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INVESTIGATIONS ON THE INFLUENCE OF GUEST MOLECULE CHARACTERISTICS AND THE PRESENCE OF MULTICOMPONENT GAS MIXTURES ON GAS HYDRATE PROPERTIES

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ABSTRACT

In this study, we investigated the molecular characteristics of hydrates which were synthesized from gas mixtures containing the two isomers of butane, or the pentane isomers neopentane and isopentane, in excess methane. Thereto various techniques, including Raman spectroscopy, powder and single crystal X-ray diffraction and ^{13}C NMR spectroscopy were employed. It turned out that shape and conformation of the guest molecule and hydrate structure both influence each other. In case of the mixed butane hydrate it could be confirmed that n-butane is enclathrated in its gauche conformation. This was verified by Raman spectroscopy, single crystal X-ray diffraction and calculated data. While isopentane is known as a structure H former, our results from powder X-ray diffraction, ^{13}C NMR and ab initio calculations show that it can be also incorporated into structure II when the hydrate is formed from a neopentane/isopentane/methane gas mixture.

Keywords: gas hydrates, guest molecular properties, constitutional isomer, rotational isomer

INTRODUCTION

Although most naturally occurring gas hydrates form structure I hydrates with methane as the main component, structure II hydrates that contain light hydrocarbon guest molecules like propane, isobutane or n-butane could be identified as well [1, 2]. Recently Lu et al. succeeded in verifying the existence of structure H hydrates in nature. The E ($5^{12}6^8$) cavity of structure H is the largest cavity which is known for naturally occurring gas hydrates. It incorporates large guest molecules such as isopentane, n-hexane and even methylcyclohexane [3].

It has been well established that the guest molecule size influences the structure obtained when a guest material reacts with water to form a hydrate. But as it was shown before the relationship between structure and molecular size is not straightforward [4]. There are still open questions regarding the influence of other molecular properties such as the guest molecule shape (conformation) as well as the presence of further guest molecules on the properties of the formed gas hydrate and vice versa. Therefore hydrates were synthesized from gas mixtures containing the two isomers of butane, or the pentane isomers neopentane and isopentane, in excess methane. The composition of these gas mixtures was kept close to natural conditions [5, 6].

Recently it was shown that depending on the formation conditions either the shape of a guest molecule or its water solubility has a great impact on

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the gas hydrate composition [7]. For a non-stirred water system the smaller isomer is preferentially incorporated into the hydrate phase. The hydrate composition is dominated by the different diffusion rates of the isomers, which are related to their shape. When the water phase is stirred diffusion becomes unimportant, and the isomer with the higher water solubility is enriched in the hydrate phase.
In order to study these multicomponent hydrates on a molecular level several analytical tools are employed to verify the crystal structure and require the hydrate composition. Thereby, the emphasis of this work was kept on the role of the guest molecular shape during the hydrate formation process and the interaction between guest molecule and hydrate lattice.

EXPERIMENTAL METHODS

Sample preparation

To synthesize hydrate 3 g freshly ground ice was loaded into a high pressure cell (internal volume: approximately 130 mL) which was precooled in a freezer at 253 K. Afterwards the pressure cell was connected to a pressure transducer and placed in a cooling bath at 271 K. Before pressurization the cell was tempered 30 min in the cooling bath. To prevent the ice powder from melting, the incoming gas was cooled and the reactor was pressurized very slowly. The pressure cell was stored in the cooling bath until no further pressure drop was observed.

In case of the isopentane hydrate sample the liquid hydrocarbon was cooled in the freezer as well. 1.9 mL isopentane were dispersed with a syringe on the ice powder. After filling a 50 mL pressure cell with 5 g ice and the liquid hydrocarbon, the cell was tempered in the cooling bath at 268 K and afterwards pressurized with methane. By the time a further pressure drop could not be observed the temperature was increased to 274 K to enhance the conversion of ice into hydrate.
A list of the gas mixtures used in this study is presented in Tables 1 and 2.

Gas mixture	CH_4 (mol %)	n-C_4H_{10} (mol %)	iso-C_4H_{10} (mol %)
Ia	96.8	3.2	-
Ib	94.4	-	5.6
Ic	96.0	2.0	2.0

Table 1. Butane gas mixtures.

