Dilute nitric or nitrous acid solution containing halide ions as effective media for pure gold dissolution

Journal:	*Physical Chemistry Chemical Physics*
Manuscript ID:	CP-ART-04-2015-002288.R1
Article Type:	Paper
Date Submitted by the Author:	11-Jun-2015
Complete List of Authors:	Hojo, Masashi; Kochi University, Chemistry Yamamoto, Masahiko; Kochi University, Chemistry Okamura, Kei; Kochi University, Marine Core Reseach

Dilute nitric or nitrous acid solution containing halide ions as effective media for pure gold dissolution

Masashi Hojo[a]*, Masahiko Yamamoto[a] and Kei Okamura[b]

[a]Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520, Japan

[b]Center for Advanced Marine Core Research, Kochi University, B200 Monobe, Nankoku, Kochi 783-8502, Japan

* Corresponding author.

Keywords: gold dissolution rate constant, crystal ion radius, bulk water structure, nitronium ion, nitrosonium ion, Raman spectrum, corrosion

ABSTRACT

The greatly enhanced oxidation ability from dilute aqueous nitric acid (0.10 – 2.0 mol L^{-1}) containing bromide and iodide salts as well as chloride salts has been examined based on the dissolution kinetics of pure gold at 30 – 60 ℃. It has been found that bromide salts are more effective than chloride salts to gain the ability of dissolving gold in dilute aqueous nitric acid solution. At 60 ℃, a piece of gold-wire (*ca.* 20 mg) is dissolved in 20 mL of as low as 0.10 mol L^{-1} HNO_3 solution containing 1.0 – 5.0 mol L^{-1} NaBr and the dissolution rate constant, log (k /s^{-1}), increases linearly (from -5.78 to -4.52) with the increasing NaBr concentration. The addition of organic solvents, such as acetonitrile and acetic acid, causes acceleration of gold dissolution in LiBr and NaBr solutions. With increasing MeCN contents, for instance, the log (k /s^{-1}) value of 0.10 mol L^{-1} HNO_3 solution containing 2.0 mol L^{-1} NaBr increases linearly from -5.30 to -4.61 at 30% (v/v) MeCN. The bromide salts affect in the order of KBr < NaBr < LiBr < $CaBr_2$ on the gold dissolution rate constant. With increasing NaI concentration (0.20 – 3.0 mol L^{-1}), some acceleration in log (k /s^{-1}) for 0.50 or 1.0 mol L^{-1} HNO_3 solution has been observed, however, the slope of acceleration as the function of NaI concentration is much smaller than that of NaCl or NaBr. The gold dissolution ability has been examined also for nitrous acid containing chloride and bromide ions at 35 ℃. The $NaNO_2$ solution containing twice or more amounts of HX (X = Cl, Br) gives the maximum efficiency for gold dissolution, according to the log (k /s^{-1}) values in the mixed solutions between $NaNO_2$ (0.10 – 2.0 mol L^{-1}) and HX of various concentrations. Oxidation mechanisms with dilute nitric and nitrous acids on the gold dissolution are discussed from the standpoint of the redox potentials in “modified” aqueous solutions and not of the changes in the activity coefficients of ions.

1. Introduction

It has been well recognized that pure gold is dissolved in *aqua regia*, that is, the mixture between concentrated hydrochloric and nitric acids. In a CRC book [1] the preparation procedure of *aqua regia* is described as follows: “Mix 1 part concentrated HNO_3 with 3 parts of concentrated HCl. This formula should include one volume of water if the *aqua regia* is to be stored for any length of time. Without water, objectionable quantities of chlorine and other gases are evolved.” Beckham *et al.* [2] has described that Geber, an Arabian chemist, mentioned of *aqua regia* in the eighth century. Many primary students in chemistry may regard *aqua regia* as the only liquid to dissolve pure gold in it. In the metallurgy of gold, however, many leaching (dissolution in liquids) methods are known [3]. Chlorine-chloride leaching was applied commercially in the 19th century, but its use diminished following the introduction of the cyanide process in 1889. Other halide solutions (*i.e.*, bromine-bromide and iodine-iodide) have been investigated in the laboratory [3]. Unfortunately, the commercial application of bromine and iodine solutions for gold leaching is restricted by the high cost of the reagents, the high cost of materials of construction to withstand the severe process conditions, and industrial hygiene and health issues associated with their use. The authors of the book [3] have continued that one possible means of achieving this is by electrochemically regenerating the bromine [4] or iodine [5] from solution, with the potential for simultaneous recovery of gold and other metals.

In preceding studies [6,7,8], we have discovered that, indeed, dilute aqueous nitric acid (< 2.0 mol L^{-1}) can exhibit unexpectedly the strong oxidation ability not only in the nano-size small water droplets of reversed micelle systems [6,7,8] but also in “bulk” water [8], providing sizes of the water droplets are small enough or the “bulk” water contains enough concentrated salts. Under these conditions, we have proposed that the “intrinsic” water properties are lost in harmony with the destruction of bulk water structure through hydrogen-bonding [8,9]. The nitronium ion (NO_2^+) has been assumed to be the intermediate species for oxidation in dilute nitric acid containing halide salts in reversed micellar and “bulk” solution systems [7,8]. We do not think that the extraordinary oxidation ability of dilute nitric acid containing salts in higher concentrations can be easily explained by the proper activities of ions which might be estimated with Debye-Hückel [10] and Pitzer [11] theories.

We can obtain chlorine (Cl_2) from chloride ions with the enhanced oxidation ability in dilute aqueous HNO_3 solution (0.1 - 2.0 mol L^{-1}) containing various chloride salts. Once obtaining Cl_2, it is an easy task for us to dissolve pure gold in the chloride solution [8], because the large complexing ability of the chloride ion toward Au^{3+} causes the redox potential from Au^0 to Au^{3+} to be much lower, compared to the potential value without the abundant Cl^-. The redox potentials [12] for the Au^{3+} species are reported as follows:

$$Au^{3+} + 3e^- \leftrightarrows Au \qquad E^o = 1.52\ V, \qquad (1)$$

$$AuCl_4^- + 3e^- \leftrightarrows Au + 4\ Cl^- \qquad E^o = 1.00\ V. \qquad (2)$$

We [8] have succeeded in dissolving other precious metals, such as Pt and Pd, as well as Au in dilute aqueous nitric acid solution contaning chloride salts. The 1:1 mixed solutions between seawater and 2.0 mol L^{-1} HNO_3 have been found to be also good media for dissolving pure gold.

The stronger complexing ability of Br^- and I^- than Cl^- toward Au^{3+} causes the redox potential (*cf.* Eq. 2) to be much lower: E^o = 0.854 and 0.56 V for $AuBr_4^-$ and AuI_4^-, respectively [12]. In the present study, we examine the gold dissolution in dilute nitric acid containing bromide and iodide salts. It may be reported that the bromide salts are much more effective than chloride salts to gain the ability of dissolving gold in dilute aqueous nitric acid solution. The influences of organic solvents, such as acetonitrile and acetic acid, are examined on the gold dissolution kinetics.

