

Poly(*N*-Vinylcaprolactam) Gel/Organic Dye Complexes as Sensors for Metal Ions in Aqueous Salt Solutions

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Received 22 March 2000; accepted 27 November 2000

ABSTRACT: The complex formation of organogels based on poly(*N*-vinylcaprolactam) (PVCa) and organic dyes [5-(4-dimethylaminobenzylidene) rhodanine, α -nitroso- β -naphthol, and dithizone] and the properties of the complexes in salt aqueous solutions were studied. PVCa gels absorbed these dyes in organic media (ethanol and chloroform). Our main focus was the behavior of the gel/dye complex immersed in a salt aqueous solution if the dye was the chelating ligand for metal ions. The behavior of the PVCa/dithizone (Dz)/chloroform system was studied in AgNO₃ aqueous solutions. The absorption spectra of gel/dye and gel/dye/metal ion systems were investigated. The results obtained indicate that Ag⁺ ions penetrate the gel phase and that the Dz/silver complexes are indeed formed inside the gel. The dependence of the optical density of the gel/dye/metal ion systems on the AgNO₃ concentration was observed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3238–3243, 2001

INTRODUCTION

Poly(*N*-vinylcaprolactam) (PVCa) is of immediate interest to the experimentalist because of its unique properties. This polymer is soluble in both aqueous and organic media. PVCa also has a high capacity for complex formation.^{1,2} These unusual properties of PVCa are governed by the amphiphilicity of its monomer chains: the PVCa monomer units contain both a polar amide group and hydrocarbon groups that provide hydrophobicity to the macromolecular monomer units. In previous studies, it was shown that in aqueous solutions, PVCa gels can absorb both ionic molecules as a result of polar interactions and nonionic organic compounds as a result of hydrophobic in-

teractions between the hydrophobic groups of PVCa and the hydrophobic groups of organic molecules.^{3,4}

It is well known that dyes are widely used in analytical chemistry for the photometric-selective quantitative determination of metal ions in aqueous solutions. The methods of determination are based on the property of the dyes to form chelate complexes with ions of certain metals.⁵ Complex formation leads to the change in the electronic spectra and, hence, to the displacement of the absorption maximum of the dye. In recent years, polymer gels with dye molecules inside them have been used for the selective absorption of metal ions from aqueous solutions. For example, articles have been devoted to the investigation of gels based on poly(vinylpyridine) modified by Dz as selective absorbents for mercury and gold ions from water solutions.^{6,7}

Sometimes, for the determination of metal ions in aqueous solutions, dyes soluble only in organic solvents are used. In these cases, the labor-consuming procedure of extraction is necessary.

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Contract grant sponsor: Russian Foundation for Basic Research; contract grant number: 98-03-33370a.

Contract grant sponsor: Russian Foundation for Basic Research; contract grant number: 00-03-33108.

Journal of Applied Polymer Science, Vol. 81, 3238–3243 (2001)
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The dyes that were investigated in this study were selective reagents for silver ions in aqueous solutions. Taking this into account, one can expect that the use of a dye-enriched polymer gel for the determination of metal ions from aqueous solutions can help to avoid the procedure of extraction because the polymer network will separate the organic and aqueous phases if the organic compound and water are immiscible.

In this study, we investigated the possibility of the use of gels based on PVCa swollen in an organic solvent for the absorption of water-insoluble dyes. We then determined that the gel/dye complexes obtained in this way could be further used as model sensors for the determination of metal ions if immersed in aqueous solutions. Therefore, the study consisted of two parts. In the first part, the swelling behavior and absorption ability of the PVCa gels in organic media (chloroform and ethanol) in the presence of dyes [Dz, 5-(4-dimethylaminobenzylidene) rhodanine (rhodanine), and α -nitroso- β -naftol] were studied. In the second part, Dz-containing PVCa organogels (Dz is a selective reagent for silver ions) were tested in salt aqueous solutions as a sensor for the determination of silver ions. The systems, which combine the properties of polymer gels and dyes, can be used for the design of new sensor systems for the determination of metal ions in aqueous solutions.

