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^{1}H NMR ANALYSIS OF THE AQUEOUS-ALCOHOLIC MIXTURES, PREPARED WITH SOFTENED WATER USING NA-CATIONIZATION

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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 (softened by using Na-cationization) 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 definition 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 water and ERS. We have experimentally established the dependence rate of accomplishment of thermodynamic equilibrium and its character, as well as obtaining conditions od optimal organoleptic characteristics of AAM prepared with the softened water using Na-cationization and ERS.

Introduction

NMR spectroscopy is widely used in physics research. 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.

The first ^{1}H NMR spectra of H_2O were obtained in 1946 (Bloch et al, 1946). The first ^{1}H NMR spectra of ethanol C_2H_5OH were developed in 1951 (Arnold et al, 1951). At the first glance, it may seem that these are fairly simple organic molecules, at the same time NMR spectroscopy exhibits grate variety (Nose et al, 2005; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) in such characteristics as chemical shift, spin-spin interactions and the effect of chemical exchange.

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 (Roberts, 2002). “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 (Richards, Hollerton, 2011). 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 (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. The 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.

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

The preliminary conducted ^{1}H NMR studies, which are described in a work (Kuzmin O., Sujkov S., Topol'nik V., 2013), 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 balance depending on the transformation of hydroxyl protons’ of ethanol and

water. Systems with unsteady balance typical for AAM used with ERS «Lux» and drinking water, with a tasting score – 9,43 points. This also includes the AAM made from ERS «Lux» and demineralized by the reverse osmosis water, with a tasting score – 9,30 points. Systems with a steady balance that are typical for AAM made of ERS «Lux» and water softened by Na- cationization, with tasting score – 9,49 points were defined.

Thus, in the work (Kuzmin O., Sujkov S., Topol'nik V., 2013) established experimental evidence of instalment nature / (non- instalment) of thermodynamic balance, taking into account the organoleptic characteristics of AAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the AAM are remain unsolved.

Therefore, the additional research is required for a detailed study of internal mechanism of thermodynamic balance and insurance in obtaining high quality vodka products - for each type of water separately.

Thus, the conducted earlier ^{1}H NMR research (Kuzmin O., Topol'nik V., Sujkov S., 2013) to study the AAM prepared with the usage of drinking water of south-eastern region of Ukraine allows us to assert that between the characteristics of ^{1}H NMR spectra of AAM traced a definite connection. Thus, the presence of such features as separate signals of OH protons' of H_2O and EtOH and abnormal waveforms of CH_3 and CH_2 characterize a product with lower tasting qualities. The presence of a combined signal H_2O+(EtOH) as well as rational form of CH_3 and CH_2 signals (triplet form of the methyl group, the quartet form a methylene group) – characterized AAM as a product with a better tasting qualities. The exchange rate of hydroxyl proton (OH) of ethanol in the first 48 hours is located in a transitional area where a separate observation of signals is possible. The protons' exchange is accelerated in interval from τ=48 h to 120 h due to the rearrangement in system's structure. Starting from τ=120 h, only single common signal of asymmetric shaped mobile protons is observed. Chemical shift's value of a summary signal $\delta_{H2O+(EtOH)}$ =4,74 ppm (τ=120 h) gradually begins to grow and becomes a «weak field» with a value: $\delta_{H2O+(EtOH)}$=4,79 ppm (τ = 312 h).

Therefore, the aim of this work is implementation of a next stage - detailed study of mechanisms of transformation of ethanol protons (ERS) and water (softened by the Na-cationization) in the process of AAM creation.

Method

^{1}H NMR analysis of the AAM 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). Physicochemical and organoleptic qualities of alcohol, water and AAM were carried out in laboratory of the following enterprises: LLC «Donetsk factory of liquor-vodka «Lik», Donetsk regional water test center.

^{1}H NMR analysis of AAM was conducted with the usage of the following: FT-NMR Bruker Avance II spectrometer 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; ERS of class «Lux» as per DSTU 4221:2003, used at LLC «Donetsk factory of liquor-vodka «Lik»; softened water as per GOST 2874-82, prepared by communal enterprise «Company «Voda Donbassa»; AAM model from ERS «Lux» and softened by Na-cationization water.