In the final section (*cf. 3-5*) of this paper, nitrous acid (HNO_2) solutions instead of HNO_3 containing the halide ions are examined, and the oxidation mechanism with nitrous acid on the gold dissolution is discussed. For a long time, it may have been believed that the oxidation ability of diluted aqueous nitric acid should be initiated by nitrous acid of a low concentration. Kinetics studies have been reported on the oxidation of bromide ions by nitric acid in the presence of nitrous acid [13,14]. However, we would like to demonstrate that diluted aqueous nitric acid (0.10 – 2.0 mol L^{-1}) itself can exhibit the oxidation ability, providing the solution contains salts and/or inert organic solvents of higher concentrations or contents.

2. Experimental section

The sample of pure gold was commercially available: gold wire (Nilaco, 99.95%, 0.25 mm diameter). Commercially available salts were used as received: LiBr, LiI xH_2O (x = 1.5 - 3), $CaBr_2$, and CaI_2 xH_2O (x = 4 - 6) from Aldrich; LiCl, NaCl, NaBr, NaI, KCl, KBr, KI, $CaCl_2$, and $NaNO_2$ (of all GR grades) from Wako Pure Chemical Industries. Nitric acid of 60% of a GR grade (JIS S), HCl (5.0 mol L^{-1}), HBr, HI, acetone, acetic acid, and acetonitrile of GR grades were purchased from Wako. Commercially obtained *o*-toluidine (TCI) was used as received. Pure water purified by a MilliQ System was used (< 0.1 μS cm^{-1}).

A 4.0 or 10.0 mol L^{-1} HNO_3 solution was utilized to make HNO_3 solutions of various concentrations such as 0.50, 1.0, or 2.0 mol L^{-1}, containing various salts. Nitrous acid solutions were prepared by mixing $NaNO_2$ with HX (X = Cl and Br) solutions. A gold sample of 19.7 ± 0.5 mg (*i.e.* 5.0×10^{-3} mol L^{-1}) in a 20 mL volumetric flask was kept at a constant temperature from 30 to 60 (±0.1) ℃ in a Yamato Shaking Incubator, model BT100, being shaken 60 times in a minute, equipped with a cooling dip (Yamato model BE-200F). The changes in mass of a piece of gold-wire (*ca.* 20 mg) were measured by a Mettler Toledo electronic analytical scale, model AB204-S. Before the dissolution, the pieces of gold-wire were rinsed with acetone and were air-dried on dried sheets of the KimWipes paper. After the partial dissolution, the pieces were washed with pure water and rinsed with acetone. The “pseudo” first–order dissolution rate constants (k/s^{-1}) were evaluated from the slope of ln [S] *vs.* t, with the correlation coefficients of more than 0.98, where [S] represents the relative mass (m_t/m_0) of gold remains at a certain time.

Raman spectra of H_2O in the presence of various contents of CH_3COOH were recorded with a Horiba-Jobin Yvon LabRam Spectrograph HR-800 at room temperature (~23 ℃). Excitation for the Raman spectroscopy was provided by a 514.5 nm argon laser.

3. Results and discussion

3-1 Effective dissolution of gold-wire in dilute nitric acid containing bromide salts

It has been found, in the present section, that various bromide salts as well as chloride salts [8] are effective to gain the ability dissolving gold in dilute aqueous nitric acid solution. At 60 ℃, for instance, gold-wire of *ca.* 20 mg is dissolved in 0.10 mol L^{-1} HNO_3 solution containing 1.0 – 5.0 mol L^{-1} NaBr and the dissolution rate constant, log (k /s^{-1}), increases linearly from -5.78 to -4.52 with increasing NaBr concentration (*cf.* Fig. 1). After *ca.* 6.4 h, needless to say, a half of the 20 mg gold-wire dissolves in the 0.10 mol L^{-1} HNO_3 solution containing 5.0 mol L^{-1} NaBr. LiBr is more effective but KBr is less effective than NaBr. An alkaline earth metal salt, $CaBr_2$, causes larger log (k /s^{-1}) values than the alkali metal salts at the corresponding concentrations over the range of 1.0 – 3.0 mol L^{-1}.

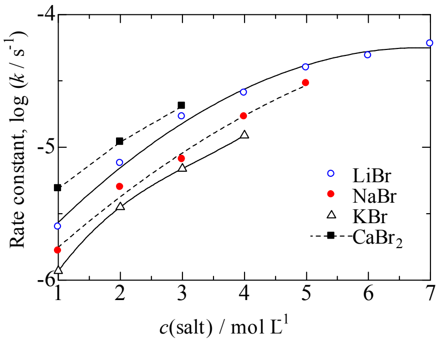

Fig. 1. Gold-wire dissolution rate constants, log (k / s^{-1}), in 0.10 mol L^{-1} HNO_3 containing bromide salts at 60℃: (○) LiBr; (●) NaBr; (△) KBr; (■) $CaBr_2$.

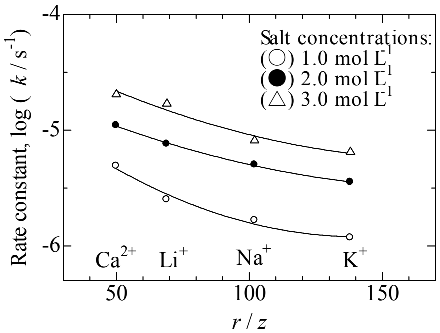

Fig. 2. The relationship between log (k / s^{-1}) and the crystal ion radii per charge number (r/z) for the metal ions in 0.1 mol L^{-1} HNO_3 containing various bromide salt at 60 ℃.

Fig. 2 shows the relationship between the log (k /s^{-1}) values and the crystal ion radii per charge number (r/z) for the metal ions [15] under the conditions in Fig. 1. The dissolution rate constants give linear curves against the r/z values for 1.0, 2.0, and 3.0 mol L^{-1} salts in 0.10 mol L^{-1} HNO_3 solutions. The smaller the crystal ionic radius per charge (r /z) of a metal ion, the faster the gold dissolution proceeds. The hydration around the lithium ion should be stronger than that around the sodium ion. The difference in the strength of hydration around metal ions may cause the difference among the gold dissolution rates. We [8] have reported similar linear curves for chloride salts of alkali metal, alkaline earth metal, and aluminum ions. In the present study, however, it has been found that the log (k /s^{-1}) values with iodide salts are hardly influenced by the kind of alkali metal ions (LiI, NaI, or KI over the range of 0.20 – 3.0 mol L^{-1}) in the 0.50 mol L^{-1} HNO_3 solution.

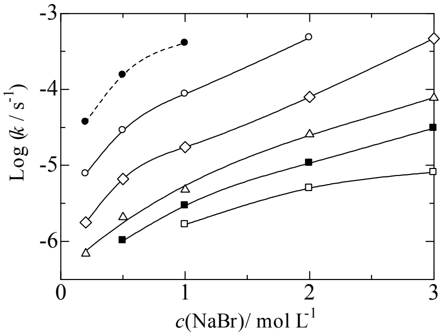

Fig. 3. Change of log (k / s^{-1}) in various concentration HNO_3 containing 0.20 - 3.0 mol L^{-1} NaBr at 60℃: (□) 0.1 (■) 0.2; (△) 0.3; (◇) 0.5; (○) 1.0; (●) 2.0 mol L^{-1} HNO_3.

