FOOD SCIENCE AND FOOD TECHNOLOGY
RECEIVED 09.08.2014 ACCEPTED 11.09.2014 PUBLISHED 15.09.2014
DOI: 10.15550/ASJ.2014.10.043

EDUCTION OF UNSTEADY EQUILIBRIUM IN VODKAS BY MEANS OF ^{1}H NMR SPECTROSCOPY

O. Kuzmin, V. Topol'nik

Donetsk National University of Economics and Trade,
31, Shchorsa Str., Donetsk 83050 Ukraine
kuzmin_ovl@mail.ru

Abstract. The aim of this publication is to identify unsteady equilibrium of hydroxyl proton of ethanol and water in various types of vodkas and flavored vodkas produced in Ukraine. The method used in the work is ^{1}H nuclear magnetic resonance (NMR) spectroscopy. This work has established fundamentally new aspects related to an internal mechanism of unsteady thermodynamic equilibrium in the finished product - vodka or flavored vodka. Unsteady equilibrium is characterized by the presence of two separate signals of H_2O and EtOH in hydroxyl group.

Keywords: ^{1}H NMR spectroscopy, hydroxyl group, methylene group, methyl group, unsteady thermodynamic equilibrium, vodka.

Introduction

In accordance to the requirements of normative documents of Ukraine (DSTU 3297:95) vodka - is an alcoholic drink with a strength of 37,5% to 56%, 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%, with a marked flavor and taste, prepared by processing AAM with a special sorbents with addition of non-volatile and volatile ingredients.

Previously, ^{1}H NMR research of AAM has been conducted and described in the work of Kuzmin O. et al, (2013-2014). 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 H_2O+(EtOH) 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 (2013-2014) 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 vodka flavored 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 unsteady equilibrium of hydroxyl proton of ethanol and water in various samples of vodkas and flavored vodkas produced in Ukraine.

Method

^{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) with operating frequency at ^{1}H -

400 MHz; specially shaped capillary with acetone-d$_6$ $(CD_3)_2CO$; high accuracy ampoules № 507-HP for high resolution NMR's spectroscopy (400 MHz); dispenser; test samples of vodkas and premium vodkas produced in Ukraine.

Work methodology: 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 (400 MHz) spectrometer.

Results

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

In this paper, we will study only 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 (figure 1).

1. Vodka «Поляна Чиста»	2. Vodka «Справа майстра Справжня»	3. Vodka «Medoff Класик»	4. Flavored vodka «Хлібна сльоза»	5. Vodka «Істинна Срібна»	6. Flavored vodka «Вдала Житня»	7. Vodka «Біленька Пшенична нива»	8. Vodka «Статус Класичний»

Fig. 1. Vodkas and flavored vodkas samples

Figure 2 shows one-dimensional proton spectra of vodkas and flavored vodkas 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 protons' 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 ethanol's methylene group of protons (CH_2) and ethanol's methyl group of protons (CH_3).

Discussion

We will examine spectra of hydroxyl group. The selected samples of vodkas and flavored vodkas with unsteady equilibrium characterized by the absence of single signal (H_2O+EtOH), therefor hydroxyl group of protons is represented by two separate peaks of water (H_2O) and alcohol (EtOH) (figure 2, c). The component of multiplet of hydroxyl (OH) protons of ethanol (EtOH) in each sample is represented as a single broad singlet (s) with a rounded shape (figure 2, c1-c8), located in a «weak field» with a chemical shift δ_{EtOH}=5,34 ppm (table 1).

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.

The difference between the chemical shifts of OH-proton (EtOH) and proton of water (H_2O) in each sample is $\Delta\delta_1$=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.

Analysis of ^{1}H NMR spectra of methyl group's protons CH_3 (figure 2, a1-a8) in vodkas and flavored vodkas 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,

