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PHASE TRANSITION AND MICROGEL FORMATION IN POLYMER SOLUTIONS WITH SALT IONS

The features of the phase transition in dilute polymer solutions leading to the formation of a new phase, which is a swollen polymer mesh, have been considered. It is shown that, under certain conditions, only small clusters, microgels, of the new phase are formed and precipitate. A formula for the time dependence of the average microgel radius is derived. Using the method of dynamic light scattering, the time dependences of the cluster size in dilute aqueous solutions of hydroxypropyl cellulose with NaF, NaCl, NaBr, and NaI salt ions are obtained. The experimental results are compared with the derived formula.

Keywords: phase transition, microgel, hydroxypropyl cellulose, salt ions.

1. Introduction

In recent years, the rapid development of gel physics has been observed, which is associated with the application of gels in medicine [1–4]. The most usable in this domain are hydrogels created on the basis of water-soluble cellulose derivatives [5–7], which is associated with such unique properties of these materials as their availability, cheapness, and biocompatibility. In addition, the mentioned gels have low values of the lower critical solution temperature [8, 9], which makes them a good choice for biomedical applications. An important role in the practical applications of hydrogels is played by the availability of information about the features of the sol-gel transition in them, which testifies to the challenging character of the problem considered in this article.

Being considered as a macroscopic system, gel is a heterogeneous continuum consisting of a solid and a liquid component, with the solid component forming the gel framework [10]. Actually, such a continuum is a porous medium whose pores contain a liquid.

The distinctive features of the gel as a porous medium are as follows:

- when describing the gel behavior, a spatial scale of about $\Delta\ell_1$ is used, where $\Delta\ell_1$ satisfies the inequality

$$\Delta\ell_1 \gg (L_1, L_2), \tag{1}$$

and L_1 is the pore size, and L_2 is the pore wall thickness. Then the gel behaves itself as a homogeneous continuum, and its shear modulus G satisfies the condition

$$G \ll G_s, \tag{2}$$

where G_s is the shear modulus of the solid;

- when the basis of the gel framework consists of polymer chains, the gel is called polymeric; in such a gel, a spatial scale of about $\Delta\ell_2$ is used, with $\Delta\ell_2$

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satisfying the condition

$$\Delta\ell_2 \sim a, \tag{3}$$

where a is the size of the polymer chain link, and the framework is a swollen polymer network.

A system with a network structure is usually called the microgel [3] if the size of the system exceeds 10^2 nm, but is smaller than 10^3 nm. The physics of microgels is a promising scientific direction, as is evidenced by a substantial number of publications dedicated to them (see works [11–14] and references therein). The relevance of microgel research follows first of all from their application in medicine, in particular as drug delivery systems [15–17].

An important place in the physics of microgels is occupied by the studies of the mechanisms through which microgels are formed [3, 18, 19]. In this article, we will consider one of them. In our opinion, it can become a basis for a new method aimed at obtaining microgels. This paper is a continuation of our works [20–22] also devoted to the study of hydrogels.

2. Phase States of Polymer Solution

As is known [23], the polymer solution can exist in two structural forms. In the first form (it is called the sol structure), the polymer chains are not connected to one another. In the second variant, the chains form a network. In the literature [10, 24–26], the thesis that the formation of a polymer network is a percolation transition prevails. In [27], it was shown that the formation of a network is a phase transition of the first kind. At one of the phase transition stages, the rate of the new phase (network formation) increases sharply. This stage was identified in work [28] as the percolation transition discussed in work [10].

In works [27, 28], the swollen polymer network was considered to be a thermodynamic phase occupying an intermediate position between the sol phase and the polymer crystal. For this reason, the mentioned network was called the mesophase.

The phase diagram of the "polymer–solvent" system corresponding to the existence of a mesophase is depicted in Fig. 1, where T is the temperature, and C is the polymer concentration in the system. In this figure, the region of the $T - C$ plane bounded from below by the SEF curve corresponds to the mesophase, the region bounded by the ARDKH curve corresponds to the sol phase, and the region bounded by the SEDRA curve is the region, where both mentioned phases coexist.

