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^{1}H NMR ANALYSIS OF THE AQUEOUS-ALCOHOLIC MIXTURES, PREPARED WITH DRINKING WATER OF SOUTH-EASTERN REGION OF UKRAINE

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Annotation

The aim of the publication is to study the mechanisms of transformation of ethanol protons (ethyl rectified spirit - ERS) and water (drinking water) in the process of creating aqueous-alcoholic mixtures (AAM). The methods used in the work: ^{1}H nuclear magnetic resonance (NMR) spectroscopy of AAM; methods of evaluation of physicochemical and organoleptic characteristics of water, ethanol, AAM. In this paper, we have established fundamentally new features in the process of creating AAM that are directly dependent on the time of contact with drinking water and ERS. We have experimentally established the dependence rate of achievement of thermodynamic equilibrium and its character, as well as obtaining optimal organoleptic characteristics of AAM prepared for drinking water and ERS. The systems are allocated, depending on the type of thermodynamic equilibrium; with unsteady, transitional and steady equilibrium, with the similar regularities.

Introduction

NMR spectroscopy is widely used in physics research, industry, agriculture and other industries. NMR plays a particularly important role in food chemistry where it used in the study of both simple organic molecules and complex macromolecular structures and their complexes. A large number of articles discuss the use of NMR for research of food products; meat, fish, dairy products, vegetables, fruits, juices, pastry, cheese and alcohol products. This method provides comprehensive information with relatively simple obtaining spectra, thus greatly facilitating and accelerating chemical research.

NMR spectroscopy is most commonly applied to the nuclei of lightest isotope of hydrogen ^{1}H (protium, ^{1}H isotope) proton. The spectra measured using such nuclei are called proton magnetic resonance (PMR) spectra. PMR accounts for about 90% of all research on NMR spectra. Most of them operate in the Fourier transform mode.

The principle of NMR spectroscopy is based on the magnetic properties of certain atomic nuclei that resonate in the radio frequency range of the electromagnetic spectrum when placed in a strong magnetic field at a certain magnetic field. This allows for the identification of nuclei in different chemical environments. This property is explained by the existence of nuclei with non-zero spin (intrinsic mechanical torque), that is determined by the sum of the spins of its constituent protons and neutrons. The spin of the isotopes' nuclei with an even number of protons and an even number of neutrons is always equal to zero (zero moment). NMR is not observed in these nuclei.

The first «low resolution» ^{1}H NMR spectra of H_2O were obtained in 1946 (Bloch et al. 1946). The first «high resolution» ^{1}H NMR spectra of ethanol C_2H_5OH were developed in 1951 (Arnold et al. 1951). At first glance, it may seem that this are fairly simple organic molecules, as many scientists (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977; Nose et al, 2005; Khausser, Kaltbitzer, 1993; Richards , Hollerton, 2011; Roberts, 2002; Hu et al, 2010) continue to conduct NMR spectroscopy of ethanol due its relative simplicity.

At the same time NMR spectroscopy exhibits variations in characteristics of ethanol such as chemical shift, spin-spin interactions and the effect of chemical exchange.

An ethanol molecule consists of 6 protons located in 3 proton-containing groups: methyl (CH_3), methylene (CH_2) and hydroxyl (OH) with a relative intensity CH_3:CH_2:OH - 3:2:1. This characteristic is proportional to the number of protons in each group with non-equivalent chemical conditions: protons of the methyl group (CH_3)

are not equivalent to the methylene (CH_2) groups and the hydroxyl (OH) groups. This quality allows the NMR to split resonance signals into separate lines, thereby creating a multiplet spectrum structure.

Groups of protons have a different chemical shift. The chemical shift (δ) is a dimensionless parameter that determines the position of the signal in the spectrum (Ionin et al, 1983; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011). The unit of measurement of chemical shift is 1 ppm (parts per million) Alternatively the field strength or the resonance frequency relative to zero-signal of the reference connection.

The positions of spectrum's components relative to the beginning of the dimensionless scale are usually described with a set of specialized terms (Khausser, Kaltbitzer, 1993). When the signal is located in the left part – it is located in a «weak field» (deshielding effect is observed). When the signal is located in the right part – it's in a «strong field» (shielding effect is observed).

The proton's signals in the ^1H spectra lie in the interval δ=0...15 ppm for the vast majority of organic compounds.

^1H NMR spectra of liquid water (T_{sample}=300K; without solvent) is a wide singlet with chemical shift δ_{OH}=4,7 ppm, a water in a vapor phase - δ_{OH}=3,4 ppm. The presence of solvents changes the signal's position. For example, water in acetone-d_6 has property of δ_{OH}=2,84 ppm.

^1H NMR spectra of ethanol in liquid form (T_{sample}=300K; anhydrous; without solvent) (Roberts, 2002) have the following properties: methyl (CH_3) - δ_{CH3}=1,2 ppm; methylene (CH_2) - δ_{CH2}=3,7 ppm; hydroxyl (OH) - δ_{OH}=5,3 ppm. Vaporous ethanol has the following properties: δ_{CH3}=3,6 ppm; δ_{CH2}=6,0 ppm; δ_{OH}=2,8 ppm. Anhydrous ethanol dissolved in acetone-d_6 demonstrates the chemical shift of the proton groups: δ_{CH3}=1,12 ppm; δ_{CH2}=3,57 ppm; δ_{OH}=5,39 ppm.

