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Thermodynamics of Solvent Extraction of Rhenium(VII) with *N*,*N*′-Di(1-methyl-heptyl)acetamide

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ABSTRACT: Equilibrium molalities of ReO_4^- were measured in the aqueous phase over the temperature range from (278.15 to 303.15) K, with NH_4Cl as a supporting electrolyte at ionic strengths from (0.1 to 2.0) $mol \cdot kg^{-1}$. The standard extraction equilibrium constants K^0 at various temperatures were obtained by Pitzer's polynomial approximation method. Thermodynamic properties for the extraction process were also calculated.

INTRODUCTION

Rhenium is a rare metal which is widely used in the petrochemical industry, aviation, electronics, medicine, and metallurgy, and so forth. Owing to the high value of rhenium, its recovery has both economic and environmental benefits.[1] Among solvent extraction, capillary electrophoresis, liquid chromatography, and ion exchange, solvent extraction provides an effective and simple separation method of recovery and enrichment of rhenium from mine tailings. The extraction equilibrium constant and thermodynamic parameters are fundamental for the extraction process technique.[2]

In this paper, concentrations of rhenium(VII) (perrhenate) in the aqueous phase at different ionic strengths in the hydrochloric acid system were measured. The standard extraction constants K^0 were obtained by the method of polynomial approximation.[3−5] The thermodynamic quantities for the extraction process were also calculated.

In the extraction process of rhenium(VII), tertiary amines are the most widely used extractant in hydrometallurgy. However, research has been almost solely focused on trioctyl amine and its homologues. To investigate the extracting ability affected by the molecular structure of the extractant, we selected a different kind of amine which contains an acyl group. The structure is given in Figure 1.

In the presence of an excess of extractant N503 (*N*,*N*′-di(1-methyl-heptyl)acetamide), the extraction reaction is:

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

where (aq) and (org) refer to the aqueous and organic phase, respectively, R_3N represents the extractant N503, and $NR_3 \cdot H^+ \cdot ReO_4^-$ is the extraction complex. The standard equilibrium constant K^0 is given by

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

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

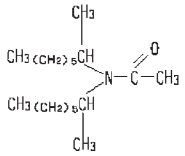

Figure 1. Structure of N503.

EXPERIMENTAL SECTION

The water used was doubly deionized, and its conductivity was $1.5 \cdot 10^{-4}\ \Omega^{-1} \cdot m^{-1}$ (Ω is ohm). The hydrochloric acid was of AR (analytical reagent) grade (99 % mass pure), and the ammonium chloride was 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 $a = 0.001\ mol \cdot kg^{-1}$, 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 from (0.1 to 2.0) $mol \cdot kg^{-1}$. The organic phase was prepared by dissolving N503 in n-C_7H_{16}, with the initial molality of N503 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

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equilibrium aqueous phase was determined using a 722 spectrophotometer (Shanghai Jinghua Instrument Co. Ltd.).

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:

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

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

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 from (0.1 to 2.0) mol·kg^{-1} are listed in Table 1, where each value of pH is the mean of three replicate measurements.

There are 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:

$$I' = 1/2\sum m_i Z_i^2 \tag{5}$$

The calculated values of I' are listed in Table 1. Equation 2 can be expressed as:

$$\begin{aligned}\log K^0 = {} & \log[m\{H^+ \cdot NR_3 \cdot ReO_4^-\}] \\ & - \log[m\{H^+\} \cdot m\{ReO_4^-\} \cdot m\{NR_3\}] \\ & - \log[\gamma\{H^+\} \cdot \gamma\{ReO_4^-\}]\end{aligned} \tag{6}$$

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:[6]

$$\begin{aligned}\ln \gamma_M = {} & z_M^2 F + \sum_a (m_a/m^0)(2B_{Ma} + ZC_{Ma}) \\ & + \sum_c (m_c/m^0)(2\Phi_{Mc} + \sum_a (m_a/m^0)\Psi_{Mca}) \\ & + \sum_a \sum_{a'} (m_a/m^0)(m_{a'}/m^0)\Psi_{Maa'} \\ & + |Z_M| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca}\end{aligned} \tag{7}$$

$$\begin{aligned}\ln \gamma_X = {} & z_X^2 F + \sum_c (m_c/m^0)(2B_{cX} + ZC_{cX}) \\ & + \sum_a (m_a/m^0)(2\Phi_{Ma} + \sum_c (m_c/m^0)\Psi_{cXa}) \\ & + \sum_c \sum_{c'} (m_c/m^0)(m_{c'}/m^0)\Psi_{cc'X} \\ & + |Z_X| \sum_c \sum_a (m_c/m^0)(m_a/m^0)C_{ca}\end{aligned} \tag{8}$$

