Calculation of HNO_2 Concentration from Redox Potential in HNO_3 - H_2O System as an Aid to Understanding the Cathodic Reaction of Nitric Acid Corrosion

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Nitrous acid affects the corrosion of metals such as stainless steels in nitric acid. However nitrous acid is not particularly stable in nitric acid and the analytical methods available are quite involved. Accordingly, the calculation of nitrous acid concentration from redox potential was tested in the HNO_3 - H_2O system as a convenient in situ analysis method. The calculation process is based on Nernst's equation and the required thermodynamic data were obtained from published values. The available thermodynamic data allow calculation of nitrous acid concentration from 273 K to 373 K for 0%-100% HNO_3 . The redox potential was measured in $8 \text{ kmol} \cdot \text{m}^{-3}$ HNO_3 under NO bubbling and the nitrous acid concentration was determined by a Colourimetric method. The calculated data were compared with the measured data and a good agreement was found. It was found that the corrosion potential of stainless steel is influenced by nitrous acid concentration in nitric acid solution. The calculation process is useful for in-situ analysis of nitrous acid species in HNO_3 - H_2O system and understanding the behavior of the cathodic reaction associated with nitric acid corrosion.

Key words : nitrous acid, in-situ analysis, nitric acid corrosion, stainless steel, cathodic reaction, thermodynamic calculation, redox potential

1. Introduction

Corrosion is an electrochemical process which consists of anodic (i.e. oxidation) and cathodic (i.e. reduction) reactions. In general, the anodic reaction is influenced by material factors, whilst the cathodic reaction is influenced by environmental factors. In the nitric acid system, the over-all cathodic reaction is known to be¹⁾:

Nitric acid corrosion of stainless steel is strongly affected by the cathodic reaction, since in sufficiently oxidising conditions (i.e. those for which the solutions exerts a high redox potential), the passivity of stainless steel breaks down and significant transpassive corrosion rates can be generated²⁾. Nitrous acid (HNO_2), which is the product of nitrate reduction (reaction (1)), exerts a powerful effect on the redox potential of nitric acid solutions owing to the fact that reaction (1) actually consists of a series of linked steps involving HNO_2 and the reaction is autocatalytic¹⁾. However it is difficult to understand the behaviour of HNO_2 which is one of the species in the above reaction because it is not particularly stable in nitric acid. In this paper, the nitrous acid concentration in nitric acid solutions was calculated from redox potential by application of Nernst's equation and the results obtained were compared with direct measure-

ment. In addition, the effect of HNO_2 concentration on the corrosion potential of stainless steel was investigated in HNO_3 solution.

2. Thermodynamic theory

Nernst's equation can be used to relate the concentration of nitrous acid in nitric acid to the solution redox potential³⁾. According to the equation, when the activity coefficient of HNO_2 is assumed to be unity (which is not unreasonable because of the expected low concentration of HNO_2), the electrode potential E for reaction (1) is given by:

$$E = E^0 + (RT/2F) \ln \{ [\text{H}^+]^3 [\text{NO}_3^-] \gamma_{\pm}^4 / [\text{HNO}_2] a_L \} \quad (2)$$

$$E^0 = 1/2F (\mu_{\text{NO}_3^-}^0 + 3\mu_{\text{H}^+}^0 - \mu_{\text{HNO}_2}^0 - \mu_{\text{H}_2\text{O}}^0) \quad (3)$$

where E^0 is the standard equilibrium potential, $[\text{H}^+]$, $[\text{NO}_3^-]$ and $[\text{HNO}_2]$ are the molality of each ion or compound (mol/kg-water), R is the gas constant ($= 1.986 \text{ cal/mol} \cdot \text{K}$), F is Faraday's constant ($= 23060 \text{ cal/V}$), μ^0 is the chemical potential of each species (cal/mol). $\gamma_{\pm}$ is the mean activity coefficient of a pure aqueous solution of HNO_3 and a_L is the water activity of a pure aqueous solution HNO_3 .

Therefore, if μ^0 , $\gamma_{\pm}$ and a_L are known for a certain HNO_3 concentration, $[\text{HNO}_2]$ can be theoretically calculated from the measured solution redox potential and vice versa.

