39	10.4	−257
283.15	3.3744	−18.32	−14.12	14.8	−253
278.15	3.4284	−18.23	−12.87	19.3	−248

The values of parameters A_i are: $A_1 = 13.97$, $A_2 = -1132$, and $A_3 = 0.0233$ with a standard deviation of $s = 6.033 \times 10^{-3}$.

The standard molar thermodynamic properties $\Delta_r G_M^0$, $\Delta_r H_M^0$, $\Delta_r S_M^0$, $\Delta_r C_{P,M}^0$ for the extraction process are simply related to the parameters in Eq 19:

$$\Delta_r G_M^0 = -(R \ln 10)(A_1 T + A_2 + A_3 T^2) \qquad \text{(Eq 20)}$$

$$\Delta_r H_M^0 = (R \ln 10)(A_3 T^2 - -A_2) \qquad \text{(Eq 21)}$$

$$\Delta_r S_M^0 = (R \ln 10)(A_1 + 2 A_3 T) \qquad \text{(Eq 22)}$$

$$\Delta_r C_{P,M}^0 = (R \ln 10)(2 A_3 T) \qquad \text{(Eq 23)}$$

where R is the gas constant. The thermodynamic quantities calculated from Eq 20-23 are listed in Table 2.

4. Conclusions

The extractant has satisfactory extraction effect at various temperatures of the experiment. $\Delta_r G^0$ and K^0 increase with decrease of experimental temperatures, which indicates low temperature benefits extraction. The negative experimental association Gibbs energy. $\Delta G_M^0 < 0$ means that the ionic association reaction can occur spontaneously under the conditions of constant temperature and pressure. The enthalpy and entropy are both the dominant thermodynamic factors.[12-14] Accompanying with the increase of temperature, the enthalpy's contribution does increase.

Acknowledgments

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