Quantitation of poly(diallyldimethylammonium chloride) by complexation with Acid Orange 7 dye (*Rapid Communication*)

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Abstract: The anionic dye Acid Orange 7 (AO7) was applied for quantitative determination of poly(diallyldimethylammonium chloride) (PDDA) in aqueous solutions. The PDDA polymer forms colloidal complexes with the AO7 dye resulting in spectral changes. Increase in the polymer concentration up to 0.10 mmol(mer)/dm^3 leads to decrease in absorbance at wavelengths in the range between 450 and 500 nm. The obtained calibration dependences between absorbance and concentration fulfill linear equation with quite small variance ($s^2 = 1.56 \cdot 10^{-2}$). The proposed method of PDDA quantitation requires weak acidic medium (pH = 3.5—6.5) and low values of ionic strength ($I \approx 20$ mM).

Keywords: poly(diallyldimethylammonium chloride), Acid Orange 7, dye-polymer complex, quantitation.

Oznaczanie ilościowe poli(chlorku diallilodimetyloamonowego) za pomocą kompleksowania oranżem kwasowym II

Streszczenie: Zdolność barwnika — oranżu kwasowego II (AO7) do tworzenia koloidalnych kompleksów z poli(chlorkiem dimetylodialliloamonowym) (PDDA) została wykorzystana do ilościowej analizy tego polimeru w roztworach wodnych. Wykazano, że oznaczenie stężenia PDDA za pomocą pomiaru absorbancji z wykorzystaniem krzywej wzorcowej jest możliwe w zakresie długości fali od 450 do 500 nm. Wzrostowi stężenia polimeru do 0,10 mmol(mer)/dm^3 towarzyszy spadek intensywności głównego piku w widmie barwnika AO7, przy czym krzywa kalibracyjna ma charakter prostoliniowy. Zaproponowana metoda oznaczania PDDA wymaga zastosowania środowiska słabo kwasowego (pH ≈ 3,5—6,5) i o małych wartościach siły jonowej ($I \approx 20$ mM).

Słowa kluczowe: poli(chlorek dimetylodialliloamonowy), oranż kwasowy II, kompleks barwnik-polimer, oznaczanie ilościowe.

Poly(diallyldimethylammonium chloride) (PDDA), is a cationic polyelectrolyte with wide variety of applications. In many cases a precise and reliable method of quantitative determination of the polymer in solution is required. A popular analytical procedure for PDDA determination is titration against potassium poly(vinyl sulfate) with the endpoint recognition by means of a streaming current detector [1—3]. The polyelectrolyte titration endpoint may be also recognized using an appropriate indicator, such as *o*-toluidine blue [1, 2, 4, 5] or crystal violet [6]. The color change of the indicator dye is usually registered by visual observation or by spectrophotometric measurements. On the other hand, direct spectrophotometry of colloidal polymer-dye complexes looks to be a less laborious method. The anionic dyes applicable for such measurements are triphenylmethane ones [7, 8] and azo one [9]. The sensitivity of the method depends on both molar extinction coefficient and the charge of the dye used as well as on solution pH and ionic strength [7, 8].

The aim of this work was to examine the anionic acid orange 7 dye as a reagent for fast spectrophotometric determination of PDDA concentration in aqueous solutions.

EXPERIMENTAL PART

Materials

The Acid Orange 7 dye {AO7, (sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene)hydrazinyl] benzenesulfonate, with molar absorption coefficient ε = 14 000 dm^3/(mol·cm)} was supplied by Boruta-Kolor (Poland).

Poly(diallyldimethylammonium chloride) (PDDA) of average molar mass of 100—200 kg/mol was obtained from Aldrich as a solution of concentration 20 % and density of 1.04 g/cm^3.

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Method of testing

The UV-Vis light absorption measurements were performed with spectrophotometer Pharo 300 (Merck) in the wavelength range between 300 and 700 nm using quartz cuvettes with 10 mm optical path and distilled water as a reference. All the measurements were performed in three independent series. Absorbance of samples was measured immediately after sample preparation.

The stock solution of the AO7 dye of concentration 1 mmol/dm^3 was prepared by dissolving an adequate mass of the dye in distilled water.

