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THE EFFECT OF A DYNAMIC PHASE TRANSITION IN WATER ON THE ELECTROPHYSICAL PROPERTIES OF AQUEOUS ALBUMIN SOLUTIONS

Introduction. *The structure of human serum albumin (HSA) in aqueous solutions undergoes significant changes depending on temperature, concentration, acid-base balance (pH), the presence of salts, etc.*

Methods. *The temperature dependence of the zeta potential of human serum albumin macromolecules (1 g/l) in a 0.075 M (0.45 wt. %) aqueous solution of sodium chloride in the temperature range (30–75) °C at the initial pH 7.4 was analyzed.*

Results. *Experimental values of the zeta potential increase sharply from –27 mV at the temperature of 30°C to zero at around 42°C, and then oscillate near zero up to the denaturation temperature. In the vicinity of 42°C a dynamic phase transition in water occurs, which divides the range of the liquid phase of water into two intervals: in the first interval, the thermal motion of water molecules has a crystal-like character, and in the second interval, water molecules move like ones in argon, i.e. the movement of molecules has an argon-like character.*

Conclusions. *The analysis shows that the temperature dependence of the zeta potential of albumin macromolecules in dilute aqueous solutions near the temperature of the dynamic phase transition in water is similar to the behaviour of magnetization around the Curie-Weiss critical point for the simplest magnets. Thus, the zeta potential can be considered as an order parameter for the thermodynamic Landau potential, which has the same structure as for the simplest magnets near their Curie-Weiss critical points. Further research will be aimed at studying the peculiarities of the applicability of the revealed analogy for the zeta potential of albumin macromolecules under different conditions of the solution.*

Keywords: *dynamic phase transition, human serum albumin, zeta potential, aqueous solutions.*

Introduction

The structure of human serum albumin (HSA) in aqueous solutions undergoes significant changes depending on temperature, concentration, acid-base balance (pH), the presence of salts, etc. With a change in the pH value in the solution, the

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charges of amino acid residues of macromolecules also change, and therefore the total charge of albumin macromolecules. The redistribution of charges on the surface of the macromolecule leads to a change in the spatial structure of the macromolecule and contributes to the processes of oligomerization of albumin macromolecules (Barbosa et al., 2010). Although a significant number of works have been devoted to the study of the structure of albumin in aqueous solutions, there is currently no effective model for the relationship between the structure and electrophysical properties of the albumin macromolecule and changes in the properties of aqueous solutions. The goal of this work is to clarify the influence of a dynamic phase transition in water on the temperature behavior of the zeta potential of HSA macromolecules in an aqueous solution of sodium chloride.

Methods

Experimental data on the temperature dependence of the zeta potential of human serum albumin macromolecules in aqueous solutions of sodium chloride are taken from (Bardik et al., 2020, p. 4). Human serum albumin powder was dissolved in 0.075 M (0.45 wt. %) aqueous sodium chloride solution at an initial pH 7.4 at 30 °C to obtain a protein concentration of 1 mg/ml. The zeta potential of albumin macromolecules was measured using a Zetasizer Nano ZS (Malvern Panalytical, UK) in the temperature range $T = (303–348)$ K (Bardik et al., 2020, p. 4). We estimated the relative errors of zeta potential and temperature measurement to be equal to $\varepsilon(\zeta) = 5$ % and $\varepsilon(T) = 0.3$ %, respectively.

Results

The electrophysical properties of macromolecules in solution are closely related to the value of the zeta potential, which can be measured experimentally. Zeta-potential (ζ) as the difference between the potentials of the aqueous medium and the stationary layer of the liquid surrounding the macromolecule allows us to draw conclusions about the total charge and stability of macromolecules in solution. One of the peculiarities of the behavior of the zeta potential of human serum albumin macromolecules in aqueous solution is the existence of a characteristic point – the isoelectric point of albumin (pH_0), at which the zeta potential of albumin is zero. This means that the total charge of the macromolecule is close to zero, so there are no repulsive electrostatic forces between macromolecules, and this can contribute to the processes of association and oligomerization of albumin macromolecules.

