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MECHANISM OF ENHANCED OXIDATION ABILITY OF DILUTE NITRIC ACID AND DISSOLUTION OF PURE GOLD IN SEAWATER WITH NITRIC ACID

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It has been discovered that dilute nitric acid in reversed micelle systems can oxidize the Br^- ion to Br_2 and we have proposed that the nitryl (or nitronium) ion NO_2^+ should be the active species in the oxidation process. Nitration of phenol in reversed micelle systems with dilute nitric acid, $CHCl_3/CTAC/H_2O$ (2.0 mol dm^{-3} HNO_3 in the 1.0% (v/v) H_2O phase), has been performed at 35 ºC to obtain 2- and 4-nitrophenols, where CTAC represents cetyltrimethylammonium chloride. In aqueous 2.0 mol dm^{-3} HNO_3 solution accompanied by 4.0 mol dm^{-3} LiCl (and a small amount of LiBr as the bromide resource), trans-1,4-dibromo-2-butene was successfully brominated to 1,2,3,4-tetrabromobutane. This result is good evidence that the Br^- ion can be oxidized to Br_2 in dilute nitric acid (2.0 mol dm^{-3}) providing it contains concentrated salts. For chloride salts, the cation effects increased as $Et_4N^+ << Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$. Even the evolution of Cl_2 has been demonstrated from < 2.0 mol dm^{-3} HNO_3 solution containing concentrated LiCl, $MgCl_2$, and $CaCl_2$ as well as $AlCl_3$. The dissolution of precious metals (Au, Pt, and Pd), especially, of gold has been demonstrated in 0.1 - 2 mol dm^{-3} HNO_3 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} HNO_3 accompanied by 1.0 mol dm^{-3} $AlCl_3$ has been shortened remarkably with temperature increase from 15 to 80 ºC. 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} HNO_3 accompanied by the metal chlorides, in general, increase with increasing salt concentrations at 40 and 60 ºC. The gold can be dissolved in the solution of <1.0 mol dm^{-3} HNO_3 and <1.0 mol dm^{-3} HCl, i.e. a "dilute aqua regia." We have achieved a total dissolution of five pieces of the gold wire (totally 0.10 g) in 100 mL of the 1:1 mixture between seawater and 2.0 mol dm^{-3} HNO_3 at ca. 100 ºC.

Keywords: nitryl or nitronium ion, CTAC, evolution of chlorine, oxidation of bromide, salt effect, bulk water structure, dilute aqua regia, tetrachloroaurate, concentrated salt, Raman spectrum.

Introduction

Nitric acid has two different functions, a strong acid and a strong oxidizing agent in diluted and in concentrate conditions, respectively, and is one of the best known and most widely applied oxidizing agents in chemistry. Although the oxidation ability of HNO_3 depends on its concentration in solution, it is common knowledge that dilute nitric acid has no oxidation ability. Airborne sea salt particles wet or dry can react with various gases, in particular various oxides of nitrogen, potentially contributing to the chemistry of the troposphere [1]. Cotton and Wilkinson [2] have described that nitric acid of 0.1 mol dm^{-3} dissociates about 93% and that nitric acid of less than 2.0 mol dm^{-3} has virtually no oxidation ability. The dissociation constants of HNO_3 at different concentration ranges in aqueous solution have been determined [3].

In a previous paper [4], however, we have reported that the Br^- ion of the surfactant, CTAB, is oxidized to Br_2 (or Br_3^-) in the $CHCl_3/CTAB/H_2O$ reversed micelle system of W = 1.0 - 4.0 with dilute nitric acid (0.25 - 2.5 mol dm^{-3} in the 1.0% (v/v) H_2O phase) at 15 – 40 °C where CTAB stands for cetyltrimethylammonium bromide and the W value is the ratio of $[H_2O]/[surfactant]$. We proposed that the NO_2^+ ion should be the active species in this oxidation process. Unfortunately, our proposal for the active species may not be recognized so much, regardless of our supplying reasonable evidence in the study. The changes in the hydrogen-bonding conditions of the water droplets in reversed micelle systems have been discussed on the basis of ^1H NMR chemical shifts [4]. The influence of salts, acids, and phenols on the hydrogen-bond structure of water-ethanol mixtures has been examined also by ^1H NMR spectroscopy [5].

For more than thirty years, we [6] have tried to demonstrate that alkali metal (M^+) and alkaline earth metal (M^{2+}) ions have potentially the ability to coordinate with simple anions, such as Cl^-, NO_3^-, RSO_3^-, RCO_2^-, etc. Such minor interactions between M^+ or M^{2+} and simple anions could not be observed normally in dilute aqueous solution because of strong hydration toward both the metal cations

and the anions. In poor solvating media such as acetonitrile, however, the chemical as well as Coulombic interaction between M^+ or M^{2+} and simple anions has been demonstrated by careful examination with electrochemical and spectroscopic techniques. Rather strong chemical interactions between alkaline earth metal ions and the benzoate ion in acetonitrile were found by UV-visible and NMR spectroscopy [7].

We have also proposed [6] that the properties of bulk water are based on the hydrogen-bond network among a huge number of H_2O molecules (e.g., $n_w > \sim 10^7$). Water can lose its property as bulk water (H-O-H) 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 destroyed in the following cases: (a) the residual water ($c(H_2O) \sim 10^{-3}$ mol dm^{-3}) in organic solvents; (b) aqueous solutions or organic solvent-water mixtures containing highly concentrated salts; (c) nanoscale water droplets in nano-tubes or reversed micelle systems; (d) water on metal electrodes, ion-exchange resins, proteins, organic solvents as the solvent extraction, and glass vessels; (e) water under supercritical conditions. Such waters can be "reduced" to the authentic singular H_2O molecules (also called "dihydrogen ether", (H)-O-(H)) [8]. Reichardt et al. [9] have concisely interpreted "dihydrogen ether" that, at high salt concentrations ($c(salt) > 5$ mol dm^{-3}), region C, according to the solvation model of Frank and Wen [10], can be abolished and only regions A and B survive, resulting in an aqueous solvent called "dihydrogen ether".

Now, we would like to point out that hydrogen-bond dynamics of both water in highly concentrated NaBr solutions and in reversed micelle systems show a similar behavior [11]. In addition, Park et al. [11] have described that the water dynamics in 4 nm nano-pools in reversed micelle systems of both ionic and non-ionic surfactants is almost identical: confinement by an interface to form a nanoscopic water pool is the primary factor governing the dynamics of nanoscopic water rather than the presence of charged groups at the interface. Spectroscopic studies of the structure of surface water as it is affected by added salts, acids, and ammonia have been presented in a review article by Gopalakrishnan et al. [12]. The OH stretch of nitric acid in CCl_4 has provided definitive proof of molecular nitric acid rather than NO_3^- [13].

With the assistance of above-mentioned two ideas, i.e., (1) chemical interaction between the metal cations and simple anions, (2) the change of water properties with the addition of concentrated salts and/or organic solvents, we have successfully explained the concentrated salt effects on solvolysis reactions of organic haloalkanes and related compounds without resorting to different types of ion pairs [8].

It is widely accepted that the NO_2^+ ion is the active species in nitration reactions. March [14] has described in his textbook: "there is a great deal of evidence that NO_2^+ is present in most nitration reactions and that it is the attacking entity".

In Part 1 of the present paper, a few examples for the nitration of phenols with dilute nitric acid (2.0 mol dm^{-3}) in various reversed micelle systems are reported. After that, we examine the oxidation of Br^- to Br_2 by dilute nitric acid in aqueous bulk solution containing concentrated salts in order to recognize that the NO_2^+ ion can be produced within nanoscale water droplets in reversed micelle systems. In the course of our experiments, even the evolution of Cl_2 as well as the oxidation of Br^- to Br_2 has been observed in dilute nitric acid in aqueous bulk solution containing concentrated salts. Finally, the distortion of bulk water structure is fully discussed for aqueous solutions containing concentrated salts, such as LiCl and NaCl, based on experimental data observed with Raman and ^1H NMR spectroscopy.

In Part 2, pure gold dissolution in seawater mixed with aqueous nitric acid is demonstrated.

Results and Discussion

Part 1 Formation of NO_2^+ as the Intermediate in Reversed Micelle Systems and Bulk Aqueous Media from Dilute HNO_3

1.1. Nitration of phenol with dilute nitric acid in CHCl₃/CTAC reversed micelle

First of all, we would like to characterize the reaction field in reversed micelle systems. Fig. 1 shows the change with time in the ^1H NMR chemical shift (δ) values of OH in water droplets (1.0% H_2O phase containing 2.0 mol dm^{-3} HNO_3) of reversed micelle systems, CHCl₃/CTAB/H₂O (W = [H₂O]/[surfactant] = 2.0) and CHCl₃/CTAC/H₂O (W = 4.0) at 25 °C. The $\delta(^1H)$ value of the CTAB micelle system decreased after two hours with changing of the color from colorless to yellow,

whereas that of the CTAC micelle system remained constant during five hours and even after 7 days. In the previous study [4], we have established that the oxidation of Br^- ions to Br_2 (or Br_3^-) occurs with $0.25 - 2.0$ mol dm^{-3} HNO_3 (in the 1.0% H_2O phase) of the $CHCl_3/CTAB/H_2O$ (W = 2.0) reversed micelle system at 25 °C. We have also suggested that the oxidizing species should be the NO_2^+ ion which is formed from the dilute nitric acid in the micelle system.

