

Cationic Polymer-Metal Complex Formation at Interfaces, Solutions and Hydrogels

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SUMMARY: The polymer-metal complex formation at interface, solution and hydrogels were comparatively investigated. The specific peculiarities of complexation of cationic polymers with metal ions having a various nature depending on the preparation conditions were found.

Introduction

The principle of analogy of hydrodynamic behaviour between slightly cross-linked polymeric hydrogel and its linear macromolecules was submitted by a number of the authors.^{1, 2)} The discussion about free thermal fluctuation of the chains between joined points of the gels, consequently, their high flexibility of conformational state has been an attractive problem in polymer science for last two decades. The question is reduced to revealing common features of swelling-compression behaviour in hydrogels and dissolution-precipitation in their linear analogues. Research of these two extreme conditions of macromolecules can be essentially useful in a prediction of the first or second order volume-phase transitions phenomena taking place in polymer. Such a volume phase transitions were found to be generated by changing of an environmental conditions: temperature, the composition of the solvent, application of electric or magnetic fields, pH and ionic strength of the solution, the presence of low or high molecular substances which can interact with the functional groups of gels³⁾ forming complexes of variable content. In this paper, we report a comparative study on behaviors of moderately cross-linked gels and their linear analogous under interaction with metal ions running from alkali to polyvalent metal cations.

The purpose of the present study is to clarify the peculiarities of the complexation process depending on the preparation conditions of complexes. Concerning this aim, the polymer-metal complexes were prepared in the bulk of the solvent, at the boundary of two immiscible liquids and in the volume of gels. The final aim is to define the common and specific features of complexation depending on conformational states of gels and linear macromolecules, respectively.

Polymer-metal complex formation at the boundary of two liquid phase

At present, the problem of obtaining and using new semipermeable membranes on the basis of composite polymer materials is actual. Well-known methods to produce membranes and films in the bulk of solution are multistage and complicated processes. In this connection, the new method of preparation of polymer-metal complexes with high structural order at the interface of two immiscible liquids was proposed.⁴⁾ The components separately dissolved in the appropriate liquids must possess a complementary relation toward each other.

It is interesting to note, that the interaction between polyvinylpyridines and both alkali salts and earth-alkali metals occurs in polar organic solvents. However such complexes did not manage to be obtained neither in pure water nor in low-polarity organic solvents, for example, in benzene, though they can be synthesized at the boundary of these two immiscible liquids. We have investigated a wide set of different polymer-metal complexes synthesized at the benzene-water interface running from alkali to transition metal ions. Table 1 shows general characteristics of the complexes thus obtained.

Table 1. The characteristics of P2VP-Meⁿ⁺ complexes

Complex	Composition [P2VP]:[Me ⁿ⁺]	Colour	Thickness of films, μm	Elemental analysis of N, %		ν , cm^{-1}
				calc.	exp.	
2VP-AgNO ₃	2	gray	30	11.0	10.6	1595
P2VP-Cu(NO ₃) ₂	4	blue	27	11.3	12.0	1595
P2VP-LiClO ₄	4	colorless	10	8.80	8.50	1600
P2VP-LiJ	4	yellow	20	-	-	1600
P2VP	-	-	-	13.3	13.3	1590

Complex formation takes place due to the coordination of electron-donating nitrogen atoms of poly(2-vinylpyridine) (P2VP) to metal ions which is in agreement with the elemental analysis of the final product and IR spectra of the film. One can see that the experimentally obtained values of nitrogen content in the complexes (N_{exp}) are in good agreement with the theoretical ones (N_{calc}) and differed from the nitrogen content in the

polymer itself. A small shift of the C=N band wave length from 1590 by 5-10 cm^{-1} in the IR spectrum evidences coordination of P2VP nitrogen atoms with metal ions.

The realization of complex formation reaction at the boundary of two phases causes the high structural order of these complexes. It was confirmed by both X-ray and DTA analysis of complexes under discussion.⁵⁾

Complexation of polymeric hydro- and organogels with metal ions in aqueous and organic media

As it was mentioned above, the most complete information on a nature and mechanism of interaction can be received from the comparative analysis of complexation of linear and cross-linked macromolecules with low molecular substances in solvents of various thermodynamic quality. The latter, as a rule, plays the extremely important role in acquiring of macromolecules or any other conformation as a result of specific interaction of the solvent molecules with hydrophobic and hydrophilic parts of the polymer. Proceeding from comparison macroscopic behaviour of macromolecules (the viscosity of linear and swelling coefficient of cross-linked polymers) one can make a decision about complex structure at microscopic level.

