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DETERMINATION OF THE SURFACE TENSION COEFFICIENT OF POLYMER GEL

A method for determining the surface tension coefficient at the sol-gel phase interface in the polymer solution is proposed. The required value is calculated on the basis of the temperature dependence of the gel phase volume fraction formed during the sol-gel transition. The method has been tested using the hydroxypropyl cellulose aqueous solution. In particular, the gel phase volume fraction is determined by measuring the temperature dependence of the solution turbidity. Using the proposed method, it is found that the surface tension coefficient of the examined solution decreases, if ions of group-I alkali metals (Li, Na, and K chlorides) are introduced, which agrees with the classical theory of electrocapillary phenomena in solutions.

Keywords: hydroxypropyl cellulose, phase transition, ions, surface tension.

1. Introduction

It is known [1–3] that the polymer solution can exist in two phase states: the gel and sol phases. The fundamental difference between them is that polymer chains form a connected polymer network in the gel phase, whereas such a network is absent in the sol phase (see Fig. 1; here polymer chains are depicted by curves, colored circles stand for network nodes, and hollow ones for solvent molecules).

The study of the structure and properties of polymer gels is a promising and actively developed scientific direction. Information about the properties of polymer networks is necessary for the development of technologies in food industry, the fabrication of personal hygiene products and drugs, the creation of functional composite materials, and so forth (see works [4,5] and references therein). Polymer networks can be used as detectors to determine the presence of a small amount of ionic impurities in the solution, which is important for the development of water purification systems. But the most important circumstance making the mentioned researches extremely challenging is the fact that polymer networks are ingredients of the human body.

The collagen network serves as a framework for biotissues that ensures their elasticity and strength. The regeneration of damaged biotissue begins precisely from the formation of such a network. As was shown in work [6], it is this process that provides the adhesion between biotissue sections, when they are joined together making use of electric welding. Furthermore, a fibrin network arises at blood clotting and is a part of blood clots [7]. By their microstructure, networks of polymer hydrogels are similar to the intercellular matrix in a lot of body tissues, and they can imitate its physical, chemical, and mechanical properties [8]. Due to their unique properties, polymer hydrogels have become widely used in ophthalmology [9, 10], wound healing [11,12], tissue engineering [13,14], and drug delivery systems [15,16].

The gel and sol phases can coexist under certain conditions. An important characteristic of the gel is the surface tension coefficient σ at the interface be-

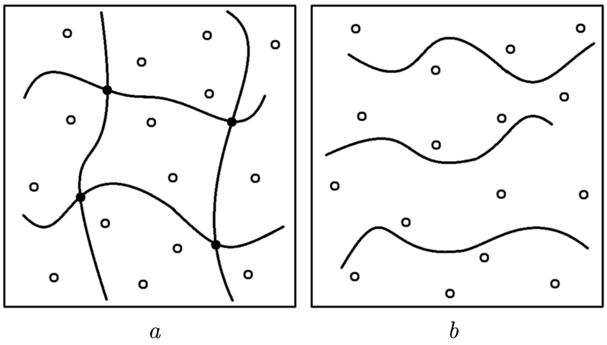

Fig. 1. Schematic structure of the gel (*a*) and sol (*b*) phases

tween both phases. However, the experimental determination of the values of this coefficient for gels is not a trivial task. Really, it is known that, according to their mechanical properties, gels occupy an intermediate position between liquids and solids. Unlike liquids, the shear modulus of which equals zero, gels are ascribed non-zero values of this parameter. However, the shear modulus of gels is much lower than that of solids.

Due to the indicated differences, the conventional experimental methods for determining σ, which were developed for liquids or solids, are practically inapplicable in the case of gels. In this article, a method for determining the surface tension coefficient σ at the interface between the sol and gel phases is proposed.

2. Formalism

The proposed method is based on the well-known fact from the physics of phase transitions that the coefficient of surface tension between two phases affects the kinetics of the phase transition between them.

