Chemistry Faculty Research & Creative Works   Chemistry

01 Jan 1974

Effects Of Surfactants On Atomic Absorption Analysis Of Dilute Aqueous Copper And Nickel Solutions

Raymond L. Venable
Missouri University of Science and Technology

Robert V. Ballad

Effects of Surfactants on Atomic Absorption Analysis of Dilute Aqueous Copper and Nickel Solutions

Raymond L. Venable and Robert V. Ballad

Department of Chemistry, University of Missouri—Rolla, Rolla, Mo. 65401

One aspect of atomic absorption spectrometry on which no studies have been reported is the effect that addition of an anionic surfactant has on the absorption by metal ions in dilute aqueous solutions.

Surfactants have been used in atomic absorption and flame photometry to prevent clogging of capillaries in highly saline solutions (1), in clinical work (2), and in combination with other organic substances to enhance sodium and potassium determinations (3). Surfactants added to aqueous solutions just to lower surface tension have been reported to have essentially no effect on atomic absorption results (4).

This paper presents results of studies that have been made in analyzing dilute ($\sim$3 μg/ml) copper and nickel solutions upon addition of the anionic surfactant, sodium dodecyl sulfate, (SDS).

One of the effects is enhancement of absorption in acidic copper and nickel solutions containing SDS above the critical micelle concentration (CMC) over the same acidic copper and nickel concentrations without surfactant present. The second effect seems to be either prevention of precipitate formation or stabilization of a colloidal dispersion in basic solutions at surfactant concentrations approaching and above the CMC.

EXPERIMENTAL

Apparatus. The primary instrument used was a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with the DCR1 digital concentration readout and also interfaced to a Leeds and Northrup Speedomax recorder. A three-slot burner head was used for most of the work, as was a corrosion resistant nebulizer. A Perkin-Elmer Model 305A with deuterium background corrector was used in some experiments. Copper and nickel were determined in an air-acetylene flame at the instrument settings recommended in the Perkin-Elmer Analytical Methods book.

Reagents. Atomic absorption standards for copper and other metals used were prepared by dissolving weighed amounts of high purity (99.999%) metal in reagent grade nitric acid and dilution of the concentrated stock solution to the desired concentration range.

The sodium dodecyl sulfate, BDH Laboratory reagent sodium lauryl sulfate, specially pure, was used without further purification. Tetradecylpyridinium bromide (TPB) was a laboratory preparation. All other chemicals were reagent grade. Solutions were made with water that had been distilled once from a Corning AG1b still followed by two distillations from alkaline permanganate.

RESULTS AND DISCUSSION

In Figure 1 instrument response which is proportional to absorption of copper is plotted as a function of pH over the pH range 2-9 for a constant copper concentration of 3.2 μg/ml. Three cases are shown; one with no added surfactant, one with 0.01 g/l. of SDS, and one with 4.0 g/l. of SDS. Dean, Bosqui, and Lanouette reported that divalent copper precipitated above pH 5.3 (5). These findings are essentially confirmed here as shown by the presence of a visible precipitate at higher pH values and by the decrease in absorption at high pH values, except for the solution containing 4.0 g/l. of SDS. At this latter SDS concentration, which is above the CMC, there is an enhancement of absorption even in acidic solutions, and a definite and visible prevention of precipitate formation, or at least a prevention of flocculation at higher pH values. Throughout this work, the surfactant was added before the pH was made neutral or basic.

The effect of increasing SDS concentration at a constant copper concentration of 3.3 μg/ml and pH of approximately 9 is shown in curve I of Figure 2. A pronounced increase in absorption with increasing SDS concentration is observed until the CMC for SDS of approximately 1.75 g/l. is reached. [The CMC of an ionic surfactant varies with added electrolyte concentration and the value of 1.75 g/l., determined by independent measurements, is valid only in electrolyte concentrations corresponding to those used here (6).] Beyond the CMC the absorption changes only slightly, but does show a small decrease at higher SDS concentrations. At concentrations above about 5 g/l. of SDS, the viscosity of the solution increases markedly above that of water, which may account for the tailing off of the curve. The overall shape of this curve is similar to the detergency curves shown by Adamson (7). Results at pH 2 for copper and nickel are shown as curve II and again show absorption enhancement even in these acidic solutions. The data points for curve II represent many analyses, and the height of the points shows the experimental uncertainty. Thus, it can readily be seen that the enhancement is far beyond the limits of experimental error.