The influences of nitric acid as well as NaBr concentrations were examined on the gold dissolution at the same temperature. Fig. 3 shows the changes of log (k /s^{-1}) in various HNO_3 concentrations (0.10 – 2.0 mol L^{-1}) containing 0.20 – 3.0 mol L^{-1} NaBr at 60 ℃. The increases in both the HNO_3 and NaBr concentrations cause enhancements in gold dissolution. In the presence of 1.0 mol L^{-1} NaBr, for instance, the log (k /s^{-1}) value increases from -5.78 to -3.39 with the increase in the HNO_3 concentration from 0.10 to 2.0 mol L^{-1} HNO_3 (*cf.* Table 1). In turn, the increase of the NaBr concentration from 0.20 to 3.0 mol L^{-1} with 0.30 mol L^{-1} HNO_3 solution results in a 100-fold acceleration of the dissolution [log (k /s^{-1}) = -6.16 to -4.11].

3-2 Comparison of the bromide salt with chloride and iodide salts

As mentioned in the **Introduction** section, the redox potentials of $AuCl_4^-$, $AuBr_4^-$, and AuI_4^- are reported to be +1.00, +0.854, and +0.56 for the following reactions: $AuX_4^- + 3e^- \leftrightarrows Au + 4X^-$, where X = Cl, Br, and I, respectively [12]. The redox potentials may predict the dissolution rate of gold metal in each halide solution. Fig. 4(a) shows the log (k /s^{-1}) values in dilute nitric acid solutions containing NaCl at 60 ℃. The log (k /s^{-1}) values with NaCl are much lower than those with NaBr of the corresponding concentrations. At 1.0 mol L^{-1} HNO_3, for instance, log (k /s^{-1}) = -5.42 and -4.06 (*cf.* Table 1) with 1.0 mol L^{-1} NaCl and NaBr, respectively, that is, *ca.* a 20-fold superiority of NaBr.

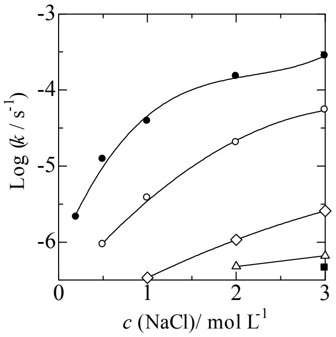

Fig. 4(a). Changes of log (k / s^{-1}) in HNO_3 solutions containing 0.20-3.0 mol L^{-1} NaCl at 60℃: (■) 0.20; (△) 0.30; (◇) 0.50; (○) 1.0; (●) 2.0 mol L^{-1} HNO_3.

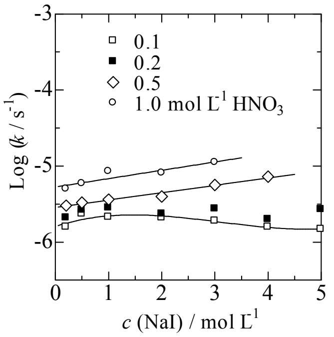

Fig. 4(b). Changes of log (k / s^{-1}) in HNO_3 solutions containing 0.20-5.0 mol L^{-1} NaI at 60℃: (□) 0.10, (■) 0.20; (◇) 0.50; (○) 1.0 mol L^{-1} HNO_3.

The effects of the iodide salt are not very ordinary, *cf.*, Fig. 4(b). Although the higher HNO_3 concentrations cause the higher rate constants, the increased segments in the rate caused by 0.10 – 1.0 mol L^{-1} HNO_3 are so small, *e.g.*, log (k /s^{-1}) increases only from -5.67 to -5.07 at 1.0 mol L^{-1} NaI. The acceleration with increasing salt concentration are also very small. With 0.50 mol L^{-1} HNO_3, for instance, the increase in the NaI concentration from 0.20 to 3.0 mol L^{-1} causes mere less than a 2-fold acceleration (from -5.52 to -5.25) in the rate constant. In 0.10 mol L^{-1} HNO_3 solution containing 0.2 and 3.0 mol L^{-1} NaI, after 140 h, the masses of *ca.* 20 mg gold-wire are lost to be 51.7 and 31.5% in 0.10 mol L^{-1} HNO_3, which result in log (k/s^{-1}) = -5.80 and -5.72, respectively. With the (salt) concentration increase from 0.20 to 3.0 mol l^{-1}, contrastingly, NaCl and NaBr cause *ca.* 130- and 260-fold increases in the rate constant, respectively, for 2.0 and 0.50 mol L^{-1} HNO_3.

Fig. 5(a) shows that, under 0.50 mol L^{-1} HNO_3 conditions, indeed, the log (k /s^{-1})

value with NaI at 0.20 mol L^{-1} exceeds that with NaBr, and should exceed largely that with NaCl at the corresponding concentration. At 3.0 mol L^{-1} salt concentration, however, the log (k /s^{-1}) value with NaI is much lower than that with NaBr and just over that with NaCl. Fig. 5(b) shows that, under 1.0 mol L^{-1} HNO_3 conditions, the log (k /s^{-1}) value with NaI at 1.0 mol L^{-1} exceeds slightly that with NaCl but, at more than 1.5 mol L^{-1}, it becomes smaller than that with any other salt.

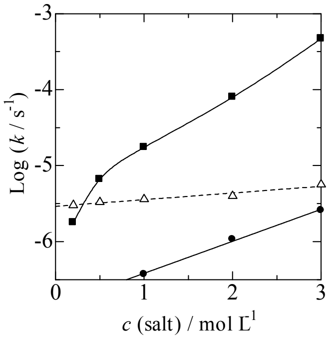

Fig. 5(a). Changes of log (k/s^{-1}) in 0.50 mol L^{-1} HNO_3 containing various salt at 60 ℃: (●) NaCl; (■) NaBr; (△) NaI.

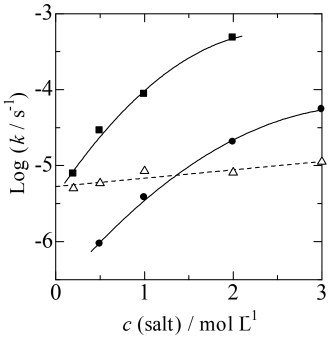

Fig. 5(b). Changes of log (k/s^{-1}) in 1.0 mol L^{-1} HNO_3 containing various salt at 60 ℃: (●) NaCl; (■) NaBr; (△) NaI.

It is known that the solubility of I_2 is very low in aqueous as well as nitric acid solutions [16], however, the triiodide ion I_3^- is soluble, therefore, addition of KI to I_2 is a common method to dissolve I_2 in aqueous solution. The specific adsorption phenomena of halide ions have been observed on the mercury electrode in aqueous solution [17]. An electrochemical quartz crystal microbalance (EQCM) has been applied to a quantitative adsorption study of halide anions on a highly ordered Au(111) electrode and it has been found the strength of halide adsorption increases in the sequence $Cl^- < Br^- < I^-$ [18]. All the iodine species, I_2, I_3^-, and I^-, are likely to adsorb strongly on gold-wire surface during the dissolution of gold in dilute nitric acid containing the iodide salts. While the I^- ion is oxidized to I_2 (probably by NO_2^+) in dilute nitric acid solution, the gold surface may be covered with I_2 and I_3^- as well as I^-. We think that the heavy coverage on gold surface with the iodine species, especially I_2, is one of the most important factors for the lower dissolution rate constant at higher nitric acid and iodide salt concentrations.

Another possible reason for the less effective role of iodide salts on gold dissolution is the oxidation of iodine in the nitric acid solution. During measuring the solubility of iodine in the system water and nitric acid at 25 ℃, Lutsyk *et al.* [16] have observed that iodine in concentrated nitric acid is completely oxidized within several minutes. The candidates of the oxidized iodine species may be such compounds as INO (nitrosyl iodide), formed by the combination between NO_x and iodine. Nitrosyl iodide in gas phase has been well characterized, which is released by freezing iodide in solution [19].