Let the sol and gel phases be denoted by the letters A and B, respectively. We consider phases A and B to be some continuums for which the spatial scale substantially exceeds the critical nucleus size [17]. In the framework of this assumption and for the case where the temperature of the system T changes linearly in time, i.e.,

$$T = T_0 + vt, \tag{1}$$

where T_0 is the temperature at which phases A and B are in equilibrium, and v is the heating rate, the following formula was obtained [17]:

$$\ln \theta_{\mathrm{A}}(T) = -D(T - T_0)^{3(1+\alpha)} \exp\left[-\frac{M}{(T-T_0)^2}\right], \tag{2}$$

where θ_{A} is the volume fraction occupied by phase A, α is the scale dimension of aggregates in phase B, and D is a constant. The quantity M is determined by the expression

$$M = \frac{16\pi T_0}{3k_{\mathrm{B}}}\frac{\sigma^3}{\lambda^2}, \tag{3}$$

where k_{B} is the Boltzmann constant, σ is the surface tension coefficient at the phase interface, and λ is the heat of phase transition per unit volume.

The scale dimension α is determined by the formula [18]

$$\alpha = \frac{d(\ln N(R))}{d(\ln R)}, \tag{4}$$

where R is the aggregate size, and $N(R)$ is the number of structural units in the aggregate.

One of the most applied methods to study the kinetics of gel formation is the measurement of the solution transparency (see, for example, work [1]), which is proportional to the volume fraction of phase A, θ_{A}.

The theory [17] can be used in two ways to experimentally obtain information about surface tension. The first variant involves the following sequence of stages:

1) by measuring the solution transparency, the experimental dependence $\theta_{\mathrm{A}}(T)$ is determined;

2) substituting this dependence into the left-hand side of formula (2), the values of the parameters M and T_0 are calculated;

3) using the calorimetric method, the value of λ is determined;

4) by substituting the found values of M, T_0, and λ into formula (3), the surface tension coefficient σ is calculated.

The second variant is used in comparative studies. Let us consider two solutions: the original solution and a solution with a structure different from the original one. Let σ_1 and σ' denote the coefficients of surface tension at the interface between phases A and B in the former and latter solutions, respectively. As the relative surface tension coefficient, we take the quantity

$$\xi = \sigma'/\sigma_1. \tag{5}$$

Let the condition

$$|\lambda_1 - \lambda'| \le \Delta\lambda \tag{6}$$

hold, where λ_1 and λ' are the heats of the transition A → B in the former and latter solutions, respectively, and $\Delta\lambda$ is the experimental determination error of the transition heat. Condition (6) obviously means that the heats of the A → B transition in both solutions are practically identical.

The second variant consists of the following stages:

1) by measuring the transparency of the original solution and the solution with the changed structure, we obtain the corresponding dependences $\theta_{\rm A}(T)$;

2) using those dependences and formula (2), we calculate two values of the parameter M, namely, M_1 for the original solution and M' for the solution with the changed structure;

3) taking condition (6) into account and bearing in mind expression (3), we calculate the relative coefficient of surface tension according to the formula

$$\xi = (M'/M_1)^{1/3}. \tag{7}$$

It is the latter variant that is used in this paper.

3. Experimental Part

For the research, we chose the 2-wt% aqueous solution of hydroxypropyl cellulose (Alfa Aesar) [19]. The molecular weight of this compound equals 10^5, and the substitution degree is 75.7%. We have already studied earlier the features of the sol-gel transition in aqueous solutions of cellulose derivatives, both experimentally [20, 21] and using a mathematical simulation [22]. It was shown that the researched sol-gel transition in those systems has a character of the first-kind phase transition.

In Fig. 2, a schematic diagram of the experimental setup is depicted. This is an improved version of the device used by us in work [20] for measuring the solution turbidity.

