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Determination of Cationic Surfactant by Laser Thermal Lens Spectrometry

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Abstract: A novel method for the determination of cationic surfactant by laser thermal lens spectrometry was developed. It was based on the reaction between 1-hydroxy-2-(5-nitro-2-Pyridylazo)-8-aminonaphthalene-3,6-disulfonic acid (5-NO2-PAH) and cationic surfactant to form 1：2 ionic association complex in a weakly basic medium (pH 9.44). The determination conditions and the mechanism were discussed. The method has been applied to the analysis of wastewater and moat water samples.

Keywords: Determination of cationic surfactant, cetylpyridinium bromide (CPB), cetyltrimethyl-ammonium bromide (CTMAB), 1-hydroxy-2-(5-nitro-2-pyridylazo)-8-aminonaphthalene-3,6-disulfonic acid (5-NO_2-PAHA), laser thermal lens spectrometry.

Surfactants have been widely applied to industry, agriculture and everyday life. It is important to develop a high sensitive method of determination for surfactants to study the biodegradability and aquatic toxicity of the surfactants in environment as well as its influence on the physiological process. There are many methods for determining surfactants, such as absorption spectrophotometry, IR, electricity tension, luminosity analytical method and HPLC [1, 2] *etc*., but the improvements in the sensitivity are not remarkable owing to the limitation of the methods themselves. Laser thermal lens spectrometry (LTLS) is a highly sensitive optical-thermal spectroscopic technology. However, up to now there are few published data on the LTLS application to determination of surfactants.

In this work, a new method for the determination of cationic surfactant by LTLS was developed. It is based on the reaction between 1-hydroxy-2-(5-nitro-2-pyridylazo)-8-aminonaphthalene-3, 6-disulfonic acid (5-NO_2-PAH) and cationic surfactant, such as cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTMAB) *etc.*, which form 1:2 ionic association complex in a weakly basic medium (pH 9.44). It is shown that the method has high sensitivity (10^{-8}mol/L), simple, and has been successfully applied to determination of low concentration of cationic surfactants CTMAB in the domestic sewage and Xian city moat with satisfactory results.

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Experimental

The instrument of laser thermal lens spectrometry used in this experiment has been previously described[3]. An Ar^+ laser (TEMoo, $\lambda_{540\ nm}$) acts as both exciting and probing laser beam. The power at the sample location is 3 mW.

To 2.0 mL borax buffer solution (pH 9.4) in a 25 mL separating funnel, added a certain amount of solution containing appropriate amount of cationic surfactant (or sample solution), and diluted to mark with water. Then, 0.5 mL of 1×10^{-3}mol/L 5-NO_2-PAH solution was added and mixed well. After 5 min, the solution was extracted with chloroform. The signal intensity of LTLS was measured and recorded.

Results and Discussion

In basic medium solution, 5-NO_2-PAH is ionized to form the anion of 5-NO_2-PAH. The cationic surfactant CPB and CTMAB can also be ionized to form their cations in the dilution solution ($<10^{-4}$mol/L)[4]. When the anion of 5-NO_2-PAH and cation of CPB or CTMAB exit in a solution, there is an interaction between the cation of the surfactant with one positive charge and the anion of 5-NO_2-PAH with two negative charges to form the ionic association complex due to the electrostatic forces, of which the ionic association ratio is 1:2. The ionic association complex can be extracted into the organic solvent and determined by LTLS. The maximum absorption of the ionic association complex lies at 530 nm in the organic solvent medium, which is similar to that of the reagent, 5-NO_2-PAH, in aqueous medium. It is shown that the spectral features, absorption peak and maximum wavelength are not altered, when the ionic association complex is formed.

It was found that the LTLS signal increased with increasing of 5-NO_2-PAH, but high concentration of 5-NO_2-PAH would produce a larger blank signal. Therefore, 0.5 mL of 1×10^{-3} mol/L 5-NO_2-PAH was chosen in the experiment

The molecule of 5-NO_2-PAH does not dissociate to form the anion of 5-NO_2-PAH and produce the complex in neutral medium or acid medium. If the reaction was in strong base medium, the ionic association complex of 5-NO_2-PAH could not be produced also. The results showed that optimum acidity to produce ionic complex was at pH 8~10. The reaction solutions were buffered to pH 9.44 with the borax buffer.

