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CERIUM(IV)-SULFITE CHEMILUMINESCENT SYSTEM. ADDITION OF SODIUM DODECYLSULFATE FOR LINEARITY IMPROVEMENT AND INTERFERENCE REDUCTION

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The range in which chemiluminescence intensity of the cerium(IV) sulfate-sulfite system changes linearly with sulfite concentration has been expanded more than one order of magnitude (0.2-600 ng SO_2 ml^{-1}) by addition of sodium dodecylsulfate (SDS) to sample solutions. In addition, interferences from nitrite and halide ions were greatly reduced. The optimum concentration of SDS was found to be 1 g l^{-1} which was lower than the critical micelle concentration. The role of SDS was briefly discussed in terms of the interaction between water and the excited molecules.

In order to determine the trace amounts of sulfite species in atmospheric water droplets in connection with the acid precipitation, we have developed sensitive and continuous methods using a chemiluminescence (CL) technique[1,2]. Although the use of cerium(IV) sulfate as a reagent[2] was successful in obtaining a higher sensitivity and a lower detection limit than with potassium permanganate, the linear dynamic range decreased and some foreign species such as nitrite still interfered with the measurement.

It has been known that the characteristics of liquid-phase luminescence such as intensity and lifetime of excited species are affected by the polarity and viscosity of solvent, by the presence of heavy atoms and paramagnetic species, and by hydrogen bonding.[3] Therefore, the effect of addition of alcohols and surfactants to the CL system was examined. Methanol and glycerol (0.1-10%) simply decreased the CL intensity, while sodium dodecylsulfate (SDS) expanded the linear dynamic range and was effective to reduce the interferences. The present CL method can be applied to analyses of river and lake waters and samples from the food, textile and wood pulp industries with simple pretreatments.

The flow type analyzer described previously[1] was used with a vortex reaction cell in order to obtain a more efficient CL. The cell is made of polymethacrylate resin and is shown in Fig. 1, together with the conventional discoidal one. The reagent solution [0.3 mM $Ce(SO_4)_2$/10 mM H_2SO_4] and standard samples were prepared in the same manner as before.[2] A 50 g l^{-1} stock solution of SDS (biochemistry grade, Wako Pure Chemicals Co.) was prepared and was added to sample solutions to give required concentrations. Each of sample and reagent solution was pumped to the cell at a flow rate of 2 ml min^{-1}. A high voltage for the photomultiplier and the counting period were -710 V and 100 s, respectively. After the measurement, the cell was washed with purified water in order to prevent it from cracking.

The CL intensity obtained with the vortex cell was about three times that with the discoidal one. A detection limit of 0.09 ng SO_2 ml^{-1} was obtained, but the linear dynamic range became smaller (0 to 20 ng SO_2 ml^{-1}). A similar result was observed before: the $Ce(SO_4)_2$ reagent with the discoidal cell was ca. 5 times more efficient than the $KMnO_4$ reagent,$^{1)}$ but the upper limit of the linear dynamic range was decreased from 100 ($KMnO_4$) to 50 ng SO_2 ml^{-1} [$Ce(SO_4)_2$]. These results imply the interdependence of the efficiency and the linear dynamic range of chemiluminescence.

The relation between sulfite concentration (x) and CL intensity (y) in the presence and absence of SDS are shown in Fig. 2. The arrows denote the upper limit of linear dynamic range. A regression analysis of curve (a) gave the following equations: $y = 3.65x + 2.5$ ($r=0.995$) for $0 < [HSO_3^-] < 20$ ng SO_2 ml^{-1}, $y = 16.0x^{0.5} + 3.9$ ($r=0.997$) for $20 < [HSO_3^-] < 300$ ng SO_2 ml^{-1}, and $y = 63.9x^{0.25} + 14.8$ ($r=0.929$) for $[HSO_3^-] > 300$ ng SO_2 ml^{-1}. It is rather troublesome and unreliable to use the complicated nonlinear calibration curve to determine high concentrations of sulfite. By adding SDS to the sample solution, the linear range of the calibration curve was significantly increased (up to 600 ng SO_2 ml^{-1}). The CL intensity was smaller than that without SDS in the concentration region lower than 500 ng SO_2 ml^{-1}, but it became greater above that concentration.