As light source *1*, we used a GNL-5013PGC G-Nor LED with a known spectral characteristic. It was powered using a micropower current stabilizer made on an LP2951 chip. Light with a wavelength of 525 nm was fed through fiber optic cable *2* into thermostatic chamber *3* filled with the polymer solution. The light beam reflected from mirror *4* returned through optical fiber cable *6* to a TLS237 digital photosensor (*7*) connected to an AVR ATmega328P microcontroller (*8*). As a result, the total intensity

$$J_\Sigma = J_t + J_r \tag{8}$$

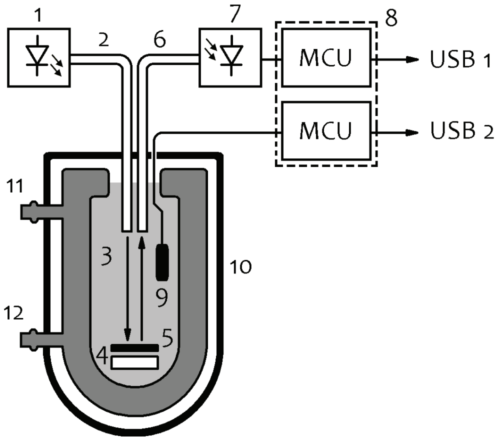

Fig. 2. Schematic diagram of the installation for measuring the solution turbidity

was measured, where J_t is the intensity of the light flux attenuated because of its passage through the specimen, and J_r is the intensity of the light flux scattered by the specimen at an angle of 180°. When measuring J_r, mirror *4* was screened with curtain *5* made of light-absorbing material (black anodized aluminum). Thus, in order to determine J_t and J_r for a specific specimen, it was necessary to perform two measurements: in the presence and in the absence of screen *5*.

The solution temperature was measured by means of a digital temperature sensor LMT01LPG (*9*) and another identical microcontroller in unit *8*. The illumination and temperature values were synchronously read out using a block of microcontrollers and transferred to USB ports of a personal computer using the RS-232 protocol. Accumulation of data, their further processing and visualization were implemented with the help of a Delphi code. The illuminance measurement error did not exceed 0.1 lux, and the temperature measurement error was ±0.1°C. The chamber with the polymer solution was placed in light-proof box *10* and connected with the help of nozzles *11* and *12* to a circulation thermostat Julabo ME-6. Structurally, elements *4*, *5*, and *9* together with the output (input) of optical fiber cables *2* and *6* were arranged in the form of a probe that was immersed into the examined solution.

In order to test the efficiency of the proposed method for determining the surface tension coefficient of polymer gel, we investigated the aqueous solutions

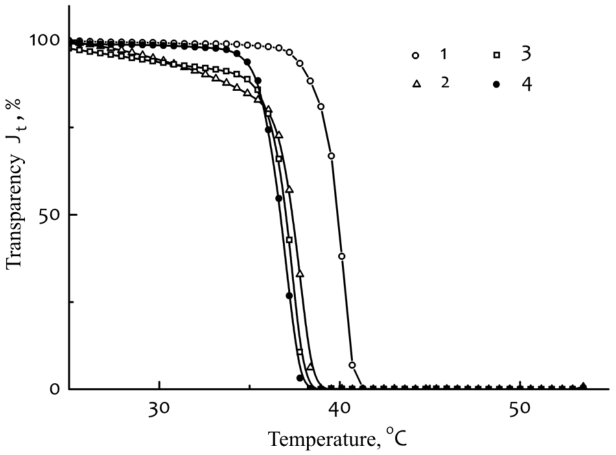

Fig. 3. Temperature dependences of the transparency J_t of the 2-wt% aqueous solutions of hydroxypropyl cellulose with no ions (*1*), and Li (*2*), Na (*3*), and K (*4*) single charged ions. The heating rate is 1.1 °C/ min

Variations of the surface tension coefficient σ if ionic impurities are introduced into the polymer solution

Specimen, n	Ions	σ_n/σ_1
2	Li	0.653 ± 0.203
3	Na	0.573 ± 0.178
4	K	0.492 ± 0.165

of hydroxypropyl cellulose with admixtures of group-I alkali metal ions (Li, Na, and K chlorides). The molar salt concentrations in all specimens were identical and equal to 0.154 mol/l.

