KAPITEL 8 / *CHAPTER 8* [8]
COMPLEX FORMATION IN SOLUTIONS

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Introduction

Intermolecular interactions between mixture components may lead to the formation of molecular complexes and associates. It affects greatly macroscopic properties of mixtures which might become nonlinear dependent on mixing ratio [1]. Knowledge of the molecular structure of mixtures allows obtaining solutions with predefined characteristics [2]. From this point of view, methanol-chloroform liquid solution is interesting due to its wide application in different areas. For example, it is used in lipids extraction and separation from microorganisms by Folch method [3]. Changing the methanol-chloroform mixing ratio allows changing dye absorption and fluorescence emission maximum [4–6]. The physical and chemical properties of methanol-chloroform solutions show nonlinear dependence on the concentration of components, temperature, etc. Concentration dependence of viscosity [7], density [7,8], and excess thermodynamic functions [9,10] are essentially nonlinear.

The reason for this is the complicated inner structure of methanol mixtures which show heterogeneity at a molecular level [11–17]. Methanol tends to be self-associated and to form molecular complexes with chloroform due to hydrogen-bond and halogenbond formation [18]. This phenomenon was investigated by different experimental techniques: core-level photoelectron spectroscopy [19], NMR spectroscopy [6,20–22], optical Kerr effect spectroscopy [23], polarized Raman spectroscopy [21] and molecular dynamics simulations [24,25].

On the other hand, vibrational spectroscopy is an extremely valuable tool for the investigation of intermolecular interactions. It is sensitive to vibration splitting due to molecular associates and complex formation. The purpose of this study is to analyze the complex formation in a methanol-chloroform solution by Fourier Transform Infrared (FTIR) absorption and Raman spectroscopy. These spectroscopic techniques provide complementary information about the investigated system. Multivariate curve

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resolution [26] (MCR) techniques are used to obtain quantitative information about mixture components. Quantum chemical calculations combined with quantum cluster equilibrium theory [27] were used to interpret experimental data. It was shown that a minimal cluster set can adequately explain MCR results and excess enthalpy of mixing.

8.1. Theoretical part

8.1.1. Multivariate curve resolution

Multivariate curve resolution (MCR) techniques allow us to obtain quantitative information about the investigated system. The main goal of MCR is to calculate concentration matrix ***C*** and spectral profiles matrix ***S*** using the measured spectra matrix ***D***.

Mathematically speaking, the main goal is the non-negative matrix factorization of ***D*** [28,29]:

$$\boldsymbol{D} = \boldsymbol{C}\boldsymbol{S}^{T} + \boldsymbol{E} \tag{1}$$

Here ***E*** - is the residuals matrix. One of the widely used decomposition methods is MCR using alternating least squares (ALS) [26,30]. Bilinear decomposition (1) is an example of blind source separation [31] because the number of all mixture components is often unknown. Principal component analysis can be used to deduce the number of components [32,33]. However, it should be used with caution because it may result in the wrong number of chemical components, especially for quasi-ideal mixtures [34].

Quantitative analysis of mixture components may suffer from ambiguities of bilinear decomposition (1) [35,36]. Rotation ambiguity is caused by spectra overlapping. Its presence means that the resulting profiles of MCR solutions are unknown linear combinations of real component profiles. It should be taken into account during MCR analysis of vibrational spectra of hydrogen-bonded liquids and solutions because the vibrational frequency shift caused by the hydrogen bond formation is small [37]. Moreover, MCR solutions suffer from intensity ambiguity. Therefore, only the shape of the true profile can be determined without using any additional information.

All prior information about the investigated system can be used to avoid non-physical solutions and to reduce or eliminate ambiguities of the obtained solutions. Examples of such information can be the non-negativity of spectra and concentration profiles, known concentration values and/or known component spectra, and the known local rank of the system. However, using all known information cannot guarantee the uniqueness of the obtained data [35,38]. To obtain band boundaries of the feasible solutions, nonlinear optimization techniques can be used [39,40].

On the other hand, multiset data (e.g., data obtained by different experimental techniques) could be used to eliminate the ambiguity of MCR decomposition.. It has been shown that this approach can essentially reduce decomposition ambiguity compared to a single dataset decomposition [41,42]. Infrared absorption spectra and Raman spectra contain complementary information, so it is possible to use the following augmented dataset for decomposition:

$$\left[\boldsymbol{D}_{Raman},\boldsymbol{D}_{ATF\ FTIR}\right]=\boldsymbol{C}\left[\boldsymbol{S}_{Raman},\boldsymbol{S}_{ATF\ FTIR}\right]^{T}+\left[\boldsymbol{E}_{Raman},\boldsymbol{E}_{ATF\ FTIR}\right] \tag{2}$$

8.1.2. Quantum cluster equilibrium theory

The basic idea of the quantum cluster equilibrium (QCE) theory is that the cluster picture of dense gases can be continuously expanded into the region of condensed states by varying the clusters distribution for each pair of values T and P [43]. The existence of the gas–liquid critical point leads to the continuity of the transition from gas to liquid. QCE thermodynamic properties of the liqliquid phase system can be represented by a finite set of clusters that are dominant in the fixed values of the thermodynamic parameters. Thus, the investigated system is considered as a mixture of clusters of different sizes and shapes (topologies) [27]. Thermodynamic properties of the system are determined using the partition function, which has the following form for the binary solution [44]:

$$Q^{tot}\left(\{N_p\},V,T\right)=\prod_{p=1}^{N}\frac{1}{N_p!}\left(q_p^{rot}\left(t\right)q_p^{vib}\left(t\right)q_p^{el}\left(t\right)\left(\frac{2\pi m_p k_B T}{h^2}\right)^{\frac{3}{2}}\left(V-V_{ex}\right)e^{\frac{u_p^{\mathrm{int}}}{k_B T}}\right)^{N_p} \tag{3}$$

Here p, N_p are the types of the particle (monomer, complex, or associate) and its quantity; $q_p^{r,vib,el}(T)$ is a contribution of the corresponding degrees of freedom to the single-particle partition function obtained by quantum chemical calculations. V_{ex} is an excluded volume correction, which for a binary solution has the form

$$V_{ex} = b_{xv} \sum_{p=1}^{N} N_p \left(i(p)v_1 + j(p)v_2 \right),$$

where $i(p)$, $j(p)$ are numbers of monomers of type 1 and 2 in the complex of type p. The residual intercluster interaction is described using mean-field approximation and has the form of $u_p^{\text{int}} = -\frac{a_{mf}\left(i(p)+j(p)\right)}{V}$.

