



Can pure gold be dissolved in seawater mixed with aqueous nitric acid?



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ABSTRACT

In order to demonstrate further the oxidation ability of diluted aqueous nitric acid containing abundant amounts of salts, the dissolution of precious metals (Au, Pt, and Pd), especially, of gold has been examined in 0.1–2 mol dm⁻³ HNO₃ accompanied by alkali metal, alkaline earth metal, and aluminum chlorides. The complete dissolution time of pure gold plate (20 ± 2 mg, 0.1 mm thickness) in 2.0 mol dm⁻³ HNO₃ accompanied by 1.0 mol dm⁻³ AlCl₃ was shortened remarkably with a temperature increase from 15 to 80 °C. The dissolution rate constants, log (k/s⁻¹), of a piece of gold wire (19.7 ± 0.5 mg) in 20 mL of 2.0 mol dm⁻³ HNO₃ accompanied by the metal chlorides, in general, increase with increasing salt concentrations at 40 and 60 °C. For instance, the log (k/s⁻¹) values linearly increase from -4.15 via -3.77, -3.45 to -3.14 by the addition of 1.0, 2.0, 3.0, and 4.0 mol dm⁻³ LiCl in a 2.0 mol dm⁻³ HNO₃ solution at 60 °C. The gold can be dissolved in the solution of 1.0 mol dm⁻³ HNO₃ and 1.0 mol dm⁻³ HCl, i.e. a “dilute *aqua regia*.” We have achieved a total dissolution of five pieces (0.10 g) of the gold wire in 100 mL of the 1:1 mixture between seawater and 2.0 mol dm⁻³ HNO₃ at ca. 100 °C, with a complete dissolution time of within 17 h and log (k/s⁻¹) = -4.52. At 60 °C, the complete dissolution experiments of the gold wire in much lower HNO₃ concentrations (down to 0.1 mol dm⁻³) with the chloride salts have been also successfully performed. The distortion of bulk water and alternation of water properties are discussed based on the Raman spectra with increasing HCl concentrations.

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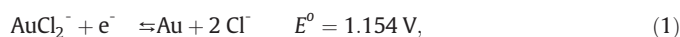
1. Introduction

It has been widely recognized that every natural element present in the earth is dissolved in seawater [1]. Concentrations of elements in seawater may depend on the amounts in the earth's crust, the solubility, the mean residence time, and so on. Sonstadt [2] reported the gold concentration in seawater to be 65 µg L⁻¹. After World War I, Haber [3] tried to recover gold from seawater in vain. So far, it is believed that the gold content in seawater amounts to 145 ± 45 fmol dm⁻³ (i.e. 29 ± 9 pg L⁻¹) in open ocean pacific waters [4], or 50–150 fmol dm⁻³ in the Atlantic and Northeast Pacific ocean [5].

In an editorial article [6] it is written that “many people have the impression that gold occurs as nuggets in streambeds and being a noble metal is only dissolved by *aqua regia*, mixture of concentrated hydrochloric and nitric acids.” Beckham et al. [7] described that Geber, an Arabian chemist, mentioned *aqua regia* in the eighth century. In the metallurgy of gold, many leaching (dissolution in liquids) methods were known [8]. Chlorine–chloride leaching was applied commercially

in the 19th century, but its use diminished following the introduction of the cyanide process in 1889. Thiosulfate, thiourea, ammonia, alkaline sulfide, and other halides (eg., bromide, iodide) solutions have been investigated extensively in the laboratory. Putnam [9] has reported that the addition of chlorides to a chlorine solution will hasten the dissolution of gold particles.

The redox potentials [10a] for gold species are as follows:



A comparison between Eqs. (1) and (2) indicates that the Au(III) complex is more stable than the Au(I) species by 0.15 V. Oxidation will occur only above approximately, 1.2 V, and therefore a strong oxidant, such as Cl₂ or O₃, is required to dissolve gold at a reasonable rate [11]. The redox potential of Cl₂ (g) to Cl⁻ (aq) is reported to be 1.358 V [10b] and that of O₃ to O₂ to be 2.075 V or 1.246 V in acidic or basic solution, respectively [10c].