Gas mixture	CH_4 (mol %)	neo-C_5H_{12} (mol %)	iso-C_5H_{12} (mol %)
IIIa	97.2	2.8	-
IIIb	79.8	-	20.2
IIIc	98.0	1.0	1.0

Table 2. Pentane gas mixtures.

Sample analysis

The hydrate crystal structure and lattice constants were obtained with a Bruker D8 Advance Powder X-ray diffractometer (Cu K_α radiation, λ = 1.5406 Å) equipped with an Anton Paar low temperature controller. The powder X-ray diffraction patterns were acquired at 153 K in a continuous scan mode. The patterns obtained were calibrated with reference to several ice Ih reflections.

The cage occupancies of the mixed hydrate samples were determined by ^{13}C magic angle spinning (MAS) NMR measurements which were carried out on a Bruker DSX-400 NMR spectrometer. For this, hydrate samples were finely ground and packed in a 7 mm zirconia rotor that was loaded into a variable temperature probe. The ^{13}C NMR spectra were recorded at 173 K with ~ 2 kHz spinning rate. In order to distinguish the solid phase signals from that of the liquid (adsorbed higher hydrocarbons) the spectra were obtained by high power proton decoupling (HPDEC) as well as cross polarization (CP) programs. The spectra were referenced to adamantane as external chemical shift reference with assigned chemical shifts of δ = 38.56 ppm and δ = 29.50 ppm at 298 K.

The compositional analysis of the hydrate samples was supported by Raman spectroscopy. The Raman spectra were recorded in the C-C stretching vibration regions at 77 K on an Acton SpectroPro 2500i spectrometer equipped with a Witec confocal microscope. An argon ion laser operating at 514.53 nm was used as excitation source. Naphthalene at 1382 cm^{-1} was used as reference.

In case of the n-butane – isobutane – methane hydrate it was possible to collect a single crystal from the bulk sample which turned out to be a multiple twin. This hydrate crystal was analyzed by single crystal X-ray diffraction. The data were collected with Mo K_α radiation (λ = 0.71073 Å, 2Θ = 50.0, ω scan mode) on a Bruker SMART CCD diffractometer at 100 K. The structure was solved by direct

methods using the SHELXTL suite of programs. All atoms were refined anisotropically.
Hydrogen atoms on guest molecules were placed in calculated positions and allowed to ride on the parent atoms.

In addition to the sample analysis, ab initio quantum mechanical calculations were performed to investigate the interaction of the guest molecule and the hydrate cage and the role of the different guest molecular conformations during the hydrate formation process in more detail. The ab initio calculations were performed with Hartree Fock (HF) and density functional (DFT) methods that are implemented in the GAUSSIAN 98 software package. The following basis set was used: 6-31 + G*. The geometries of the hydrate cages and the entrapped guest molecules were fully optimized using HF and B3LYP levels of theory. A more detailed description for this method is provided in the literature [8]. To support the experimental results from ^{13}C NMR measurements the chemical shifts were calculated for the synthesized hydrates as well.

RESULTS AND DISCUSSION

All hydrate samples were analyzed with powder X-ray diffraction, Raman spectroscopy and ^{13}C NMR spectroscopy to determine the crystal structure and the composition of the hydrate. The measurements were performed in regard to the shape and conformation of the guest molecule and the gas hydrate structure. In the following, three examples for the interaction of guest molecular properties and molecular properties of the formed gas hydrate are presented.

Butane hydrates

Isobutane – Methane SII Hydrate

This hydrate was formed at 2.1 MPa for several days while the main pressure drop was observed during the first hours after pressurization. After verifying the crystal structure by powder X-ray diffraction the hydrate was analyzed by ^{13}C MAS NMR methods (Figure 1). The measured chemical shifts coincide with literature data of mixed isobutane – methane hydrates (Table 3) [3]. Please note, that the carbon signals for isobutane in the hydrate phase are reversed relative to their order in the pure compound isobutane [9].

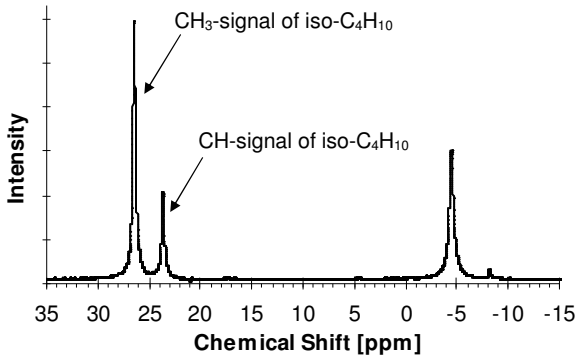

Figure 1. CP/MAS ^{13}C NMR spectra of isobutane – methane hydrate; measuring temperature 173 K.