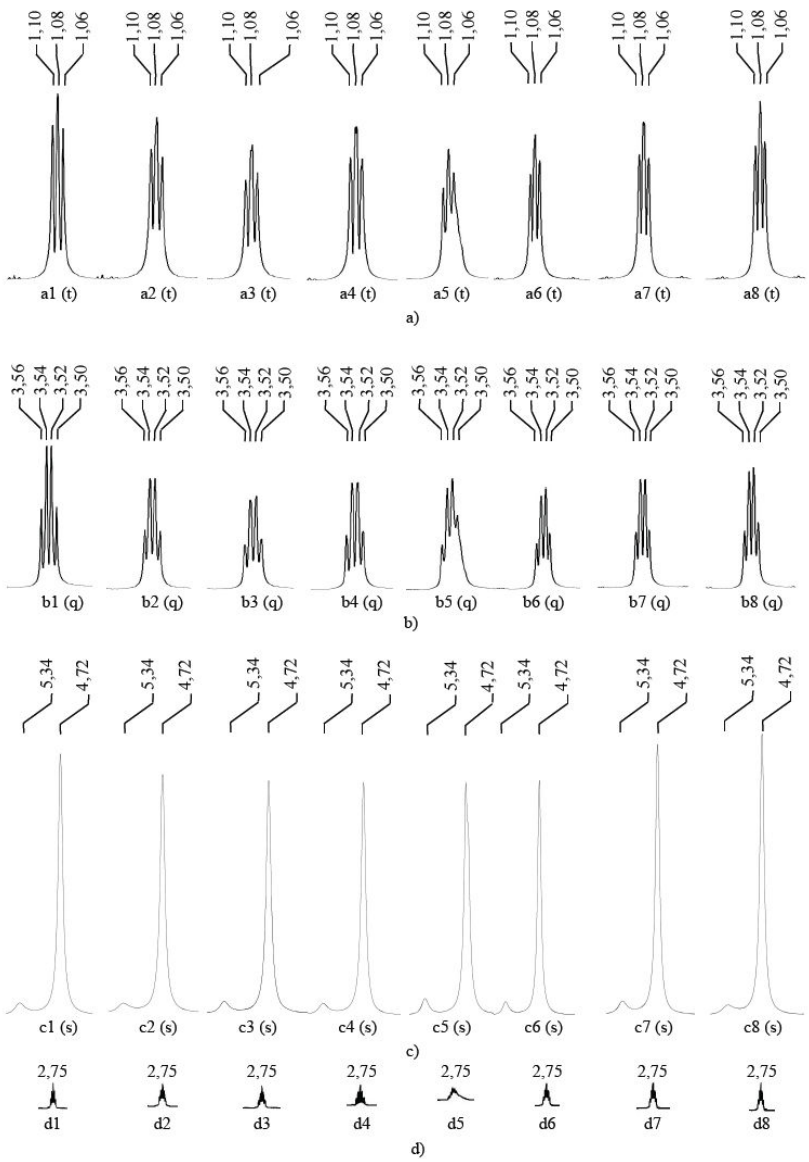

Fig. 2. Modifications of ^{1}H NMR spectra of proton groups: a - CH_3; b - CH_2; from - H_2O + EtOH; d - acetone-d_6; 1 ... 8 - number of sample (table 1)

Table 1

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

Sample number	Name	Chemical shift (δ), ppm						
		EtOH	$\Delta\delta_1$	H_2O	$\Delta\delta_2$	CH_2	$\Delta\delta_3$	CH_3
1.	Vodka «Поляна Чиста»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
2.	Vodka «Справа майстра Справжня»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
3.	Vodka «Medoff Класик»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
4.	Flavored vodka «Хлібна сльоза»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
5.	Vodka «Істинна Срібна»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
6.	Flavored vodka «Вдала Житня»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
7.	Vodka «Біленька Пшенична нива»	5,34	0,62	4,72	1,19	3,53	2,45	1,08
8.	Vodka «Статус Класичний»	5,34	0,62	4,72	1,19	3,53	2,45	1,08

apart from methylene group (CH_2) can affect methyl group (CH_3). Thus, methyl group of protons (CH_3) is located in a strong field with an average value of chemical shift δ_{CH3}=1,08 ppm that has individual characteristics of chemical shift of peaks δ_{CH3}=(1,10; 1,08; 1,06) ppm. The distance between each peak of quartet is 0,02 ppm.

The analysis of ^1H NMR spectra of methylene group's protons CH_2 (figure 2, b1-b8) indicates that the group is represented as a quartet (q) with intensity (1:3:3:1). This is confirmed by the spin-spin interaction of protons of methyl (CH_3) group. This group has to split signal of the methylene group (CH_2) into four components and form a quartet (q) with intensity ratio of 1:3:3:1. In turn, the protons of hydroxyl (OH) groups should split every component of methylene (CH_2) group's quartet into two components and form a double quartet. The absence of spin-spin interaction between hydroxyl (OH) and methylene (CH_2) groups should make signal of methylene (CH_2) group a quartet by means of chemical exchange between these groups.

At the same time methylene group of protons (CH_2) is located in a weak field, with an average value of chemical shift δ_{CH2}=3,53 ppm (table 1), with individual chemical shifts of quartet's peaks (q) 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 of water (H_2O) in each sample is $\Delta\delta_2$=1,19 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.

Fundamentally new aspects that are related to an internal mechanism of unsteady 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 H_2O+EtOH in hydroxyl group. Unsteady and transient equilibrium is characterized by the presence of two separate signals of H_2O and EtOH 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 authors express their gratitude to the participants of the experimental studies: Sujkov S. - senior researcher at the Institute of Physical-Organic Chemistry and Coal Chemistry named after L.M. Litvinenko NAS Ukraine, Ph.D. (Chem.), senior researcher, (Donetsk, Ukraine); Onosova I. - associate professor of merchandising and examination of food, Donetsk National University of Economics and Trade named of Mykhailo Tugan-Baranovsky (Donetsk, Ukraine), Ph.D. (Econ.), associate professor. The authors thank Mukherjee O. for adapting translation.

References

The State Committee for Standardization Metrology and Certification of Ukraine, (1995). *DSTU 3297:95 Alcoholic beverage industry. Terms and definitions*. Kyiv: Government of Ukraine.

Kuzmin, O., Topol'nik, V. and Sujkov, S. (2013) ^1H NMR analysis of the aqueous-alcoholic mixtures, prepared with drinking water of south-eastern region of Ukraine. *The Advanced Science Journal*, 2013(8) pp. 21-31.

Kuzmin, O., Sujkov, S. and Topol'nik, V. (2013) The change of the hydroxyl protons in aqueous alcoholic mixtures under the process of making vodkas. *The Advanced Science Journal,* 2013(Special Issue for China), pp. 15–27.

Kuzmin, O. et al. (2014) ^1H NMR analysis of the aqueous-alcoholic mixtures, prepared with softened water using Na-cationization. *The Advanced Science Journal,* 2014(7) pp. 9–14.

Kuzmin, O., et al. (2014) ^1H NMR analysis of the aqueous-alcoholic mixtures, prepared in demineralized by reverse osmosis water. *The Advanced Science Journal*, 2014(Special Issue for China), pp. 235–240.

Kuzmin, O.V. (2014) Usage of ^1H NMR spectroscopy in the process of creating vodkas. *Visnyk Donetskoho natsionalnoho universytetu ekonomiky i torhivli imeni Mykhaila Tuhan-Baranovskoho*, 2014(61) pp. 169-184.