Change in the redox potential of animal protein solutions in electrochemically activated water

L G Ipatova, A L Kuznetsov, O A Suvorov, A G Pogorelov
Institute for Theoretical and Experimental Biophysics RAS, 3, Institutskaya st., Pushchino, Moscow region, 142290, Russia
E-mail: agpogorelov@rambler.ru

Abstract. The change in the redox potential of water and solutions of bovine serum albumin and gelatin in electrochemically activated water with a reduced value of the redox potential obtained in the cathode chamber of a diaphragm electrochemical reactor is considered. The dependence of the relaxation rate of a protein solution in electrochemically activated water on its concentration in the range 0.01%-0.2% is shown. An increase in the concentration of proteins contributes to the restoration of the RP of solutions with different kinetics for albumin and gelatin. Reagent-free control of the characteristics of protein solutions can find application in technologies for processing livestock products, for example, in meat technologies.

1. Introduction
The water used in the production of food products in the initial state differs significantly in terms of the concentration of impurities, microbial contamination, mineralization and acid-base characteristics. In this regard, an important stage is water treatment, which ensures the specified characteristics of water, such as pH, salt composition and total mineralization, hardness. An essential indicator that determines the structure of the aquatic environment and its energy status, affecting the redox properties of water, is the redox potential (RP). The RP of water can be directionally changed in a wide range using the method of electrochemical activation (ECA) of water and aqueous solutions in the area adjacent to one of the electrodes of the diaphragm electrochemical reactor (electrolyser) - the anode or cathode. The result is obtaining, respectively, anolyte or catholyte, which have several anomalous properties during the relaxation period, lasting from several minutes to several days, depending on the conditions of energy exchange with the environment [1,2].

In the process of obtaining an ECA solution, not only the RP changes, but also the pH, biological and chemical activity, while the ionic (mineral) composition remains unchanged. After cathodic treatment, fresh or slightly mineralized water acquires an alkaline reaction due to the conversion of some of the dissolved salts into hydroxides. RP indices, surface tension, the content of dissolved oxygen and nitrogen, electrical conductivity decrease, at the same time the concentration of hydrogen and free hydroxyl groups increases, the structure of not only the hydration shells of ions changes, but also the free volume of water. As a result of anodic electrochemical treatment, the RP and acidity of water, the content of dissolved gases, and electrical conductivity increase. At the same time, the concentration of hydrogen decreases, the surface tension, and the structure of water changes [1,3,4]. In foreign and domestic literature, water treated in this way is called electrochemically activated, electrolysis, ionized, superoxidized or super-reduced [4,5].
Electrochemical activation is a modern method of water treatment for the purpose of purification, conditioning and directed change of the physicochemical properties of water and aqueous solutions without the introduction of chemical reagents. In various areas of agriculture and food industry, ECA solutions are known not only as effective and safe disinfectants [6], but also as promising extracting, hydrolyzing and modifying agents [7, 8, 9].

The method of electrochemical activation of water creates favorable conditions for its use in the meat industry. ECA water and solutions are considered from the point of view of increasing the efficiency of hydrolysis, extraction, emulsification, preparation of brines for processing meat products and several other processes. ECA catholyte has the properties of a catalyst for reducing physicochemical and biochemical processes. A change in the state of aggregation of cathode activated water when exposed to a meat substrate has a great impact on the quality and safety of the final finished product [9, 10]. In the case of using meat raw materials with a high content of connective tissue, the use of ECA catholyte is advisable for enzymatic biomodification [11]. At a catholyte pH of 6.8-7.7, a temperature of 50-55 °C, and the concentration of sodium chloride in the initial activated solution - up to 0.7%, the proteolytic activity of the enzyme preparation significantly increases. Several experimental studies have confirmed that the use of catholyte in brines does not require the addition of chemical components and improves the rheological properties of meat. When raw meat is salted in a catholyte medium, the pH of the meat shifts towards alkaline values, causing an increase in the moisture-binding capacity of the meat substrate [9, 10, 12].