It is worth noting that particle concentration $\{N_p\}$, and pressure P are calculated due to the minimization of Gibbs energy. Additional experimental data (for example, density, isobars, or phase transition temperature) are required to obtain values of the empirical parameters a_{mf} and b_{xv} . The detailed algorithm of the thermodynamic functions calculation using QCE theory can be found elswere [43,45,46].

8.2. Experimental part

8.2.1. Samples

Methanol and chloroform with the purity of 99.9 % and 99.8 % were used in this research (Sigma-Aldrich numbers 646,377 and 366927, respectively). The temperature of the liquid samples was 25 ± 0.4C. The concentration of components in the methanolchloroform solutions was changed from 0 % to 100 % (in volume %). Diluted samples of binary liquid solutions with 5 ± 0.1 % increments were prepared with the usage of Eppendorf Pipette Research Plus (volume 100–1000 μL). Each sample was stored in glass vials with a screw cap (volume 1.5 ml).

8.2.2. FTIR spectroscopy

Reflection spectra in the mid-infrared region were registered using FTIR spectrometer Thermo Scientific Nicolet iS50 equipped with a single-bounce diamond attenuated total reflection (ATR) accessory. All the ATR spectra were measured with the spectral resolution of 4 cm^{-1}. The number of scans for each spectrum was 32. The obtained spectral resolution is sufficient to study the IR spectra of molecular liquids where the half-width of vibration bands is rarely smaller than 5 cm^{-1}. ATR-FTIR measurements were carried out with the usage of an aluminum cylinder with a round through-hole (diameter 4 mm) located between the ATR crystal and high-pressure clamp accessory. Liquid samples were inserted in the hole of the aluminum cylinder with Eppendorf Pipette Research Plus (volume 100–1000 μL) and tightly fixed with a high-pressure clamp accessory to avoid evaporation of liquid outside the assembly during the measurement time of several minutes.

8.2.3. Raman spectroscopy

All Raman spectra were measured with the spectral resolution of 3 cm^{-1} at the excitation wavelength of 785 nm. Laser power was 100 mW for each measurement. Heating of the sample almost did not occur during the measurements due to the small value of absorption coefficient at the excitation frequency. Liquid samples were inserted in the hole of the aluminum cylinder with Eppendorf Pipette Research Plus (volume 100–1000 μL) and covered with a lid. More details about the experimental setup could be found in the paper [47].

8.3. Results and discussion

8.3.1. Raman and ATR FTIR spectra

The vibrational spectra of the methanol-chloroform solutions were measured within the ranges 900–1300 cm^{-1} and 2700–3700 cm^{-1}. Residual spectra were calculated to separate the regions where spectral intensity depends nonlinearly on the concentration. The calculation of residual or excess spectra SE is like the calculation of excess thermodynamics functions: the ideal mixture spectrum is subtracted from the real spectrum [48,49]:

$$S^E\left(\varphi_1,\varphi_2,\nu\right)=S\left(\varphi_1,\varphi_2,\nu\right)-S_{id}\left(\varphi_1,\varphi_2,\nu\right)=S\left(\varphi_1,\varphi_2,\nu\right)-\varphi_1 S_1^0\left(\nu\right)-\varphi_2 S_2^0\left(\nu\right). \qquad (4)$$

Here S_1^v, S_2^v are volume fractions of mixture component. S_1^0 and S_2^0 are spectra (optical density or Raman intensity) of the corresponding pure component. Equation (4) differs from the original form of the excess spectrum, which were calculated for molar absorptivity and molar fractions were used instead of volume fractions. If there are several types of molecular complexes in the solution, they should cause residual spectral intensity extrema in the corresponding spectral and concentration ranges.

Mid-IR ATR and Raman spectra of the methanol-chloroform solution are presented at different mixing ratios in Fig. 1 and Fig. 2. Residual spectra were calculated using Eq. (4) with interpolated densities from [8] and presented in Figs. 3-4. Volume fractions were recalculated into molar fractions for better representation.

The residual optical density map (Fig. 3a) and residual Raman intensity map (Fig. 3b) in the range of 900–1300 cm^{-1} show that residual intensity at 1215 cm^{-1} (CH bending vibration of chloroform [50]) is decreased, while a new vibration peak at 1240 cm^{-1} similar to the diethyl ether-chloroform [51] and acetone-chloroform [52] solutions appeared. The presence of this peak is connected to the bending vibration of the chloroform molecule as part of the complex with methanol. The maximal residual intensity is reached at approximately 0.65 mol. fraction of methanol. At the same time, the new residual peak at 3017 cm^{-1} reaches its minimal value for Raman spectra (Fig. 4 b), but its residual ATR FTIR intensity is positive. It can be interpreted as red-shifted CH stretching vibration of chloroform as a part of a complex. Another vibration peak appears at 3629 cm^{-1}1 both in IR and Raman spectra (Fig. 2). It is the region of free OH stretching vibrations of methanol. The residual spectral maps (Fig. 4) show that this peak reaches maximal residual intensity at 0.3 M fraction of methanol. During complex formation, changes in the vibration frequency occur not only in the OH stretching vibration of methanol but for C-O stretching vibration as well. C-O stretching vibration of methanol (1029 cm^{-1}) splits at the low concentration of methanol, a new peak appears at 1016 cm^{-1} and it indicates the hydrogen bonding of methanol with chloroform.

Excess spectra provide higher spectral resolution compared to the analysis of raw spectra. Thus, the analysis of residual maps (Figs. 2, 3) indicates the presence of at least two types of complexes in the investigated solution. The non-zero residual intensity of corresponding peaks indicates that the complexes exist in the whole concentration range of the investigated solution.