First it is worth noting that in (Bardik et al., 2020, p. 3) it was established that the addition of NaCl ions changes the value of the hydrodynamic radii of HSA macromolecules in the range of (5.0 ± 0.3) nm. Nevertheless, the values of the hydrodynamic radii of HSA macromolecules remain practically constant in the temperature interval (30–50) °C.

The values of the zeta potential of HSA macromolecules in aqueous solutions of sodium chloride in the temperature range (30–75) C are presented in Fig. 1. As can be seen, the value of the zeta potential increases sharply from –27 mV at the temperature of 30 C up to zero at about 42 C, and then it oscillates near zero up to the denaturation temperature. It should be noted here that in vicinity of 42 C the zeta

potential takes a zero value, which is characteristic of the isoelectric point (pH_0), and the liquid system is not particularly stable in this region. In (Bulavin et al., 2020, p. 795) it was shown that the temperature of 42 C divides the region of the liquid state of pure water into two intervals: $T_{tr} < T < (T_{tr} + 42)$ and $(T_{tr} + 42) < T < T_c$, where T_{tr} is the triple point and T_c is the critical point of pure water. In the first interval, the thermal motion of water molecules has the crystal-like character, while in the second interval, water molecules move in the same way as in argon, i.e. the molecular motion has argon-like character. Therefore, it can be concluded that a dynamic phase transition in water takes place in the region of 42 C.

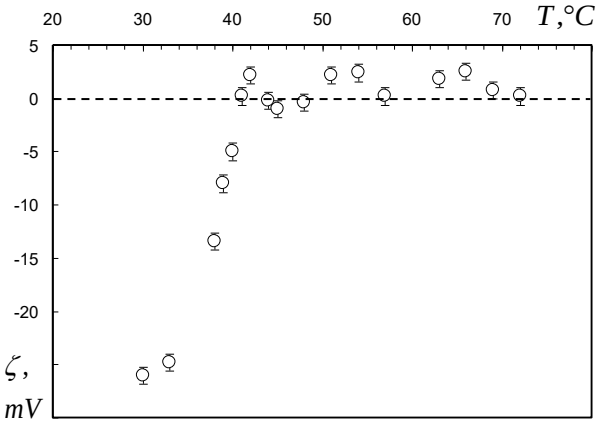


Fig. 1. Temperature dependence of the zeta potential of macromolecules of human serum albumin in 0.075 M aqueous solution of sodium chloride at an initial pH 7.4 at 30 °C (Bardik et al., 2020, p. 4)

Here it is necessary to pay attention to the fact that the temperature dependence of the zeta potential of HSA macromolecules in aqueous salt solutions near the 42 C is similar to the behavior of magnetization (m_z) near the Curie–Weiss critical point (T_{CW}) of magnet (Snoke, 2020). Indeed,

$$m_z = \begin{cases} 0, & T > T_{CW}, \\ \neq 0, & T < T_{CW}. \end{cases} \quad (1)$$

The behaviour of the zeta potential (ζ) could be reproduced the same:

$$\zeta \approx \begin{cases} 0, & T > T_H, \\ \neq 0, & T < T_H, \end{cases} \quad (2)$$

where $T_H = 42$ C and can be called a peculiar point for the subsystem of ions, which reflects the peculiarities of thermal motion in water.

Thus, the zeta potential in the aqueous albumin-salt solution near the peculiar point 42 C behaves similarly to the order parameter near the critical point of the magnetic system. This allows us to interpret this singular point as one for a dynamic

phase transition (Bardik et al., 2020, pp. 1–2). Near this point, thermodynamic properties, similar to volume properties (the size of albumin macromolecules), remain practically unchanged, while the electrophysical properties of protein molecules change very significantly. In particular, this is manifested in the specific dependence of the zeta potential on pH. Thereby, the dependence of zeta potential on the difference pH – pH_0 should be similar to the behavior of the magnetization (M_z), which is considered as a function of the magnetic field strength (H) for the simplest ferromagnetic:

$$M_z(T,H) \sim \tanh \beta H \,, \tag{3}$$

where $\beta = T_* / T$ and T_* is so called the Curie–Weiss critical point. Given the similarity, the zeta potential can be described by a similar expression, where α is some function of temperature:

$$\zeta(T, \mathrm{pH}) \sim \tanh \alpha(\mathrm{pH} - \mathrm{pH}_0) \,. \tag{4}$$

This result is quite surprising and it requires a physical explanation. To understand the similarity mechanism for zeta potential and magnetization, we have to apply the thermodynamic Landau potential depending on the order parameter. Identifying the order parameter with the magnetization in the case of a magnet and the zeta potential in the case of aqueous albumin solutions, in our next publication we will construct a thermodynamic Landau potential, assuming a conceptually similar framework for magnets and solutions.