System	Chemical shift [ppm]	Peak assignment
isobutane – methane hydrate	-4.46	CH_4 in small cage
	-8.16	CH_4 in large cage
	26.46	CH_3-signal of iso-C_4H_{10}
	23.69	CH-signal of iso-C_4H_{10}
isobutane (liq.) [9]	25.2	CH-signal
	24.3	CH_3-signal

Table 3. Chemical shifts and peak assignments for isobutane and methane in the hydrate phase and isobutane in the liquid phase.

It is important to mention that the peak assignments for the CH- and CH_3-signal of pure isobutane are not consistent in the literature [10, 11]. For this reason we decided to compare our data with calculated ^{13}C NMR data.
In this case our peak assignments for ^{13}C NMR spectra were also confirmed by the calculated data (Figure 2). In comparison to the pure compound (dashed lines) the CH-signal and CH_3-signal of isobutane are reversed in the hydrate phase (solid lines). The peak positions of the calculated spectra (calculation temperature 0 K) differ from those of the experimental spectrum as they were referenced to the methane peak that was also calculated for this structure.

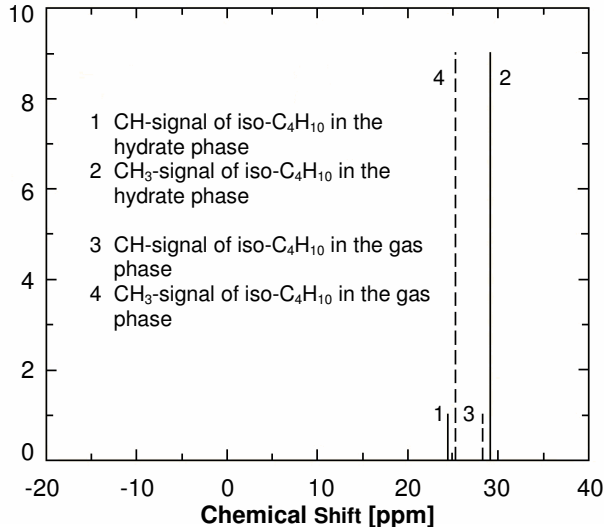

Figure 2. Calculated ^{13}C NMR spectra of isobutane in the hydrate phase (solid lines) and in the gas phase (dashed lines); calculation temperature 0 K.

Apart from that it should be noted that peak positions can be shifted due to changes in temperature [12-14]. So, one might assume that the change of the peak order is a consequence of the different measuring and calculation temperatures, respectively. But to the authors' knowledge it was not reported so far that a change of the temperature can cause a change in the peak order. Therefore we suppose that the change of the peak order results from the enclathration of isobutane in the hydrate lattice.

This assumption is supported by single crystal analyses (Figure 3). As mentioned before, it was possible to collect a single crystal from a hydrate sample that was synthesized from a gas mixture containing 2% isobutane 2% n-butane and 98% methane (gas mixture Ic). This combination of guest molecules results in a structure II hydrate. The unit cell parameter was determined with a = 17.213 Å (space group Fd-3m). The measurement has shown that the small cavities are completely filled with methane. 65% of the large cavities are filled with isobutane and 35% are filled with n-butane. As presented in Figure 3 it was found for isobutane that the molecule has moved out of the cavity centre closer to the edge of the hydrate cage. Therefore an interaction of the guest molecule and the hydrate cage appears to be possible which might arise in a change of the peak order in the ^{13}C NMR spectrum.

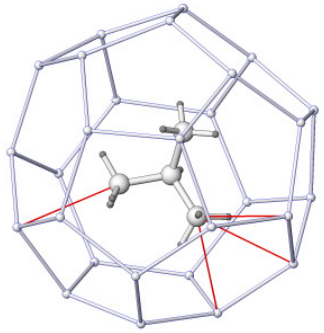

Figure 3. Guest molecule isobutane in the H ($5^{12}6^4$) cavity of structure II.

n-Butane – Methane SII Hydrate

A conformational analysis of n-butane encaged in the hydrate lattice is presented as the second example for an interaction between guest molecule and hydrate cage.