Nuclear spin-spin interaction is observed between the three proton-containing groups of ethanol, all of which have different resonant frequencies (Roberts, 2002). "N" number of equivalent protons of one group (spin 1/2) split the signal of the nearest group into (n+1) lines with the intensity of a Pascal triangle (Silverstein et al, 1977; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011). The ability to observe spin-spin interactions may depends on the rate of the intermolecular proton exchange (if exist). It should be noted that NMR is a slow method in comparison with the other types of spectroscopy.

The presence of proton exchange in the water-ethanol is a well-known fact (Roberts, 2002). Hydroxyl proton (OH) of ethanol can exchange with free hydrogen ions, which are generated in water (self-dissociation), or in trace amounts of acids, alkalis or dissociated ethanol. The speed of exchange is proportional to the concentration of free ions. Exchange with acidic and basic impurities also impacts the position of average signal of water. The NMR spectra of AAM protons have a different appearance depending on the pH.

Slow exchange of OH (less than 1 second) is observed in conditions of a neutral environment (pH=7) (Ionin et al, 1983; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011; Roberts, 2002):

- Protons of the methyl group (CH_3) split the signal of the methylene group (CH_2) into four components (quartet - q) with an intensity ratio of 1:3:3:1;
- Protons of the methylene group (CH_2) split the signal of the methyl group (CH_3) into three components (triplet - t) with an intensity ratio of 1:2:1;
- A proton of the hydroxyl group (OH) splits each component of the methylene group quartet (CH_2) into two components in two quartets;
- Protons of the methylene group (CH_2) split the signal of the hydroxyl group (OH) into three components of the triplet (t) with an intensity ratio (1:2:1).

Quick exchange of OH takes place under acidic conditions (pH<7) (Ionin et al, 1983; Silverstein et al, 1977; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011; Roberts, 2002):

- The mutual influence of the methyl protons (CH_3) and methylene (CH_2) groups results in signal splitting similar to that of a neutral environment;
- There is a lack of observed spin-spin interactions between the methylene (CH_2) and a hydroxyl (OH) groups by chemical exchange. As a result, the triplet signal of hydroxyl group (OH) is converted into a single narrow or broad signal (singlet - s), situated in the area of weak field at 4...6 ppm. The signal of a methylene group (CH_2) is a quarter.

Adding a small quantity of water as a proton solvent into pure ethanol results in relatively slow proton exchange; allowing individual signals of OH protons and H_2O to be registered (Roberts, 2002). The exchange of OH can be accelerated by increasing the proportion of water. Individual resonance peaks of OH merge and take

the weighted average position. This position is determined by the chemical shifts of the OH groups and the relative concentration of ethanol and water.

Addition of an acid (Silverstein et al, 1977; Richards, Hollerton, 2011) into a AAM catalyzes the exchange of hydroxyl proton (OH) of alcohol with water. This leads to the disappearance of splitting and the conversion of the OH-group alcohol signal into a singlet.

A high speed exchange is required (less than 10^{-6} seconds) in order to «average-out» the electronic surroundings of a proton and nullify possibility of observing the spin-spin coupling with protons of adjacent CH_2-group. The speed of exchange can be reduced by applying a solution or solvent of soda ash (Na_2CO_3), aluminum oxide or zeolites (Silverstein et al, 1977).

The addition of alkali (Ionin et al, 1983) catalyzes proton exchange of the OH group. The exchange is so quick that it averages the effect of spin-spin interactions. Thus it leads to a single peak of ethanole OH group. The addition of alkali reduces the lifetime of the proton in each of these states, forcing the individual signals to merge into a single resonant peak, which occupies an intermediate position.

^{1}H-NMR spectra of compounds with labile hydrogen atoms, in particular OH-group of ethanol, strongly depend on external factors (Zhunke, 1974; Ionin et al, 1983): the nature of the solvent, substrate concentration, temperature and pH. Chemical shift of CH-protons is much more resistant to external factors in comparison with the OH-protons. The dependence of hydroxyl proton's resonance (OH) and its chemical shift on the nature of the solvent is explained by the formation of hydrogen bonds (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977; Roberts, 2002). The hydrogen bond reduces electron density around the hydroxyl proton. It weakens the screening and the displacement of the signal in a weak field. Polar solvents impact the effects of a hydrogen bond, because they can form it themselves. Intramolecular hydrogen bonds are less susceptible to the environment as compared to intermolecular bonds.

Hydroxyl proton appears in a spectrum of pure ethanol as a triplet with δ_{OH}=5,35 ppm. The chemical shift of the hydroxyl proton group, is shifted to the area δ_{OH}=2...4 ppm in a nonpolar solvent (deuterochloroform) with 5...20% concentration. The signal shifts to a stronger field to δ_{OH}=0,5 ppm when extrapolating to the infinite dilution or gas phase. The use of a different solvent shifts the signals of the hydroxyl proton (Silverstein et al, 1977).

Unlike OH-protons, the chemical shifts of C-H protons are weakly dependent on the concentration of substrate (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977). When developing a solution with an« inert» solvent, the hydroxyl proton signal is shifted as diluting the solution to the strong field results in the rupture of the intermolecular hydrogen bonds. The signal is shifted to the weak fields with the increasing of association degree.

