^{1}H NMR-spectroscopy of water-alcohol systems in the process of electrochemical activation of drinking water

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Abstract

The aim of the work is to study the process of establishing the equilibrium state in alcohol water systems at the main stages of creating vodka with electrochemical activation of drinking water. The formation of alcohol-water (drinking) system occurs during the weakening of hydrogen bonds in the presence of water associates and ethanol that have a chemical shift of hydroxyl protons of water δ_{H_2O} 4,36 ppm and of ethanol – δ_{EtOH} 4,96 ppm and the difference in chemical shifts between EtOH and H_2O, which is $\Delta\delta$ 0,60 ppm. (Δf 240 Hz), that do not undergo significant changes after the treatment of alcohol water mixture with activated carbon. Conditions for the formation of stable complexes in the system of alcohol-water (drinking) have not been revealed, the absence of formation of ethanol hydrates characterizes a system with unstable equilibrium. Prepared with electrochemical activation drinking water leads to the immediate formation of hydrates of $EtOH \cdot 5H_2O$ type in the alcohol-water system: in the anode cell – an anolyte with ethanol hydrates $EtOH \cdot 4{,}81H_2O$; in a cathode cell – a catholyte with ethanol hydrides $EtOH \cdot 4{,}69H_2O$. The strongest hydrogen bond of OH-groups in the alcohol-water system is observed in water prepared by electrochemical activation that is characterized by a constant equilibrium.

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DOI: 10.24263/RES-2018-3

Introduction

Nowadays, ^{1}H NMR spectroscopy is the most popular among spectroscopic methods due to its simplicity and completeness of information that facilitates chemical researches, especially in the food industry.

The first ^{1}H NMR water and ethanol spectra were obtained more than 60 years ago but even today there are a lot of researches [1-9] of these formally simple systems that demonstrate complex and diverse behavior. In particular, ^{1}H NMR spectroscopy is a highly sensitive method for studying the equilibrium in solutions. Considering that the establishment of the equilibrium state of the alcohol solution in water is being one of the main processes that provide stable and predicted characteristics of vodka products, we used this method for the defining what affect the preliminary water preparation actions may have.

The hydroxyl proton of ethanol can exchange with free ions H^+ in the matrix, that are generated due to dissociation of water, or with the trace amount of acid [7,10-11]. The speed of exchange is proportional to the number of free ions H^+ [11]. For this reason the actual location of the center of ^1H NMR signal, that is averaged for moving forms of protons in this case, depends on the difference in the chemical shifts of protons in two environments – water and alcohol [9].

That is why the creation of an equilibrium state of the solution with help of ^1HNMR may become an efficient mean for controlling the efficiency in usage of technical solutions in the process of vodka production.

The aim of the research – applying the method of ^1H NMR spectroscopy to study the process of equilibrium establishment in water-alcohol mixtures at the main stages of vodka production with electrochemical activation of drinking water.

Materials and methods

The following equipment and materials have been used during the research:

– Fourier NMR spectrometer Bruker Avance II – 400 MHz (Fig.1);

– dispenser (15); ampoules 5 mm with specimens (16); capillaries with deuteroacetone;

– external standard and signal for the system LOCK‘a (17); ampoules with capillary (18) (Fig. 1, b);

– drinking water; drinking water – catholyte; drinking water – anolyte;

– rectified ethyl alcohol;

– drinking water based water-alcohol mixture; catholyte based water-alcohol mixture; anolyte based water-alcohol mixture;

– water-alcohol mixture based on drinking water after treatment with activated carbon (vodka); water-alcohol mixture based on catholyte after treatment with activated carbon; water-alcohol mixture based on anolyte after treatment with activated carbon.

Fig.1,a. shows the principal scheme designed for this research experimental stand with the diaphragm electrochemical reactor.

The drinking water (1.0) goes through the open tap into two lines (9) – line for water preparation by electrochemical activation and the line for preparation of water-alcohol mixture. On the electrochemical activation preparation line the water reaches the electrochemical reactor (6), the anodic and cathodic space of which is separated with a porous diaphragm. The electrons are transferred into water near the cathode, and removed from the water – near the anode that leads to the formation of a catholyte (1.1) and anolyte (1.2).

