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HYDROGEL COMPOSITES OF NEUTRAL AND SLIGHTLY CHARGED POLY (ACRYLAMIDE) GELS WITH INCORPORATED BENTONITE. INTERACTION WITH SALT, LINEAR POLYELECTROLYTES AND IONIC SURFACTANTS

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SUMMARY The swelling behavior in the solutions of sodium chloride, linear polyelectrolytes and ionic surfactants of the composites based on clay mineral bentonite (BENT) embedded in neutral and slightly charged poly(acrylamide) (PAAm) gels is studied. Negatively charged flat clay particles incorporated into polymer gel adsorb oppositely charged surfactant and linear polyelectrolyte and attract the charged chains of cationic polymer matrix. The results of SAXS study manifest the formation of lamella structure of the cationic surfactant adsorbed by the clay plates. The gels loaded with the clay show a strong response to changes in the nature and the composition of the ionic environment.

Introduction

It is well known that slightly cross-linked polyelectrolyte gels and neutral gels loaded with linear polyelectrolytes undergo drastic conformational transitions induced by a small change of external parameters such as composition of a medium, temperature, mechanical tension etc.[1-4] The properties of the gels can be significantly modified by incorporation of self-organizing organic or inorganic systems, in particular surfactants[5] and clays[6-8], into the cross-linked polymer matrix. The paper is devoted to a study of the composites of neutral and slightly charged PAAm gels containing clay mineral, BENT[9]. The main aim of the work was to study the effect of BENT on the absorption of linear polyelectrolytes and ionic surfactants

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by the gels and to investigate the response of the composites to adsorption. The charged gels contained 10 mol % of diallyldimethylammonium chloride (DADMA) or sodium salt of 2-acrylamide-2-methyl-1-propane-sulfonic acid (AMPS). Poly(DADMA) (PDADMA) sodium polystyrenesulfonate (PSS), sodium dodecylbenzenesulfonate (SDBS) and cetylpyridinium chloride (CPC) were used as polyelectrolytes and ionic surfactants.

Experimental Results

Fig. 1 shows the dependence of the swelling ratio m/m_0 on the concentration of sodium chloride c for the neutral PAAm gel and for the composites. Here m and m_0 are the values of the mass of the samples at equilibrium and after the preparation. The swelling ratio of PAAm network containing BENT decreases slightly with the increase of c, while for the neutral PAAm gel it does not depend on c (Fig. 1 (1,2)). The analogous decrease of m/m_0 is much more pronounced for anionic gel intercalated with BENT (Fig. 1 (3)).
These results can be explained in the framework of the recent theory[10)] which describes the swelling behavior of inhomogeneous polyelectrolyte gels. Most of the couterions of the clay, which plays a role of inhomogeneuty, remain in the local volume around the clay particles or between the plates and do not contribute strongly to the total osmotic pressure inside the gel. The reversed swelling behavior is observed for the cationic gel composite. The increase of the ionic strength of the solution results in significant swelling of the gel composite (Fig. 1 (4)). This result shows that without the screening effect of salt there is a strong electrostatic attraction between cationic DADMA groups attached to the chains of the network and the anionic surface of the clay. This attraction leads to significant contraction of the gel.
Fig. 2 shows the effect of the cationic and anionic surfactants (a) and polyelectrolytes (b) on the conformational state of the cationic gel containing anionic particles of BENT. In the region of low concentration the addition of any of these compounds results in a marked swelling of the composite. In the region of high concentration the ionic strength of the solutions becomes high and the values of the swelling ratio decreases approaching that of the gels in the solution of 1,1-salt. The study of adsorption of CPC by the cationic PAAm-BENT composite has shown that in parallel with the swelling of the composite the absorption of ionic surfactant by the gels occurs. The corresponding isotherms of absorption have a tendency to saturate when

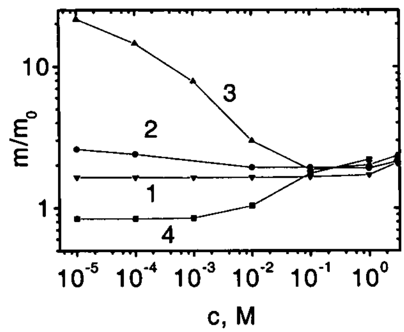

Fig. 1. Dependencies of the swelling ratio m/m_0 of the gels on the concentration c of sodium chloride for the neutral PAAm gel (1); PAAm-BENT gel composite (2); anionic PAAm (3) and cationic PAAm-BENT gel composite (4).

the number of surfactant ions exceeds the number of mobile ions of the clay or of the cationic network in the gel. The obtained results can be explained by the formation of polyelectrolyte complexes between the ions of DADMA and BENT in the cationic gel-clay composite. During the interaction with the surfactants the competition reactions of the formation of the new complexes between BENT and CPC or between the cationic network and SDBS occur (reactions (1) and (2)). This leads to the break of the ionic bonds between the network and the clay. The breaking of the ionic bonds which play a role of additional physical cross-links results in the swelling of the composite.