8.3.2. Multivariate curve resolution method

Four component decomposition of methanol-chloroform spectra was performed. Such models are supported by the analysis of residual spectra and PCA analysis of ATR FTIR and Raman datasets. All calculations were performed using MATLAB graphical user interface [53]. ‘Pure’ spectra obtained by SIMPLISMA [54] were used as the initial estimates of the spectral profiles. The following constraints were applied during the optimization processes: spectra and concentrations non-negativity, closure condition, and known values for the concentrations (in the ranges of pure methanol and pure chloroform). Non-linear optimization by MCR-BANDS [40] was used to determination of the band boundaries of the feasible solutions obtained by MCR-ALS.

It seems that we should obtain identical concentration profiles of the mixture components because both figures represent the same system. However, the profile shapes and the concentration values were different. We also observed that MCR-ALS results were dependent on the spectral range chosen for the analysis. This can be explained by the fact that spectral regions with vibrational modes which are directly involved in the intermolecular bond formation provide a much more significant impact on the spectral intensity compared to the spectral regions with vibration modes unrelated to the formation of the intermolecular bond. A similar concept can be applied to the differences in the concentration profiles obtained after the separate analysis of ATR FTIR and Raman data. In some cases, the ATR FTIR part of the vibrational spectrum can be more sensitive to the complexation effects than Raman data and vice versa.

To avoid ambiguities connected with the choice of the type of vibrational spectra and spectral ranges, we carried out the four-component decomposition of the extended matrix of the spectral data which includes ATR FTIR and Raman datasets in both ‘‘fingerprint” and high-frequency spectral ranges (Figs. 1, 3). Obtained spectral and concentration profiles of the mixture components are presented in Figs. 5-6. Components were identified as ‘pure’ chloroform, ‘pure’ methanol, complex 1, and complex 2. It should be noted that we consider complex as some ‘effective’ structure unit due to the dynamical structure of liquid.

The obtained concentration profiles are not unique due to the presence of rotation ambiguity (Fig. 6). The concentration profile of methanol is resolved with the least ambiguity, because of Manne’s theorem 1 condition is satisfied [55,56]. The condition is the following: all interfering component that appear inside the concentration window of methanol should also appear outside this window. As can be seen from Fig. 6 that if the total molar fraction of methanol is small (0.0–0.2), then the only two components are present in the solution: the ‘pure’ chloroform and complex 2. Further increase in the concentration of methanol leads to the formation of complex 1. The concentration of the ‘pure’ methanol becomes non-zero when the total molar fraction of methanol becomes greater than 0.4. The maximal population of the complex 1 is achieved at 0.75 total molar fraction of methanol. It corresponds to the chloroform/methanol ratio of 1:3. It can also be said that this ratio represents the stoichiometry of the dominant complex type in this range. The maximum population of complex 1 is approximately 0.43 mol. The complex 2 is the dominant structural unit in the region where the total concentration of chloroform is large. The maximal population of the complex 2 is achieved at the total molar fraction of methanol 0.45. The ratio of chloroform and methanol is 1.2:1. The maximum fraction of the complex is in the range from 0.28 to 0.46. The resulting spectra of the ‘pure’ chloroform and ‘pure’ methanol (Fig. 5) obtained by the decomposition were practically identical to the corresponding bulk liquid spectra (Fig. 1). It means that there are spatial regions in the solution with the same local structure as in the bulk methanol and chloroform. As it can be seen from Fig. 5 that both ATR FTIR and Raman spectra of the complex 2 have a peak maximum at the frequency of 3670 cm^{-1}. This peak corresponds to stretching vibrations of the free and quasi-free OH groups of methanol [50]. The absence of the corresponding peaks in the spectra of the complex 1 and ‘pure’ methanol can indicate that the dominated structural units contain cyclic methanol associates formed due to the OH. . .O hydrogen bond [57,58]. Species which contain free and quasi-free OH group are not dominant and corresponding vibrations are not detectable [59].

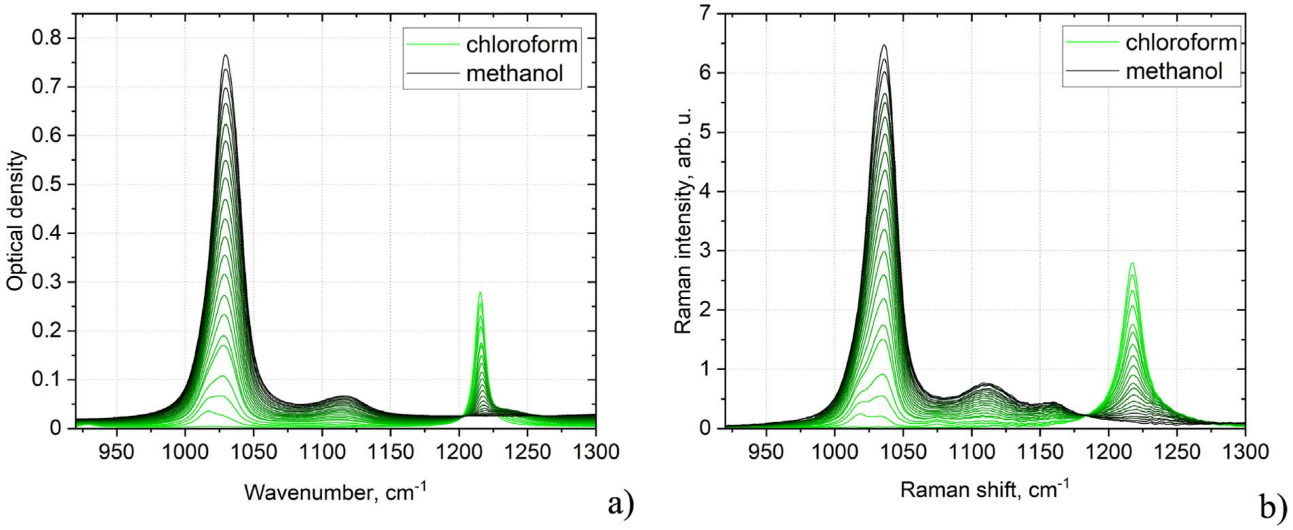

Figure 1 - ATR FTIR absorption (a) and Raman spectra (b) of the methanol-chloroform solution at different compositions (step 5 % vol.) in the range of 900–1300 cm^{-1}1.