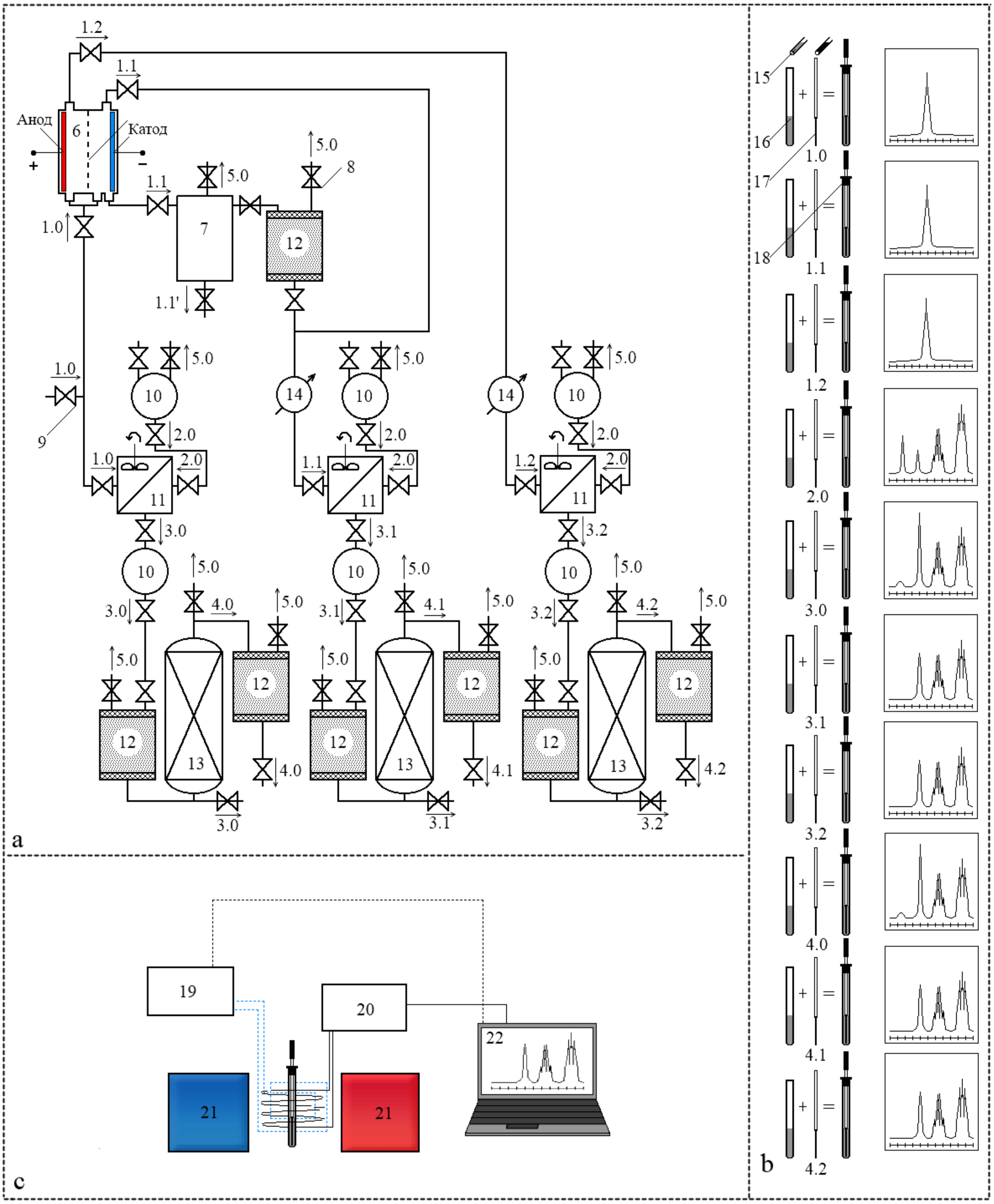

Figure 1. Scheme of conducting the research:
a – the principal scheme of the experimental stand;
b – scheme of sample preparation for ^{1}H NMR research;
c – block scheme of a ^{1}H NMR spectrometer;
1-5 –flows (samples); 6-14 – technological equipment;
15-22 – laboratory equipment

As the result of electrochemical reactions low-solubility calcium and magnesium carbonates, as well as heavy metal and ferrum hydroxides are created in cathode cell. There is an additional line with receiving container (7) for drainage and filtration of the catholyte concentrate (1.1'), sand filter (12) and air taps (8) –for removing the air (5.0).