The effects noted are not seen for all surfactants, as shown in Figure 3. Here the results obtained with the cationic surfactant TPB are compared with those obtained with SDS, both at pH 9. It is obvious that if addition of TPB causes anything, it is a decrease in absorption. There is a large amount of scatter in the data which is characteristic of solutions where the substance being analyzed is precipitated. This behavior is quite in contrast with that of solutions containing SDS as shown by the pronounced increase in absorption with that surfactant. It should be noted that the CMC for TPB is less than 2 g/l. and, of course, does depend on the electrolyte concentration. These results would eliminate simple surface tension lowering and "detergency," or indiscriminate suspending power of a surfactant as the causes of the enhancement. The enhancement has also been seen for basic solutions of nickel and zinc containing SDS.

(1) J. Ramirez-Munoz. "Atomic Absorption Spectroscopy," Elsevier, New York, N.Y., 1968, p 310.

(2) J. A. Dean. "Flame Photometry," McGraw-Hill, New York, N.Y., 1960, p 54.

(3) K. Sugawara, T. Koyama, and N. Kawasaki, *Bull. Chem. Soc. Jap.*, **29**, 679 (1956).

(4) J. A. Dean and T. C. Rains. "Flame Emission and Atomic Absorption Spectrometry." Marcel Dekker, New York, N.Y., 1969, p 306.

(5) J. G. Dean, F. L. Bosqui, and K. H. Lanouette, *Environ. Sci. Technol.*, **6**, 518 (1972).

(6) U. M Oko. Ph.D. Thesis, University of Missouri—Rolla, Rolla, Mo., 1968.

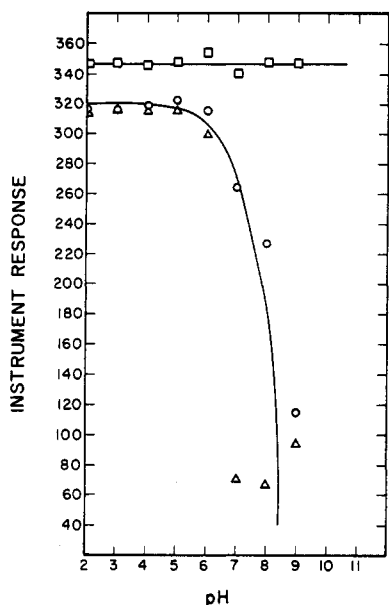(7) A. W. Adamson. "Physical Chemistry of Surfaces," 2nd ed., Interscience Publishers, New York, N.Y., 1967, p 491.

Figure 1. Absorption by copper as a function of pH from pH 2 to 9

O, 3.2 µg/ml Cu; △, 3.2 µg/ml Cu + 0.01 g/l. SDS; □, 3.2 µg/ml Cu + 4.0 g/l SDS
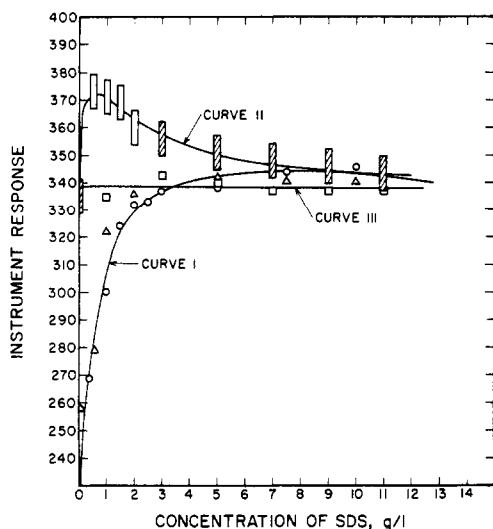

Figure 2. Absorption by 3.3 µg/ml copper and nickel solutions as a function of surfactant concentration

▯ Copper at pH 2; ▨, copper and nickel at pH 2; O, copper at pH 9 with air–acetylene flame; △, copper at pH 9 with nitrous oxide flame; □, copper at pH 7.3 with THAM present

Interferences in atomic absorption, here taken to mean any factors which cause erroneous results, may be roughly classified into physical factors such as viscosity, surface tension, temperature, light scattering by particles in the flame, etc.; and chemical factors such as reactions in the solution or flame which affect results.