2.1 Calculations of μ^0 and E^0

In this work, the calculated data of chemical potentials at 373 K published by EPRI⁴⁾ were used to calcu-

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Table 1 Chemical potentials at 298 K and 373 K.

	NO ₃ (aq., m=1)	H ⁺ (aq., m=1)	HNO ₂ (aq., m=1)	H ₂ O (liq.)	H ₂ (g)
$\mu^\circ_{298\text{K}}[\text{kJ/mol}]$	-111,389	0	-55,674	-237,292	0
$G^\circ_{373\text{K}}[\text{kJ/mol}]$	-122,001	+435	-65,733	-243,198	-10,051

late E° from equation (3). μ° at 298 K and G° at 373 K are shown in Table 1. G° shows Gibb's free energy and it needs to consider equation (4) in addition to equation (3) to apply G° at 373 K in the table to the calculation of E° (vs. NHE). Accordingly, E° at 373 K is calculated by equation (5).

$$E^\circ = 1/2F (G^\circ_{\text{NO}_3^-} + G^\circ_{\text{H}^+} + G^\circ_{\text{H}_2} - G^\circ_{\text{HNO}_2} - G^\circ_{\text{H}_2\text{O}}) \quad (5)$$

Assuming that enthalpy and entropy are linearly related to temperature, E° in the range from 273 K to 373 K was calculated from equation (6).

$$E^\circ_T = E^\circ_{298\text{K}} + ((E^\circ_{373\text{K}} - E^\circ_{298\text{K}})/75) * (T - 298) \quad (6)$$

2.2 Calculations of a_L and $\gamma_\pm$

In order to calculate a_L and $\gamma_\pm$, Clegg and Brimblecombe's data were used⁵⁾. They presented values for a_L and $\gamma_\pm$ in the range from 273 K to 373 K for 0%-100% HNO₃ as a function of total mole fraction of ions (X_i).

In their paper, a_L and $\gamma_\pm$ at 298 K are expressed by equations (7)-(9) :

$$f_\pm = \gamma_\pm (1 + (M_1/1000) \sum m_i) \quad (7)$$

where $f_\pm$ is the mean activity coefficient at 298 K expressed as a molar fraction and $\gamma_\pm$ is the mean activity coefficient at 298 K expressed as a weight concentration. M_1 is the molar mass of the solvent (18.0152 g for H₂O). $\sum m_i$ means the summation of over all solute species i . In this case, $\sum m_i$ equals $m[\text{H}^+] + m[\text{NO}_3^-]$, where m is molality (i.e. mol/kg-H₂O).

$$\ln(f_\pm) = -A_x \{ (2/\omega) \ln(1 + \omega I_x^{1/2}) + (I_x^{1/2} - 2I_x^{3/2}) / (1 + \omega I_x^{1/2}) \} + X_i^2 (W + 2X_i U + X_i^2 V) - W \quad (8)$$

$$\ln(a_L) = \ln(X_L) + 2A_x I_x^{3/2} / (1 + \omega I_x^{1/2}) + X_i^2 [\{ W + (2X_i - 1) U \} - V X_i (X_i - 1/3)] \quad (9)$$

where A_x is the Debye-Hückel constant (=2.917 at 298 K). X_i means total mole fraction of ions ($X[\text{H}^+] = X[\text{NO}_3^-] = n[\text{H}^+] / (n[\text{H}^+] + n[\text{NO}_3^-] + n[\text{H}_2\text{O}])$, n : mole number) and I_x means ionic strength ($=1/2(X[\text{H}^+] + X[\text{NO}_3^-])$). ω , W , U and V are constants and their values are shown in Table 2⁵⁾.

Table 2 Each value of parameters for calculation of activity coefficient.