The use of liquid systems based on ECA water allows for reagent-free, environmentally friendly regulation of the functional, technological and quality properties of minced meat systems. Thus, the use of an alkaline fraction of electrochemically activated water (pH 10-12) as an aqueous phase in combination with cavitation disintegration of a liquid medium ensures the production of stable protein-fat emulsions that serve as the basis to produce emulsified minced meat products. When dispersed in electrochemically activated water, the water-absorbing and emulsifying capacity of the protein increases, due to which the separation of the fat fraction begins to occur at an oil concentration in the system of 70-80%, while when using drinking water - already at 52% [13].

In a study [14], the blood plasma of slaughtered animals, a source of complete protein and a valuable ingredient in minced meat products, with unique technological polyfunctional properties, was treated. Blood plasma (pH 7.7) after activation was divided into two fractions - acidic (anolyte, pH 5.8-6.0) and alkaline (catholyte, pH 9.9-10.1). The addition of activated plasma fractions to sausage minced meat under cutting conditions caused changes in the physicochemical and structural-mechanical characteristics of the minced meat (ultimate shear stress, plastic viscosity, fat globule size, water binding capacity, electrostatic charge, etc.).

The physical model proposed by the authors explains these changes by the formation of coagulation contacts in the minced meat between the protein molecules and the surface of the fat globules, leading to the formation of adsorption layers, which are a structural and mechanical barrier for the aggregation of the balls and ensure the stability and homogeneity of the minced meat. Activated blood plasma fractions have a different effect on these structures, as well as on aggregation processes in the myofibrils of muscle tissue [14].

Of great interest is the study of the interaction of ECA water with food ingredients the determination of the relationship between the redox potential of water and the properties of solutions of food substances.

2. Materials and methods
The object of the study was BSA100 bovine serum albumin (Merck, Sigma-Aldrich) and food gelatin P-11 (Russian Grocery Company LLC, Russia). The catholyte fraction of electrochemically activated water (ECAW) with a negative RP value was obtained in a FEM-3 flow-through electrochemical module. Water from the water pipe was passed sequentially through the anode chamber of the module, the reaction-flotation reactor, the heterophase catalytic reactor, and the cathode chamber of the module. The ECA values of the water corresponded to pH 7.3 and RP = -223 mV. The control was
water from the city water supply (pH 7.3, RP = +190 mV). The pH value and redox potential of water were measured using a SevenExellence S470 multivariable device (METTLER TOLEDO, Switzerland) equipped with a pH electrode (Inlave Routine Pro, Mettler Toledo), an RP electrode (InlaB Redox Pro, Mettler Toledo).

3. Results and Discussion
The shift of the RP value to the region of negative values can affect the quality and efficiency of the interaction of the dissolved macromolecules. In an aqueous medium, a protein as a polyelectrolyte with high conformational mobility can be susceptible to the redox properties of a solvent electrochemically activated (ECA) water. We investigated electrochemically activated water with normal acidity (pH ~ 7.3), but abnormally low (-223 mV) redox potential at the starting point (Fig. 1).

Figure 1. Change over time of the redox potential of electrochemically activated water and tap water at 20 °C

It can be seen (Fig. 1) that over time, ECAP shows an increase in RP, demonstrating relaxation of the metastable state, against the background of an almost unchanged indicator for the original tap water. If the RP value of tap water (control) at 20 °C remained at a constant damage of +190 mV during the entire observation period (24 hours), then the RP ECA value of water equal to -223 mV gradually increased due to the relaxation of the metastable state. The highest relaxation rate was noted in the first 6 hours, after which the process slows down, RP goes into the region of positive values, reaching +69 mV in 24 hours, which is significantly lower than the level of the control water sample.

Figure 2 shows the characteristics of RP solutions after adding albumin and gelatin to ECA water.

The data obtained (Fig. 2a, b) show that the dissolution of both albumin and gelatin in ECA water causes the growth of RP solutions. The effect becomes more pronounced with increasing protein content. At the initial moment, the RP, while remaining negative, does not reach the value of +190 mV, which is typical for the initial water from the mains.