The electrochemical activation process is accompanied by an increase of water temperature $t_{1\text{-}2}$=32 ºC, that is unacceptable for the production of water alcohol mixture. Consequently, the water flows (1.1, 1.2) are additionally cooled down in the chiller (14).

On the line of the water-alcohol mixture preparation rectified ethyl alcohol (2.0), and afterwards – the water (1.0-1.2), is added to the sorting tanks (11) from gravity tanks (10), where they are mixed with the help of high-speed propeller mixers. In the course of mixing the total volume of water-alcohol mixture undergoes pressure (contraction) with the following heat release. After mixing the strength of water-alcohol mixtures is determined with the help of density analyzer «Anton Paar DMA 4500». In case it is different from the givenparameters, it is adjusted, than mixed again with the following samples collection (3.0-3.2).

Having been mixed the water-alcohol mixture goes to the gravity tanks (10), than it is filtered on the sand filters (12) and treated with the activated carbon in absorbers (13). In order to remove tiny parts of carbonate from the vodka it is filtered again with the following samples collection.

Methodology of ^{1}H NMR research: the study sample is placed with the help of dosimeter (15) into ampoule (16). Necessary for LOCK'a system work – deuterium stabilization of the NMR spectrometer deuteroacetone, an external standard which is separated from study material, is placed into ampoule (16) in the capillary of a specific shape (17); according to the methodology spectrum recording the spectrum of sample in deuteroacetone is recorded. The obtained primary materials, free induction decays, are processed with Bruker TopSpin v2.6 program.

Results and discussions

Fig. 2 shows one-dimensional ^{1}H NMR spectra of CH_3-, CH_2-, OH-groups of protons of study substances, taking into account chemical shift. Rectified ethyl alcohol with a volume fraction of ethanol –96,37% and water ≈ 3,63% have been used in the research. ^{1}H NMR spectra of OH-protons of alcohol are represented by two separate signals of ethanol EtOH and water H_2O (Fig. 2, a). The EtOH component is a symmetric singlet with an expanded base and a top of a regular form with a chemical shift δ_{EtOH} 5,65 ppm. The component H_2O is a singlet from δ_{H2O} 4,85 ppm. The difference in chemical shifts between EtOH and $H_2O$is $\Delta\delta$ 0,80 ppm. (Δf 320 Hz).

