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TEMPERATURE-INDUCED EVOLUTION OF A CLUSTER STRUCTURE IN *n*-NONAN-1-OL: EXPERIMENTAL STUDY AND QUANTUM-CHEMISTRY CALCULATIONS

UDC 532.74

*It is well known that alcohols belong to the class of partly ordered liquids, which can form aggregates or clusters with different numbers of molecules. The object of our investigation is *n*-nonan-1-ol. The experimentally obtained temperature-induced evolution of *n*-nonan-1-ol in the temperature range from -20 to 0 °C is analyzed. Experimental results are compared with the results of the quantum-chemistry computer simulation. It is shown that, at the liquid-solid phase transition, one can observe a change of the cluster structure from smaller to bigger associates.*

Keywords: cluster structure, *n*-nonan-1-ol.

1. Introduction

Investigations of molecules with one or more hydroxyl groups are a promising, topical, and popular field of research in modern physical science. There are many articles devoted to the research of partly ordered liquids (water, alcohols, *etc.*) in different scientific journals [1–6], and a lot of scientific groups present their reports every year at various workshops and conferences all around the world.

The substances with hydrogen bonds are interesting not only for physicists, chemists, and other scientists, but they also are very important for industrial and technical applications. Methanol and other alcohols are widely used in medicine, food industry, cosmetic and perfumery industries as solvents, various industrial chemical processes, for example, in the synthesis of polymer materials, *etc.* That is why these substances are in focus of our interest.

Experimental and theoretical investigations of alcohol molecules bigger than methanol and ethanol are not so popular, because they are more complicated. We have not seen any articles about the cluster structure of *n*-nonan-1-ol at all. Thus, *n*-nonan-1-ol is an object of our research. Its molecule is schematically shown in Fig. 1.

Vibrational spectroscopy is the most powerful and informative experimental tool for the investigation of

molecular structures and particularly for the study of intra- and intermolecular hydrogen bonds. Our previous works were devoted to the cluster structure of partly ordered liquids studied by experimental and theoretical methods and techniques [7–10]. In this paper, the analysis of the temperature-induced evolution of the cluster structure in *n*-nonan-1-ol and quantum-chemistry calculations for this substance are presented.

2. Experimental and Calculation Details

All experimental spectra presented in our article were registered in the Laboratory of Fourier-transform infrared (FTIR) absorption spectroscopy at the Vilnius University (Lithuania). Liquid *n*-nonan-1-ol with purity >99.9% from Fluka was used as-received. The spectra were registered by the attenuated total reflection (ATR) method, by using a FTIR spectrometer VERTEX 70 from Bruker in the spectral region from 500 to 4000 cm^{-1} . A single-pass ZnSe ATR crystal was used for capturing the ATR spectra. The incidence angle of an IR beam was set to 70 degree, which insured the total reflection from the ZnSe/alcohol interface. The spectral resolution was set to 1 cm^{-1} . In order to increase the signal-to-noise ratio, each spectrum was taken as an average of 64 scans. The spectrometer was equipped with a liquid-N₂-cooled mercury cadmium telluride (MCT) detector. The Blackman–Harris 3-term apodization function was used during the processing of interferograms. The inves-

tigations were carried out in the temperature range from -20 to 0 °C. A LINKAM cryostat (model FTIR 600) was used for the thermostabilization.

To make our analysis of experimental data more detailed, the quantum-chemistry calculations were made, by using the Gaussian 03 software and the B3LYP functional of DFT with basis set 6-31G(d,p).

3. Results and Discussion

In Fig. 2, *a*, the temperature-induced evolution of the registered FTIR spectra of *n*-nonan-1-ol in the spectral region 900 – 1200 cm^{-1} is presented. One can observe some changes in the structure of the registered bands at the temperature changing from -20 to 0 °C (melting point is -10.6 °C). For example, we can observe the disappearing of bands at 915 , 965 , 1015 and 1120 cm^{-1} . The bands in the region from 1025 to 1100 cm^{-1} lose their structured form, and the peak near 1060 cm^{-1} shifts toward 1055 cm^{-1} .

In Fig. 3, *a*, the temperature-induced evolution of the registered FTIR spectra of *n*-nonan-1-ol in the spectral region 3000 – 3700 cm^{-1} is presented. This is the spectral region of O–H stretching vibrations. Here, we can see drastic changes near the temperature of the solid-liquid-phase transition. The position of the maximum shifts toward the high frequency region, as the temperature increases.