Chemical shifts of C-H protons do not change substantially with changing temperature (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977). The temperature significantly affects the position of «movable» signals and protons (OH-group) that are prone to the formation of hydrogen bonds. Changes in temperature affect the formation of associates and thereby to change the chemical shift. Increasing the temperature usually results in the signal of the hydroxyl proton shifting into the strong field due to the rapturing of intermolecular hydrogen bonds and the equilibrium shifting towards the monomer.

In most cases, the proton exchange reaction is fast as per the NMR time scale, i.e. we can observe the averaged value of the chemical shift δ in a spectrum. The magnitude of the chemical shift in the simplest case is determined by the pH (Khausser, Kaltbitzer, 1993).

During changes in ^{1}H of NMR for different pH values in the field of rapid exchange, a signal is observed when chemical shift changes depending on the concentration of OH ions (Khausser, Kaltbitzer, 1993).

If the connections contain protons with heteroatoms in the solvent, providing a rapid exchange of mobile protons (in water), then all the moving protons will demonstrate a single common signal. Its position depends on the pH value. The lower the pH value, the weaker field of signal's location.

In accordance to the requirements of the normative documents of Ukraine (DSTU 3297:95) vodka – is an alcoholic drink with strength from 37,5% to 56% (DSTU 4256:2003), obtained by mixing ERS (DSTU 4221:2003) with water, prepared in accordance with SOU 15.9-37-237:2005, and treated with activated carbon BAU-A (GOST 6217-74), with addition of non-volatile ingredients or without them.

In the opinion Hu N. and others (2010) vodka is a fairly simple physicochemical system: a mixture of alcohol and water. However, each brand has its own distinctive taste and features on the molecular level.

Research conducted by Hu N. and others (2010) confirm that these differences are significant both during the stage of creating AAM, and in the final product - the commercial vodka. The major differences are associated with hydrogen bonds, in particular their strength, as confirmed by various research methods such as ^{1}H NMR spectroscopy, FTIR spectroscopy, Raman spectroscopy. ^{1}H NMR and FTIR Spectroscopy demonstrates the presence of water in the hydrate structure EtOH*(5,3±0,1)H_2O. Water can also be observed in AAM as well as in vodka. The authors (Hu N. and others, 2010) attribute this value with the perception of organoleptic characteristics of vodka.

Lots of attention in the work of Hu N. and others, 2010 has been given to ^{1}H NMR spectra of hydroxyl proton of OH water and alcohol. Water protons are represented as narrow singlets with δ_{OH}=5 ppm. The spectra of some samples are represented by the appearance of a second broadened OH signal of ethanol at a level of δ_{OH}=5,5 ppm. The presence in the samples of a single signal of OH ethanol (according Hu N. et al, 2010) is attributed to the weak hydrogen bonds of ethanol.

In their paper, the authors (Hu N. and others, 2010) introduced the concept of «structurability» - defined as the ability to maintain structure - a parameter that determines the ability of vodka (alcohol) to streamline its structure.

The effect of impurities (such as salts, acids, phenols) strengthening the hydrogen bonds in AAM as well as in the finished product such as sake, has been studied by Nose et al. (2005). Hu N. and et al have identified that the impurity of compounds has an effect on the molecular dynamics in ethanol's hydration process.

Therefore, the aim of this work is to study the transformation of ethanol protons (ERS) and water (drinking water) in the process of creating of AAM.

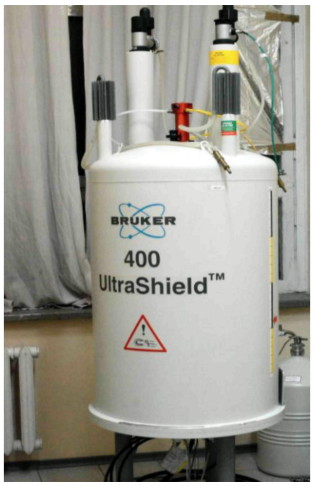
A pilot study of ethanol and water in the process of creating AAM has been conducted to achieve this goal.

Method

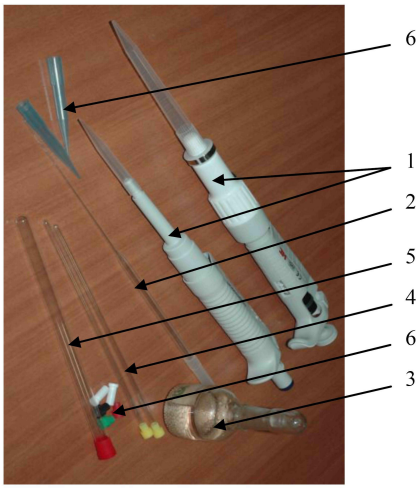
^{1}H NMR analysis of the AAM conducted in a laboratory of the L.M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry NAS Ukraine (Donetsk city). Physicochemical and organoleptic properties of alcohol, water and AAM carried out in laboratory's conditions at the following enterprises: LLC «Donetsk liquor-vodka factory «Lik», Donetsk regional test center of water, communal enterprise «Company «Voda Donbassa».

