

Internal mechanisms of establishment of the equilibrium state of water-alcohol mixtures in vodka technology

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Abstract

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Introduction. The aim of the publication is to study the mechanism of the establishment of relaxation of water-alcohol mixtures (WAM) in the main stages of creating vodka in the application of electrochemical activation (ECA) at the stage of Na-cationization process water softening.

Materials and methods. ¹H NMR analysis was performed using: FT-NMR Bruker Avance II spectrometer (400 MHz); special capillary with acEtOHe-d₆; high accuracy ampoules № 507-HP; dispenser; ethyl alcohol rectified (EAR); water softened by Na-cationization; WAM from EAR and softened water.

Results and discussion. In this work, the equilibrium state of vodkas in the creation of WAM in the process of ECA of softened water by Na-cationization is investigated. It has been established that electrochemical reactions lead to a change in the system of intermolecular interactions. Charging states of molecules in anolyte and catholyte lead to differences in the electron distribution, which affects the chemical displacements of hydroxyl protons. In relation to the softened water ($\delta_{H_2O}=4.65$ ppm), the anolyte with $\delta_{H_2O}=(4.23; 4.22)$ ppm has a displacement of the hydroxyl proton in the «strong field» at $\Delta f=170$ Hz. The catholyte with $\delta_{H_2O}=(4.56; 4.54)$ ppm has a displacement in the «strong field» at $\Delta f=40$ Hz. It has been proved that the WAM on anolyte (pH=2.43) and EAR has an acidic medium (pH=3.10), WAM in a catholyte (pH=11.08), and EAR has a meadow medium (pH=11.75). These polar ratios of H_3O^+ to OH^- for anolyte and catholyte lead to a restructuring of the structure in the alcohol/water system. It can be assumed that the proton exchange is accelerated, while there is one general signal of mobile protons $EtOH+H_2O$.

On the basis of the study a fundamental difference between the behavior of the WAM and the vodka prepared on softened water and water after ECA treatment was established. Found systems (alcohol/water) with a stable equilibrium, which are characterized by a high degree of generalization of protons, as well as characteristic rates of exchange for it.

Conclusions. The experimental data obtained prove the dependence of the speed and nature of the establishment of the thermodynamic equilibrium due to the relaxation of the WAM. It is shown that relaxation occurs at the simultaneous stabilization of the hydroxyl group of water and ethanol protons.

Introduction

Today, 1H NMR spectroscopy is the most popular among spectroscopic methods due to its simplicity (Rutledge, 1996) [26] and completeness of information (Majumdar et al., 2017; Richards, Hollerton, 2011) [23, 27], thus accelerating chemical research, especially in the food industry (Abraham, Mobli, 2008) [20]. A large number of articles discuss the use of NMR for research of food products: honey, fruits, juices, vegetables, pastry, cheese, meat, fish, dairy products, starch and alcohol products (Zuriarrain et al, 2015; Minoja, Napoli, 2014; Zhu, 2017; Campo et al, 2016; Pinto et al, 2018; Oh et al, 2018; Shi et al, 2018; Youssouf et al, 2017; Li et al, 2018; Kuballa et al, 2018; Yuan et al, 2017) [1, 2, 5, 6, 9, 10, 11, 17, 25, 28, 32]. This method provides comprehensive information with relatively simple obtaining spectra, thus greatly facilitating and accelerating chemical research (Hu et al, 2010; Nose et al, 2005; Roberts, 2002; Richards, Hollerton, 2011) [8, 18, 24, 27].

Since the first 1H NMR spectra of water and ethanol have been obtained more than 60 years, today there are many works (Batta et al, 1997; Albert, 2002; Meusinger, 2010; Rutledge, 1996; Holzgrabe et al, 2008) [7, 12, 21, 26, 29] in which the spectra of water and ethanol are given – which are understandable from the analytical point of view of the substance. But these relatively simple molecules have a large variety of details that occupy a deserved place both in works (Arnold, 2002; Becker et al, 2002; Oliveira et al, 2007; Ababneh, 2018; Richards, Hollerton, 2011; Xu et al, 2012; Mori et al, 2018) [3, 4, 19, 22, 27, 30, 31] and are of interest to our work (Kuzmin et al, 2017) [15, 16].

We will consider a complex of issues related to intermolecular proton exchange. The hydroxyl proton of ethanol can be exchanged with free H^+ ions in the matrix, which are generated by the introduced water or by residual quantities of acid (Arnold, 2002; Becker et al, 2002; Abraham, Mobli, 2008) [3, 4, 20]. The rate of exchange is proportional to the number of free ions H^+ , so the actual location of the center of the signal depends on the availability of an alternative exchange point (water), as well as on the difference in chemical changes in the protons of the two milieus (Arnold, 2002; Richards, Hollerton, 2011) [3, 27].

Previously, we have conducted primary research of 1H NMR of water-alcohol mixtures (WAM), which were described in the work of Kuzmin et al, 2017 [15, 16]. The obtained results give grounds to assert a fundamental difference in the behavior of the WAM prepared from the alcohol and water passing through various processes. This may indicate the presence of such features as separate signals of *OH*-protons of H_2O and *EtOH*. Also abnormal waveforms of CH_3 and CH_2 characterize a product with a lowered tasting properties. The presence of the combined signal of $H_2O+(EtOH)$ and a «clear» form of CH_3 and CH_2 signals (triplet – for CH_3 , quartet – for CH_2) – characterizes the WAM with the best tasting properties.

Thus, in the work of Kuzmin et al, 2017 [15, 16] established experimental evidence or instilment nature/(non- installment) of thermodynamic balance, taking into account the organoleptic characteristics of WAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the WAM are remain unsolved.

Therefore, the additional research is required for a detailed study of internal mechanism of thermodynamic balance and insurance in obtaining high quality vodka products – for each type of water separately.

Conducting a set of technical solutions at the main stages of production of vodka, due to electrochemical activation (ECA) of technological water, will allow us to study the mechanism for establishing the equilibrium state of WAM by stabilizing the position of *OH*-protons of ethanol and water, using 1H NMR spectroscopy. Since there is no such information

in the literature, the purpose of the work was to study the mechanism of establishing the thermodynamic equilibrium – the relaxation of the WAM at the major stages of creating vodka when applying ECA at the stage of *Na*-cationization softening of technological water to predict the quality of the final product.

For the set goal, the following tasks were solved:

- to obtain experimental evidence of the rate and nature of the establishment of the thermodynamic equilibrium of WAM;
- to establish a mechanism of thermodynamic equilibrium – the relaxation of WAM;
- to investigate the stabilization of the hydroxyl group of water and ethanol protons.