Two of the physical factors, surface tension and viscosity, were discussed along with the discussion of the results presented in Figures 2 and 3. A third factor, background absorption, was investigated using a Perkin-Elmer Model 305A spectrophotometer equipped with a deuterium background corrector. The results of these measurements are shown on curve I of Figure 4 for 3.6 µg/ml copper at pH 7. Curve II shows results obtained on the Perkin-Elmer 303 with the original nebulizer. The curve shapes are similar and roughly reproducible. It can be concluded that nei-
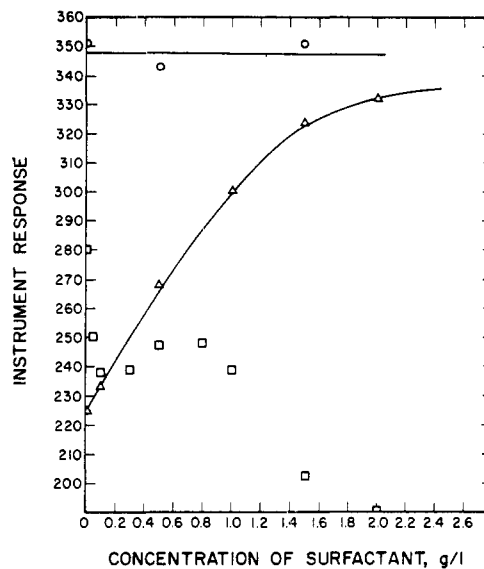

Figure 3. Comparison of effects of cationic surfactant TPB with anionic surfactant SDS

□, 3.5 µg/ml Cu at pH 9 with TPB; △, 3.3 µg/ml Cu at pH 9 with SDS; O, 3.5 µg/ml Cu at pH 1.5 with TPB
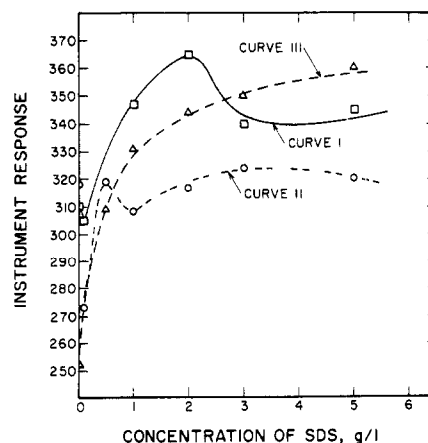

Figure 4. Deuterium background correction and effect of aspiration rate on apparent concentration

□, Deuterium background correction 3.30 µg/ml Cu at pH 6.4; O, high flow rate nebulizer with 3.2 µg/ml Cu at pH 7.3; △, corrosion resistant (low flow rate) nebulizer with 3.2 µg/ml Cu at pH 7.3

ther the pronounced increase in absorption by copper with increasing surfactant concentration at high pH nor the enhancement over the results obtained in acid solutions can be due to background absorption or scattering.

An interesting side light here is the effect that the type of nebulizer has on the results. The original nebulizer on the 303 had a 0.023-in. i.d. polyethylene capillary with a flow rate of 9 ml/min, which was similar to the 305A nebulizer, which also had a flow rate of 9 ml/min. A new corrosion resistant nebulizer (P.-E. No. 303-0404), with a 0.015-in. i.d. Teflon capillary and flow rate of 3.4 ml/min was used for most of this work. The results obtained with it are shown as curve III of Figure 4. The new nebulizer gave a more reproducible curve for the results shown.

Possible interference caused by the presence in the flame of non-absorbing copper species, such as CuO, which are either destroyed or not allowed to form by concentrations of SDS near the CMC can be tested in two ways. One is the use of a nitrous oxide–acetylene flame instead of an air–acetylene flame. The hotter nitrous oxide flame should reduce all forms of copper to the atomic

state. As shown in curve I of Figure 2, the use of the nitrous oxide flame has no effect on the results. A second way would be burner height studies (the height of the sample beam above the burner head). If non-absorbing species are present, they are more likely to be reduced to the atomic state higher in the flame. Burner height studies show the effect is present regardless of where the sample beam passes through the flame.

Another possible explanation for the increased solubility of copper in the basic solutions studied here is that addition of an electrolyte (such as SDS) caused an increase in solubility by a "salting in" type mechanism. This possibility is negated by the results with TPB which is also an electrolyte and by some studies with added sodium sulfate, using SDS as the surfactant. In these latter studies the total anionic electrolyte concentration [DS^- + SO_4^{2-}] was held constant as the concentration of SDS was increased. Curves very similar to curve I of Figure 2 were obtained, completely ruling out a "salting in" effect. Those studies also eliminated the possibility that the bright sodium flame was affecting the results.

