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Eduction of equilibrium state in vodkas by means of ^{1}H NMR spectroscopy

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Abstract

Introduction. The aim of this work is to identify equilibrium state of hydroxyl proton of ethanol and water in various samples of vodkas and flavored vodkas produced in Ukraine, using ^{1}H NMR spectroscopy.

Materials and methods. Volumetric pipette were used to set up a required volume (0,3 ml) of vodka or flavored vodka. External standard separated from testing substance which is required for LOCK's system operation deuterium solvent (acetone-d_6) of NMR's deuterium stabilization spectrometer is added into an ampoule in a special form capillary. ^{1}H NMR spectra records and data processing were performed according to the instruction of FT-NMR Bruker Avance II spectrometer (400 MHz).

Results and discussion. Experimentally determined elements thermodynamic equilibrium of hydroxyl proton of ethanol and water in vodkas and flavored vodka, using ^{1}H NMR spectroscopy. In this work, we set three groups of samples with equilibrium of hydroxyl protons of water and ethanol: unsteady; transitional; steady equilibrium.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of EtOH+H_2O ($\delta_{EtOH+H2O}$=4,75...4,80 ppm). Unsteady and transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of EtOH (δ_{EtOH}=5,34 ppm) and H_2O (δ_{H2O}=4,72…4,75 ppm). Unsteady equilibrium is characterized by the presence of hydroxyl proton of ethanol (EtOH), which is obvious. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium.

Conclusion. The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas and flavored vodkas, using ^{1}H NMR spectroscopy. Equilibrium systems allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

Keywords:

Vodka
Equilibrium
Hydroxyl
Proton

^1H NMR spectroscopy

Встановлення рівноважного стану горілок за допомогою ^1H ЯМР спектроскопії

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Вступ. Метою статті є виявлення рівноважного стану гідроксильних протонів етанолу і води у горілках і горілках особливих, вироблених в Україні, за допомогою ^1H ЯМР спектроскопії.

Матеріали і методи. За допомогою мірної піпетки задавали необхідний об'єм (0,3 мл) горілки або горілки особливої. Необхідний для роботи системи LOCK'a - дейтерієвій стабілізації ЯМР спектрометра ацетон-d6 - зовнішній стандарт, який відокремлений від досліджуваної речовини, вносили до ампули у капілярі спеціальної форми; запис спектрів ^1H ЯМР та обробку даних проводили відповідно до інструкції, що додається до Фур'є ЯМР спектрометра Bruker Avance II (400 MHz).

Результати. Експериментально визначені елементи встановлення термодинамічної рівноваги гідроксильних протонів етанолу та води у горілках і горілках особливих за допомогою ^1H ЯМР спектроскопії. В роботі виділено 3 групи зразків виходячи з рівноваги гідроксильних груп протонів води та етанолу: несталої; перехідної; сталої рівноваги.

Стала рівновага характеризується наявністю в гідроксильній групі об'єднаного унітарного сигналу $EtOH+H_2O$ ($\delta_{EtOH+H2O}$=4,75...4,80 ppm). Нестала і перехідна рівновага характеризуються наявністю в гідроксильній групі двох роздільних сигналів EtOH (δ_{EtOH}=5,34 ppm) і H_2O (δ_{H2O}=4,72…4,75 ppm). Відмітною їх особливістю є те, що нестала рівновага характеризується явною присутністю гідроксильного протона етанолу (EtOH), а перехідна рівновага - наявністю ледве помітного сигналу EtOH, що характеризує перехід від сталої до несталої рівноваги.

Висновки. На підставі проведеного дослідження встановлена принципова відмінність поведінки гідроксильних протонів етанолу та води у горілках і горілках особливих за допомогою ^1H ЯМР спектроскопії. Отримані в роботі рівноважні системи дозволяють удосконалити технологічний процес виробництва горілок на лікеро-горілчаних підприємствах для стабілізації якості готової продукції.

Ключові слова: горілка, рівновага, гідроксил, протон, ^1H ЯМР спектроскопія.