EXPERIMENTAL

Gels were obtained by the radical polymerization of *N*-vinylcaprolactam in an ethanol solution with the crosslinking agent *N,N'*-methylene-bis-acrylamide (1 crosslinking unit per 100 monomer molecules) and with the initiator 2,2'-azobis(2-methylpropionitrile). The initial content of *N*-vinylcaprolactam was 70%.

For the film formation, the solution was bubbled with argon for 10 min to remove oxygen and transferred between glass plates. Polymerization was carried out in an argon medium at 58°C, for 1 day. Then films were removed and washed with distilled water for 2 weeks. After being washed with water, the gels were air-dried at 20°C and immersed in organic solvents.

For the determination of polymer contents in the gels swollen in different solvents, the parameter β was used, the weight ratio of the dry polymer network to the swollen polymer network.

Values of β obtained for gels were 0.022 for PVCa in ethanol and 0.035 for PVCa in chloroform.

Photometric measurements were performed on a Hewlett-Packard 8452A spectrophotometer (Germany). The solvents were measured in 0.1-cm and 1-cm quartz cells in a wavelength interval of 200–800 nm. The pure solvent used for the preparation of the solution was measured to obtain a comparison signal. The colored films were measured between glass plates in a wavelength interval of 300–700 nm. A film swollen in pure solvent was measured to obtain a comparison signal. The thickness of the films was obtained in micrometers (to an accuracy of 0.01 mm).

The content of silver ions in aqueous solutions was evaluated by photometric measurements in the presence of 5-(4-dimethylaminobenzylidene) rhodanine and acetone.⁸

RESULTS AND DISCUSSION

Swelling Behavior and Absorption Ability of PVCa Gels in Organic Media in the Presence of Dyes

The first part of this study was the investigation of the interaction of PVCa gels with the organic dyes 5-(4-dimethylaminobenzylidene) rhodanine and α -nitroso- β -naftol in ethanol and Dz in chloroform.

Figure 1 presents the dependencies of the ratio between the equilibrium dye concentration inside the gel and the dye concentration in the external solution ($C_{\text{gel}}/C_{\text{ext}}$) on the initial dye concentration in the solution for the rhodanine and α -nitroso- β -naftol in ethanol (curves 1 and 2) and for the Dz in chloroform (curve 3). For rhodanine and α -nitroso- β -naftol in an ethanol solution, the ratio of $C_{\text{gel}}/C_{\text{ext}}$ was well above 1 (the dye concentrations inside the gel were 3–10 times larger than the concentrations in the external solution). Thus, the effective absorption of rhodanine and α -nitroso- β -naftol by the PVCa gel was observed. The different characters of the curves can be explained by the different natures of the dyes under investigation and the different concentration ranges that were used.

For the chloroform solution of Dz, the ratio of the equilibrium dye concentrations inside and outside the gel ($C_{\text{gel}}/C_{\text{ext}}$) was slightly above 1, which indicates insignificant absorption of Dz by the gel. From these data, it is obvious that the absorption capacity of the PVCa gel was higher in ethanol than in chloroform. This can be explained

