Microheterogeneity in CH₃OH/CD₃OH mixture

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A B S T R A C T

Recently, we demonstrated the presence of microheterogeneity in binary mixtures of unlike alcohols. [*RSC Adv.* 2016, 6, 37195–37202] The aim of this work was examination if this phenomenon occurs also in the mixture of very similar alcohols like CH₃OH and CD₃OH. Theoretical calculations suggest that the isotopic substitution in methyl group influences properties of the OH group. Hence, one can expect that this effect may lead to partial separation of CH₃OH and CD₃OH at a molecular level and it contributes to deviation from the ideal mixture. This work evidences that CH₃OH/CD₃OH mixture also deviates from the ideal one, but the extent of this deviation is much smaller as compared with the mixtures of other alcohols. It is of particular note that this deviation results mainly from the difference between the CH₃ and CD₃ groups, while the contribution from the OH groups is small. The structure of CH₃OH/CD₃OH mixture at a molecular level is similar to the structure of binary mixtures of other alcohols. The mixture is composed of the homoclusters of both alcohols and the mixed clusters. The homoclusters existing in the mixture are similar to those present in bulk alcohols. The highest population of the heteroclusters and the largest deviation from the ideal mixture were observed at equimolar mixture. Both the experimental and theoretical results reveal that in CH₃OH/CD₃OH mixture dominate the cyclic tetramers and larger clusters, while the population of the linear clusters is negligible. Though the extent and strength of hydrogen bonding in both alcohols are the same, the position and intensity of the $2\nu(OH)$ band for CH₃OH and CD₃OH are different. We propose possible explanation of this observation.

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1. Introduction

Mello et al. reported separation at a molecular level for macroscopically homogeneous mixture of methanol with ethanol [1]. Based on two-dimensional (2D) correlation analysis of concentration-dependent Raman spectra the authors suggested presence of separate methanol and ethanol clusters. Recently, microheterogeneity in this mixture was confirmed by MIR/NIR spectroscopy coupled with 2D correlation analysis and chemometrics methods [2]. In addition, it was demonstrated that this effect is also present in the mixtures of methanol with short chain aliphatic alcohols [2]. As shown, in the binary mixtures of alcohols exist homoclusters of both alcohols in equilibrium with heteroclusters. The largest population of the heteroclusters was found at equimolar mixture. At the same composition was observed the highest degree of deviation from the ideal mixture. The extent of this deviation was shown to increase with the chain length and the order of the alcohol.

The structure of liquid methanol was a subject of numerous experimental and theoretical studies [3–12]. A vibrational overtone study of liquid methanol by Bourdéron et al. demonstrated the presence of

oligomers and monomers [3,4]. In contrast, in the fundamental region occurs a strong and broad band due to polymeric species. Comparing X-ray emission spectra with DFT calculations Kashtanov et al. reported that liquid methanol is a combination of rings and chains clusters, dominated by six and eight methanol units [5]. The theoretical calculations (DFT and quantum cluster equilibrium) by Ludwig suggested that in liquid methanol appear mainly cyclic and/or lasso structures [6]. The cyclic hexamer is the most highly populated cluster, followed by the cyclic pentamer. On the other hand, the linear structures fail to fit experimental values. Another DFT studies by Boyd and Boyd demonstrated that the cyclic clusters of five to six methanol molecules are the most stable structures and they are sufficient to mimic the liquid methanol behaviour [7]. In contrast, Zoranic et al. concluded from molecular dynamics study that methanol is weakly associated liquid, forming different open and closed chainlike structures [8]. Neat methanol in the liquid phase is partially or fully microstructured under ambient conditions, and this phenomenon results from the local heterogeneity. Lin et al. recorded temperature-dependent Raman spectra of liquid methanol from 3000 to 3700 cm⁻¹ [9]. The authors identified four components in the spectra. These components were assigned to chain/ring trimer, chain tetramer and chain pentamer and they consist of >50% of total clusters. The comprehensive theoretical study by Vrhovšek et al. reveals that

cyclic clusters are important constituents of liquid methanol structure (10–35% depending on the model) [10]. Linear chains are smaller than the cyclic and acyclic branched clusters. A statistical model of hydrogen bonds in liquid methanol used by Sillrén et al. has shown that an average cluster size is close to six [11]. Yet, the authors do not provide information on the structure of these clusters. The recent study of methanol and methanol/water clusters in helium nanodroplets by MIR spectroscopy and DFT calculations reveals that starting from the trimer all larger clusters have cyclic structure [12].

Our previous results evidenced the existence of microheterogeneity in binary mixtures of methanol with different aliphatic alcohols [2]. In this work we examine if this phenomenon is also present in the mixture of very similar alcohols like methanol/methanol d_3 and what is an extent of this separation at a molecular level. Methanol is the simplest alcohol and its vibrational spectra are not complicated by presence of different conformational rotamers. Besides, due to small size of methanol molecule, the theoretical modeling of its clusters is not as demanding as that of the higher alcohols. It seems that CH_3OH/CD_3OH mixture should be close to the ideal mixture since both alcohols have similar properties. On the other hand, the theoretical calculations show that the isotopic substitution influences properties of the OH group in CD_3OH [13]. Hence, it is likely that this difference leads to partial separation of CH_3OH and CD_3OH at a molecular level, and deviation from the ideal mixture behaviour. The manifestation of this phenomenon should be visible in the excess absorption spectra [2,14,15], 2D correlation spectra [2,15] or in results of chemometric analysis [2,15]. Additional details were obtained from the theoretical calculations (DFT) of the structure and vibrational spectra of clusters of different size and composition.