The decrease of the $\delta(^1H)$ value in the CTAB micelle system has been attributed to the decrease in the nitric acid concentration, which should accompany the oxidation of Br^- ions of the surfactant, CTAB. Contrastingly, it is obvious that 2.0 mol dm^{-3} HNO_3 in the $CHCl_3/CTAC/H_2O$ (W = 4.0) micelle system could not oxidize the Cl^- ions (of the surfactant, CTAC) into Cl_2, thus, no decrease in the HNO_3 concentration was observed. In brief conclusion, Eq. 1 can take place but not Eq. 2 in the two reversed micelle systems.
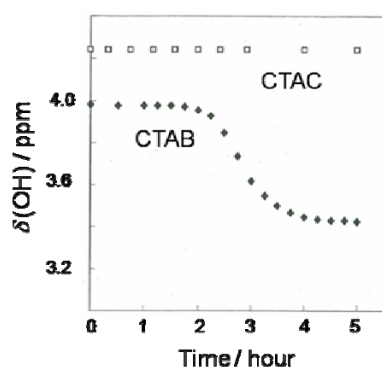
$$2Br^- + NO_2^+ \rightarrow Br_2 + NO_2^- \tag{1}$$

$$2Cl^- + NO_2^+ \rightarrow Cl_2 + NO_2^- \tag{2}$$

Figure 1. Time-dependent chemical shifts of $\delta(OH)$ in reversed micelle systems, $CHCl_3/CTAB/H_2O$ (W = 2.0) and $CHCl_3/CTAC/H_2O$ (W = 4.0), containing 2.0 mol dm^{-3} HNO_3 (in the 1.0% H_2O phase) at 25 °C.
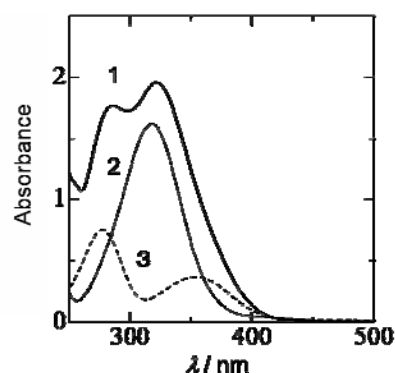
Figure 2. UV absorption spectra (0.1 cm path-length) of the products from 2.5×10^{-3} mol dm^{-3} phenol formed in the reversed micelle system $CHCl_3/CTAC/H_2O$ (W = 4.0), containing 2.0 mol dm^{-3} HNO_3 (in the 1.0% H_2O phase) at 35 °C and the candidate compounds in the reversed micelle system: (1) products formed after four days; (2) 1.0×10^{-3} mol dm^{-3} 2-nitrophenol; (3) 1.0×10^{-3} mol dm^{-3} 4-nitrophenol.

Fig. 2 shows the UV spectrum based on the reaction products from 2.5×10^{-3} mol dm^{-3} phenol in the reversed micelle ($CHCl_3/CTAC/H_2O$) at W = 4.0 containing 2.0 mol dm^{-3} HNO_3 (in the 1.0 % H_2O phase) after four days at 35 °C. Two bands at λ_{max} = 285 and 323 nm were observed. The UV spectrum of the reaction products was able to be fit with 1.6×10^{-3} mol dm^{-3} 2-nitrophenol and 1.4×10^{-3} mol dm^{-3} 4-nitrophenol, that is, the ratio of (1.14):(1.00) for 2- and 4-nitrophenols with a reaction yield of 80 % from phenol. This result seems to be reasonable since the OH-group of phenol has an ortho- and para-orientation tendency [15]. The production of 3-nitrophenol and 2,4-dinitrophenol was excluded based on their UV absorption spectra: reaction conditions are so gentle that 3-nitro- and dinitro-derivatives were not produced.

1.2. Nitration of 4-methylphenol with dilute nitric acid in CTAC and AOT reversed micelle systems

Nitration of 4-methylphenol with dilute nitric acid was examined in the $CDCl_3/CTAC/H_2O$ reversed micelle system at 35 °C. Fig. 3(a) shows the ^1H NMR spectrum of 0.010 mol dm^{-3} 4-methylphenol in the reversed micelle ($CDCl_3/CTAC/H_2O$) at W = 8.0 containing 2.0 mol dm^{-3} HNO_3 (in the 1.0 % H_2O phase) just after solution preparation. Two doublet signals characterize the reactant 4-methylphenol. The ^1H NMR spectrum (for $\delta(^1H)$ = 5 – 10 ppm) of 4-methylphenol in the $CDCl_3/CTAC/H_2O$ reversed micelle system was almost identical with that of a commercial compound in $CDCl_3$ solution. After completion of the reaction (two days later), the ^1H NMR signals shifted to the down-field direction; one singlet (3H) and two doublet signals (5H and 6H), shown in Fig. 3(b), indicated the formation of 2-nitro-4-methylphenol and the absence of the reactant 4-methylphenol.
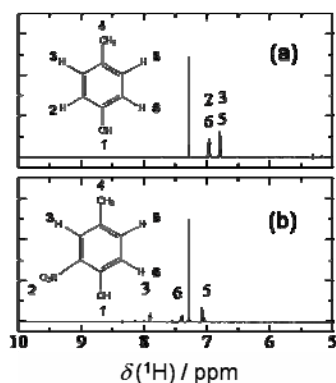
Figure 3. ^{1}H NMR spectra of (a) 0.01 mol dm^{-3} 4-methylphenol in CDCl$_3$/CTAC/H$_2$O (W= 4.0) reversed micelle in the presence of 2.0 x 10^{-3} mol dm^{-3} HNO$_3$ (in the 1.0% H$_2$O phase) just after solution preparation and (b) the product formed from 0.01 mol dm^{-3} 4-methylphenol in the reversed micelle system after reaction completion (two days later at 35 ºC).
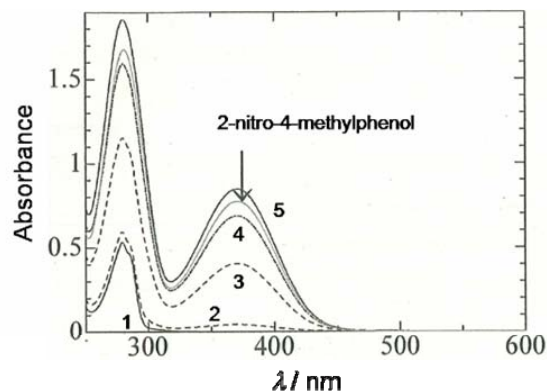

Figure 4. Changes of UV and visible spectra (0.1 cm path-length) from 2.5 x 10^{-3} mol dm^{-3} 4-methylphenol to 2-nitro-4-methylphenol with time in reversed micelle, CHCl$_3$/AOT/H$_2$O (W = 2.0), containing 2.0 mol dm^{-3} HNO$_3$ (in the1.0% water phase) at 35 ºC: (1) 0; (2) 2.0; (3) 4.0; (4) 5.0; (5) 6.0 h later. Commercially obtained 2-nitro-4-methylphenol of 2.0 x 10^{-3} mol dm^{-3} is also displayed.

The reaction yield was evaluated by means of UV spectroscopy of 2-nitro-4-methylphenol from 2.5 x 10^{-3} mol dm^{-3} 4-methylphenol in the CHCl$_3$/CTAC/H$_2$O reversed micelle system. The yield of the product increased with increasing W value, e.g. 88.5, 91.7, and 95.7 % for W = 1.2, 2.0, and 8.0, respectively, and the reaction time (for completion) was prolonged by smaller W values: 2, 3, and 5 days for W = 2 - 8, 1.5, and 1.2, respectively. One can expect some superiority in the yields and reaction rates for the smaller W values because of more remarkable distortion of the water structure. However, the experimental data indicates the opposite tendency. Similar opposite tendency have been reported for the oxidation of Br$^-$ in CTAB reversed micelle system [4].

The cationic surfactant, CATC, was then replaced by an anionic surfactant, AOT. Fig. 4 shows the formation of 2-nitro-4-methylphenol from 2.5 x 10^{-3} mol dm^{-3} 4-methylphenol in the reversed micelle (CHCl$_3$/AOT/H$_2$O) at W = 2.0 containing 2.0 mol dm^{-3} HNO$_3$ (in the 1.0 % H$_2$O phase) at 35 ºC. Two hours later, a reaction to some extent could be observed with a slight increase of absorbance at around λ = 280 and 370 nm. The reaction was completed after six hours to give a UV spectrum with two bands at λ = 281 and 371 nm for 2-nitro-4-methylphenol with a reaction yield of 93.2 %. The influence of the W value on reaction time and yield was examined only for W = 1.0 – 3.0, since the reversed micelle system was unstable for W = 4.0 or more. Smaller W values caused slightly lower yields and longer reaction times: 92.1 % (8 h) and 94.0 % (6 h) for W = 1.0 and 3.0, respectively.

