Chemiluminescence Determination of Thiourea Using Tris(2,2′-bipyridyl)ruthenium(II)–$KMnO_4$ System

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The emission produced by thiourea in oxidation by permanganate in acidic solution in the presence of $Ru(bipy)_3^{2+}$ is used to determine 1.8×10^{-8} to 1.8×10^{-6} mol/l thiourea. The limit of detection is 1.0×10^{-8} mol/l and the relative standard deviation is 1.1% for a 1×10^{-5} mol/l thiourea solution (n=10). The method was applied satisfactorily to the determination of thiourea.

Keywords Thiourea, chemiluminescence, tris(2,2′-bipyridyl)ruthenium(II)

Thiourea (TU) has various industrial, agricultural and analytical applications. The material is widely used in photography as a fixing agent and to remove stains from negatives, and in agriculture as fungicide, herbicide and rodenticide. TU is also used as a spectrophotometric reagent for the determination of several metals.

Various methods have been proposed for the determination of TU, such as Raman spectrometry[1], polarography[2], stripping voltammetry[3], high-performance liquid chromatography[4], kinetic methods[5,6], piezoelectric detection[7], potentiometric method[8], pulsed amperometry[9], oxalate-catalyzed oxidimetric method with $KMnO_4$[10], electrokinetic reversed-phase chromatography[11] and FIA fluorometry.[12]

Despite the large number of methods, most of them lack either sensitivity or simplicity. The CL method has been widely used because of its high sensitivity and simplicity. $Ru(bipy)_3^{2+}$ is a widely used electrogenerated CL reagent[13] and has become a useful CL reagent. It has been used for the determination of some organic acids in the $Ru(bipy)_3^{2+}$–Ce(IV) chemiluminescence system.[14,15] We used it in TU–$KMnO_4$ system to determine TU.

In this paper the development of the TU–$KMnO_4$ CL method for the determination of thiourea and its application to the sample analysis is presented. The emission intensity of the system is greatly enhanced by the presence of $Ru(bipy)_3^{2+}$ and surfactant sodium dodecylbenzene sulfonate (SDBS). It was used for the determination of thiourea in grape wine.

Experimental

Apparatus

An LKB 1251 luminometer with a Dispenser SVD and a Dispenser controller DC (Pharmacia LKB Biotechnology AB, Sweden) and an Epson LX-800 printer were used.

Reagents

All solutions were prepared from analytical-reagent grade materials in doubly distilled water.

A 0.1 mol/l stock solution of thiourea was prepared daily by dissolving 0.741 g of thiourea in water and diluting with water to 100 ml. $Ru(bipy)_3^{2+}$ (prepared in our laboratory[15]) solutions were prepared by dissolving a weighed amount of $Ru(bipy)_3Br_2$ in water and diluting to volume. The concentration of the stock solution is 4.48×10^{-3} g/ml.

Potassium permanganate stock solutions were prepared by dissolving a weighed amount of $KMnO_4$ in water and adding a pre-determined volume of 1.0 mol/l H_2SO_4 and diluting to volume. Working solution were prepared by dilution of the stock solution with 1.0 mol/l H_2SO_4 and water.

The 2.0 % solutions of Tween-20, Tween-40, Tween-80 and Triton X-100 were prepared by dissolving 2.0 g in water and diluting with water to 100 ml. The 1.0×10^{-2} mol/l solutions of sodium dodecyl benzene sulfonate (SDBS), tetradecyl pyridine bromide (TPB), cetyl pyridine bromide (CPB), cetyl trimethyl ammonium bromide (CTAB) were prepared by dissolving 0.348, 0.356, 0.384, or 0.364 g of them in water and diluting with water to 100 ml.

Procedure

A 0.2 ml amount of thiourea and 0.2 ml of 2×10^{-3}

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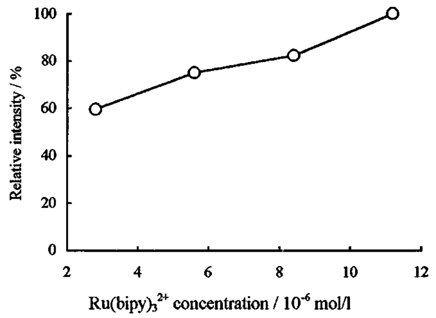

Fig. 1 Effect of $Ru(bipy)_3^{2+}$ concentration on the emission intensity from 1×10^{-5} mol/l thiourea at 2.5×10^{-5} mol/l $KMnO_4$ in the presence of 7.5×10^{-3} mol/l H_2SO_4 and 5×10^{-4} mol/l SDBS.