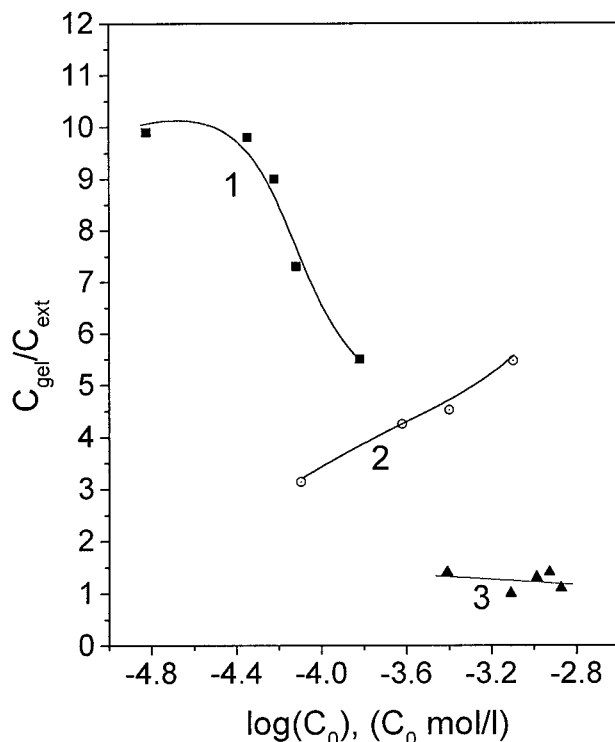


Figure 1 Relation between the equilibrium dye concentration inside the gel (C_{gel}) and the dye concentration in the external solution (C_{ext}) as a function of the log of the initial dye concentration (C_0): (1) 5-(4-dimethylaminobenzylidene) rhodanine, (2) α -nitroso- β -naftol, and (3) Dz.

by the so-called solvophobic interactions that can take place in ethanol.⁹ These interactions are analogous to hydrophobic interactions in water. As a result of solvophobic interactions, the hydrocarbon groups of rhodanine and α -nitroso- β -naftol molecules associate with the hydrocarbon groups of PVCa.

Figure 2 presents the dependencies of the gel swelling degree, $\frac{m_{\text{sw}} - m_{\text{dry}}}{m_{\text{dry}}}$, on the initial dye concentration in the solution, where m_{sw} and m_{dry} are the weights of the swollen and dry polymer gels, respectively. From these data, it is obvious that the swelling degree was independent of the dye concentration and the dye type. The swelling degree for PVCa gel was higher in ethanol than in chloroform.

Of particular interest were the direct measurements of the absorption spectra of dye immobilized inside the gel. For these purposes, the absorption spectra of Dz-containing PVCa films were measured by the spectrophotometer. Figure 3 shows the absorption spectra of Dz in a chloro-

form solution and the Dz/PVCa gel film. The spectra match almost exactly. This shows that Dz did not interact strongly with the PVCa network chains.

Behavior of the Organogel/Dye Complex in Salt Aqueous Solutions

The second part of this study was devoted to the investigation of the behavior of PVCa organogel/Dz (with chloroform as a solvent for the gel phase) films in an aqueous solution of AgNO_3 . Dz is one of the sensitive organic reagents used for the extractive-photometric determination of small amounts of Ag^+ ions in aqueous solutions. The extraction is usually carried out by chloroform in acidic solutions at $\text{pH} < 1$. It is known that in aqueous solutions, Dz forms one-charged HDz^- and two-charged Dz^{2-} ions according to the pH of the solvent. Therefore, the AgHDz and Ag_2Dz complexes are formed as a result of the interaction of Dz with Ag^+ ions in acidic and basic solutions, respectively.¹⁰

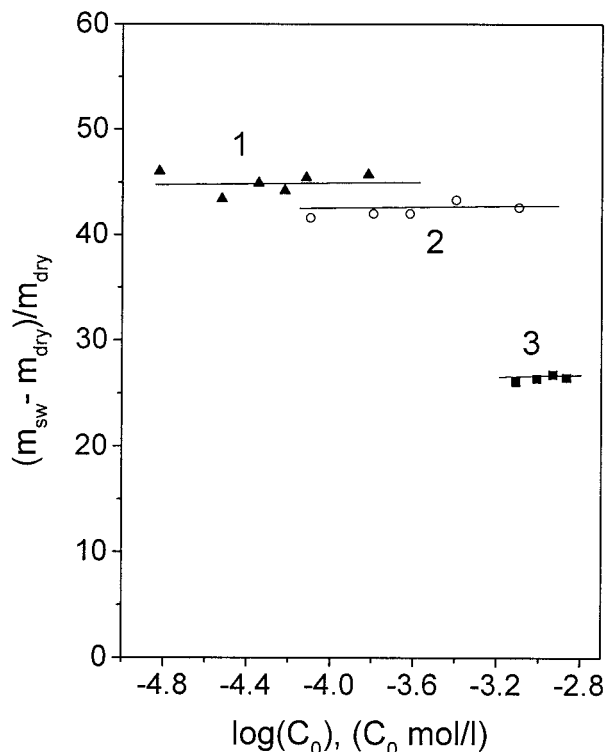


Figure 2 Swelling degree $\left(\frac{m_{\text{sw}} - m_{\text{dry}}}{m_{\text{dry}}}\right)$ as a function of the log of the initial dye concentration: (1) 5-(4-dimethylaminobenzylidene) rhodanine in ethanol, (2) α -nitroso- β -naftol in ethanol, and (3) Dz in chloroform.

