EDUCTION OF TRANSITIONAL EQUILIBRIUM IN VODKAS BY MEANS OF $^1$H NMR SPECTROSCOPY

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Abstract: The aim of this publication is to identify transitional equilibrium of hydroxyl proton of ethanol and water in various vodkas and flavored vodkas produced in Ukraine. The methods 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 transitional thermodynamic equilibrium in the finished product - vodka or flavored vodka. Transitional equilibrium is characterized by the presence of two separate signals $^2$H$^2$O and EtOH. Also the transitional equilibrium assumes a presence of a subtle signal of EtOH. Presence of this signal characterizes transition from steady to unsteady equilibrium.

Keywords: $^1$H NMR spectroscopy, hydroxyl group, methylene group, methyl group, transitional thermodynamic equilibrium, vodka.

Introduction

In accordance to the requirements Ukraine’s normative documents (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.

$^1$H NMR research of AAM has been previously conducted and described in the work of Kuzmin O. et al, (2013 and 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$_2$O 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$_2$O+(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, experimental evidence of steady / unsteady thermodynamic equilibrium of AAM was established in the work of Kuzmin O. et al (2013-2014). 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 transitional 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 transitional thermodynamic equilibrium to insure provision of high quality characteristics of finished products (vodka, flavored vodka).

The aim of this work is to identify transitional 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.
This group has included 8 samples of vodkas of different manufacturers, brands, names and formulations in Ukraine.

Work methodology: volumetric pipette is 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-d₆) of NMR’s deuterium stabilization spectrometer is added into an ampoule in a special form capillary. ¹H 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 ¹H NMR spectroscopy. These samples were divided into 3 groups with unsteady equilibrium, transitional and steady equilibrium of protons’ hydroxyl group.

In this paper, we will study only second group of vodkas and flavored vodkas with transitional equilibrium. This group has included 8 samples of vodkas of a different manufacturers, brands, names and formulations (figure 1).

![Vodkas and flavored vodkas samples](image)

**Fig. 1. Vodkas and flavored vodkas samples**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Name</th>
<th>The chemical shift (δ), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flavored vodka «Українська березова особлива»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>2</td>
<td>Vodka «Green Day»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>3</td>
<td>Vodka «Перепилка Класична»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>4</td>
<td>Flavored vodka «Чиста сльоза М'яка»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>5</td>
<td>Vodka «Хуторок Експортна»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>6</td>
<td>Flavored vodka «Пшениця українська відбірна»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>7</td>
<td>Vodka «Мороша Карпатська»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>8</td>
<td>Vodka «Луга-Нова Російська»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>9</td>
<td>Flavored vodka «На березових бруньках»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>10</td>
<td>Flavored vodka «Луга-Нова Біла королева»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
<tr>
<td>11</td>
<td>Vodka «Українка Джерельна»</td>
<td>5.34, 0.59, 4.75, 1.22, 3.53, 2.45, 1.08</td>
</tr>
</tbody>
</table>

Table 1

Figure 2 shows one-dimensional proton spectra of vodkas and flavored vodkas for the following groups of protons: CH₃; CH₂; H₂O; EtOH; acetone-d₆. The general characteristic of the obtained spectra is presented in table 1. where Δδ₁ – is deviation between chemical shifts of protons’ hydroxyl group of ethanol (EtOH) and water (H₂O), Δδ₂ – is deviation between chemical shifts of proton’s hydroxyl group of water (H₂O) and a methylene group of protons of ethanol (CH₂), Δδ₃ – is deviation between chemical shifts of ethanol’s methylene group of protons (CH₂) and ethanol’s methyl group of protons (CH₃).
**Discussion**

In this work we will examine spectra of hydroxyl group. 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 (H$_2$O+EtOH) therefor hydroxyl group of protons is presented by two separate picks of H$_2$O and EtOH (figure 2, c1-c11). Component of multiplet of hydroxyl (OH) protons of ethanol (EtOH) in each sample is represented as a separate subtle signal of a rounde d shape located in a «weak field» with a chemical shift $\delta_{\text{EtOH}}=5,34$ ppm (table 1).

Component of proton of water (H$_2$O) in each sample is represented as a singlet with a chemical shift $\delta_{\text{H2O}}=4,75$ ppm. Waveform of H$_2$O 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 OH-proton (EtOH) and proton of water (H$_2$O) in each sample is $\Delta\delta=0,59$ ppm. This may indicate that certain prerequisites are created to establish equilibrium structure (unsteady/steady equilibrium).

Analysis of $^1$H NMR-spectra of methyl group of protons CH$_3$ (figure 2, a1-a11). Methyl group of protons (CH$_3$) in each sample is located in a strong field and represented as a triplet (t) with a relative intensity of (1:2:1). The average value of chemical shift is $\delta_{\text{CH3}}=1,08$ ppm (figure 1). Individual characteristics of each chemical shift’s peak is $\delta_{\text{CH3}}=(1,10; 1,08; 1,06)$ ppm. The distance between each peak of quartet is 0,02 ppm.
1H NMR spectra of proton’s methylene group (CH\textsubscript{2}) is shown on a figure 2, b1-b11. The group is represented as a quartet (q) with intensity ratio of (1:3:3:1) and average value of chemical shift of δ\textsubscript{CH2}=3.53 ppm (figure 1). Individual chemical shifts of quartet’s peaks are δ\textsubscript{CH2}=(3.56, 3.54; 3.52; 3.50) ppm. The distance between each peak of quartet is 0.02 ppm.

The difference between the chemical shifts of ethanol’s protons of methylene group (CH\textsubscript{2}) and hydroxyl group of water (H\textsubscript{2}O) in each sample is Δδ=1.22 ppm. The difference between the chemical shifts of ethanol’s protons of methylene group (CH\textsubscript{2}) and methyl group of ethanol (CH\textsubscript{3}) in each sample is Δδ=2.45 ppm.

Fundamentally new aspects that are related to an internal mechanism of transitional thermodynamic equilibrium in 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\textsubscript{2}O+EtOH in hydroxyl group. Unsteady and transient equilibrium is characterized by the presence of two separate signals of H\textsubscript{2}O 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.

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References