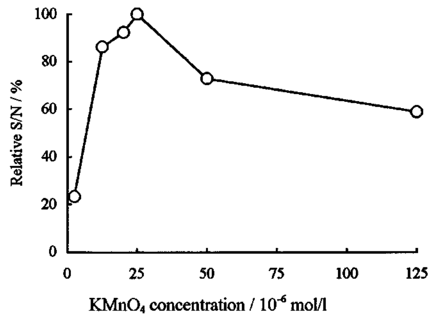

Fig. 2 Effect of $KMnO_4$ concentration in 7.5×10^{-3} mol/l sulfuric acid on the emission intensity from 1×10^{-5} mol/l thiourea in the presence of 5.6×10^{-6} g/ml $Ru(bipy)_3^{2+}$ and 5×10^{-4} mol/l SDBS.

Table 1 Effect of oxidant on the emission intensity (mV)

Oxidant					
$KMnO_4$	$KBrO_3$	KIO_4	$K_2S_2O_8$	I_2	$Ce(SO_4)_2$
18.0	0.52	0.51	0.50	0.60	34.0

mol/l SDBS and 0.2 ml of 2.24×10^{-5} g/ml $Ru(bipy)_3^{2+}$ were mixed in this order in the sample cuvettes and then transferred into the measuring chamber at a constant temperature of 25˚C. After the start button was pressed, 0.2 ml of 1×10^{-4} mol/l $KMnO_4$ (3×10^{-2} mol/l H_2SO_4) was injected automatically and the peak height was recorded. The reagent blank was recorded with the same procedure except that the thiourea was replaced with doubly distilled water.

Calibration graphs of emission intensity [I(mV)] *versus* thiourea concentration [C(mol/l)] were prepared to determine the thiourea content of the samples. A standard sample solution was included after every 5 samples.

Results and Discussion

Effect of concentration of $Ru(bipy)_3^{2+}$

The emission intensity increases with increasing concentration of $Ru(bipy)_3^{2+}$. This is shown in Fig. 1: 5.6×10^{-6} g/ml of $Ru(bipy)_3^{2+}$ was used in this study.

Effect of oxidants

Six oxidants have been tested. The emission intensity with $KMnO_4$ is the highest among them except $Ce(SO_4)_2$, which has higher blank intensity, as was shown in Table 1.

Effect of concentration of $KMnO_4$ *and sulfuric acid*

The effect of the concentration of $KMnO_4$ in 7.5×10^{-3} mol/l sulfuric acid is shown in Fig. 2. The optimum concentration for the oxidant is 2.5×10^{-5} mol/l when 1×10^{-5} mol/l thiourea, 5×10^{-4} mol/l SDBS and 5.6×10^{-6} g/ml $Ru(bipy)_3^{2+}$ were used.

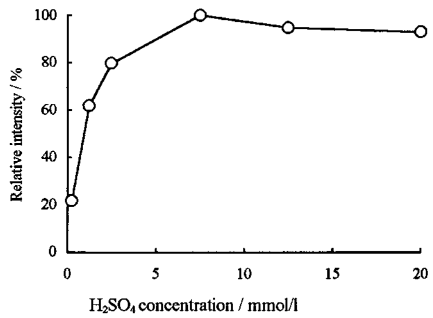

Fig. 3 Effect of H_2SO_4 concentration on the emission intensity from 1×10^{-5} mol/l thiourea at 2.5×10^{-5} mol/l $KMnO_4$ in the presence of 5.6×10^{-6} g/ml $Ru(bipy)_3^{2+}$ and 5×10^{-4} mol/l SDBS.

$KMnO_4$ is a strong oxidant in sulfuric acid solution and the CL intensity was affected by the concentration of the acid (see Fig. 3). The optimum concentration of sulfuric acid was 7.5×10^{-3} mol/l.