Materials and methods

Scheme of conducting research (basic scheme of the experimental stand, the scheme of sample preparation for the 1H NMR study and block diagram of the 1H NMR spectrometer) is presented in Figure 1.

The following devices, materials and raw materials were used for research:

- dispenser (15); ampoules 5 mm (400 MHz) with specimens (16); capillaries with deuterioacEtOHe (DAC) (17); ampoules with capillary (18) (Figure 1, b);
- drinking water (0.0) with characteristics: hydrogen index 6.91 unit pH; redox potential (ORP) «+» 269.0 mV; mass concentration (MC) $MC_{Ca} - 104.342 \text{ mg/dm}^3$; $MC_{Mg} - 22.835 \text{ mg/dm}^3$; $MC_{Na} - 91.966 \text{ mg/dm}^3$; total hardness – 8.04 mmol/dm³; total alkalinity – 5.38 mmol/dm³;
- softened water (1.0) with characteristics: hydrogen index 7.18 unit pH; ORP «+» 288.0 mV; $MC_{Ca} - 0 \text{ mg/dm}^3$; $MC_{Mg} - 0 \text{ mg/dm}^3$; $MC_{Na} - 266.131 \text{ mg/dm}^3$; total hardness – 0.05 mmol/dm³; total alkalinity – 4.12 mmol/dm³;
- anolyte (1.2) with characteristics: hydrogen index 2.43 unit pH; ORP «+» 451.0 mV; $MC_{Ca} - 0 \text{ mg/dm}^3$; $MC_{Mg} - 0 \text{ mg/dm}^3$; $MC_{Na} - 156.626 \text{ mg/dm}^3$; total hardness – 0.90 mmol/dm³; total alkalinity – 0.00 mmol/dm³;
- catholyte (1.1) with characteristics: hydrogen index 11.08 unit pH; ORP «+» 44.0 mV; $MC_{Ca} - 0 \text{ mg/dm}^3$; $MC_{Mg} - 0 \text{ mg/dm}^3$; $MC_{Na} - 380.009 \text{ mg/dm}^3$; total hardness – 0.15 mmol/dm³; total alkalinity – 10.85 mmol/dm³;
- ethyl alcohol rectified (EAR) of the class «Lux» (2.0): volume fraction of ethanol – 96.37%, at $T=293 \text{ K}$; $MC_{aldehydes} - 1.28 \text{ mg/dm}^3$; $MC_{fusel \text{ oil}} - 1.47 \text{ mg/dm}^3$; $MC_{esters} - 1.30 \text{ mg/dm}^3$; volume fraction of methanol – 0.0022%;
- WAM for EAR of a class «Lux» and water softened by *Na*-cationization (3.0): volume fraction of ethanol – 39.90%; hydrogen index 7.84 unit pH; ORP «-» 35 mV; $MC_{aldehydes} - 1.31 \text{ mg/dm}^3$; $MC_{fusel \text{ oil}} - 1.41 \text{ mg/dm}^3$; $MC_{esters} - 1.41 \text{ mg/dm}^3$; volume fraction of methanol – 0.0020%; alkalinity – 2.40 ml; tasting score – 9.49 points;
- WAM on softened water – anolyte (3.2): volume fraction of ethanol – 39.91%; hydrogen index 3.10 unit pH; ORP «+» 146 mV; $MC_{aldehydes} - 1.80 \text{ mg/dm}^3$; $MC_{fusel \text{ oil}} - 1.26 \text{ mg/dm}^3$; $MC_{esters} - 1.55 \text{ mg/dm}^3$; volume fraction of methanol – 0.0022%; alkalinity – 0.00 ml; tasting score – 9.51 points;
- WAM on softened water – catholyte (3.1): volume fraction of ethanol – 39.95%; hydrogen index 11.75 unit pH; ORP «-» 174 mV; $MC_{aldehydes} - 1.43 \text{ mg/dm}^3$; $MC_{fusel \text{ oil}} - 1.20 \text{ mg/dm}^3$; $MC_{esters} - 1.42 \text{ mg/dm}^3$; volume fraction of methanol – 0.0021%; alkalinity – 2.40 ml; tasting score – 9.42 points;