Figure 3 illustrates the measurement results of the polymer solution transparency. All curves in Fig. 3 are calibrated with respect to a transparency level of 100%, which was taken as a value of the photosensor illumination for the curve corresponding to the ion-free specimen at a temperature of 25°C. The corresponding experimental errors are smaller than the symbol size.

In order for formula (2) to be applicable to interpret the experimental results, it is necessary to change from the transparency J_t to the relative fraction of the volume occupied by the phase, $\theta(T)$. Table contains the values of the parameters α and M, as well as the relative change of the surface tension coefficient (4) and (5), obtained by minimizing the root mean square deviation

$$\chi^2(N) = N^{-1}\sum_{j=1}^{N}(\theta_{\mathrm{A}}(T_j) - \theta(T_j))^2, \tag{9}$$

where N is the number of experimental (approximated) points $\theta(T_j)$. The data quoted in Table were obtained under the conditions $D = 0.1 \times \times 10^{-13}\ \mathrm{K}^{-3(1+\alpha)}$, $T = 296$ K, and $\alpha = 3$ (these are optimal values for the entire measurement series).

From the analysis of the data presented in Table, it follows that the surface tension coefficient (4) is lower, if there are ions in the specimen. This result can be explained qualitatively in the framework of the theory of electrocapillary phenomena in liquids [23, 24]. As was already indicated above, in this paper, we study binary symmetric solutions of electrolytes. If such a solution comes into contact with another liquid, the concentrations of ions of opposite signs are identical at a sufficiently large distance from the interface. However, their concentrations near the interface are different owing to the predominant absorption of ions of a certain sign. The surface charge that is formed at the interface is compensated by the charge of excess ions located in the adjacent layer of the solution. It is the interaction forces between ions associated with such a compensation that lead to the reduction of the surface tension coefficient of the polymer gel, which was observed in our experiment.

4. Conclusions

The behavior of a two-phase system consisting of the gel and sol phases is significantly affected by the interface layer that separates those phases. In particular, it is one of the factors governing the kinetics of the sol-gel transition. On the basis of this fact, the authors developed a method for determining the surface tension coefficient at the interface between the sol and gel phases. The essence of the method is expounded in Section 2, and its verification is carried out in Section 3.

The authors have not found any information in the literature concerning the analyzed coefficient and the methods of its determination.

With the help of the developed method, it is found that the introduction of ions into the polymer solution reduces the indicated coefficient. According to formula (2), the reduction of the surface tension coefficient increases the rate of the sol-gel transition. Therefore, the introduction of ions into the polymer solution speeds up the process of the polymer network formation. In our opinion, this result can be applied in technologies dealing with polymer gels.

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ВИЗНАЧЕННЯ КОЕФІЦІЄНТА ПОВЕРХНЕВОГО НАТЯГУ ПОЛІМЕРНОГО ГЕЛЮ

Запропоновано метод визначення коефіцієнта поверхневого натягу на межі золь- та гель-фаз полімерного розчину. Для розрахунку цього коефіцієнта використана температурна залежність кількості гель-фази, яка утворюється під час золь-гель переходу. Запропонований метод апробовано на водному розчині гідроксипропілцелюлози. Кількість гель-фази визначалася на основі вимірювань температурної залежності мутності. За допомогою запропонованого методу встановлено, що коефіцієнт поверхневого натягу вказаного розчину внаслідок введення в нього іонів лужних металів I-ї групи (хлориди Li, Na і K) зменшується, що узгоджується з теорією електрокапілярних явищ у розчинах.

Ключові слова: гідроксипропілцелюлоза, фазовий перехід, іони, поверхневий натяг.