Specific Interactions of CH_2- and CH_3-Groups of n-Paraffins with PFTB

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Dedicated to Professor Dr. Kurt Dehnicke, Universität Marburg, on the occasion of this 60th birthday

The OH stretching frequency ν_{OH} of perfluoro-tert.-butanol (PFTB) dissolved in different liquid n-paraffins decreases with increasing chain length n of the solvent. This observation is explained by an overlapping of two different ν_{OH} absorption bands induced by interactions between CH_2- resp. CH_3-groups and the OH-oscillators of PFTB. The decrease of ν_{OH} demonstrates an increase of the intermolecular interaction energies. These mean interaction energies between the OH-groups and the solvent molecules increase with n in a similar way as the densities ϱ of the paraffins. The frequency shifts $\Delta\nu_{OH}$ ($\Delta\nu_{OH} = \nu_{OH\,(Gas)} - \nu_{OH}$) of PFTB as well as the specific volumes V of the paraffins can be described by a sum of CH_2- and CH_3-group contributions. In this way the role of the cohesion energy for $\Delta\nu_{OH}$ is demonstrated. The $OH \cdots CH_2$-interaction has been found as 2.5 times larger than $OH \cdots CH_3$-interactions. The $I \cdots CH_2$ Lennard-Jones parameter ε has been found too as 2.5 times larger than the value of $I \cdots CH_3$ interactions. This agreement demonstrates the efficiency of the intermolecular IR spectroscopy.

The sum of group contributions for interactions of linear molecules seems to have some advantages and may be more intuitive by its simplicity in comparison to explanations with parameter for "non-central forces" as e.g. the acentric factors ω of Pitzer et al.

Introduction

The so-called Badger-Bauer rule [1] predicts a proportionality between the frequency shift $\Delta\nu_{OH} = \nu_{OH\,(Gas)} - \nu_{OH}$ and the interaction energy ΔH_H in H-bonds. To illustrate this, the spectra of saturated solutions of H_2O in different solvents are shown in Figure 1 [2]. The combination band of water ($\nu_2 + \nu_3$) is shifted to lower frequencies with increasing H-bond acceptor strength of the solvent. The spectrum with the strongest base in this experiment, diethylamine, reveals the broad absorption band of the H-bonded OH-groups at $\sim 5125\ cm^{-1}$ and in addition a narrow band at $\sim 5300\ cm^{-1}$. Likewise in ketones and alcohols as solvents absorptions around $5300\ cm^{-1}$ are observed. These bands can be assigned to the absorptions of non H-bonded OH-groups in the neighbourhood of hydrophobic CH_x-groups of the solvents.

For these weaker interactions a similar proportionality for $\Delta\nu_{OH}$ with a proportionality factor different from that given by the Badger-Bauer rule for H-bonds is valid [3].

Consequently we could show recently that OH-groups interacting with perhalogenated solvent molecules containing different halogen substituents yield different shifted ν_{OH} absorption bands induced by $OH \cdots FC$-, $OH \cdots ClC$-, $OH \cdots BrC$- resp. $OH \cdots IC$-interactions [4].

First attempts to correlate ν_{OH} absorption band shoulders with interactions between OH groups and different sites in larger molecules have been described by Szczepaniak et al. [5] and by Schriver and Burneau [6].

With the low temperature matrix isolation spectroscopy we obtained clearly separated ν_{OH} bands which we assigned to the above mentioned interactions. We were able to confirm these assignments by comparison with solution spectra at room-temperature [4].

According to this, one could expect that OH-groups surrounded by n-paraffin molecules should induce only one ν_{OH} absorption band independent of the chain length n. However, precise measurements with perfluoro-tert.-butanol (PFTB), containing an OH-oscillator whose force constant is very sensitive to changes of its molecular environment, have shown that the observed frequency shift $\Delta\nu_{OH}$ depends on n [7].