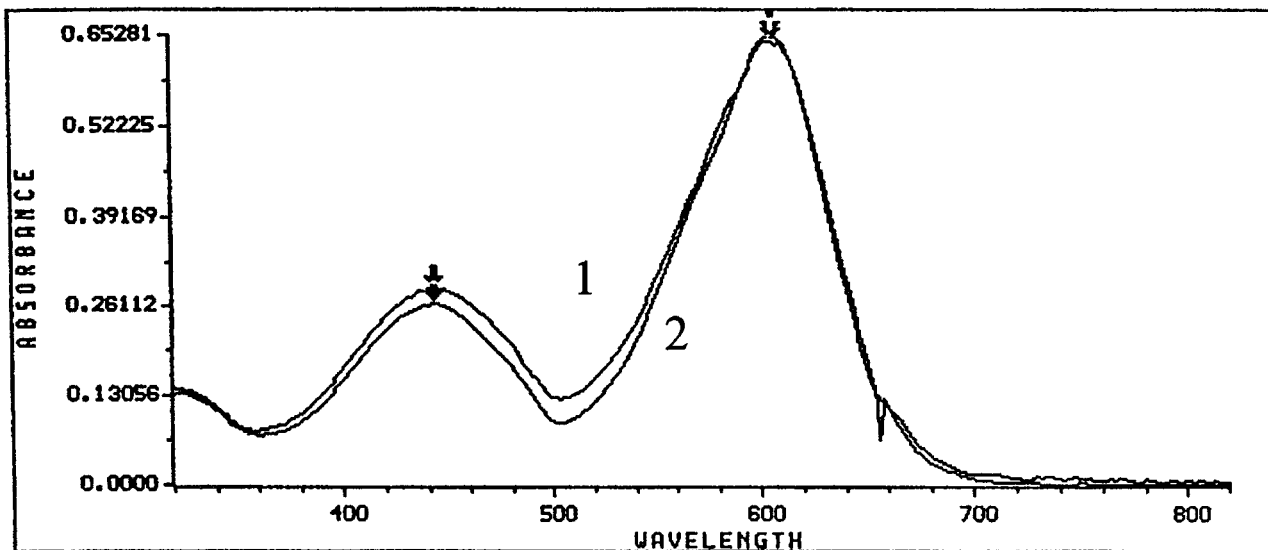


Figure 3 Absorption spectra of Dz in (1) a chloroform solution and (2) inside the gel.

To analyze the behavior of the organogel/dye complexes in salt aqueous solutions, gel samples containing a fixed amount of dye (with chloroform as a solvent in the gel phase) were immersed in aqueous solutions of AgNO_3 acidified with nitric acid. The pH of the solvent was kept at the level of approximate unity. After a 1-min immersion in the AgNO_3 aqueous solution, the gel films were analyzed by the spectrophotometer. The change of the sample color from green to yellow and the shift of the absorption band from 606 to 460 nm

(Fig. 4) showed that Ag^+ ions were absorbed by the gel and formed AgHDz complexes inside the gel. It is known that the absorption maximum of AgHDz complex is about 456 nm.¹⁰

To understand the process of the complex formation and estimate the amount of the absorbed ions, the content of the Ag^+ ions inside the Dz-containing gel was compared with the content of the Ag^+ ions inside the Dz-free gel. Note that AgNO_3 is not soluble in chloroform, so Ag^+ ions cannot penetrate the gel phase as a result of dif-