2. Experimental Details

Methanol (>99.9%, J. T. Baker, The Netherlands) was distilled and dried under freshly activated molecular sieves (4A). Due to limited amount of methanol d_3 (>99.5%, Sigma-Aldrich Chemical Co, Germany) it was used as received. All spectra were recorded on Nicolet Magna 860 spectrometer with DTGS detector and 256 scans were accumulated. ATR-IR spectra were recorded with multi-reflection ZnSe crystal (HATR Flow Cell, 45 Degrees, PIKE Technologies) at a resolution of 2 cm^{-1}, while NIR spectra were measured in a temperature-controlled quartz (Suprasil) cell of 2 mm thickness (Hellma) at a resolution of 4 cm^{-1}. The spectra of CH_3OH/CD_3OH mixture were recorded at 25 °C in the whole range of mole fractions with a step of X = 0.04. The mixtures were automatically prepared with a high precision and dosed to the cell by a computer-controlled flow-system constructed in our laboratory [2,15].

3. Computational Details

Prior to further analysis, we minimized the baseline fluctuations between different spectra in the series by making an offset at a reference point. For this purpose, an absorbance at a reference point (3800 cm^{-1} for ATR-IR spectra and 9000 cm^{-1} for NIR spectra) was subtracted from the entire spectrum [16]. The peak positions and integrated intensities were calculated by using standard Matlab/PLS Toolbox functions, *peakfind* and *trapz*, respectively. From principal component analysis (PCA) and evolving factor analysis (EFA), [17,18] we estimated the number of significant components in the mixture, and the initial approximations of the concentration profiles for each component. The actual concentration and spectral profiles of all components were resolved by multivariate curve resolution-alternating least squares (MCR-ALS) method with constraints [19,20]. During calculation of synchronous and asynchronous 2D correlation spectra [21,22] a composition-average spectrum was used as a reference. To facilitate interpretation of asynchronous peaks, the asynchronous intensity was multiplied by the sign of the corresponding synchronous intensity. The excess

absorption spectra and the values of ER were calculated as previously described [2,15]. The data handling was performed with MATLAB R2016a (The Math Works Inc.) and PLS-Toolbox 8.2 (Eigenvector Research Inc.).

The structures and vibrational spectra of various homo and heteroclusters were calculated by DFT method at B3LYP/6-311++G(d,p) level of theory using Gaussian 09 [23]. Numerous literature reports show that this level of theory is sufficient for explanation of the experimental results for various hydrogen-bonded systems [24–26]. Selected model clusters were also calculated by using dispersion corrected M06X method (not shown). The obtained results indicate only the systematic shift towards higher wavenumbers for most of the bands as compared with those calculated at B3LYP/6-311++G(d,p) level. For further analysis, we used only the results where all harmonic frequencies were positive. DFT calculations were performed in WCSS (grant no. 163).

4. Results and Discussion

As can be seen from Fig. 1, variations in composition of the mixture lead to significant changes both in MIR and NIR spectra. The assignments of main spectral features (Table 1) were compared with results of other spectroscopic and theoretical studies of methanol [4,12, 27–30]. In addition, the band assignment was guided by theoretical calculations of the structure and vibrational spectra of different model clusters from trimers to octamers. For tetramers and hexamers we calculated the spectra of all possible mixed clusters $[CH_3OH]_n[CD_3OH]_{4-n}$ (for n = 0 to 4) and $[CH_3OH]_m[CD_3OH]_{6-m}$ (for m = 0 to 6). Optimized structures of cyclic tetramers and cyclic hexamers are shown in Fig. 2. Our calculations lead to two important conclusions: (a) the linear clusters are much less stable than the cyclic ones; (b) the isotopic substitution (from CH_3OH to CD_3OH) does not affect the properties of the OH group. This way, all cyclic clusters of the same size have the same length and symmetry of O—H···O bonding. An average O···O distance for tetramers was found to be 2.726 (± 0.000015) Å. As expected, the corresponding value for hexamers was slightly smaller: 2.701 (± 0.0003) Å, suggesting that the cyclic hexamers are more stable structures as compared with the cyclic tetramers [6]. In the cyclic clusters (Fig. 2) all OH groups are involved in the hydrogen bonding. The dominance of cyclic species in liquid methanol is confirmed by analysis of MIR and NIR spectra. As can be seen (Fig. 1), near 3600 cm^{-1} (MIR) or 7100 cm^{-1} (NIR) does not appear any significant absorption from the free OH. This observation agrees with the other literature reports showing that the cyclic species are more stable than the linear ones [6,7,10,12]. It is of particular note that absorption of the ν(OH) band does not change with CD_3OH
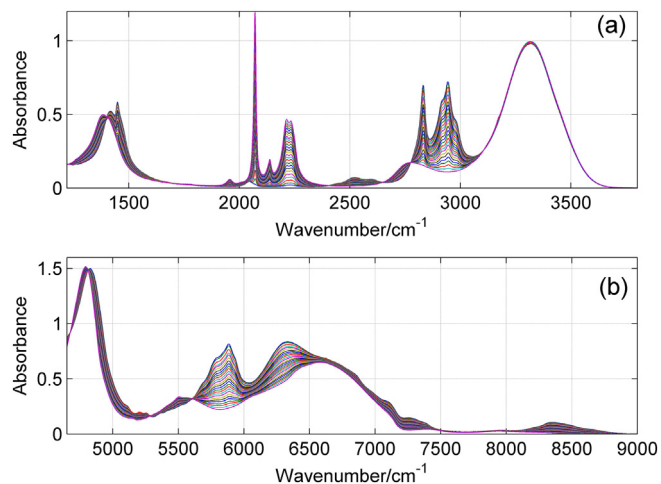

Fig. 1. ATR-IR (a) and NIR (b) spectra of CH_3OH/CD_3OH mixture in the entire range of mole fractions with a step of 0.04.