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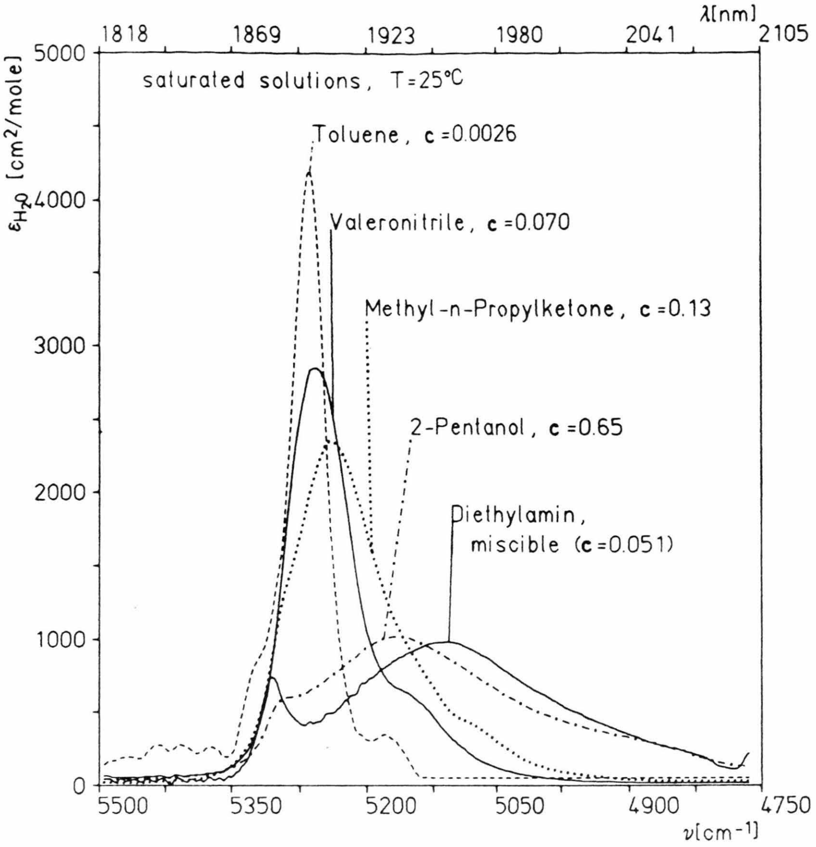

Fig. 1. The combination band $(\nu_2+\nu_3)$ of water solved saturatedly in different solvents at 25 °C. c [mol H_2O/mol solvent]: saturation concentration of H_2O (for diethylamine no saturation is obtained). $\Delta\nu$ is proportional to the acceptor strength (Badger-Bauer-rule) of the solvent and proportional to c. – The small band at ~5300 cm^{-1} with diethylamine as solvent is induced by CH_x-groups and indicates that different groups in a solvent molecule cause separated OH-bands.

The intention of this paper is to study the cause of this observation in order to explain the detailed mechanism of n-paraffin solvent effects.

Parallel to the observed dependence of $\Delta\nu_{OH}$ on n, macroscopic properties of n-paraffins also change continuously with n, as e.g. the mole volume [8], the second virial coefficient [9], the compressibility factor [10] and the solubility of rare gases in paraffins [11]. For instance, the Ostwald solubility coefficient for Krypton at 25 °C decreases from $1.27 \cdot 10^{-2}$ in hexane to $0.756 \cdot 10^{-2}$ in tetradecane.

Based on the idea that deviations from the hypothesis of *corresponding states* may depend on the deviation of the spherical symmetry of molecules [12], Pitzer et al. described the influence of the chain length n of paraffins in thermodynamic terms by an acentricity factor ω [9, 10].

Altenburg [13] treated properties of paraffins with mean values of summed radii of the molecule groups. He needs 5 terms with 5 fitted constants.

Spectra are the language of molecules. Therefore it seemed to be reasonable to study the intermolecular interactions directly with vibrational spectroscopy based on the Badger-Bauer rule and to modify the more geometrical treatments of Pitzer et al. and of Altenburg.

Experimental

The IR absorption spectra have been recorded on a Perkin Elmer 325 grating spectrometer which was connected to a personal computer via an A/D-converter for the digitizing and the subsequent working up of the spectra. 10 data points were collected per wavenumber (10/cm^{-1}).

The used thermostated QI cells with an optical pathlength (d) of 1 mm were from Fa. Hellma (Mülheim, Germany). A calibration series to relate the temperature measured inside the cells with the tempera-