For the AOT system at W = 2.0, the replacement of CHCl$_3$ with heptane as the organic phase caused the reaction rate of the nitration of 4-methylphenol to be much faster. The nitration reaction was completed in two hours with a yield of 98 %. At various W values (W = 1.0 – 8.0), the yield and reaction time were obtained for 2-nitro-4-methylphenol from 2.5 x 10^{-3} mol dm^{-3} 4-methylphenol in the reversed micelle (heptane/AOT/H$_2$O) containing 2.0 mol dm^{-3} HNO$_3$ (in the 1.0 % H$_2$O phase) at 35 ºC. The reaction or completion time was always 2 h, except for W = 1.0 (3.5 h), and the yields were within 93 – 98 %. However, the insolubility of the CTAC surfactant in heptane prevented us from examining the reaction in a heptane/CTAC/H$_2$O reversed micelle system.

Onori and Santucci [16] have investigated water structure in CCl$_4$/AOT/H$_2$O reversed micelle systems. They have stated that the IR spectra can be expressed as sum of the contributions from interfacial and bulk-like water. Without doubt, the conditions in the nanoscale water droplets are quite different from that of intrinsic bulk water.

In 10 mL of heptane without surfactants, the nitration of 2.5 x 10^{-3} mol dm^{-3} 4-methylphenol with 2.0 mol dm^{-3} HNO$_3$ (0.1 mL) was examined at 35 ºC. Turbidity was observed in heptane when sonication was performed for several minutes in order to mix the solvent and the small amount of dilute nitric acid. After one day at 35 ºC, however, the solution became clear and the UV spectrum of the solution indicated the formation of 2-nitro-4-methylphenol of 93 % yield. In this case, nitration took place in the absence of surfactants. In the review article of Gopalakrishnan et al. [12] they commented that

infrared spectra of saturated solutions of water in CCl_4 at room temperature can be assigned to water monomers or dimers. The water molecules mixed into heptane, including the turbidity particles, may exist in a variety of forms from the monomer to hydrogen-bonded oligomers, $(H_2O)_n$.

In 10 mL of $CHCl_3$, on the other hand, 4-methylphenol could not be nitrated by 2.0 mol dm^{-3} HNO_3 (0.1 mL) even after two weeks. Now, we would like to discuss briefly the reactivity (formation of NO_2^+ as intermediate) in both solvents: the most obvious difference between two organic solvents must be in their acceptor numbers: ~ 0 and 23.1 for heptane and $CHCl_3$, respectively [17], whereas the donor numbers of both solvents should be quite small (~0). Chloroform with the larger acceptor number (i.e., the larger basicity) can accept the hydrogen bond from the H-atoms of nitric acid, which might cause a lower tendency to produce the NO_2^+ ion.

Now, we wonder what kind of function surfactants may have for the reaction in reversed micelle systems. Additionally, the question is where the NO_2^+ ion is generated, either within the aqueous phase or in the organic phase. In order to solve these problems, we examined the oxidation ability of dilute nitric acid in bulk water containing concentrated salts, as described in the following sections.

1.3. Oxidation of Br⁻ to Br₂ with dilute nitric acid in aqueous bulk solution containing abundant salts

Fig. 5 shows the UV-visible absorption spectra of a 2.0 mol dm^{-3} HNO_3 aqueous solution, after addition of 4.0 mol dm^{-3} LiCl and 0.010 mol dm^{-3} LiBr at 35 ºC. Note that the concentration of nitric acid is less than 2.0 mol dm^{-3} (actually found to be 1.83 mol dm^{-3}) because a substantial part of the volumetric flask is occupied by a large amount of the salt, LiCl, and only 2.0 mol dm^{-3} HNO_3 was handled for preparation of the solution. The solution turned soon from colorless to yellow. In the UV-visible spectra, a band of at around 371 nm developed gradually with time until 30 min passed. Commercially available Br_2 gave UV absorption band at around 371 nm (absorptivity, e /cm^{-1} mol^{-1} dm^3 = ca. 200) in 4.0 mol dm^{-3} LiCl aqueous solution, cf., ε = ca. 180 at λ = 390 nm in 2 mol dm^{-3} $HClO_4$ [18]. Based on the absorptivity of Br_2, the oxidation of the Br⁻ ion (LiBr) is suggested to be completed after 30 min. The presence of Br_2 in the concentrated salt solution (e.g., 4.0 or 5.0 mol dm^{-3} LiCl) after the reaction was detected by the Rosaniline method [19]; the appearance of a red color (l = ca. 570 nm) proved the formation of Br_2.
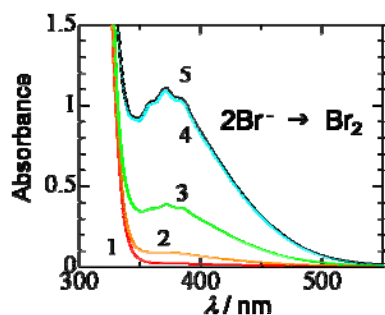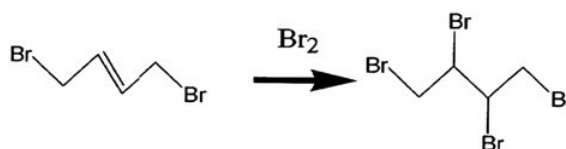

Figure 5. Formation of Br_2 (1.0 cm path-length) from 0.010 mol dm^{-3} LiBr in 2.0 mol dm^{-3} HNO_3 solution, accompanied by 4.0 mol dm^{-3} LiCl at 35 ºC: (1) 0; (2) 5; (3) 10; (4) 25; (5) 30 min later.

Scheme 1. The bromination of a butene to the butane.

The formation of Br_2 from LiBr with 2.0 mol dm^{-3} HNO_3 accompanied by 4.0 mol dm^{-3} LiCl (and 0.010 mol dm^{-3} LiBr) was confirmed also by means of ${}^1H$ NMR as follows: before and after the reaction, each solution of 10 mL in the presence of trans-1,4-dibromo-2-butene (0.010 mol dm^{-3}) was extracted with 2 mL of $CDCl_3$. After the completion of reaction, the formation of 1,2,3,4-tetrabromobutane was demonstrated by the disappearance of a signal at $\delta({}^1H)$ = ca. 6.0 ppm stemming from trans-1,4-dibromo-2-butene as well as the appearance of signals between $\delta({}^1H)$ = 3.5 – 5.0 ppm. The formation of 1,2,3,4-tetrabromobutane from trans-1,4-dibromo-2-butene (cf. Scheme 1) is a good evidence for the oxidation of Br⁻ with dilute nitric acid in the presence of LiCl. It is true that the lithium ion has an advantage for getting good oxidation ability with dilute nitric acid, however, we would like to stress that Li^+ is not the essential ion component. At 35 ºC, a solution of 2.0 mol dm^{-3} HNO_3 accompanied by sodium chloride (3.0 mol dm^{-3}) and bromide (0.010 mol dm^{-3}),

which contains no lithium ions, produced also Br_2, though the reaction rate and the yield of Br_2 (ca. 25 %) was low.

At various temperatures, examined were the time-dependent changes of absorbance at l = ca. 371 nm of Br_2 in 2.0 mol dm^{-3} HNO_3 accompanied by 4.0 mol dm^{-3} LiCl (and 0.010 mol dm^{-3} LiBr). With increasing temperature, the reaction rate increases. The activation energy for 20 – 35 °C was evaluated to be 67.2 kJ mol^{-1} for the 4.0 mol dm^{-3} LiCl solution. With decreasing salt concentration, however, the reaction rate decreased remarkably; the activation energies were evaluated to be 58.6 and 45.0 kJ mol^{-1} for 3.7 and 3.5 mol dm^{-3} LiCl. Naturally, with increasing LiCl concentration, the reaction rate increased. In 2.0 mol dm^{-3} HNO_3 accompanied by 5.0 mol dm^{-3} LiCl (and 0.010 mol dm^{-3} LiBr), the oxidation reaction proceeded too fast to evaluate the rate constant precisely, therefore, nitric acid of 1.0 mol dm^{-3} was used for 5.0 mol dm^{-3} LiCl to obtain log (k/s^{-1}) = -3.87 at 25 °C.

In the case of 9.0 mol dm^{-3} LiCl, at last, the nitric acid concentration was decreased down to 0.1 mol dm^{-3} to get reasonable experimental conditions. In Table 1 are listed the apparent oxidation-reaction rate constants, log (k/s^{-1}), for 0.10 – 2.0 mol dm^{-3} nitric acid accompanied by LiCl in high concentrations (3.5 – 9.0 mol dm^{-3}). It should be mentioned that the rate constants are not very precise values because the apparent molarity concentrations of nitric acid are always reduced by the volumes of a large amount of salts (vide supra); the actual molarity values are also listed in the table.