Considering the lower efficiency for gold dissolution with iodide salts in the nitric acid solutions, which is brought about through by-productive phenomena or species, one had better make use of the iodine-iodide system in the absence of nitric acid. Molecules of iodine (I_2) can be successfully generated by the electrochemical oxidation of iodate ions [5]. However, we would like to stress that the dilute nitric acid systems containing chloride or bromide salts are still useful for gold dissolution.

3-3 Temperature influence on the dissolution rate constant

Fig. 6 shows the temperature influence on the dissolution rate constant in 1.0 mol L^{-1} HNO_3 containing NaBr at 30 – 60 ℃. At any temperature, the log (k /s^{-1}) value increases monotonously with increasing NaBr concentration. Fig. 7 shows the Arrhenius plots for the gold-wire dissolution rate constants, log (k /s^{-1}), in 1.0 mol L^{-1} HNO_3 containing 2.0 and 1.0 mol L^{-1} NaBr and $CaBr_2$, respectively. The linear curves from 30 to 60 ℃ give the activation energies (E_a) of 55.4 and 56.9 kJ mol^{-1}. Larger activation energies have been reported for NaCl and $CaCl_2$ in 2.0 mol L^{-1} HNO_3 to be E_a = 86.4 and 89.2 kJ mol^{-1} [8]. Obviously, the E_a values with the bromide salts are much smaller than those with the chloride salts. The activation energies with NaI, KI, and CaI_2 under similar conditions are also smaller values of 56.0, 49.8, and 52.6 kJ mol^{-1}, respectively.

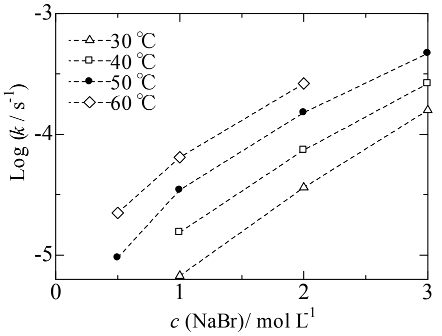

Fig. 6. Temperature dependence of the dissolution rate constant in 1.0 mol L^{-1} HNO_3 containing NaBr at various temperatures: (△) 30; (□) 40; (●) 50; (◇) 60 ℃.

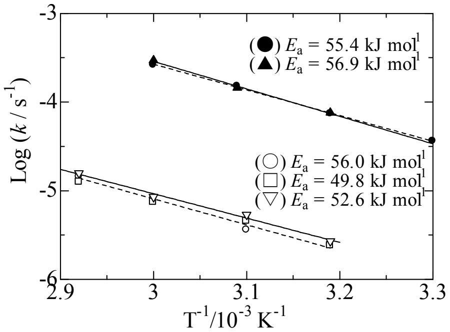

Fig. 7. Arrhenius plot for gold-wire dissolution rate constants in 1.0 mol L^{-1} HNO_3 containing 1.0 mol L^{-1} $CaBr_2$ (▲), CaI_2 (▽) and 2.0 mol L^{-1} NaBr (●), NaI (○), KI (□).

3-4 Influence of organic solvents on the dissolution rate constant

By means of Raman spectroscopy, we have reported that the hydrogen-bonding structure of bulk water is greatly destroyed by the addition of organic solvents, such as sulfolane [20], acetonitrile (MeCN) [21], and *N,N*-dimethylacetamide (DMA) [22]. In preliminary studies, we have noticed that the addition of MeCN to a HNO_3 solution containing NaCl makes a superior media for pure gold dissolution. It takes just three hours for the 1:1 mixture between MeCN and 2.0 mol L^{-1} HNO_3 aqueous solution (the mixture contains 1.0 mol L^{-1} HNO_3 and NaCl) to dissolve a piece of *ca.* 20 mg gold-wire completely, whereas more than ten hours for even 2.0 mol L^{-1} HNO_3 solution containing 1.0 mol L^{-1} NaCl to do so. However, the separation between water and MeCN phases from the mono-phase by the addition of NaCl kept us from further examining with the NaCl system. The phase separations between water and MeCN in the presence of chloride salts are well known phenomena [23].

Fig. 8 shows the influence of added MeCN on log (*k* /s^{-1}) in 0.10 mol L^{-1} HNO_3 containing 2.0 and 1.0 mol L^{-1} of NaBr and NaI, respectively. The log (*k* /s^{-1}) value for 2.0 mol L^{-1} NaBr increases linearly with increasing MeCN contents from -5.30 to -4.61 at 30% (v/v) MeCN. For 1.0 mol L^{-1} NaI, the log (*k* /s^{-1}) value also increases linearly with increasing MeCN contents from -5.67 to -5.18 at 50% (v/v) MeCN. As mentioned above, LiBr causes larger rate constants in 0.10 mol L^{-1} HNO_3 aqueous solution than NaBr does (*cf.* Fig. 1). The acceleration in log (*k* /s^{-1}) by the addition of MeCN for 2.0 mol L^{-1} LiBr is parallel to that for NaBr, and the log (*k* /s^{-1}) values are -5.12 and -4.37 for non- and 30% (v/v) MeCN, respectively.

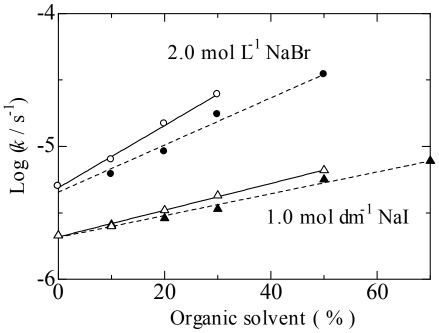

Fig. 8. Influence of organic solvents on log (*k* / s^{-1}) in 0.1 mol L^{-1} HNO_3 containing 2.0 or 1.0 mol L^{-1} NaBr or NaI, respectively, at 60℃: (○,●) NaBr; (△,▲) NaI. The open and solid symbols represent MeCN and CH_3COOH, respectively.

Not only MeCN but also acetic acid can promote the gold-wire dissolution rate. The log (*k* /s^{-1}) value increases linearly with increasing contents of CH_3COOH in aqueous HNO_3 solution, admittedly, the effects of CH_3COOH are weaker than those of MeCN in both the cases with NaBr and NaI. We may mention that Nakano [24] have succeeded in dissolving Au in MeCN solvent systems containing Cl_2-Et_4NCl and Br_2-Et_4NBr.

We would like to discuss from several points of view why these organic solvents have the promotion effects on the gold-wire dissolution in 0.1 mol L^{-1} HNO_3 aqueous solution. (1) Diluted HNO_3 solutions can exhibit the stronger oxidation ability if the more additional protons are provided in the solutions. Needless to mention, acetic acid is a (week) acid, however, it may be difficult to expect that additional protons are provided from acetic acid in solution containing the strong acid, HNO_3. (2) The decreased permittivity of water with the addition of organic solvents (ε_r = *ca.* 36 and 6.17 for MeCN and acetic acid, respectively [25]) may cause the decreased proton dissociation of HNO_3, which should result in the stronger oxidation ability from diluted HNO_3 solutions. Obviously, however, the experimental results between MeCN and acetic acid are contradictory, therefore, the factor of the permittivity decrease must be less affective. (3) The oxidation ability of diluted HNO_3 can be promoted by the distortion or destruction of bulk water structure through hydrogen-bonding. By means of ^{1}H NMR [9] and Raman spectroscopy [21], we have already demonstrated that the bulk water structure through hydrogen-bonding are destroyed by the increased contents of MeCN in water. Finally, the promoted ability in the gold dissolution with added MeCN is reasonably accounted for by the increased distortion of bulk water structure.