Effect of sensitizers

Eight kinds of sensitizers have been investigated in our study. They are SDBS, Tween-20, Tween-40, Tween-80, Triton X-100, TPB, CPB and CTAB. SDBS has the highest enhancement among them. The effect of the concentration of SDBS in the system is shown in Fig. 4. The optimum concentration for SDBS is 5×10^{-4} mol/l.

Effect of mixing order of reagents

The emission intensity is affected by the mixing order of reagents. This is shown in Table 2.

Effects of various ions and solvents

Various ions and solvents commonly used in the laboratory were tested from high to low concentration. It was shown that the CL intensity was not much changed for the determination of 5×10^{-6} mol/l thiourea when any of the following were present: 2000-fold Na^+, NO_3^-, 1500-fold Ac^-, 650-fold Pb^{2+}, Mn^{2+}, K^+, Cl^-, 400-fold CO_3^{2-}, 200-fold Mg^{2+}, NH_4^+, 20-fold Ba^{2+}, Co^{2+}, Ni^{2+}, Br^-, 2-fold $C_2O_4^{2-}$, 0.1 mol/l F^-, 3×10^{-4} mol/l Al^{3+}.

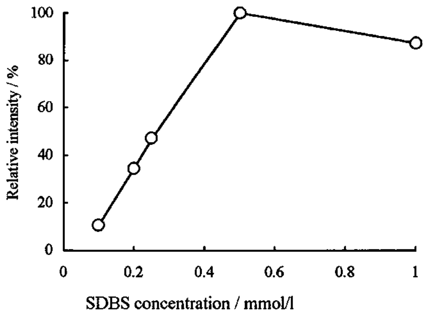

Fig. 4 Effect of SDBS concentration on the emission intensity from 1×10^{-5} mol/l thiourea at 2.5×10^{-5} mol/l $KMnO_4$ in the presence of 5.6×10^{-6} g/ml $Ru(bipy)_3^{2+}$ and 7.5×10^{-3} mol/l sulfuric acid.

Calibration and detection limit

Under the recommended conditions, the calibration graph was stepwise linear from 1.8×10^{-8} to 1.8×10^{-6} mol/l thiourea. The maximum peak height increased linearly within two thiourea concentration ranges, as expressed by the equations $I_1=8.3+2.3\times10^7C_1$, $r=0.9999$, (C_1: 1.8×10^{-8} to 1.8×10^{-7} mol/l), $I_2=98+1.7\times10^7C_2$, $r=0.9939$, (C_2: 1.8×10^{-7} to 1.8×10^{-6} mol/l). The detection limit is 1.0×10^{-8} mol/l (DL=$3s/r$), and the relative standard deviation (RSD) is 1.1% for the 1×10^{-5} mol/l thiourea solution (n=10).

The determination of thiourea in grape wine

The method was applied to the determination of thiourea in white grape wine. The sample was diluted 1000-fold with distilled water. The spiked samples were prepared by mixing the standard and the diluted sample solution with equal volume. The recoveries were good enough for practical use and all determination results are listed in Table 3.

In conclusion, the CL reaction of $Ru(bipy)_3^{2+}$-thiourea-$KMnO_4$ can be satisfactorily applied to sensitive and reproducible determination of thiourea in white grape wine. Our reported method is simple and easy. It has high sensitivity and wide linear range compared with those of the other methods described in the introduction.

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Table 2 Effect of the mixing order of reagents

The order of reagents added	Emission intensity/mV
$Ru(bipy)_3^{2+}$ + SDBS + thiourea	574.6
$Ru(bipy)_3^{2+}$ + thiourea + SDBS	540.0
SDBS + thiourea + $Ru(bipy)_3^{2+}$	581.5
Thiourea + SDBS + $Ru(bipy)_3^{2+}$	603.2
Thiourea + $Ru(bipy)_3^{2+}$ + SDBS	606.7

Table 3 The determination of thiourea in white grape wine

Added/10^{-6} mol l^{-1}	Found/10^{-6} mol l^{-1}	Recovery, %
6.08	6.30	103.6
15.2	14.87	97.8
304.0	297.0	97.6

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