Table 1. The apparent rate constants, log (k/s^{-1}),[a] of formation of Br_2 from dilute nitric acid (and 0.010 mol dm^{-3} LiBr as the Br$^-$ resource) solution containing alkali metal and alkaline earth metal chlorides at 20 – 40 °C.

salt/mol dm^{-3}	HNO$_3$/ mol dm^{-3}	40°C	35°C	30°C	25°C	20°C
LiCl, 4.0	2.0[b] (1.83)[c]		-2.57	-2.76	-2.96	-3.24
LiCl, 5.0	1.0 (0.894)		-3.23	-3.63	-3.87	-4.13
LiCl, 6.5	0.5 (0.431)		-3.36	-3.72	-3.94	-4.22
LiCl, 8.0	0.2 (0.167)	-3.70	-3.80	-4.03		
LiCl, 9.0	0.1 (0.081)	-3.87	-3.97	-4.20		
NaCl, 3.5	2.0 (1.84)		-4.81	-5.19	-5.43	
MgCl$_2$, 1.7	2.0 (1.60)			-2.51	-3.14	-3.49
CaCl$_2$, 2.5	2.0 (1.83)		-2.68	-2.93	-3.47	-3.51

[a] Evaluated from the slope of ln $(A_\infty - A_t)$ vs. t, where A_∞ and A_t represent the absorbance at reaction completion and at each time, respectively.
[b] The concentration of HNO_3 solution, with which the salt was dissolved.
[c] The actual HNO_3 concentration in the reaction flask, evaluated by the weight and the total volume values.

All the log (k/s^{-1}) values observed are between ca. -4.0 to ca. -2.5 at 25 – 35 °C, in other words, the reaction rates were adjusted by controlling the concentrations of both HNO_3 and LiCl for obtaining appropriate experimental data. In the case of sodium chloride, 3.5 and not 4.0 mol dm^{-3} salt solution was utilized because of the smaller solubility of NaCl in 2.0 mol dm^{-3} HNO_3. A 2.0 mol dm^{-3} HNO_3 aqueous solution accompanied by 3.5 mol dm^{-3} NaCl (and 0.010 mol dm^{-3} LiBr) at 25 °C gave the log (k/s^{-1}) value of -5.43 and this value is much smaller than that (-3.75) for 3.5 mol dm^{-3} LiCl. Note that the actual concentration of "2.0 mol dm^{-3} HNO_3", accompanied by 3.5 mol dm^{-3} LiCl or NaCl were found to be each 1.84 mol dm^{-3}. The large difference in the log (k/s^{-1}) values between LiCl and NaCl is probably caused not only by some interaction between M^+ and NO_3^- but also by the change of the water structure through hydrogen bonding in the presence of these salts. In the final section of Part 1, the water structure through hydrogen bonding will be discussed based on the Raman and ^{1}H NMR spectral data of D_2O or H_2O containing LiCl, NaCl, and other salts.

As for non-metallic salts, a 2.0 mol dm^{-3} HNO_3 solution accompanied by 3.5 mol dm^{-3} Et$_4$NCl (and 0.010 mol dm^{-3} LiBr) at 30 and 35 °C gave no Br_2 even 50 h later, although we have observed the production of Br_3^- salts (brown-color) on Et$_4$NBr crystals from a 2.0 mol dm^{-3} HNO_3 solution, saturated with Et$_4$NBr after several days at room temperature. It is obvious that the metal ions play an important role in the oxidation process with dilute nitric acid. Magnesium and calcium chlorides promoted remarkably the oxidation reaction with dilute nitric acid: it was necessary for us to employ lower concentrations for these salts to obtain appropriate experimental data. The log (k/s^{-1}) values for MgCl$_2$ and CaCl$_2$ are also listed in Table 1. The effects by alkali metal and alkaline earth metal chlorides were

classified as $Et_4NCl \ll NaCl < LiCl < CaCl_2 < MgCl_2$. This order of cations is just similar to that of the cation effect on solvolysis reaction rates of S_N1 substrates [8].

After examining the heterogeneous reactions of oxides of nitrogen with NaCl as a model for sea salt particles, Langer et al. [1] inferred that NaCl may not be the component of sea salt which is most reactive with HNO_3. Rossi [20] has summarized the study by Langer et al. [1] in a review article, "this study indicates that HNO_3 and NO_2 appear to react preferentially with hydrate salts such as $MgCl_2·6H_2O$, which is one of the constituents of natural sea salt". Admitting that they studied in heterogeneous phases, our observation is consistent with the result obtained by them [1].

1.4. Evolution of Cl_2 in concentrated chloride salt solutions and mechanism of the oxidation of the Br^- ion

In 2.0 mol dm^{-3} HNO_3 accompanied by 1.0 mol dm^{-3} $AlCl_3$ (and 0.010 mol dm^{-3} LiBr) at 20 – 35 °C, the reaction proceeded quickly to give Br_2 but yields were not so high. In addition, we noticed that Cl_2 gas seemed to be produced from the solution. Therefore, the Cl_2 formation was examined by the o-tolidine method [21] for 2.0 mol dm^{-3} HNO_3 accompanied by 1.0 mol dm^{-3} $AlCl_3$ at room temperature. Chlorine was detected by the absorption band at $\lambda = 437.5$ nm in the test solutions, sampled from the vapor phase as well as from the condense phase (the HNO_3 solution). By the same method, the formation of Cl_2 was demonstrated in 2.0 mol dm^{-3} HNO_3 accompanied by LiCl, $MgCl_2$, and $CaCl_2$ of 4.0, 1.7, and 2.5 mol dm^{-3}, respectively. Although we failed to determine Cl_2 from 2.0 mol dm^{-3} HNO_3 accompanied by 3.5 mol dm^{-3} NaCl in a preliminary experiment, we believe that the formation of Cl_2 is possible from all the (dilute) nitric acid solutions containing concentrated chloride salts which we have examined.

The standard redox potentials, E^o, of $NO_2^+/NO_2^·$ and NO_2^+/N_2O_4 are reported to be 1.35 and 1.50 V [22], respectively, cf. $E^o = 1.396$ V for $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ [23]. Olah [24] has described that the reversible potential for reduction of NO_2^+ in acetonitrile is 1.45 V (vs. NHE), citing an electrochemical paper [25]. The oxidation of Cl^- to Cl_2 with NO_2^+ must be possible according to the redox potentials of NO_2^+ and Cl_2.

Behnke et al. [26] have stated that NO_2^+ reacts with water to form $2H^+$ and NO_3^- or with Cl^- to produce nitryl chloride ($ClNO_2$) in their atmospheric chemical experiment of N_2O_5 on liquid NaCl aerosols or bulk NaCl solution at 291 K. However, it is known that [27] nitryl chloride is soluble in water and it decomposes to nitric and hydrochloric acids. The mixture (aqua regia) of concentrate HNO_3 and HCl is ready to evolve Cl_2 and nitrosyl chloride (NOCl) [28]. Coincidentally, nitration of a calixarene compound by anhydrous $AlCl_3$ and KNO_3 in CH_2Cl_2 has been reported [29]. Another aluminum salt, $Al(H_2PO_4)_3$, serves as an efficient solid acid catalyst of nitration of a variety of organic substances with 70 % nitric acid [30].

Having the evolution of Cl_2 is demonstrated, the oxidation mechanism of the Br^- to Br_2 should be reconsidered. The oxidation of the Br^- ion of LiBr in concentrated LiCl solution can occur not only directly by NO_2^+ but also indirectly through Cl_2, as expressed by Eqs. 2 and 3:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^- \qquad (3)$$

The reaction given in Eq. 3 was inferred from the formation profile of Br_2 in the dilute nitric acid containing chloride salts, that is, the absorbance of Br_2 increased gradually from the beginning of reaction time. On the other hand, the formation profile of Br_2 in dilute nitric acid containing non-chloride salts is completely different from that of chloride salts. Fig. 6 shows the change of Br_2 concentration with time in 2.0 mol dm^{-3} HNO_3 (and 0.010 mol dm^{-3} LiBr) accompanied by lithium trifluoromethanesulfonate, perchlorate, and nitrate salts. The absorbance of Br_2 increased not from the initial time but after an induction period for each salt. The oxidation reaction of other non-chloride lithium and sodium salts, such as CH_3SO_3Na or $NaHSO_4$, also need a long induction period before the formation of Br_2 starts. The details of the influence of cation and anion components on the generation of NO_2^+ as the active species from dilute nitric acid will be reported later. We just mention that the basicities of anions from salts in higher concentrations may influence on the generation of NO_2^+ from dilute HNO_3. Kinetics and mechanism of the autocatalytic oxidation with nitric acid have been reviewed by Bazsa [31].

1.5. Distortion of bulk water structure in the presence of concentrated LiCl and NaCl

According to Frank and Wen [10], Li^+ and Cs^+ ions in aqueous solution are regarded to be structure making and breaking, respectively. This classification for cations or salts is widely accepted in solu-

tion chemistry. However, we would like to point out that this argument must be limited to lower salt concentrations in solution. In the presence of salts in high concentrations (e.g., 5 mol dm^{-3}), bulk water molecules are consumed for hydrating the ions, therefore, the bulk water part (properly structured with an enormous number of water molecules) in solution is reduced or even disappears and only isolated water molecules should be left for solvating foreign chemical species [6].
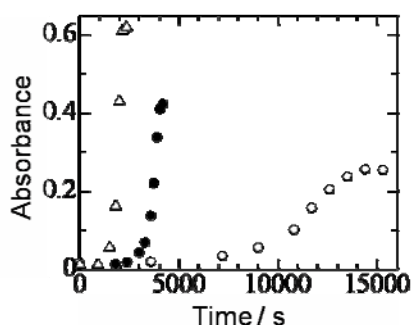

Figure 6. Time-dependent absorbance (1.0 cm path-length) at around l = 371 nm of a 2.0 mol dm^{-3} HNO$_3$ solution, accompanied by 3.5 mol dm^{-3} lithium salts (and 0.010 mol dm^{-3} LiBr) at 35 °C: (△) CF$_3$SO$_3$Li; (●) LiClO$_4$; (○) LiNO$_3$.
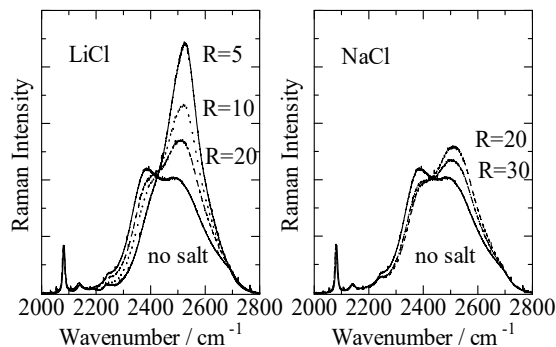
Figure 7. The changes of Raman spectra of D$_2$O with changing R values of LiCl and NaCl, where R = [D$_2$O] / [salt].

