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Study of the formation of structures in solutions of chitosan – polyvinyl alcohol polymer blends

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Abstract

The aim of this work was the investigation of the formation of structures in solutions of individual polymers, as well as their blends with each other in buffer solvents with different values of pH. In this study we used a sample of chitosan (degree of deacetylation ~ 84 %, M = 130,000), which is a polycation when dissolved, and polyvinyl alcohol ($\rho = 1.25 \text{ g/cm}^3$, M = 5000). Buffer systems based on acetic acid and sodium acetate with pH = 3.8, 4.25, and 4.75 were used as solvents. Viscosimetry was used to determine the intrinsic viscosity, the degree of structuring, and the Huggins constant. The Kriegerbaum method was used to determine the nature of the aggregates formed by the blend of the studied polymers.

In the course of the research, it was shown that an increase in the pH of the acetate buffer used as a solvent was accompanied by a compression of the macromolecular coil (a decrease in intrinsic viscosity values), a deterioration in the quality of the solvent (an increase in Huggins constant values), and an increase in the degree of polymer aggregation in a solution for chitosan polyelectrolyte. At the same time for a solution of polyvinyl alcohol the pH of the buffer practically did not affect the nature of the polymer-solvent interaction. It has been proved that polymer blends are characterized by an increase in aggregation processes and a decrease in the thermodynamic quality of the solvent in comparison with solutions of individual polymers. The size of the “combined” macromolecular coil, characterized by the intrinsic viscosity value for the polymer blend, which can be both above (buffer solvent with pH = 3.80) and below (buffer solvent with pH = 4.25 and 4.75) additive values, changed depending on the type of formed polymer-polymer aggregates (homo- or hetero-). It was established that the type of aggregates (homo- or hetero-) formed in solutions of polymer blends was determined not only by the thermodynamic quality of the used solvents, but also by the concentration of the polymers in the initial solutions.

Keywords: Polymer blends, Viscometry, Structure formation, Chitosan, Polyvinyl alcohol

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1. Introduction

It is known that the prehistory of the formation of a polymer material from a solution can affect a number of its characteristics: elasticity, strength, thermal stability, and many others [1–4]. This is due to the fact that even after the careful removal of the solvent, the nature and thermodynamic quality of the solvent used, the initial concentration of polymers in the solution, and the ratio of the components in the blend affect the properties and structure of films or fibres formed from a solution [4–7]. For example, due to the use of solvents of different thermodynamic qualities in relation to the polymer, various supramolecular structures were created in solutions, which remain in the metastable systems formed after the removal of solvents and further in the solid phase [8]. Thus, even in the case of obtaining materials from polymer-solvent systems, the hierarchy of the structures being formed, both in a dilute solution and in a condensed state, is complex and diverse, not to mention polymer-polymer-solvent systems.

Taking these facts into account, it becomes clear that it is extremely important to study the formation of the structures of polymers, as well as their blends in solutions, not only for the solution of specific applied problems, but also for obtaining new knowledge about the structures of polymers in solutions. The aim of this study was the investigation of the formation of structures in solutions of individual polymers (chitosan (ChTS) and polyvinyl alcohol (PVA)), as well as their blends with each other. The choice of polymers was due to their physiological activity [9], as well as a number of properties, such as biocompatibility, biodegradability, atraumaticity, high sorption capacity, minimal immune response of the organism, etc. [10–

17]. It should be noted that, when dissolved in acidic media, ChTS acquires the properties of a polyelectrolyte, namely, a polycation, which has a major effect on its physiological activity.

2. Experimental

For the study we used a sample of chitosan ChTS (manufactured by ZAO Bioprogress, Shchelkovo), obtained by the alkaline deacetylation of crab chitin (degree of deacetylation ~ 84 %), $M = 130000$, which, upon dissolution is a polycation (Fig. 1a), and polyvinyl alcohol PVA (Fig. 1b), grade 11/2 produced by OOO Reakhim $\rho = 1.25 \text{ g/cm}^3$, $M = 5000$.

