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Polymer Gel/Organic Dye Complexes in Aqueous Salt Solutions

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SUMMARY: The present work is devoted to the study of the complex formation of polymer gel with organic dye and their properties in the aqueous salt solutions. Two systems were studied: 1) polyelectrolyte gel based on poly(diallyldimethylammonium chloride) and water soluble oppositely charged organic dyes (alizarin red S and catechol violet) and 2) organogel based on poly(N-vinylcaprolactam) and dithizone. The collapse of the polyelectrolyte gels in the presence of oppositely charged dyes together with the effective absorption of dyes was observed. The shrinking degree and the dye absorption by the gel depends on the dye concentration. In the case of PVCa gel in organic media the dye absorption takes place.

The main attention has been concentrated on the study of the behaviour of gel/dye complex immersed in the salt solution if dye is the chelating ligand for metal ions. It was shown that polyelectrolyte gels generally form stable complexes with oppositely charged dyes.

The behaviour of PVCa-dithizone-chloroform system was studied in $AgNO_3$ aqueous solution. The release of dithizone to the external aqueous solution of $AgNO_3$ reservoir is completely suppressed.

Absorption spectra of gel/dye and gel/dye/metal ion systems were studied. It was shown that metal ions penetrate inside the gel phase and the dye/metal ion complexes form within the gel. The dependence of the optical density for the systems of gel/dye/metal ion on the salt concentration is observed.

Introduction

The complexes of water-soluble polymers with different high- and low-molecular-weight compounds excite great interest at present. They are formed as a result of specific noncovalent interactions and have all the features of individual compounds displaying unique properties different from those of the initial components[1-2]. There are a number of works that deal with the interaction of dyes with linear polymers in aqueous solutions[3-5] and polyelectrolyte gels[6-8]. Coulombic, hydrophobic and steric interactions are major factors governing the thermochemical and dynamic aspects of complex formation.

The present work deals with the products of the interaction of 1) polyelectrolyte positively charged gel based on poly(diallyldimethylammonium chloride) (DADMAC) with alizarin red S,

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catechol violet and 2) organogel based on poly(N-vinylcaprolactam) (PVCa) with dithizone. Here we report (a) the swelling characteristics and absorption properties of these systems and (b) the complex behaviour in salt solutions.

Taking into account that the certain dyes are the selective reagents for metal ions in aqueous solutions, the practical aspects of the present research are connected with the design of new materials (selective absorbents for metal ions) based on gels possessing the combination of properties of the gel and feature dye.

Results and discussion

After immersion of the polyelectrolyte gel in the solution of the oppositely charged organic dye gel collapse occurs (Fig.1, curves 1,2) and the effective dye absorption by the gel is observed (Fig. 1, curves 3,4). Here initial dye concentration in the solution θ is expressed by molar ratio between added dye and charged monomer unit of polymer network and dye absorption γ is the molar ratio of dye absorbed by gel to charged monomer unit of polymer network.

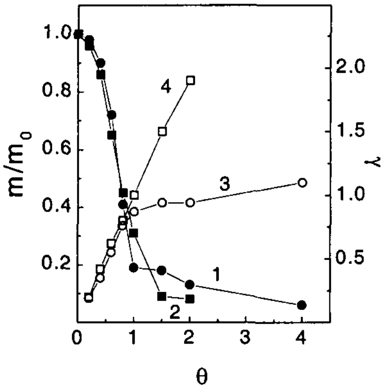


Fig. 1: The swelling ratio m/m$_0$ of gel (1, 2) and absorption γ (3, 4) as a function of dye concentration. Catechol violet (1, 3) and alizarin red S (2, 4).
m$_0$ -initial mass of gel swollen in water; m - gel mass after incubation in dye solution.

It is natural to assume that the gel collapse is caused by the dye absorption. Due to the strong Coulombic interaction between opposite charges, the dye molecules are concentrated in the gel phase and their aggregation induced by hydrophobic interactions leads to the gel collapse. This is exactly the kind of phenomena which take place for the polyelectrolyte gel -

oppositely charged surfactants system. After immersion of polyelectrolyte gel in the solution of the oppositely charged surfactant due to ion exchange reaction and hydrophobic interactions the surfactants are concentrated and aggregated inside the gel phase; simultaneously the gel collapses [9-10]. The aggregation of charged species with hydrophobic groups is enhanced in the oppositely charged gel as a result of fact that the dye aggregates charge is neutralised by the initially immobilised charges fixed on the gel chains.

