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Reentrant conformational transition of polyelectrolyte network in water alcohol mixtures in the presence of oppositely charged surfactant

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SUMMARY. Reentrant conformational transitions are observed in polyelectrolyte networks of sodium methacrylate - acrylamide copolymers in water - alcohol mixtures in the presence of cetylpyridinium bromide. At low alcohol content, gel shrinking is induced by complex formation between charged network and oppositely charged surfactant. In media with high alcohol content the complex dissociates and the collapse comes as a result of volume interactions between charged network and the solvent. At intermediate alcohol concentration, hydrophobic interactions between hydrocarbon groups of surfactant ions are suppressed and the gel swelling is observed.

INTRODUCTION. Charged networks form stable polyelectrolyte complexes (PEC) with oppositely charged ions of surfactants /1,2/. The ions of a surfactant in a gel aggregate due to hydrophobic interactions /1,3/. Column interaction between the charged surface of this aggregates and the ions of a network result in gel collapse. The theory of this phenomena is developed in /4/. This paper presents a new type of conformational transitions in polyelectrolyte networks in the presence of charged surfactant namely the reentrant transition in binary solvent.

First observation of reentrant volume transitions in charged gels swollen in binary solvent, and the first theoretical explanation of the phenomena has been described in /5,6/. The more general theory, which explains the phenomena of the so-called double reentrant transitions is presented in /7/.

EXPERIMENTAL. The object of this investigation was the network of copolymer sodium methacrylate (SMA) with acrylamide (AA). The gel was prepared by free radical

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polymerization of SMA (30,5 mol.%), AA (69,0 mol.%) and N,N'-methylenebisacrylamide (0,5 mol.%) in aqueous solution. The total concentration of monomers was 10%. The crosslinker was bisacrylamide. Ammonium persulphate (concentration .4·10^{-3} mol/l) and (N,N,N',N'-tetramethylethylendiamine concentration 4.4 10^{-3}mol/l) were respectively the initiator and the accelerator of the polymerization reaction. Gelation was carried out in cylindrical tubes having an inner diameter of 3,0 mm at room temperature. The prepared gel was washed in a large amount of distilled water for 3 weeks, cut into thin disks, and then immersed in water-isopropanol or aqueous solutions, containing the surfactant. The amount of solvent was 4.10^{2}l per one mole of the charged unit of the network. The surfactant was cetylpyridinium bromide (CPB).

The value m/m_o characterizes the relative mass of the samples where m and m_o are the equilibrium mass values in solution and in pure water respectively. The initial equilibrium content of dry polymer in the sample was 0,010%. The efficiency of the CPB absorption by the gel was characterized by the distribution constant **K** = C_g/C_s where C_g and C_s are the concentrations in the gel phase and in the solution. respectively. The **K** value was calculated by the formula $\mathbf{K}=(M - D\,V_s\,\varepsilon^{-1})\varepsilon/VD$, where M is the amount of the CPB moles in the system, ε is the extinction coefficient at $\lambda = 259$ nm, V_s is the solution volume, D is optical density of the solution. Optical density was measured by spectrophotometer Hitachi 150-20 Japan.

RESULTS AND DISCUSSION Fig.1 shows the m/m_o values as a function of the surfactant content in the volume of the system ϑ. Here ϑ is the relation between the initial number of CPB cations in the solution and the number of the charged units of the network. The obtained curve is typical for polyelectrolyte network - surfactant systems /1,2/. At low ϑ the degree of swelling decrease slowly. Then the transition in collapsed state is observed, followed by a slight increase in the sample volume.