Fig. 1a and 1b demonstrate the dependences of intrinsic viscosity and swelling coefficient of linear and cross-linked poly(2methyl-5vinylpyridine) (P2M5VP) macromolecules on relative salt concentration of NaClO_4 (1) and CaCl_2 (2) in methanol respectively. It is visible, that the characteristic curves of viscosity as well as K_{sw} with increasing of salts concentration are identical and passes through two clearly expressed maximums. At small metal ion concentrations the maximum has a higher value in comparison with the second one. We believe that the presence of maxima is caused by formation of coordination bond between metal ions and their ionic pairs with electron donating nitrogen atoms of P2M5VP. This behaviour can be explained in terms of the polyelectrolyte swelling effect both in linear and in cross-linked polymer because of electrostatic repulsive force between positive charges of cations associated with the macromolecule chains.⁶⁾ The further decrease of the parameters characterizing hydrodynamical volume of macromolecules can be caused by suppression of polyelectrolyte swelling effect due to high ionic strength of a solution created by dissociated ions of low molecular salts. The second peak is caused by the interaction of functional groups of polymer which was not entered in interaction at the first stage of complexation with ionic

pairs of salts.⁸⁾ The maximal values of viscosity in complexes $[P2M5VP]:[CaCl_2]$ is equal to 4:1 and 8:1, while in system gel $[P2M5VP]:[CaCl_2]$ corresponds to the ratios 5:1 and 8:1 respectively.

The existence of complexes are inferred from the examination of IR and X-ray data. The new band (1100 or 1096 cm^{-1} depending on complex composition) in complex gel $P2M5VP-NaClO_4$ was observed. The behaviour of the band 1724 cm^{-1} corresponding to the valent vibration of the piridinium ring is very interesting. At the change of a ratio of interacting components the band at 1724 cm^{-1} gradually turns into the shoulder of the band

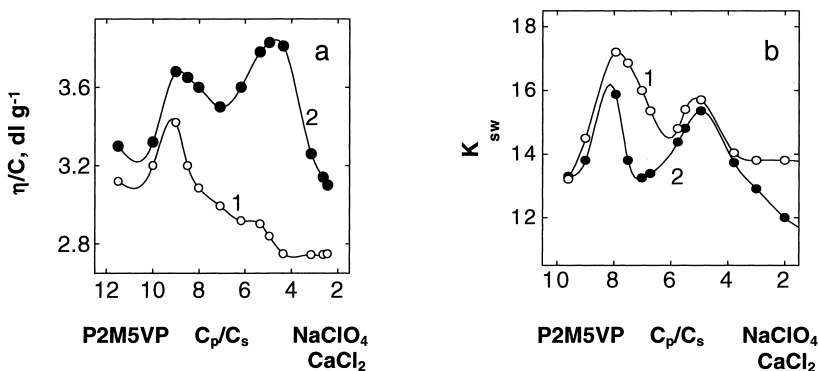


Fig. 1. Dependences of reduced viscosity (a) and swelling degree (b) of linear and cross-linked P2M5VP on relative concentration of $NaClO_4$ (1) and $CaCl_2$ (2).

1604 cm^{-1} that provide evidence for the fact that the interaction takes place in the ring. For other bonds the shifts are small (of order 4 cm^{-1}). From these data a conclusion can be made that obtained complexes are qualitatively new compounds. The behaviour of the bonds with frequencies 1456 and 1400 cm^{-1} in the spectra of $CaCl_2$ differs from the system discussed above. Both of them shifts to the region of low frequencies by 4 and 16 cm^{-1} , respectively. For the system with $NaClO_4$ the first bond lies in the region of higher frequencies and the second one changes only by 4 cm^{-1} to the low wavelength. This fact may be explained by different interaction mechanism of alkali and earth-alkali metal ions, particularly by the participation in the complexation process of two types of divalent metal.⁶⁻⁸⁾

X-ray investigation of $P2M5VP$ -salt complexes shows two new crystalline lines with $d=3.0248$ and 5.0025 \AA for the systems gel- $CaCl_2$ and gel- $NaClO_4$, respectively. Maximum of amorphous halo of polymer actually does not change, but the decrease of

intensity takes place in both cases. This process is somewhat differ from the behaviour of linear PVP where destruction of polymer matrix and obvious change of d-values were observed.⁸⁾