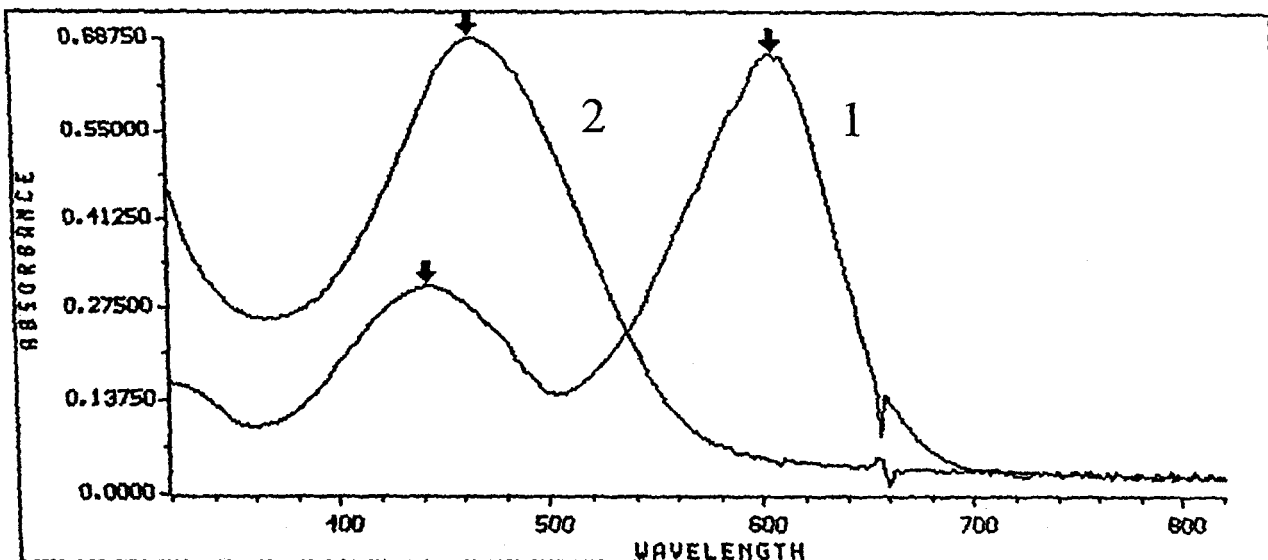


Figure 4 Absorption spectra of Dz-containing film (1) before and (2) after interaction with a solution containing silver ions.

Table I Evaluated Concentrations of AgNO_3 Inside Dithizone-Free and Dithizone-Containing PVCa Gels

C_0 AgNO_3	$C_{\text{gel}}/C_{\text{ext}}$	$C_{\text{gel}}/C_{\text{ext}}$ Dit	ν_0	ν	ν_{dit}
$8.3 \cdot 10^{-2}$	3.3	5.4	7.5	0.8	1.2
$8.3 \cdot 10^{-3}$	—	4.1	$6.4 \cdot 10^{-1}$	—	$0.9 \cdot 10^{-1}$
$8.3 \cdot 10^{-4}$	5.8	7.1	$6.9 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
$8.3 \cdot 10^{-5}$	13.4	28.8	$5.9 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$

$C_0 \text{AgNO}_3$ = initial concentration of AgNO_3 in the external solution; $C_{\text{gel}}/C_{\text{ext}}$ = ratio between the AgNO_3 concentrations inside and outside the gel; $C_{\text{gel}}/C_{\text{ext}} \text{Dit}$ = ratio between the AgNO_3 concentrations inside and outside the gel in the dithizone-containing gel; ν_0 = initial molar ratio of AgNO_3 to monomer units of the network chains; ν = molar ratio of absorbed silver to monomer units of the polymer chains for the dithizone-free gel; ν_{dit} = molar ratio of absorbed silver to monomer units of the polymer chains for the dithizone-containing gel.

fusion. Hence, the absorption of silver ions by the PVCa/organogel may depend on two factors: (1) the complex formation of silver ions with amide groups of PVCa chains and (2) the complex formation of silver ions with dye molecules within the gel.