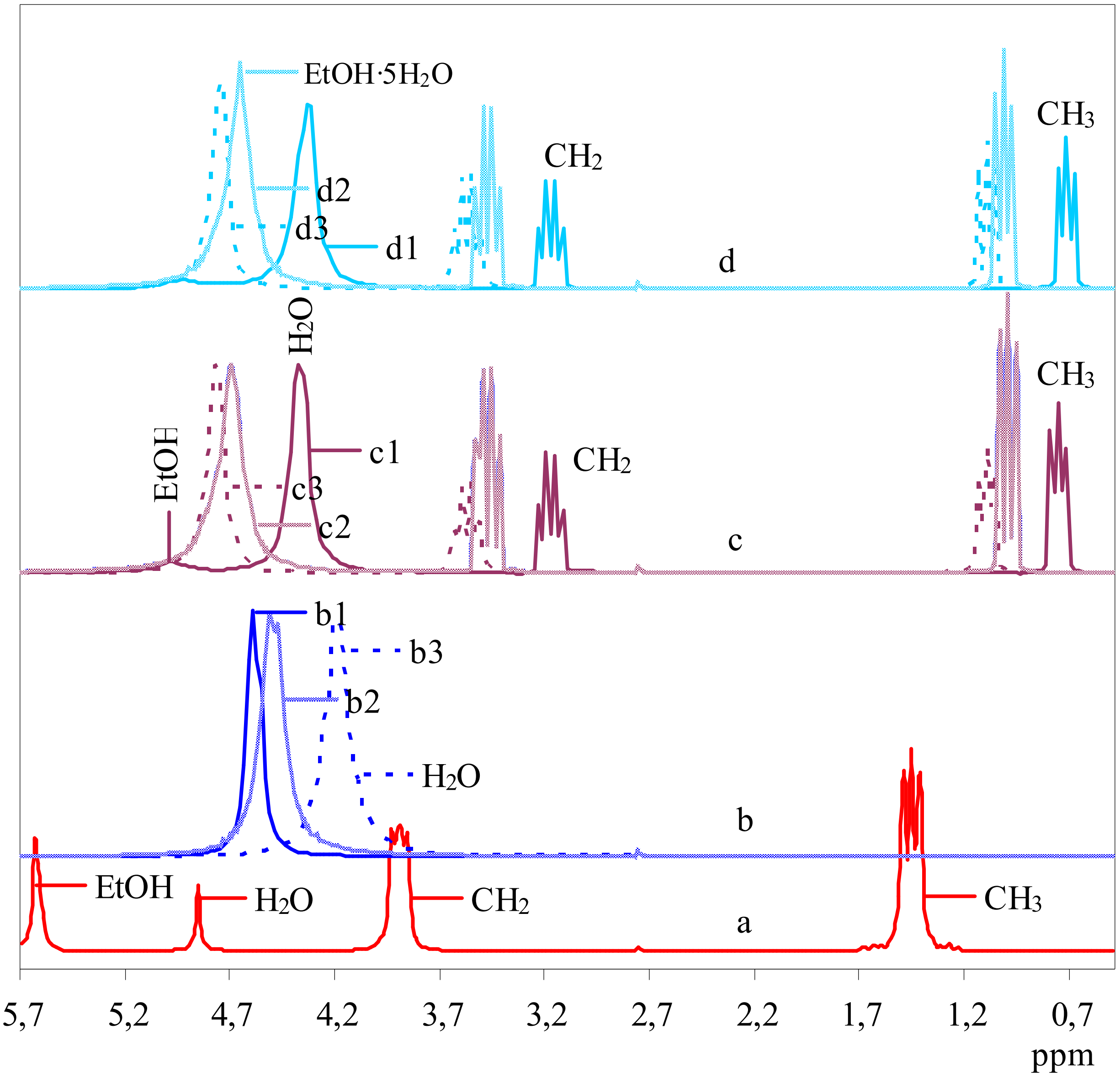

Figure 2. ^{1}H NMR spectra of molecular complexes of resonance CH_3-, CH_2-, OH-groups of protons for water-alcohol mixtures obtained through electrochemical activation of drinking water:

a – rectified ethyl alcohol;
b – water;
c – water-alcohol mixture;
d –water-alcohol mixture after treatment with activated carbon; in the process:
    1 – without processing with electrochemical activation;
    2 – cathode electrochemical activation;
    3 – anode electrochemical activation

The ^{1}H NMR spectrum of drinking water (Fig. 2,b1) has the single signal in the form of a singlet with an expanded base and an irregular vertice at δ_{H2O} 4,60ppm. ^{1}HNMR spectra of drinking water after electrochemical activation: catholyte – singlet from δ_{H2O} (4,50; 4,48) ppm. (Fig. 2, b2); anolyte – singlet with δ_{H2O} (4,19; 4,18)ppm (Fig. 2,b3). In relation to drinking water the catholyte has a displacement of the hydroxyl proton into a «strong field» with an average value of $\Delta\delta$ 0.110 ppm, the anolyte has a displacement into the «strong field» at $\Delta\delta$ 0,415 ppm.

In the process mixing alcohol (Fig. 2,a) with drinking water (Fig. 2,b1), a water-alcohol mixture is created (Fig. 2,c1), ^{1}H NMR spectra of which are represented by two signals of hydroxyl protons EtOH and H_2O. The EtOH component is depicted in the form of a convexity, which is situated in the «weaker field» with δ_{EtOH} 4,96 ppm., the H_2O component is represented as a symmetric singlet with δ_{H2O} 4,36 ppm. The difference in chemical displacements between EtOHi$H_2O$is$\Delta\delta$ 0,60 ppm (Δf 240 Hz).

The water-alcohol mixture based on drinking water with a pH 6.91 and rectified ethyl alcohol has a pH of 8.32 that corresponds to a lower concentration of ions of hydroxonium H_3O^+in relation to OH^- hydroxyl ions. At constant concentration of alcohol in a water-alcohol mixture (volume fraction of ethanol – 39,94%) and thermostatting system at ^{1}H researches (t = 23,5 ºC), the exchange speed of EtOH is at the intermediate level, with the possibility of separate observation of signals.