Acetate buffers with pH = 3.8 (buffer solution 1), 4.25 (buffer solution 2), and 4.75 (buffer solution 3) were used as solvents. The acetate buffers were prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate: pH = 3.8–12 ml and 88 ml, pH = 4.25–32 ml and 68 ml, pH = 4.75–60 ml and 40 ml, respectively.

For the determination of the intrinsic viscosity $[\eta]$, the polymer was dissolved in an acetate buffer (for the exclusion of the effect of polyelectrolyte swelling for chitosan) for 24 h at room temperature with constant stirring. The intrinsic viscosity was determined viscometrically according to the standard method using an Ubbelohde viscometer at 25 °C [8] (by extrapolating to zero using the Huggins and Kroemer equations), the polymer concentration in the solution was varied from 0.1 to 0.5 g/dl. The experimental error was not higher than 1 %.

The degree of structuring of the solution (d) was determined as the slope of the line of the experimental dependences of the specific viscosity of solutions on the concentration of the polymer in the solution in logarithmic coordinates [18] (Fig. 2a).

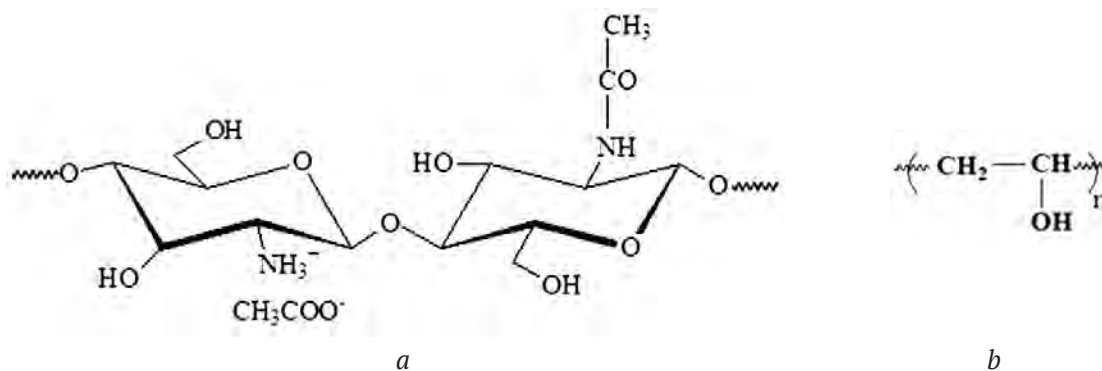


Fig. 1. Structural formulas of chitosan (a) and polyvinyl alcohol (b)

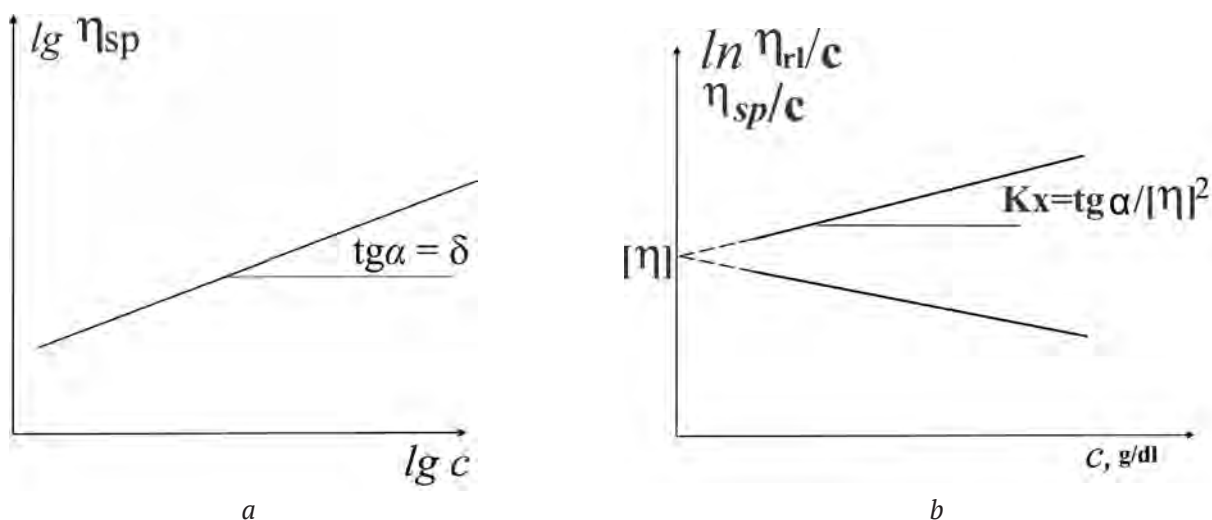


Fig. 2. Graphical methods for determining the degree of structuring of the solution (a) and Huggins constant (b)