Fig. 7 shows the changes of Raman spectra of D$_2$O with changing R values of LiCl and NaCl where R = [D$_2$O] / [salt]. Excitation for the Raman spectroscopy was provided by a 514.5 nm argon laser. The two peaks at ca. 2390 and 2500 cm^{-1} of D$_2$O in the absence of salts can be attributed to O-D stretching bands of strongly and weakly hydrogen-bonded D$_2$O molecules, respectively [8c-8e,32]. With decreasing R values (i.e., with increasing salt concentration), the intensity of the band of weakly hydrogen-bonded water increases at the expense of that of strongly hydrogen-bonded water for both LiCl and NaCl solutions. The Raman spectra obviously indicate that the water structure through hydrogen-bonding is much destroyed in concentrated LiCl as well as NaCl solution. Furthermore, examining the distortion of the water structure, we found, LiCl has a stronger impact than NaCl. At R = 20, for instance, the ratio of Raman intensities (I$_2$/I$_1$) is 0.64 and 0.72 for LiCl and NaCl, respectively, where I$_1$ and I$_2$ represent Raman intensities at ca. 2500 and 2390 cm^{-1}. The smaller Raman ratio for the D$_2$O solution of LiCl, as compared with that of NaCl, indicates that the water structure is more distorted by LiCl, rather than NaCl of the same molality concentration: R value of 20 corresponds to 2.5 mol kg^{-1}.

Coincidently, Pastroczak et al. [33] have demonstrated how the intensity ratio of two main band components of H$_2$O (around 3200 and 3400 cm^{-1}) depends on the excitation laser wavelength in the visible range. Note that the ratio (I$_2$/I$_1$) is 1.08 for pure D$_2$O and that D$_2$O is somewhat more structured than H$_2$O (I$_2$/I$_1$ = 0.90 for 3250 and 3400 cm^{-1}, laser excitation at 514.5 cm^{-1}). Gordon [34] has already mentioned that D$_2$O is a more structured liquid than H$_2$O.

1.6. Integration of apparent contradiction between NMR and Raman spectroscopy

Now, we have to declare that ^{1}H NMR chemical shifts of H$_2$O containing the salts were found to be apparently controversy to the Raman results. Fig. 8 shows the $\Delta\delta$ values changed by various cations or anions of 1.0 mol dm^{-3} in 2.0 % (v/v) EtOH-H$_2$O solution. We have found that these $\Delta\delta$ values observed in 2.0% are not so much different from those observed in 20% (v/v) EtOH-H$_2$O solution, previously reported [5]. We can notice that the difference of the $\Delta\delta$ values between Mg^{2+} and Ca^{2+} are definitely smaller than that observed in 20% (v/v) EtOH-H$_2$O solution, though.

The separation of the effects by the anion and cation components in a salt was performed according to Hindman's method [35] ($\Delta\delta$ (NH$_4^+$) = 0): the details of the procedure have been described previously [5]. Magnesium, calcium, and lithium ions having smaller ionic sizes (r/z) gave positive $\Delta\delta$ values while Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ gave negative values; where r and z are the crystal ion radius and the

number of charges, respectively. Positive and negative $\Delta\delta$ values should be correspondent to structure making and breaking, respectively. Based on the ^{1}H NMR data, Li^+ is structure making while Na^+ and Cl^- are structure braking. Thus, the ^{1}H NMR data for these ions are in good accordance with the model of Frank and Wen [10].
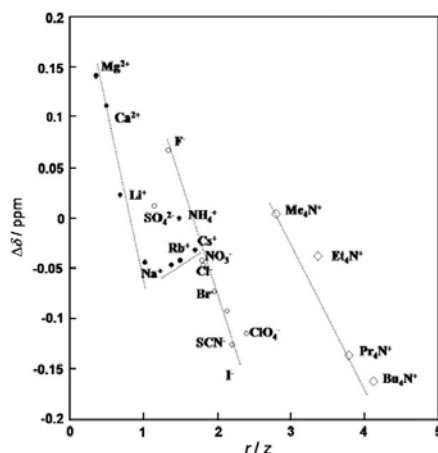

Figure 8. The $\Delta\delta$ values vs. r/z for various cations and anions at 1.0 mol dm^{-3} in 2.0 % (v/v) EtOH-H$_2$O solution, where r and z are the crystal ion radius and the number of charge, respectively. The signal of the methyl group in EtOH served as the internal standard for the chemical shift.

As discussed above, however, the Raman spectra supply us with the information that the water structure is more distorted by higher concentration of LiCl than of NaCl. Such an apparent contradiction between Raman and NMR data has been one of the most difficult points to clear in solution chemistry. Now we suppose that ^{1}H NMR system may reflect the ion hydration (neighboring part of ions) even though the bulk water is almost lost in the presence of salts in higher concentrations, whereas Raman spectroscopy seems to be able to evaluate the degree how much an aqueous solution is changed from the initial bulk water as the result of adding salts. Note that the condition of water structure around a metal ion (e.g., Li^+ or Fe^{2+}), developed by its ionic field or coordination ability, must be quite different from that of the bulk water. Raman spectra may distinguish the difference between hydration and bulk water molecules but NMR spectra may not. As mentioned above, we have proposed of change in the properties of bulk water into those of "dihydrogen ether" [8] in the presence of highly concentrated salts. It is, indeed, necessary for us to arrange slightly the idea of Frank and Wen [10] (structure-making or breaking ions) in order to account for the controversy feature between Raman and ^{1}H NMR spectroscopy.

The influence of MgCl$_2$ and CaCl$_2$ on the water structure has been examined by means of ^{17}O NMR and Raman spectroscopy [36]. Changes in Raman spectra indicated the break of the fully hydrogen bonded water structure with increasing concentration of MgCl$_2$ and CaCl$_2$. However, the $\delta(^{17}OH_2)$ values increased (down-field shift) with increasing concentration of MgCl$_2$ and CaCl$_2$. The authors have described that results from ^{17}O NMR and Raman measurements are "compatible" with each other. Obviously, in the truth, they have had encountered the contradiction just similar to ours. However, they evaded the difficult situation by describing, "though CaCl$_2$ and MgCl$_2$ destroy four hydrogen-bonded water structures, they promote the water structure in the mass".
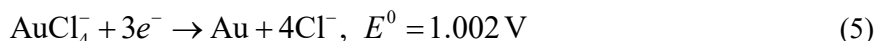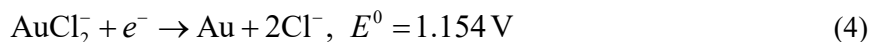
Yonehama et al. [37] reported the O-D stretching frequency in aqueous electrolyte solutions. Although they paid their precise attention only to the frequency changes but not to the intensities in Raman spectra, they cast a most important comment as follows: the term "structure-making and structure-breaking" is a confusing expression in that incorporation of small ions in water invites a new structure (hydration structure) formation different from the intrinsic water structure.

Part 2 Pure gold dissolution in seawater mixed with aqueous nitric acid

In an editorial article [38] 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. [39] 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 [40]. Chlorine-Chloride leaching was applied commercially in the 19th century, but its use diminished following the introduction of the cyanide process in 1887.

The redox potentials [23] for gold species are as follows:

$$Au^+ + e^- \rightarrow Au, \; E^0 = 1.83 \, V \; \text{ and } \; Au^{3+} + 3e^- \rightarrow Au, \; E^0 = 1.52 \, V$$

$$AuCl_2^- + e^- \rightarrow Au + 2Cl^-, \; E^0 = 1.154 \, V \tag{4}$$

$$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-, \; E^0 = 1.002 \, V \tag{5}$$

The comparison between Eqs. 4 and 5 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 Cl_2 or O_3, is required to dissolve gold at a reasonable rate [41]. The redox potential of Cl_2 (g) to Cl^- (aq) is reported to be 1.358 V [41] and that of O_3 to O_2 to be 2.075 V or 1.246 V in acidic or basic solution, respectively [41].

We have recognized 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. 6 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 [4] as well as in bulk water containing higher concentrations of salts.

$$2HNO_3 \rightarrow NO_2^+ + NO_3^- + H_2O \tag{6}$$

With an intimate examination of Eq. 6, we may notice that enhanced formation of HNO_3 in its molecular state and not dissociated ($H^+ + NO_3^-$) is essential for a favorite NO_2^+ generation. In bulk aqueous solution, however, many people may be suspicious that diluted nitric acid 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. $\varepsilon_r < 10$) 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"[8], 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 [42] and Pitzer [43] 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.

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, at the same time, coordinated by the abundant Cl^- ions, when the aqueous nitric acid is accompanied by sufficient amounts of chloride salts.

In Part 2, we would like to demonstrate the dissolution of precious metals (Au, Pt, and Pd), and to give detailed reports on gold dissolution in aqueous nitric acid (< 2 mol dm^{-3}) containing alkali metal, alkaline earth metal, and aluminum chlorides at 15 – 100 ºC.

2.1. Total dissolution of pure gold in 2 mol dm^{-3} aqueous HNO_3 solution containing concentrated salts

The gold dissolution has been examined with gold plate. Fig. 9 shows the period (time in hour) needed for the complete dissolution of a piece of gold plate (20±2 mg, the thickness of 0.1 mm) in a 20 mL solution of 2.0 mol dm^{-3} HNO_3, accompanied by 1.0 mol dm^{-3} $AlCl_3$, at various temperatures. It takes a long time, ca. 35 hours at 15 ºC, however, the dissolution period was shortened with increasing temperature, e.g. less than 30 minutes at 70 or 80 ºC. The aqueous HNO_3 solution acquires the increased dissolution ability with the temperature increase.

Next, the gold dissolution into the aqueous HNO_3 solution has been examined with the gold wire instead of the gold plate. Fig. 10 shows the time for complete dissolution of a piece of gold wire (19.7±0.5 mg, diameter of 0.25 mm) in a 20 mL solution of 2.0 mol dm^{-3} HNO_3, accompanied by various chloride salts, at 60 ºC. With increasing salt concentrations (from 1.0 mol dm^{-3}), generally speaking, the complete dissolution time is shortened. However, an interesting reversal trend is observed for

more than 5.0 mol dm^{-3} LiCl: the gold dissolution in a 2 mol dm^{-3} HNO$_3$ solution needs longer time in the presence of 7.0 or 9.0 than 5.0 mol dm^{-3} LiCl. The most remarkable reversal effect is exhibited by CaCl$_2$. The dissolution time reaches its minimum at around 2.5 mol dm^{-3} CaCl$_2$ and get longer again after reaching a concentration of 3.0 mol of the salt.
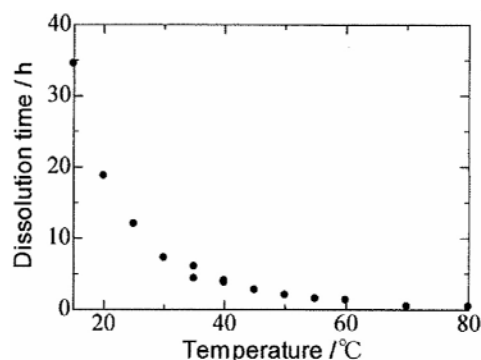

Figure 9. Time for the complete dissolution of gold plate (20 ± 2 mg) in 2.0 mol dm^{-3} HNO$_3$, accompanied by 1.0 mol dm^{-3} AlCl$_3$ at various temperatures.

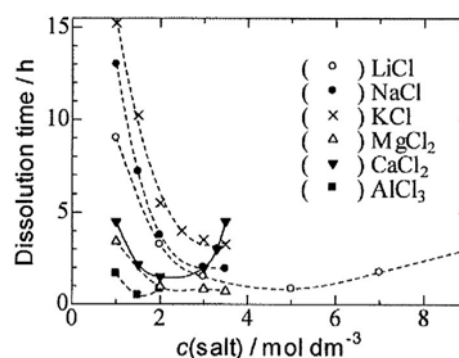**Figure 10.** Time for the complete dissolution of gold wire (19.7 ± 0.5 mg) in 2.0 mol dm^{-3} HNO$_3$, accompanied by various chloride salts at 60 °C.

As to dissolving gold, MgCl$_2$ is more effective than CaCl$_2$. The influence of metal chlorides (at 1.0 mol dm^{-3}) for the rate of gold dissolution increases in the order KCl < NaCl < LiCl < CaCl$_2$ < MgCl$_2$ < AlCl$_3$. At a lower temperature, 40 °C, much longer time is needed for complete dissolution of the gold wire in a 20 mL solution of 2.0 mol dm^{-3} HNO$_3$ than at 60 °C. For instance, it takes 13 hours for the solution with 3.0 mol dm^{-3} NaCl at 40 °C, but only 2 hours at 60 °C. In any case, all the results obtained with the metal chlorides at 40 °C were very similar to those observed at 60 °C. We would like to mention that the complete dissolution experiments of the gold wire in the solutions of much lower HNO$_3$ (down to 0.1 mol dm^{-3}) concentrations containing the chloride salts have been also successfully performed at 60 °C.

The dissolution capacity for Au has been examined as follows: a 2 mL solution of 2.0 mol dm^{-3} HNO$_3$ is poured to 0.57 g of MgCl$_2$ (ca. 3 mol dm^{-3}) in a small beaker, and gold wire of 0.10 g is put in the solution. The beaker is placed on a hot-plate at ca. 80 °C, the gold wire dissolved completely in 40 minutes: the capacity can be estimated to be 50 g Au/L of 2 mol dm^{-3} HNO$_3$, accompanied by 3 mol dm^{-3} MgCl$_2$. On the other hand, it takes several days for a 0.040 g Pt wire (0.1 mm diameter) to be dissolved in 10 mL of 2 mol dm^{-3} HNO$_3$, accompanied by 3 mol dm^{-3} MgCl$_2$ at 80 °C, giving a Pt capacity of at least 4 g Pt/L. We will also note that Pd can be dissolved in a 1:1 mixture between 2.0 mol dm^{-3} HNO$_3$ and seawater (vide infra).

For other precious metals, Ir and Ru, dissolution experiments have been performed. However, these metals (in powder) are not dissolved in 2 mol dm^{-3} HNO$_3$, accompanied by 3 mol dm^{-3} MgCl$_2$. It is well known that both Ir and Ru are not dissolved even in proper aqua regia [44]. Our method for dissolving precious metals (such as Au, Pt, or Pd) has a similar but weaker function than normal aqua regia. However, we would like to stress that our method has a higher efficiency of chemicals, without useless evolution of NO and Cl$_2$ during gold dissolution in regular aqua regia.

2.2. Dissolution rate constants and cation effects

The UV-visible spectroscopy has been employed to identify the dissolved species formed from the gold wire. Fig. 11 shows the changes with time in the absorption spectra (in 0.1 cm path-length) of a 2.0 mol dm^{-3} HNO$_3$ solution containing a piece of gold wire (ca. 19.7 mg) in the presence of 3.5 mol dm^{-3} NaCl. A band appears and increases with time, which is accompanied by a peak at λ ~ 306 nm and a shoulder around 400 nm, while the initial HNO$_3$ gives a band at λ ~ 300 nm. The spectrum observed after 12 hours in a 0.05 cm cuvette is consistent to that of 5.0 x 10^{-3} mol dm^{-3} NaAuCl$_4$ dissolved in a 2.0 mol dm^{-3} HNO$_3$ solution. Therefore, we can safely conclude that the species dissolved in the 2 mol dm^{-3} HNO$_3$ and 3.5 mol dm^{-3} NaCl solution is definitely the AuCl$_4^-$ ion. Jones et al. [45] have reported the single crystal X-ray structure of Mg[Au(OH)$_4$]$_2$ and Ca[Au(OH)$_4$]$_2$, which have been obtained from reactions between HAuCl$_4$ and Ca(OH)$_2$.

Beckham et al.[39] noted that, when nitric acid is mixed with solid sodium chloride, there are formed sodium nitride, chlorine, and nitrosyl chloride: $3\,NaCl + 4\,HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2\,H_2O$. They mentioned that "the system is similar to aqua regia." Concentrated NOCl in solution, such as aqua regia, should give a more dark orange or reddish color. The UV-visible absorption cross-sections of NOCl have been reported [46].
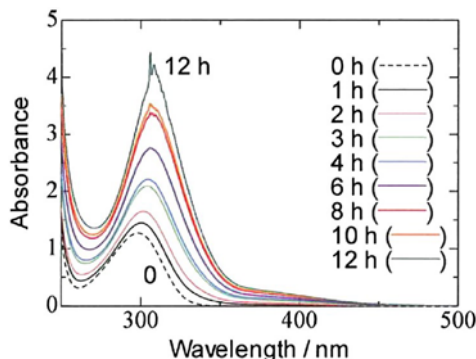

Figure 11. Changes in the UV–vis absorption spectra with time of $AuCl_4^-$ in 2.0 mol dm^{-3} HNO$_3$ containing 3.5 mol dm^{-3} NaCl at 40 °C.

The dissolution reaction rate constants (the first-order reaction) have been evaluated with the changes in the solid gold mass as well as the absorbance at $\lambda \sim 375$ nm, for avoiding the rather large HNO$_3$ absorbance (at $\lambda \sim 300$ nm). We have adopted the linear part of the plots of ln [S] vs. t, since the plots tend to deviate from the linearity downward (i.e., reaction accelerated) after the half-life period. It should be mentioned that the rate constant is for the initial dissolution process and that effects of the surface area on the reaction rate can be minimized by taking the values obtained with the initial part of each experiment.

Table 2. The gold dissolution rate constant, $\log (k/s^{-1})$, measured in 2.0 mol dm^{-3} HNO$_3$, accompanied by various added chloride salts at 40 °C.

c(salt)/mol dm^{-3}	LiCl	NaCl	MgCl$_2$	CaCl$_2$	AlCl$_3$
0.5					-4.67[a]
					-4.63[b]
1.0			-4.49	-4.59	-4.00
			-4.48	-4.57	-3.97
1.5			-4.09		-3.61
			-4.07		-3.60
2.0	-4.39	-4.62	-3.82	-4.09	
	-4.37	-4.69		-4.06	
3.0	-4.10	-4.29	-3.51	-3.99	
	-4.03	-4.27			
3.5		-4.21			
		-4.27	-3.54	-4.26	
4.0	-3.84				
	-3.84				
5.0	-3.59				
6.0	-3.62				

[a] The (k/s^{-1}) values in the upper rows are evaluated from the loss of the gold mass, ln (M_t/M_0) vs. t/s where M_0 and M_t are the gold masses at the initial and a certain time, respectively.
[b] The (k/s^{-1}) values in the lower rows are evaluated from the absorbance values at 375 nm, ln $(A_\infty - A_t)$ vs. t/s where A_∞ and A_t are absorbance values after the complete gold dissolution and at a certain time, respectively.

In general, rate constants obtained by the different two ways are consistent to each other (cf. Table 2). However, the results from the absorbance method can be fluctuated, especially, when the concentrations of the chloride ion are quite high; in such cases, the solution turns already to a yellow color

before placing gold. For its simplicity, we may take the rate constants obtained by the loss of the gold mass, except for some cases in which the mass method could not be appropriately applied. In the present paper, the rate constants evaluated by the mass method are given, unless otherwise noted.

2.3 Gold dissolution into seawater and the seawater assisted by added chloride salts

Seawater is an electrolyte solution. Its chemistry is dominated by the presence of six ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) which constitute more than 99.5% of the dissolved constituents [47]. The concentrations of the main components have been reported to be 0.468, 0.010, 0.053, 0.010, 0.545, and 0.028 mol kg^{-1}, respectively, for the 35‰ seawater [48]. Taking into account its density (d = 1.025 as the average)[49], we can regard the seawater as a 0.55 ~ 0.56 mol dm^{-3} chloride solution with mainly sodium and partly magnesium cations.

All experimental results in the present work strongly suggest that pure gold should dissolve in seawater if it is mixed with aqueous nitric acid and then heated. We have utilized "Muroto Deep Seawater" as a standard sample of seawater. The main components in the seawater are well consistent with the typical 35‰ seawater. By mixing 50 mL seawater with 50 mL of 2.0 mol dm^{-3} HNO_3, we have a 100 mL solution of 1.0 mol dm^{-3} HNO_3 containing 0.278 mol dm^{-3} Cl^-, 0.225 mol dm^{-3} Na^+, 0.026 mol dm^{-3} Mg^{2+} (0.014 mol dm^{-3} SO_4^{2-}) and other ions. The mixed solution is heated up to ca. 100 ºC in a flask, equipped with a condenser. When boiling starts, then five pieces of gold wire (totally 0.10 g) are placed into the solution. Occasionally, samplings are carried out from the boiling solution and the pieces of gold wire are dissolved completely within 17 hours. The absorbance values at l = 375 nm are utilized for evaluating the dissolution rate constant to give log (k /s^{-1}) = -4.52. Another Pacific seawater off Hawaii (1,000 m depth) gives a value (-4.54) similar to that of "Muroto Deep Seawater". Although ten pieces of gold wire (totally ca. 0.20 g) have appeared to dissolve completely in the 100 mL (seawater and nitric acid mixture) solution, after cooling down, some residue is noticed on the solution surface. Therefore, we keep five pieces (0.10 g) of gold wire as the limit for the seawater experiments. Incidentally, platinum is too tough to be dissolved in the seawater and 2.0 mol dm^{-3} HNO_3 (1:1) mixture even after 10 days at ca. 100 ºC. However, within 24 hours, a piece of Pd wire (0.04 g, 0.25 mm diameter, 99.9%) has dissolved in a 50 mL mixed (1:1) solution between the seawater and 2.0 mol dm^{-3} HNO_3 at ca. 100 ºC.

Fig. 12 shows the increasing dissolution rate constant with increasing NaCl added to the seawater. The solution preparation procedure is as follows: The seawater is poured to 11.69 g NaCl crystals up to 50 mL in a volumetric flask to prepare an additional 4.0 mol dm^{-3} NaCl seawater solution. Mixing between 50 mL of 2.0 mol dm^{-3} HNO_3 and 50 mL of the additional 4.0 mol dm^{-3} NaCl seawater solution gives 100 mL of 1.0 mol dm^{-3} HNO_3 containing additional 2.0 mol dm^{-3} NaCl seawater solution (totally ca. 2.23 mol dm^{-3} Na^+ and ca. 2.28 mol dm^{-3} Cl^-).

The log (k /s^{-1}) value increases remarkably from -4.52 to -3.71 with additional 0.5 mol dm^{-3} NaCl and it remains almost a constant value up to 2.0 mol dm^{-3} NaCl. As for platinum, however, a 2.8 mg Pt mass has been left without dissolving out of ca. 20 mg platinum wire (0.1 mm diameter) in 100 mL of the 1.0 mol dm^{-3} HNO_3 and 0.5 mol dm^{-3} NaCl added seawater after six days. Without the support by additional salts, however, no Pt can be dissolved in the 1:1 mixture between seawater and 2.0 mol dm^{-3} HNO_3 (vide supra).

We just mention that the "excellent" dissolution ability of seawater mixed with 2.0 mol dm^{-3} HNO_3 for gold has been successfully applied to collecting of gold from waste electronic devises, just mechanically tipped. The ICP-atomic emission spectrometry has demonstrated the dissolution of Au out of the waste electronic devices, as well as Cu, Ni, Al, Si, Zn, and B. Recovery of gold from secondary sources has been widely reviewed by S. Syed [50].

2.4 "Dilute aqua regia" of various HNO_3 and HCl concentrations

In the CRC book [51] 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". According to this description, it has been well known that dilution with water is essential for the long term storage of active aqua regia. Assuming 16 mol dm^{-3} HNO_3 (70%) and 12 mol dm^{-3} HCl, the original aqua regia is composed of 4 mol dm^{-3} HNO_3 and

9 mol dm^{-3} HCl, while the water added solution is calculated to contain still 3.2 mol dm^{-3} HNO$_3$ and 7.2 mol dm^{-3} HCl.
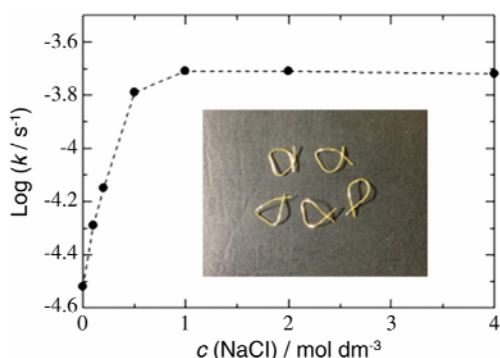

Figure 12. The increase of the dissolution rate constant of gold wire with increasing added NaCl concentration in the 1.0 mol dm^{-3} HNO$_3$ and seawater (a half-concentration) solution at ca. 100 °C. The rate constants have been evaluated by means of spectroscopy.
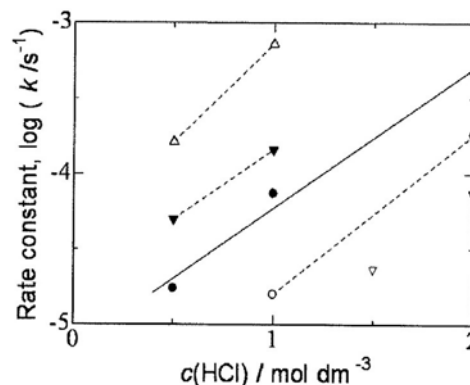
Figure 13. The dissolution rate constants of gold wire (19.7 ± 0.5 mg) in various concentrations of "dilute aqua regia" at 60 and ca. 100 °C: (▽) 0.5 mol dm^{-3} HNO$_3$ 60 °C; (○) 1.0 mol dm^{-3} HNO$_3$ 60 °C; (●) 2.0 mol dm^{-3} HNO$_3$ 60 °C; (▼) 0.5 mol dm^{-3} HNO$_3$ 100 °C; (△) 1.0 mol dm^{-3} HNO$_3$ 100 °C. The rate constants at 60 and ca. 100 °C have been evaluated by the mass and spectroscopy, respectively.

The gold dissolution in "dilute aqua regia" has been examined with different HNO$_3$ and HCl combinations in various concentrations: 0.5, 1.0, and 2.0 mol dm^{-3} HNO$_3$; 0.5, 1.0, (1.5), and 2.0 mol dm^{-3} HCl at 60 ºC (cf. Fig. 13). The [1.0, 1.0] "dilute aqua regia" (of 1.0 mol dm^{-3} HNO$_3$ and 1.0 mol dm^{-3} HCl) gives a dissolution rate constant of log (k /s^{-1}) = -4.80 at 60 ºC. With increased HCl concentration, i.e., of 2.0 mol dm^{-3}, the rate constant increases: the [1.0, 2.0] "dilute aqua regia" gives -3.74. The [2.0, 0.5], [2.0, 1.0], and [2.0, 2.0] solutions give a linear relation between log (k /s^{-1}) and c(HCl) values, to be -4.76, -4.13, and -3.33. Comparing the [0.5, 2.0] with the [2.0, 0.5] solution, we have noticed that the [0.5, 2.0] (-4.13) is faster than the [2.0, 0.5] (-4.76), probably because the ratio between c(HNO$_3$) and c(HCl) in the [0.5, 2.0] may be more favorable than that of the [2.0, 0.5] as the "dilute aqua regia" medium. Similarly, the [1.0, 2.0] (-3.74) is faster than the [2.0, 1.0] (-4.13) at 60 ºC. At 100 ºC, the rate constant of "dilute aqua regia" increases remarkably, e.g. the [1.0, 1.0] (-3.14) at ca. 100 ºC is 46 times faster than the [1.0, 1.0] (-4.80) at 60 ºC. In a very "dilute aqua regia," it takes a very long time to dissolve gold wire (ca. 19.7 mg) completely: 8 days in both the [0.5, 1.0] and the [1.0, 0.5] solutions at 60 ºC.

Conclusion

Nitration of phenols was performed by dilute nitric acid (2.0 mol dm^{-3}) in reversed micelle systems at 35 ºC. Even dilute nitric acid in bulk water system, provided it contains salts in high concentrations, can oxidize the Cl$^-$ ion to Cl$_2$ as well as Br$^-$ to Br$_2$. The nitronium ion (NO$_2^+$), the active species for nitration or oxidation, can be generated not only in water phase of reversed micelle systems but also in bulk water containing salts in high concentrations. Just as the water structure of nanoscale water droplets in reversed micelle systems is distorted, that of "bulk" aqueous solution can be also distorted by salts in high concentrations and, consequently, "bulk" aqueous solutions should lose the properties of the bulk water.

Although aqueous nitric acid (< 2 mol dm^{-3}) itself exhibits no oxidation ability, it acquires the strong oxidation ability to oxidize Cl$^-$ to Cl$_2$ in the presence of chloride salts. The chlorine (Cl$_2$)–chloride (Cl$^-$) systems provided by aqueous nitric acid containing enough amounts of chloride salts, have been found to be excellent media for dissolving precious metals, especially, pure gold. In general, the increasing concentrations of chloride salts cause the advanced ability for gold dissolution. At higher temperatures, such as 60 or 100 ºC, gold can easily be dissolved into the mixed solution between diluted aqueous HNO$_3$ and HCl, i.e. "dilute aqua regia", which can be applied to prepare a 1000 ppm gold stock solution easily. The "excellent" gold dissolution ability of the mixture of sea-

water with aqueous nitric acid can be applied to the recovery of gold from waste electronic devices. In electrochemical operation, the Au or Pt electrodes can be dissolved naturally in concentrated halides salt solutions.

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М. Ходжо. Механизм повышенной окисляющей способности разбавленной азотной кислоты и растворение металлического золота в азотной кислоте, разбавленной морской водой.

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Обнаружено, что разбавленная азотная кислота в обращённых мицеллах может окислять ион Br^- до Br_2, и предложено использовать нитроний, NO_2^+, как активный реагент в окислительном процессе. Нитрование фенола разбавленной азотной кислотой в водной дисперсной фазе обращённой мицеллярной системы $CHCl_3$/хлорид цетилтриметиламмония/H_2O (2.0 моль дм$^{-3}$ HNO_3 при содержании воды 1.0 % (v/v), проведённое при 35 ºC, привело к образованию 2- и 4-нитрофенолов. В водном растворе HNO_3 с концентрацией 2.0 моль дм$^{-3}$ в присутствии 4.0 моль дм$^{-3}$ LiCl и небольшого количества LiBr как источника бромида *транс*-1,4-дибром-2-бутен успешно бромируется до 1,2,3,4-тетрабромбутана. Этот результат является хорошим подтверждением возможности окисления иона Br^- до Br_2 в разбавленной до 2.0 моль дм$^{-3}$ азотной кислоте в присутствии концентрированных солей. Для серии хлоридов эффект катиона возрастает в ряду: Et_4N^+ << Na^+ < Li^+ < Ca^{2+} < Mg^{2+}. Наблюдалось даже выделение Cl_2 из раствора HNO_3 с концентрацией < 2.0 моль дм$^{-3}$, содержащего высокие концентрации LiCl, $MgCl_2$ и $CaCl_2$, а также $AlCl_3$. Показано растворение благородных металлов (Au, Pt, and Pd) и особенно золота в 0.1 - 2 моль дм$^{-3}$ HNO_3 в присутствии хлоридов щелочных и щелочноземельных металлов, а также хлорида алюминия. Время полного растворения пластины из металлического золота массой 20±2 мг и толщиной 0.1 мм в 2.0 моль дм$^{-3}$ HNO_3 в присутствии 1.0 моль дм$^{-3}$ $AlCl_3$ заметно сокращается при повышении температуры от 15 до 80 ºC. Скорость растворения кусочка золотой проволоки массой 19.7±0.5 мг в 20 мл раствора HNO_3 концентрации 2.0 моль дм$^{-3}$ в

присутствии хлоридов металлов в целом возрастает при увеличении концентрации солей при 40 и 60 ºC. Золото может растворяться при концентрациях HNO₃ и HCl менее 1.0 моль дм⁻³, т.е. в "разбавленной царской водке". Нами достигнуто полное растворение пяти кусочков золотой проволоки суммарной массой 0.10 г в 100 мл смеси морской воды с 2.0 моль дм⁻³ HNO₃ в соотношении 1: 1 при ≈ 100 ºC.

Ключевые слова: нитроний ион, хлорид цетилтриметиламмония, выделение хлора, окисление бромида, солевой эффект, структура объёмной воды, разбавленная царская водка, тетрахлораурат, концентрированная соль, Рамановский спектр.

М. Ходжо. Механізм підвищеної окислюючої здатності розведеної нітратної кислоти і розчинення металевого золота в нітратній кислоті, розведеній морською водою.

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Знайдено, що розведена нітратна кислота в обернених міцелах може окислювати іон Br⁻ до Br₂, та запропоновано використовувати нітроній, NO₂⁺, як активний реагент в окислювальному процесі. Нітрування фенолу розведеною нітратною кислотою в водній дисперсній фазі оберненої міцелярної системи CHCl₃/хлорид цетилтриметиламонію/H₂O (2.0 моль дм⁻³ HNO₃ при вмісті води 1.0 % (v/v), проведене при 35 ºC, привело до створення 2- та 4-нітрофенолів. У водному розчині HNO₃ з концентрацією 2.0 моль дм⁻³ в присутності 4.0 моль дм⁻³ LiCl і невеликої кількості LiBr як джерела броміду *транс*-1,4-дибром-2-бутен успішно хромується до 1,2,3,4-тетрабромбутану. Цей результат є добрим підтвердженням можливості окислення іону Br⁻ до Br₂ в розведеній до 2.0 моль дм⁻³ нітратній кислоті у присутності концентрованих солей. Для серії хлоридів ефект катіону зростає у послідовності: Et₄N⁺ << Na⁺ < Li⁺ < Ca²⁺ < Mg²⁺. Спостерігалося також виділення Cl₂ з розчину HNO₃ з концентрацією < 2.0 моль дм⁻³, який містить високі концентрації LiCl, MgCl₂ и CaCl₂, а також AlCl₃. Показано повне розчинення благородних металів (Au, Pt, and Pd) і особливо золота в 0.1 - 2 моль дм⁻³ HNO₃ в присутності хлоридів лужних та лужноземельних металів, а також хлориду алюминию. Час повного розчинення пластини з металевого золота масою 20±2 мг і товщиною 0.1 мм в 2.0 моль дм⁻³ HNO₃ в присутності 1.0 моль дм⁻³ AlCl₃ помітно зменшується при підвищенні температури від от 15 до 80 ºC. Швидкість розчинення шматочка золотого дроту масою 19.7±0.5 мг в 20 мл розчину HNO₃ з концентрацією 2.0 моль дм⁻³ в присутності хлоридів металів в цілому зростає при підвищенні концентрації солей при 40 і 60 ºC. Золото може розчинятися при концентраціях HNO₃ і HCl менших ніж 1.0 моль дм⁻³, тобто в «розведеній царській водці». Нами досягнуте повне розчинення п'яти шматочків золотого дроту сумарною масою 0.10 г в 100 мл суміші морської води з 2.0 моль дм⁻³ HNO₃ у співвідношенні 1:1 при ≈ 100 ºC.

Ключові слова: нітроній іон, хлорид цетилтриметиламонію, виділення хлору, окислення броміду, сольовий ефект, структура об'ємної води, розведена царська водка, тетрахлораурат, концентрована сіль, Рамановський спектр.