Установление равновесного состояния водок с помощью ^{1}H ЯМР спектроскопии

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Введение. Целью статьи является выявление равновесного состояния гидроксильных протонов этанола и воды в водках и водках особых, произведенных в Украине, с помощью ^{1}H ЯМР спектроскопии.

Материалы и методы. С помощью мерной пипетки задавали необходимый объем (0,3 мл) водки или водки особой. Необходимый для работы системы LOCK'а - дейтериевой стабилизации ЯМР спектрометра ацетон-d_6 - внешний стандарт, который отделен от исследуемого вещества, вносили в ампулу в капилляре специальной формы, запись спектров ^{1}H ЯМР и обработку данных проводили в соответствии с инструкцией, которая прилагается к Фурье ЯМР спектрометру Bruker Avance II (400 MHz).

Результаты. Экспериментально определены элементы установления термодинамического равновесия гидроксильных протонов этанола и воды в водках и водках особых с помощью ^{1}H ЯМР спектроскопии. В работе выделены 3 группы образцов исходя из равновесия гидроксильных групп протонов воды и этанола: неустановившегося; переходного; установившегося равновесия.

Установившееся равновесие характеризуется наличием в гидроксильной группе объединенного унитарного сигнала EtOH+H_2O ($\delta_{EtOH+H2O}$=4,75...4,80 ppm). Неустановившееся и переходное равновесие характеризуются наличием в гидроксильной группе двух раздельных сигналов EtOH (δ_{EtOH}=5,34 ppm) и H_2O (δ_{H2O}=4,72…4,75 ppm). Отличительной их особенностью является то, что неустановившееся равновесие характеризуется явным присутствием гидроксильного протона этанола (EtOH), а переходное равновесие - наличием едва заметного сигнала EtOH, который характеризует переход от установившегося к неустановившемуся равновесию.

Выводы. На основании проведенного исследования установлено принципиальное отличие поведения гидроксильных протонов этанола и воды в водках и водках особых с помощью ^{1}H ЯМР спектроскопии. Полученные в работе равновесные системы позволяют усовершенствовать технологический процесс производства водки на ликеро-водочных предприятиях для стабилизации качества готовой продукции.

Ключевые слова: водка, равновесие, гидроксил, протон, ^{1}H ЯМР спектроскопия.

Introduction

NMR spectroscopy is widely used in physics research, industry, agriculture and other industries [1]. 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 ^1H (protium, ^1H isotope) proton [2-4]. 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 [1, 3-7]. 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 [4-7]. 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 [1, 7].

The first «low resolution» ^1H NMR spectra of H_2O were obtained in 1946. The first «high resolution» ^1H NMR spectra of C_2H_5OH were developed in 1951. At first glance, it may seem that this are fairly simple organic molecules, as many scientists [1, 4, 8-22] 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 [1, 11-14].

In accordance to the requirements of normative documents of Ukraine vodka - is an alcoholic drink with a strength of 37,5% to 56,0%, made of aqueous-alcoholic mixtures (AAM) processed by a special sorbents with or without volatile ingredients. Flavored vodka is an alcoholic drink with a strength of 37,5% to 56,0%, with a marked flavor and taste, prepared by processing AAM with a special sorbents with addition of non-volatile and volatile ingredients.

In the opinion Hu N. and others [23] 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 [23] 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 ^1H NMR spectroscopy, FTIR spectroscopy, Raman spectroscopy. ^1H NMR and FTIR spectroscopy demonstrates the presence of water in the hydrate structure $EtOH*(5{,}3\pm0{,}1)H_2O$. Water can also be observed in AAM as well as in vodka. The authors [23] attribute this value with the perception of organoleptic characteristics of vodka.

Lots of attention in the work of Hu N. and others [23] has been given to ^1H NMR spectra of hydroxyl proton of OH water and ethanol. Water protons are represented as narrow singlets with δ_{H2O}=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_{EtOH}=5,5 ppm. The presence in the samples of a single signal of OH ethanol is attributed to the weak hydrogen bonds of ethanol.

