Chinese Chemical Letters Vol. 10, No. 1, pp. 51–54, 1999

A Highly Sensitive Kinetic Spectrophotometric System and Its Analytical Potential for Chromatographic Detection of Metal Ions

Xi Rong HUANG*, Wen Juan ZHANG, Shu Hua HAN, Gui Ying XU

College of Chemistry, Shandong University, Jinan 250100

Abstract: Based on the inhibitory effect of metal ions on the decolourization reaction of a dye taking place in a mixed micellar medium, a differential rate method was developed for the detection of metal ions. The present kinetic spectrophotometric system has several advantages due to introduction of the mixed micelles.

Keywords: Mixed micellar media, decolourization reaction, bromopyrogallol red, metal ions, inhibitor, spectrophotometry, method development.

Micelles, microemulsions, vesicles, etc., are organic microheterogeneous media. Use of these media in analytical reactions for developing new kinetic-based determinations or improving previously established kinetic methods has been reported[1, 2]. In recent years, a mixed micellar medium composed of ionic and non-ionic surfactants is preferred[3-6] due to the advantage that its microenvironment, which usually has a remarkable effect on analytical reactions, can be easily changed by varying the temperature and/or the composition ratio. In this paper, the decolourization reaction of bromopyrogallol red (BPR) in a mixed micellar medium composed of cetyltrimethylammonium bromide (CTAB) and nonylphenoxypolyethoxyethanol (OP) has been studied. Due to the introduction of the mixed micelles, the rate of the decolourization reaction of BPR is accelerated (micellar catalysis) and high concentration of BPR is tolerated (solubilization). Based on the effects of metal ions on the reaction, a highly sensitive kinetic spectrophotometric system has been established, which could be developed further for chromatographic detection of metal ions in postcolumn reaction (PCR) absorbance mode. To facilitate the narration, the authors choose Ti (IV) as a representative of metal ions studied. Systems with and without Ti (IV) are hereafter referred to as samples and blanks, respectively. The optimum reaction time is the time by which the blank has decolourized completely (from purple red to golden yellow) at 532nm while absorbance of the sample remains almost unchanged.

Results and Discussion

Absorption spectra of the sample and the blank (heated for 3′45″ at 90°C after initiation by H_2O_2 and then taken out and cooled with cold water) are given in **Figure. 1**. It shows that Ti (IV) has an obvious inhibitory effect on the decolourization reaction of BPR.

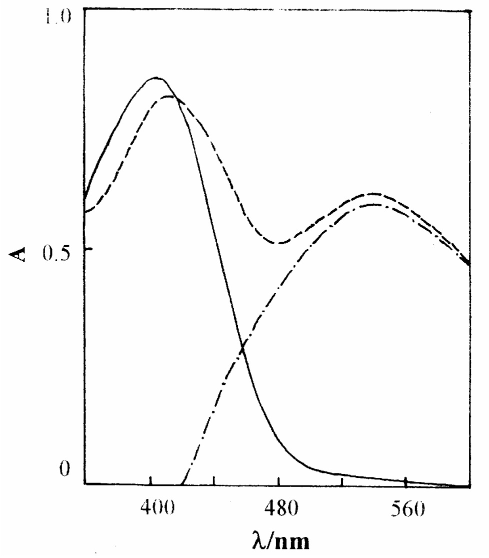

Figure 1. Absorption spectra. Dash line, sample against water; solid line, blank against water; dot-and-dash line, sample against blank. Conditions: T=90°C, pH=2.0, [BPR]=6×10^{-5}mol/L, [CTAB]=0.1%, [OP]=0.8%, Ti=0.1μg/mL, [H_2O_2]=1×10^{-3}%.

At 90 ℃, CTAB/OP mixed micelles had an obvious catalytic effect on the decolourization reaction of BPR. At a given concentration of CTAB, the reaction rates of both the blank and the sample increased with the increase of [OP], but they showed different dependence on [OP]. By the time the blank had decolourized completely, the absorbance of the sample decreased little. Further increase of [OP], however, caused the sample and the blank to be turbid if [CTAB] was not high, thereby resulting in incomplete decolourization of the blank. To avoid phase separation, it was necessary to keep the [CTAB] high. If [OP] was fixed at 0.8 % (w/v), then [CTAB] should be no less than 0.05 % (w/v). When [CTAB] exceeded 0.15 % (w/v), however, appreciable decrease in the reaction rate for both the sample and the blank was observed. Moreover, the sample had begun to decolourize at a perceivable rate prior to complete decolourization of the blank. Results showed that the optimum concentration of CTAB was 0.10±0.02% for 0.8 % OP.