As a linear alkane, the CH_3CH_2 fragments are able to rotate around the central C-C bond which results in different rotational isomers. The energetically most stable conformer of n-butane is the trans (also called anti) form that has a C_{2h} symmetry. A rotation of 120° about the central C-C bond results in the gauche conformer (symmetry C_2) [15]. Several studies dealing with the rotational isomerism of n-butane demonstrate that Raman spectroscopy is an appropriate tool to distinguish the conformers [15-17].

In the presence of a help gas like methane, n-butane forms a structure II hydrate. Two studies deal with the conformation of n-butane in the hydrate cage. Davidson et al. have performed dielectric relaxation measurements on an S II hydrate consisting of hydrogen sulphide and n-butane [18]. The condition for dielectric absorption is a permanent dipole moment of the guest molecule. In contrast to trans n-butane gauche n-butane does have a permanent dipole moment. Apart from that, trans n-butane (van-der-Waals diameter: 7.9 Å) is supposed to be too large to fit into the large cage of structure II. As a dielectric absorption was observed for this hydrate Davidson et al. assumed that the smaller conformer gauche n-butane (van-der-Waals diameter: 7.1 Å) is encaged in the hydrate lattice.

Secondly, Subramanian and Sloan presented Raman data for an n-butane – methane hydrate synthesized at 0.22 MPa and 273.7 K [19]. Comparing the Raman spectra of liquid n-butane and the gas hydrate they showed that trans-gauche band pairs

occurring in the liquid spectrum reduce to single bands in the hydrate spectrum. They claimed that these single bands correspond to the gauche bands of the pure liquid n-butane. As they found only bands generated by the gauche form of n-butane in the hydrate spectrum they concluded that the trans form is excluded from the hydrate lattice.
For this work an n-butane – methane hydrate was synthesized at 4.3 MPa and 271 K. In addition to the hydrate sample liquid n-butane was analyzed by Raman spectroscopy as well. The liquid n-butane was measured at room temperature and the hydrate spectrum was recorded at 77 K.
While the Raman spectra of Subramanian and Sloan cover a wave number region of 700 cm^{-1}– 1150 cm^{-1} this study shows a region of 750 cm^{-1} – 1600 cm^{-1} (Figure 4) [19].

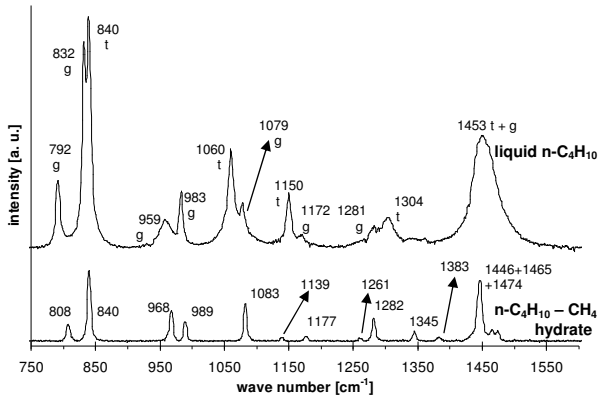

Figure 4. Comparison of the Raman spectra of pure n-butane (liquid) and n-butane – methane hydrate. The bands of the liquid n-butane spectrum were labelled with "t" and "g" corresponding to the trans and gauche rotational isomers of n-butane.

The liquid and hydrate spectra obtained correspond very well to the literature data [15-17, 19-22]. A complete overview of all peak positions and vibrational assignments for the liquid and the hydrate phase spectra is presented in Table 4. Based on the literature data the observed bands for liquid n-butane were assigned to the corresponding trans and gauche conformer, respectively [15-17, 20-22]. Accordingly the peaks were labelled as "t" (trans) and "g" (gauche). The band at 1453 cm^{-1} is very broad and can be attributed to both conformers. Due to its width it interferes with several neighbouring bands which are assigned to both conformers as well. It is important to mention that the literature data are not consistent in this frequency area.

