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Structure Formation of Fibrillar Protiens at the Electrodialysis of Ions in a Shift Stream

[1]S.O. Eshbekova and [2]A.A. Kholmuminov

[1]The Dzhizak Polytechnical Institute, 704126, Dzhizak, Street Halklar Do'stligi, 35
[2]Institute of Polymer Chemistry and Physics of UzAS, 700128, Tashkent, Street. A.Kadiri 7 "b"

Abstract: Opportunities of application of an electrodialysis for regulation of the contents of ions are revealed at structure formation of silk fibroin in a shift stream. Received "gels-plastics" can be considered as ion containing electro conducting compositions with an average degree of orderliness of circuits.

Key words: Silk fibroin . protein solution . shift stream . ion electrodialysis . gelation . electroconductivity . birefringence

INTRODUCTION

Processing of fibrous waste products fibrillar proteins to polymeric materials can be carried out through solutions at the presence of ions of salts and alkalis [1]. However, presence of ions in a solution interferes with formation intermacromolecular connections at formation of spatial structure of proteins in a stream. Removal of ions from solutions probably by means of an electrodialysis and application of the given way represents practical interest [2]. In the given work influence of an electrodialysis of ions of salts on structure formation of fibrillar protein is investigated at a shift stream for silk fibroin salt solution.

MATERIALS AND METHODS

Proceeding from a principle of work of device Reotest-2 (Germany) with a cell "cylinder-cylinder" have collected the installation represented on Fig. 1 for carrying out of experiences. Between in parallel fixed coal electrodes (1, 1'), taking place in the glass cylinder, have established cylindrical hydrocellulose membrane (3). Inside the membrane cylinder have coaxially placed the glass cylinder (5) which rotation provided with the electromotor (M). Thus the distance between cylinders made about 3 mm. The (7) is a direct of ions from membrane to electrodes.

Through the given space passed a polarizing beam (6) for definition of the factor of orientation of macromolecules (β) in a stream with the help of polarizing microscope (PM)

$$\beta \approx (\Delta n/\Delta n_{\infty})^{0.5} \quad (1)$$

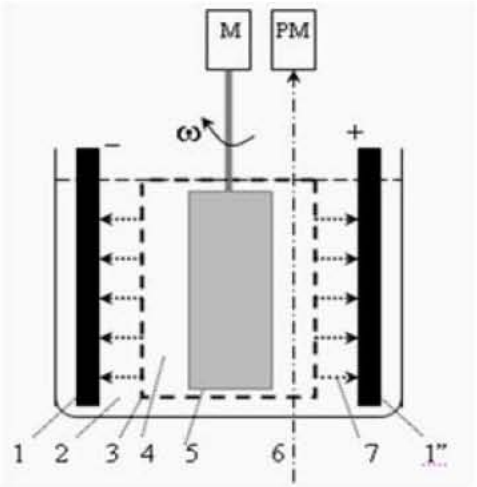

Fig. 1: The circuit of carrying out of an electrodialysis of ions at shift current ion containing solutions of fibrillar proteins

Where, Δn is the birefringence of the anisotropic region of the solution, which is determined from the phase difference Δf between the ordinary and extraordinary beams that pass through an anisotropic region of thickness d. For this purpose the device of Frank-Keller is used [1, 2]:

$$\Delta n \approx \lambda \Delta f / 180d \quad (2)$$

$\lambda \approx 0.56 \times 10^{-4}$ cm is the wavelength of a monochromatic light beam.

The quantity Δn_{∞} corresponds to the maximally attainable birefringence of the uncoiled chains. The parallel alignment of fibroin chains in the fiber makes it possible to assume that the fiber corresponds to the

Corresponding Author: Dr. A.A. Kholmuminov, Institute of Polymer Chemistry and Physics of UzAS, 700128, Tashkent, Street. A.Kadiri 7 "b"

maximally extended state of macromolecules [3]. Then, the birefringence

$$\Delta n_f \tilde{} \Delta n_\infty \qquad (3)$$

The direction of moving of ions (7) through membranes to the electrodes which are taking place in dialysiats (2) coincides with a direction of deformation of proteins molecules due to centrifugal force $F_{cf} = V\rho\omega^2 r$ (where V-volume and ρ-density of a solution, ω-angular speed of rotation, r-distance from an axis of rotation).

Fluidity (τ_r) for the fibroin solution determined under formula Margulies [4] supervising change of speed of rotation of the cylinder by submission on the electromotor of the certain electric voltage

$$\tau_r \approx 1/\eta_r \approx 2\pi\omega hR^3/bM \qquad (4)$$

Where η_r-viscosity of a solution; *h*-height of the cylinder; $R = (R_1+R_2)/2$-parameter of a hydrodynamic cell (R_1-radius of the internal glass cylinder, R_2-radius external of the membrane cylinder); b-distance between cylinders; $M = rF_{cf}$the moment of rotation.