The reaction of ionic association occurred at 0~25°C. When the reaction temperature was over 25°C，the complex would be dissociated and the intensity of LTLS decreased with the raising of reaction temperature. Therefore, the ionic association complex between 5-NO_2-PAH and CPB or CTMAB could be carried out at room temperature. It was found that the ionic association complex did not change within 1 h after adding 0.5 mL of 1×10^{-3}mol/L 5-NO_2-PAH to produce the complex. Therefore, the complex was determined 5 min after adding 5-NO_2-PAH to the reaction system at room temperature.

It is known that the intensity of the LTLS signal not only depends on the optical absorption of the sample but also the thermal-physical characteristics of the solvent under a certain energy of irradiation laser[5]. The solvent selected should both have high signal enhancement coefficient of TLS and good extraction rate, which increases as the dielectric constant of solvent increases, especially in extraction of the ionic pair. In addition, the absorption maximum of the complex in the selected solvent should not change the absorption maximum. Chloroform was selected as extraction solvent and determination medium for LTLS in the experiment. The dielectric constant of chloroform is greater than benzene, toluene and cyclohexane *etc*., and there is no absorption peak at the measuring wavelength. The enhancement factor of chloroform (10.1) is greater than that of water (0.3)[6]. Therefore, chloroform as solvent medium for LTLS measurement can enhance the determination sensitivity.

Under the chosen experimental condition, the calibration graph was obtained by the general procedure. Good linearity was over the range of $0\sim3.5\times10^{-6}$mol/L for CPB and $0\sim2.4\times10^{-6}$mol/L for CTMAB, respectively. The linear regression equation was $S_{TLS}= 6.812\times10^{5}C - 0.0053$. The correlation coefficient r=0.9976. The detection limit of CPB and CTMAB, which was calculated according to the 3_s-criterion, was 4.96×10^{-8}mol/L and 2.63×10^{-8}mol/L, respectively.

The influence of more than 30 foreign species on the determination of a solution containing 5.0×10^{-6}mol/L of cationic surfactant, such as CPB and CTMAB *etc*. was examined by adding various amounts of these foreign species. The error of the measurement was no more than 5% in the tolerance limit. The results showed that the large amount of anionic surfactant and non-ionic surfactant did not interfere, and a 1×10^{5}-fold amount of I^-; 5000-fold $S_2O_3^{2-}$, F^-, K^+; a 1500-fold Hg^{2+}, As^{3+}, Zn^{2+}, Sr^{2+}; a 500-fold Bi^{3+}, Cd^{2+}, Pb^{2+}; 50-fold Mn^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, EDTA could be tolerated. Although the cation of Cr^{3+}, Co^{2+} and Ni^{2+} can form the complex with 5-NO_2-PAHA, the absorption maximum of formed complex is not different. Therefore, no significant interference arose from the foreign species for the determination of cationic surfactant.

The proposed method has been applied to the determination of CTMAB in domestic sewage and water of Xian city moat. The determination results are shown in **Table 1**.

Table 1 Determination results in samples*

Sample	CTMAB added ($\times10^{-6}$mol/L)	Found[a] ($\times10^{-6}$mol/L)	RSD(%)	Recovery(%)
Domestic sewage I	-----	1.414	1.1	
	2.00	3.320		95.3
	3.00	4.450		101.2
	4.00	5.246		95.8
Domestic sewage II	-----	5.972	2.1	
	2.00	7.925		99.1
	3.00	9.095		104.1
	4.00	10.085		102.8
Xian city moat water	-----	0.181	1.7	
	2.00	2.101		96.0
	3.00	3.145		98.8
	4.00	4.077		97.4

* Expressed as CTMAB; [a]Average value of eight determinations.

It is demonstrated that the method could be used for the routine determination of low concentrations of surfactant in formulated products and environmental samples.

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