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. [24]. Hu N. and others [23] have identified that the impurity of compounds has an effect on the molecular dynamics in ethanol's hydration process.

Previously, ^1H NMR research of AAM has been conducted and described in the work of Kuzmin O. et al [25-27]. The obtained results of this work have proved a fundamental difference in AAM behavior prepared from ethyl rectified spirit (ERS) and water that has been passed through a various processing. It is indicated by the presence of such features as divided signals of OH-protons of H_2O and EtOH, abnormal waveforms of CH_3 and CH_2. Presence of these features characterize product with a lower tasting properties. In the contrary presence of combined signal of EtOH+H_2O and rational form of CH_3 and CH_2 signals (triplet - for CH_3, quartet - for CH_2) - characterizes AAM with the best tasting properties. In this regard, we have established systems with a steady and unsteady equilibrium depending on transformation of hydroxyl protons of ethanol and water. Unsteady balance is typical for AAM used with ERS «Lux» and drinking water, with a tasting score – 9,43 points. This also include the AAM made from ERS «Lux» and demineralized water by reverse osmosis, with a tasting score – 9,30 points. The systems with a steady equilibrium are typical for AAM made of ERS «Lux» and water softened by Na-cationization, with a tasting score of 9,49 points.

Thus, in the work of Kuzmin O. et al [25-27] experimental evidence of steady/unsteady thermodynamic equilibrium of AAM were established. The established equilibriums affect organoleptic characteristics of AAM depending on water treatment method and time of system's functioning. However, the questions related to internal mechanism and speed of unsteady thermodynamic equilibrium of finished product - vodka or flavored vodka were not yet clarified.

Therefore, additional studies were required to be conducted for a more detailed study of the internal mechanism of unsteady thermodynamic equilibrium to insure provision of a high quality characteristics of finished products (vodka, flavored vodka).

The aim of this work is to identify equilibrium state of hydroxyl proton of ethanol and water in various samples of vodkas and flavored vodkas produced in Ukraine, using ^1H NMR spectroscopy.

Materials and methods

^1H 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 $^1H \pm 0{,}0005$ ppm; 5-mm broadband inverse probe with Z-gradient;

thermostatic system (+25°C ... +100°C);

- 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 $\delta = 2,75$ ppm;
- High accuracy ampoules №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;
- The 31 sample of vodkas, flavored vodkas and moonshine, produced in Ukraine (Table 1) were used as experimental material for ^1H NMR spectroscopy.

Experimental studies of ^1H NMR were carried out in the following order:

- Preparation of samples to research;
- Recording of ^1H NMR spectrum;
- Conclusion and interpretation of work results.

Work methodology:

- 0,3 ml of vodka or flavored vodka 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 and discussions

The 31 sample of vodkas and flavored vodkas, produced in Ukraine were used as experimental material for ^1H NMR spectroscopy. These samples were divided into 3 groups with unsteady equilibrium, transitional and steady equilibrium of protons hydroxyl group (Fig. 1-3).

We will study first group of vodkas and flavored vodkas with unsteady equilibrium. This group has included 8 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 1).

The selected samples of vodkas and flavored vodkas with unsteady equilibrium characterized by the absence of single signal ($EtOH+H_2O$), therefor hydroxyl group of protons is represented by two separate peaks of ethanol (EtOH) and water (H_2O).

The component of multiplet of hydroxyl protons of ethanol (EtOH) in each sample is represented as a single broad singlet (s) with a rounded shape, located in a «weak field» with a chemical shift δ_{EtOH}=5,34 ppm.

