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Determination of systems with a steady equilibrium in vodkas, depending on transformation of hydroxyl protons

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Abstract

Introduction. The aim of this work is to identify a steady equilibrium of hydroxyl proton of ethanol and water in various types of vodkas and moonshine, which are produced in Ukraine.

Materials and methods. Volumetric pipette were used to set up a required volume (0,3 ml) of vodka (flavored vodka, moonshine). 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.

Results and discussion. Fundamentally new aspects that are related to an internal mechanism of steady thermodynamic equilibrium in the finished product - vodka (flavored vodka, moonshine) were established during the studies. The study has proved that steady equilibrium is characterized by the presence of combined unitary signal EtOH+H_2O in hydroxyl group ($\Delta\delta_1$=0 ppm). Unsteady and transitional equilibrium is characterized by the presence of two separate signals of EtOH and H_2O in hydroxyl group.

The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group EtOH+H_2O for 7 samples - $\Delta\delta_2$=1,23 ppm, for 5 samples – $\Delta\delta_2$=1,27 ppm. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3$=2,45 ppm, which specifies on stability of chemical shifts between these groups, and strong links between methyl (CH_3) and methylene (CH_2) groups.

Conclusion. The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas, flavored vodkas and moonshine, 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
^{1}H NMR spectroscopy

Виявлення систем із сталою рівновагою у горілках, які залежать від трансформації гідроксильних протонів

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Вступ. Метою публікації є виявлення сталої рівноваги гідроксильних протонів етанолу і води для різних видів горілок та самогону, які виробляються в Україні.

Матеріали і методи. За допомогою мірної піпетки задавали необхідний об'єм (0,3 мл) горілки (горілки особливої, самогону). Необхідний для роботи системи LOCK'a - дейтерієвій стабілізації ЯМР спектрометра ацетон-d_6 - зовнішній стандарт, який відокремлений від досліджуваної речовини, вносили до ампули у капілярі спеціальної форми. Запис спектрів ^{1}H ЯМР та обробку даних проводили відповідно до інструкції, що додається до Фур'є ЯМР спектрометра Bruker Avance II.

Результати. В ході проведених досліджень встановлені принципово нові аспекти, які пов'язані з деталізацією внутрішнього механізму визначення сталої термодинамічної рівноваги у готовому продукті – горілці (горілці особливої, самогоні). При цьому стала рівновага характеризується наявністю в гідроксильній групі об'єднаного унітарного сигналу EtOH+H_2O і відсутністю хімічного зрушення між ними ($\Delta\delta_1$=0 ppm). Нестала і перехідна рівновага характеризуються наявністю в гідроксильній групі двох роздільних сигналів EtOH і H_2O.

Різниця в хімічних зрушеннях між метиленовою групою протонів етанолу (CH_2) і гідроксильною групою (EtOH+H_2O) для 7 зразків складає $\Delta\delta_2$=1,23 ppm, для 5 зразків - $\Delta\delta_2$=1,27 ppm. Різниця в хімічних зрушеннях між метиленовою групою протонів етанолу (CH_2) і метильною групою етанолу (CH_3) для всіх зразків складає $\Delta\delta_3$=2,45 ppm, що може свідчити про стабільність хімічних зрушень між цими групами, та міцність зв'язків між метильною (CH_3) і метиленовою (CH_2) групами.

Висновки. На підставі проведеного дослідження встановлена принципова відмінність у поведінці гідроксильних протонів етанолу та води у горілках, горілках особливих та самогоні за допомогою ^{1}H 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, ^{1}H ЯМР спектроскопія.

Выявление систем с установившимся равновесием в водках, которые

зависят от трансформации гидроксильных протонов

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Введение. Целью публикации является выявление установившегося равновесия гидроксильных протонов этанола и воды для различных видов водок и самогона, которые производятся в Украине.

Материалы и методы. С помощью мерной пипетки задавали необходимый объем (0,3 мл) водки (водки особой, самогона). Необходимый для работы системы LOCK'a - 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.