Now we shall consider the peculiarities of complexation process between metal ions and hydrogels and their linear macromolecules in aqueous solution as well. Fig. 2a shows

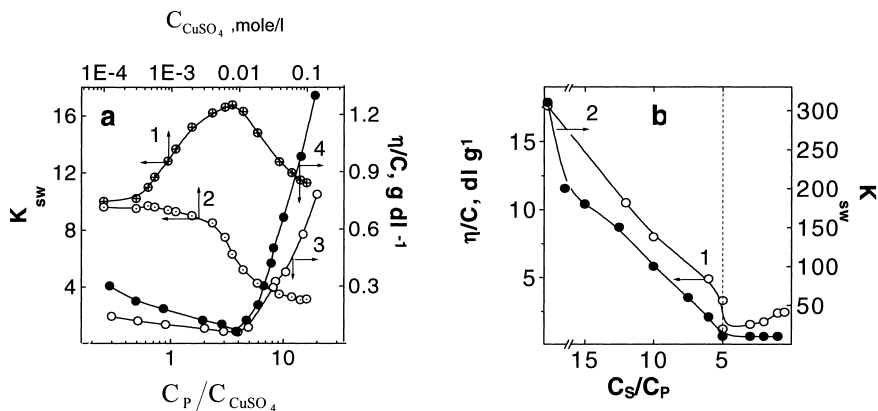


Fig. 2a. Dependences of PEI (1, 2) and PAA•HCl (3) gels swelling degree and reduced viscosity its linear polymer (4) on $CuSO_4$ concentration at pH 8,3 (1) and 6,5 (2).

Fig. 2b. Dependences of reduced viscosity (1) and swelling degree (2) of 2M5VP-BMA on the ratio $[H_2PtCl_6]/[N]$ in linear and cross-linked forms respectively.

the dependences of change of the hydrogel swelling coefficient of poly(ethylenimine) (PEI) and polyallylamine (PAA•HCl) hydrochloride hydrogel and reduced viscosity of its linear polymer on concentration of copper sulfate (C_{CuSO_4}) in the solution (1, 2) and ratio of polymer functional groups (C_P) to metal ions concentration (3, 4). Characteristics of both investigated systems is the strong compression of hydrogel volume (or reduction of weight) with increasing of transition metal ions mole fraction in the system. An attention must be paid to the fact of influence of the degree of macroligand ionization on character of conformational change of linear segments of the gel. From Fig. 2a one can see that under high pH the swelling coefficient of the PEI gel passes through a maximum in gel-metal ion systems at concentration of salt equal to $8 \cdot 10^{-3}$ mole/l for Cu^{2+} (the molar ratio corresponding to the number of macroligand functional groups which has entered into coordination with metal ions ($\beta = [Me^{2+}]/[PEI]$) is equal to 0.25). The increase of hydrogels swelling degree under complexation with metal ions at high pH can be explained in terms of arising additional charge in the slightly-charged gel by bivalent metal ions coordinated with

amiono-groups of PEI. The latter promotes increase of electrostatic energy of the system that results in increasing swelling coefficient. The swelling proceeds so long as the copper ions will not achieve completely the maximal coordination saturation of vacant orbitals. The compression after an extreme point can be treated from a position of suppression of electrostatic repulsion between the coordinated metal ions at the excess ionic strength of a solution.

For PAA·HCl hydrogel the decreasing of the swelling coefficient caused by intramolecular chelation between metal ions and polyligands is observed. It, in turn, results in additional cross-linking in a network due to the donor-acceptor bonds and compactization of linear parts of polymers between covalently cross-linked points. At low value of pH the complexation proceeds by substitution mechanism of hydrogen ions of protonized nitrogen atoms of the gel by metal ions avoiding the stage when polymer chain acquires charge as it was observed at high pH value (see Fig. 2a, gel PEI-Cu²⁺, curve 1 and 2 also). The appropriate correlation between changing of K_{sw} and reduced viscosity of the gel and linear polymer is observed (Fig. 2a, curves 3 and 4). Complexes of PAA·HCl, copolymer of 2M5VP-butylmethacrylate (2M5VP-BMA·HCl) and PEI hydrogels with metal ions existing in the form of complex anions, e.g. [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻, [PtCl₆]²⁻ were also obtained.⁹⁾