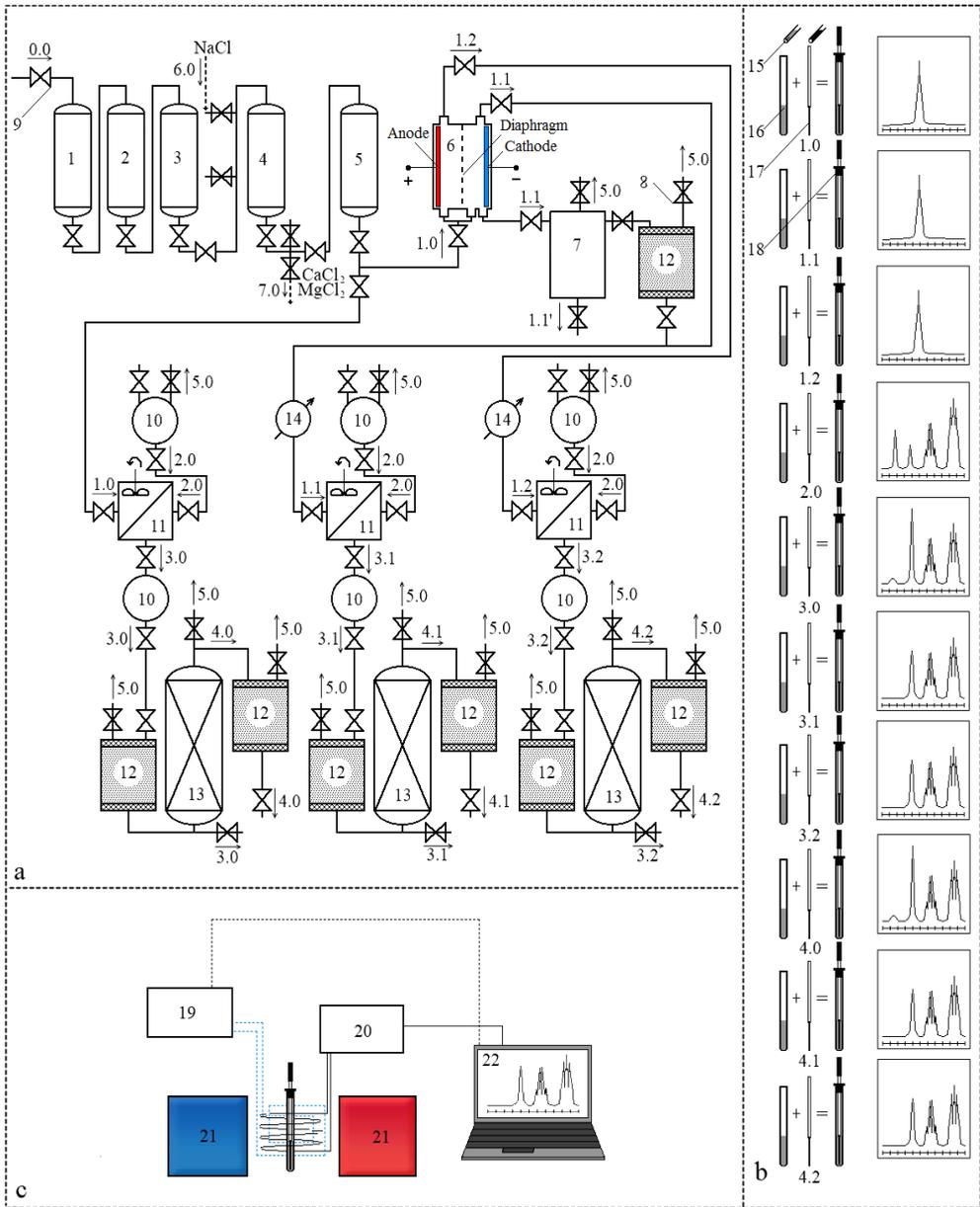


Figure 1. Scheme of research:

a – the principle scheme of the experimental stand;

b – sample preparation scheme for 1H NMR study;

c – block diagram of a 1H NMR spectrometer;

0.0–7.0 – streams; 1–14 – technological equipment; 15–22 – laboratory equipment

- WAM on EAR and water softened at the expense of *Na*-cationization after treatment with activated carbon (AC) (4.0): volume fraction of ethanol – 39.81%; hydrogen index 9.14 unit pH; ORP – «+»122 mV; $MC_{\text{aldehydes}}$ – 1.72 mg/dm³; $MC_{\text{fusel oil}}$ – 1.34 mg/dm³; MC_{esters} – 1.82 mg/dm³; volume fraction of methanol – 0.0023%; alkalinity – 2.3 ml; tasting score – 9.63 points;
- WAM on softened water – anolyte after AC (4.2): volume fraction of ethanol – 39.82%; hydrogen index 3.12 unit pH; ORP – «+»360 mV; $MC_{\text{aldehydes}}$ – 4.54 mg/dm³; $MC_{\text{fusel oil}}$ – 1.57 mg/dm³; MC_{esters} – 3.52 mg/dm³; volume fraction of methanol – 0.0024%; alkalinity – 0.0 ml; tasting score – 9.61 points;
- WAM on softened water – catholyte after AC (4.1): volume fraction of ethanol – 39.80%; hydrogen index 10.45 unit pH; ORP – «+»92 mV; $MC_{\text{aldehydes}}$ – 2.22 mg/dm³; $MC_{\text{fusel oil}}$ – 1.44 mg/dm³; MC_{esters} – 1.60 mg/dm³; volume fraction of methanol – 0.0024%; alkalinity – 2.4 ml; tasting score – 9.65 points;

Methods: ¹H NMR spectroscopy; methods for assessing physical-chemical and organoleptic characteristics of water, EAR, WAM and vodka.

Work methodology of ¹H NMR (Kuzmin et al, 2017) [15, 16]: using the dispenser (15) in the ampoule (16) the test specimen is given. Necessary for the system LOCK – deuterial stabilization NMR spectrometer DAC – external standard, which is separated from the test substance, is introduced into the ampule (16) in the capillaries of a special form (17); in accordance with the method of recording ¹H NMR spectra, the spectrum of the sample in the DAC (18) is recorded and processed using the Bruker TopSpin v2.6 program.

Apparatus. For the ¹H NMR study, the *Fourier NMR* spectrometer Bruker Avance II 400 MHz (Figure 1, c) (19–22) was used.

In Figure 1 a, the principal scheme of the experimental stand with the diaphragm electrochemical reactor is given.

Drinking water (0.0) through the open tap (9) enters the line for preparation of technological water, which consists of the following elements:

- mechanical filter (1) of polypropylene fiber with a filtration rating of 5 μm, which removes mechanical impurities of more than 5 μm from the water;
- carbon filter (2) with porous carbon materials (PCM), which is prepared from alternative materials – food industry wastes by method of chemical activation using H_3PO_4 (Kuzmin O., Shendrik T., Zubkova V., 2017) [14], which provides clearing of active chlorine, iron;
- a mechanical filter (3) with a filtration rating of 1 μm which removes mechanical impurities from the water, which are in the form of weighted particles of varying degrees of dispersion sized by more than 1 μm;
- a filter with ion exchange resin cationic type granules (4). The installation is equipped with mechanisms of automatic regeneration of ion exchange resin *NaCl* (6.0) and a drain of water concentrate from *CaCl₂* and *MgCl₂* (7.0);
- a barrier filter (5), which is designed for control softened water filtration before supplying reverse osmosis with a particle lag rating of 1 μm.

Results and discussions

On the ECA preparation line, softened water enters the electrochemical reactor (6), the anodic and cathodic space of which is separated by a porous partition, a diaphragm that is permeable to ions and impervious to products of electrolysis. In this case, the arrival of electrons in water occurs near the cathode, and the removal of electrons from water – near

the anode, which leads to the formation in a cathode chamber – a catholyte (1.1), and in the anode – anolyte (1.2).

For drainage and filtration of the catholyte concentrate (1.1') there is an additional line with a receiving capacity (7), a sand-filter (12) and air cocks (8) – for air separation (5.0).

The ECA process leads to an increase in the water temperature to $T_{1.1-1.2}=310$ K, which is unacceptable for the manufacture of WAMs, so the water flows (1.1, 1.2) are additionally cooled using a chiller (14).

On the WAM preparation line from the pressure tanks (10) to the sorting tanks the EAR (2.0) and then the water (1.0–1.2) are added (11), where they are mixed by high-speed propeller mixers with the asynchronous electric motor Vemat VTB80B–8. In the process of mixing there is contraction of the total volume of the WAM with heat release. After mixing using the density analyzer «Anton Paar DMA 4500», if the strength of the WAM is determined with deviations from the given, adjust it, re-mix and carry out sampling (3.0–3.2).

After mixing, the WAM enters the pressure vessels (10), after which it is filtered on the sand filters (12) and treated with AC in adsorbers (13). AC used from pyrolyzed wood wastes, obtained by the method of alkaline activation of *KOH* (Kuzmin O., Tamarkina J., Shendrik T., Zubkova V. et al, 2017) [13]. In order to get rid of small particles of coal, WAM (vodka) is filtered again and sampled (4.0–4.2).