The calculated IR spectra for different cluster structures (from monomeric to tetrameric) of *n*-nonan-1-ol in the spectral region from 3000 to 3700 cm^{-1} are presented in Fig. 4. These spectra were scaled due to the half-width and position of the C–H₂ and C–H₃ stretching vibration bands, which are constant for all temperatures in the experiment.

The absence of the free O–H vibration band can be easily seen from the experimental data. As a result, we can conclude that there are no monomeric, dimeric, or chain structures in the condensed phase of *n*-nonan-1-ol. In this case, we can use the results of calculations for bigger clusters only and ignore the chain clusters with free O–H bonds. In addition, our calculations have shown that the cyclic clusters are more energetically favorable than the chain ones. These facts confirm the consistency of the obtained theoretical results.

In Figs. 5, 6, and 7, the experimentally obtained FTIR spectra at various temperatures are compared

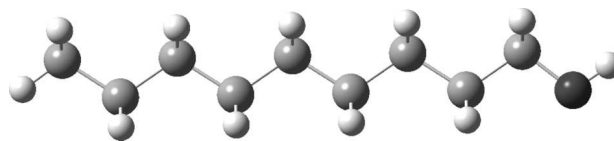


Fig. 1. Molecule of *n*-nonan-1-ol

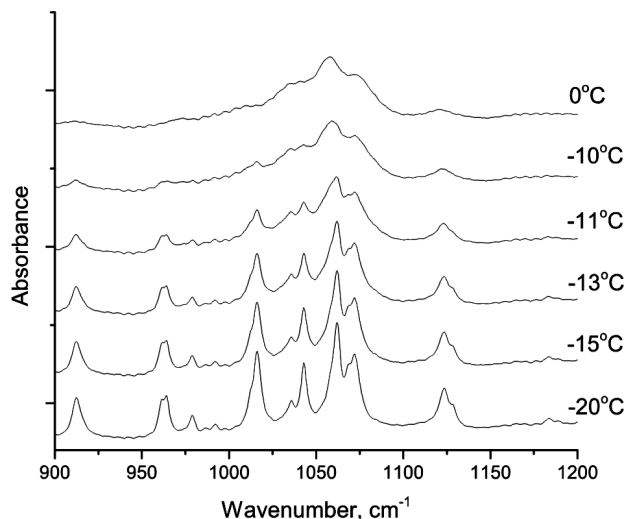


Fig. 2. Experimental FTIR spectra of *n*-nonan-1-ol for various temperatures in the spectral region 900 – 1200 cm^{-1}

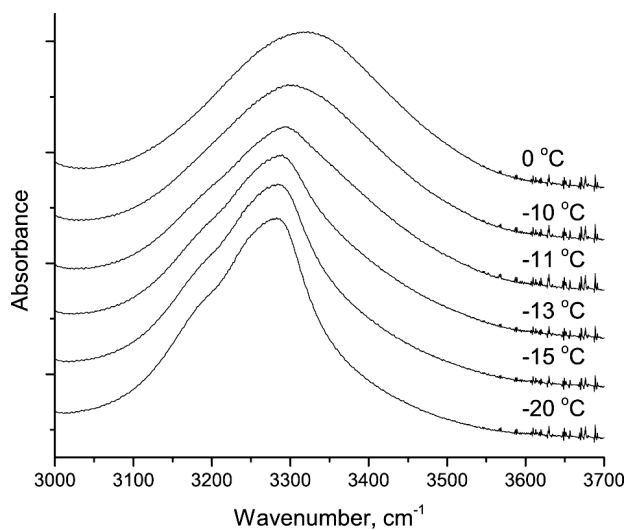


Fig. 3. Experimental FTIR spectra of *n*-nonan-1-ol for various temperatures in the spectral region 3000 – 3700 cm^{-1}

with the calculated data for *n*-nonan-1-ol in the O–H stretching region.