Результаты. В ходе проведенных исследований установлены принципиально новые аспекты, которые связаны с детализацией внутреннего механизма определения установившегося термодинамического равновесия в готовом продукте – водке (водке особой, самогоне). При этом установившееся равновесие характеризуется наличием в гидроксильной группе объединенного унитарного сигнала EtOH+H_2O и отсутствием химического сдвига между ними ($\Delta\delta_1$=0 ppm). Неустановившееся и переходное равновесие характеризуются наличием в гидроксильной группе двух раздельных сигналов EtOH и H_2O.

Разница в химических сдвигах между метиленовой группой протонов этанола (CH_2) и гидроксильной группой (EtOH+H_2O) для 7 образцов составляет $\Delta\delta_2$=1,23 ppm, для 5 образцов – $\Delta\delta_2$=1,27 ppm. Разница в химических сдвигах между метиленовой группой протонов этанола (CH_2) и метильной группой этанола (CH_3) для всех образцов составляет $\Delta\delta_3$=2,45 ppm, что может свидетельствовать о стабильности химических сдвигов между данными группами, и крепости связей между метильной (CH_3) и метиленовой (CH_2) группами.

Выводы. На основании проведенного исследования установлено принципиальное отличие в поведении гидроксильных протонов этанола и воды в водках, водках особых и самогоне 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.

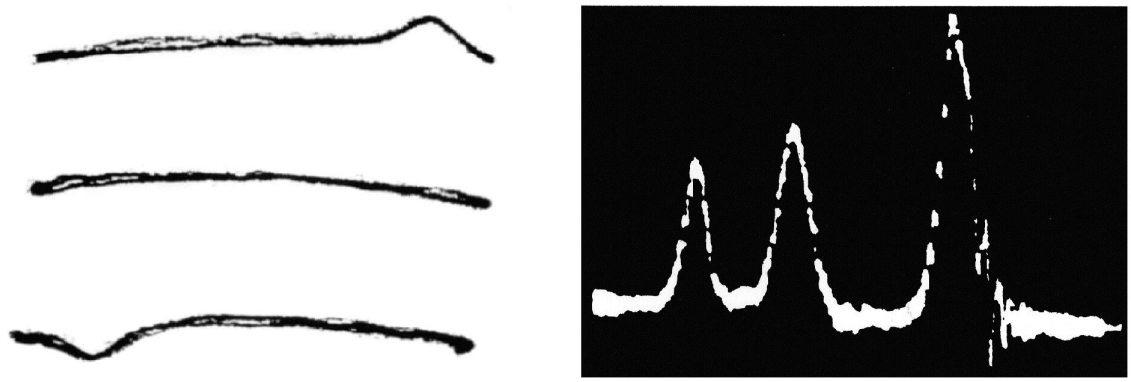
Ключевые слова: водка, равновесие, гидроксил, протон, ^{1}H ЯМР спектроскопия.

Introduction

NMR spectroscopy is widely used in physics research [1, 2]. NMR accounts for about 90% of all research of the proton magnetic resonance spectroscopy (^{1}H NMR).

Most of them operate in the Fourier transform mode.

Bloch F. obtained ^{1}H NMR spectra with «low-resolution» of H_2O (Fig. 1, a) for the first time in 1946 [3], and in 1951 Arnold J.T. for the first time obtained ^{1}H NMR spectra with «high-resolution» of ethanol C_2H_5OH (Fig. 1, b) [4]. At the first glance, it may seem that these are fairly simple organic molecules [5-10], at the same time NMR spectroscopy exhibits grate variety [11-14] in such characteristics as chemical shift, spin-spin interactions and the effect of chemical exchange.



a b

Fig.1. ^{1}H NMR spectra:
a - H_2O [3]; b - C_2H_5OH [4] – (from left to right) protons of hydroxyl (OH), methylene (CH_2) and methyl (CH_3) groups

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

Nuclear spin-spin interaction is observed between the three proton-containing groups of ethanol, all of which have different resonant frequencies [14]. «N» number of equivalent protons of one group split the signal of the nearest group into (N+1) lines with the intensity of a Pascal triangle [12]. The ability to observe spin-spin interactions depends on the rate of the intermolecular proton exchange.

