

## Turbidimetric Monitoring of Phase Separation in Aqueous Solutions of Thermoresponsive Polymers

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A method for the experimental determination of turbidity in thermoresponsive polymer solutions is presented. The method is based on measuring the intensity of light streams: weakened and backscattered from the sample, which is in the region of the volume phase transition. The turbidimeter developed by us, unlike industrial devices of this type, is equipped with a thermostat that allows to study the dependence of the solution turbidity on the temperature. The device operates automatically, the values of luminosity and temperature from digital sensors are processed by the microcontroller and transmitted via the RS-232 protocol to USB ports of a personal computer. The error of luminosity measurement does not exceed 0.1 lux, the temperature measurement accuracy is  $\pm 0.1$  °C. This article demonstrates an example of using the designed turbidimeter to study the first-order phase transition in an aqueous solution of hydroxypropylcellulose (2 wt. %) in the presence (absence) of NaCl ions. It is assumed that the sol-gel transition in the investigated solution is due to swelling of polymer coils and their subsequent aggregation. In our opinion, the displacement of the phase transition temperature is due to additional swelling of polymer coils owing to shielding of the electrostatic interaction of monomers in the presence of NaCl ions. It is shown that the intensity of backscattered light corresponds to the kinetics of the formation of the gel network, which makes it possible to establish the dimensions of formed aggregates in the network nodes.

**Keywords:** Turbidimetry, Phase transition, Hydroxypropyl cellulose.

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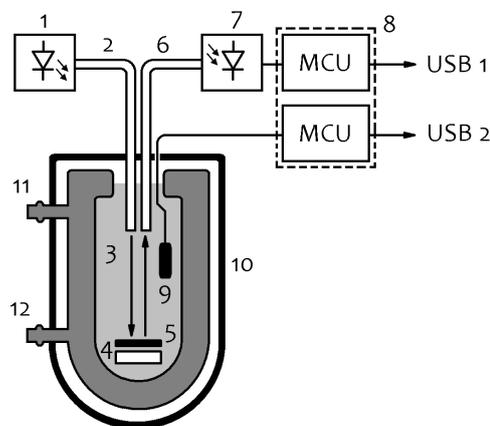
### 1. INTRODUCTION

Phase transition in aqueous solutions of thermoresponsive polymers – simple cellulose ethers – is an intensive area of research based on promising technologies in various fields, including food processing, personal care products, medicine, pharmacology, and environmentally friendly materials [1, 2]. Phase separation in solutions of cellulose derivatives is a rather complex process, the understanding of which is necessary to create materials with specified physicochemical properties. Aqueous solutions of thermoresponsive polymers undergo a sol-gel transition upon heating, returning to their original state upon cooling [3, 4]. Gelation of such a system is associated with an increase in the solution turbidity resulting from phase separation. To date, the mechanism of gelation is still not well understood, although many different hypotheses have been proposed ([5] and references therein).

Turbidimeters (turbidity analyzers) are devices based on measuring the luminosity when the light flux passes through a scattering (dispersed) system. A typical turbidimeter consists of a stabilized light source, a transparent cuvette containing the test solution, and a photodetector that records the luminous flux after the passage of light through the sample. One of the disadvantages of industrial devices of this type, along with the high cost, is often the impossibility to change the temperature of the solution (no thermostatic chamber). Therefore, according to the tasks studying the phase transition kinetics, our laboratory has developed and manufactured a device that allows us to research the temperature dependences of turbidity in the sample under study.

### 2. EXPERIMENTAL SETUP

Fig. 1 illustrates a block diagram of a turbidimetric setup, which is an improved version of the instrument used in [6] for turbidity measurements.



**Fig. 1** – Installation diagram of turbidity measurements (explanations are in the text)

As a light source 1, a GNL-5013PGC LED was used, which was powered by a micropower current stabilizer made on an LP2951 microcircuit. A light beam with a wavelength of 525 nm was fed through the fiber-optic cable 2 into the thermostated chamber 3 filled with a polymer solution. The beam reflected from the mirror 4 returned through the fiber optic cable 6 to the digital optical sensor 7 (TLS237) connected to the microcontroller 8 (AVR ATmega328P). As a result, the total in-