From Fig. 5, it is obvious that, in the spectrum of liquid *n*-nonan-1-ol, there is a wide band with a max-

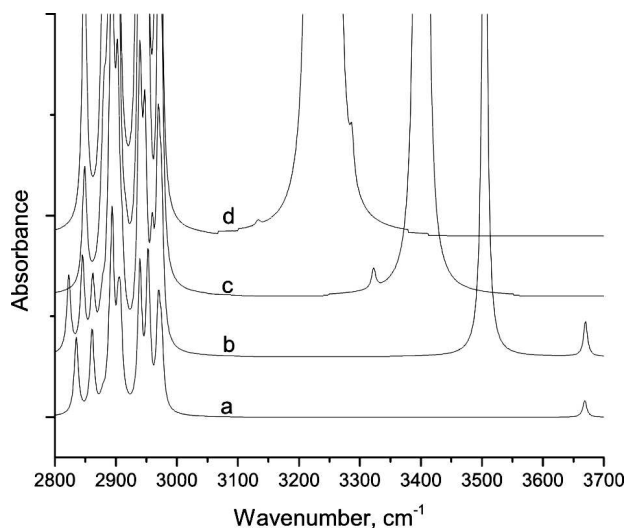


Fig. 4. Calculated IR spectra for different clusters (monomer *a*, dimer *b*, trimer *c*, and tetramer *d*) in the spectral region 3000–3700 cm^{-1}

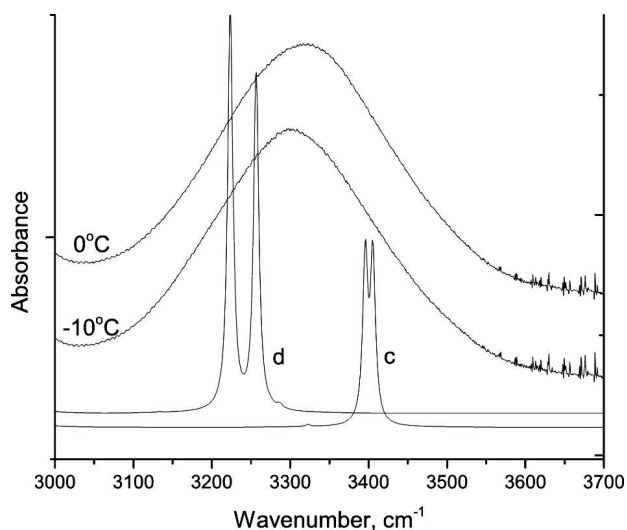


Fig. 5. Comparison of experimental FTIR spectra at 0 and $-10\text{ }^{\circ}\text{C}$ with the calculated ones for a trimer (*c*) and a tetramer (*d*) in the O–H stretching region

imum at higher frequencies (3318 cm^{-1} at $0\text{ }^{\circ}\text{C}$ and 3300 cm^{-1} at $-10\text{ }^{\circ}\text{C}$), than that of O–H vibrations for a tetrameric cluster (bands with the highest intensity at 3223 and 3257 cm^{-1}). On the other hand, the bands of O–H vibrations for a trimer (3396 and 3405 cm^{-1}) are by 1.77–2.09 times weaker than those for a tetramer. In addition, the experimental band is symmetric relative to the maximum. These facts

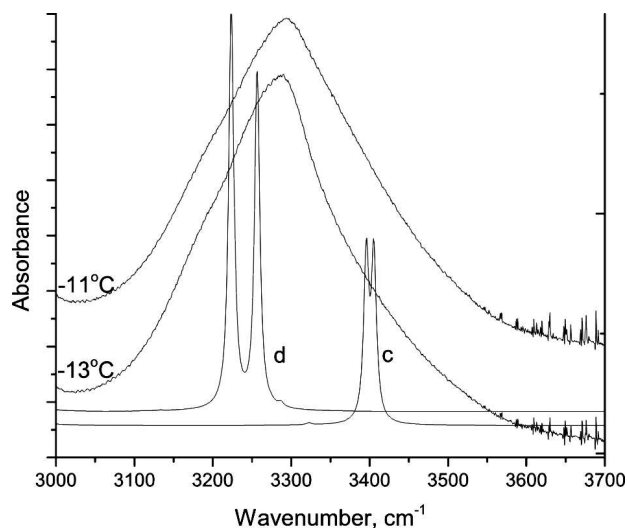


Fig. 6. Comparison of experimental FTIR spectra at -11 and $-13\text{ }^{\circ}\text{C}$ with the calculated ones for a trimer (*c*) and a tetramer (*d*) in the O–H stretching region