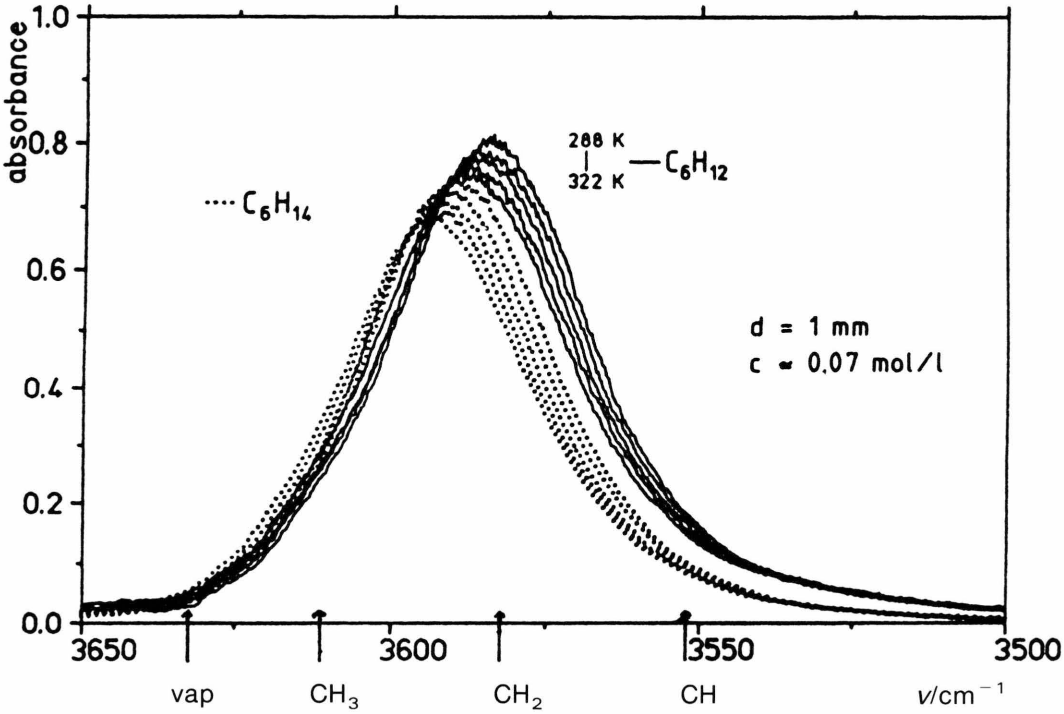

Fig. 2. Fundamental OH stretching band of perfluoro-tert.-butanol (PFTB) solved in n-hexane (dotted lines) and in cyclohexane (full lines) at different temperatures *T* (*T* decreases from the top of the bottom). For the partial bands indicated at the abscissa see text.

ture of the thermostate has been used to determine the exact temperature of the samples during the experiments.

The spectra shown in Fig. 5 were recorded with a self-constructed cell for low-temperature experiments ($d = 1$ mm) [7] which was placed in vacuum to prevent the condensation of atmospheric moisture on the optical windows and was cooled by a regulative flow of liquid helium.

PFTB was obtained from SCM Chemicals (Gainesville, Florida, USA). The n-paraffins had the quality UVASOL® or per synthesis and were obtained from Fa. Merck (Darmstadt, Germany).

The concentration of PFTB in the solvents was ~ 0.07 mol · l⁻¹. During the recording of a solution spectrum the pure solvent was placed in the reference beam of the spectrometer in order to eliminate disturbing spectral features of the solvent.

Results and Discussion

Figure 2 illustrates the ν_{OH} absorption band of PFTB dissolved in n-hexane and in cyclohexane at different temperatures (*T*). Three observations are made:

(i) At the same temperature ν_{OH} of PFTB is different for the two solvents.

(ii) Both $\Delta\nu_{OH}$ and the intensities of the bands increase by lowering the temperature *T*.

The increase of $\Delta\nu_{OH}$ is effected by the decrease of the intermolecular distances resp. by the increase of intermolecular interactions [3]. The intensity of the band is proportional to $\Delta\nu_{OH}$ caused by a change of the dipole moment derivatives of the OH-oscillators [14].

(iii) The low-frequency side of the ν_{OH} band seems to change more with *T* than the high-frequency side of the band.

This effect may indicate the existence of two overlapping ν_{OH} bands which may be caused by different interactions, i.e. two different configurations, $OH \cdots H_3C$ and $OH \cdots H_2C$, in the solution.

Recently we have shown that $d\nu/dT$ of the ν_{OH} absorption is proportional to $\Delta\nu_{OH}$ [3, 7]. If the absorp-

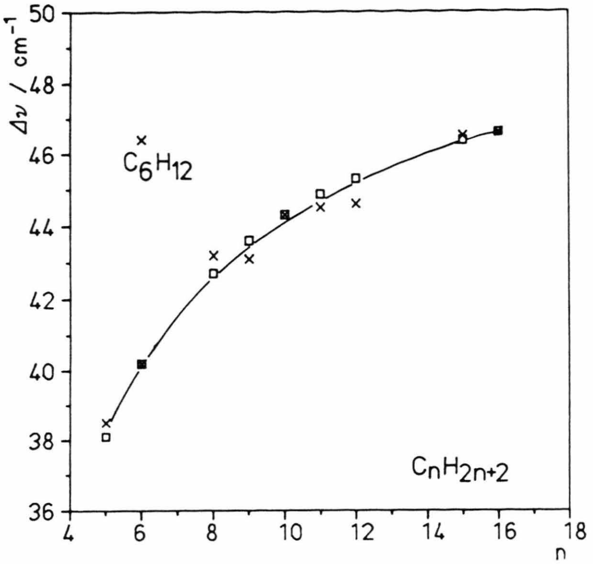

Fig. 3. Band maxima $\Delta\nu_{OH}$ of PFTB in different n-paraffins C_nH_{n+2} at 30 °C in dependence on the chain length n (×: experimental, □: calculated with (1)).