[clay-.DADMA+] + CPC+ = [clay- CPC+] + DADMA+ (1)

[DADMA+.clay-] + SDBS- = [DADMA+ SDBS-] + clay- (2)

The study of the adsorption of PDADMA by the cationic gel-BENT composite shows that the amount of the absorbed polymer cations is much less than the number of charges of BENT. However, the addition of PDADMA results in the marked increase of the swelling ratio of the composite (Fig. 2 (b)). The obtained result shows that the most ionic groups of the clay do not interact with polycation. As it is known, the clay minerals consist of flat particles which have a strong tendency to form parallel packing[9]. It can be assumed that the BENT plates forms such parallel aggregates in the composite gels and that the distance between the flat surfaces is so small that the charged coils of BENT can not penetrate there. Still the PDADMA molecules can react with a surface of such clay aggregates and induce the swelling of the composite via

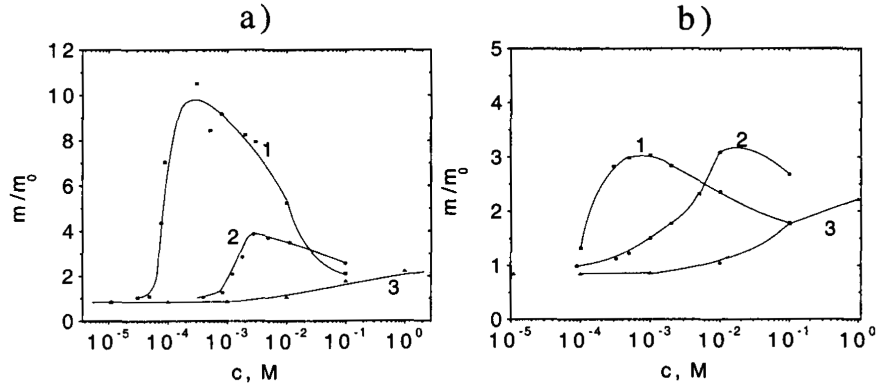

Fig. 2. Dependencies of the swelling ratio m/m_0 of the cationic PAAm-BENT gel composite on the concentration of CPC ((a), 1), SDBS ((a), 2) PDADMA ((b), 1), PSS ((b), 2) and sodium chloride ((a), (b), 3).

the reaction analogous to the reaction (1). In the case of PSS the possible mechanism of the gel swelling is the same as in the case of SDBS.

Fig. 3 shows the effect of the surfactants and PDADMA on the swelling behavior of the neutral PAAm gel intercalated with BENT. For comparison the analogous dependence of the swelling ratio on salt concentration is also listed. The addition of 1,1-salt, SDBS and PDADMA leads to monotonous decrease of the swelling ratio of the gel. At the same time in the region of low concentration of CPC a pronounced contraction of the gel is observed and the swelling ratio of the gel becomes lower in comparison with that in the solution of 1,1-salt with high ionic strength (Fig. 3, (1)). Further increase of the concentration of CPC leads to the gel swelling and at high concentration of the surfactant the value of m/m_0 becomes the same as in the solution of salt. The study of the absorption of CPC by the composite gel shows that the position of the maximum of the contraction corresponds to partial or complete replacement of sodium ions of the clay by the ions of the surfactant. The reswelling of the gel occurs in the region of concentration of CPC where the number of the surfactant ions is in excess over the number of the charges of the network. The observed contraction of the gel induced by cationic surfactant can be explained by the ion exchange between the sodium counter ions of the clay and the cations of CPC and further aggregation of surfactant ions due to hydrophobic interaction. As a result the osmotic pressure of the counterions of BENT decreases and the gel shrinks. Also, aggregates of surfactant on the clay surface causes additional electrostatic attraction between parallel surfaces (Fig. 4 b). Therefore, the gel shrinks. At higher concentration of CPC it can be expected that the excess of positively charged ions is adsorbed due to hydrophobic interaction between the ions of the surfactant. The effective charge of the surface of BENT particles becomes positive, they start to repel each other due to Coulomb interactions and the gel swells.