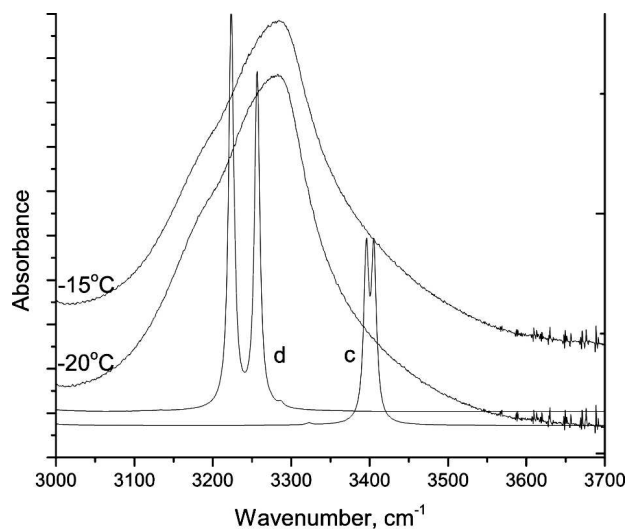


Fig. 7. Comparison of experimental FTIR spectra at -15 and $-20\text{ }^{\circ}\text{C}$ with the calculated ones for a trimer (*c*) and a tetramer (*d*) in the O–H stretching region

show us that the amount of trimers is much bigger than that of tetramers (not less than by 2.5 times).

At $-10\text{ }^{\circ}\text{C}$, we can observe a small red shift in experimental FTIR spectra, which indicates a redistribution of the amounts of clusters. At this temperature, a quantity of tetramers grows up.

After the phase transition at $-11\text{ }^{\circ}\text{C}$ (Fig. 6), we can observe significant changes in the spectral struc-

ture, e.g., changes of a half-width of the O–H vibrational band, namely a transformation to a more complex band with wide wing at lower frequencies. Moreover, the symmetry of the band relative to the maximum breaks. Such changes are clear signs of the cluster redistribution.

At $-13\text{ }^{\circ}\text{C}$, the process of cluster redistribution continues. A new peak (at about 3180 cm^{-1}) appears at the wing of the O–H vibrational band, and the main peak shifts to 3285 cm^{-1} (33 cm^{-1} -shift from the 3318 cm^{-1} position at $0\text{ }^{\circ}\text{C}$). The subsidence of the high frequency wing shows that the amount of trimeric clusters slumps.

After the cooling to -15 and $-20\text{ }^{\circ}\text{C}$ (Fig. 7), changes become more significant. We can observe the almost complete absence of trimeric clusters. On the other hand, the band becomes wider and structured on the both sides of the calculated frequencies for a tetrameric cluster. Such big half-width of the vibration band can be explained by the presence of different conformers of tetrameric clusters. Moreover, a higher intensity of the high-frequency band in the experiment means that this band is common for all conformers unlike the low-frequency band.

4. Conclusions

It is shown that there is no absorption band corresponding to the free O–H stretching vibrations (near 3670 cm^{-1}) in the experimental spectrum of *n*-nonan-1-ol. This fact indicates a lack of monomeric and dimeric structures in a condensed phase of *n*-nonan-1-ol.

At the liquid–solid phase transition, we can observe a change of the cluster structure from trimers to tetramers. It is important to note that similar investigations of the temperature-induced evolution of the cluster structure for smaller alcohols (methanol, ethanol, *etc.*) have demonstrated the opposite result

(smaller clusters for the solid phase and bigger ones for the liquid one).

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ТЕМПЕРАТУРНА ЕВОЛЮЦІЯ
КЛАСТЕРНОЇ СТРУКТУРИ *n*-НОНАН-1-ОЛУ:
ЕКСПЕРИМЕНТАЛЬНЕ ДОСЛІДЖЕННЯ
ТА КВАНТОВО-ХІМІЧНІ РОЗРАХУНКИ

Резюме

Як відомо, спирти належать до частково впорядкованих рідин, які можуть формувати агрегати – кластери з різною кількістю молекул в них. На даний момент об'єктом наших досліджень є *n*-нонан-1-ол. В цій роботі ми представляємо експериментально отримані дані про температурну еволюцію *n*-нонан-1-олу для температур від -20 до $0\text{ }^{\circ}\text{C}$. Ми порівнюємо наші результати з результатами квантово-хімічного комп'ютерного моделювання. Результати наших досліджень показали, що при фазовому переході рідина–тверде тіло спостерігається зміна кластерної структури від менших кластерів до більших. З іншого боку, для менших спиртів спостерігається протилежний результат – менші кластери для твердої фази і більші для рідкої.