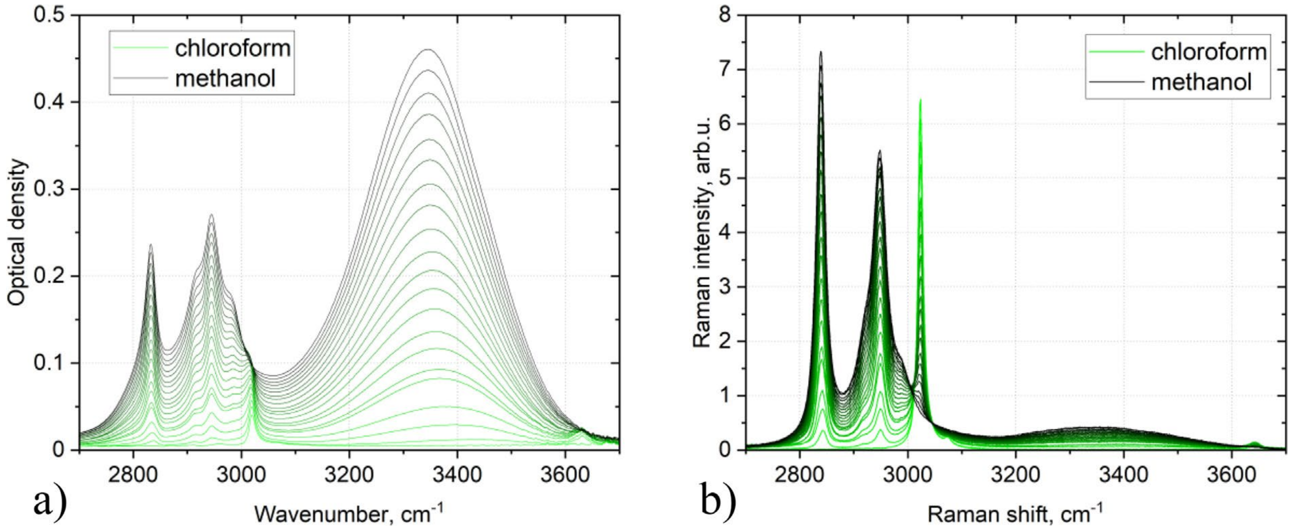

Figure 2 - ATR FTIR (a) and Raman spectra (b) of the methanol chloroform solution at different compositions (step 5 % vol.) in the range of 2700–3700 cm^{-1}.

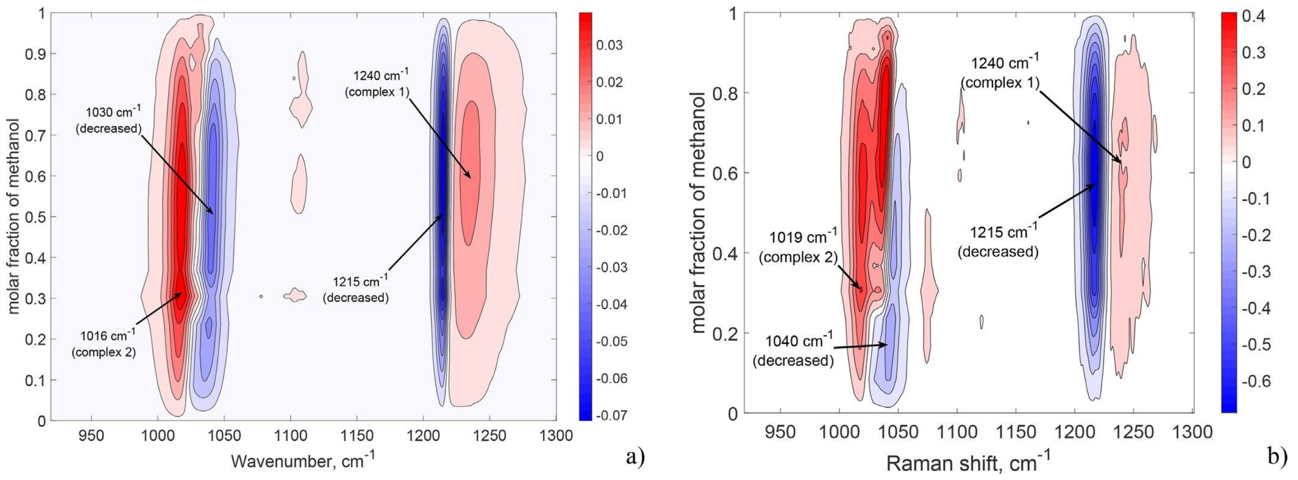

Figure 3. 2D maps of ATR FTIR (a) and Raman (b) residual spectra of the methanol-chloroform solution in the range of 900–1300 cm^{-1}.

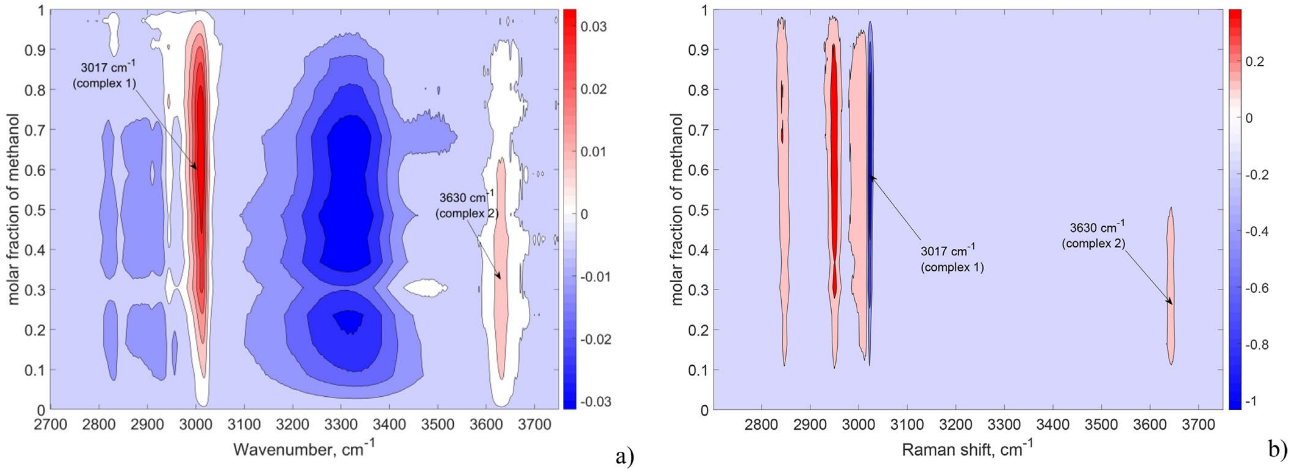

Figure 4 - 2D maps of ATR FTIR (a) and Raman (b) residual spectra of the methanol chloroform solution in the range of 2700–3700 cm^{-1}.