The stock solution of PDDA with concentration of 1 mmol(mer)/dm^3 was prepared by diluting the basic solution with distilled water and then stored in the dark. The calibration solutions have been prepared in 100 cm^3 volumetric flasks, taking 15 cm^3 of the stock dye solution and adequate quantity of the PDDA stock solution. A dose of 0.1 mol/dm^3 NaOH or HCl solution or/and a dose of NaCl solution of concentration 50 mmol/dm^3 were added for regulation of pH and ionic strength, respectively.

RESULTS AND DISCUSSION

The UV-Vis spectra of the AO7 dye in presence of various PDDA polymer concentrations are shown in Fig. 1. The spectrum of AO7 dye (without polymer) contains two peaks: the lower one in the range of wavelength near ultraviolet (at 310 nm) and the higher one in the visible range (at 485 nm). The spectra of AO7 change when PDDA is added to the solution.

The absorbance values corresponding to both the UV and Vis spectral peaks decrease with an increase in PDDA concentration, suggesting the reduction of the AO7 dye concentration in the solution. The most probable cause of the observed spectral changes is electrostatic complexation of the dye with polymer. The positive charges of the polymer macromolecule attract the negative charges of the dye molecules resulting in complex formation. The polymer-dye complex is low soluble in water and forms a colloidal suspension causing slight turbidity of the sample. The isosbestic point observed around 540—550 nm (Fig. 1) suggests that the formed complex is rather stoichiometric. For samples with PDDA concentrations higher than 0.12 mM an additional peak appears at about 430—440 nm. The peak intensity increases following the increase in polymer content probably due to adsorption of PDDA macromolecules on colloidal particles.

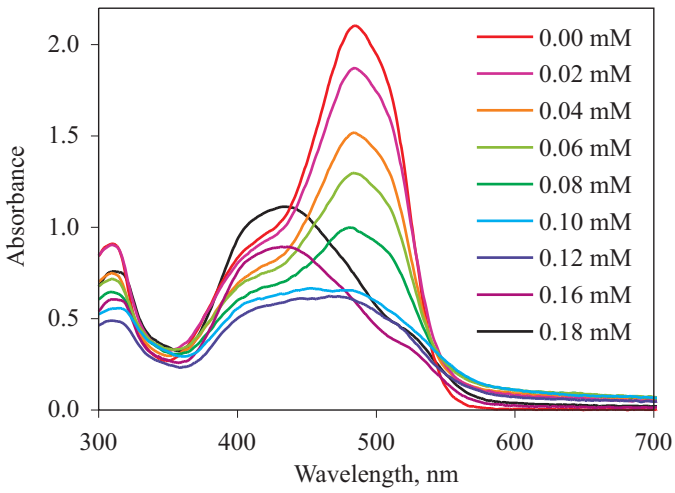

Fig. 1. Absorption spectra of the AO7 dye at pH = 6 in the presence of various PDDA concentrations

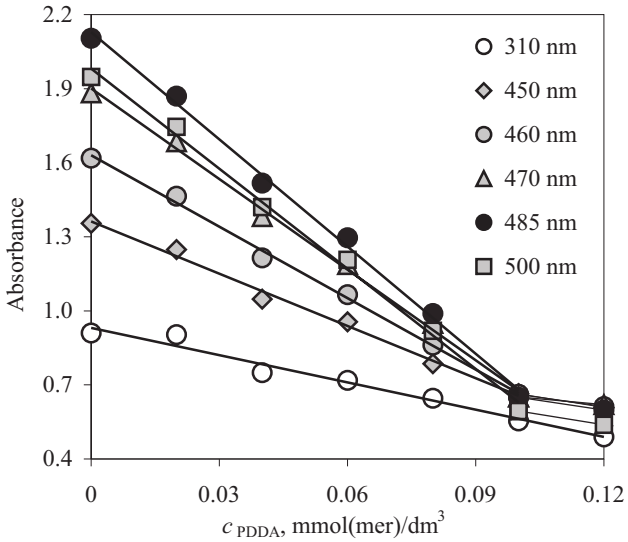

Fig. 2. Absorbance of the AO7 dye solution at different wavelengths versus PDDA concentration at pH = 6

As it was shown in Fig. 2, the absorbance at the peak wavelength changes linearly in a wide range of the polymer concentration. This fact creates the basis of analytical procedure for PDDA quantitation. In order to provide maximal sensitivity of determination the measurements at the wavelengths corresponding to the main peak of AO7 spectrum are recommended.