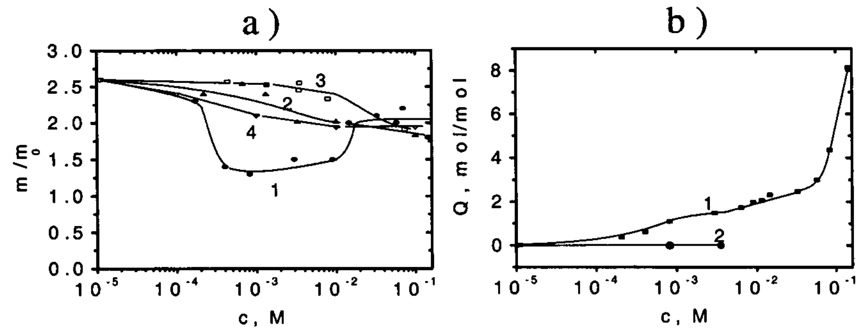

Fig. 3. a) Dependencies of the swelling ratio m/m_0 of the neutral PAAm-BENT gel composite on the concentration c of CPC (1), sodium chloride (2), SDBS (3) and PDADMA (4). b) Isotherms of absorption of CPC (1) and PDADMA (2) by the composite.

This assumption is confirmed by the data obtained by SAXS. It was shown that the surfactant ions adsorbed by BENT in the gel composite forms lamella structures. For instance, for the gel with the ratio Q between the number of surfactant ions and the charges of BENT Q=2.0 the positions of maximums in the X-ray intensity profile correspond to the values of the wave vector q=0.15, 0,30 and 0.43 nm^{-1} i.e. the surfactant ions forms lamella structure. At the absence of CPC no pronounced maximums were observed in the q range studied (q<0.55).

Conclusion

Negatively charged flat plates of clay mineral, BENT embedded in neutral and slightly charged PAAm gels play a role of "2-d polyelectrolyte", which induce additional sweling of a neutral gel and significant shrinking of the gel containing cationic groups in the polymer matrix. Both

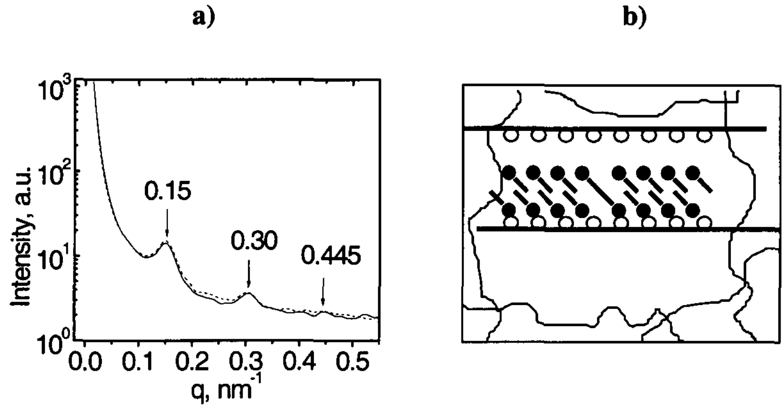

Fig. 4. a) SAXS profiles of PAAm gel-BENT composite with Q=1.1 and 2.0 (upper curve). b) Schematic representation of the structure of BENT-CPC complex embedded in the PPAm gel.

the charges of the gel and of BENT play a role of the centers of adsorption of oppositely charged surfactants and linear polyelectrolytes. Ionic surfactants and polymers participate in a competition interaction with the charges of the amphoteric composite and their absorption leads to the marked swelling of the gel. The results of SAXS study manifest the formation of lamella structure of the cationic surfactant adsorbed by the clay plates.

References

1. T. Tanaka, T. *Phys. Rev. Lett.* **40**, 820 (1978)
2. T. Tanaka, D. Fillmore, S. T. Sun, J. Nishio, G. Swislow, A. Shan, *Phys. Rev. Lett.* **45**, 1636 (1980)
3. Y. Hirokawa, T. Tanaka, *J. Chem Phys.* **81**, 6379 (1984)
4. A. R. Khokhlov, S. G. Starodoubtsev, V. V. Vasilevskaya, *Adv. Pol. Sci.* **109**, 123 (1993)
5. A. R. Khokhlov, E. Yu. Kramarenko, E. E. Makhaeva, S. G. Starodoubtsev, *Macromolecules* **25**, 4779 (1992)
6. D. Gao, *Preparation and Property Improvement of a Superabsorbent Polymer Composite*; Alberta Reseach Council: Edmonton, Canada, 1992, Charter 1
7. D. Gao, R. B. Heimann, *Polymer Gels and Networks*, **1**, 225 (1993)
8. N. A. Churochkina, S. G. Starodoubtsev, A. R. Khokhlov, *Polymer Gels and Networks*, **6**, 205 (1998).
9. B. K. G. Theng, *Formation and Properties of Clay-Polymer Complexes*; Elsevier: Amsterdam, Oxford, New York, 1979, Chapter 1.
10. Zeldovich, K.B.; Khokhlov, A.R. *Macromolecules*, in press.