^{1}H NMR analysis of AAM was conducted with the usage of:

- FT-NMR Bruker Avance II spectrometer (400 MHz); measurement error of the chemical shifts for ^{1}H ± 0,0005 ppm; 5-mm broadband inverse probe with Z-gradient; thermostatic system (+25°C ... +100°C) - (fig. 1, a);



a)



b)

Figure 1. Appearance of devise and materials used for the ^{1}H NMR analysis: a - magnet block FT-NMR Bruker Avance II spectrometer (400 MHz); b - sample preparation materials for liquid sensor usage: 1 – dispensers; 2 - dimensional pipette; 3 - flask with acetone-d_6; 4 - 5 mm ampoules; 5 - 10 mm ampoule; 6 – caps

- Specially shaped capillary with acetone-d_6 $(CD_3)_2CO$ (atomic fraction of deuterium – 99,88%; moisture content – 0,018%; bp=+56,3 ºC, mp=-94 ºC; chemical shift of the residual proton ^1H δ = 2,75 ppm;
- High accuracy ampoules No.507-HP for high resolution NMR's spectroscopy (400 MHz) standard length - 178 mm; outside diameter - 4,97±0,006 mm; internal diameter - 4,20±0,012 mm; curvature ± 0 0006 mm;
- Volumetric pipette;
- Dispenser;
- ERS of class «Lux» as per DSTU 4221:2003, used at LLC «Donetsk liquor-vodka factory «Lik»;
- Drinking water as per GOST 2874-82, prepared by communal enterprise «Company «Voda Donbassa»;
- AAM model from ERS «Lux» and drinking water.

Drinking water characteristics (ionic composition) were determined using an ion chromatograph «Metrohm 792» with measurement error ± 0,1 mg/dm^3.

Characteristics of alcohol and AAM were determined using gas chromatography «Chromatec Crystal 5000.1» with measuring error of methanol ± 0,002 % vol., the rest of positions - ± 0,5 mg/dm^3.

Experimental studies of ^1H NMR were carried out in the following order:
- Preparation of AAM;
- Recording of the AAM ^1H NMR spectrum;
- Conclusion and interpretation of work results.

Work methodology:
- 0,3 ml of a AAM prepared with a volumetric pipette with a predetermined strength (40,0 ± 0,2)% vol. External standard separated from the testing substance which is required for LOCK's system operation (deuterium solvent (acetone-d_6) of NMR 's deuterium stabilization spectrometer) is added in a special form of a capillary into an ampoule. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other;
- ^1H NMR spectra records and data processing were performed according to the instruction of FT-NMR Bruker Avance II spectrometer (400 MHz).

Results

The following characteristics of south-eastern region of Ukraine drinking water (Donetsk city tap water) were determined: dry residue - 867 mg/dm^3; specific electrical conductivity - 1150 µS/cm; pH – 7,01; redox (ORP) - «+» 271 mV; total hardness – 7,93 mmol/dm^3; permanganate oxidation – 4,27 mg O_2/dm^3; mass concentration (MC) of sodium – 90,75 mg/dm^3; MC potassium – 4,87 mg/dm^3; MC ammonium - <2,0 mg/dm^3; MC calcium – 106,03 mg/dm^3; MC magnesium – 23,91 mg/dm^3; total alkalinity – 5,38 mmol/dm^3. Chromatogram of drinking water's ion composition is shown on fig. 2.