It is noticeable that the absorbance at about 485 nm is decreased up to certain polymer concentration. Further increase in PDDA content results in the disappearance of this band due to the limited quantity of the dye.

The exemplary calibration plots presented in Fig. 2 indicate that the straight-line relationships between light absorption and PDDA concentration exist from 0 to about 0.1 mmol(mer)/dm^3. The obtained calibration equations are characterized with high values of R^2 coefficients (*e.g.* at 485 nm $A = -14.5 \cdot c_{PDDA} + 2.13$, $R^2 = 0.9965$). Possibility of calibration curve description with the straight-line equation is much more convenient comparing to the polynomial calibration characteristic for the Bradford reagent [7]. Another advantage as compared to the Brad-

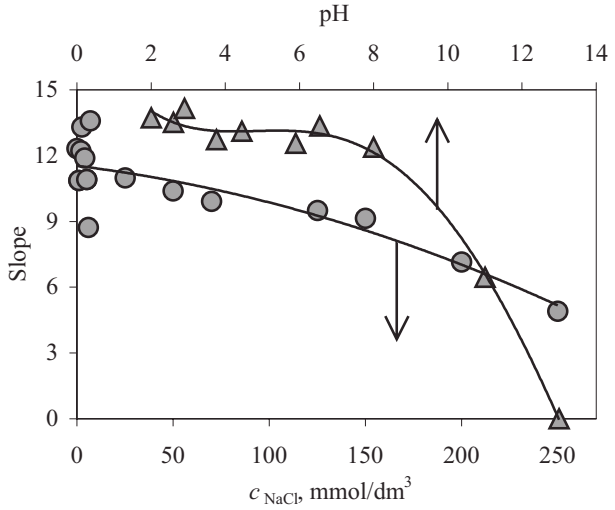

Fig. 3. Dependences of calibration line slope (at 485 nm) on pH and ionic strength of solution

ford reagent is twice as wide range of determination at comparable sensitivity. Unfortunately, further extension of the concentration range of PDDA determination is not possible, because an increase in polymer concentration above 0.1 mmol(mer)/dm^3 results in stabilization and further increase in absorbance values (Fig. 2).

It has been proved that results of PDDA analysis by means of the AO7 dye depend on both pH and ionic strength of solution. Dependence of calibration line slope on pH and ionic strength of solution is presented in Fig. 3.

The repeatability of calibration, being rather low in the absence of salt, improves considerably at small ionic strength ($I \approx 10—25$ mM). Unfortunately, at higher salt concentration the slope of calibration line decreases. The calibration slope remains stable in acidic solutions and is dependent on solution pH in neutral and alkaline ones (pH > 6.5). For the above-mentioned reasons, weak acidic pH buffered at rather small ionic strength $I \approx 20$ mM may be recommended as the optimal condition for the PDDA analysis. The results obtained at the optimal conditions proved good repeatability. The data measured at 485 nm and 0.05 mmol(mer)/dm^3 and averaged on 13 sample series result in mean recovery, variance and standard deviation values equal to 98 %, $2 \cdot 10^{-4}$ and $1.56 \cdot 10^{-2}$, respectively.

CONCLUSIONS

The AO7 dye has been found to be useful for quantitative analysis of PDDA in aqueous solutions. The main absorption band of the AO7 dye spectrum is rather narrow and is characterized with high intensity. The peak absorbance value decreases in mixtures of AO7 and PDDA following the dye-polymer complex formation. The calibration curves derived at the wavelength between 450 and 500 nm are straight lines decreasing with an increase in PDDA concentration. Using the AO7 dye and cuvettes of 10 mm optical path, PDDA concentration can be determined in the range between approximately 0.01 and 0.10 mmol(mer)/dm^3. Statistical parameters have satisfactory values when the analyzed solutions are buffered at pH = 6.

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