Work technique: 0,3 ml of AAM prepared with a volumetric pipette at 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.

Results

The following characteristics of water softened by Na-cationization in accordance to SOU 15.9-37-237:2005, were determind: solid residual – 695 mg/dm^3; electrical conductivity – 1070 μS/cm; pH – 6,71; ORP – "+" 288 mV; total hardness – <0,05 mM/dm^3; permanganate oxidability – 2,36 mg O_2/dm^3; MC of sodium – 266,1 mg/dm^3; MC of potassium – <2,0 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – <2,0 mg/dm^3; MC of magnesium – <2,0 mg/dm^3; total alkalinity – 4,12 mM/dm^3.

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. %.

AAM made of EAR of class "Lux" and process water softened by Na-cationization has the following characteristics: alcoholic strength – 39,85 % vol.; electrical conductivity – 255 μS/cm; ORP – "-" 35 mV; pH level – 7,84; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,3 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,4 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,4 mg/dm^3; content of methanol in anhydrous alcohol – 0,0020 % vol.; alkalinity – 2,4 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 of sorting; oxidability test – 9 min.; taste evaluation – 9,49 points (appearance – colourless liquid without sediment; odor – strong alcoholic; taste – bitterish, softened).

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

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
Chemical shift (δ), ppm	CH_3	1,07	1,07	1,07	1,07	1,08	1,08
Chemical shift (δ), ppm	CH_2	3,53	3,53	3,53	3,53	3,54	3,54
Chemical shift (δ), ppm	H_2O+(EtOH)	4,76	4,81	4,79	4,78	4,82	4,80
Organoleptic evaluation of AAM, point		9,47	9,48	9,48	9,48	9,49	9,49
- appearance		colorless liquid with no sediment					
- odor		sharp, alcohol					
- taste		bitterish				bitterish, softened	

Discussion

Will examine spectra of hydroxyl group of water (H_2O), alcohol (EtOH), AAM (H_2O+EtOH), prepared with the usage of softened water, using Na-cationization and ERS «Lux» at different times of operation (life after mixing).

At the initial time of AAM formation- operation of the system (τ=0 h), hydroxyl protons' group is represented by a single summary peak - OH of ethanol (EtOH) and water (H_2O). Components of OH proton of H_2O and OH proton of C_2H_5OH are represented as the joint singlet H_2O+(EtOH), with a chemical shift $\delta_{H2O+(EtOH)}$=4,76 ppm. The form of joint singlet is distorted Gaussian curve, with a broader base and a certain asymmetry of apex.

The second spectrum (τ=48 h) is also characterized by a single summary peak - OH of ethanol (EtOH) and water (H_2O). Its' form is a symmetric singlet. The hydroxyl group of protons has shifted towards weak field at $\Delta\delta_0$=0,05 ppm with a chemical shifts $\delta_{H2O+(EtOH)}$=4,81 ppm relatively to the initial position (τ=0 h) . The form a summary H_2O+(EtOH) signal is distorted Gaussian curve, with a broader base and a partial asymmetry of apex.

The third spectrum (τ=120 h) is characterized by a summary peak of OH of ethanol (EtOH) and water (H_2O). The components of OH-proton of H_2O and OH-proton of C_2H_5OH represented as a mutual singlet H_2O+(EtOH). The hydroxyl group of protons has also shifted towards weak field at $\Delta\delta_0$=0,03 ppm with a chemical shifts $\delta_{H2O+(EtOH)}$=4,79 ppm relatively to the initial position (τ=0 h). The form of a summary singlet - distorted Gaussian curve, with a broader base and partial asymmetry of apex.

The fourth spectrum (τ=192 h) is characterized by a single summary peak of OH-proton (H_2O+EtOH), which is represented as a symmetric singlet. The hydroxyl group of protons has shifted towards weak field at $\Delta\delta_0$=0,02 ppm with a chemical shifts $\delta_{H2O+(EtOH)}$=4,78 ppm relatively to the initial position (τ=0 h). The form the summary H_2O+(EtOH) signal is distorted Gaussian curve, with a broader base and partial asymmetry of apex.