where

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

Table 1. Values of pH, Molalities of 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
$ReO_4^-(\cdot 10^{-4})$	5.51	6.02	6.24	6.42	6.60	6.75
pH	1.26	1.20	1.11	1.07	1.03	1.00
			I = 0.2			
I'	0.223	0.182	0.189	0.184	0.184	0.186
$ReO_4^-(\cdot 10^{-4})$	5.84	6.13	6.27	6.76	6.96	7.02
pH	1.26	1.17	1.06	1.07	1.05	1.00
			I = 0.4			
I'	0.383	0.379	0.385	0.394	0.399	0.399
$ReO_4^-(\cdot 10^{-4})$	6.09	6.25	6.42	6.79	7.19	7.25
pH	1.23	1.12	1.02	1.02	1.03	0.98
			I = 0.5			
I'	0.481	0.493	0.486	0.491	0.499	0.513
$ReO_4^-(\cdot 10^{-4})$	6.24	6.40	6.46	6.83	7.22	7.30
pH	1.23	1.12	1.00	1.00	1.01	0.96
			I = 0.6			
I'	0.582	0.585	0.586	0.596	0.602	0.611
$ReO_4^-(\cdot 10^{-4})$	6.27	6.47	6.51	6.93	7.22	7.36
pH	1.22	1.11	0.99	1.00	0.98	0.95
			I = 0.8			
I'	0.782	0.779	0.785	0.793	0.808	0.833
$ReO_4^-(\cdot 10^{-4})$	6.27	6.51	6.57	6.97	7.25	7.41
pH	1.18	1.08	0.96	0.96	0.95	0.92
			I = 1.0			
I'	0.976	0.981	0.985	1.000	1.018	1.024
$ReO_4^-(\cdot 10^{-4})$	6.36	6.58	6.67	7.04	7.33	7.48
pH	1.16	1.06	0.94	0.94	0.93	0.90
			I = 1.2			
I'	1.173	1.185	1.185	1.198	1.211	1.243
$ReO_4^-(\cdot 10^{-4})$	6.42	6.67	6.83	7.09	7.33	7.49
pH	1.15	1.04	0.94	0.92	0.90	0.87
			I = 1.4			
I'	1.376	1.386	1.385	1.393	1.413	1.421
$ReO_4^-(\cdot 10^{-6})$	6.50	6.69	6.83	7.09	7.37	7.51
pH	1.13	1.02	0.91	0.89	0.88	0.85
			I = 1.6			
I'	1.576	1.587	1.582	1.605	1.626	1.655
$ReO_4^-(\cdot 10^{-6})$	6.53	6.72	6.80	7.14	7.40	7.51
pH	1.12	1.00	0.88	0.88	0.86	0.82
			I = 1.8			
I'	1.776	1.790	1.782	1.801	1.820	1.830
$ReO_4^-(\cdot 10^{-6})$	6.53	6.76	6.85	7.15	7.43	7.55
pH	1.10	0.99	0.87	0.86	0.84	0.81
			I = 2.0			
I'	1.977	1.986	1.981	1.999	1.992	2.062
$ReO_4^-(\cdot 10^{-6})$	6.56	6.78	6.79	7.33	7.49	7.60
pH	1.08	0.97	0.84	0.86	0.84	0.80

$$f^{\mathrm{r}} = -A_{\mathrm{P}}[(I/m^0)^{1/2}/[1 + 1.2(I/m^0)^{1/2}] + (2/1.2)\ln[1 + 1.2(I/m^0)^{1/2}] \quad (10)$$

$$Z = \sum_{\mathrm{c}}(m_{\mathrm{c}}/m^0)|Z_{\mathrm{c}}| = \sum_{\mathrm{a}}(m_{\mathrm{a}}/m^0)|Z_{\mathrm{a}}| \quad (11)$$

$$C_{ij}^{\mathrm{P}} = C_{ij}^{\mathrm{P}}/2(|z_i z_j|)^{1/2} \quad (12)$$

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[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, 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 that are not all of the same sign. According to Pitzer and Kim,[9]

$$B_{\mathrm{ca}} = \beta_{\mathrm{cs}}^{(0)} + \beta_{\mathrm{ca}}^{(1)} y_1 \quad (13)$$

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

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

$$y_1 = 2[1 - (1 + \alpha\{I/m^0\}^{1/2})\exp(-\alpha\{I/m^0\}^{1/2})/(\alpha^2\{I/m^0\}) \quad (15)$$

$$y_2 = 2[-1 + (1 + \alpha\{I/m^0\}^{1/2}) + (\alpha^2\{I/m^0\}/2)\exp(-\alpha\{I/m^0\}^{1/2})]/(\alpha^2\{I/m^0\}^2) \quad (16)$$