Discussions and conclusions

The paper analyzes the temperature dependence of the zeta potential of human serum albumin macromolecules in a 0.075 M (0.45 wt. %) aqueous solution of sodium chloride at an initial pH 7.4 at 30 °C. The analysis shows that the temperature dependence of the zeta potential of albumin macromolecules in diluted aqueous solutions near the temperature of the dynamic phase transition in pure water (near the 42 °C) is similar to the behavior of magnetization in the vicinity of the Curie–Weiss critical point for the simplest magnets. It is concluded that the zeta potential can be considered as an order parameter for the thermodynamic Landau potential having the same structure as the one for the simplest magnets near their Curie-Weiss critical points. In order to guarantee the similarity of the magnetic and polarization properties, we conclude that the difference pH – pH_0 takes the sense of the field conjugate to the order parameter, i.e. is the analogue of the magnetic field for magnets. Further research will be aimed at studying peculiarities of applicability of the revealed analogy for the zeta potential of albumin macromolecules under different conditions.

Authors' contribution: Oleksii Khorolskyi – conceptualization, methodology, investigation, visualization, writing – original draft preparation, writing – reviewing and editing; Natalia Fudulei – investigation, validation, writing – original draft preparation; Oksana Stoliaryk – formal analysis, investigation, writing – original draft preparation; Wei Zhang – data curation, writing – original draft preparation.

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ВПЛИВ ДИНАМІЧНОГО ФАЗОВОГО ПЕРЕХОДУ У ВОДІ НА ЕЛЕКТРОФІЗИЧНІ ВЛАСТИВОСТІ ВОДНИХ РОЗЧИНІВ АЛЬБУМІНУ

Вступ. ***Структура сироваткового альбуміну людини (ЧСА) у водних розчинах зазнає значних змін залежно від температури, концентрації, кислотно-лужної рівноваги (pH), наявності солей тощо.***

Методи. ***Проаналізовано температурну залежність дзета-потенціалу макромолекул сироваткового альбуміну людини в 0,075 М (0,45 мас. %) водному розчині хлориду натрію в інтервалі температур (30–75) °С за початкового pH 7,4.***

Результати. ***Експериментальні значення дзета-потенціалу різко зростають від – 27 мВ при температурі 30 °С до нуля в околі 42 °С, а потім коливаються поблизу нуля аж до температури денатурації. Нульове значення дзета-потенціалу характерно для ізоелектричної точки альбуміну, коли загальний заряд макромолекули дорівнює нулю і між макромолекулами майже відсутні електростатичні сили відштовхування, що може сприяти процесам асоціації та олігомеризації макромолекул альбуміну. З іншого боку, в околі температури 42 °С у воді відбувається динамічний фазовий перехід, який розбиває діапазон рідкої фази води на два інтервали: у першому інтервалі тепловий рух молекул води має кристалоподібний характер, а в другому інтервалі молекули***

води рухаються подібно молекулярним рухам в аргоні, тобто рух молекул має аргоноподібний характер.

В и с н о в к и . ***Аналіз показує, що температурна залежність дзета-потенціалу макромолекул альбуміну в розведених водних розчинах поблизу температури динамічного фазового переходу у воді подібна до поведінки намагніченості в околі критичної точки Кюрі–Вейса для найпростіших магнітів. При цьому дзета-потенціал можна розглядати як параметр порядку для термодинамічного потенціалу Ландау, який має таку саму структуру, як і для найпростіших магнітів поблизу їхніх критичних точок Кюрі–Вейса. Подальші дослідження будуть спрямовані на вивчення особливостей застосовності виявленої аналогії для дзета-потенціалу макромолекул альбуміну за різних умов водного оточення.***

К л ю ч о в і с л о в а : ***динамічний фазовий перехід, сироватковий альбумін людини, дзета-потенціал, водні розчини.***

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