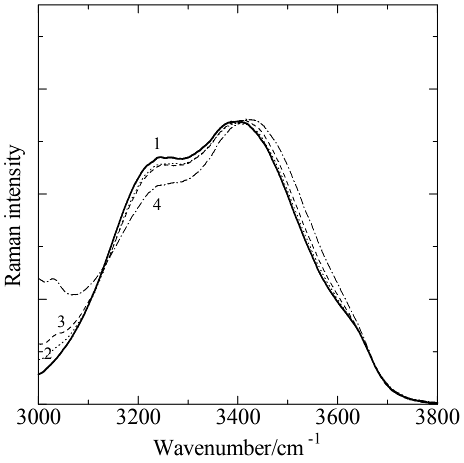

Fig. 9. The Raman spectra of H_2O solutions containing CH_3COOH at room temperature: (——) 0; (·········) 5.7; (-----) 11.5; (–·–·–) 28.7% (v/v) CH_3COOH.

Fig. 9 shows the Raman spectra of H_2O containing different volumes of CH_3COOH. With increasing contents of CH_3COOH, the band intensity at around 3250 cm^{-1} decreases, compared to that at around 3400 cm^{-1}. The bands at 3250 and 3400 cm^{-1} of H_2O (both OH-stretching) have been attributed to strongly hydrogen-bonded H_2O molecules and weakly hydrogen-bonded ones, respectively [8,26].

According to the Raman spectra, indeed, bulk water structure is distorted by the addition of acetic acid, although acetic acid can strengthen the hydrogen bonding among water molecules when observed by ^1H NMR [27]. We [7,8] have integrated successfully the apparent discrepancy between NMR and Raman spectroscopy and argued that the concept of "structure-making" and "structure-braking" by Frank and Wen [28] should be rearranged for solutions containing salts of high concentrations. Our most important contention is as follows: the water structure induced by the ions or solutes of higher concentrations in aqueous solution must be completely different from the intrinsic bulk water structure, naturally self-assembled by the huge number of water molecules ($n_w >$ $\sim 10^8$), even though both (induced and natural) structures seem to be similar to each other by some observation means.

Nishi *et al.* [29] have reported the decreases in the intensity at 3200 cm^{-1} of the hydrogen-bonded O-H stretching Raman band of H_2O with the increase of acetic acid in H_2O. They have suggested that acetic acid breaks the hydrogen-bond networks of water.

We would like to point that Gutmann's donor number (*DN*) [30] of H_2O changes with the different conditions of water. The original value to be $DN = 18.0$ has been given for H_2O of lower concentration ($\sim 10^{-3}$ mol L^{-1}) dissolved in 1,2-dichloroethane. Under such conditions, we have argued, it should be impossible for water molecules to construct their natural huge structure self-assembled through hydrogen-bonding and their properties may alter just like alcohols (R-O-H) or even ethers (R-O-R) [7,8,9]. Only under bulk water conditions (dilute aqueous solution at lower temperatures), water molecules can gain their "intrinsic" properties. Much larger values have been given by Marcus [31] for such bulk water conditions, $DN_{\text{bulk}} = 40.3$ and 42.3.

3-5 Gold dissolution in nitrous acid containing halide ions

Making use of dissolution phenomena of pure gold, we have examined thoroughly the enhancement in oxidation ability of dilute nitric acid containing concentrated salts. However, someone may suspect that the oxidation ability comes from nitrous acid (it might be present) as the impurity in nitric acid, and not from dilute HNO_3 itself. At any rate, it must be worth examining the oxidation ability of nitrous acid on the dissolution of pure gold.

In a preliminary study, we have found that the concentration ratio of HCl to $NaNO_2$ is an important factor for dissolving gold. For instance, the mixture between 1.0 mol L^{-1} HCl and 1.0 mol L^{-1} $NaNO_2$ has no actual ability to dissolve pure gold at 35 ℃, however, with increasing HCl concentration (*e.g.*, 1.5 and 2.0 mol L^{-1}), the $NaNO_2$ solution of that concentration causes the dissolution of pure gold. Fig. 10 shows the gold-wire dissolution rate constants in various concentration combinations between HCl and $NaNO_2$. The log (k /s^{-1}) increases as -6.61, -5.66, -4.89, and -4.63 in 1.0 mol L^{-1} $NaNO_2$ solution containing 1.5, 2.0, 2.5, and 3.0 mol L^{-1} HCl, respectively. It is true that some irregularities are observed for the $NaNO_2$ concentrations, but the increased concentration of HCl causes always the increased log (k /s^{-1}) value. At 1.0 or *ca.*1.2 mol L^{-1} $NaNO_2$, a maximum value is observed for 2.5 mol L^{-1} HCl. This result may suggest that twice or 2.5 times HCl concentration is appropriate for $NaNO_2$ to dissolve pure gold. As for other HCl concentrations, shown in Fig. 10 (and Table 2), a similar ratio between HCl and $NaNO_2$ may give an effective result.

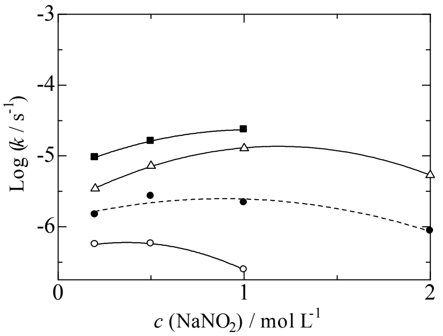

Fig. 10. Changes of log (k / s^{-1}) in 0.20 - 2.0 mol L^{-1} $NaNO_2$ containing HCl at 35℃: (○) 1.5; (●) 2.0; (△) 2.5; (■) 3.0 mol L^{-1} HCl.

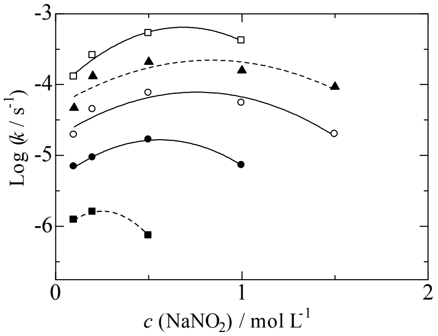

Fig. 11. Changes of log (k /s^{-1}) in 0.10 - 1.5 mol L^{-1} $NaNO_2$ containing HBr at 35℃: (■) 0.50; (●) 1.0; (○) 1.5; (▲) 2.0; (□) 2.5 mol L^{-1} HBr.