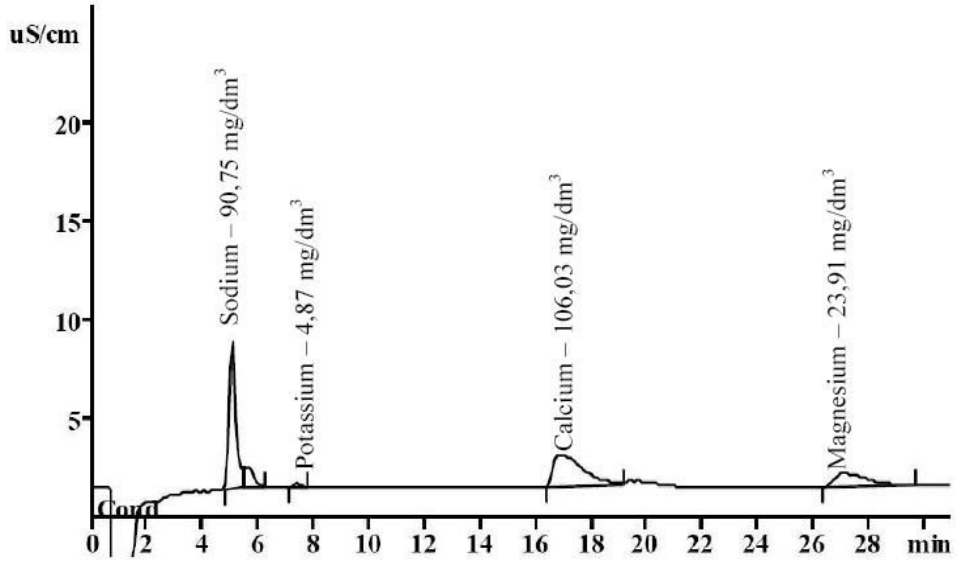
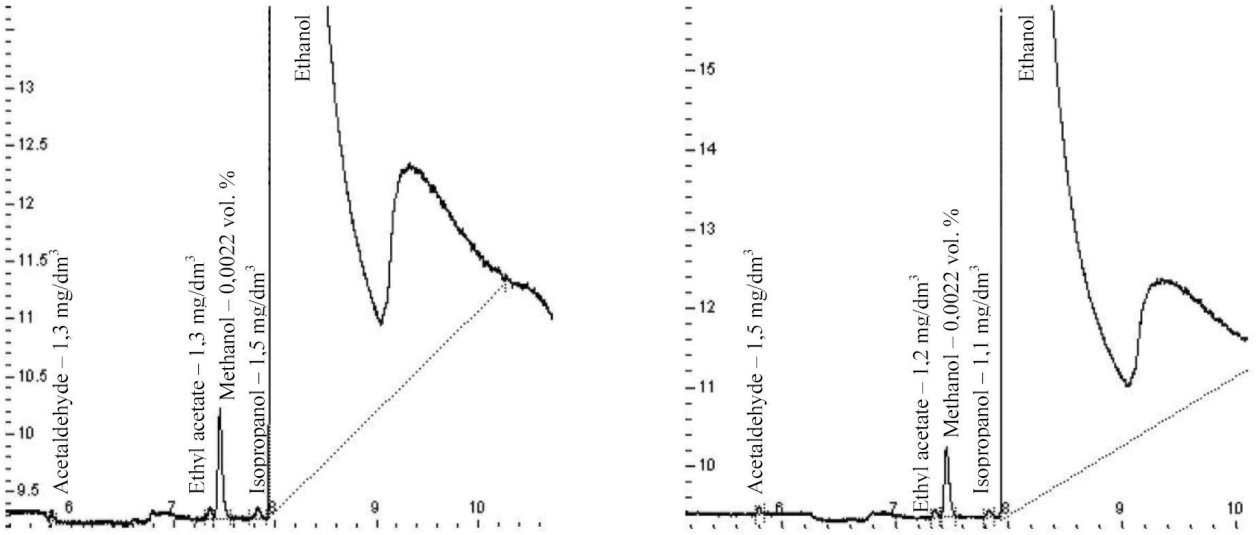


Figure 2. Ion chromatogram of drinking water

Characteristics of ERS «Lux» as follows: the content of aldehydes in anhydrous alcohol (a.a.), based on acetaldehyde – 1,3 mg/dm^3, the content of fusel oils in a.a.: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,5 mg/dm^3; the content of esters in a.a., based on of ethyl acetate – 1,3 mg/dm^3; the methanol content in the a.a. – 0,0022 vol. %. Gas chromatogram of ERS «Lux» is show in fig.3, a and fig. 3, b – AAM's gas chromatogram of ERS «Lux» and drinking water.



a) b)

Figure 3. Chromatograms: a) ERS «Lux»; b) AAM prepared by mixing alcohol «Lux» with drinking water

AAM sample of ERS «Lux» and drinking water has the following physicochemical and organoleptic characteristics: fortress – 39,94 % vol.; specific electrical conductivity - 183 μS/cm; ORP - «+» 37 mV; pH – 8,32; aldehyde content in a.a., based on acetaldehyde – 1,5 mg/dm^3; content of fusel oils in a.a.: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,1 mg/dm^3; the content of esters in a.a., based on acetic acid ethyl ester – 1,2 mg/dm^3; methanol content in a.a. – 0,0022 vol. %; alkalinity – 2,5 cm^3 of 0,1 M hydrochloric acid for titration of 100 cm^3 of AAM; oxidation test – 13,5 min; tasting score – 9,43 points (appearance - colorless liquid with residue; smell - sharp alcohol; flavor - heavy).

The figure 4 shows the proton group ^{1}H NMR spectras of freshly prepared AAM sample and a sample taken after the few days, with an interval of 2-3 days, indicating the chemical shift. The generalized characteristics of the spectra and the organoleptic characteristics of AAM are presented in table 1.

Discussion

We will analyze the spectra of hydroxyl group of water (H_2O), alcohol (EtOH) and AAM (H_2O+EtOH) prepared in water and ERS «Lux» at different periods of operation (after substances have been mixed).

Hydroxyl group of protons are represented by two separate peaks; (fig. 4, c) at the time of the initial formation of the AAM and at the time of the functioning of the system, (τ= 0 h). A component is represented as a single broad singlet rounded shape, located in a «low field» with the chemical shift δ_{EtOH} = 5,32 ppm. A component of water (H_2O) proton is represented as singlet with a chemical shift of δH2O = 4,71 ppm. The form of H_2O protons' signal is a distorted Gaussian curve, with a broadened base and a certain asymmetry. The difference between the OH-proton (EtOH) and the proton of water (H_2O) in the chemical shifts at the initial point of «living systems» is Δδ = 0,61 ppm.

The second spectrum (τ= 48 h) is also characterized by two separated peaks – of OH ethanol (EtOH) and water (H_2O). Component of EtOH is represented as a single singlet with a rounded chemical shift δ_{EtOH}= 5,37 ppm. Component of H_2O protons represented as a singlet. This singlet is also located in a weak field with a chemical shift δ_{H2O} = 4,76 ppm. The form of H_2O proton is asymmetric, with a broadened base and apex of irregular shape. The peak of apex is shifted to the left in relation to center line. The difference in chemical shifts between the OH protons of ethanol and water is Δδ=0,61 ppm.