ν liquid n-butane [cm^{-1}]	ν n-butane – methane hydrate [cm^{-1}]	**Vibrational mode**	
		trans conformer	**gauche conformer**
792	808		C-C stretch, $CH_{3/2}$ rock
832	840		C-C stretch, CH_3 rock
840	–	C-C stretch	
959	968		C-C stretch
983	989		CH_3 rock
1060	–	C-C stretch	
1079	1083		C-C stretch
1137 [21]*	1139		CH_3 rock
1150	–	CH_3 rock	
1172	1177		$CH_3/_2$ rock
1263 [21]*	1261		CH_2 twist, CH_3 rock
1281	1282		CH_2 twist
1304	–	CH_2 twist	
1343 [16]*	1345		CH_2 wag
1383 [21]*	1383	CH_3 sym deform	CH_3 sym deform
1453 (very broad)	1446** 1465** 1474**	CH_3 deg deform	CH_3 deg deform

Table 4. Observed Raman frequencies ν [cm^{-1}] and assignments to the main vibrational modes for liquid n-butane and n-butane – methane hydrate (stretch = stretching, rock = rocking, twist = twisting, scis = scissors, wag = wagging, deform = deformation, deg = degenerate, sym = symmetric)
* Literature data for pure n-butane that were not observed in the liquid phase spectrum
** Due to overlapping vibrational modes of both conformers a reliable assignment is not possible.

The measured region in the Raman spectra of liquid n-butane contains four trans-gauche band pairs. These band pairs are 832 cm^{-1} (g) – 840 (t) cm^{-1},

1060 cm^{-1} (t) – 1079 cm^{-1} (g), 1150 cm^{-1} (t) – 1172 cm^{-1} (g) and 1281 cm^{-1} (g) – 1304 cm^{-1} (t). On the basis of the Pimentel-Charles "Loose Cage – Tight Cage Model" Subramanian and Sloan determined that the Raman bands for n-butane trapped in the hydrate cage are slightly shifted to higher frequencies compared to the liquid phase spectrum [19]. Thus, we can assign the band occurring at 808 cm^{-1} in the hydrate spectrum as the C-C stretching vibration that was detected at 792 cm^{-1} in the liquid spectrum. Considering the trans-gauche band pairs of the liquid spectrum we can designate the single bands in the hydrate phase spectrum at 840 cm^{-1}, 1083 cm^{-1}, 1177 cm^{-1} and 1282 cm^{-1} as the remaining gauche bands. The four corresponding trans bands are nonexistent in the hydrate phase spectrum. In contrast to the liquid spectrum the hydrate spectrum includes four bands at 1139 cm^{-1}, 1261 cm^{-1}, 1345 cm^{-1} and 1383 cm^{-1}. As shown in Table 4 these four bands were compared with literature data of n-butane. Keeping in mind that the vibrational frequencies of n-butane trapped in the hydrate cage are slightly shifted, the bands at 1139 cm^{-1}, 1261 cm^{-1}, 1345 cm^{-1} and 1383 cm^{-1} presumably correspond to bands of pure n-butane which are located at 1137 cm^{-1}, 1263 cm^{-1}, 1343 cm^{-1} and 1383 cm^{-1}. The literature bands at 1137 cm^{-1}, 1263 cm^{-1} and 1343 cm^{-1} are assigned to gauche n-butane. The signal at 1383 cm^{-1} which is caused by a symmetric CH_3 deformation vibration can result from both conformers [20]. Therefore we assume that compared to the liquid phase the gauche conformer was enriched in the hydrate phase which results in the appearance of these four bands. Regarding the multiple peak at 1450 cm^{-1} it was already mentioned that several vibrational modes of both conformers overlap at this position. For this reason an exact assignment of the three bands appearing in the hydrate phase Raman spectra is only speculative. Thus, the presence of a vibrational mode resulting from the trans conformer cannot be excluded, but it is very unlikely.

To sum up, four distinctive trans bands present in the liquid spectrum of n-butane are absent in the hydrate phase spectrum. The signal at 1383 cm^{-1} as well as the multiple peak at 1450 cm^{-1} can include vibrational modes of both conformers in theory. Considering these results and due to fact that the hydrate spectrum shows three additional bands resulting from the gauche conformer it can be concluded that the gauche conformer of n-butane is incorporated into the hydrate phase.

These results are supported by the single X-ray diffraction data which were obtained for the n-butane – isobutane – methane hydrate. As shown in Figure 6 n-butane occupies the H ($5^{12}6^4$) cavity of structure II. It turned out that n-butane is encaged in its higher energy gauche form.