The experimental data were analysed using the Kriegbaum method: according to the Huggins equation:

$$\eta_{\text{specific}}/C = [\eta] + bC;$$

where $b = [\eta]^2 K_x$.

The parameter of intermolecular interaction for individual polymers (b_{11}, b_{22}) was determined as the slope of the linear part of the dependence of the reduced viscosity on the polymer concentration (Fig. 2b).

Then, at each fixed concentration, the experimental parameter of intermolecular interaction ($b_{12(\text{exp})}$) for a blend was determined according to the formula:

$$b_{12(\text{exp})} = \frac{h_{\text{blend}} - [h]_1 C_1 - [h]_2 C_2 - b_{11} C_1^2 - b_{22} C_2^2}{2C_1 C_2}.$$

The parameter of intermolecular interaction Δb_{12} ($\Delta b_{12} = b_{12(\text{exp})} - b_{12(\text{theor})}$; $b_{12(\text{theor})} = (b_{11} b_{22})^{0.5}$) was determined by comparing $b_{12(\text{exp})}$ and $b_{12(\text{theor})}$. The types of the associates formed can be determined by the change of Δb_{12} : positive values of Δb_{12} indicate the presence of associates between dissimilar macromolecules in the solution and negative values indicate the presence of homoassociates.

3. Results and discussions

The study of the dynamic properties of macromolecules in solutions, in particular their hydrodynamic behaviour, provides information on the intermolecular interactions. In the description of the viscosity properties of dilute solutions,

as a rule, the interaction of macromolecules is neglected and their description is based on the linear dependence of the increase in viscosity on the concentration of the polymer solution. In the region of transition from dilute to semi-dilute solutions (crossover region), where the mechanism of mass transfer and the conformational regime of macromolecules change, and the formation of entangled network occurs. In accordance with the scaling theory in this region there is a deviation from the linearity of the concentration dependence of viscosity $\eta \sim c^\delta$. This is revealed by the change in the slope of the corresponding dependence in double logarithmic coordinates. According to generally accepted concepts, the tangents to the initial and final sections of this dependence intersect in the region of c^* , and the slopes are equal to 1 and 15/4 [19, 20].

Indeed, as was shown by viscometric studies of ChTS and PVA solutions in aqueous solutions with different values of pH (buffer solution 1 – pH = 3.80, buffer solution 2 – pH = 4.25, buffer solution 3 – pH = 4.75), the representation of the dependences of the specific viscosity of polymer solutions on concentration in logarithmic coordinates allows determining the concentration of c^* as the value from which the experimental curve deviates from a straight line. It should be noted that in the case of ChTS solutions, which have a polyelectrolyte nature, the value of c^* changes with changes in the pH of the medium (see Table 1).

As can be seen from Table 1, with an increase in the pH of the aqueous solution, the crossover

Table 1. Characteristics of the studied polymers obtained from viscometric data

Polymer	Solvent	c^* , g/dl	δ	K_χ	$[\eta]$, dl/g
ChTS	Buffer1 (pH = 3.80)	0.24	1.25	0.54	6.80
	Buffer2 (pH = 4.25)	0.26	1.28	0.60	5.70
	Buffer3 (pH = 4.75)	0.28	1.35	0.62	5.00
PVA	Buffer1 (pH = 3.80)	–	1.10	0.80	0.50
	Buffer2 (pH = 4.25)	–	1.15	0.80	0.50
	Buffer3 (pH = 4.75)	–	1.20	0.81	0.49

occurred somewhat later, which indicates a slight decrease in the size of the macromolecular coils. For PVA solutions, a crossover in the studied concentration range (up to 1 g/dL) was not observed due to the low molecular weight of PVA.