A characteristic feature of the first two spectra of ethanol (EtOH) and water (H_2O) is that the spectra are located separately from each other with a similar difference in a chemical shift $\Delta\delta$=0,61 ppm. This suggests that conditions for the formation of structure of water with the hydroxyl proton of alcohol were not created. Therefor it can be said that thermodynamic balance does not happen at τ=48 h.

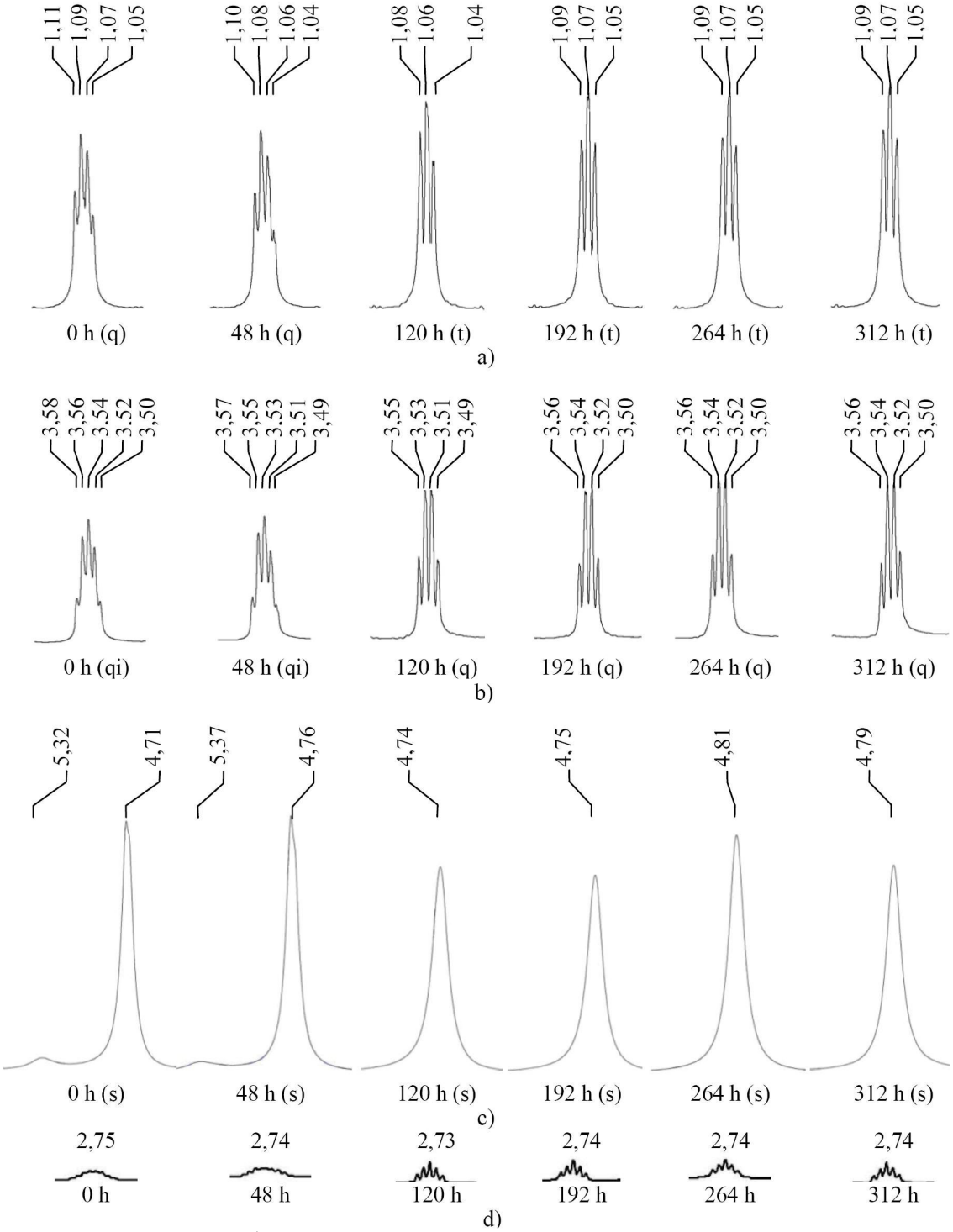


Figure 4. Modifications of ^{1}H NMR spectra of AAM's proton groups prepared in water and ERS «Lux»: a - CH_3; b - CH_2; c - H_2O+(EtOH); d - external standard (acetone-d_6), depending on the operation system time

Table 1. Characteristic of main parameters that evaluate chemical structure of AAM in ^{1}H NMR spectra