Fig. 2b shows the dependence of the reduced viscosity (curve 1) of linear and the swelling coefficient K_{sw} (curve 2) of its hydrogel upon the molar ratio m of interacting components ($m=[H_2PtCl_6]/[N]_{gel}$). Complexation between linear polymers with [PtCl₆]²⁻ ions leads to the formation of bridges and to a folding of linear macromolecule due to electrostatic interactions of oppositely charged complex metal ions and functional groups of polymer. A similar behaviour is shown by the system of hydrogel 2M5VP-BMA·HCl-[PtCl₆]²⁻. For both linear and cross-linked polymers the continual contraction takes place in the interval of $m=15:1$ reaching minimal value at $m=5:1$. The minima of reduced viscosity and swelling coefficient correspond to the latter composition.

In the literature the problem of complexation between three complementary components were discussed: for example, polyacid – polybase – transition metal ions or polybase – transition metal ions – surfactant¹⁰⁾. Obviously, driving force of the process should be joint cooperation of electrostatic forces, hydrophobic interactions and donor-acceptor bonds.

Fig. 3a and 3b represent the dependences of change of K_{sw} and degrees of binding of sodium dodecylsulfate (SDS) and Cu²⁺ ions on copper acetate concentration under its

addition it to the gel PEI-SDS complex. The addition of copper acetate solution to the complex of PEI-SDS results in significant growth of K_{sw} from 4,6 up to 16,6 and decrease of pH (Fig. 3a). The presence of the opposite charged surfactant ions in the hydrogel volume promotes easy penetration of copper ions inside of the network. The reason may be explained by decreasing of hydrogels surface potential.

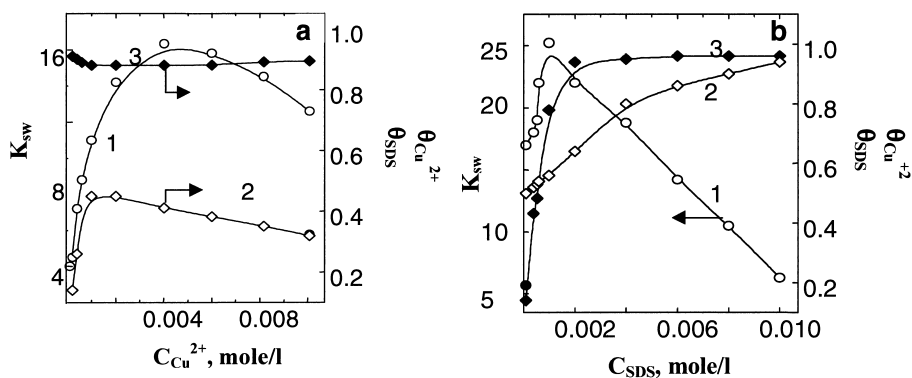


Fig.3. Dependences of swelling degree of PEI gels (1), degrees of binding of Cu^{2+} (2) and SDS (3) on concentration of $Cu(Ac)_2$ (a) and SDS (b).

The increase of K_{sw} can be caused by both purchase of a positive charge and increase of osmotic pressure inside of network volume created by acetate counter-ions at the excess amount of copper ions. According to the principle of an electroneutrality, acetate ions should compensate a superfluous positive charge of the gel created by copper ions. The experiment which has been carried out in the return order (Fig. 3b), that is with constant β ($\beta = [Me^{2+}]/[PEI] = 0.25$) and varying n ($n = [SDS]/[PEI]$) shows also strong increase of K_{sw} of the gel PEI- $Cu(Ac)_2$ from 16,5 up to 25 under adding SDS solution. The maximal value of K_{sw} of the polymer-metal complex corresponds to $n = 0,1$. In this case appearance of charges in the network due to the coordination with copper ions, promotes effective sorption of the opposite charged surfactant ions. The prompt decrease of K_{sw} at value $n > 0,1$ can be explained by reduction of counter-ions osmotic pressure both of copper ions (acetate-ions) and SDS (sodium-ions). The mechanism of interaction can be presented as an ion exchange reaction between the acetate-ions and SDS ions. The strengthening of hydrophobic interactions between unipolar parts of surfactant and PEI macromolecules provides also strong compression of the gel, extruding from it easily migrated sodium and acetate ions to the environmental solution.

Thus we have considered some important features of behaviour of polymers depending on a condition of their existence in the system: either as free macromolecules with maximal conformational freedom of the chains or as moderately cross-linked gels with some limitations of chains flexibility.

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