A characteristic feature of the first four spectra of OH-proton (EtOH+H_2O) of AAM is that the spectra is located in a range of chemical shift's value of δ=4,76...4,81 ppm. The time of system's life after the mixing is τ=0...192 h. The form of a summary signal of H_2O+(EtOH) for all the samples is distorted Gaussian curve, with a broader base and partial asymmetry of apex. The absence of separate peaks of OH ethanol (EtOH) and water

(H_2O) may indicate that the initial stage of AAM creation (τ=0 h) has set conditions for the formation of an equilibrium structure of AAM.

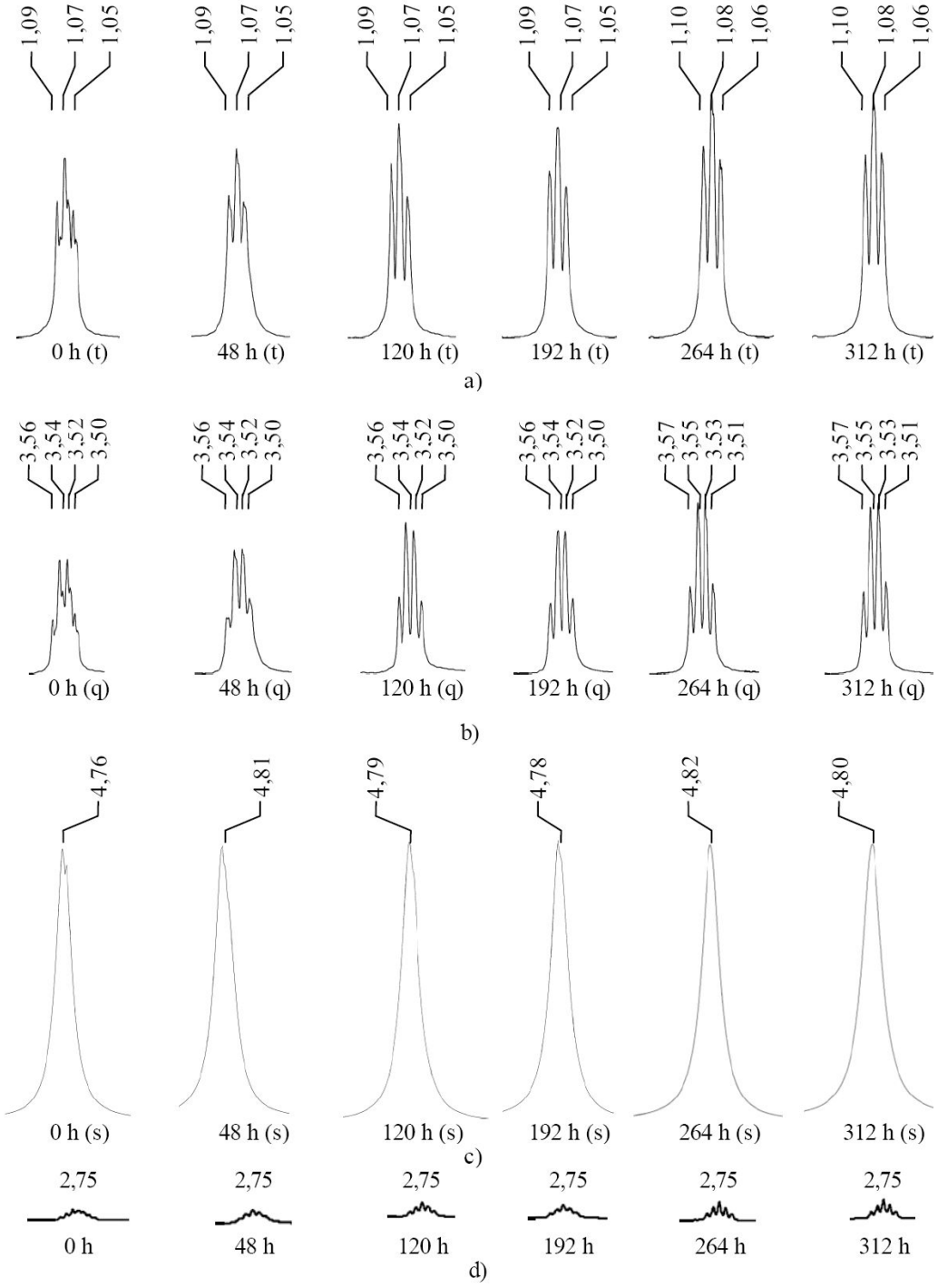

Figure 1. Modifications of ^1H NMR spectra of AAM's proton groups prepared with softened water using Na-cationization and ERS «Lux»: a - CH_3; b - CH_2; c - H_2O+(EtOH); d - external standard (acetone-d_6), depending on operation system time.

Fifth spectrum (τ=264 h) is characterized by a single summary peak - H_2O+(EtOH) as a singlet. The hydroxyl group of protons has shifted to the weak field at $\Delta\delta_0$=0,06 ppm with a chemical shifts $\delta_{H2O+(EtOH)}$=4,82

ppm relatively to the initial position (τ=0 h). The form of a summary signal is symmetric with a broader base and the apex of a regular shape.

The sixth spectrum (τ=312 h) is characterized by a single summary peak H_2O+(EtOH) of ethanol and water, which is represented in a form of symmetric singlet. The hydroxyl group of protons shifted to the weak field at $\Delta\delta_0$=0,04 ppm with chemical shifts $\delta_{H2O+(EtOH)}$=4,80 ppm relatively to the initial position (τ=0 h). The form of a summary signal is symmetric with a broader base and the apex of a regular shape.

The characteristic feature of the last two spectra of OH proton H_2O+(EtOH) of AAM, that were in the range of δ=4,80...4,82 ppm with the system's life time after mixing of τ=264...312 h, is the shape of the summary signal. The shape is symmetrical with the broadened base and the apex's regular form. This feature guarantees the conditions for the formation of equilibrium structure of AAM.