The presence of proton exchange in the water-ethanol is a well-known fact [14]. 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. The exchange with acidic and basic impurities also impacts the position of average signal of water. The NMR spectra of aqueous-alcoholic mixtures (AAM) protons have a different appearance depending on the pH.

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 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.

The preliminary conducted ^{1}H NMR studies, which are described in a works [15-19], relate to the study of hydroxyl protons of AAM modifications in the process of making vodkas. The obtained results give grounds to assert a fundamental difference in the behavior AAM prepared from the alcohol and water passing through various processes. During the study we have determined the systems of unsteady and steady equilibrium depending on the transformation of hydroxyl protons of ethanol and water.

In works [20, 21] we set two groups of samples (vodkas, flavored vodkas) with equilibrium of hydroxyl protons of water (H_2O) and ethanol (EtOH) – unsteady and transitional equilibrium. 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.

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

The aim of this work is to identify a steady equilibrium of hydroxyl proton of ethanol and water in various types of vodkas and moonshine, which are produced in Ukraine.

Materials and methods

^{1}H NMR analysis of vodkas and flavored vodkas has been conducted in a certified laboratory of the Institute of Physico-Organic Chemistry and Coal Chemistry named after L.M. Litvinenko NAS Ukraine (Donetsk city), using:

- 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);
- Specially shaped capillary with acetone-d_6 $(CD_3)_2CO$ (atomic fraction of deuterium – 99,88%);
- 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 samples of vodkas, flavored vodkas and moonshine, produced in Ukraine (Table 1), were used as experimental material for ^{1}H NMR spectroscopy.

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

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

Work methodology:

- 0,3 ml of vodka (flavored vodkas, moonshine) 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;

- ^{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 discussions

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

In other works [20, 21], we already in detail considered two groups of samples – unsteady and transitional equilibrium.

In this paper, we will study only third group of vodkas flavored vodkas and moonshine with a steady equilibrium. This group has included 12 samples of vodkas (Fig. 2) of a different manufacturers, brands, names and formulations (Table 1).

Fig. 2. Vodkas, flavored vodkas and moonshine samples:
1…12 - number of sample (Table 1)

In figures 3-4 presented one-dimensional proton spectra of vodkas, flavored vodkas and moonshine for the following groups of protons: CH_3; CH_2; H_2O; EtOH; acetone-d_6. General characteristic of the obtained spectra is presented in table 1, where $\Delta\delta_1$ – is deviation between chemical shifts of proton's hydroxyl group of ethanol (EtOH) and water (H_2O), $\Delta\delta_2$ – is deviation between chemical shifts of proton's hydroxyl group of water (H_2O) and a methylene group of protons of ethanol (CH_2), $\Delta\delta_3$ – is deviation between chemical shifts of protons of ethanol's methylene group of protons (CH_2) and ethanol's methyl group protons (CH_3).