Over time, a change in the RP of the solution is observed (Fig. 3). Note that an increase in the concentration of both albumin and gelatin promotes a faster recovery of the RP ECA solution, but with different kinetics.
Figure 2. Influence of protein concentration on RP values of electrochemically activated water solution: (a) - RP value of solution with different concentration of albumin at the initial moment; (b) - RP value of a solution with different concentrations of gelatin at the initial moment

Figure 3. Influence of Protein Concentration on Change in RP During Storage of a Solution in ECA water: (a) - albumin; (b) - gelatin

The considered results demonstrate the process of RP reduction in solutions of bovine serum albumin and gelatin. With an increase in the concentration of proteins in the range of values 0.01% - 0.2%, the relaxation rate increases gradually. The addition of proteins promotes a faster recovery of the RP ECA solution, and depending on the concentration and type of protein, the kinetics of the process differs, and the maximum values after 24 hours for both proteins remain significantly lower than the RP of the control sample without additives (+190 mV).

4. Conclusion
The content of protein molecules in solutions based on ECA water affects the relaxation process of activated solutions, which is manifested in the reduction of RP in the aqueous medium. Revealing the regularities of the interaction of ECA water with molecules of nutrients bovine serum albumin and gelatin, is interesting from the point of view of the prospects for reagent-free control of the physicochemical properties of food systems, improving their rheological properties, accelerating and optimizing technological processes in food production.
Acknowledgments
This work was supported by the Russian Science Foundation grant № 20-16-00019.

References
[1] Bakhir V M 2014 Electrochemical activation. Inventions, technique, technology (Moscow: VIVA-STAR)
[2] Gluhchev G 2015 Electrochemically Activated Water: Biophysical and Biological Effects of Anolyte and Catholyte Types of Water European Journal of Molecular Biotechnology 7(1) 12–26. DOI: 10.13187 / ejmb.2015.7.12 www.ejournal8.com
[3] Henry M, Chambron J 2013 Physico-Chemical, Biological and Therapeutic Characteristics of Electrolyzed Reduced Alkaline Water (ERAW) Water 5 2094-2115. DOI: 10.3390 / w5042094
[4] Kashiwagi T, Yan H, Hamasaki T, Kinjo T, Nakamichi N, Teruya K, Kabayama S, Shirahata S 2014 Electrochemically Reduced Water Protects Neural Cells from Oxidative Damage Hindawi Publishing Corporation Oxidative Medicine and Cellular Longevity 18 Article ID 869121. DOI: http://dx.doi.org/10.1155/2014/869121
[5] Johansson B 2017 Functional water-in promotion of health beneficial effects and prevention of disease Internal Medicine Review 32
[6] Athayde D R, Flores D R M, Silva J S et al 2018 Characteristics and use of electrolyzed water in food industries International Food Research Journal 25(1) 11-16
[7] Plutakhin G A, Aider M, Koschaev A G, Gnatko E N 2013 Practical application of electrochemically activated aqueous solutions Scientific journal KubSAU 92(08)
[8] Gorbacheva M V, Tarasov V E, Kalmanovich S A, Sapozhnikova A I 2021 Electrochemical activation as a fat rendering technology Foods and raw materials 9(1) 32–42. DOI: 10.21603 / 2308-4057-2021-1-32-42
[9] Dydykin A S 2012 Theoretical foundations and practical application of electrochemical activation of water Meat industry 1 44–48
[10] Shamaeaeva E A et al 2007 Electrochemical activation as a method of reagent-free regulation of the properties of liquid food media: Monograph (Stavropol: Publishing House of the North Caucasus State Technical University)
[11] Borisenko A A, Borisenko L A, Bratsikhin A A et al 2001 The use of activated liquid systems to produce deli meats Meat industry 6 12-13
[12] Bal-Prilepko L V, Leonov B I, Naumenko V I 2009 Application of activated water as the main component of brines for meat products Scientific result of business and service technology 8 24–31
[13] Borisenko L A, Borisenko A A, Lagereva A V, Zorin A V, Bratsikhin A A 2008 Development of technology to produce sausages using activated liquid systems Bulletin of the North Caucasus Technical University SevKavGTU 2(15) 45–46
[14] Antipova L V, Titov S A, Ilyina N M, Popova N N, Sayko D S 2001 Physical model of the formation of coagulation contacts in minced meat with the addition of electrochemically activated blood plasma Izvestiya VUZov. Food technology 1 10–12
[15] Chichko A A, Borisenko L A 2002 Research of functional and technological properties of activated protein-containing preparations Modern achievements of biotechnology: Materials of the 2nd All-Russian scientific and technical conference Stavropol SevKavSTU vol 2 pp 96-976