	ω	W	U	V
Value	14.065	-3.82721	0.202749	-2.57620
Standard error	0.368	0.0193	0.0498	0.231

a_L and $\gamma_\pm$ in the range from 273 K to 373 K ($=\gamma_{\pm,T}$, $a_{L,T}$) were calculated by using a_L and $\gamma_\pm$ at 298 K on the basis of the following equations :

$$\log(f_{\pm,T}) = \log(f_\pm) + (y/v) L_2 - (z/v) J_2 + (\Omega/v) \Gamma_2 \quad (10)$$

$$\log(a_{L,T}) = \log(a_L) + y/L_1 - z/J_1 + \Omega \Gamma_1 \quad (11)$$

where

$$y = (T_r - T) / (2.303 R T_r T) \quad T_r: 25(^{\circ}\text{C}) \quad (12)$$

$$z = T_r y - \log(T_r/T) / R \quad (13)$$

$$\Omega = T_r (z + 1/2 (T - T_r) y) \quad (14)$$

$$\Gamma_2 = 1.7722 X_i (X_i - 2) - 0.35496 X_i^{2.5} (5 X_i - 7) \quad (15)$$

$$\Gamma_1 = X_i^2 (0.8861 - 0.8874 X_i^{1.5}) \quad (16)$$

L_2 , L_1 , J_2 and J_1 were calculated on the basis of Clegg and Brimblecombe's data⁵⁾. The Tables list the Chebyshev polynomial coefficients for the calculation of the partial molal functions L_2 , L_1 , J_2 and J_1 for $0 \leq X_i \leq 1$. Data fitting was carried out as a function of $I_x^{1/2}$ and the variable X was defined by the following equation.

$$X = I_x^{1/2} \quad (17)$$

The polynomial is represented in Chebyshev series form by the normalised variable α :

$$\alpha = (2X - X_{\max} - X_{\min}) / (X_{\max} - X_{\min}) \quad (18)$$

where $X_{\max}$ and $X_{\min}$ are the upper and lower limits of the fit respectively (given in each table). The polynomial representation, with $N+1$ coefficients, of each partial molal function $f(\alpha)$ is given by

$$f(\alpha) = 0.5 \alpha_0 T_0(\alpha) + \alpha_1 T_1(\alpha) + \alpha_2 T_2(\alpha) + \alpha_3 T_3(\alpha) + \dots + \alpha_N T_N(\alpha) \quad (19)$$

where $T_0(\alpha) = 1$, $T_1(\alpha) = \alpha$ and, for $n \geq 2$:

$$T_n(\alpha) = 2\alpha T_{n-1}(\alpha) - T_{n-2}(\alpha) \quad (20)$$

As an example, those parameters of $8 \text{ kmol} \cdot \text{m}^{-3} \text{HNO}_3$ ($X = I_x^{1/2} = 0.374$) are shown in Table 3.

From the above process, $[\text{HNO}_2]$ is calculated from the measured E in HNO₃. The advantage of this method is that a_L and $\gamma_\pm$ can be calculated at various temperature and HNO₃ concentration. Fig. 1 shows

Table 3 L_2 , L_1 , J_2 and J_1 values of $8 \text{ kmol} \cdot \text{m}^{-3} \text{HNO}_3$.

X_i	$X(I_x^{1/2})$	L_2	L_1	J_2	J_1
0.2799	0.3740	10911.16	-1263.01	205.9	-10.9512

Fig. 1 Relationship between total mole fraction of ions (X_I) and water activity (a_L) as a function of temperature.

the relationship between total mole fraction of ions (X_I) and water activity (a_L). From this result, a_L is

Fig. 2 Relationship between total mole fraction of ions (X_I) and mean activity coefficient (f) as a function of temperature.

Table 4 $\gamma_{\pm,T}$ of representative HNO_3 concentrations and temperatures.