In Figure 2–11 shows one-dimensional 1H NMR spectra of hydroxyl protons of the studied substances, taking into account the chemical shift.

The studies used EAR with a volume fraction of ethanol – 96.37% and water – 3.63%, so the 1H NMR spectra of *OH*-proton WAMs are represented by two separate signals of ethanol *EtOH* and *H₂O* water (Figure 2). The component *EtOH* is a symmetric singlet with an expanded base and an apex of the correct form with a chemical shift $\delta_{EtOH}=5.65$ ppm. The *H₂O* component is a singlet from $\delta_{H_2O}=4.85$ ppm. The difference in chemical shifts between *EtOH* and *H₂O* is $\Delta\delta=0.80$ ppm ($\Delta f=320$ Hz).

The 1H NMR spectrum of softened water due to *Na*-cationization (Figure 3) is presented as a singlet with an expanded base and an irregular vertex and $\delta_{H_2O}=4.65$ ppm. The 1H NMR spectrum of water softened by *Na*-cationization after ECA: anolyte is a singlet from $\delta_{H_2O}=(4.23; 4.22)$ ppm (Figure 4); catholyte is a singlet from $\delta_{H_2O}=(4.56; 4.54)$ ppm (Figure 5). In relation to the water softened by *Na*-cationization, anolyte has displacement in the «strong field» at $\Delta\delta=0.425$ ppm ($\Delta f=170$ Hz), catholyte has a displacement of the hydroxyl proton in a «strong field» with an average value of $\Delta\delta=0.10$ ppm ($\Delta f=40$ Hz).

In the process of mixing the EAR class «Lux» (Figure 2) with water softened by *Na*-cationization (Figure 3), the WAM is formed (Figure 6), whose 1H NMR spectra are represented by one single singlet – *EtOH+H₂O* with an expanded base and the vertex of the correct form and $\delta_{EtOH+H_2O}=4.41$ ppm. The difference in chemical shifts between *EtOH* and *H₂O* is $\Delta\delta=0.0$ ppm.

When creating a WAM (Figure 7) on an EAR of the class «Lux» (Figure 2) with the anolyte (Figure 4), the proton spectra are represented by one single singlet – *EtOH+H₂O* with $\delta_{EtOH+H_2O}=(4.82; 4.81)$ ppm. The form of the *EtOH+H₂O* signal is a distorted gaussian, with an extended base and a certain asymmetry of the vertex, which has one principal peak and one additional low-peak peak.

When creating a WAM (Figure 8) in the catholyte (Figure 5), the proton spectra are characterized by a total singlet *EtOH+H₂O* with $\delta_{EtOH+H_2O}=(4.76; 4.75)$ ppm.

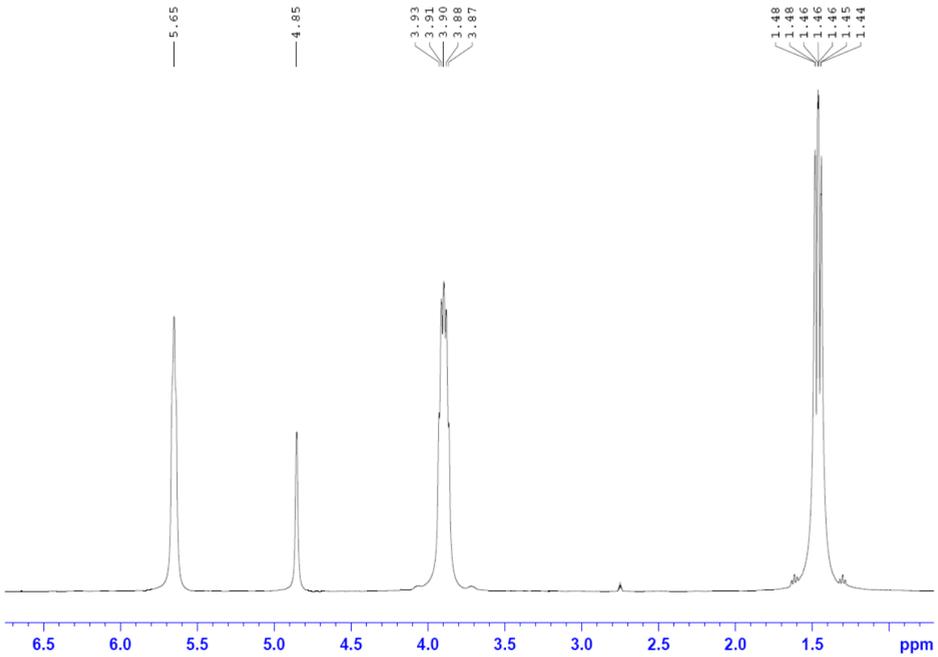


Figure 2. 1H NMR spectra of proton groups EAR: CH_3 ; CH_2 ; H_2O ; $EtOH$

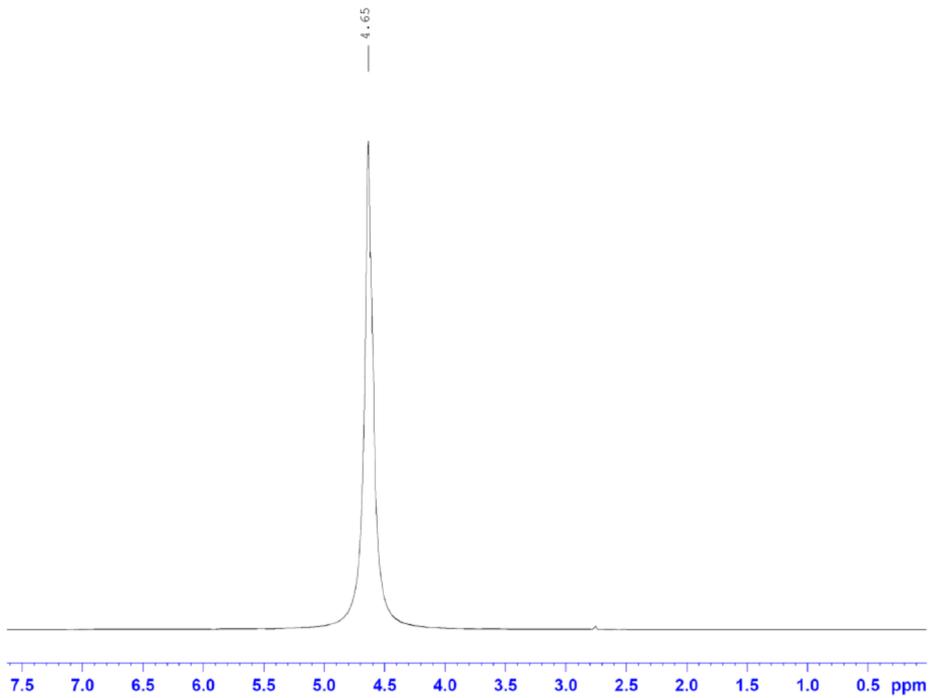


Figure 3. 1H NMR spectra of hydroxyl proton of Na -cationization softening of technological water