The transition in collapsed state is a result of a strong volume interaction between hydrocarbon residues of surfactant ions in gel. This interaction causes aggregation of the hydrophobic groups of the surfactant. Due to this fact (i) the concentration of mobile counterions inside the gel decreases leading to the essential decrease in

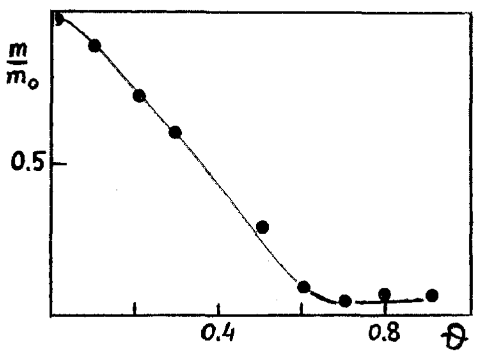

Fig.1 Dependence of the relative mass m/m_o on the relation between the number of the CPB cations and SMA units in the system ϑ.

internal osmotic pressure of gel; (ii) strongly charged aggregates are attracted to the oppositely charged network chains inducing their additional crosslinking. As a result, the pronounced collapse of gel is observed. Further slight increasing of gel volume can be explained by introducing of large surfactant ions in collapsed network with low water content /2/.

Fig.2 illustrates the dependence of distribution constant **K** on ϑ. The resulting curve has a sharp maximum at $\vartheta=0,5$. Near this point, the values of concentration of CPB cations in gel phase are 10^4 times higher than in surrounding solution so the efficiency of CPB cations absorption by the gel is very high. Sharp increasing of **K** values at low ϑ is a result of significant decreasing of the gel volume. At high ϑ, the saturation of the charged network by surfactant ions is observed.

It is well known that charged gels undergo sharp and often discontinious volume transitions in response to small changes in the temperature or solvent composition /8-9/. Many examples of such transition including gels with high charge density /10/ are known now. One should expect that for the network used in this work the same behavior will be observed.

Fig.3 shows the degree of swelling m/m_0 of the gel as a function of water - isopropanol composition. As it could be expected the phase transition from highly swollen to collapsed state is observed. The phase transition occurs at the volume fraction of isopropanol $\mathbf{v}_2=0,55$.

Now let us consider what kind of transitions should be expected for the network in the binary solvent in the presence of an oppositely charged surfactant. The result should strongly depend on the concentration of components. At low surfactant and isopropanol concentration, the network should swell due to the high osmotic pressure of the network counterions. The increasing of the volume fraction of alcohol should result in increasing of the attractive interactions between polymer units. As a result, at high alcohol content the gel collapse will be observed.

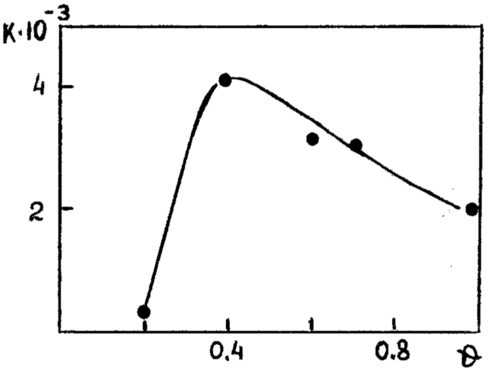

Fig.2 Dependence of the destribution constant **K** on the relation between the number of CPB cations and SMA units in the system ϑ.

At an intermediate CPB concentration, the degree of swelling of the anionic gel in water will be lowered due to network - surfactant interaction. The adding of isopropanol in solution should result both in weakening of the hydrophobic interactions and in increasing of the attractive forces between monomer units of the network. So the final picture should strongly depend on the interaction parameters, osmotic pressure, elastic forces etc. and the experimental investigation of each system is needed. In the case under investigation the gel collapse proceeds at rather high isopropanol content. Therefore, one should expect that the addition of alcohol will lead to the destruction of the hydrophobic interactions in the concentration region where the binary solvent is a good one. In this case the increasing of a bad solvant (isopropanol) content will result in significant gel swelling.