The change of the linear dynamic range with the SDS concentration in sample solution (0.01-8 g l^{-1}) is shown in Fig. 3(a). Nearly identical linear calibration curves were obtained with SDS concentrations ranging from 0.5 to 2.0 g l^{-1}. SDS concentrations above and below the optimum range

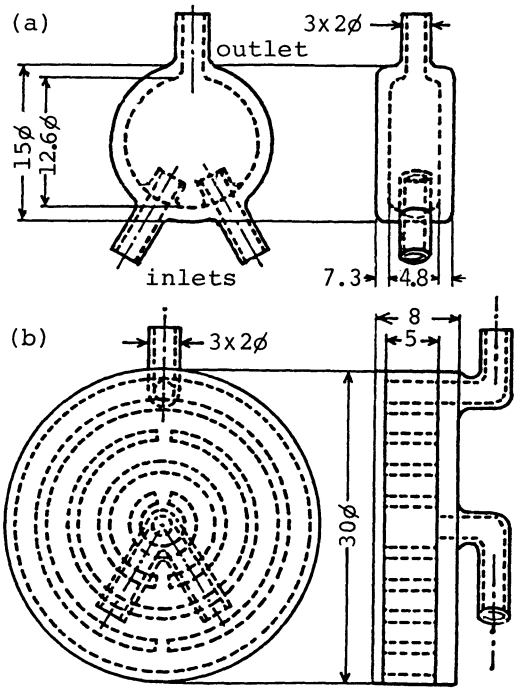

Fig. 1. Discoidal (a) and vortex-type (b) CL reaction cells (in mm).

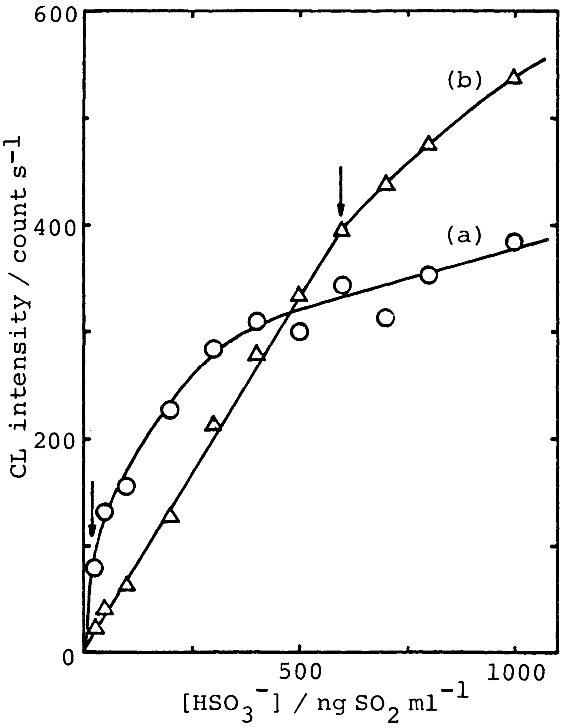

Fig. 2. CL intensity vs. [HSO_3^-]. Reagent: 0.3 mM $Ce(SO_4)_2$/0.01 M H_2SO_4. (a) without SDS, (b) with SDS (1 g/l). The arrows show the upper limit of linear dynamic range.

were less effective, and a higher background luminescence (curve b) was found with the higher SDS concentrations. Sample solutions containing 1 g l^{-1} of SDS was thus used in the following experiment. Although the addition of SDS resulted in the decrease in the slope of the calibration curve, the detection limit of 0.2 ng SO_2 ml^{-1} was maintained by using the vortex cell. The critical micelle concentration (CMC) of SDS under the optimum conditions for sulfite determination was measured conductometrically . The CMC was 2.3 g l^{-1} (7.9 mM) for standard sample solution and 1.37 g l^{-1} for the mixed solution in the cell (diluted with equal volume of the reagent solution). Figure 3 shows that no micelles exist at the optimum SDS concentration and that the micelle formation rather deteriorates the CL response.

The interferences from foreign species are shown in Table 1. The concentrations of interfering species which decreased the CL intensity of 20 ng SO_2 ml^{-1} samples by 10% and 50% are shown as $C_{90\%}$ and $C_{50\%}$, respectively, and those without SDS[2)] are given in parentheses. Interferences from NO_2^- and halide ions, which had been most significant interfering species, were remarkably reduced. Interferences from cationic and non-ionic species such as transition metal ions, H_2O_2 and aldehydes were also reduced, although the effect of SDS was not so remarkable as that for anionic species.

The use of surfactants and similar compounds has often been tried to produce some improvements in photometric analysis. The roles of them are generally classified into two categories. One is the enhancement of molar absorption coefficient due to coordination/association of surfactants (especially, cationic surfactants)[4,5)] with the molecule to be determined. The other is the stabilization of excited species and the elongation of the luminescence lifetime due to the formation of different environment isolated from the