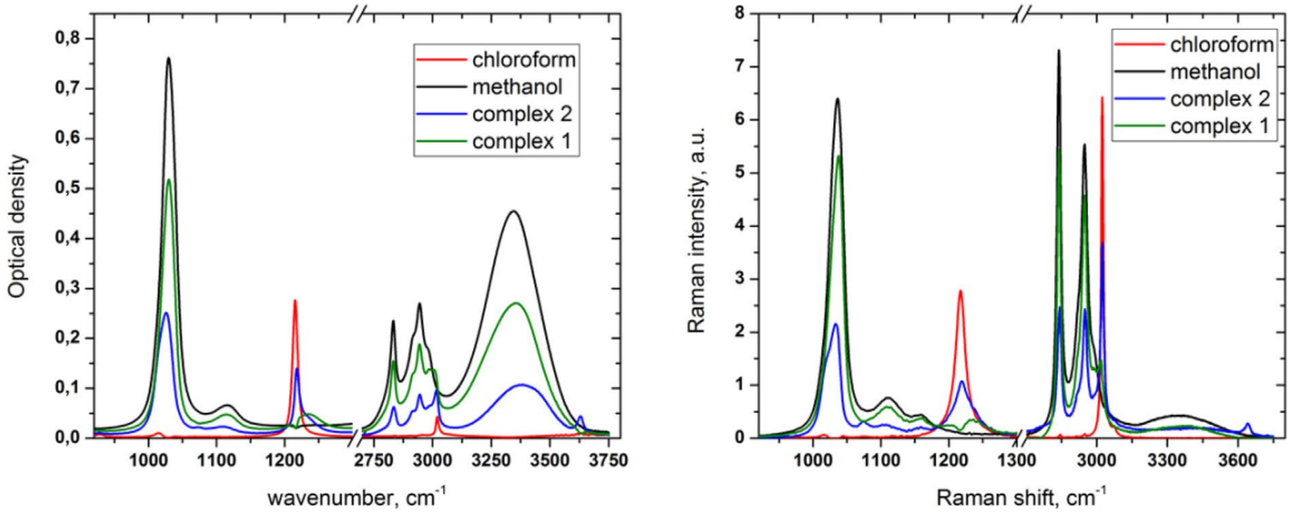

Figure 5 - Spectral profiles (left - optical density; right - Raman intensity) of the

mixture components obtained using MCR-ALS decomposition.

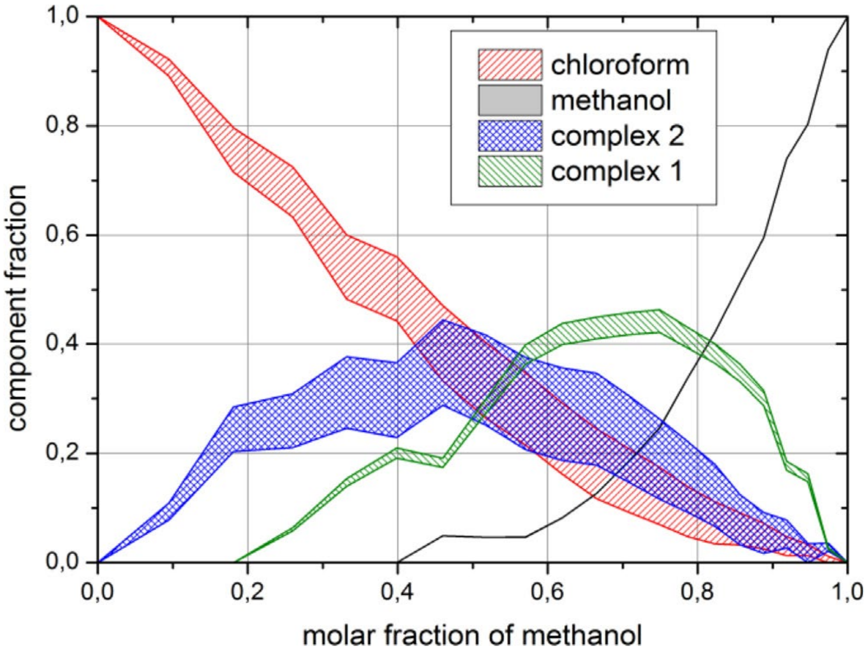

Figure 6 - Concentration profiles of the mixture components. Stained areas – regions of feasible solutions obtained by MCR-BANDS.

8.3.3. QCE calculations

As was mentioned in 2.2, the given set of clusters should be used to calculate the partition function which is necessary to obtain the thermodynamic functions of the investigated system. Since liquid-phase systems are modeled by finite sets of clusters, the determination of the set of dominant structures making the major contribution to the macroscopic characteristics is not an easy task [27,44,60]. In particular, it has been shown that it is important to highlight dominant topologies (for example, cyclic or linear clusters) and, using even the small set of clusters, we can adequately describe thermodynamics of pure liquids [27,60] and binary mixtures [44,61].

The cluster set used for the QCE calculations is shown in Fig. 7. The quantum chemical calculations were displayed on the charts using the GAMESS [62,63] package by the method of density functional (DFT) at the B3LYP/cc-pVTZ theory level. Gradient convergence tolerance was set to 10^{-7}. SCF density convergence critear was set to 10^{-6}. We consider a minimal set of clusters to describe qualitative features of the methanol-chloroform solution. We consider monomer, dimer and trimers of methanol. We limit ourselves with cyclic trimers of methanol because it was reported that cyclic clusters of methanol are the most stable [57,58]. We consider monomer and dimers of chloroform since chloroform can form weakly bonded dimers [64,65]. Initial geometries of clusters were built manually using the optimized structure of monomers of chloroform and methanol. The absence of imaginary frequencies was the confirmation of the optimized geometry.