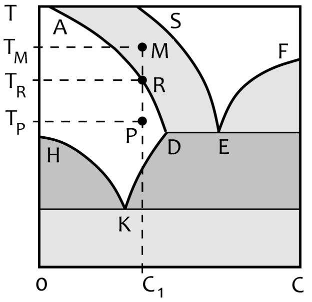

Fig. 1. "Polymer–solvent" phase diagram

Let the concentration of the examined mesophase equal C_1, and the temperature of the system increases from T_P to T_M. In this case, as one can see from Fig. 1, if the temperature T_R is exceeded, a phase transition of the first kind "sol–mesophase" has to occur.

3. Mechanism of Microgel Formation

Currently, the following mechanism of the first-kind phase transition is generally accepted [29]. Let us consider a transition from phase A to phase B. It begins with the formation of nuclei of phase B in initial phase A. These nuclei are formed due to thermal fluctuations and become the growth centers of clusters of phase B. After the end of the transition A → B, the volume previously occupied by phase A turns out to be occupied by phase B.

In our case, phase A is a sol, and phase B is a mesophase. Therefore, after the end of the transition A → B, the system, in principle, should have been composed exclusively of the mesophase. However, this rule can be violated in the case where the inequality

$$C \ll 1 \tag{4}$$

holds. The matter is that the theory [29] does not involve the influence of gravitational forces on the phase transition course. Indeed, let the density of phase B exceed the density of phase A. In this case, along with the thermodynamic factor, which favors the growth of clusters of phase B and their fusion, there appears another factor, gravitational attraction, which contributes to the precipitation of phase B.

There is a competition between those factors. If the condition

$$w \gg u, \tag{5}$$

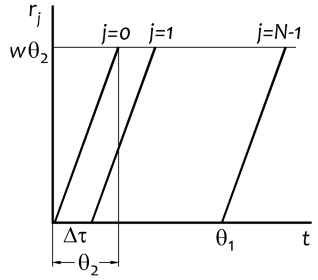

Fig. 2. Time dependences of cluster radius r_j

where w is the linear growth rate of the clusters of phase B, and u is their speed of motion under the action of gravity, is satisfied, then there is enough time for the clusters of relatively large size to be formed. Moreover, the probability of the cluster contact with one another increases in this case, which favors the cluster merging into aggregates with even larger sizes. As the size of the aggregate increases, the resistance force that opposes the movement of the aggregate during its sedimentation increases, and, if the aggregate size is substantial, practically excludes the possibility of aggregate movement. This situation corresponds to the zero approximation for the small parameter ratio u/w, and it is precisely this approximation in which the theory [29] was developed.

However, if condition (5) is obeyed, the clusters of phase B practically do not contact with one another, which thereby prohibits the formation of aggregates of considerable sizes. This circumstance brings about the inequality

$$w \le u, \tag{6}$$

which promotes the precipitation of clusters and does not allow them to reach substantial sizes.

Thus, if inequality (4) is valid, the phase transition A → B is reduced to the formation of relatively small clusters of phase B, which precipitate. During the phase transition A → B, the polymer concentration C in the system decreases. Accordingly, the phase transition terminates when the polymer in the "polymer-solvent" system becomes exhausted.

As was mentioned above, phase B is a swollen polymer network. Therefore, having in mind the above definition of the term "microgel", we will call small clusters of phase B that precipitate during the phase transition A → B as "microgels" and, accordingly, consider the described mechanism of the formation of such clusters as the mechanism of microgel formation.