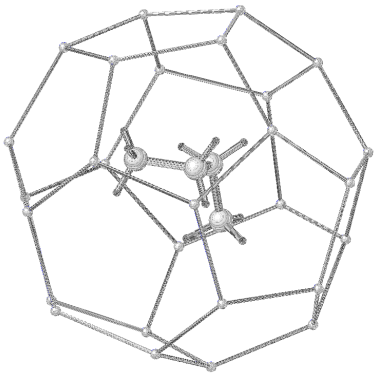

Figure 6. Guest molecule n-butane in a gauche conformation inside the large cavity of structure II.

On the basis of ab initio calculations it was possible to generate a picture of n-butane in the large cavity of structure II. At the end of the optimization process it was found as well that n-butane can be incorporated in its gauche conformation as shown in Figure 7.

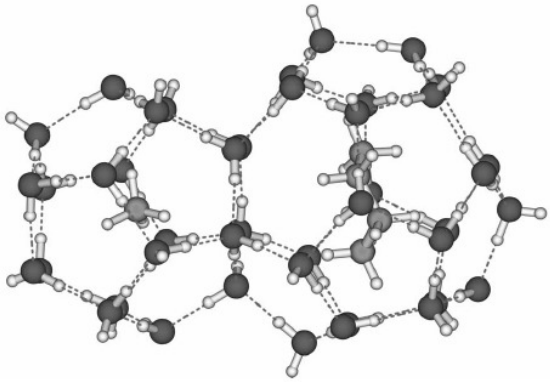

Figure 7. Optimized structure of n-butane – methane hydrate. n-Butane is encaged in its gauche conformation.

Pentane hydrates

Isopentane – Neopentane – Methane Hydrate

As the existence of structure H hydrates in nature could be recently verified this study was extended to hydrates containing constitutional isomers with five carbon atoms [3]. Isopentane is known as

structure H former [23]. Its smaller structural isomer is neopentane which occupies the large cavity of structure II [24]. Isopentane has two stable conformations – trans and gauche with C_1 and C_s symmetry, respectively [25].
To come close to natural conditions, a gas mixture was employed which included 1% isopentane 1% neopentane and 98% methane (gas mixture IIIc). In order to evaluate the results from this gas mixture hydrate samples were synthesized which contained only one pentane isomer and methane. According to the ^{13}C NMR spectra and powder X-ray diffraction pattern it could be verified for the samples containing only one isomer that neopentane is incorporated into the H ($5^{12}6^4$) cavity of structure II and isopentane is encaged in the E ($5^{12}6^8$) cavity of structure H (Figure 8a and 9a and 8b and 9b, respectively).
Figure 8 shows the results of CP/MAS ^{13}C NMR measurements for all three mixed hydrates. The peak positions and assignments, which were confirmed by literature data, are presented in Table 5 [9, 26].

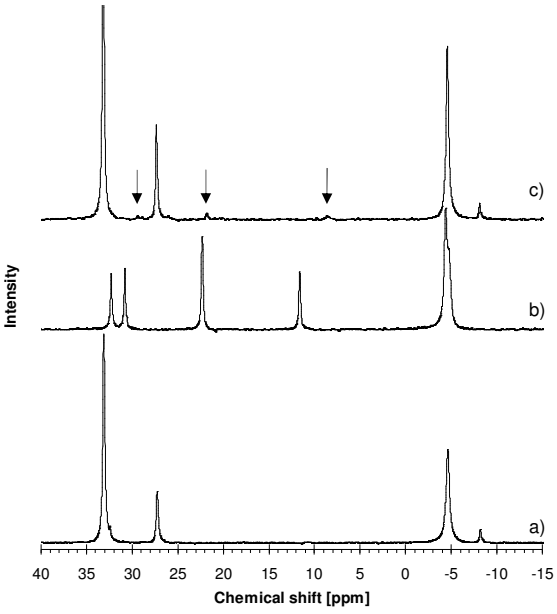

Figure 8. CP/MAS ^{13}C NMR spectra of a) neopentane – methane hydrate, b) isopentane – methane hydrate, c) isopentane – neopentane – methane hydrate. In order to show the isopentane signals (marked by an arrow) the CH_3-signal for neopentane was cut.

The carbon skeleton of isopentane was numbered according to IUPAC rules. It should be noted that Shin et al. have shown before that isopentane is incorporated in its gauche conformation into $5^{12}6^8$ cavity of structure H [26]. Although the trans conformer is the low energy form and would fit into the large cavity of structure H, Shin et al. confirmed by HPDEC ^{13}C NMR techniques that the smaller gauche conformer is preferred.