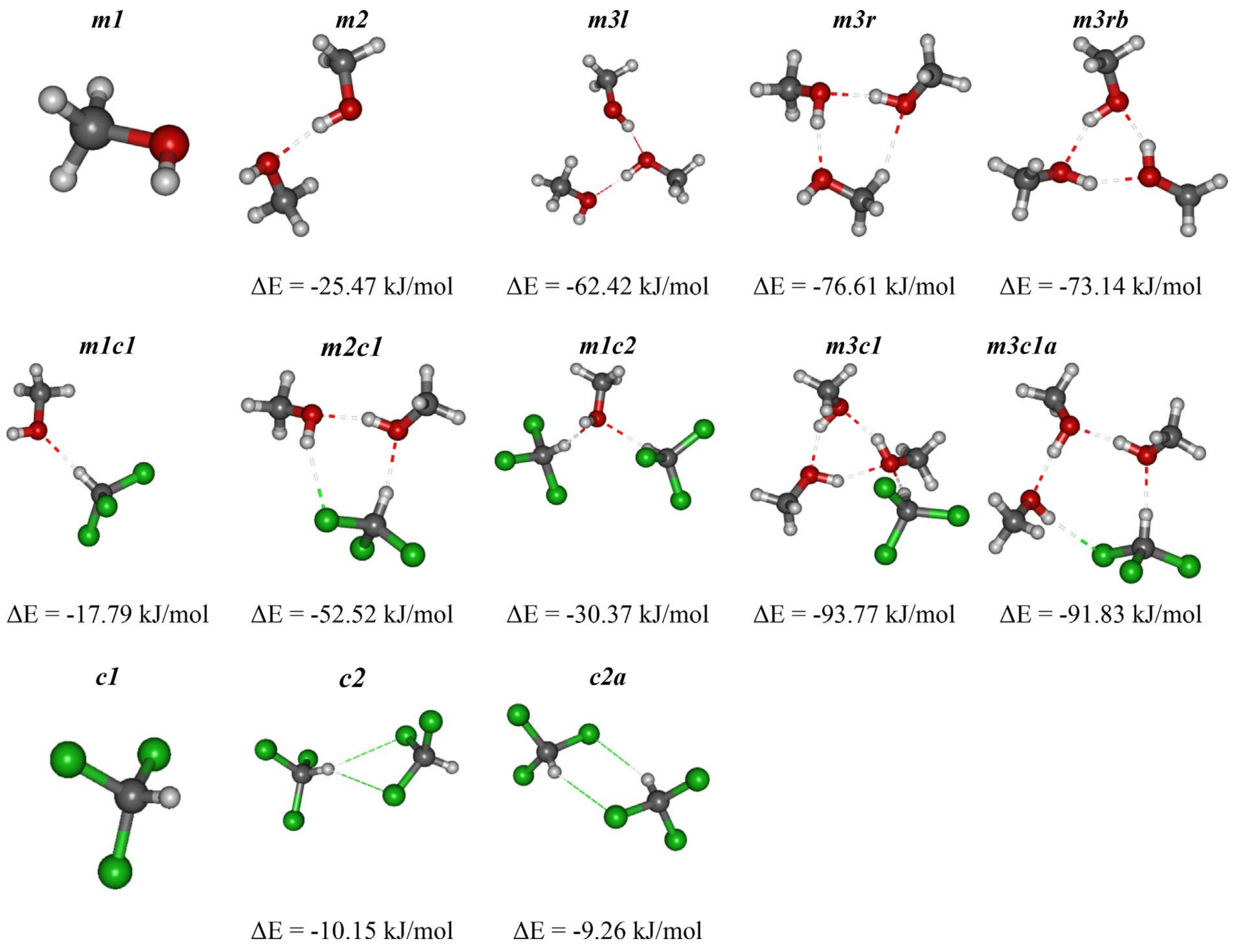

Figure 7 - The cluster set used for QCE calculations.

The QCE calculations were performed using PEACEMAKER [45,46] software. Theoretical calculations were performed in two ways: a) ‘fully sampled’ model with reference data, and b) using the linear mixing rule with effective parameters a_{mf} and b_{xv} found as a linear combination of the corresponding pure liquid values. The density of the methanol-chloroform solution at different mixing ratios [8] and its boiling temperature were used as the reference data. The methanol-chloroform solution is azeotropic not for all concentrations and there are temperature intervals of the coexistence of two phases [66]. Therefore, the average temperatures of the two-phase coexistence region were chosen as the values of the boiling point. The calculations were performed for a fixed pressure 101.325 kPa and temperature range 278.15–378.15 K. The cluster volumes were calculated as van der Waals volumes, where corresponding radii values were taken from Bondi’s compilation [67]. The parameters a_{mf} and b_{xv} were optimized in the range of 0.01–2.0 to get the best reproduction of boiling temperature and density of the mixture.

The resulting concentration profiles of the mixture components for ‘fully sampled’ model are shown in Fig. 8.. Concentration profiles obtained by different models are very similar. It can be seen that the cyclic trimers of methanol are dominant, and the linear trimer concentration is negligible in the pure methanol. This is consistent with the absence of the free OH stretching vibrations in the spectrum of pure methanol (Figs. 1, 2). It is also in line with the literature results which indicate the domination of cyclic structural units of different stoichiometry [57,68,69]. Monomers are dominant units in the liquid chloroform. Molecular complexes are the dominant structural units in the region of medium concentrations. The complex m3c1 reaches the maximal molar fraction of 0.55 at the methanol molar fraction of about 0.70. The position of the maximum and stoichiometry of the complex correlate with the results obtained by the method of multivariate curve resolution. The population of the complex m3c1a, which contains linear methanol trimer, also reaches its maximal value of 0.05 at this fraction of methanol. The population of the complex m1c1 is much smaller and reaches its maximal value of 0.065 at the methanol molar fraction of 0.3 (Fig. 8 b).

The integral concentration profiles of the mixture components are shown in Fig. 9. The complexes were divided into two groups to correlate with the concentration profiles obtained by the MCR decomposition. Group 1 contains only the complex m3c1. This complex contains the cyclic trimer of methanol (Fig. 9) and it is in line with the fact that the corresponding MCR spectral profile does not contain free OH stretching vibrational peaks (Fig. 5).