In addition, the description of the viscosity properties of polymer solutions, should consider the possibility of reversible aggregation processes, which can occur not only in the region of high concentrations, but also in the region $c < c^*$.

It is known that in the translational mechanism of mass transfer in aggregated suspensions, the contribution to the viscosity is made not by individual particles with a volume V_0 , but by their aggregates, the volume of which $V(n)$ depends not only on the number of constituent particles n , but also on the density of their packing, characterized by the fractal dimension D :

$$V(n) = V_0 \cdot n^{3/D}. \quad (1)$$

As a result of the loose packing of the suspension particles in the aggregate, their contribution to the viscosity starts to depend non-linearly on the concentration:

$$\Delta\eta \sim \eta_0 \cdot C^\delta, \quad \delta > 1. \quad (2)$$

A similar reasoning extends to polymer solutions when considering the dynamic properties of polymer coils taking into account the excluded volume effect (the model of impermeable coils) [18].

The processing of the experimental dependences of the specific viscosity of polymer solutions on the concentration in double logarithmic coordinates allows determining the power value d in the scaling dependence (2), the corresponding values of which are presented in Table 1.

A comparison of the obtained values shows that in all considered cases, the values of the scaling parameter exceed 1, which unambiguously

indicates that the processes of aggregation in the polymer solution begin in the region of dilute solutions.

Table 1 shows the values of the intrinsic viscosity and the Huggins constant (K_χ) of the studied polymers, which allowed the quality of the used solvents to be estimated. An analysis of these data for PVA and ChTS solutions in buffer solutions with different pH confirms the conclusions about the deterioration of the solvent quality and a decrease in the coil size with increasing pH in the case of ChTS. The sizes of PVA coils practically did not change with a change in the pH of the medium, which should be expected, considering that PVA is not a polyelectrolyte.

As a result of mixing ChTS and PVA solutions with equal concentrations, both the additive behaviour of the mixed solutions and deviations from additivity due to the rearrangement of the structure of polymer solutions, caused by both the different nature (ChTS is polyelectrolyte, PVA is not), and by the difference in molecular weight of macromolecules can be expected. An increase in the structuring of mixed solutions in comparison with solutions of individual polymers can be indicated, first of all, by the degree of aggregation (δ).

As can be seen from data presented in Fig. 3, polymer blends and solutions of individual polymers, are aggregated systems in all used buffers, regardless of the pH of the solvent, and for all compositions of ChTS: PVA blends. It should be noted that the values of the degree of aggregation are always higher than the additive values, which characterizes an increase in the intermolecular interaction of macromolecules. However, a general pattern was noted: with the deterioration of the thermodynamic quality of the solvent, e.g. with the transition to a more alkaline buffer, higher deviations from the additive values were observed.

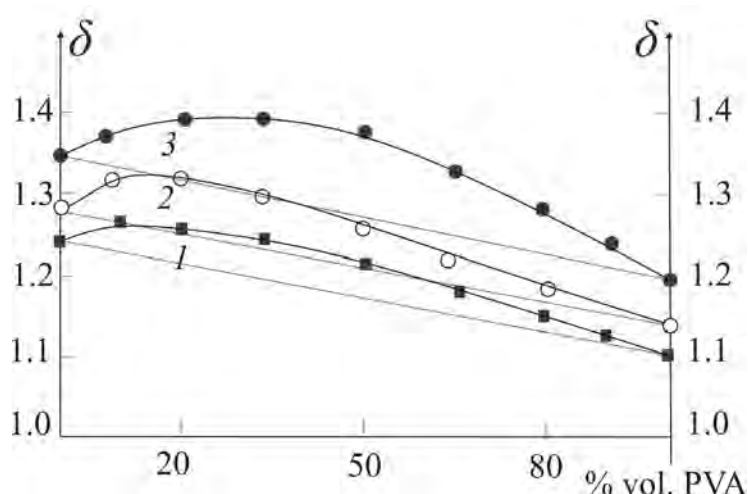


Fig. 3. The dependence of the aggregation δ degree of ChTSZ-PVA solutions in buffer solution 1 (1), in buffer solution 2 (2), in buffer solution 3 (3)