System	Chemical shift [ppm]	Peak assignment
a) neopentane – methane hydrate	-4.62	methane in small cage
	-8.19	methane in large cage
	33.10	CH_3-signal of neo-C_5H_{12}
	27.24	C-signal of neo-C_5H_{12}
b) isopentane – methane hydrate	-4.39	methane in small cage
	-4.77	methane in medium cage
	22.31	CH_3-signal of iso-C_5H_{12} (C1)
	30.79	CH-signal of iso-C_5H_{12} (C2)
	32.29	CH_2-signal of iso-C_5H_{12} (C3)
	11.62	CH_3-signal of iso-C_5H_{12} (C4)
c) isopentane – neopentane – methane hydrate (2.3 MPa)	-4.58	methane in small cage
	-8.13	methane in large cage
	33.17	CH_3-signal of neo-C_5H_{12}
	27.33	C-signal of neo-C_5H_{12}
	29.42	CH-signal of iso-C_5H_{12} (C2)
	21.83	CH_3-signal of iso-C_5H_{12} (C1)
	8.61	CH_3-signal of iso-C_5H_{12} (C4)

Table 5. Chemical shifts and peak assignments for the pentane hydrates.

The ^{13}C NMR spectra of the isopentane – neopentane – methane hydrate sample (Figure 8c) shows only traces of isopentane in the hydrate phase. Neopentane is the dominant pentane isomer that was trapped in the hydrate cage. In order to influence the hydrate composition the samples were synthesized at four different pressures: 2.3 MPa, 3.0 MPa, 3.5 MPa and 4.0 MPa. But no distinctive change in the hydrate composition could be achieved. Therefore the sample that was synthesized at 2.3 MPa was chosen as representative (Figure 8c and Figure 9c).
For isopentane in the mixed pentane hydrate only carbon signals for C1, C2 and C4 could be observed which were marked by an arrow in Figure 8c. Please note that the peak positions for isopen-

tane in the mixed pentane hydrates are slightly shifted upfield compared to isopentane in the isopentane – methane hydrate (Figure 8b). Only the isopentane – neopentane – methane sample that was prepared at 3.0 MPa shows a double peak for the CH_3-group of isopentane where one peak coincides with the peak position of the C1-signal for isopentane in the structure H hydrate.

To verify the crystal structure of the isopentane – neopentane – methane hydrates powder X-ray diffraction measurements were performed and compared with hydrate samples containing only one pentane isomer (Figure 9). As both pentane isomers are known to form different hydrate structures a mixture of reflections from structure II and structure H was expected. In fact, for the mixed pentane samples only structure II reflections could be recorded. Once again only the isopentane – neopentane – methane sample synthesized at 3.0 MPa shows one small reflection that can be assigned to structure H hydrate.

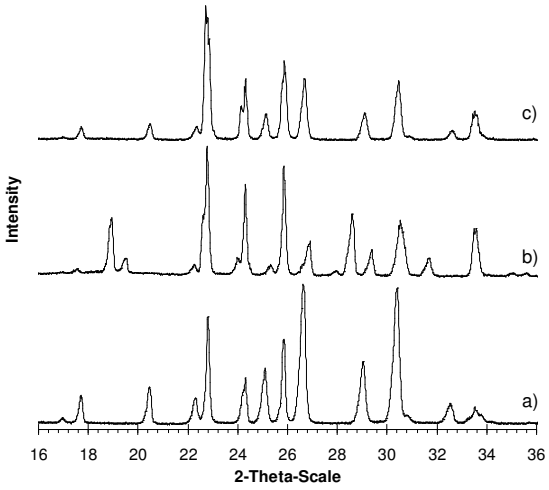

Figure 9. Powder X-ray diffraction pattern of a) neopentane – methane hydrate, b) isopentane – methane hydrate, c) isopentane – neopentane – methane hydrate.

The ^{13}C NMR measurements have shown that the amount of isopentane is very low in the hydrate phase. So one might assume that the concentration of structure H hydrate was too low to be detected by powder X-ray diffraction.