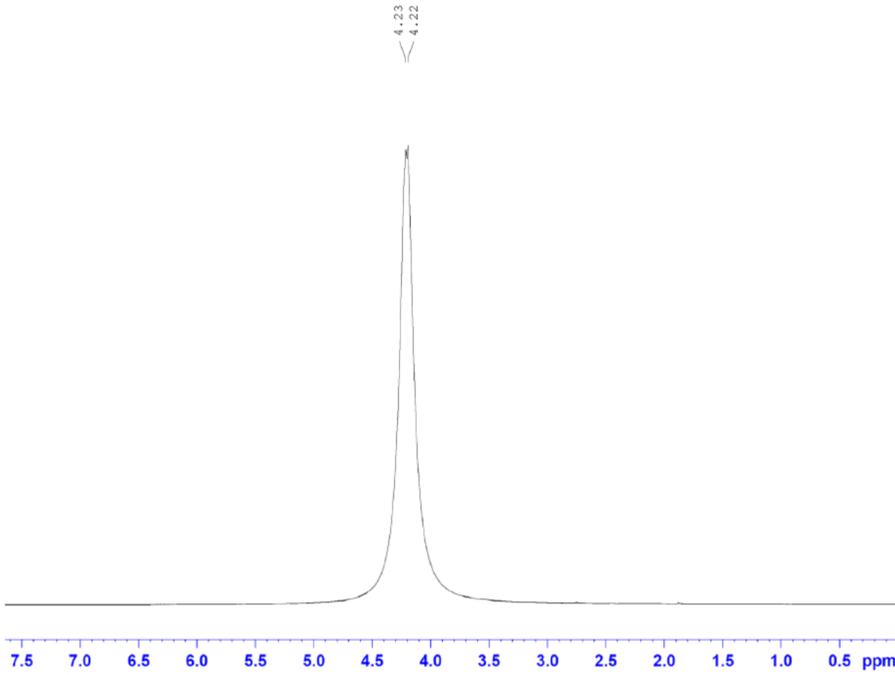


Figure 4. ^1H NMR spectra of hydroxyl proton of water softened by *Na*-cationization after ECA (anolyte)

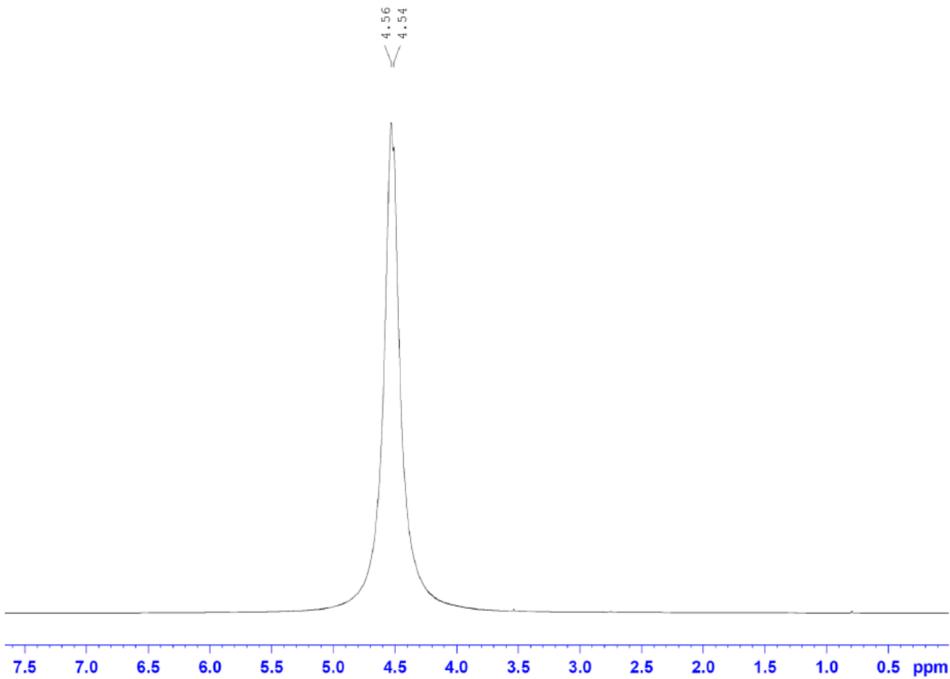


Figure 5. ^1H NMR spectra of hydroxyl proton of water softened by *Na*-cationization after ECA (catholyte)