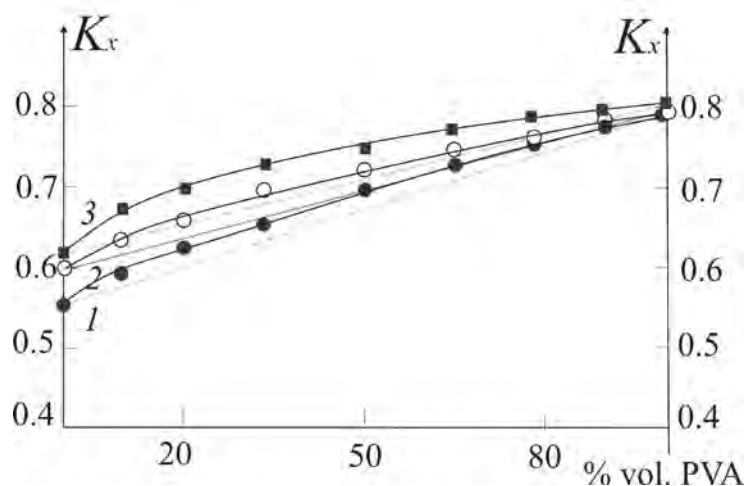


Fig. 4. The dependence of the Huggins constant of ChTS-PVA solutions in buffer solution 1 (1), buffer solution 1 (2) and in buffer solution 3 (3)

The increase in the degree of structuring of the solution was also evidenced by the values of Huggins constant (Fig. 4). As can be seen from the data presented, deviations from the additive values were observed for all solvents (buffer systems) used in the study.

Based on the values of the degree of aggregation and Huggins constant it can be stated that the formation of structures in solutions increases with polymer mixing. However, the analysis of the dependence of the intrinsic viscosity (reflecting the conformational state of macromolecules) on the composition of the polymer blend solutions indicates that the nature of the formed aggregates is different when using solvents with different values of pH (Fig. 5).

As can be seen from the data in Fig. 5, representing the dependence of the intrinsic viscosity on the composition of the blend for solutions with different pH, in a more acidic medium (with pH = 3.8) the mixed macromolecular coils “swell”, while in a more alkaline buffer - 3, the coils are “squeezed”, as evidenced by the negative nature of the deviation of the intrinsic viscosity from the additive values.

The processing of the viscometric data by the Krigbaum method allowed determining the nature of the aggregates formed by the PVA-ChTS blend. It was found that the nature of the aggregates in the polymer blend depends not only on the pH of the used solvent, but also on the concentration of the initial polymer solutions (Fig. 6).

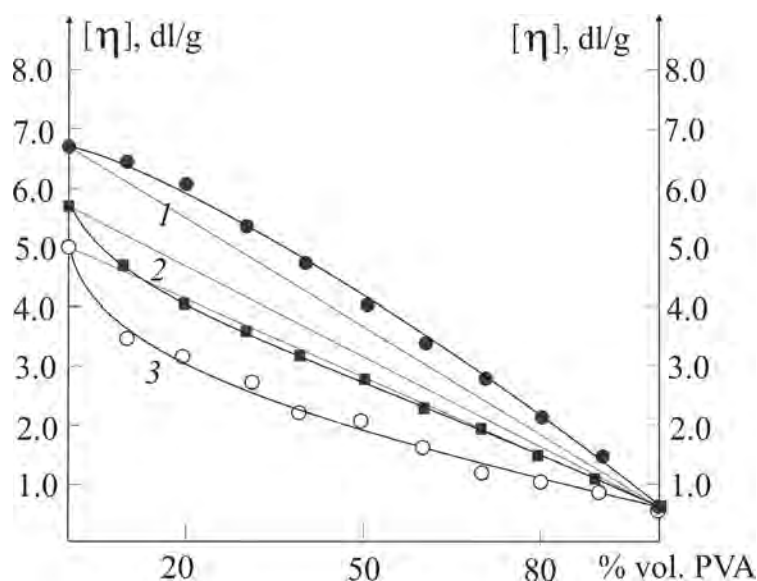


Fig. 5. The dependence $[\eta]$ of ChTS-PVA solutions in buffer solution 1 (1), in buffer solution 2 (2), in buffer solution 3 (3)

Thus, in buffers with $\text{pH} = 4.25$ and 4.75 , the formation of homoaggregates from macromolecules occurred with all investigated concentrations of the initial solutions of ChTS and PVA. This was evidenced by the negative values of the intermolecular aggregation parameter (Δb_{12}) (Fig. 6 b, c).