Effect of pH

The effect of pH on the optimum net absorbance (obtained at optimum reaction time) of the sample (against the blank) was studied. Results showed that the optimum pH ranged from 2.0 to 2.7.

Effect of Temperature

At room temperature, the reaction rate was very slow for both the sample and the blank. No obvious changes in their absorption spectra were observed even if they were kept for 30min at 30°C. At higher temperature (>60°C), the reaction rate was accelerated for both the blank and the sample and, moreover, their difference in reaction rate was enlarged. When the temperature exceeded 95°C, the sample had already begun to decolourize prior to complete decolourization of the blank.

Effect of BPR

The net absorbance, ΔA, increased rapidly with the increase of the concentration of BPR, which was accompanied by a gradual hypsochromic shift of the peak of the sample (against the blank) (from 542nm to 532nm). When the concentration of BPR exceeded 2.5×10^{-4}mol/L, however, only slow increase in ΔA was observed over the range of 2.5×10^{-4}mol/L—4×10^{-4}mol/L. Considering that the increase of the concentration of BPR prolonged the reaction time, the final concentration of BPR was fixed at 2.5×10^{-4} mol/L.

Effect of H_2O_2

Without H_2O_2, much time (>20min) was needed for complete decolourization of the blank, but large amounts of H_2O_2 reduced the difference in reaction rate between the sample and the blank. Experiment showed that the optimum volume for 0.01% H_2O_2 ranged from 0.4mL up to 1.2mL.

Analytical characteristics and analytical potential

Under the optimum conditions, Beer's law was obeyed over the range of 2-10 ng/mL Ti (IV) with molar absorptivity of 4.7×10^{6} $L\cdot mol^{-1}\cdot cm^{-1}$ and limit of detection (3σ) of 1.2 ng/mL. For 6.0 ng/mL Ti (IV), the relative standard deviation (n=9) was 3.8 %. To our knowledge, this kinetic spectrophotometric system seems to be the most sensitive system ever reported for the determination of Ti (IV)[6]. Its high sensitivity and low limit of detection should be attributed to the high molar ratio of BPR to Ti (IV) as well as the large difference in reaction rate between the blank and the sample.

Like Ti (IV), Ge (IV), Sn (IV), Cr (VI), Mo (VI), W (VI), V (V), Zr (IV), Cu (II), Ni (II), Zn (II), Mg (II), and Ga (III) also had an obvious inhibitory effect on the decolourization reaction of BPR (results not shown), which indicated that these metal ions could be sensitively detected, after separation, by kinetic spectrophotometric technique, i.e., the present kinetic spectrophotometric system could be developed further for chromatographic detection of metal ions in PCR absorbance mode. To our knowledge, catalytic effects have seldom been used for this purpose[7]. Exploitation of the compatibility of the combined system and its applicability for chromatographic analysis of metal ion-spiked distilled-water samples is under way.

Acknowledgments

The authors gratefully acknowledge financial support from Natural Science Foundation of Shandong Province, China.

References

1. M. L. Carreto, S. Rubio and D. Perez-Bendito, *Analyst*, 1996, *121*, 33R.
2. D. Perez-Bendito and S.Rubio, *Trends Anal. Chem*., **1993**, *12*, 9.
3. X. Huang, W. Zhang, Z. Zhang, G. Xu and C. Li, *Spectrochim. Acta Part A*, **1998**, *54*, 617.
4. X. Huang, W. Zhang, Y. Yin, G. Xu and X. Wang, *Talanta*, **1997**, *45*, 127.
5. X. Huang, N. Jie, S. Han, W. Zhang and J. Huang, *Mikrochim. Acta*, **1997**, *126*, 329.
6. Y. Xu, W. Shi and Y. Ci, *Journal of Beijing University*, **1988**, *24*, 430.
7. P. K. Dasgupta, *J. Chromatogr. Sci.*, **1989**, *27*, 442.

Received 2 August 1998