Table 1

Characteristics of vodka's chemical structure under ^{1}H NMR spectroscopy

Name of product	Name of enterprise	Chemical shift (δ), ppm				
		EtOH +H_2O	$\Delta\delta_2$	CH_2	$\Delta\delta_3$	CH_3
1. «Berezovyi tsvit»[2]	LLC «Beveridge group»	4,76	1,23	3,53	2,45	1,08
2. «Khortytsa Absoliutna»[1]	SE «Image Holding» JSC «Image Holding AnC»	4,77	1,23	3,54	2,45	1,09
3. «Malynivka Lahidna»[2]	LLC «Distillery «Prime»	4,80	1,27	3,53	2,45	1,08
4. «Zolotyi Lviv Panska»[1]	JSC «Lviv distillery»	4,80	1,27	3,53	2,45	1,08
5. «Prime World class»[1]	LLC «Distillery «Prime»	4,75	1,23	3,52	2,45	1,07
6. «Pulse active»[1]	LLC «Artemovsk Distillery-Plus»	4,80	1,27	3,53	2,45	1,08
7. «Baika Liuksova yakist Pom'iakshena»[2]	LLC «National Vodka Company»	4,76	1,23	3,53	2,45	1,08
8. «Nova Rublovka Klasychna»[2]	LLC «Latona-Invest»	4,76	1,23	3,53	2,45	1,08
9. Moonshine[3]	smt. Novgorodskoe	4,76	1,23	3,53	2,45	1,08
10. «Poltavska bytva»[2]	CJSC «Poltava Distillery»	4,80	1,27	3,53	2,45	1,08
11. «Khortytsa Platinum»[1]	SE «Image Holding» JSC «Image Holding AnC»	4,76	1,23	3,53	2,45	1,08
12. «Artemivska Klasychna»[1]	LLC «Distillery Altera»	4,80	1,27	3,53	2,45	1,08

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

We will examine spectra of hydroxyl group. The selected samples of vodkas, flavored vodkas and moonshine with a steady equilibrium characterized by a unitary signal of hydroxyl group of EtOH+H_2O (Fig. 3-4, c1…c12). 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.