Similarly, many different combinations between HBr and $NaNO_2$ have been examined, and it has been found that HBr causes more remarkable effects than HCl on the gold dissolution. Fig. 11 shows that the log (k /s^{-1}) value for a $NaNO_2$ solution increases monotonously with increasing HBr concentration at a constant $NaNO_2$ concentration. For instance, the log (k /s^{-1}) values at 1.0 mol L^{-1} $NaNO_2$ are -5.14, -4.26, -3.80, and -3.38 with 1.0, 1.5, 2.0, and 2.5 mol L^{-1} HBr, respectively. A 1.0 mol L^{-1} $NaNO_2$ solution containing 2.0 mol L^{-1} HBr is ca. 70 times as effective for pure gold dissolution as that containing 2.0 mol L^{-1} HCl. A maximum is observed for 1.0 mol L^{-1} HBr at 0.5 mol L^{-1} $NaNO_2$. Similarly, for 1.5 mol L^{-1} HBr, a maximum is given at 0.5 or *ca.* 0.7 mol L^{-1} $NaNO_2$. These results indicates that two- or three-fold concentrations of HBr to $NaNO_2$ give the maximum dissolution rates. Other cases are also support this theory. If the concentration ratio between $NaNO_2$ and HX (X = Cl, Br) is 1:2, then the solution consists of equi-molar HNO_2, HX, and NaX. Coincidently, a violent reaction between aqueous $NaNO_2$ and HI to produce I_2 at room temperature prevented us from practicing further examination. However, we suppose that this system also can be applied to gold dissolution with careful operation at lower temperatures since iodine are spontaneously produced from HI.

Nitrous acid is a weak acid (pK_a = 3.37 at 12.5 ℃)[1], therefore, the proton from HX are apt to combine with the NO_2^- ion from $NaNO_2$ to produce the molecule of HNO_2 in solution. Because of much stronger (Brønsted) basicity of NO_2^- than NO_3^-, nitrous acid exhibits its oxidation ability more easily than nitric acid at lower concentrations. Regardless of the superiority for oxidation, it needs unexpectedly large amounts of protons even for nitrous acid to exhibit strong oxidation ability, otherwise, the NO_2^- ion is easily oxidized by halogens. In kinetic studies [32,33], for instance, it is reported that the nitrite ion is even oxidized to NO_2Br by Br_2 (pH *ca.* 3 – 6) [32] and to NO_2Cl by Cl_2 (pH 0 – 1) [33] in aqueous acid solutions.

For the exhibition of oxidation ability with not only nitrous but also nitric acid, we believe, the formation of molecular HNO_2 or HNO_3 in solution is essential. Two molecules of HNO_2 may easily produce NO^+ (nitrosonium ion) and NO_2^- even at lower HNO_2 concentrations (*cf.* Eq. 3). While two molecules of HNO_3 should give NO_2^+ (nitronium ion) and NO_3^- in concentrated HNO_3 solution [34], otherwise, in diluted aqueous nitric acid solution containing concentrated salts (Eq. 4).

$$2\ HNO_2 \leftrightarrows NO^+ + NO_2^- + H_2O, \qquad (3)$$

$$2\ HNO_3 \leftrightarrows NO_2^+ + NO_3^- + H_2O. \qquad (4)$$

The NO^+ as well as the NO_2^+ ion should oxidize the Cl^- and Br^- ions to Cl_2 and Br_2, respectively. Olah [35] has described that "the reversible potentials for reduction of NO_2^+ and NO^+ in acetonitrile are known to be 1.45 and 1.51 V (vs. NHE)," citing an electrochemical paper [36]. Judging from the cited paper [36], we believe, the potentials for NO_2^+ and NO^+ should be 1.51 and 1.45 and not 1.45 and 1.51 (vs. NHE), respectively. Another literature [12] reports $E^o = 1.45$ V for $NO^+ + e^- \rightarrow NO$ (g) in 0.1 - 4 mol L^{-1} H_2SO_4. At any rate, their potentials seem to be high enough for the oxidation of Cl^- to Cl_2 (also Br^- to Br_2) with NO^+ and NO_2^+ (Eqs. 5 and 6), compared to those of Cl_2 and Br_2, that is, $E^o = 1.396$ and 1.087 V for $X_2 (aq) + 2e^- \leftrightarrows 2 X^- (aq)$ where X = Cl and Br, respectively [12].

$$NO^+ + 2 X^- \leftrightarrows NO^- + X_2, \quad (5)$$

$$NO_2^+ + 2 X^- \leftrightarrows NO_2^- + X_2. \quad (6)$$

The Cl_2 and Br_2 evolved in Eqs. 5 and 6 can oxidize the gold metal to Au^{3+} with the assistance of complexing by the halide ions (Eq. 7).

$$2Au + 3 X_2 + 2 X^- \leftrightarrows 2 AuX_4^-. \quad (7)$$

The following Eqs. 8 and 9 are also promising reaction schemes for oxidation of Br^- to Br_2, however, the redox potentials of the reactions ($E^o = 1.20$ and 0.996 V, respectively [12]) are not high enough to oxidize Cl^- to Cl_2.

$$NO_2^- + 2 H^+ + e^- \leftrightarrows NO (g) + H_2O \qquad E^o = 1.20 \text{ V}, \quad (8)$$

$$HNO_2 + H^+ + e^- \leftrightarrows NO (g) + H_2O \qquad E^o = 0.996 \text{ V}. \quad (9)$$

It may be worth mentioning that the evolution of Cl_2 has been demonstrated by the *o*-toluidine method [37] for a sample collected from the gas phase over a 1.25 mol L^{-1} HCl solution containing 1.0 mol L^{-1} $NaNO_2$.

Eqs. 10 and 11 show the exhibition of rather strong oxidation by NO_3^- in the presence of abundant protons [12].

$$NO_3^- + 3 H^+ + 2 e^- \leftrightarrows HNO_2 + H_2O \qquad E^o = 0.94 \text{ V}, \quad (10)$$

$$2 NO_3^- + 12 H^+ + 10 e^- \leftrightarrows N_2 + 6 H_2O \qquad E^o = 1.25 \text{ V}. \quad (11)$$

However, both reaction schemes could not give the potential high enough to oxidize Cl^- to Cl_2 ($E^o = 1.396$). We [7] have detected successfully the evolution of Cl_2 from 2.0

mol L^{-1} HNO_3 solution containing LiCl, $MaCl_2$, $CaCl_2$, or $AlCl_3$. We may mention once more that the oxidation of Cl^- to Cl_2 should take place through the NO_2^+ ion, produced by the association of two molecules of HNO_3 and releasing of H_2O (*cf.* Eq. 4).

The shortage of H^+, compared to NO_2^-, should cause a lower oxidation ability in the mixture between $NaNO_2$ and HX. Le Chatelier's principal in Eq. 3 suggests that the increasing NO_2^- ($NaNO_2$) concentration results in the decreased NO^+ concentration. Previously, we have discussed [8] the effects of NO_3^- ($LiNO_3$) on the promotion in oxidation ability of 2.0 mol L^{-1} HNO_3 accompanied by 3.5 mol L^{-1} LiCl (observed in ref. [7]). It has been suggested [8] that the NO_3^- ion causes lesser influences on the promotion than ClO_4^- because of Le Chatelier's principal in Eq. 4.

Fig. 12(a) shows the temperature dependence of the log (k /s^{-1}) value in 0.50 mol L^{-1} $NaNO_2$ solution containing HCl. Not only at 35 ℃ but also at another temperature (40, 45, or 50 ℃), the log (k /s^{-1}) value increases monotonously with increasing HCl concentrations. With increasing temperature, the log (k /s^{-1}) value increases as expected. Fig. 12(b) shows the Arrhenius plots for the log (k /s^{-1}) values in 0.50 mol L^{-1} $NaNO_2$ solution containing HCl of 2.0, 2.5, and 3.0 mol L^{-1}. The activation energies over 35 – 50 ℃ are given to be 69.9, 72.4, and 72.8 kJ mol^{-1} for 2.0, 2.5, and 3.0 mol L^{-1} HCl, respectively.