The Dz-free and Dz-containing (the Dz concentration inside the gel was about 4.5×10^{-4} mol/L) PVCa gels were immersed in AgNO_3 aqueous solutions. The content of Ag^+ ions was evaluated by the change in the silver concentration in the external solution after the incubation of the samples in the AgNO_3 solution. The results of the investigation are presented in Table I. From the presented data, it is obvious that both Dz-free gels and Dz-containing gels absorbed silver ions from the solution. For all systems under consideration, the silver concentration within the gels was several times higher than that in the external solution. Consequently, PVCa absorbed the silver ions from the external solution. The content of silver ions absorbed by Dz-containing gels was higher than by Dz-free gels (the ratio of the concentration of silver ions in the Dz-free gel to the concentration of silver ions in the Dz-containing gel was about 0.8). This shows that the presence of Dz slightly enhanced the absorption capacity of the gel because of the complex formation of Dz molecules with the silver ions. Nevertheless, the special convenience of Dz-containing gels is connected to the fact that because of the complex formation of Dz molecules with the silver ions, their visible absorption spectra are changed and, therefore, such gels can be used as sensors for the determination of the presence of silver ions. The polymer network of the gel plays the role of container for water-insoluble organic dyes and separates the dye-containing and water phases. In

this case, smaller amounts of dye can be used, and the labor-consuming procedure of extraction can be avoided.

The optical density of the AgHDz complex inside the gel was a function of the AgNO_3 concentration in the external solution (Fig. 5). The increase in the AgNO_3 concentration in solution led

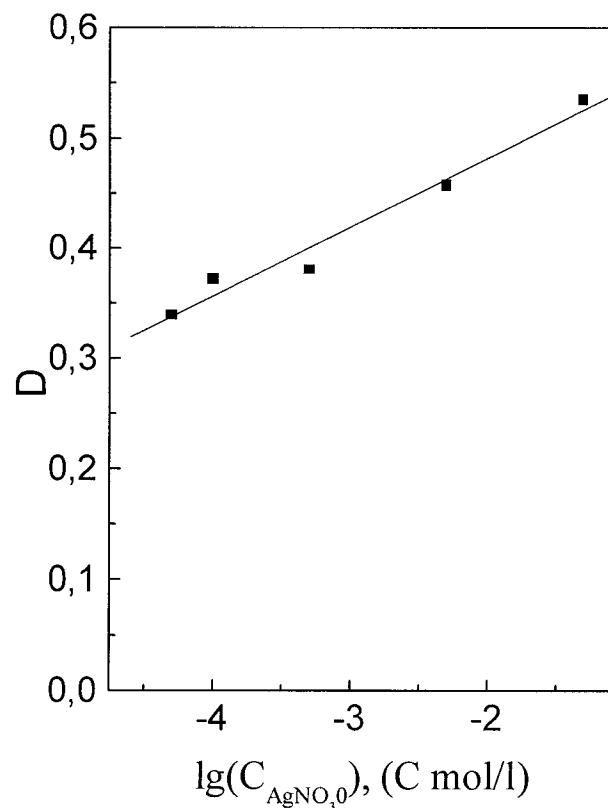


Figure 5 Optical density of the AgHDz complex inside the gel as a function of the initial AgNO_3 concentration in the external solution.

to the increase in the optical density of the system.

CONCLUSIONS

The efficiency of the absorption of dyes by PVCa gels depends on the nature of the organic solvent. PVCa organogel/dye systems absorb metal ions from aqueous solutions because of the absorption properties of PVCa and the formation of chelate complexes between dye molecules and metal ions. The photometric data for Dz-containing PVCa gels (with chloroform as a solvent in the gel phase) immersed in AgNO_3 aqueous solutions indicates that metal ion/dye complexes are formed inside the gel phase. Because the water and chloroform are immiscible liquids and Dz is insoluble in water, the Dz molecules are not released into the external solution. The optical density of the metal ion/dye complexes inside the gel depends on the salt concentration in the external solution.

Thus, a principle possibility for the design of sensors of metal ions based on dye-containing PVCa gels was shown. The solubility of PVCa in both water and organic media makes possible the use of these systems for the determination of the presence of metal ion concentration in water solutions if the dye is insoluble in water and soluble in organic liquids. In this case, the polymer network acts as a container of water-insoluble organic dyes and separates the dye-containing and

water phases. The use of the systems based on PVCa gel for the photometric determination of metal ions has several advantages over the extraction methods commonly used in analytical chemistry because, in this case, the separation of two compounds is not needed.

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