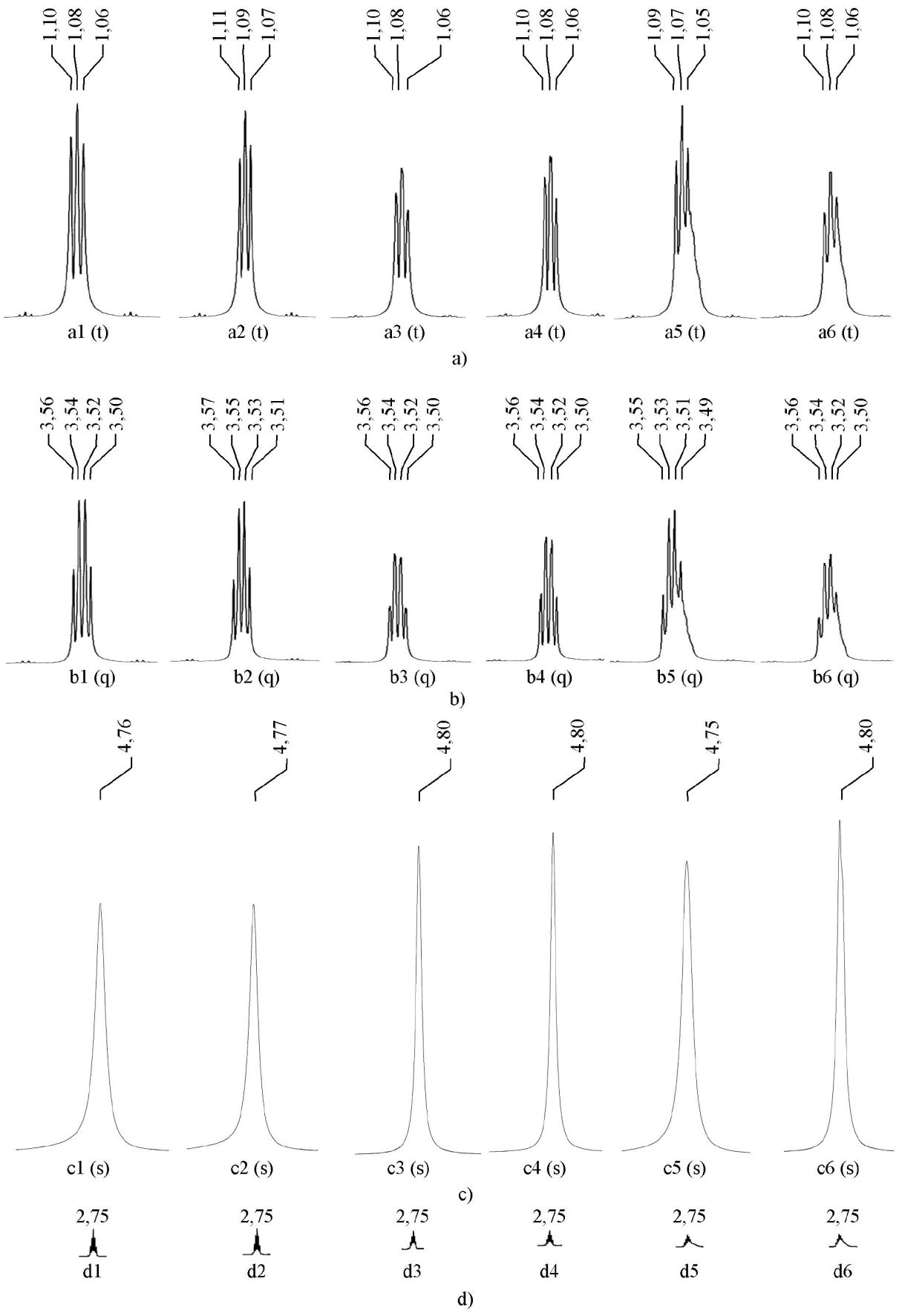


Fig. 3. Modifications of ^{1}H NMR spectra of proton groups:
a - CH_3; b - CH_2; c – EtOH+H_2O; d - acetone-d_6;
1...6 - number of sample (Table 1)