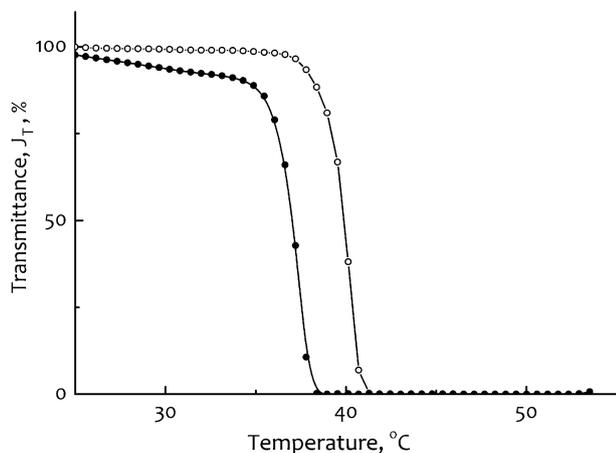
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tensity was measured:  $J_E = J_T + J_R$ , where  $J_T$  is the intensity of the weakened light flux due to the passage through the sample,  $J_R$  is the intensity of the light flux reflected (backscattered) by the sample. To measure  $J_R$ , mirror 4 was shielded by the shutter 5 made of light-absorbing material (black anodized aluminum). Thus, in order to determine  $J_T$  and  $J_R$  for a specific sample, it was necessary to perform two measurements: with and without screen 5.

The solution temperature was measured by the digital temperature sensor 9 (LMT01LPG) connected to the second identical microcontroller in block 8. The values of luminosity and temperature were synchronously read by the unit 8 and transmitted via the RS-232 protocol to USB ports of a PC. Data collection, their subsequent processing and visualization were implemented by a program written in Delphi. The luminosity measurement error did not exceed 0.1 lux, and the temperature measurement accuracy was  $\pm 0.1$  °C. Chamber 3 was enclosed in the light-tight case 10 and connected through outputs 11 and 12 to a Julabo ME-6 circulation thermostat. Structurally, elements 4, 5, and 9 together with the output (input) of fiber-optic cables 2 and 6 were designed as a probe immersed in the solution to be tested.

### 3. ANALYSIS OF EXPERIMENTAL RESULTS

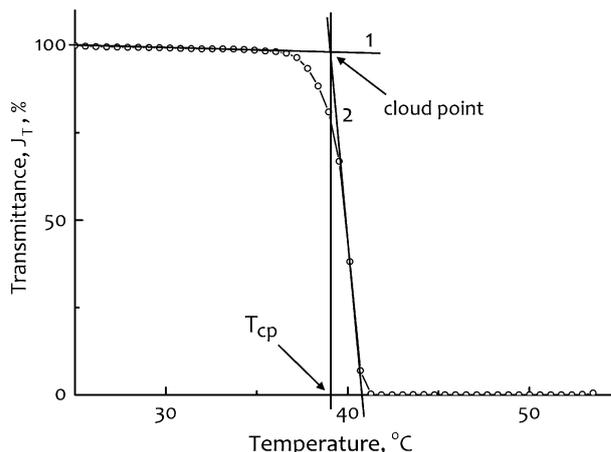
Fig. 2 demonstrates the results of measuring the transmitted light flux for a 2 wt. % aqueous solution of hydroxypropyl cellulose (Alfa Aesar, molecular weight  $10^5$ , substitution degree 75.7 %) with and without NaCl ions. The sodium chloride concentration was 0.9 wt. %.



**Fig. 2** – Temperature dependences of the transmittance  $J_T$  for 2 wt. % aqueous solutions of hydroxypropyl cellulose:  $\circ$  – without sodium chloride ions,  $\bullet$  – with sodium chloride ions. The heating rate was 1.1 °C/min

All curves in Fig. 2 were calibrated to 100 % transmittance that corresponds to the optical sensor luminosity for the sample without ions at 25 °C. The phase transition temperature,  $T_{cp}$ , was determined as the temperature of the so-called cloud point [5, 7], corresponding to the intersection of lines 1 and 2 (Fig. 3).

It follows from Fig. 3 that for the solution without ions  $T_{cp} = 38.9$  °C. The obtained temperature is in agreement with the data of other authors:

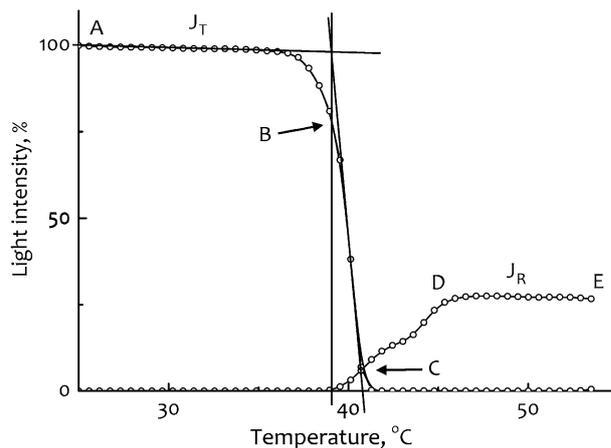


**Fig. 3** – Determination of the phase transition temperature for the sample without ions

$T_{cp} = 39 \pm 1$  °C [8],  $T_{cp} = 40.3$  °C [9]. It also follows from Fig. 2 that  $T_{cp} = 36.2$  °C for the sample with NaCl ions.