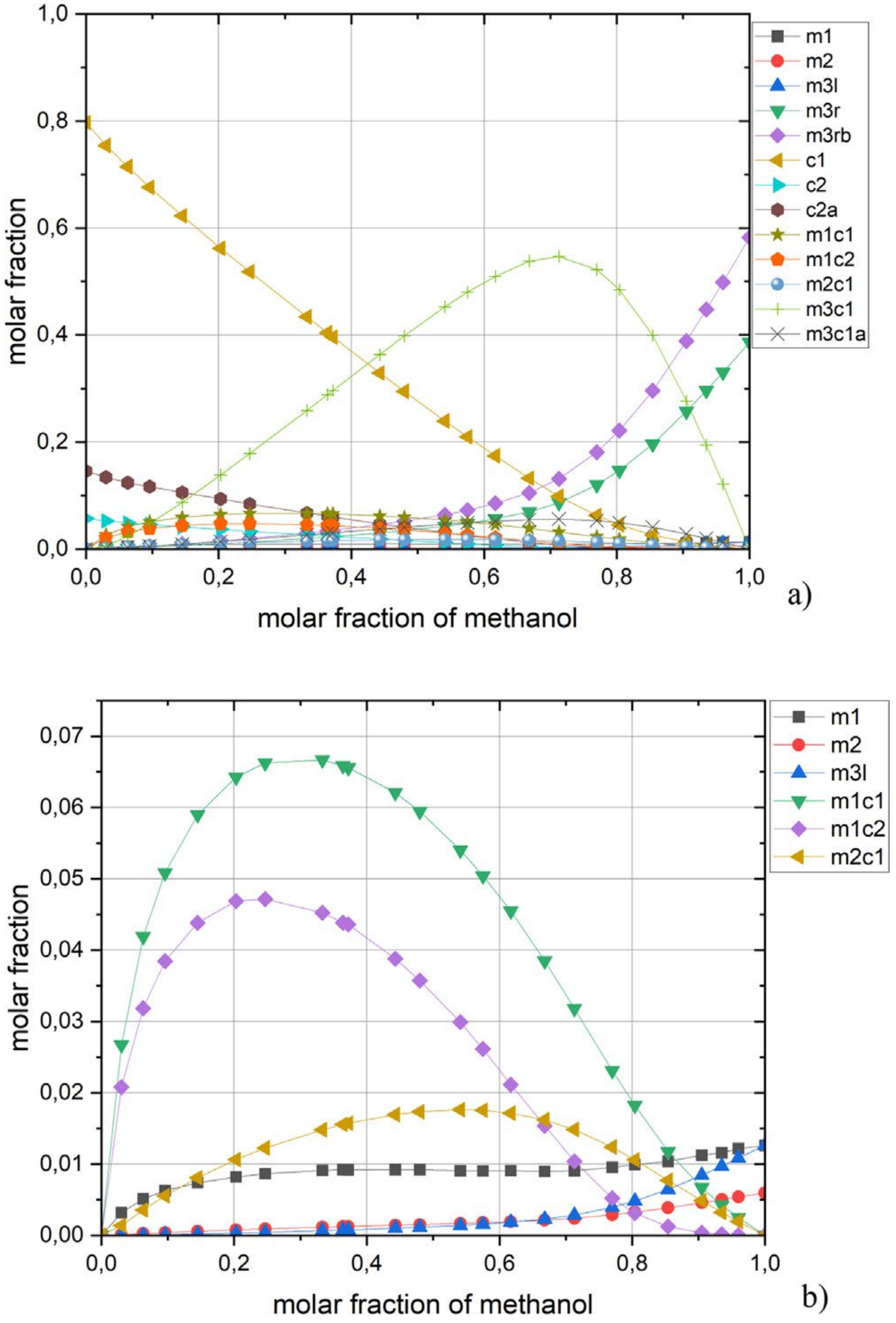

Figure 8 - Theoretically calculated concentration profiles of all components using 'fully sampled' approach (a); (b) – concentration profiles with the smallest concentrations.

Group 2 contains the complexes m1c1, m1c2, m2c1, m3c1a. The maximum value of the integral population is 0.2 and it is reached at th methanol molar fraction of 0.5. It also correlates with the position of the complex 2 maximal concentration obtained by MCR (Fig. 6). The absence of cyclic structures of methanol supports such interpretation of the complex 2. As it was discussed above, the spectral profile of complex 2 contains the free OH stretching vibrational peak (Fig. 5).

The comparison of the integral concentration profiles obtained by the QCE calculations (Fig. 9) and MCR concentration profiles (Fig. 6) shows that the MCR profiles should be interpreted as profiles of averaged or 'effective' structures.

We computed the concentration dependence of excess enthalpy using the given cluster set. The calculated and experimental excess enthalpy is presented in Fig. 10. Both models, 'fully sampled' and the model with linear mixing rule are able to explain features of excess enthalpy. However, the 'fully sampled' way allows us to explain this dependence more quantitatively.