In the case of a more acidic solution with $\text{pH} = 3.80$, a complex dependence of the values of the intermolecular aggregation parameter on the concentration of the initial polymer solutions was observed. Thus, at concentrations lower and slightly exceeding c^* , positive Δb_{12} values (Fig. 6, curves 1, 2, 3) were revealed, which

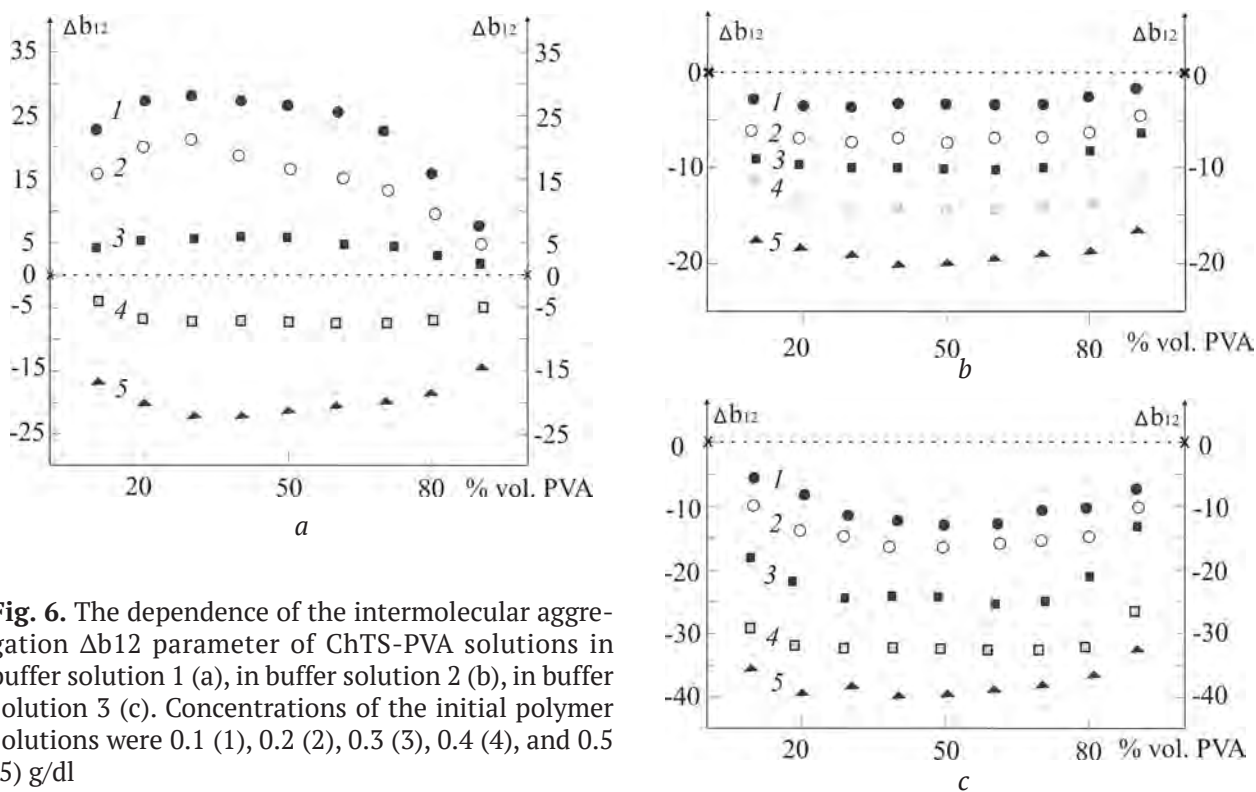


Fig. 6. The dependence of the intermolecular aggregation Δb_{12} parameter of ChTS-PVA solutions in buffer solution 1 (a), in buffer solution 2 (b), in buffer solution 3 (c). Concentrations of the initial polymer solutions were 0.1 (1), 0.2 (2), 0.3 (3), 0.4 (4), and 0.5 (5) g/dl

indicate the formation of mixed associates. At high concentrations of the initial ChTS and PVA solutions, negative values of intermolecular aggregation (Fig. 6, curves 4, 5) and, accordingly, the formation of homoaggregates were detected.