HNO_3 concentration ($\text{kmol}\cdot\text{m}^{-3}$) at 298K	1.0	3.0	4.0	8.0	9.0	13.0
Density [kg/l] at 298K	1.0302	1.0955	1.1270	1.2449	1.2709	1.3611
X_I	0.03589	0.1065	0.1413	0.2799	0.3152	0.4633
$\gamma_{\pm}$ 273K	0.8405	1.0844	1.2501	2.0818	2.3224	3.3217
$\gamma_{\pm}$ 298K	0.7216	0.9313	1.0738	1.7892	1.9962	2.8562
$\gamma_{\pm}$ 333K	0.5321	0.6873	0.7928	1.3226	1.4759	2.1132
$\gamma_{\pm}$ 353K	0.4336	0.5614	0.6481	1.0848	1.2114	1.7377
$\gamma_{\pm}$ 373K	0.3482	0.4528	0.5238	0.8821	0.9862	1.4198
$a_{L, 298K}$	0.9638	0.8679	0.8106	0.5546	0.4905	0.2645

hardly influenced by temperature. Fig. 2 shows the relationship between X_I and mean activity coefficient as a standard of molar fraction ($f_{\pm,T}$). $\gamma_{\pm,T}$ can be calculated by equation (7). $\gamma_{\pm,T}$ of representative nitric acid concentrations and temperatures are shown in Table 4.

3. Experimental

Electrochemical tests were performed to measure the redox potential (E) of nitric acid solution and the corrosion potential of stainless steel (E_{corr}) as a function of NO purging. The redox potential in $8\text{ kmol}\cdot\text{m}^{-3}$ HNO_3 (i.e. the potential adopted by clean Pt) was measured at 353K and 373K in this experiment. Corrosion potential measurements for stainless steel were made in $8\text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 373K, again as a function of NO purging. The stainless steel used was NAG (nitric acid grade) 18/10 L, manufactured in the United Kingdom. The composition of this steel is

Table 5 Chemical composition of NAG18/10 L electrode.

C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu
0.015	0.008	0.015	0.32	1.54	9.64	18.77	0.03	0.07	0.03
Sn	Al	Ti	Co	B	N	As	Nb	W	Fe
0.008	0.008	<0.01	0.04	0.0005	0.044	0.007	<0.01	0.04	bal

wt%

Fig. 3 Basic structure of electrochemical test.

given in Table 5 and it can be seen that it is closely related to AISI 304L.

The basic structure of electrochemical test is shown in Fig. 3. A Pt coil was used as working electrode. The electrochemical test cell was immersed in a thermostatically-controlled water bath which was adjusted to maintain the desired temperature in the test liquor as measured by a PTFE-coated thermocouple immersed in it. The desired purge gas was supplied to the test liquor via microbore PTFE tubing and the gas flowrate was regulated by a stainless steel flow-meter. NO flow rate was adjusted at 10 cm³/min in this work. The test vessel was open to the atmosphere via a water-cooled condenser and the purge gas was vented to an operating fume cupboard. The reference electrode was a Saturated Calomel (SCE) which was connected to the test liquor by a series of Luggin capillaries designed to prevent Cl⁻ contamination of test liquor and nitrite contamination of the SCE. The Luggin capillaries were threaded with glass-fibre string in order to prevent loss of electrolytic connection due to solution off-gassing. The technical grade of pure NO was used for this test.

From the redox potential measured as a function of time, [HNO₂] was calculated on the basis of equation (2). The analysis was performed in the range from 0.88 to 0.97 [V vs. SCE] at 353 K and 0.915 to 0.98 [V vs. SCE] at 373 K to determine the relationship between redox potential and HNO₂ concentration.

Table 6 Measurement results of HNO₂ concentration by colourimetric method at 353 K.

E _{SCE} [V vs SCE]	E _{NHE} [V vs NHE]	Mea.[HNO ₂] [mg/l]
0.89	1.0947	9200
0.9	1.1047	5200
0.91	1.1147	2800
0.92	1.1247	1600
0.93	1.1347	800
0.94	1.1447	400
0.95	1.1547	210
0.96	1.1647	85
0.97	1.1747	31
0.98	1.1847	17

The adjustment of redox potential in this experiment was not difficult. The desirable potential can be chosen because it increases automatically by stopping NO. The actual [HNO₂] resulting in the solution was determined by a Colourimetric method using Cleve's acid⁶⁾ in order to allow comparison with the calculated HNO₂ concentration. This method employs an initial dilution by a factor of one hundred and is thus suitable for determining HNO₂ in initially hot and concentrated nitric acid solutions.

Table 7 Measurement results of HNO_2 concentration by colourimetric method at 373 K.