Characteristics	Signal	Time (τ), h					
		0	48	120	192	264	312
The hydroxyl group							
Chemical shift (δ), ppm	H_2O	4,71	4,76	-	-	-	-
Signal shape		(s)	(s)				
Chemical shift (δ), ppm	EtOH	5,32	5,37	-	-	-	-
Signal shape		(s)	(s)				
Chemical shift (δ), ppm	(H_2O+ EtOH)	-	-	4,74	4,75	4,81	4,79
Signal shape				(s)	(s)	(s)	(s)
The methyl group							
Chemical shift (δ), ppm	CH_3	1,08	1,07	1,06	1,07	1,07	1,07
Signal shape		(q)	(q)	(t)	(t)	(t)	(t)
The methylene group							
Chemical shift (δ), ppm	CH_2	3,54	3,53	3,52	3,53	3,53	3,53
Signal shape		(qi)	(qi)	(q)	(q)	(q)	(q)
Organoleptic properties							
Organoleptic evaluation the AAM, point		9,40	9,41	9,43	9,43	9,43	9,43
- appearance		colorless liquid		colorless liquid with sediment			
- the smell		very harsh, alcoholic		harsh, alcoholic			
- the taste		very heavy		heavy			

The third spectrum (τ=120 h) is characterized by a single summarized peak of OH ethanol (EtOH) and water (H_2O). Components of OH-protons H_2O and OH-protons C_2H_5OH are represented as a total singlet H_2O+(EtOH), with the chemical shift $\delta_{H2O+(EtOH)}$=4,74 ppm. The form of a summarized singlet is symmetrical with a broadened base and with apex of a regular shape.

Fourth spectrum (τ=192 h) is characterized by a single summarized peak of OH-proton (EtOH+H_2O). It is represented by symmetric singlet with a chemical shift $\delta_{H2O+(EtOH)}$=4,75 ppm. The form of a summarized signal H_2O+(EtOH) is symmetric with a broadened base and with apex of a regular shape.

Fifth spectrum (τ=264 h) is characterized by a single summarized peak of H_2O+(EtOH). It is represented by symmetric singlet with a chemical shift $\delta_{H2O+(EtOH)}$=4,81. The form of the summarized signal is symmetric with a broadened base and with apex of a regular shape.

Sixth spectrum (τ=312 h) is characterized by a single summarized peak of ethanol and water - H_2O+(EtOH). It is represented by a symmetric singlet with a chemical shift $\delta_{H2O+(EtOH)}$=4,79 ppm. The form of the summarized signal is symmetric with a broadened base and with apex of a regular shape.

The analysis of the ^{1}H NMR-spectra of protons methyl group (CH_3) AAM allows us to state the following:

τ=0 h. The protons' methyl group is represented as a quartet (q) with a relative intensity (1:3:3:1) in the initial part of system's operation. This is abnormity as according to Pascal's triangle and on the assumption of protons' methyl group spin-spin interactions, methylene group's (CH_3) signal has to be split by an adjacent protons' group (CH_2) as a triplet (t) with intensity ratio (1:2:1). Besides the methylene group (CH_2), no other group of protons can have an effect on the active spectrum of the methyl group (CH_3).

τ=48 h. Methyl group of protons (CH_3) has shifted by a distance of 0,01 ppm towards the strong field from its original position (τ=0 h) with an average value of the chemical shift δ_{CH3}=1,07 ppm. It has the following individual characteristics of signals' chemical shift's peaks δ_{CH3}=(1,10; 1,08; 1,06; 1,04) ppm; distance between the peaks is 8 Hz relative to each other. Signal's form is quartet (q), which is also an abnormity for the

interaction of the above spectrum with methylene group (CH_2).

First two spectra, in our view, belong to the group with an unsteady balance, because signals form is abnormal - quartered (q). It has to be represented as a triplet (t) in theory.

τ = 120 h. Methyl spectrum has shifted by a distance of 0,02 ppm from its original position (τ=0 h) with a average value of the chemical shift δ_{CH3}=1,06 ppm. Signal's form is triplet (t), which indicates it's stability. This is based on spin-spin interaction with methylene (CH_2) group's protons. Chemical shift of triplet's individual peaks is δ_{CH3}=(1,08; 1,06; 1,04) ppm.

Time interval from 120 to 192 h (5 ... 8 days) is characterized by the transition mode of equilibration.

A complete structuring of methyl group's (CH_3) signal, both in shape as triplet (t), and in location - δ_{CH3}=1,07 ppm, takes place after 8 hours (192 h) expiration, which remains unchanged. It is shifted towards the stronger field by a distance of 0,01 ppm, if to compare it's average position to it's original position (τ=0 h). The distance between the peaks remains unchanged – 8 Hz.

The analysis of methylene group's (CH_2) ^{1}H NMR's protons shows the following:

The methylene group's protons (CH_2) are represented as quintet (qi) with the intensity (1:4:6:4:1) at the beginning of AAM's formation process (τ=0 h). This is an abnormity. Protons of methyl (CH_3) groups must split the signal of methylene group (CH_2) into four components and form a quartet (q) with an intensity ratio of 1:3:3:1, as based on the spin-spin interaction. In turn, protons of hydroxyl (OH) groups should split each quartet's component of methylene (CH_2) group into two components to form a double quartet. The signal of methylene (CH_2) groups should remain as quartet. This happens due to the absence of spin-spin interaction between the hydroxyl (OH) and methylene (CH_2) groups by the chemical exchange.

The methylene group of protons (CH_2) is in a weak field, with the average value of the chemical shift of δ_{CH2}=3,54 ppm, each peak of quartet is located at a distance of 8 Hz from each other.

The methylene group of protons (CH_2) has shifted from its original position towards the strong field by 0,01 ppm after the 48 hours. The average value of its chemical shift is δ_{CH2}=3,53 ppm. The distance between the peaks is 8 Hz. Signal's form is quintet (qi). This is an abnormity for the above proton's spectrum.