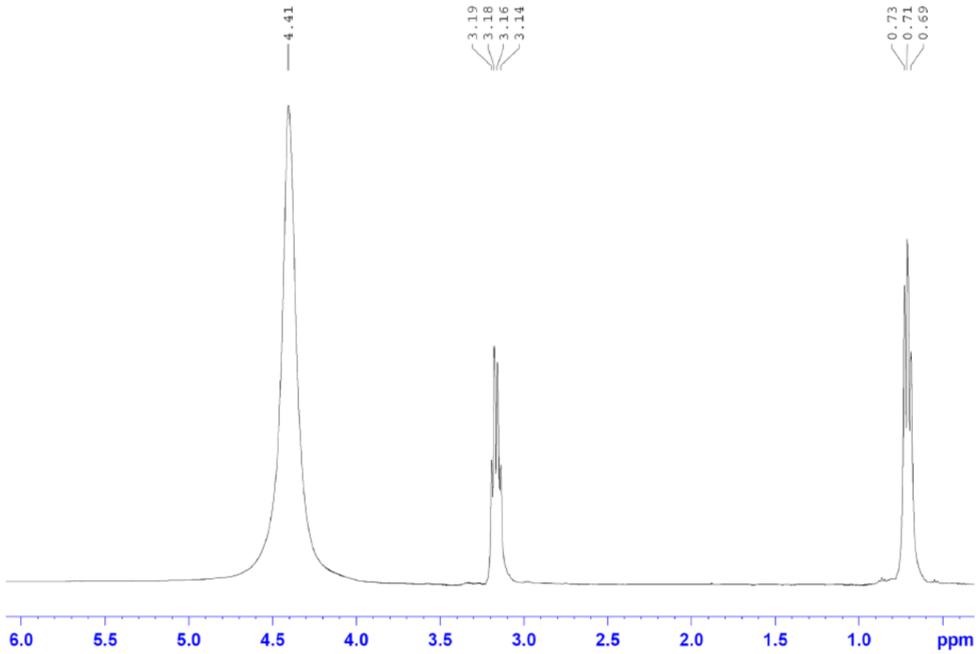


Figure 6. 1H NMR proton spectra of WAM for EAR and softening of water

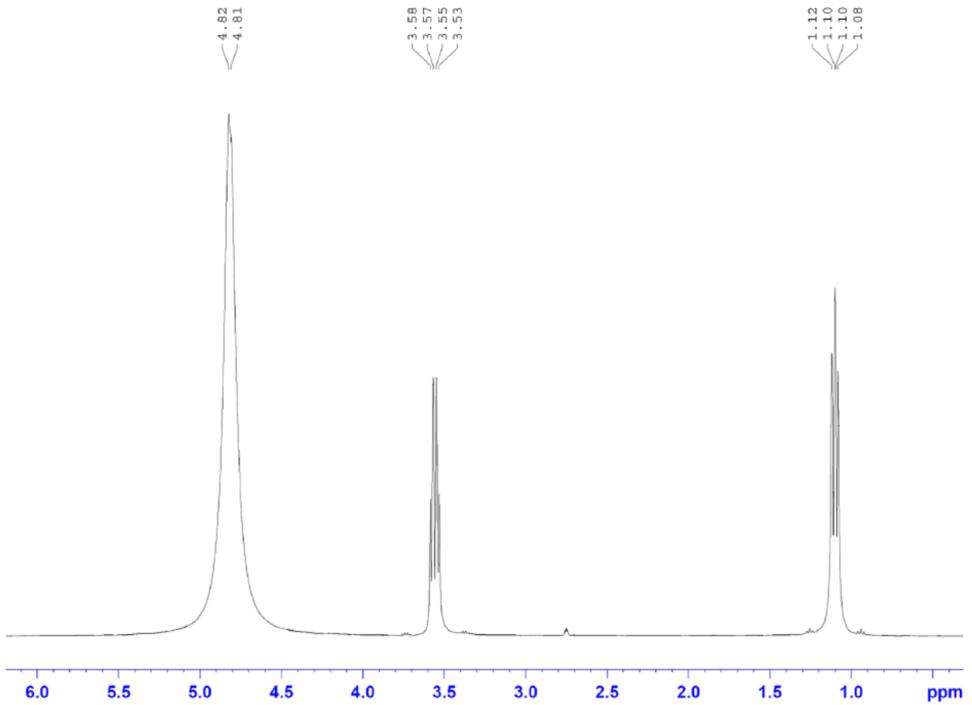


Figure 7. 1H NMR proton spectra of WAM for EAR and softening of water after ECA (anolyte)

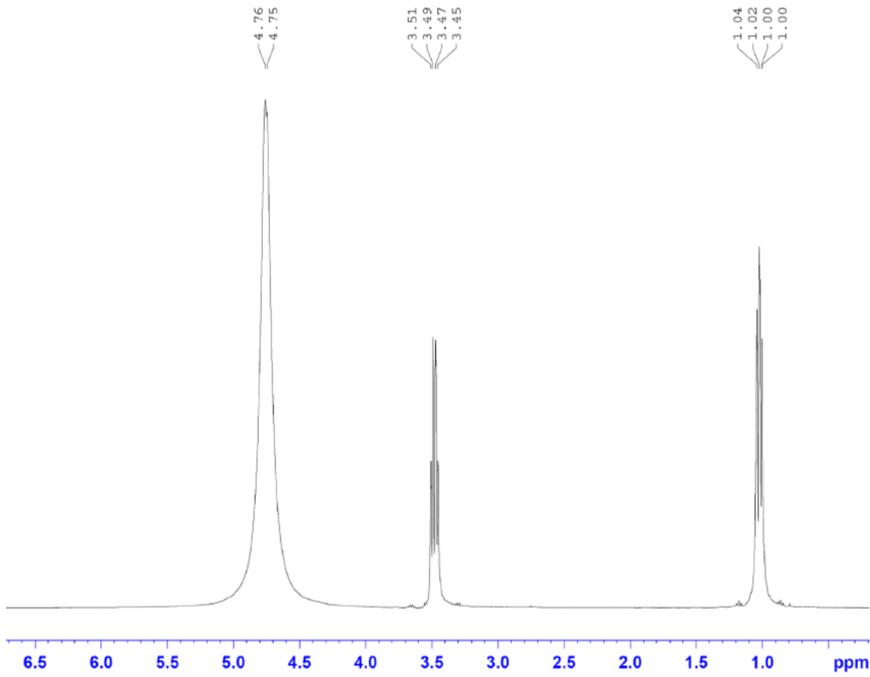


Figure 8. 1H NMR proton spectra of WAM for EAR and softening of water after ECA (catholyte)

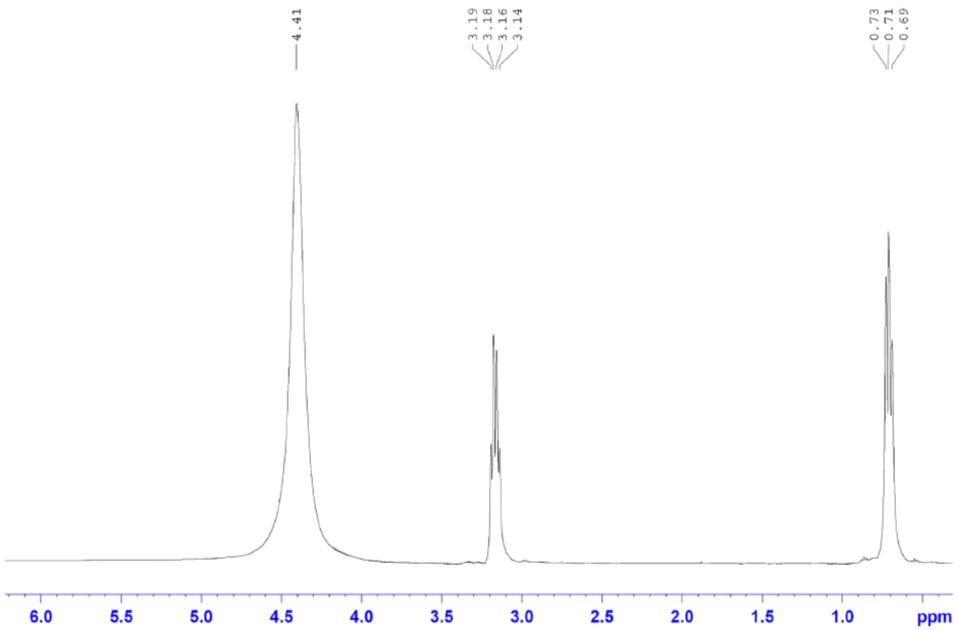


Figure 9. 1H NMR proton spectra of WAM for EAR and softening of water after treatment with AC