The data shown in Fig.3 support such assumption. At low surfactant concentration the increase of the alcohol content results in the shrinking and the collapse of the gel (Fig.3, curve 2). The increase of CPB concentration in medium with low alcohol content, leads to the gel shrinking (Fig.3, curve 3). UV-measurements show that in this concentration region practically all the surfactant is included in the gel (Fig.4). Then the increase of the alcohol content results in the gel swelling due to the weakening of the hydrophobic interaction between the surfactant ions. Finally, the increase of isopropanol content results in the gel collapse. Both, the swelling and the collapse of the gel proceed continiously. It should be noted, that after the collapse of the network the content of CPB ions in the gel is very small. It is less than it should be expected for the case of a nonspecific ion exchange.

In conclusion, it should be noted that in aqueous medium complexes, formed by polyelectrolyte networks and oppositely charged surfactants, are effective absorbers of organic compounds. The present paper shows that dissociation of such complexes can be easily achieved by addition of organic solvents in an aqueous medium.

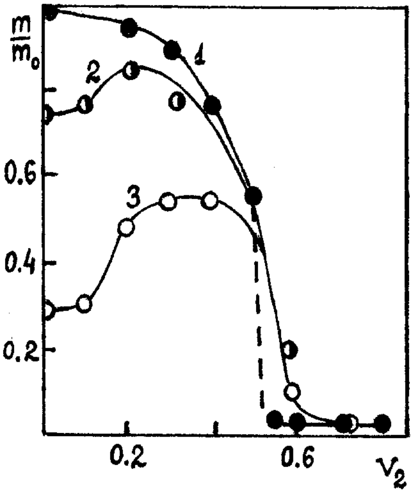

Fig.3 Dependence of the gel relative mass m/m_0 on the isopropanol content v_2 (vol%) in isopropanol-water mixtures. ϑ=0 (1), 0,2 (2) and 0,5 (3).

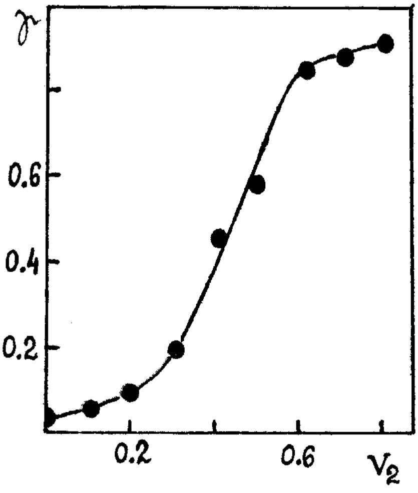

Fig.4 Dependence of the fraction of CPB moles in solution γ on the isopropanol content v_2 (vol.%) in isopropanol-water mixtures.

REFERENCES

1.STARODUBTZEV S.G., RYABINA V.R. and KHOKHLOV A.R.: Vysokomolek. Soed. V.32A, P. 969 (1990).
2.STARODUBTZEV S.G.: Vysokomolek. Soed. V.31B, P. 925 (1990).
3.BISENBAEV A.K., SALETSKY A.M., MACHAEVA E.E. and STARODOUBTZEV S.G.: in Networks 91. Conference Polymer Networks: Synthesis, Structure and Properties, Moscow, 91. P.51.
4.VASILEVSKAJA. V.V., KRAMARENKO E.Yu. and KHOKHLOV A.R.: Vysokomolek. Soed. V.33A, P. 1062 (1991).
5.KATAYAMA S., HIROKAWA Y. and TANAKA T.: Macromolecules V.17, P. 2641 (1984).
6.AMIYA T., HIROKAWA Y., HIROSE Y., LI Y. and TANAKA T.: J. Chem. Phys. V.86, P.2375 (1987).
7.VASILEVSKAJA. V.V., RYABINA V.R.,STARODUBTZEV. S.G. and KHOKHLOV A.R.: Vysokomolek. Soed. V.31A, P. 713 (1989).
8.TANAKA T.: Phys. Rew. Lett. V.40, P.820.
9.TANAKA T., FILLMORE D.J., SUN S.T., NISHIO L., SWISLOV G., and SHAH.S.: Phys., Rew. Lett. V.45, P.1636.
10.STARODUBTZEV S.G., and RYABINA V.R.: Vysokomolek. Soed. V.29B, P. 224 (1990).

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