The first two spectra, in our view, belong to a group with unsteady balance, since the signals' form is abnormal.

Methylene spectrum with an average value of the chemical shift as δ_{CH2}=3,52 ppm has shifted into the strong field with respect to the initial position (τ=0 h) by 0,02 ppm after 120 hours expiration. Signal's form is quartet (q), typical for the above proton group, based on the spin-spin interaction with the protons of the methyl (CH_3) group and chemical exchange between hydroxyl (OH) and methylene (CH_2) groups. This is the form's stabilization.

Complete structuring of methylene group's (CH_2) signal takes place approximately after 8 days (τ=192 h): signal's form is quartet (q); location - chemical shift with an average value of δ_{CH2}= 3,53 ppm, which remains unchanged. The distance between the peaks also remains unchanged – 8 Hz.

Therefore, we can assume that the time of τ= 120…192 hours is characterized as transitional balance.

Generalizing the findings, it is necessary to note the formation of AAM includes three periods in thermodynamics of chemical equilibrium between the proton groups of water and alcohol:

1 - unsteady equilibrium;

2 - transition mode;

3 - steady equilibrium.

The duration of these periods is different for the individual characteristics of AAM. Based on the obtained data, we have detected two groups of signals by thermodynamic equilibrium with a similar pattern: τ – time of drinking water hookup with ERS; δ - chemical shift; signal's form; organoleptic assessment of AAM.

The first group of signals:

- with an unsteady equilibrium (τ_1=0÷48 h);
- with the transitional mode (τ_2=48÷120 h);
- with steady equilibrium (τ_3=120÷312 h).

The second group of signals:

- with an unsteady equilibrium (τ_1=0÷120 h);
- with the transitional mode (τ_2=120÷192 h);
- with steady equilibrium (τ_3=192÷312 h).

The first group includes: H_2O; EtOH; H_2O+(EtOH); organoleptic assessment of AAM (appearance, smell, taste). Unsteady thermodynamic equilibrium (at the time of drinking water hookup with ERS τ_1=0÷48 h) is characterized by the presence of two separated signals H_2O and EtOH in hydroxyl group; by worst organoleptic evaluations of 9,40-9,41 points (in appearance - colorless liquid; scent - very sharp, smell of alcohol, flavor - very heavy). We established that the transitional balance between unsteady and steady equilibrium during the period of (τ_2=48÷120 hours) is characterized by varying features that can be considered for both periods. The steady state equilibrium (τ_3=120÷312 h) is characterized by the presence of a combined signal H_2O+(EtOH) in hydroxyl group ; by stabilization of organoleptic features: tasting evaluation provides the same value at 9,43 points. It leads to stabilization of appearance - colorless liquid with sediment; scent - sharp alcohol; flavor - heavy. Furthermore, transformation of CH_2 and CH_3 signals' form with an abnormal form at unsteady equilibrium and rational form at steady equilibrium can be attributed to transition period (mode).

Second group of signals includes: CH_3; CH_2. Unsteady equilibrium (τ_1=0÷120 h) is characterized by unstable location of signals in methyl group (CH_3), in methylene group (CH_2). Unstable signals shifted to the strong field with the increase of hookup duration in all three groups. We established that the transitional equilibrium (τ_2=120÷192 h) between the unsteady and steady equilibrium has varying features. Steady equilibrium (τ_3=192÷312 h) is characterized by stabilization of signal's location: CH_3 - 1,07 ppm; CH_2 - 3,53 ppm.

Based on the test results, we can confirm the existence of a correlation between AAM's ^{1}H NMR-spectra's features: the obtained values of proton groups are correlated. That is, the presence of such features as separate signals of OH-protons of H_2O and EtOH, and an abnormal form of CH_3 and CH_2 leads to products with lower tasting properties. The presence of combined signal of H_2O+(EtOH), and rational form of CH_3 and CH_2 signals (triplet form of methyl group, quarter form of methylene group) characterize a high level of tasting properties of AAM.

The following conclusion can be made: during the process of creation of AAM by mixing drinking water with pH=7,01 and ERS «Lux» we created a product with pH = 8,32. This value is characterized by a reduced content of free H^+ ions relative to the OH^-, i.e. general alkaline reaction of the system. Hydroxyl proton (OH) of ethanol exchange rate is in intermediate area. It happens during the first 48 hours when the concentration of alcohol is constant (strength AAM - 39,94 % vol.) and the system is thermostatic (t=+23,5 ºC). Signals are separately located. Protons' exchange is accelerated due to the rearrangement of system's structure, during the interval of τ=48 h to 120 h. Since τ=120 h, there is only one common signal of mobile protons of asymmetrical shape. The size of chemical shift of the summed signal $\delta_{H2O+(EtOH)}$= 4,74 ppm (τ=120 h) is starting to grow and shifts to the «weak fields» with the value of $\delta_{H2O+(EtOH)}$=4,79 ppm (τ=312 h).

The article studies the mechanisms of transformation of ethanol's protons and drinking water during the creation of AAM. The paper presents experimental evidence of speed and nature of the thermodynamic equilibrium dependence as well as dependence of obtaining of optimal organoleptic characteristics of vodka on hookup time of AAM's components.

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