The observed decrease in the  $T_{cp}$  value in the presence of NaCl ions can be qualitatively explained as follows. Cellulose derivatives are moderately rigid-chain polymers [10], the macromolecules of which in various solvents are characterized by a certain conformation that depends on the type of solvent, polymer concentration, etc. For example, hydroxypropyl cellulose macromolecules are elongated in ethanol solutions [11] and in highly diluted aqueous solutions [12]. In [13], it was shown that the polymer chain of hydroxypropyl cellulose in a 2 wt. % aqueous solution has the conformation of a statistical coil.

The equilibrium state of a polymer coil (conditional point A in Fig. 4) is characterized by its root-mean-square radius  $R$ , which is determined by the balance of electrostatic repulsion forces acting between monomers (that leads to an increase in  $R$ ) and elastic forces preventing coil swelling.



**Fig. 4** – Temperature dependence of the recorded light intensity for the sample without ions:  $J_T$  – transmittance,  $J_R$  – backscattered (reflected) light. Letter designations are explained in the text

The transition from A to B (cloud point) is accompanied by a temperature increase and further swelling of the polymer coil (P. Flory, [14]). The presence of ions

is a factor that causes additional coil swelling due to the screening of interaction forces between the links of the polymer chain. On the other hand, the same effect can be obtained by slightly heating of the non-ionic solution. We suppose that this is one of the possible mechanisms qualitatively describing the observed decrease in the phase transition temperature in the presence of NaCl ions.

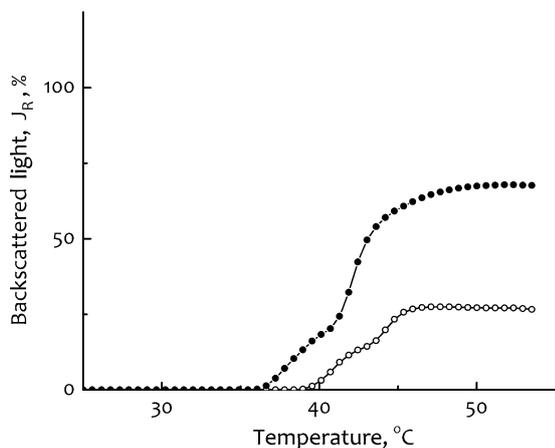


Fig. 5 – The same as in Fig. 2, but for backscattered light

Section BC in Fig. 4 corresponds to the sol-gel transition which is characterized by the aggregation of swollen coils that leads to the formation of a 3D gel network. In the CD region, the gel structure continues to form with a further increase in the polymer concentration in the network and its simultaneous depletion in the solution. Finally, in the area marked by point E, we observe saturation: the gel network has formed, and its structure does not grow any more.

Data analysis in the saturation region (Fig. 5) leads to the conclusion that the structure fragments of the gel network with NaCl ions have larger sizes. This follows, for instance, from the well-known fact [15] that the scattering intensity  $J_R$  is proportional to the square of the dispersed particle volume. In general, it can be said that additional swelling of the polymer coil due to the presence of ions determines the final size of the gel network fragments.

#### 4. CONCLUSIONS

The results obtained in this work are in full agreement with the results of other authors [8, 9, 16, 17]. Here, we did not analyze the influence of the ion radius on the cloud point temperature, since this requires additional research (for example, setting up an experiment on dynamic light scattering). It should also be noted that the mechanism of phase separation in solutions of thermoresponsive polymers is spinodal decomposition ([5] and references therein), which can be modeled using the Cahn-Hilliard equation [18, 19] that is the goal of our further studies.