We can make a preliminary conclusion: the instantaneous velocity of protons' exchange leads to the generalization of hydroxyl signal and the subsequent structuring of AAM system. The position of hydroxyl proton relatively to the conventional zero (τ=0 h) $\delta_{H2O+(EtOH)}$=4,76 ppm, during the lifetime of the system leads to a shift of signal towards the weak field with a divergence of $\Delta\delta_0$=(0,02...0,06) ppm.

The analysis of ^{1}H NMR spectra of proton's methyl group of AAM allows to state the following:

τ=0 h. In the initial time of system's functioning methyl group of protons (CH_3) is represented as a triplet (t), due to the spin-spin interaction with protons of adjacent methylene group (CH_2). The intensity ratio as per Pascal triangle is (1:2:1). Not a single group of protons can affect the spectra of methyl group (CH_3) besides the methylene group (CH_2). Thus, the methyl group of protons (CH_3) is located in a strong field with the average value of chemical shift as δ_{CH3}=1,07 ppm. The chemical shift has individual characteristics of chemical shift's peaks - δ_{CH3}=(1,09; 1,07; 1,05) ppm. The distance between every peak of triplet is 0,02 ppm.

τ=48...192 h. The methyl group of protons (CH_3) hasn't change it's positioning (positioning is stable) relatively to the initial position (τ=0 h). The average value of a chemical shift is δ_{CH3}=1,07 ppm. The methyl group of protons (CH_3) has the following particular characteristics of chemical shift's peaks δ_{CH3}=(1,09; 1,07; 1,05) ppm: distance between each peaks - 0,02 ppm, waveform is triplet (t).

τ=264...312 h. The methyl group of protons (CH_3) has shifted from its original position (τ=0 h) towards the weak field by 0,01 ppm. The average value of a chemical shift is δ_{CH3}=1,08 ppm. It has the following particular characteristics of chemical shift's peaks δ_{CH3}=(1,10; 1,08; 1,06) ppm: distance between each peaks - 0,02 ppm relative to each other, waveform is triplet (t).

The following initial conclusion can be made: the range (0...312 h) is characterized by a complete structuring signal of methyl group as a triplet (t) in its form and by the middle positioning of a chemical shift - δ_{CH3}=1,07…1,08 ppm, which remains unchanged. There is no abnormal change in the spectra's structure during this period of time. Its position is stable. The distance between the peaks also remain unchanged - 0,02 ppm.

The analysis of ^{1}H NMR spectra of methylene group (CH_2) reveals the following:

At the beginning of the formation of AAM (τ=0 h) methylene group of protons (CH_2) is presented as a quartet (q), which is confirmed by the spin-spin interaction of protons of methyl (CH_3) groups, that should split signal of the methylene group (CH_2) into four components, form a quartet (q) with intensity ratio of 1:3:3:1. In turn, protons of hydroxyl (OH) group should cleave every component of methylene (CH_2) group's quartet into two components to form a double quartet. The absence of spin-spin interaction between hydroxyl (OH) and methylene (CH_2) groups due to chemical exchange would have to ascertain that the signal of the methylene (CH_2) group must remain as quartet.

Methylene group of protons (CH_2) is in a weak field, with an average value of a chemical shift of δ_{CH2}=3,53 ppm, with individual chemical shifts of quartet's peak δ_{CH2}=(3,56; 3,54; 3,52; 3,50) ppm; the distance between each peak of quartet is 0,02 ppm.

τ=48...192 h. Methylene group of protons (CH_2) is in a stable position relatively to the its initial position with an average value of chemical shift as δ_{CH2}=3,53 ppm and a distance between the peaks - 0,02 ppm. Waveform is quartet (q).

τ=264...312 h. Methylene spectrum with an average value of chemical shift δ_{CH2}=3,54 ppm is shifted to the weak field by 0,01 ppm relatively to its initial position (τ=0 h). Waveform - quartet (q), which is typical for the above proton group, on the assumption of spin-spin interaction with protons of the methyl (CH_3) group and chemical exchange between the hydroxyl (OH) and methylene (CH_2) groups.

The following initial conclusion can be made: the range (0...312 h) is characterized by a complete structuring signal of the methylene group (CH_2) as quartet (q) in its form and by the middle positioning of the

chemical shift - δ_{CH2}=3,53…3,54 ppm, which remains unchanged. There is no abnormal change in the spectra's structure during this period of time. Its position is stable. The distance between the peaks also remain unchanged - 0,02 ppm.

To generalize the obtained results, we must note the presence of chemical equilibrium in thermodynamic of AAM formation process between the protons' groups of water and alcohol. Also the absence of division between hydroxyl protons of ethanol (EtOH) and water (H_2O) says about structuring of AAM. The improvement of organoleptic characteristics, based on testing evaluation of AAM and system's operation time, is characterized by a change of mark points from 9,47 to 9,49. Wherein, the external appearance is a colorless liquid with no sediment; odor – sharp and alcoholic; taste – from bitter to softened bitter.

Based on experimental data, we can conclude that in the process of creating of AAM by mixing softened by Na- cationization water with pH=6,71 and ERS «Lux» we have obtained AMM with a pH=7,84. The obtained value characterizes low content of free ions H^+ in relation to OH^- i.e. total alkaline reaction of the system. The instantaneous structuring of system occurs throughout whole length of its life (τ=0...312 h) when the concentration of alcohol remains unchanged (strength of AAM- 39,85 % vol.) and system's temperature is controlled (t=+23,5 ºC). The protons exchange is so quick that only one mutual signal of hydroxyl protons of ethanol (EtOH) and water (H_2O) is observed.

Thus, this article describes mechanisms of transformation of ethanol's protons and water softened by Na-cationization in the process of AAM creation. The paper presents experimental evidence of speed and nature of determination of thermodynamic equilibrium dependence as well as dependence of obtainment of maximized organoleptic characteristics of AAM from contact time of water and alcohol after mixing.

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