The component of proton of water (H_2O) in each sample presented as singlet (s) with a chemical shift δ_{H2O}=4,72 ppm. Waveform of H_2O protons - is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

Table 1

List of samples, used as an experimental material

№ sample	Name of product	Name of enterprise
1.	«Poliana Chysta»[1]	LLC «First Ukrainian Vodka Standard»
2.	«Sprava maistra Spravzhnia»[1]	LLC «Distillery Altera»
3.	«Medoff Classic»[1]	LLC «Crimean Vodka Company»
4.	«Khlibna sloza»[2]	LLC «Distillery «Karat»
5.	«Istynna Sribna»[1]	LLC «Distillery «Prime»
6.	«Vdala Zhytnia»[2]	CJSC «Crimean Wine and Cognac Factory «Bakhchysarai»
7.	«Bilenka Pshenychna nyva»[1]	LLC «Distillery «Prime»
8.	«Status Klasychnyi»[1]	LLC «Zolotonosha Distillery «Zlatogor»
9.	«Nemiroff Ukrainska berezova osoblyva»[2]	SC «Ukrainian Vodka Company «Nemiroff»
10.	«Green Day»[1]	LLC «Atlantis»
11.	«Perepilka Klasychna»[1]	LLC «National Vodka Company»
12.	«Zlatohor Chysta sloza M'iaka»[2]	LLC «Zolotonosha Distillery «Zlatogor»
13.	«Khutorok Eksportna»[1]	LLC «Crimean Vodka Company»
14.	«Nemyrivska Pshenytsia ukrainska vidbirna»[2]	SC «Ukrainian Vodka Company «Nemiroff»
15.	«Morosha Karpatska»[1]	LLC RPE «Hetman»
16.	«Luga-Nova Rosiiska»[1]	PJSC «Lugansk distillery Luga-Nova»
17.	«Na berezovykh brunkakh»[2]	LLC «Crimean Vodka Company»
18.	«Luga-Nova Bila koroleva»[2]	PJSC «Lugansk distillery Luga-Nova»
19.	«Ukrainka Dzherelna»[1]	LLC «Atlantis»
20.	«Berezovyi tsvit»[2]	LLC «Beveridge group»
21.	«Khortytsa Absoliutna»[1]	SE «Image Holding» JSC «Image Holding AnC»
22.	«Malynivka Lahidna»[2]	LLC «Distillery «Prime»
23.	«Zolotyi Lviv Panska»[1]	JSC «Lviv distillery»
24.	«Prime World class»[1]	LLC «Distillery «Prime»
25.	«Pulse active»[1]	LLC «Artemovsk Distillery-Plus»
26.	«Baika Liuksova yakist Pom'iakshena»[2]	LLC «National Vodka Company»
27.	«Nova Rublovka Klasychna»[2]	LLC «Latona-Invest»
28.	Moonshine[3]	smt. Novgorodskoe
29.	«Poltavska bytva»[2]	CJSC «Poltava Distillery»
30.	«Khortytsa Platinum»[1]	SE «Image Holding» JSC «Image Holding AnC»
31.	«Artemivska Klasychna»[1]	LLC «Distillery Altera»