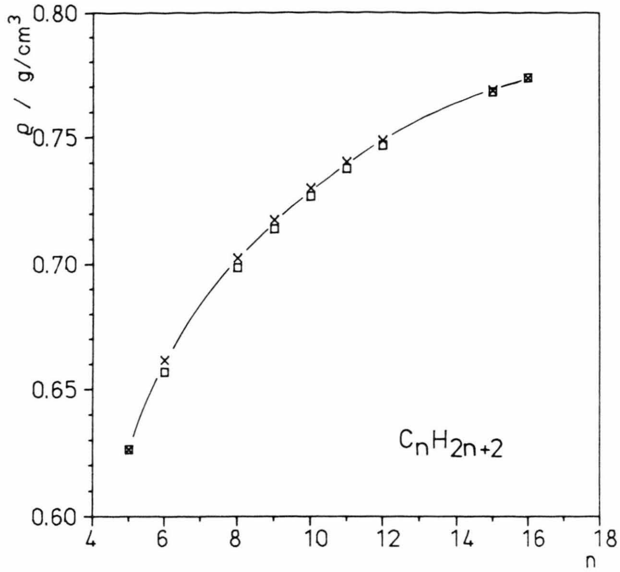

Fig. 4. Densities ϱ of n-paraffins C_nH_{n+2} at 20 °C in dependence on the chain length n (×: experimental, □: calculated with (2)).

tion bands in Fig. 2 consist of two overlapping bands, then consequently the low frequency component should have a larger T-dependence. This should explain observation (iii).

In Fig. 3 we have plotted the experimentally obtained ν_{OH} band positions at 30 °C (× in Fig. 3) versus n of the solvent. Assuming that the band maximum is determined by the two different absorptions of OH-groups in the neighbourhood of CH_2- or CH_3-groups, we can calculate $\Delta\nu_{OH}$ in dependence on the relative amounts x of CH_2 and CH_3 in the paraffin:

$$\Delta\nu_{OH} = x(CH_2)\cdot\Delta\nu(CH_2) + x(CH_3)\cdot\Delta\nu(CH_3),$$
$$x(CH_2) + x(CH_3) = 1 \qquad (1)$$

with

$\Delta\nu(CH_2)$ OH···H_2C-frequency shift,

$\Delta\nu(CH_3)$ OH···H_3C-frequency shift.

In Fig. 3 the values calculated in this way are included (□ in Figure 3).

$\Delta\nu(CH_2) = 50.6\ \mathrm{cm}^{-1}$ and $\Delta\nu(CH_3) = 19.2\ \mathrm{cm}^{-1}$

gave the best agreement with the experimental data. The deviations between experimental and calculated data are inside the error limit for $\Delta\nu_{OH}$.

The ratio of the two fitted frequency shifts for interactions with the CH_2- and CH_3-groups, $\Delta\nu(CH_2)/\Delta\nu(CH_3) = 2.64$, seems to be unexpectedly large. However, the specific volumes V (at 20 °C) of the different paraffins show a similar dependence on n. This is shown in Fig. 4 where we have plotted the densities ϱ versus the chain length n (× in Figure 4).

The specific volumes V ($V = 1/\varrho$) of the paraffins can be described by

$$V = x(CH_2)\cdot V(CH_2) + x(CH_3)\cdot V(CH_3) \qquad (2)$$

with

$V(CH_2) = 1.1551\ \mathrm{cm^3\,g^{-1}}$

resp. $\varrho(CH_2) = 0.8657\ \mathrm{g\cdot cm^{-3}}$,

$V(CH_3) = 2.2597\ \mathrm{cm^3\,g^{-1}}$

resp. $\varrho(CH_3) = 0.4425\ \mathrm{g\cdot cm^{-3}}$.

In this way the specific volume V of a paraffin can be understood to be given by the sum of contributions of its CH_2- and CH_3-segments. The densities of the paraffins calculated with (2) are included in Fig. 4 (□ in Figure 4).

The lower density of the CH_3-group is in accordance with a lower OH···H_3C-interaction (correspondingly $\Delta\nu_{OH}$) compared with the value or the CH_2-group.

Cyclohexane induces a relative large shift $\Delta\nu_{OH} = 46.4\ \mathrm{cm}^{-1}$ as against $\Delta\nu_{OH} = 40.2\ \mathrm{cm}^{-1}$ of PFTB in n-hexane. