Notes

Effects of Nonaqueous Solvents on the Polarographic Reduction of Nitrate Ion in the Presence of Zirconium(IV)

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The electrochemical reduction of nitrate ions at mercury electrodes in the presence of various electrode-inert metal ions has been investigated for various purposes.1-3 We have studied the reduction of nitrate to discover why the nitrate ion (nitric acid) is a powerful oxidizing agent in acidic solution, although it is not an oxidizing agent in neutral or alkaline solution. In general, a reluctant and a proton supplier are needed for the reduction of nitrate. In the electrochemical reduction of nitrate, the reluctant is the electrons in the electrode and the proton supplier should be water or something in the neutral or weakly acidic solution. We found that the nitrate reduction potential becomes 1.3–1.5 V more positive in the presence of zirconium(IV) ion than in its absence (in the presence of 0.1 M LiCl alone).1 These research results1-3 indicated that the metal ion acted as an intermediary for the charge transfer from the electrode to the nitrate ion and as a proton supplier to the nitrate by hydrolysis of the metal ion itself in the proximity of the electrode. However, because only the effects in the vicinity of the electrode have been discussed so far, we tried to consider in this study how the bulk properties affect the electrochemical reduction of nitrate. Therefore, because, as far as we know1-3, zirconium(IV) has the largest effect on the reduction of nitrate of the many electrode-inert metal ions, the zirconium(IV)–nitrate system was selected and nonaqueous solvents were mixed with the aqueous solution of this system in order to determine the bulk effects.

Experimental

Materials

Commercially obtained dimethyl sulfoxide (DMSO), methanol (MeOH), acetone (AC), acetonitrile (AN), N,N-dimethylformamide (DMF), 1,4-dioxane (DX) [Dojin Chemical Lab., Spectrosol Grade], ethanol (EtOH) [Wako Pure Chemical Industries, Super Special Grade], formamide (FA) [Wako, GR Grade] and hexamethylphosphoric triamide (HMPA) [Wako, 95+% Pr. Grade] were used after drying with molecular sieves [Wako, 4A 1/8]. These solvents were kept with the molecular sieves in a silica gel desiccator. Commercially obtained ferrocene [Wako, GR Grade] was purified by recrystallizing twice from methanol [Wako, GR Grade]. All other chemicals were of guaranteed-reagent grade [Wako].

Apparatus and procedure

The indicator electrode for the dc polarography was a dropping mercury electrode (DME); the mercury flow rate was 1.660 mg s⁻¹ at a height of 70 cm and the drop time was 4.60 s in 0.1 M KCl aqueous solution at open circuit. A glassy carbon disk electrode, Nikko Keisoku, NED-2 (3 mm) (Tokai Carbon GC20 covered with a Teflon tube) and/or a platinum disk electrode, Yanagimoto, P171 (3 mmφ) were used as the indicator electrode for recording the cyclic voltammogram of the ferrocene/ferricinium couple. The electrochemical instrumentation consisted of a function generator (Nikko Keisoku, Model NFG-3), a potentiostat (Nikko Keisoku, Model NPOT-2501) and an X−Y recorder (Yokogawa, Type 3086).

The electrochemical cell for mixed solvents was

Ag | AgCl, sat.KCl aq. | 0.1 M LiClO₄ aq. | Sample solution | DME or other electrode.

An agar salt bridge with 1 M KCl was used as a junction between the Ag/AgCl reference electrode and the 0.1 M LiClO₄ aqueous solution. Another agar salt bridge with 0.1 M LiClO₄ was between the 0.1 M LiClO₄ aqueous solution and the sample solution containing 0.1 M LiClO₄ in mixed solvents. After we measured the polarogram of the sample using the above cell, we added
0.015 g of ferrocene to the sample solution (40 ml) to make 2 mM or saturated ferrocene solution and we recorded the cyclic voltammogram (scan rate, \(v=50 \text{ mV/s}\)) for the ferrocene/ferricinium couple at the glassy carbon and/or the platinum disk electrodes. The peak potential difference was 54 - 65 mV in all sample solutions; this indicated a reversible process. Therefore, the \(E_{1/2}(\text{Fc}) = (E_p + E_a)/2\) of the ferrocene/ferricinium system was employed as a reference potential for the mixed solvent samples although this redox system has some problems in water solution for example, bis(biphenyl)chromium(I) cannot be used in water because of its low solubility. The \(E_{1/2}(\text{Fc})=0.397 \text{ V vs. NHE}\) at the glassy carbon electrode in water (cf. 0.400 V8 and 0.390 V9) was obtained in this work. In all sample solutions, the same potential was obtained using either the glassy carbon or the platinum electrode. The liquid junction potential was not corrected because this potential difference would be small for our cell system of \(x_s \approx 0.3\), where \(x_s\) was the molar fraction of nonaqueous solvent in the solution.

**Results and Discussion**

Figure 1 shows the polarograms of nitrate ions in the presence of Zr(IV) in various mixed solvents \((x_s=0.00 - 0.97)\) of methanol and water. The 0.2 mM Zr(IV)+10 mM LiNO3+1.0 mM HClO4+90 mM LiClO4 solution was selected in order to compare with our previous aqueous solution \((x_s=0.00)\) results.1 The limiting current for nitrate ions \(i_d\) decreased, and the half-wave potential \((E_{1/2}(\text{NO}_3^-))\) shifted in the negative direction with an increase in the molar fraction of methanol. When the molar fraction, \(x_s\), is greater than 0.5, we can observe the proton wave but not the nitrate wave because

![Fig. 1](image-url)  
*Fig. 1 The polarograms of nitrate ions in the presence of Zr(IV) in mixed solvents of water and methanol for various molar fractions \((x_s)\): 0.2 mM ZrOCl2+10 mM LiNO3+1 mM HClO4+90 mM LiClO4.*

![Fig. 2](image-url)  
*Fig. 2 The dependence of \((A) E_{1/2}(\text{NO}_3^-)\) and \((B) i_d\) on \(x_s\) in water–various organic solvents.*
of the precipitation of zirconium(IV). Therefore, in order to compare the effects of the addition of nine nonaqueous solvents to water on \( i_d \) and \( E_{1/2}(\text{NO}_3^-) \), the polarograms were recorded in mixed solvents whose molar fractions \( (x_i) \) were 0.1 and 0.3. The polarograms in the mixed solvents of water and the organic solvent except methanol were similar in shape to those of water–methanol. The results for \( i_d \) and \( E_{1/2}(\text{NO}_3^-) \) are given in Fig. 2. In every mixed solvent, the limiting current decreased, and the half-wave potential moved in the negative direction with an increase in the molar fraction of organic solvent as in the case of water–methanol, though this was not the case for \( i_d \) in water–HMPA. This shows that, with regard to the solvents used, the nitrate ion is less reducible in the mixed solvent than in water.

We tried to plot the half-wave potentials as the ordinate versus various characteristics of the medium as the abscissa. In those plots, a linear relationship was observed between the half-wave potential of the nitrate ions and the acceptor number of the mixed solvent as shown in Fig. 3. The equation for this line is \( \left( E_{1/2}(\text{NO}_3^-)/V \right) = 4.00 - 0.055 \times \text{(acceptor number)} \) with a correlation coefficient, \( r=0.910 \) (if a point for DMF was excluded from the plots, though we have no reasons for this exclusion, the line equation would be \( \left( E_{1/2}(\text{NO}_3^-)/V \right) = 3.83 - 0.052 \times \text{(acceptor number)} \), \( r=0.972 \)). The \( E_{1/2}(\text{NO}_3^-) \) only for \( x_i=0.1 \) is used for the plots because even if a potential difference caused by the liquid junction and/or by the reference potential \( (E_{1/2}(\text{Fe}) \) is included in the \( E_{1/2}(\text{NO}_3^-) \) value, it will be small or within experimental error at \( x_i=0.1 \). In general, the acceptor number can be explained by the effects of the polarity/polarizability and the proton dionicity of the solvent. These results indicate that, as the proton dionicity of the solvent to the nitrate ions is increased, the nitrate ion becomes more reducible in the presence of \( \text{Zr}^{IV} \). As also mentioned in our previous papers, an electron supplier and a proton donor are necessary for the reduction of nitrate. Therefore, we suggested that the electrode-inert metal ion (e.g., \( \text{Zr}^{IV} \)) had two roles in the reduction, as follows: an intermediary for the charge transfer and a proton supplier by the hydrolysis of the metal ion itself near the electrode. In this work, we also suggest that the medium (water–organic solvent) acts as a proton supplier to the nitrate ions.

The effect of the medium on the nitrate reduction kinetic mechanism will be investigated in more detail. In particular, the dissolved zirconium(IV) species will be studied using a spectroscopic method, and the double layer effect will be investigated by ac polarography.

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References


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