Note. 1 – vodka, 2 - flavored vodka; 3 – moonshine

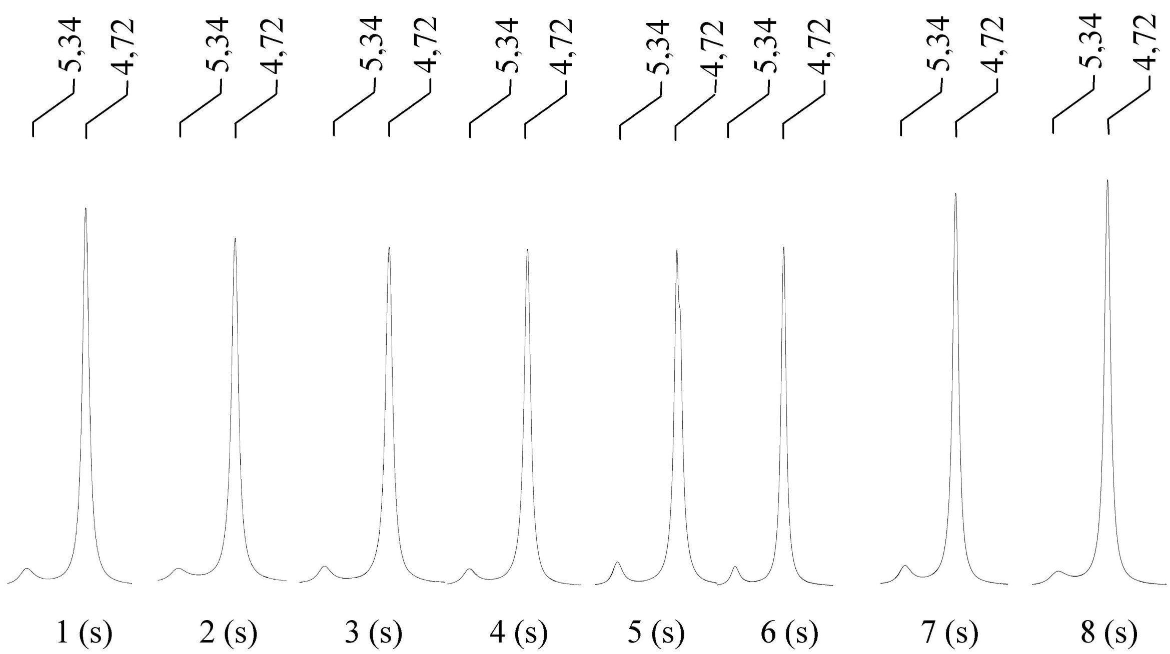

Fig. 1. ¹H NMR spectra of hydroxyl group protons of ethanol (EtOH) and water (H_2O) with unsteady equilibrium:
1...8 - number of the sample (Table 1)

The difference between the chemical shifts of hydroxyl protons of ethanol (EtOH) and water (H_2O) in each sample is $\Delta\delta$=0,62 ppm. This may indicate that conditions for the formation of water structure with hydroxyl proton of alcohol were not yet set, therefor we can state that thermodynamic equilibrium didn't appear in any of the samples.

We will study second group of vodkas and flavored vodkas with transitional equilibrium. This group has included 11 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 2).

The samples of vodkas and flavored vodkas with the transitional equilibrium as well as samples with unsteady equilibrium are characterized by the absence of unitary signal (EtOH+H_2O) therefor hydroxyl group of protons is presented by two separate picks of H_2O and EtOH.

Component of multiplet of hydroxyl protons of ethanol (EtOH) in each sample is represented as a separate subtle signal of a rounded shape located in a «weak field» with a chemical shift δ_{EtOH}=5,34 ppm.

Component of proton of water (H_2O) in each sample is represented as a singlet with a chemical shift δ_{H2O}=4,75 ppm. Waveform of H_2O signals is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

The difference between the chemical shifts of hydroxyl protons of ethanol (EtOH) and proton of water (H_2O) in each sample is $\Delta\delta$=0,59 ppm. This may indicate that certain prerequisites are created to establish equilibrium structure (unsteady/steady equilibrium).

We will consider the third group of vodkas and flavored vodkas with steady equilibrium. This group has included 12 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 3).