4. Kinetics of Microgel Formation

Let N denote the total number of formed clusters (microgels). Obviously, the number of nuclei must be the same. For the number of nuclei $n(t)$ formed within the time interval t, we have the formula

$$n(t) = vt, \tag{7}$$

where v is the number of nuclei formed per unit time. In this case, the time θ_1 during which the nuclei are formed is determined by the equality

$$\theta_1 = N/v. \tag{8}$$

Accordingly, for the average time interval $\Delta\tau$ between the successive formation of two nuclei, we have the equality

$$\Delta\tau = 1/v \tag{9}$$

so that the nuclei are formed at the time moments

$$\tau_j = j\Delta\tau = j/v \quad (j = 0, 1, 2, ..., N-1). \tag{10}$$

Let us denote, by θ_2, the time of cluster deposition, i.e., the time interval between the moment of cluster formation and the moment of its removal from the system. We also assume that the cluster has a spherical shape. The radius r_j of the j-th cluster will be determined by the formula

$$r_j = w(t - \tau_j)H(t - \tau_j - \theta_2), \tag{11}$$

where $H(x)$ is the Heaviside function. The plots of functions (11) are shown in Fig. 2.

Next, let $R(t)$ denote the average value of the cluster radius at the time moment t. Consider the time interval $[0, \theta_2]$ and choose an arbitrary time moment $t = m\Delta\tau$ within it. For this time moment, the average value of the cluster radius is determined by the equality

$$R(t) = \frac{1}{m}\sum_j r_j(t). \tag{12}$$

Substituting formula (11) into expression (12) and performing the summation, we obtain

$$R = \frac{wt}{2}, \quad t \in [0, \theta_2]. \tag{13}$$

Obviously, within the time interval $[\theta_2, \theta_1]$, the value of R is constant, namely,

$$R = \frac{w\theta_2}{2}, \quad t \in [\theta_2, \theta_1]. \tag{14}$$

As can be seen from Fig. 2, the dependences $r_j(t)$ within the time interval $[\theta_1, \theta_1{+}\theta_2]$ are similar to analogous dependences within the time interval $[0, \theta_2]$, which allows us to write the formula

$$R = \frac{w(\theta_2 - t)}{2}, \quad t \in [\theta_1, \theta_1 + \theta_2]. \tag{15}$$

Figure 3 shows the plot of the dependence $R(t)$, which is expressed by formulas (13)–(15).

5. Experiment

Hydroxypropyl cellulose (HPC, a water-soluble cellulose ether) was manufactured by Alfa Aesar [30]. The manufacturer's specification stated that the weight-average molecular weight of HPC is equal to 10^5, the degree of substitution to 75.7%, and the viscosity of the aqueous polymer solution at 25 °C equals to 112 cPs. The analytical-grade salts (NaF, NaCl, NaBr, NaI) were manufactured by Sigma-Aldrich.

The initial aqueous solution of HPC with a concentration of 0.2 wt% was prepared by dissolving the required amount of polymer in deionized water under continuous stirring at a temperature of 60 °C for 4 h to ensure complete dissolution. As a result, a homogeneous and transparent solution was obtained.

This initial solution was divided to prepare four specimens, into which salts were introduced and mixed until they were completely dissolved. The molar concentrations of the salts in the specimens were identical and equal to 15.4 mmol/l.

Using a Zetasizer Nano ZS device (Malvern), dynamic light scattering in those samples was studied. The experimental results obtained for the temperature dependences of the hydrodynamic diameters of polymer clusters existing in the solutions are exhibited in Fig. 4. As can be seen from this figure, the experimental temperature dependences of the hydrodynamic diameter of HPC clusters are in agreement with the results of theoretical calculations (the doubled radius $R(t)$ shown in Fig. 3).

The values of the parameters w and θ_2 corresponding to the data presented in Fig. 4 are quoted in Table.