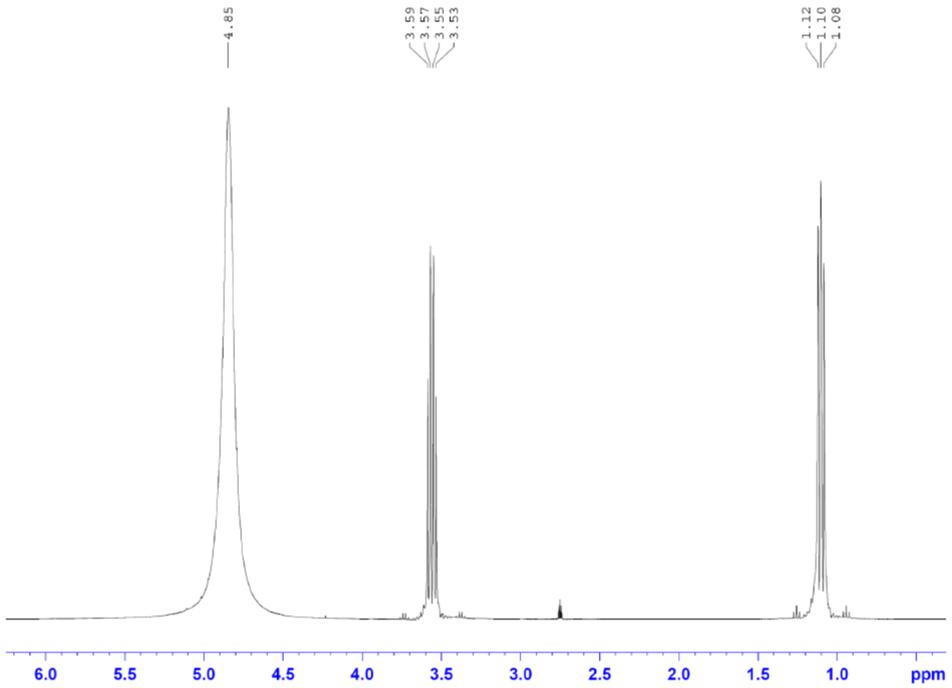


Figure 10. 1H NMR proton spectra of WAM for EAR and analyte after treatment with AC

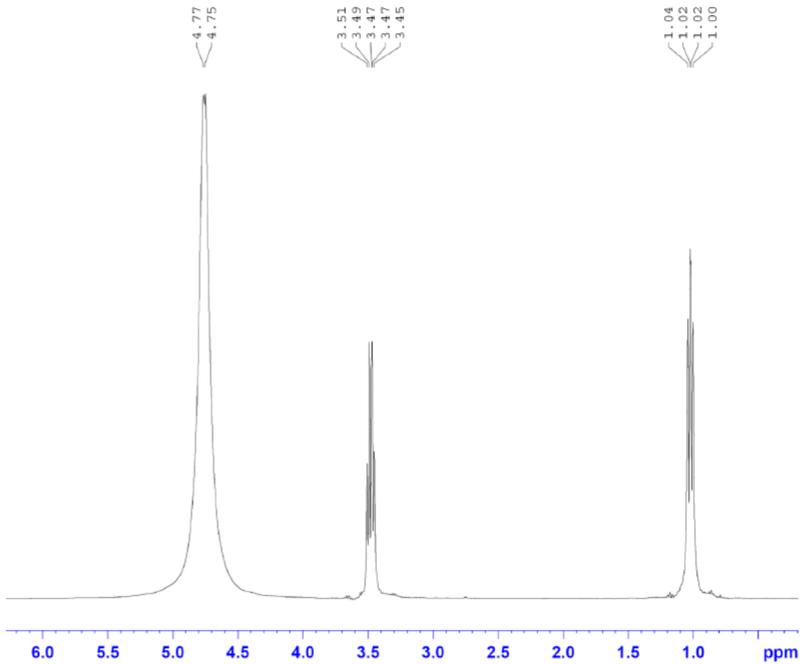


Figure 11. 1H NMR proton spectra of WAM for EAR and catholyte after treatment with AC

It can be concluded that in the process of creating a WAM in water softened by *Na*-cationization with a pH level of 7.18 and an EAR of the «Lux» class, the obtained WAM has a pH level of 7.84, which characterizes the reduced concentration of ions of hydroxonium H_3O^+ in relation to OH^- hydroxyl ions. At constant concentration of alcohol in WAM (volume fraction of ethanol – 39.94%) and thermostating system at 1H studies ($T=296.5$ K) there is an instantaneous structuring of the system, the proton exchange is so fast that there is only one general signal of hydroxyl protons ethanol (*EtOH*) and water (H_2O), although with a certain asymmetry.

At the expense of the ECA when WAM is created in anolyte with a pH level of 2.43 and an EAR of the Lux class, the WAM obtained has a pH level of 3.10, which characterizes the acidic medium. WAM on a catholyte with a pH level of 11.08 has a strongly alkaline medium (pH=11.75).

These polar ratios of H_3O^+ to OH^- concentrations for anolyte and catholyte lead to a restructuring of the structure in the alcohol/water system, therefore, the proton exchange is accelerated and there is also only one general signal of mobile protons *EtOH+H₂O* asymmetric.

In this case, the ECA water intensifies the oxidation-reduction reactions when creating WAM, due to the increase of MC aldehydes and esters. Aldehydes are acetaldehyde, which is formed by oxidation of ethanol with oxygen. Esters are represented by ethyl acetate, by oxidation of part of acetaldehyde to acetic acid by oxygen and by the interaction of acetic acid with ethanol to form ethyl acetate.

After processing AC WAM on water softened by *Na*-cationization (Figure 9), the resulting vodka is characterized by a single total signal of hydroxyl protons, *EtOH+H₂O*, represented as a symmetric singlet with a chemical shift $\delta_{EtOH+H_2O}=4.41$ ppm. In the process of processing AC WAM in the anolyte (Figure 10), which is characterized by a total peak – *EtOH+H₂O*, represented as a symmetric singlet with $\delta_{EtOH+H_2O}=4.85$ ppm. In the process of AC WAM treatment on the catholyte (Figure 11), 1H NMR spectra of *OH*-groups are characterized by a total peak – *EtOH+H₂O* with a chemical shift $\delta_{EtOH+H_2O}=(4.77; 4.75)$ ppm. The form of the total signal is a distorted Gaussian with an extended base and a vertex that has one main high-field peak and an additional low-field peak.