E_{SCE} [V vs SCE]	E_{NHE} [V vs NHE]	Mea.[HNO_2] [mg/l]
0.925	1.1135	2600
0.93	1.1185	1900
0.94	1.1285	1000
0.95	1.1385	500
0.96	1.1485	240
0.97	1.1585	120
0.98	1.1685	50
0.99	1.1785	20

Fig. 4 Effect of HNO_2 concentration on redox potential of $8 \text{ kmol} \cdot \text{m}^{-3}$ HNO_3 at 353 K.

4. Results and discussion

First of all, the reasonability of the calculation process is discussed by comparing measured data. Tables 6 and 7 show the measured values of HNO_2 concentration obtained by the Colourimetric method. Figs. 4 and 5 compare the calculated values of HNO_2 with the measured ones. Consequently, the agreement between the calculated and measured data is good and this calculation process based on Nernst's equation applying calculated activity coefficients is useful to follow the change of $[\text{HNO}_2]$. Also, it is roughly considered that the effect of temperature on the thermodynamic data is correctly discussed in the calculation process. The error of calculated value to measured one was within 30% for $[\text{HNO}_2] > 50 \text{ ppm}$. For lower HNO_2 concentrations, it is considered that the colourimetric technique used to measure HNO_2 was not sufficiently sensitive and hence that some

Fig. 5 Effect of HNO_2 concentration on redox potential of $8 \text{ kmol} \cdot \text{m}^{-3}$ HNO_3 at 373 K.

Fig. 6 Change of Redox potential and HNO_2 concentration calculated from it in $8 \text{ kmol} \cdot \text{m}^{-3}$ HNO_3 under NO bubbling

improvement could be made here.

Fig. 6 shows the change of redox potential with NO bubbling and $[\text{HNO}_2]$ calculated from these potentials. The relationship between E_{SCE} and E_{NHE} was calibrated by the following equation as a function of temperature from the data presented in Table 8⁷⁾.

$$E_{\text{NHE}} = E_{\text{SCE}} + 0.3522 - 10^{-6} T (T + 63.7) \quad (21)$$

$$[283 \text{ K} \leq T \leq 313 \text{ K}]$$

where $T(\text{K})$ is the temperature of the saturated KCl solution for SCE.

The redox potential of 8M HNO_3 is lowered and HNO_2 concentration increased by NO bubbling from the Fig.6. This means that NO acts as a reducing

Table 8 Standard half-cell potentials as a function of temperature in absolute volts.

Temperature (K)	Saturated KCl (V)
273	0.2602
283	0.2541
288	0.2509
293	0.2477
298	0.2444
303	0.2411
308	0.2377
311	0.2357
313	0.2343
323	0.2272
333	0.2199
343	0.2124
353	0.2047
363	0.1967
373	0.1885

Fig. 7 Effect of HNO_2 concentration on corrosion potential of NAG18/10 L.

agent in HNO_3 . HNO_2 is more stable in HNO_3 solution at lower temperature. In this way, the HNO_2 concentration in HNO_3 can be easily obtained by calculation from redox potential measurements which are relatively simple to make.

Fig. 7 shows the effect of HNO_2 concentration on the corrosion potential of NAG18/10L. Again, HNO_2 concentration was calculated from the solution redox potential which was measured at the same time as the corrosion potential of the stainless steel. Fig. 7 shows that increase in HNO_2 concentration has a pronounced effect on the corrosion potential of stainless steel, elevating it towards transpassivity. The change of corrosion potential is due to the autocatalytic effect of HNO_2 on nitrate reduction¹⁾—reaction (1).

5. Conclusions

In general, the in-situ determination of HNO_2 is not easy because it is not particularly stable in HNO_3 and the analytical techniques are quite involved. But, from relatively simple measurement of redox potential, $[\text{HNO}_2]$ can be reliably calculated, thus obviating the need for direct analytical determination. This is of

course applicable only to the simple HNO_3 - H_2O system, but can be applied over the range from 273 K to 373 K for 0%-100% HNO_3 .

HNO_2 increases the corrosion potential of stainless steel and hence has a significant effect on nitric acid corrosion.

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