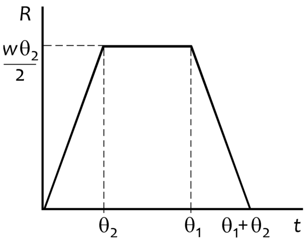

Fig. 3. Time dependence of average cluster radius R

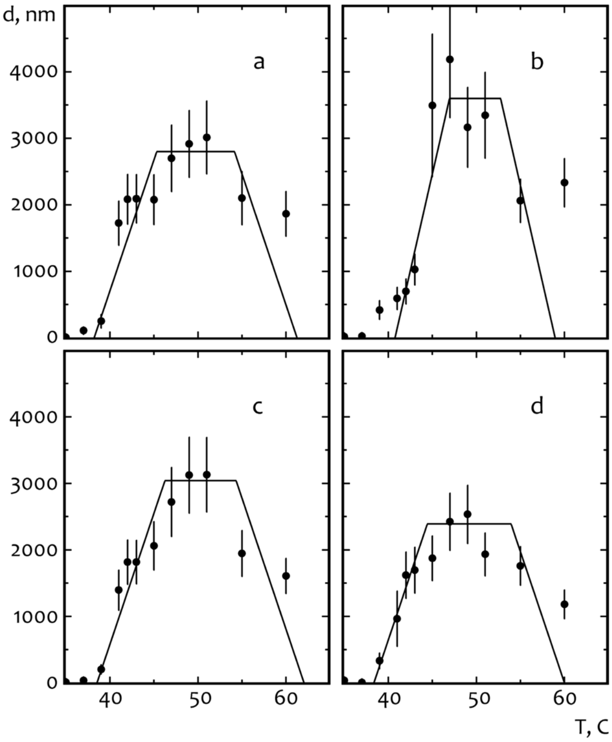

Fig. 4. Temperature dependences of hydrodynamic cluster diameter d for aqueous solutions of HPC with salt ions NaF (a), NaCl (b), NaBr (c), and NaI (d). Trapezoidal figures (solid lines) demonstrate the simulation of the cluster growth and cluster deposition processes according to formulas (13)–(15). The heating rate equals 0.3 °C/min

Parameters of the phase transition and polymer cluster deposition processes in aqueous solution of HPC with salt ions

Salt	w, nm/s	θ_2, s
NaF	1.9	1412
NaCl	3.1	1252
NaBr	1.9	1556
NaI	1.9	1221

6. Conclusions

The mechanism of microgel formation discussed in this article is as follows.

Under certain conditions, a phase transition occurs in the polymer solution: the sol phase (phase A) transforms into a swollen polymer network (phase B). For the transition A → B, as for any other first-order phase transition, the formation of phase B begins due to the appearance of the nuclei of phase B in phase A due to thermal fluctuations. These nuclei serve as centers around which polymer aggregates (clusters) of phase B are formed. The density of phase B exceeds the density of phase A, so under certain conditions these clusters have to precipitate.

In aqueous solutions of cellulose derivatives with a concentration $C \geq 1$ wt%, the precipitation practically does not occur [21]. The reason for this behavior is that the clusters in such solutions are in a suspended state owing to the high viscosity of the medium (as compared with that in dilute solutions).

In dilute polymer solutions, the clusters of phase B practically do not contact with one another. Therefore, provided that the cluster growth rate is considerably lower than the rate of its precipitation, the mentioned clusters precipitate, even if they have relatively small sizes [31,32]. Such small clusters of phase B are usually called microgels.

In our opinion, the described mechanism of formation and precipitation of microgels in dilute solutions in the presence of salt ions has an important practical value for the development of promising technologies, such as catalysts with the regulated activity and film nanocomposite materials [33–36] (in particular, bactericidal polymer films used for wound treatment).

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ФАЗОВИЙ ПЕРЕХІД І УТВОРЕННЯ МІКРОГЕЛІВ У ПОЛІМЕРНИХ РОЗЧИНАХ З ІОНАМИ СОЛЕЙ

Розглядаються особливості фазового переходу, який відбувається в розбавлених полімерних розчинах і який приводить до утворення нової фази, що є набухлою полімерною сіткою. Показано, що за певних умов утворюються лише невеликі кластери нової фази – мікрогелі, які випадають в осад. Виведено формулу залежності середнього радіуса мікрогеля від часу. За допомогою методу динамічного розсіяння світла одержано часові залежності розміру кластерів, що утворюються в розбавленому водному розчині гідроксипропілцелюлози з іонами солей NaF, NaCl, NaBr і NaI. Результати експерименту порівнюються з результатами, що випливають із виведеної формули.

Ключові слова: фазовий перехід, мікрогель, гідроксипропілцелюлоза, іони солей.