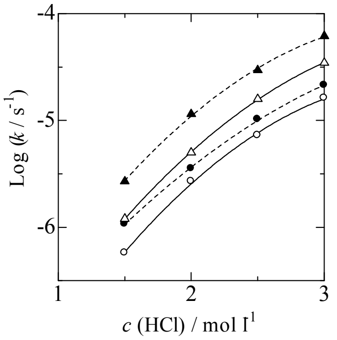

Fig. 12(a).Temperature dependence of log (k / s^{-1}) in 0.50 mol L^{1} NaNO$_2$ containing HCl of various concentrations: (○) 35; (●) 40; (△) 45; (▲) 50 ℃.

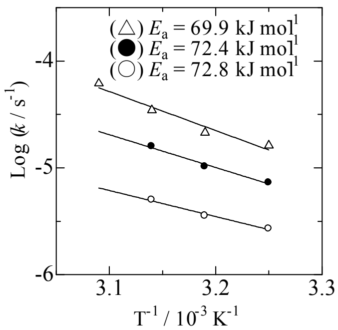

Fig. 12(b). Arrhenius plots in 0.50 mol L^{-1} NaNO$_2$ containing HCl of various concentrations: (○) 2.0; (●) 2.5; (△) 3.0 mol L^{-1} HCl.

As the summery of this section, the NaNO$_2$ solutions containing twice or more amounts of HCl or HBr have been found to be also good media for gold dissolution. The log (k /s^{-1}) values in 0.50 mol L^{-1} NaNO$_2$ containing 1.5, 2.0, and 2.5 mol L^{-1} HBr are larger by *ca.* 100 times than those containing corresponding HCl concentrations. We suppose that the gold dissolution mechanism in the nitrous acid systems containing halide ions are quite similar to the (dilute) nitric acid systems containing concentrated halide salts, despite the difference in the intermediate species of oxidation (NO$^+$ or NO$_2^+$).

Conclusion

Dilute aqueous nitric acid can exhibit the oxidation ability in "bulk" solution modified with salts and/or inert organic solvents of higher concentrations or contents. Under such conditions, molecules of HNO$_3$ may easily produce the active intermediate species, the nitronium ion (NO$_2^+$), of a higher oxidation potential. The X$_2$-X$^-$ systems (X = Cl, Br and I) for dissolving pure gold are readily prepared in dilute nitric acid containing halide salts. The bromide and iodide salts in aqueous (even as low as 0.10

mol L^{-1}) nitric acid are effective for dissolving pure gold at 60 ℃. The mixtures between $NaNO_2$ and HCl or HBr also are effective for pure gold dissolution, in which, HNO_2 molecules may produce another intermediate species, the nitrosonium ion (NO^+), of the oxidation potential as high as NO_2^+. These findings would supply us with a clue for elucidation of stainless steel corrosion mechanism in environmental conditions. Dilute aqueous HNO_3 or HNO_2 solutions containing halide ions can be useful for the recovery of gold from waste electronic devices.

Acknowledgement

The present work was partially supported by a Grant-in-Aid for the commission project of "Research Program on Climate Change Adaptation" from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] R. C. Weast, Handbook of Chemistry and Physics, CRC, Boca Raton, Florida, 70th ed., 1989.

[2] L. J. Beckham, W. A. Fessler and M. A. Kise, *Chem. Rev.*, 1951, **48**, 319.

[3] J. O. Marsden and C. I. House, The Chemistry of Gold Extraction, Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, Colorado, 2nd ed., 2006, p. 233.

[4] H. Yalçin, T. Koç and V. Pamuk, *International J. Hydrogen Energy*, 1997, **22**, 967.

[5] B. N. Grgur, M. M. Gvozdenovic, J. S. Stevanovic, B. Z. Jugovic and Lj. T. Trisovic, *Chem. Engineering J.*, 2006, **124**, 47.

[6] M. Hojo, T. Ueda, C. Daike, F. Takezaki, Y. Furuya, K. Miyamoto, A. Narutaki and

R. Kato, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 1215.

[7] M. Hojo, R. Kato, A. Narutaki, T. Maeda and Y. Uji-yie, *J. Mol. Liquids*, 2011, **163**, 161.

[8] M. Hojo, Y. Uji-yie, S. Tsubota, M. Tamura, M. Yamamoto, K. Okamura and K. Isshiki, *J. Mol. Liquids*, 2014, **194**, 68.

[9] M. Hojo, *Pure Appl. Chem.*, 2008, **80**, 1539.

[10] D. Fraenkel, *J. Phys. Chem. B*, 2011, **115**, 14634.

[11] K. S. Pitzer, Activity Coefficients in Electrolyte Solutions, CRC, Boca Raton, Florida, 2nd ed., 1991.

[12] Standard Potentials in Aqueous Solution, ed. by A. J. Bard and R. Parsons, J. Jordan, IUPAC, Marcel Dekker, New York, 1985.

[13] J. V. L. Longstaff, *J. Chem. Soc.*, 1957, 3488.

[14] H. Feilchenfeld, S. Manor and J. A. Epstein, *J. Chem. Soc. Dalton Trans.*, 1972, **23**, 2675.

[15] Y. Marcus, Ion Properties, Marcel Dekker, New York, 1997, p. 43.

[16] A. L. Lutsyk, S. Yu. Suikov, V. S. Chuprina and V. Yu. Portnyanskii, *Russian J. Appl. Chem.*, 2004, **77**, 1210.

[17] D. C. Grahame, *Chem. Rev.*, 1947, **41**, 441.

[18] H.-W. Lei , H. Uchida and M. Watanabe, *Langmuir*, 1997, **13**, 3523.

[19] P. O'Driscoll, K. Lang, N. Minogue and J. Sodeau, *J. Phys. Chem. A*, 2006, **110**, 4615.

[20] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki and D. Fujimura, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 751.

[21] L. D. Bayissa, Y. Ohmae and M. Hojo, *J. Mol. Liquids*, 2014, **199**, 294.

[22] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki and T. Nakano, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 401.

[23] T. Takamuku, Y. Noguchi, E. Yoshikawa , T. Kawaguchi, M. Matsugami and T. Otomo, *J. Mol. Liquids*, 2007, **131-132**, 131.

[24] Y. Nakano, *Chem. Commun.*, 1992, 426.

[25] J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, 4th ed. John Wiley & Sons, New York, 1986.

[26] D. E. Irish and M. H. Brooker, in Advences in Infrared and Raman Spectroscopy, ed. R. J. H. Clark and R. E. Hester, Heyden, London, 1976, vol. 2, Chapter 6.

[27] A. Nose, M. Hojo and T. Ueda, *J. Phys. Chem. B*, 2004, **108**, 798.

[28] H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

[29] N. Nishi, T. Nakabayashi and K. Kosugi, *J. Phys. Chem. A*, 1999, **103**, 10851.

[30] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.

[31] Y. Marcus, *J. Solution Chem.*, 1984, **13**, 599.

[32] J. N. Pendlebury and R. H. Smith, *Aust. J. Chem.*, 1973, **26**, 1847.