Nitric acid has two different functions: it is a strong acid and a strong oxidizing agent in dilute and concentrated aqueous solutions, respectively. Cotton and Wilkinson [12] have described that 0.1 mol dm⁻³

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aqueous nitric acid is dissociated by about 93% and that the oxidizing power of nitric acid is very dependent on concentration, and below about 2 mol dm^{-3} the acid has virtually no oxidizing power. The dissociation constants of HNO_3 at different concentration ranges in aqueous solution have been determined [13]. The OH stretch IR absorption of nitric acid in CCl_4 has provided definitive proof of molecular nitric acid rather than NO_3^- [14].

We have proposed an innovative idea [15] that the properties of bulk water originate from the intermolecular hydrogen-bonded network among a huge number of H_2O molecules (e.g., $n_w > \sim 10^7$). Water can lose its properties as bulk water to get that of a non-aqueous solvent, such as an alcohol (R–O–H) or even an ether (R–O–R) if the highly “self-assembled structure” of bulk water is disturbed in the following causes: (a) the residual water ($c(\text{H}_2\text{O}) \sim 10^{-3} \text{ mol dm}^{-3}$) in organic solvents; (b) aqueous solutions or organic solvent–water mixtures containing salts at high concentrations; (c) nanoscale water droplets in nano-tubes or reversed micellar systems; (d) water on metal electrodes, ion-exchange resins, proteins, organic solvents in the solvent extractions, and glass vessels; (e) water at higher temperatures or under supercritical conditions. Such water can be “reduced” to authentic singular H_2O molecules (also called “dihydrogen ether,” $(\text{H})-\text{O}-(\text{H})$) [16]. Reichardt et al. [17] have concisely interpreted “dihydrogen ether” that, at high salt concentrations [$c(\text{salt}) > 5 \text{ mol dm}^{-3}$], region C, according to the solvation model of Frank and Wen [18], can be abolished and only regions A and B survive, resulting in an aqueous solvent called “dihydrogen ether.”

Our two ideas are combined by chance: (1) the ion association can take place between simple [15,19] or poly-anions [20] and alkali metal or alkaline earth metal cations, (2) the bulk water may lose its properties completely by the addition of salts and/or organic solvents at high concentrations. Then, for the first time, we have been able to explain successfully the concentrated salt effects on solvolysis reactions of organic haloalkanes and related compounds without resorting to different types of ion pairs [16]. The exponential increases in solvolysis rates of $\text{S}_{\text{N}}1$ substrates in the presence of concentrated alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates are attributed to the favorable formation of carbocations (R^+) through association (direct “chemical” interaction) between metal cations (M^+ or M^{2+}) and the leaving group anion (X^-) of a substrate (R–X) in the modified solvent.

Previously [21], we have managed to demonstrate that the Br^- ion of the surfactant, CTAB, is oxidized to Br_2 (or Br_3^-) in the $\text{CHCl}_3/\text{CTAB}/\text{H}_2\text{O}$ reversed micelle system with diluted nitric acid ($0.25\text{--}2.5 \text{ mol dm}^{-3}$ in the 1.0% (v/v) H_2O phase) at $15\text{--}40^\circ\text{C}$ (CTAB stands for cetyltrimethylammonium bromide). We have proposed that the NO_2^+ ion should be the active species in this oxidation process. In a following study [22] the nitration of phenols has been performed by aqueous nitric acid (2.0 mol dm^{-3}) in reversed micelle systems.

Our most important finding in the current work [22] is that nitric acid of below 2 mol dm^{-3} in bulk water, provided it contains salts in high concentrations, can oxidize the Cl^- ion to Cl_2 as well as Br^- to Br_2 at $20\text{--}40^\circ\text{C}$. Thus, we recognize that the nitronium ion (NO_2^+), the active species for nitration or oxidation, can be generated not only in the water phase of reversed micellar systems but also in bulk water containing salts in higher concentrations. Eq. (3) is the common reaction scheme to produce NO_2^+ in concentrate nitric acid and we have assumed that the same scheme can be applied to even the diluted nitric acid in reversed-micellar water droplets [21,22] as well as in bulk water containing higher concentrations of salts [22].