But due to the fact that the carbon signals for isopentane of the mixed pentane hydrate are shifted upfield these results can also lead to another assumption. We calculated the van-der-Waals diameter of gauche isopentane at first from the molar volume with an assumed spherical structure of the molecule: 6.23 Å and secondly from an Onsager cavity: 7.86 Å. As gauche isopentane has no ideal spherical structure the "real" van-der-Waals diameter lies between those two values. Regarding the ratio of the molecular diameter of gauche isopentane to the cavity diameter of the $5^{12}6^4$ cage of structure II this leads to the conclusion that the gauche isopentane does also fit into the $5^{12}6^4$ cavity. Thereto, ab initio calculations were performed which should show if the large cavity of structure II could be occupied by the gauche conformer of isopentane as well. In fact, the optimizing process for a structure II hydrate with isopentane in its gauche conformation was successful (Figure 10) and shows that this conformer can also occupy the large cavity structure II. Thus, the observed upfield shift for isopentane in the mixed pentane hydrate might result from its enclathration in the $5^{12}6^4$ of structure II. The driving force for this effect is supposedly the presence of neopentane, another higher hydrocarbon guest molecule that forms structure II.

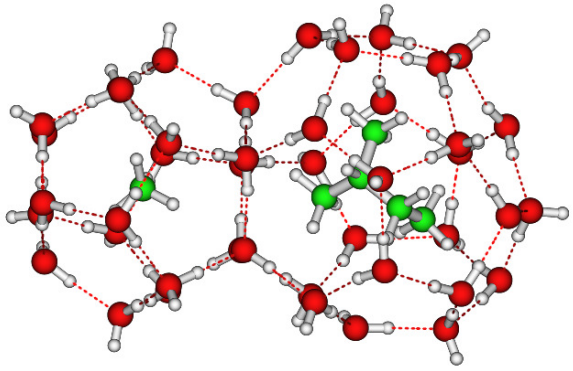

Figure 10. Optimized structure of isopentane – methane hydrate. Isopentane is encaged in its gauche conformation in the H ($5^{12}6^4$) cavity of structure II.

For this reason it can be concluded that although isopentane is a typical structure H former it might be also incorporated into the large cavity of structure II when another higher hydrocarbon guest molecule is present. There is only one mixed pentane sample that shows traces of a structure H hydrate. But the diffraction pattern of all other samples shows only structure II reflections. Therefore we conclude that depending on the formation conditions isopentane is able to form either a structure II or a structure H hydrate or probably even coexisting structure II and structure H hydrates. But to

verify this assumption further investigations are necessary.

CONCLUSION

The aim of this study was to investigate the interaction of guest molecular properties e.g. the conformation and molecular properties of the gas hydrate formed. Therefore gas hydrates were synthesized which contained the constitutional isomers of butane or two constitutional isomers of pentane in excess methane, respectively. By means of three examples this interaction was illustrated.

For the isobutane – methane hydrate it was observed that the peak positions for isobutane in the ^{13}C NMR spectrum are reversed relative to their order in the pure compound. With the help of single crystal X-ray measurements it could be shown that isobutane is moved out of the cavity centre. The resulting interaction of the guest molecule and the cavity wall is assumed to be the reason for the change in the peak positions.

On the basis of Raman spectra, single crystal X-ray diffraction data and quantum mechanical calculations it could be verified that n-butane occupies the large cavity of structure II in its gauche conformation.

The results for isopentane – neopentane – methane hydrates led to the assumption that similar to n-butane the conformation of isopentane plays an important role during the hydrate formation process although the conformation itself is not expected to change significantly. Depending on the formation conditions e.g. the presence of another higher hydrocarbon like neopentane the "ambivalent" gauche conformer of isopentane does influence the crystal structure of the hydrate and vice versa. In order to examine this phenomenon in more detail single crystal X-ray measurements for these hydrates and additional ab initio calculations are under way.

SUPPLEMENTARY INFORMATION

Details of single crystal data collections and refinement:

Structure II isobutane – n-butane – methane hydrate. Crystal size 0.15 x 0.15 x 0.15, cubic, space group: Fd-3m, a=17.213(1)Å, V = 5099.9(2)Å^3, T=100.0(1)ºK, ρ_{calc}= 1.033 mg/m^3, 2θMax=50.00º, 117 parameters, 33 restrains, residual electron density max. 0.53, min. -0.22 eÅ^{-3}. Final R indices (I>2σ(I)): R_1= 0.064, wR_2= 0.172 (28603 reflections total, 275 unique, 246 (I>2 σ (I)).

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