[33] J. N. Pendlebury and R. H. Smith, *Aust. J. Chem.*, 1973, **26**, 1857.

[34] M. B. Smith and J. March, March's Advanced Organic Chemistry Reactions, Mechanisms, and Structure, 6th ed., Wiley-Interscience, Hoboken, NJ, USA, 2007, p. 689.

[35] G. A. Olah, R. Malhotra and S. C. Narang, Nitration: Methods and Mechanisms, VCH, New York, 1989, p. 192.

[36] G. Bontempelli, G.-A. Mozzocchin and F. Magno, *J. Electroanal. Chem.*, 1974, **55**, 91.

[37] J. D. Johnson and R. Overby, *Anal. Chem.*, 1969, **41**, 1744.

Table 1

The gold-wire dissolution rate constant, log (k /s^{-1}), in various concentration HNO_3 solutions containing 0.20 - 3.0 mol L^{-1} NaCl (upper), NaBr (middle), and NaI (lower) at 60 ℃.

c(NaX) X = C, Br, I	0.20	0.50	1.0	2.0	3.0 mol L^{-1}
$c(HNO_3)$ = 0.10 mol L^{-3}	(Cl) -	-	-	-	-
	(Br) -	-	-5.78	-5.30	-5.09
	(I) -5.80	-5.63	-5.67	-5.68	-5.72
0.20	(Cl) -	-	-	-	-6.34
	(Br) -	-5.99	-5.53	-4.97	-4.51
	(I) -5.68	-5.58	-5.55	-5.63	-5.56
0.30	(Cl) -	-	-	-6.32	-6.18
	(Br) -6.16	-5.68	-5.32	-4.59	-4.11
	(I) -	-	-5.53	-	-
0.50	(Cl) -	-	-6.47	-5.97	-5.59
	(Br) -5.75	-5.18	-4.76	-4.10	-3.33
	(I) -5.52	-5.48	-5.44	-5.40	-5.25
1.0	(Cl) -	-6.03	-5.42	-4.69	-4.26
	(Br) -5.11	-4.54	-4.06	-3.32	-
	(I) -5.30	-5.23	-5.07	-5.09	-4.95

2.0	(Cl) -5.67	-4.91	-4.41	-3.82	-3.55
	(Br) -4.43	-3.81	-3.39	-	-
	(I) -	-	-	-	-

Table 2

The gold-wire dissolution rate constants, log (k /s^{-1}), in various concentration $NaNO_2$ solutions containing HCl (upper) and NaBr (lower) at 35 ℃.

c(HX) X = Cl, Br	0.50	1.0	1.5	2.0	2.5	3.0 mol L^{-1}
$c(NaNO_2)$ = 0.10 mol L^{-1}	(Cl) -	-	-	-	-	
	(Br) -5.91	-5.16	-4.71	-4.33	-3.89	
0.20	(Cl) -	-	-6.25	-5.83	-5.46	-5.02
	(Br) -5.80	-5.03	-4.35	-3.88	-3.59	-
0.50	(Cl) -	-	-6.24	-5.57	-5.14	-4.79
	(Br) -6.13	-4.78	-4.12	-3.68	-3.28	-
1.0	(Cl)	-	-6.61	-5.66	-4.89	-4.63
	(Br)	-5.14	-4.26	-3.80	-3.38	-
1.5	(Cl)		-	-		
	(Br)		-4.70	-4.03		
2.0	(Cl)			-6.06	-5.27	
	(Br)			-	-	
2.5	(Cl)				-5.75	
	(Br)				-	

Figure Captions

Fig. 1. Gold-wire dissolution rate constants, log (k /s^{-1}), in 0.10 mol L^{-1} HNO_3 containing bromide salts at 60 ℃: (○) LiBr; (●) NaBr; (△) KBr; (■) $CaBr_2$.

Fig. 2. The relationship between the log (k /s^{-1}) values and the crystal ion radii per charge number (r/z) for the metal ions in 0.10 mol L^{-1} HNO_3 containing various bromide salts at 60 ℃.

Fig. 3. Changes of log (k /s^{-1}) in various concentration HNO_3 containing 0.20 - 3.0 mol L^{-1} NaBr at 60℃: (□) 0.10 (■) 0.20; (△) 0.30; (◇) 0.50; (○) 1.0; (●) 2.0 mol L^{-1} HNO_3.

Fig. 4(a). Changes of log (k /s^{-1}) in HNO_3 solutions containing 0.50 - 3.0 mol L^{-1} NaCl at 60 ℃: (■) 0.20; (△) 0.30; (◇) 0.50; (○) 1.0; (●) 2.0 mol L^{-1} HNO_3.

Fig. 4(b). Changes of log (k /s^{-1}) in HNO_3 solutions containing 0.20 - 5.0 mol L^{-1} NaI at 60 ℃: (□) 0.10, (■) 0.20; (◇) 0.50; (○) 1.0 mol L^{-1} HNO_3.

Fig. 5(a). Changes of log (k /s^{-1}) in 0.5 mol L^{-1} HNO_3 containing various salts at 60 ℃: (●) NaCl; (■) NaBr; (△) NaI.

Fig. 5(b). Changes of log (k /s^{-1}) in 1.0 mol L^{-1} HNO_3 containing various salts at 60 ℃: (●) NaCl; (■) NaBr; (△) NaI.

Fig. 6. Temperature dependence of the dissolution rate constant in 1.0 mol L^{-1} HNO_3 containing NaBr: (△) 30; (□) 40; (●) 50; (◇) 60℃.

Fig. 7. Arrhenius plots for gold-wire dissolution rate constants in 1.0 mol L^{-1} HNO_3 containing 2.0 mol L^{-1} NaBr (●), NaI (○), KI (□), and 1.0 mol L^{-1} $CaBr_2$ (▲), CaI_2 (▽).

Fig. 8. Influences of organic solvents on log (k /s^{-1}) in 0.10 mol L^{-1} HNO_3 containing 2.0 or 1.0 mol L^{-1} NaBr or NaI, respectively, at 60 ℃: (○,●) NaBr; (△,▲) NaI. The open and solid symbols represent MeCN and CH_3COOH, respectively.

Fig. 9. The Raman spectra of H_2O solutions containing CH_3COOH at room temperature: (1) 0; (2) 5.7; (3) 11.5; (4) 28.7% (v/v) CH_3COOH.

Fig. 10. Changes of log (k /s^{-1}) in 0.20 - 2.0 mol L^{-1} $NaNO_2$ containing HCl at 35 ℃: (○) 1.5; (●) 2.0; (△) 2.5; (■) 3.0 mol L^{-1} HCl.

Fig. 11. Changes of log (k /s^{-1}) in 0.10 – 1.5 mol L^{-1} $NaNO_2$ containing HBr at 35 ℃: (■) 0.50; (●) 1.0; (○) 1.5; (▲) 2.0; (□) 2.5 mol L^{-1} HBr.

Fig. 12(a) Temperature dependence of the log (k /s^{-1}) value in 0.50 mol L^{-1} $NaNO_2$ solution containing HCl of various concentrations: (○) 35; (●) 40; (△) 45; (▲) 50 ℃.

Fig. 12(b) Arrhenius plots in 0.50 mol L^{-1} $NaNO_2$ solution containing HCl of various concentrations: (○) 2.0; (●) 2.5; (△) 3.0 mol L^{-1}.