It is possible that the SDS prevents precipitate formation by complexing the copper although it is very difficult to imagine such a process causing the observed enhancement at low pH where the copper should be completely in solution anyway. If a complexation mechanism is the source of the stabilization, addition of another complexing agent such as tris(hydroxymethyl)aminomethane (THAM) should also prevent precipitation. As seen in curve III of Figure 2 this is indeed the case. However, this is not the most interesting aspect of these results. There is virtually no increase in absorption with increasing SDS concentration in contrast with the results shown in curve I for low pH or curve II at pH 9.

This latter result would rule out the possibility that the enhancement is due to combustion of organic matter when SDS is present. There is more organic matter present at any given SDS concentration in the solution containing THAM than when no THAM is present.

CONCLUSIONS

From these results, it is concluded that the presence of certain anionic surfactants can cause erroneous results in the analysis of dilute aqueous metal ion solutions by atomic absorption. Analysts should be aware of this fact. A more positive conclusion is that SDS and perhaps other anionic surfactants can potentially be used to keep metals in solution where acidic pH values are not tolerable.

ACKNOWLEDGMENT

Dye Laser Intra-Cavity Enhanced Absorption Measured Using a Photodiode Array Direct Reading Spectrometer

Gary Horlick and Edward G. Codding

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Enhancement of absorption when a relatively weak and narrow band absorber is placed inside the cavity of a dye laser has recently been reported by several workers. This enhancement has been demonstrated for Na and I_2 vapors (1), $Eu(NO_3)_3$ solutions (2), and Sr and Ba^+ atomic species in an air–acetylene flame (3). Enhanced absorption of nitric oxide inside the cavity of a carbon monoxide gas laser has also been reported (4). Enhancements in the range of two orders of magnitude have been found for some of the above systems, which should make this effect analytically useful in determining a number of weak absorbers. The observation of the effect for atomic species in a flame cell inside the dye laser cavity (3) should be particularly important with respect to atomic absorption techniques. However, few quantitative data have been presented in the sense of an analytical curve relating the enhanced or apparent absorption to the concentration of the absorbing species placed in the dye laser cavity. In this investigation, solutions of $Pr(NO_3)_3$, $Eu(NO_3)_3$, $NdCl_3$, and $HoCl_3$ were used to study the enhanced absorption as a function of concentration. Analytical curves are presented for both praseodymium and europium.

A key factor in this investigation which greatly facilitated the acquisition of the necessary spectral data was the utilization of a photodiode array direct reading spectrometer (5, 6). With this instrument, the entire spectrum of a dye laser pulse (~ 125 Å) could be measured and displayed on an oscilloscope essentially instantaneously after firing the pulsed dye laser.

EXPERIMENTAL

Apparatus. A block diagram of the experimental system is shown in Figure 1. A frequency doubled, Q-switched pulsed ruby laser (Korad Model K-1QP) with an output power of approximately 10 MW at 3472 Å was used to pump the dye laser (7). The ruby laser was passively Q-switched with cryptocyanine. The frequency multiplier (Korad Model K-M) was an ADP crystal which converted the 6943-Å ruby output to 3472 Å with an efficiency of about 10%.

The output of the frequency multiplier constitutes the pump for the dye laser. It was focused onto a 1-cm square quartz cell

(1) N. C. Peterson, M. J. Kuvylo, Walter Brawn, A. M. Bass, and R. A. Keller, *J. Opt. Soc. Amer.*, **61**, 746 (1971).
(2) R. A. Keller, E. F. Zalewski, and N. C. Peterson, *J. Opt. Soc. Amer.*, **62**, 319 (1972).
(3) R. J. Thrash, H. von Weyssenhoff, and J. S. Shirk, *J. Chem. Phys.*, **55**, 4659 (1971).
(4) C. Chackerian, Jr., and M. F. Weisbach, *J. Opt. Soc. Amer.*, **63**, 342 (1973).

(5) Gary Horlick and E. G. Codding, *Anal. Chem.*, **45**, 1490 (1973).
(6) E. G. Codding and Gary Horlick, *Appl. Spectrosc.*, in press.
(7) B. B. McFarland, *Appl. Phys. Lett.*, **10**, 208 (1967).