With an intimate examination of Eq. (3), we may notice that enhanced formation of HNO_3 in its molecular state and not dissociated ($\text{H}^+ + \text{NO}_3^-$) is essential for a favorite NO_2^+ generation. In bulk aqueous solution, however, many people may think that nitric acid diluted enough is apt to dissociate completely. How could we keep the nitric

acid molecules from dissociating to protons and nitrate ions? Reducing the solvent's permittivity (e.g. $\epsilon_r < 10$) may be an excellent way for that purpose. However, the permittivity of bulk aqueous solutions cannot be reduced so well. Then, our idea, the alternation of H_2O into “dihydrogen ether” [16], could resolve some of the problems. Both the “strong” acidity and basicity of water are lost at once when the water molecules in the huge network are broken into isolated molecules by some of the causes already mentioned, such as, the abundant addition of salts and increased temperature. For solutions with very high salt concentrations, we may not rely so much on the Debye–Hückel [23] and Pitzer [24] theories, even though being highly developed, because such new or extraordinary phenomena have not been predicted in advance by calculations making use of these theories, at least at the moment. We have already mentioned that the redox potential of NO_2^+ generated in diluted nitric acid should be high enough to oxidize Cl^- into Cl_2 [22].

The present adventure, that is, dissolving gold in aqueous nitric acid, has been initiated not by any coincidence but by our reasoned deduction. As described above, dilute nitric acid in bulk water, provided it contains salts in high concentrations, can oxidize the Cl^- ion to Cl_2 . Therefore, it is an inevitable theory that the evolved Cl_2 should oxidize Au^0 into Au^{3+} , which is then coordinated by the abundant Cl^- ions, when the aqueous nitric acid is accompanied by sufficient amounts of chloride salts.

In the present paper, we examine the dissolution of precious metals (Au, Pt, and Pd), and give detailed reports on gold dissolution in aqueous nitric acid ($< 2 \text{ mol dm}^{-3}$) containing alkali metal, alkaline earth metal, and aluminum chlorides at $15\text{--}100^\circ\text{C}$. The periods for complete gold dissolution as well as the corresponding rate constants are measured, and the accelerating influence of cations on the rate constants will be related to the crystal ion radii of the metal ions. Examined and discussed are the dissolution ability of “dilute *aqua regia*” (e.g., an aqueous 1.0 mol dm^{-3} HNO_3 and 1.0 mol dm^{-3} HCl solution) and the acceleration and deceleration phenomena of the dissolution rate caused by the addition of salts. At last, pieces of gold wire are dissolved into a mixture between seawater with aqueous nitric acid. The distortion of the bulk water structure is discussed based on IR Raman spectra measured at increasing HCl concentrations.

2. Experimental

2.1. Materials

The samples of gold were all commercially available: gold plate (Aldrich, 99.99%, 0.1 mm thick) and gold wire (Nilaco, 99.95%, 0.1, 0.25, and 0.5 mm diameter). Both Pt and Pd were also obtained commercially, Pt (Nilaco, 99.98%, 0.10 mm diameter) and Pd wire (Aldrich, 99.9%, 0.25 mm diameter). Powdered samples of Ir and Ru were complementarily given by Tanaka Precious Metals. Commercially available salts were used as received: NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, and MgCl_2 from Aldrich; LiClO_4 , LiCl , NaCl , NaBr , KCl , CaCl_2 , AlCl_3 , LiNO_3 , NaNO_3 , Li_2SO_4 , Na_2SO_4 (of all GR grades) from Wako Pure Chemical Industries. $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ was obtained from Aldrich. Nitric acid of 60% of a GR grade (JIS S), HCl (5.0 mol dm^{-3}), and acetonitrile of a GR grade were purchased from Wako. Pure water purified by a MilliQ System was used. The seawater of “Muroto Deep Seawater” (sampled from a 350 m depth) off Muroto, Kochi, Japan, was utilized as a standard seawater. The other seawater sampled at a 1000 m depth in the Pacific Ocean off Hawaii, USA, which was filtered in a common procedure, was also used.

2.2. Procedure and equipments

As the first stage, we measured the periods for the complete dissolution of gold plate at various temperatures. In a 20 mL volumetric flask, a piece of gold plate (Aldrich, 99.99%) of $20 \pm 2 \text{ mg}$ ($0.1 \text{ mm} \times 2 \text{ mm} \times 5 \text{ mm}$) was placed into 2.0 mol dm^{-3} nitric acid, which is accompanied by 1.0 mol dm^{-3} AlCl_3 . At the second stage, the gold plate was displaced

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