When producing vodka on the EAR class «Lux», technological water must meet the requirements of the organization standard and have the following characteristics: dry residue – no more than 350 mg/dm³; hydrogen index – from 6.0 to 8.0 units pH; total hardness – not more than 0.1 mmol/dm³; alkalinity total – from 1.0 to 2.0 mmol/dm³; ORP is not standardized.

Due to the conducted research, water after *Na*-cationization has an elevated pH=7.18 relative to drinking water (pH=6.91), as well as elevated ORP=«+»288.0 mV for drinking water (ORP=«+»269.0 mV). Anolyte and catholyte samples are characterized by a change in the pH and ORP levels relative to the initial values: with the anode ECA, the hydrogen index becomes more acidic (pH=2.43); ORP – increased to positive (oxidative) values (ORP=«+»451 mV); at catholyte – the pH=11.08 acquires a more alkaline reaction; ORP=«+»44.0 mV.

In Figure 12 is represented the dependence of hydrogen indicator of the ORP for water, WAM, WAM after AC without processing and after ECA. In this case, three areas of samples can be observed: a_0 – without treatment; a_1 – samples in the catholyte; a_2 – samples on anolyte.

It can be argued that in the process of creating vodka there is relaxation of the WAM in terms of the level of pH and ORP, which in this case are «markers» of stabilization. The values of pH and ORP tend to shift to a stationary area of values that will not undergo critical

changes throughout the «life cycle» of the finished product, while maintaining optimal storage conditions. Although in real storage conditions, there is a slight increase in pH and decrease in ORP, which are already dependent on the interaction of the product with the glass in which the product is stored.

A slight change in the value of total alkalinity in *Na*-cationization (4.12 mmol/dm³) relative to drinking water (5.38 mmol/dm³) is a major disadvantage of this process. Therefore, in the process of ECA on anolyte there is a decrease in alkalinity to 0 mmol/dm³, and after ECA (catholyte) – an increase in alkalinity to 10.85 mmol/dm³. Therefore with the help of anolyte it is possible to further acidify the water to reduce the total alkalinity of water.

It can be concluded that the electrochemical reactions occurring in the anode and cathode chambers of the diaphragm electrolyzer lead to a change in the entire system of intermolecular interactions, with different charge states of molecules in the anolyte and catholyte leading to differences in the electron distribution, which affects the values of chemical shifts hydroxyl protons.

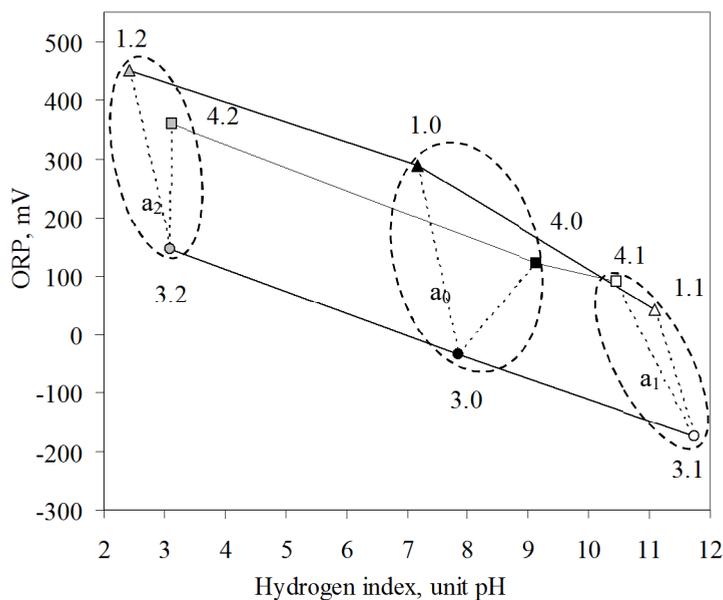


Figure 12. Dependence of hydrogen index of the ORP for water, WAM, WAM after AC without processing and after ECA:

- a_0 – area of samples without processing – control (1.0 – water softened by *Na*-cationization, 3.0 – WAM on softened water, 4.0 – WAM on water softened after treatment AC);
- a_1 – area of samples after ECA (catholyte);
- a_2 – area of samples after ECA (anolyte)

The vodka from the EAR class «Lux» should correspond to the following indicators: MC aldehydes in terms of acetic aldehyde – no more than 4 mg/dm³; MC of fusel oil, calculated on the mixture of propyl, isobutyl and isoamyl alcohols – not more than 4 mg/dm³; MC esters in terms of acetic-ethyl ester – no more than 5 mg/dm³; volume fraction of methyl alcohol – not more than 0.01%; alkalinity – from 0.5 to 3.5 cm³.

As water is softened by *Na*-cationization and water softened after ECA – do not meet all

the requirements of the normative documentation, the vodka created on this water, conditionally meets the requirements of regulatory documentation, except for alkalinity and MC aldehydes – for vodka on anolyte. In this case there are significant changes in the level of pH and ORP in the WAM in the catholyte after processing with AC. At the primary pH=11.75 for the WAM, after the AC WAM processing at the catholyte, the pH level 10.45, with the primary ORP=«-»174 mV, after the AC WAM treatment at the ORP cathode «+» 92 mV.

It can be argued that at the stage of treatment of AC WAM in water softened by *Na*-cationization and ECA there is a relaxation of the WAM, which results in the return of the values of pH and ORP to the new equilibrium values while simultaneously stabilizing the hydroxyl groups of protons of ethanol and water, due to generalizing of signals.

Conclusions

On the basis of the study, a fundamental difference was found between the behavior of WAM and vodka prepared on water softened by *Na*-cationization and water treated by the ECA. Systems with unstable equilibrium were not detected. The system of alcohol/water with a constant equilibrium and a high degree of generalization of protons, as well as its characteristic exchange rates, is characteristic of the WAM from the EAR of the Luxury class and the water softened by *Na*-cationization as well as the water that passed the ECA in the diaphragm electrolyzer.

Thus, experimental evidence is obtained of the dependence of the rate or time and nature of the establishment of the thermodynamic equilibrium due to the relaxation of the water-alcohol systems with the simultaneous stabilization of the hydroxyl group of water and ethanol protons.

The purpose of the work is to study the mechanism of establishing the equilibrium state of vodkas during the creation of water-alcohol mixtures in the process of electrochemical activation of technological water at the stage of *Na*-cationization softening. Experimentally proved the dependence of the time and nature of the establishment of the thermodynamic equilibrium – the relaxation of the water-alcohol systems during the stabilization of the hydroxyl group of protons of ethanol and water.

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