While preparing water-alcohol mixture (Fig.2, c2) based on alcohol (Fig. 2, a) with catholyte (Fig. 2, b2) proton spectra are represented by a single total singlet – EtOH +$H_2O$with an extended base and a vertex of the regular form and $\delta_{EtOH+H2O}$ 4,69 ppm. During preparation of the water-alcohol mixture (Fig. 2, c3) based on the anolyte (Fig. 2, b3) the proton spectra are characterized by a total singlet EtOH+$H_2O$with$\delta_{EtOH+H2O}$ (4,82; 4,81; 4,80) ppm. EtOH+H_2Osignal is represented in the form of a distorted Gaussian with an expanded base and a certain asymmetry of the vertex that has one high-polar peak and two additional low-polar peaks. Thus, drinking water prepared with electrochemical activation leads to the instant formation of hydrates of $EtOH\cdot5H_2O$type in the alcohol-water system: in the cathode cell – catholyte with ethanol hydrates $EtOH\cdot4{,}69H_2O$, in the anode cell – anolyte with ethanol hydrates $EtOH\cdot4{,}81H_2O$.

The water-alcohol mixture based on catholyte with pH 9,84 has high alkaline environment (pH 11,60). Due to electrochemical activation while creating a water-alcohol mixture based on anolyte with pH 2,40 and alcohol, the received water-alcohol mixture has pH 3,01, which is a characteristic of an acidic environment. These polar correlations of concentrations H_3O^+до$OH^-$for catholyte and anolyte lead to restructurization in the alcohol-water system, therefore, the proton exchange is accelerated and there is only one common signal of moving protons EtOH+$H_2O$of asymmetric form observed. In this case the electrochemical activation of water intensifies redox reactions during the preparation of water-alcohol mixtures due to the increase of mass concentration of aldehydes and esters. Aldehydes are represented by acetaldehyde, which is created by oxidation of ethanol with oxygen. Esters are represented by ethylacetate due to oxidation of a part of acetaldehyde to acetic acid and interreacting of acetic acid with ethanol.

After treatment of water-alcohol mixture based on drinking water (Fig. 2, d1), with activated carbon [15] obtained vodka is characterized by two signals of hydroxyl protons EtOHтаH_2O. EtOH component is represented in the form of convexity that is placed in the «weaker field» with δ_{EtOH}=4,93 ppm. The component $H_2O$is represented as a symmetric singlet with δ_{H2O}=4,33 ppm. The difference in chemical shifts between EtOHiH_2Omakes$\Delta\delta$=0,60 ppm. (Δf 240 Hz).

In the process of treatment of water-alcohol mixture based on catholyte (Fig.2, d2) ^{1}H NMR spectra of OH-group are characterized with one total peak – EtOH+H_2O represented in the form symmetric singlet with a chemical shift $\delta_{EtOH+H2O}$ 4,67 ppm. In the process of treatment of water-alcohol mixture with activated carbonate based on the anolyte (Fig. 2, d3), the component is characterized by one total peak –EtOH+H_2O, represented in the form of a symmetric singlet with $\delta_{EtOH+H2O}$ (4,77; 4,76) ppm. The form of the total signal is a distorted Gaussian with an extended base and a vertex that has one main high-polar and an additional low-polar peaks. Thus, the electrochemical activation of drinking water leads to the formation of hydrates in vodka: in the cathode cell – catholyte with ethanol hydrates $EtOH\cdot 4,67H_2O$, in the anode cell – anolyte with ethanol hydrates $EtOH\cdot 4,765H_2O$.

Conclusion

There has been established the fundamental difference between the behavior of water-alcohol mixtures and vodka that are prepared on drinking water and water treated with electrochemical activation. The system with unstable equilibrium is a characteristic of water-alcohol mixture made of alcohol and drinking water.

The alcohol-water system with stable equilibrium and a high degree of protons generalization, as well as specific exchange speed, is a peculiarity of water-alcohol mixture made of alcohol and drinking water that has undergone electrochemical activation in a diaphragm electrolyzer. Thus, the study has confirmed the possibility and practicability of using ^{1}H NMR spectroscopy for the current control of the technological process of production water-alcohol mixtures with water that has undergone electrochemical activation. It is shown that this method is an effective way for establishing the completeness of balance of the alcohol-water system in the presence of additional solution components typical for technological water-alcohol mixtures. There's been demonstrated an efficiency of using electrochemical activation when dealing with water preparation problems during the production of alcohol products.

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