From Figure 1 one can see the difference of the absorption of alizarin and catechol violet. The gel absorbs practically all of the added alizarin and γ is close to 2 namely 2 dye molecules per one charged unit of polymer chain. In the case of catechol violet at $\theta>1$ the amount of absorbed dye (γ) is close to 1.

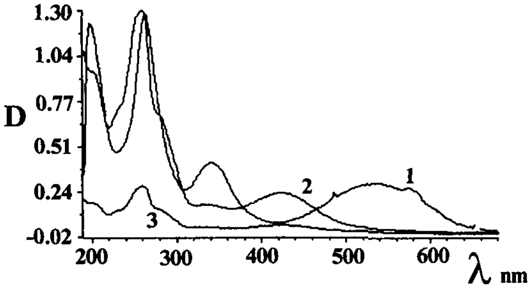
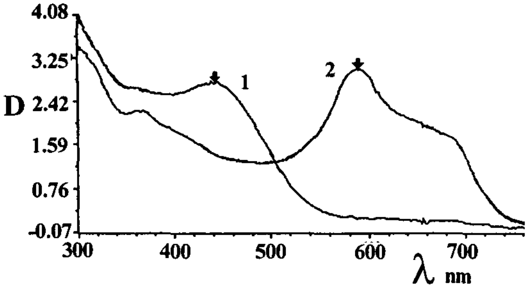


Fig. 2: Absorption spectra of alizarin red S within the gel film (1) and in solutions (2, 3). Alizarin concentration is $7.0 \cdot 10^{-4}$ (1, 2), and $1.4 \cdot 10^{-4}$ mol/L (3)

The different absorption for alizarin and catechol violet can be explained by the different state of dye molecules inside the gel. Absorption spectrum of dye immobilised inside the gel is different from the spectrum of aqueous solution at the same dye concentration (Fig. 2). In the case of alizarin the shift of absorption maximum and new maximum at $\lambda=538$ nm is observed. The effect can be explained firstly, by the formation of donor-acceptor complexes between dye molecules and polymer units. It is known that the formation of donor-acceptor complexes is accompanied by some additional electron transitions in which the electron is transferred from the ground state of donor to the excited state of acceptor. In this case the appearance of a new absorption band in the UV or in the visible domain of the spectrum and the shift of the spectrum take place[11]. Secondly, under certain conditions in concentrated enough aqueous solutions (at concentration above 10^{-3} mol/L)[12] the dye molecules aggregate forming dimers, trimers due to their hydrophobic attraction. The aggregation can take place at lower concentration of the dye in the presence of the polymers with specific binding sites for the dye[5]. Absorption band for dimer ion is shifted to short-wave region in comparison with one for monomer ion. Therefore, the analysis of absorption spectra of alizarin within the gel points out the formation of ***a)*** donor-acceptor complex and ***b)*** dye dimers. This fact explains two-fold excess of dye absorption in comparison with charged monomer units.

One of the important aspects of the studied systems is the behaviour of polymer gel/dye complexes in aqueous salt solutions. The main feature of the studied systems is that the dyes and metal ion pairs capable to form the chelating complexes are used. These organic dyes can be applied for the determination of the metal ion in the analytic chemistry. Alizarin and catechol violet are chelating ligands for specific adsorption of aluminium ions[13)].

Alizarin and catechol violet/gel complexes with different compositions were immersed in the solution of aluminium sulfate. For all studied systems the instantaneous colour change of the gel phase which is characteristic for dye solution in the presence of aluminium salt is observed. Figure 3 demonstrates the absorption spectra for catechol violet (a) and alizarin (b)/gel complexes after incubation in $Al_2(SO_4)_3$. The change of absorption spectra points out the dye/Al^{3+} complexes formation within the gel.



a)

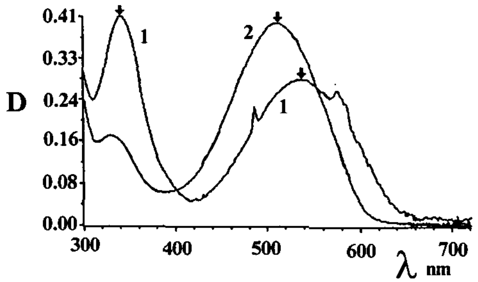


Fig. 3.: Absorption spectra of catechol violet (a) and alizarin red S (b) within the gel film (1) and after immersion of gel/dye film in the $Al_2(SO_4)_3$ solution (2). $Al_2(SO_4)_3$ concentration is 2 10^{-4} mol/L(a), 0.4 10^{-4} mol/L (b)

The *complex stability* in salt solutions was characterised by the distribution coefficient *S* which is the ratio of the amount of dye within the gel phase after incubation during 2 weeks in the salt solution to the initial amount of dye absorbed by the gel. Figure 4 shows the dependencies of *S* on the gel/complex composition in $Al_2(SO_4)_3$ solution. The decrease of the fraction of the released dye from gel in the salt solution with the increase of the dye fraction in the complex is observed.