Probably, in a more acidic solution with concentrations slightly exceeding the crossover, the capture of PVA molecules by the ChTS macromolecules with the corresponding formation of heteroaggregates occurs. In more basic media (buffer solvents 2 and 3) and when c^* in buffer solvent 1 is exceeded, ChTS macromolecules were compressed, as a result of which each of the polymers aggregates separately from each other.

Thus, the performed studies showed that the formation of aggregates from macromolecules is possible in the case of solutions of individual polymers and in the case of their blends even in the region of dilute and semi-dilute solutions of polymer blends, which are a single-phase solution without a visible interface. The type of formed aggregates was largely determined by the nature and thermodynamic quality of the selected solvent, as well as by the concentration of the initial polymer solutions.

4. Conclusions

1. It was shown that for ChTS polyelectrolyte solutions, an increase in the pH of the acetate buffer used as a solvent is accompanied by a shrinkage of the macromolecular coil (a decrease in the intrinsic viscosity values), a deterioration in the quality of the solvent (an increase in the Huggins constant), and an increase in the degree of polymer aggregation in the solution. For PVA solutions, the pH of the solution practically did not affect the nature of the polymer-solvent interaction.

2. It has been proven that polymer blends are characterized by an intensification of aggregation processes and a decrease in the thermodynamic quality of the solvent in comparison with solutions of individual polymers. The size of the “combined” macromolecular coil (intrinsic viscosity value for a polymer blend) in this case can be both higher (buffer 1 with pH = 3.80) and below (buffer 2 with pH = 4.25 and buffer 3 with pH = 4.75) the additive values, which is determined by the type of (homo- or hetero-) formed polymer-polymer aggregates.

3. It was found that the type of aggregates formed in solutions of polymer blends (homo- or hetero-) are determined not only by the thermodynamic quality of the used solvents, but also by the concentration of polymers in the initial solutions.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

- Matevosyan M. S., Askadskii A. A., Slonimskii G. L. Mechanical relaxational properties of polymer films as a function of the prehistory of their preparation from solutions. *Polymer Science U.S.S.R.* 1987;29(4): 843–850. [https://doi.org/10.1016/0032-3950\(87\)90457-6](https://doi.org/10.1016/0032-3950(87)90457-6)
- Kulish E. I., Chernova V. V., Vildanova R. F., Volodina V. P., Kolesov S. V. The influence of the prehistory of the formation of film samples of chitosan on the process of their enzymatic decomposition. *Bulletin of the Bashkir University.* 2011;16(2): 339–340. Available at: <https://elibrary.ru/item.asp?id=16461557> (In Russ., abstract in Eng.)
- Kulish E. I., Lazdina R. Yu., Shurshina A. S., Kolesov S. V., Zakharova E. M., Zakharov V. P. Structure formation as a method of forming physicommechanical characteristics of films obtained from aqueous solutions of certain polysaccharides. *Polymer Science, Series A.* 2021;63 (1): 54–62. <https://doi.org/10.1134/s0965545x21010053>
- Alig I., Lellinger D., Skipa T. Influence of thermorheological history on electrical and rheological properties of polymer-carbon nanotube composites. In: *Polymer-Carbon Nanotube Composites.* 2011; 295–328. <https://doi.org/10.1533/9780857091390.2.295>
- Mazinov A. S., Tyutyunik A. S., Gurchenko V. S. Changes in the spectral characteristics and conductivity of fullerene films depending on the type of solvent. *Applied Physics = Prikladnaya Fizika.* 2020;2: 64–70. Available at: <https://elibrary.ru/item.asp?id=43064333> (In Russ., abstract in Eng.)
- Gorodnyakova I. S., Shcherbina L. A., Budkute I. A. Influence of the composition of the precipitation bath on the structure and properties of the fiber obtained by the wet method from solutions of poly [acrylonitrile-co-methyl acrylate-co-2-acrylamide-2-methylpropane sulfonic acid] in aprotic and hydrotropic solvents.