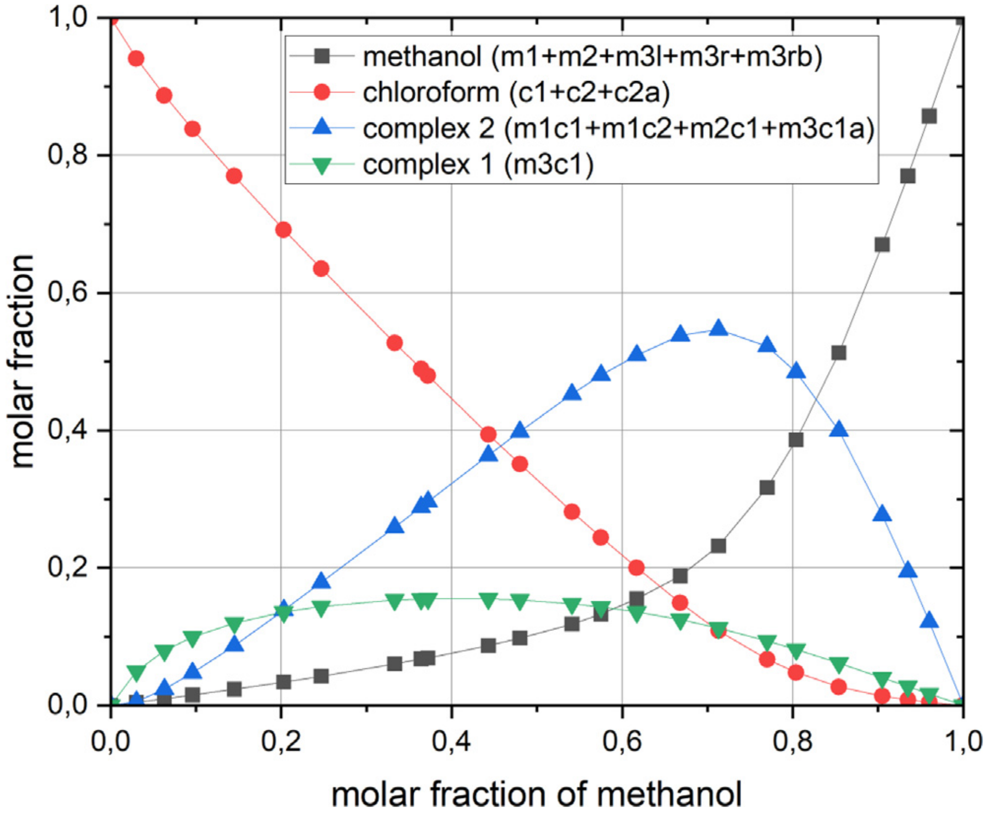

Figure 9 - Theoretically calculated integral concentration profiles of the mixture components using 'fully sampled' approach.

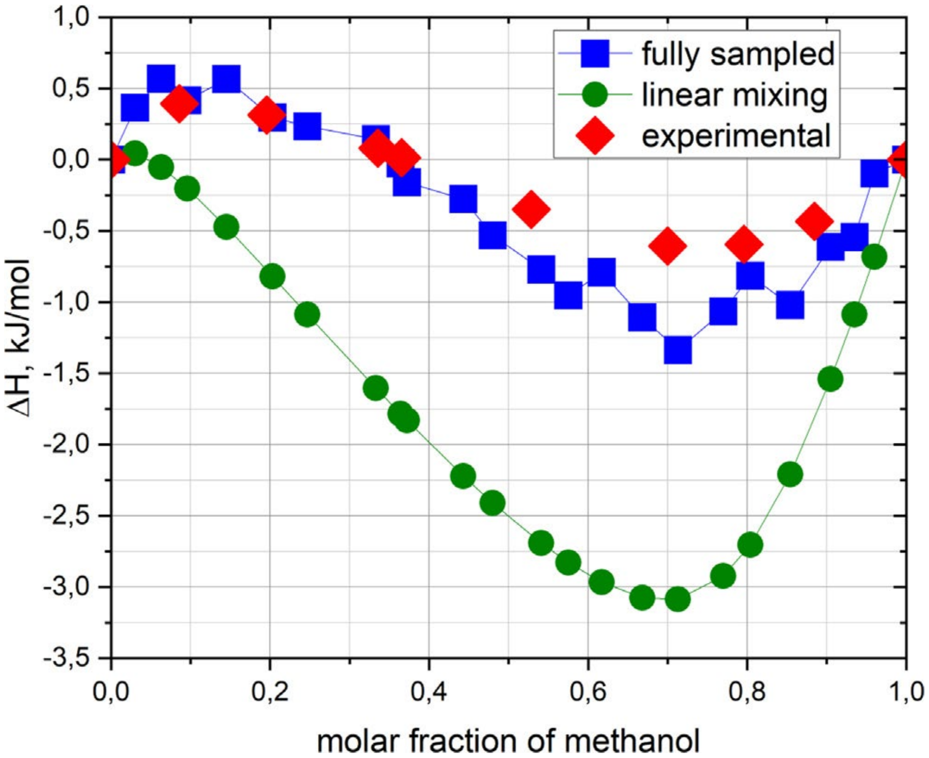

Figure 10 - Comparison of the experimental [72] and theoretically calculated values of excess enthalpy.

Non-monotonic concentration dependence of excess enthalpy can be explained by the presence of the associates of methanol in pure methanol and its complex formation with chloroform. The methanol associates dissociation requires additional external energy. The exothermic effect of the complex formation is low at a low concentration of methanol due to the small amount of molecular complexes (m1c1, m1c2). It can explain the positivity of the excess enthalpy value at the low concentration of methanol. When the concentration of methanol increases, the concentration of the complex m3c1 is maximal. The complex contains a cyclic structure of methanol which is also the dominant structural unit in pure methanol. Thus, the exothermal effect of the complex formation prevails over the endothermic effect of the methanol associates dissociation and therefore the excess enthalpy is negative. The interaction between the associates dissociation and the complex formation leads to the alternating sign of the excess enthalpy concentration dependence [70]. It is worth noting that the obtained results correlate with the results obtained in the framework of the model of ideal associated solution [71], non-ideal associated solution [10,72], athermal associated solution [20] and quasi-chemical non-ideal associated solution [73].

Summary and conclusions.

We studied complex formation in methanol-chloroform mixtures using ATR FTIR and Raman spectroscopy with the assistance of quantum cluster equilibrium modeling.

The analysis of vibrational spectra shows that the investigated solutions consist of four kinds of species: ‘pure’ methanol, ‘pure’ chloroform, and two types of hydrogen-bonded molecular complexes. Molecular complexes exist in the whole concentration range. Local surroundings of ‘pure’ components are similar to those in the bulk state due to the great similarity of their vibrational spectra.

QCE calculations help to explain the obtained MCR results qualitatively by introducing dominated cluster topologies. The obtained concentration dependences of the mixture components correlate with the experimental ones obtained by MCR-ALS. There are two dominant complexes in the methanol-chloroform solution according to QCE calculations: complex m3c1 which contains the cyclic structure of methanol and complex m1c1. This correlates with the shapes of spectral profiles obtained by MCR decomposition. The spectral profile of the complex m1c1 contains the free OH stretching vibration at 3670 cm^{-1}. Spectral profiles of the complex m3c1 and pure methanol do not contain such a peak, thus it allows to conclude the dominating contribution of cyclic structures to the corresponding spectra. The simplified cluster set used for the QCE calculation can explain the sign alternating of the concentration dependence of excess enthalpy of mixing. A more accurate description can be obtained with an extended cluster set.