However the release of alizarin from gel to the external solution of $Al_2(SO_4)_3$ reservoir is lower in comparison with catechol violet, that can be also explained by the donor-acceptor complex formation. The increase of the salt concentration in the solution leads to the slight increase of the released dye.

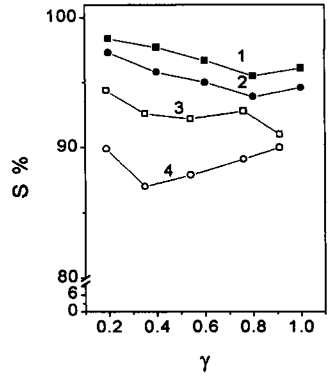


Fig. 4: Dependence of *S* on a gel/dye complex composition γ in $Al_2(SO_4)_3$ solution. Alizarin (1,2) and catechol violet (3,4). Molar ratio of salt amount in solution to amount dye absorbed by gel is 1 (1,3) and 2 (2,4).

Complex formation of Ag^+ and dithizone within the PVCa gel

The second direction of the present work is the study of the behaviour of PVCa organogel-dithizone (Dz) (chloroform as a solvent for gel phase) systems in the aqueous solution of $AgNO_3$. Here it should be noted that the main PVCa feature is its solubility in water and organic solvents. One of the great advantage of system based on PVCa gel in comparison with polyelectrolyte gel is the use of chloroform as a solvent for gel phase. In this case the dye release from gel phase into external solution is not observed because water and chloroform do not mix and dithizone is insoluble in water.Dithizone is one of the sensitive organic reagent using for extractive-photometric determination of little amount of Ag^+ ions.

PVCa organogel-dithizone films were designed by the dithizone absorption by PVCa gel in chloroform media. Dithizone concentration within PVCa gel is $4.5 \cdot 10^{-4}$ mol/L.

After immersion PVCa organogel/dithizone in aqueous solution of *$AgNO_3$* the colour change is immediately observed. Figure 5 shows the absorption spectra of PVCa/dithizone film and PVCa/dithizone film after incubation in *$AgNO_3$* solution.

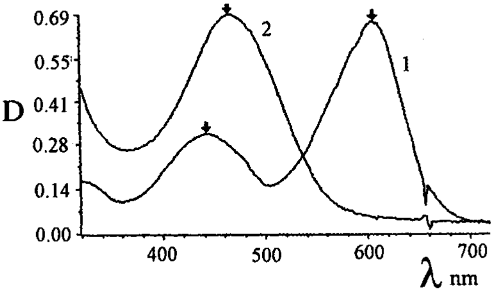


Fig. 5: Absorption spectra of ditizone within the gel film (1) and film immersed in the *$AgNO_3$* solution (2). *$AgNO_3$* concentration is 10^{-3} mol/L.

Absorption spectrum of the film after incubation in *$AgNO_3$* aqueous solution is similar to one of AgHDz complex. This fact demonstrates 1) the formation of AgHDz complex inside the gel and 2) spectra for AgHDz complex are unaffected by PVCa film.

In this case the value of optical density of AgHDz complex inside the gel is a function of *$AgNO_3$* concentration in the external solution (Fig.6). The increase of *$AgNO_3$* concentration in solution leads to the increase of the optical density of the system.

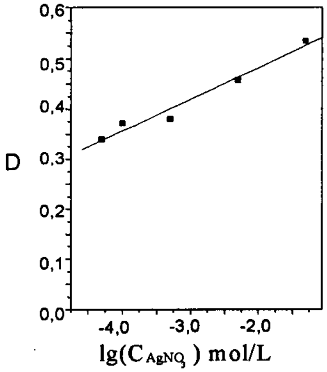


Fig. 6: Optical density of AgHDz complex within the gel as a function of $AgNO_3$ concentration in the external solution

Analysis of the absorption data for PVCa gel with dithizone and without dithizone points out that in both cases Ag^+ ions are absorbed from solution and Ag^+ concentration inside the gel is significantly higher in comparison with the solution concentration. The dithizone presence leads to the increase of the Ag^+ absorption by gel.

The principle of gel/dye complex formation allows to design and simplify synthesis of a variety of materials. The complex stability and the instantaneous colour change of the gel phase after the immersion in the salt solution with specific adsorption of metal ions by the dye molecules is perspective for the elaboration of dye-gel complex system as sensors for metal ions.

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