Polimernye materialy i tekhnologii. 2020;6(4): 42–57. <https://doi.org/10.32864/polymmattech-2020-6-4-42-57> (In Russ., abstract in Eng.)

7. Liu B., Zhang H., Ren J., Ma T., Yu M., Xie L., Lu D. Effect of solvent aromaticity on poly(9,9-dioctylfluorene) (PFO) chain solution behavior and film condensed state structure. *Polymer*. 2019;185(17): 121986. <https://doi.org/10.1016/j.polymer.2019.121986>

8. Rafikov S. R., Budtov V. P., Monakov Yu. B. *Vvedeniye v fiziko-khimiya rastvorov polimerov* [Introduction to the physicochemistry of polymer solutions]. Moscow: Khimiya Publ.; 1978. 320 p. (in Russ.)

9. Plate N. A., Vasilyev A. Ye. *Fiziologicheski aktivnyye polimery* [Physiologically active polymers]. Moscow: Khimiya Publ., 1986. 296 p. (in Russ.)

10. Anwar H., Ahmad M., Minhas, M. U., Rehmani S. Alginate-polyvinyl alcohol based interpenetrating polymer network for prolonged drug therapy, Optimization and in-vitro characterization. *Carbohydrate Polymers*. 2017;166: 183–194. <https://doi.org/10.1016/j.carbpol.2017.02.080>

11. Timofejeva A., D'Este M., Dagnija L. Calcium phosphate/polyvinyl alcohol composite hydrogels: A review on the freeze-thawing synthesis approach and applications in regenerative medicine. *European Polymer Journal*. 2017;95: 547–565. <https://doi.org/10.1016/j.eurpolymj.2017.08.048>

12. Matyjaszewski K., Möller M. Copper-mediated atom transfer radical polymerization. In: *Polymer Science: A Comprehensive Reference*. Elsevier Science; 2012;3: 377–428. <https://doi.org/10.1016/b978-0-444-53349-4.00071-6>

13. Schmitz C., Auza L. G., Koberidze D., Rasche S., Fischer R., Bortesi L. Conversion of chitin to defined chitosan oligomers: current status and future prospects. *Marine Drugs*. 2019;17(8): 452. <https://doi.org/10.3390/md17080452>

14. Crini G. Historical review on chitin and chitosan biopolymers. *Environmental Chemistry Letters*. 2019;17: 1623–1643. <https://doi.org/10.1007/s10311-019-00901-0>

15. Shukla S. K., Mishra A. K., Arotiba O. A., Mamba B. B. Chitosan-based nanomaterials: a state-of-the-art review. *International Journal of Biological Macromolecules*. 2013;59: 46–58. <https://doi.org/10.1016/j.ijbiomac.2013.04.043>

16. Keong L. C., Halim A. S. In Vitro models in biocompatibility assessment for biomedical-grade chitosan derivatives in wound management. *International Journal of Molecular Sciences*. 2009;10(3): 1300–1313. <https://doi.org/10.3390/ijms10031300>

17. Li J., Wu Y., Zhao L. Antibacterial activity and mechanism of chitosan with ultra high molecular weight. *Carbohydrate Polymers*. 2016;148: 200–205. <https://doi.org/10.1016/j.carbpol.2016.04.025>

18. Arinshtein A. E. Effect of aggregation processes on the viscosity of suspensions. *Sov. Phys. JETP*. 1992;74(4): 646–648. Available at: http://jetp.ac.ru/cgi-bin/dn/e_074_04_0646.pdf

19. Doi M., Edwards S. F. *The theory of polymer dynamics*. New York: The Clarendon Press, Oxford University Press; 1986. 391 p.

20. Gennes P. G. de *Scaling concepts in polymer physics*. Ithaca, N.Y.: Cornell University Press; 1979. 324 p.

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