Thus change of dynamics of fluidity of solutions supervised comparison with a reference value of fluidity ($\tau_r°$). Parity $\tau_r/\tau_r° \rightarrow 0$ characterizes losses of independent current of solutions with their transition to gel condition.

RESULTS AND DISCUSSION

Electrodialysis carried out for 10 % fibroin solution in 2.5 M LiCl-DMFA with use of water in quality

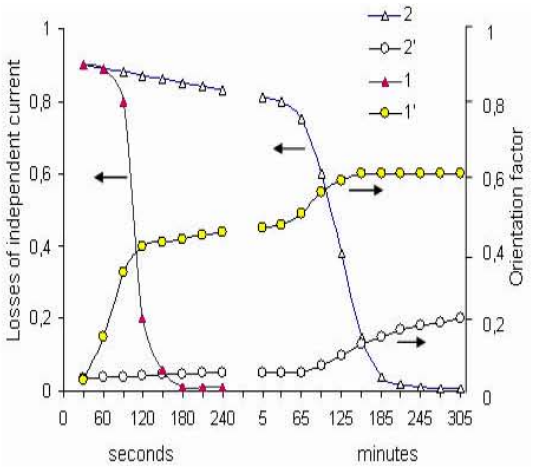

Fig. 2: Dependence of losses of independent current (1, 2) and the orientation factor (1', 2') from time of an electrodialysis (1, 1') and a dialysis (2, 2') ions at shift current of fibroin solution

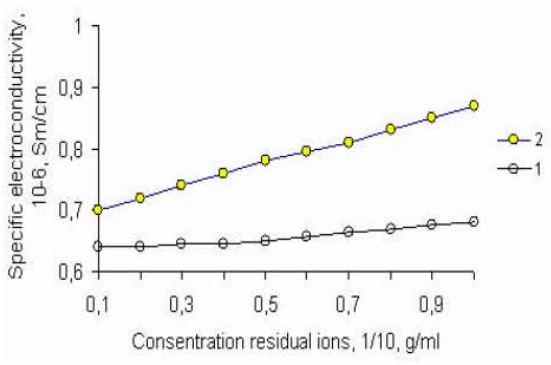

Fig. 3: Dependence of specific electroconductivity (σ) from concentration residual ions *(n)* in "gels-plastics" of fibroin at 25°C (1) and 50°C (2)

dialysiats. Efficiency of an electrodialysis estimated comparison with a usual dialysis of ions in a stream. From the data Fig. 2 it is visible, that the received curves have S-shaped kind, characteristic for non-Newton solutions currents [4].

It is revealed, that at an electrodialysis (I ≈ 5mA) solutions (volume V ≈50 cm^3), taking place under action of a constant shift pressure (100 Pa) observes intensive reduction of fluidity in an interval 100-150 seconds and loss of fluidity at > 180 seconds (a curve 1). At a usual dialysis under action of a shift field the solution loses fluidity during 180-200 minutes (a curve 2). Results of measurement of birefringence have shown that increase of the factor of orientation of macromolecules begins in case of an electrodialysis of ions (curve 1') in comparison with a usual dialysis (curve 2') much earlier. It testifies that the electrodialysis promotes acceleration of intermolecular interactions of deformation circuits in a shift field with the adjustable contents of ions in a solution.

As gelation of solutions at an electrodialysis of ions begins within 120 minutes value β ≈ 0.4 achieved for such time, testifies to a presence of macromolecules in gels with ordered enough condition. The further influence of a shift field appreciably increased deformation ordering fibers and has imparted to achievement of size β ≈ 0.6. Thus there was a phase division in a solution, i.e. at a plane of a wall of a membrane formed compressed gel phase as "gel-plastic". The given sample kept the structure after the discontinuance of shift current. The contents of residual ions in "gels-plastics" defined by extraction them on device Sokslet. Have revealed, that in 10 ml of "gel-plastic" residual ions from 0,1 up to 1 Γ which quantity depends on size of the enclosed constant electric current at an electrodialysis contain.

Residual ions give to "gels-plastics" электропроводящие properties. Results of definition

of electroconductivity at different temperature are resulted on Fig. 3. It is visible, that electroconductivity is higher in the samples containing the rests of ions in a lot. And, rise in temperature up to 50°C results in linear displacement of curves in area of the greater size σ. Basically, the found out displacement and values of electroconductivity are characteristic for ion containing polymeric compositions [5]. However, the mechanism of electroconductivity, apparently, mixed, obviously, it includes itself both ionic conductivity and electronic as, ions can easily come off fibers under action of an electric field.

CONCLUSIONS

Thus, influence of an electrodialysis of ions on structure formation deformed silk fibroin proteins in a shift stream is established. The opportunity of regulation of the given process and reception of samples of fibroin with the residual ions providing electroconductivity is shown.

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