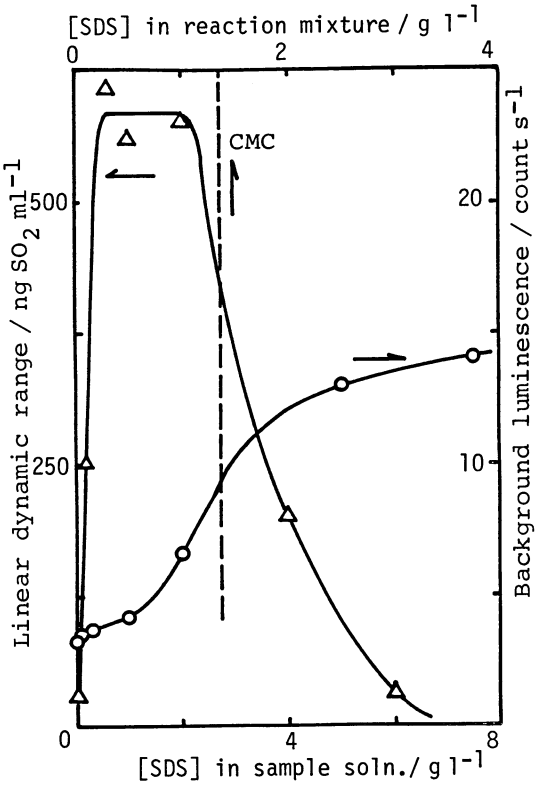

Fig. 3. Effect of SDS concentration on the upper limit of linear dynamic range and the background luminescence. Reagent: 0.3 mM $Ce(SO_4)_2$/0.01 M H_2SO_4.

Table 1. Interferences from foreign species with and without SDS[a)]

Species	$C_{90\%}$/ppm	$C_{50\%}$/ppm
NO_2^-	0.06 (0.008)	1.00(0.14)
Cl^-	10 (0.07)	>1000 (50)
Br^-	40 (0.016)	>500 (0.13)
I^-	0.012(0.002)	0.12(0.022)
Fe^{2+}	1.30 (1.10)	1.8 (1.7)
Mn^{2+}	0.082(0.045)	0.32(0.26)
HCHO	0.07 (0.15)	2.2 (1.1)
CH_3CHO	0.43 (0.057)	- (-)
H_2O_2	0.040(0.025)	0.65(0.18)

a) For $C_{90\%}$ and $C_{50\%}$, see text. Samples: 20 ng SO_2 ml^{-1} containing 1 g l^{-1} of SDS (values in parentheses are obtained without SDS).

bulk solution.6) It has been reported that SDS micelle7) and cyclodextrin8) enhance the fluorescence which otherwise is quenched by the medium (water). However, different mechanisms may be involved in our system, because the concentration of SDS is too low to form complexes or micelles.

According to Stauff and Jaeschke,9) the CL reaction associated with sulfite oxidation is rather complicated involving HSO_3 radical formation, recombination of them, and disproportionation to form an excited SO_2 molecule. The non-linear response to sulfite may be attributed to an interaction between the intermediates involved and the solvent (water) or other solute molecules. Since the slope of the calibration curve became smaller and the linearity became better than without SDS, it is considered that SDS interacts with the excited (or intermediate) molecule more strongly than water and weakens the interaction between the excited molecules and water or other solutes. Clifford and Pethica10) measured the ^{1}H-NMR spectra of aqueous SDS solution and found that the chemical shift of water protons moved to upfield with the increase in SDS concentration but the upfield shift disappeared when micelles were formed. Since the change in the chemical shift was similar to that due to the increase in temperature, they concluded that SDS caused disruption of hydrogen bonds or increased the covalent character of the hydrogen bonding. Therefore SDS can change the structure of solutions even at the concentration lower than the CMC and decreased the interaction between the excited species and water.

Quenching of luminescence by foreign species in the liquid-phase is generally explained either in terms of the collision between the quencher and the excited molecule or in terms of the long-range energy transfer.3) The interferences from nitrite and halide ions seems to be due to the long-range energy transfer, because the interferences were observed at quite low concentrations and were not so much reduced by dilution of the sample solution. Consequently, the reduction of interferences by SDS can be understood by the decrease of the long-range energy transfer through the hydrogen bonds.

References

1) K. Takeuchi and T. Ibusuki, Bunseki Kagaku, 33, E107 (1984).
2) K. Takeuchi and T. Ibusuki, Anal. Chim. Acta, 174, 359 (1985).
3) W. R. Seitz, "Treatise on analytical chemistry," 2nd ed, ed by P. J. Elving, Wiley-Interscience, New York (1981), Part I, Vol. 7, pp. 159-248.
4) K. Ueno, Bunseki Kagaku, 20, 736 (1971).
5) K. Goto, S. Taguchi, K. Miyabe, and K. Haruyama, Talanta, 29, 569 (1982).
6) M. Almgren, F. Grieser and J. K. Thomas, J. Am. Chem. Soc., 101, 2021 (1979).
7) L. J. Cline Love, M. Skrilec and J. G. Habarta, Anal. Chem., 52, 754 (1980).
8) F. J. DeLuccia and L. J. Cline Love, Talanta, 32, 665 (1985).
9) J. Stauff and W. Jaeschke, Z. Naturforsch., 33B, 293 (1978).
10) J. Clifford and B. A. Pethica, Trans. Faraday Soc., 60, 1483 (1964).

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