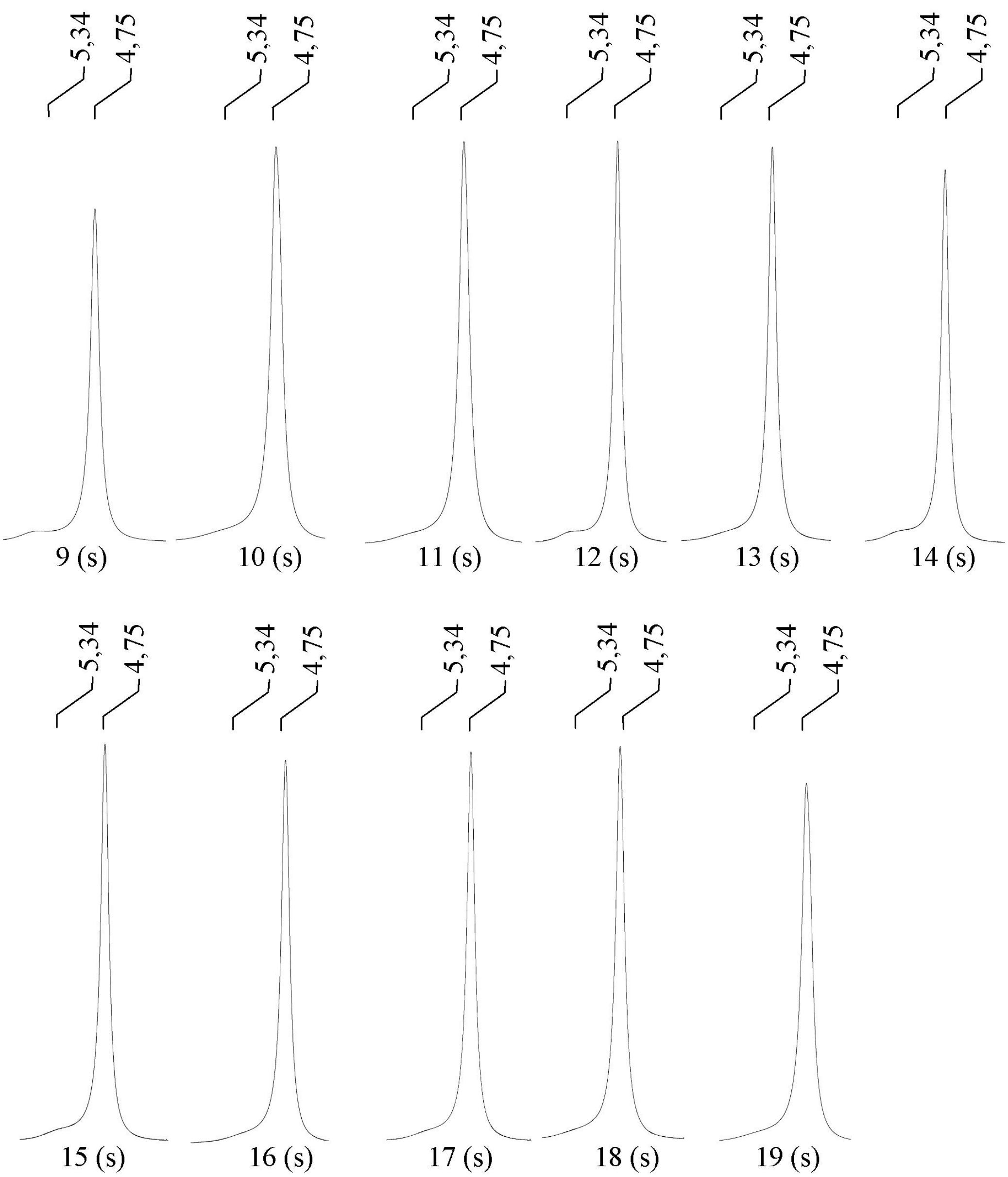

Fig. 2. ^{1}H NMR spectra of hydroxyl group protons of EtOH+H_2O with transitional equilibrium:

9...19 - number of the sample (Table 1)

The selected samples of vodkas and flavored vodkas with a steady equilibrium characterized by a unitary signal of hydroxyl group (EtOH+H_2O). The component of protons of EtOH+H_2O in each sample presented as singlet (s), located in a «weak field» with a chemical shift, which is in a range $\delta_{EtOH+H2O}$=4,75...4,80 ppm. Waveform of EtOH+H_2O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

Conclusions

We will draw conclusions on establishing of equilibrium hydroxyl proton of ethanol and water in vodka and flavored vodka by [1]H NMR spectroscopy. We identified three groups of samples based on the equilibrium of the hydroxyl groups of protons of ethanol (EtOH) and water(H_2O): unsteady; transitional; steady.