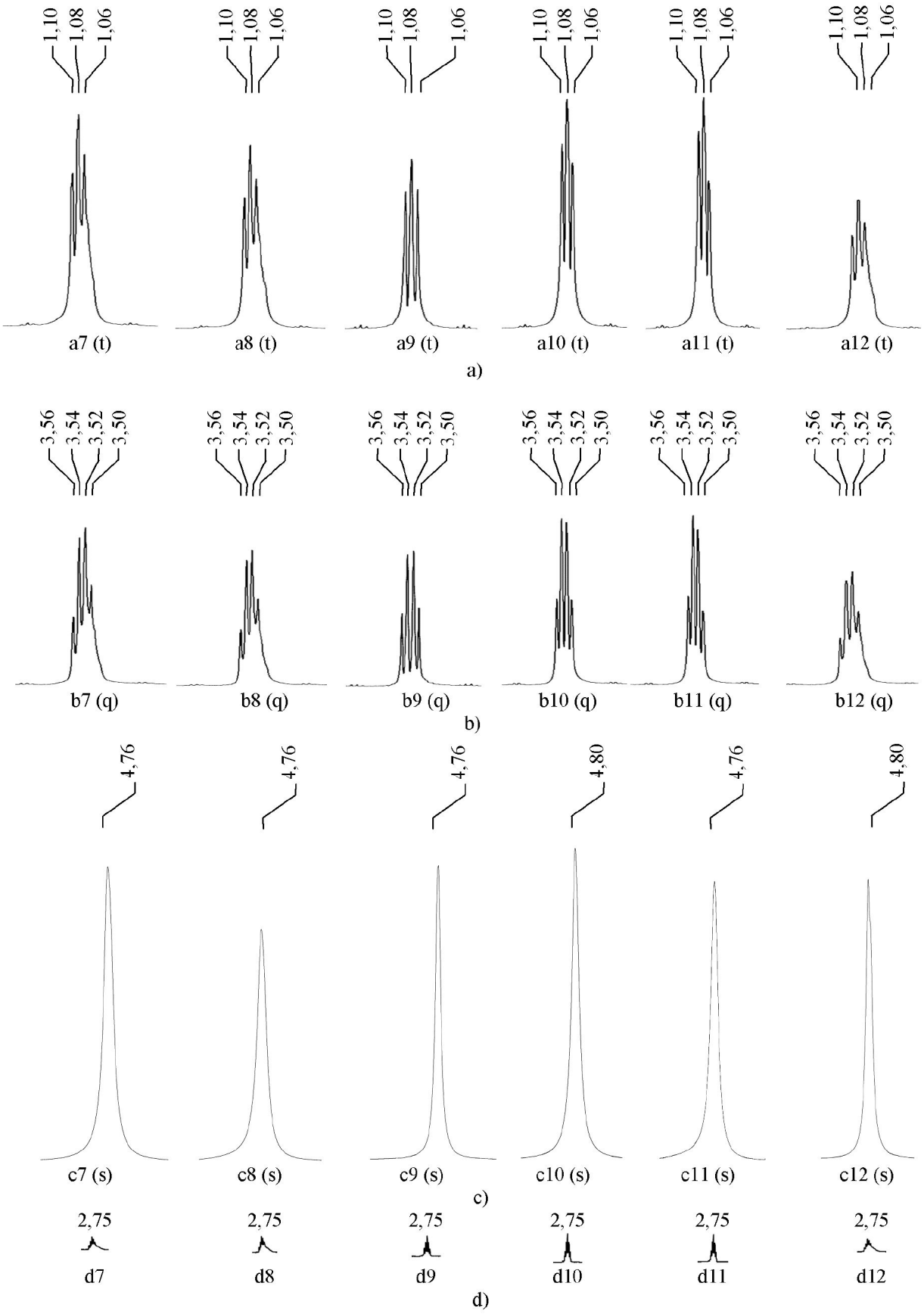


Fig. 4. Modifications of ^{1}H NMR spectra of proton groups:
a - CH_3; b - CH_2; c – $EtOH+H_2O$; d - acetone-d_6;
7...12 - number of sample (Table 1)

Analysis of ^{1}H NMR spectra of methyl group's protons CH_3 (Fig. 3-4, a1…a12) in vodkas, flavored vodkas and moonshine allows to state the following: methyl group of protons in each sample is located in a strong field and represented as a triplet (t) with a relative intensity (1:2:1). Based on spin-spin interaction of groups of protons, the methyl group's signals (CH_3) must be split by neighboring protons of the methylene group (CH_2) into a triplet (t), in accordance with Pascal's triangle with intensity ratio of (1:2:1). No other group of protons, apart from methylene group (CH_2) can affect methyl group (CH_3). The average value of the chemical shift of the methyl group for the 12 samples is within δ_{CH3}=1,07...1,09 ppm (table 1), most of which (10 samples) have an average value δ_{CH3}=1,08 ppm and private chemical shifts of the peaks of the triplet δ_{CH3}=(1,10; 1,08; 1,06) ppm. The distance between each peak of quartet is 0,02 ppm.

The analysis of ^{1}H NMR spectra of methylene group's protons CH_2 (Fig. 3-4, b1…b12) indicates that the group is represented as a quartet (q) with intensity (1:3:3:1), with an average value of the chemical shift δ_{CH2}=3,52...3,54 ppm (Table 1). Most of the components of the methylene group (10 samples) have an average value of the chemical shift δ_{CH2}=3,53 ppm partial chemical shifts of the peaks quartet δ_{CH2}=(3,56; 3,54; 3,52; 3,50) ppm. The distance between each peak of quartet is 0,02 ppm.

The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group EtOH+H_2O for 7 samples - $\Delta\delta_2$=1,23 ppm, for 5 samples – $\Delta\delta_2$=1,27 ppm. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3$=2,45 ppm, which specifies on stability of chemical shifts between these groups, and strong links between methyl (CH_3) and methylene (CH_2) groups.

Conclusions

Fundamentally new aspects that are related to an internal mechanism of steady thermodynamic equilibrium in the finished product - vodka or flavored vodka were established during the studies. The study has proved that steady equilibrium is characterized by the presence of combined unitary signal EtOH+H_2O in hydroxyl group ($\Delta\delta_1$=0 ppm). Unsteady and transient equilibrium is characterized by the presence of two separate signals of EtOH and H_2O in hydroxyl group. The unsteady equilibrium is characterized by the presence of hydroxyl proton of ethanol (EtOH). Transition equilibrium by the presence of a subtle signal of EtOH, that characterizes the transition from steady 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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