#### REFERENCES

1. P.T. Anastas, J.C. Warner, *Green chemistry: theory and practice* (Oxford University Press: 1998).
2. K. Kamide, *Cellulose and Cellulose Derivatives* (Amsterdam: Elsevier Science: 2005).
3. H. Garate, K.-W. Li, D. Bouyer, P. Guenoun, *Soft Matter*, **13**, 7161 (2017).
4. T.P. Lodge, A.L. Maxwell, J.R. Lott, P.W. Schmidt, J.W. McAllister, S. Morozova, F.S. Bates, Y. Li, R.L. Sammler, *Biomacromolecules* **19** No 3, 816 (2018).
5. J.P.A. Fairclough, H. Yu, O. Kelly, A.J. Ryan, R.L. Sammler, M. Radler, *Langmuir* **28**, 10551 (2012).
6. O.M. Alekseev, Yu.F. Zabashta, V.I. Kovalchuk, M.M. Lazarenko, L.A. Bulavin, *Ukr. J. Phys.* **64** No 3, 238 (2019).
7. S.A. Vshivkov, E.V. Rusinova, N.V. Kudrevatykh, A.G. Galyas, M.S. Alekseeva, D.K. Kuznetsov, *Polym. Sci. A*, **48**, 1115 (2006).
8. D. Desai, F. Rinaldi, S. Kothari, S. Paruchuri, D. Li, M. Lai, S. Fung, D. Both, *Int. J. Pharm.* **308**, 40 (2006).
9. P. Khumana, W. Binod Kumar Singh, S. Dushila Devi, H. Naorem, *J. Macromol. Sci. A*, **51**, 924 (2014).
10. V.G. Kulichikhin, L.K. Golova, *Sov. J. Wood Chemistry* No 3, 9 (1985) [in Russian].
11. S.V. Troshenkova, E.S. Sashina, N.P. Novoselov, K.-F. Arndt, *Rus. J. Gen. Chem.* **80** No 3, 501 (2010).
12. O.M. Alekseev, Yu.F. Zabashta, V.I. Kovalchuk, M.M. Lazarenko, E.G. Rudnikov, L.A. Bulavin, *Ukr. Phys. J.* **65** No 1, 50 (2020).
13. S.A. Vshivkov, *Phase transitions of polymer systems in external fields* (Ekaterinburg: MBA Press: 2015).
14. T.P. Lodge, P.C. Hiemenz, *Polymer Chemistry* (CRC Press: 2020).
15. E. Berrocal, D.L. Sedarsky, M.E. Paciaroni, I.V. Meglinski, M.A. Linne, *Opt. Express* **15** No 17, 10649 (2007).
16. M. Lazarenko, A. Alekseev, Y. Zabashta, S. Tkachev, V. Kovalchuk, D. Andrusenko, Y. Grabovsky, L. Bulavin, *Cellul. Chem. Technol.* **54** No 3-4, 199 (2020).
17. *Handbook of Pharmaceutical Wet Granulation: Theory and Practice in a Quality by Design Paradigm* (Eds. A.S. Narang, S.I.F. Badawy) (Academic Press: 2018).
18. F.J. Vermolen, M.G. Gharasoo, P.L.J. Zitha, J. Bruining, *Int. J. Multiscale Comput. Eng.* **7** No 6, 523 (2009).
19. X. Li, G. Ji, H. Zhang, *J. Comp. Phys.* **283**, 81 (2015).

**Турбідиметричний моніторинг розділення фаз у водних розчинах термореактивних полімерів**

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У роботі представлено метод експериментального визначення мутності розчину термореактивних полімерів в області об'ємного фазового переходу. Метод заснований на вимірюванні інтенсивностей світлових потоків: ослабленого і зворотно розсіяного зразком. Розроблений нами турбідиметр, на відміну від промислових приладів такого типу, оснащений термостатом, що дозволяє вивчати залежність мутності розчину від його температури. Прилад працює в автоматичному режимі, значення освітленості та температури від цифрових датчиків оброблюються мікроконтролером і передаються по протоколу RS-232 в USB-порти персонального комп'ютера. Похибка вимірювання освітленості не перевищує 0.1 люкс, точність вимірювання температури складає  $\pm 0.1$  °C. В роботі продемонстровано приклад використання турбідиметру для вивчення фазового переходу першого роду у 2 мас. % водному розчині гідроксипропілцелюлози за наявності (відсутності) іонів NaCl. Висловлено припущення, що золь-гель перехід у дослідженому розчині обумовлений набуханням полімерних клубків та подальшою їх агрегацією. Зміщення температури фазового переходу пояснюється додатковим набуханням полімерних клубків через екранування електростатичної взаємодії мономерів у присутності іонів NaCl. Показано, що інтенсивність зворотно розсіяного світла відображає кінетику утворення гелевої сітки, що дає можливість встановити кінцеві розміри її агрегатів.

**Ключові слова:** Турбідиметрія, Фазовий перехід, Гідроксипропілцелюлоза.