Following the advice of Pitzer and Mayorga,[10,11] ψ_{Mca} is considered to be independent of ionic strength. In estimating $\gamma\{\mathrm{ReO_4}^-\}$ and $\gamma\{\mathrm{H}^+\}$, 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:

$$\begin{aligned}\ln \gamma_{\mathrm{MX}} = {} & |z_{\mathrm{M}} z_{\mathrm{X}}|F + (\nu_{\mathrm{M}}/\nu)\sum_{\mathrm{a}} m_{\mathrm{a}}[2B_{\mathrm{Ma}} + ZC_{\mathrm{Ma}} \\ & + 2(\nu_{\mathrm{X}}/\nu)\Phi_{\mathrm{Xa}}] + (\nu_{\mathrm{X}}/\nu)\sum_{\mathrm{c}} m_{\mathrm{c}}[2B_{\mathrm{Cx}} + ZC_{\mathrm{Cx}} \\ & + 2(\nu_{\mathrm{M}}/\nu)\Phi_{\mathrm{Mc}}] + \sum_{\mathrm{c}}\sum_{\mathrm{a}} m_{\mathrm{c}} m_{\mathrm{a}} \nu^{-1}[2\nu_{\mathrm{M}} Z_{\mathrm{M}} C_{\mathrm{Ca}} \\ & + \nu_{\mathrm{M}}\Psi_{\mathrm{Mca}} + \nu_{\mathrm{X}}\Psi_{\mathrm{CaX}}] + \sum_{\mathrm{c<c'}}\sum m_{\mathrm{c}} m_{\mathrm{c'}}(\nu_{\mathrm{X}}/\nu)\Psi_{\mathrm{cc'X}} \\ & + \sum_{\mathrm{a<a'}}\sum m_{\mathrm{a}} m_{\mathrm{a'}}(\nu_{\mathrm{M}}/\nu)\Psi_{\mathrm{Maa'}} \\ & + 2\sum_{\mathrm{n}} m_{\mathrm{n}}(\nu_{\mathrm{M}}\lambda_{\mathrm{nm}} + \nu_{\mathrm{X}}\lambda_{\mathrm{nX}})/\nu \end{aligned} \quad (17)$$

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

$$\begin{aligned}\log K' = {} & \log K_{\mathrm{m}} - \log m\{\mathrm{H}^+\} - \ln[\gamma\{\mathrm{H}^+\}\cdot\gamma\{\mathrm{ReO_4}^-\}]/\ln(10) \\ = {} & \log K^0 + 2/\ln(10)\cdot m_{\mathrm{NH_4}}\beta_{\mathrm{NH_4\cdot ReO_4}}^{(0)} \\ & + 2/\ln(10)\cdot y_1 m_{\mathrm{NH_4}}\beta_{\mathrm{NH_4ReO_4}}^{(1)} + 2/\ln(10)\cdot Z m_{\mathrm{NH_4}} C_{\mathrm{NH_4ReO_4}} \end{aligned} \quad (18)$$

Table 2. Standard Molar Thermodynamic Properties for the Extraction Process in the Temperature Range (278.15 to 303.15) K

T		$\Delta_{\mathrm{r}}G_{\mathrm{m}}{}^0$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}{}^0$	$\Delta_{\mathrm{r}}S_{\mathrm{m}}{}^0$	$\Delta_{\mathrm{r}}C_{\mathrm{pm}}{}^0$
K	$\log K^0(\mathrm{P})$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot (K \cdot mol)^{-1}}$	$\mathrm{J \cdot (K \cdot mol)^{-1}}$
303.15	3.1862	−18.51	−2.591	52.52	514
298.15	3.2025	−18.27	−5.141	44.03	506
293.15	3.2227	−18.07	−7.649	35.55	497
288.15	3.2497	−17.91	−10.11	27.07	489
283.15	3.2828	−17.80	−12.54	18.59	480
278.15	3.3277	−17.73	−14.92	10.11	472

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

Thermodynamic Properties for the Extraction Process. The values of $\log K^0$ obtained at various temperatures obtained by Pitzer's equation are fitted to the following equation.[12−14]

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

The values of parameters A_{i} are: $A_1 = -631.01$, $A_2 = 95163.5$, and $A_3 = 1.0598$ with a standard deviation of $s = 0.189$.

The standard molar thermodynamic properties $\Delta_{\mathrm{r}}G_{\mathrm{M}}{}^0$, $\Delta_{\mathrm{r}}H_{\mathrm{M}}{}^0$, $\Delta_{\mathrm{r}}S_{\mathrm{M}}{}^0$, and $\Delta_{\mathrm{r}}C_{\mathrm{P,M}}{}^0$ for the extraction process are simply related to the parameters in eq 19:

$$\Delta_{\mathrm{r}}G_{\mathrm{M}}{}^0 = -(R\ln(10))(A_1 T + A_2 + A_3 T^2) \quad (20)$$

$$\Delta_{\mathrm{r}}H_{\mathrm{M}}{}^0 = (R\ln(10))(A_3 T^2 - A_2) \quad (21)$$

$$\Delta_{\mathrm{r}}S_{\mathrm{M}}{}^0 = (R\ln(10))(A_1 + 2A_3 T) \quad (22)$$

$$\Delta_{\mathrm{r}}C_{\mathrm{P,M}}{}^0 = (R\ln(10))(2A_3 T) \quad (23)$$

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

■ CONCLUSIONS

The extractant N503 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 temperature, which indicates low temperature benefits extraction of Re(VII) by using N503. The negative experimental association Gibbs energy $\Delta G_{\mathrm{M}}{}^0 < 0$ 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 factor.[12−14] Accompanying the increase of temperature, the entropy increases.

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