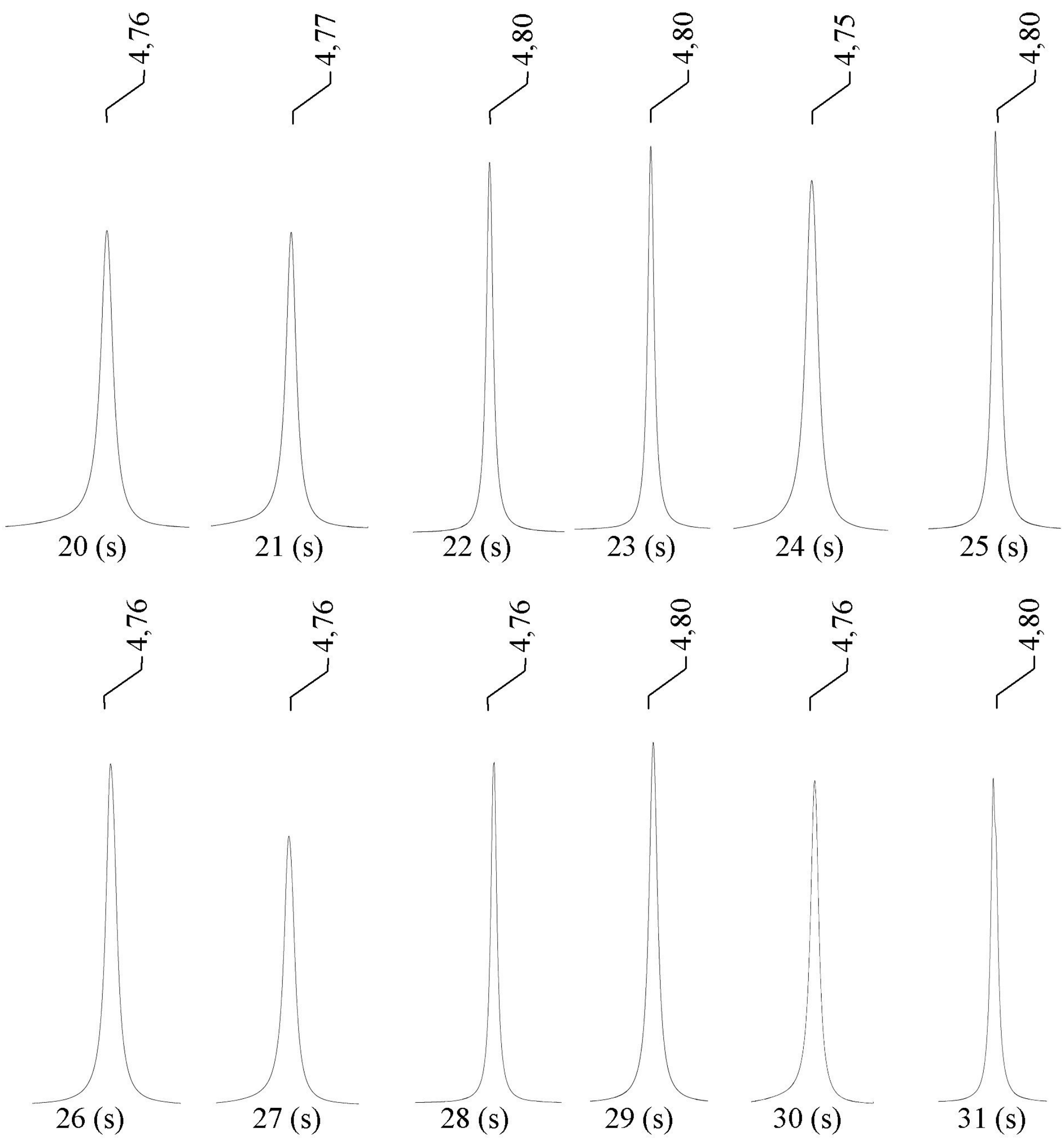

Fig. 3. ^{1}H NMR spectra of hydroxyl group protons of EtOH+H_2O with a steady equilibrium:

20...31 - number of the sample (Table 1)

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of EtOH+H_2O. Unsteady and transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of EtOH and H_2O. Unsteady equilibrium is characterized by the presence of hydroxyl proton of ethanol (EtOH), which is obvious. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium.

The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas and flavored vodkas, using ^{1}H NMR spectroscopy. Equilibrium systems allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

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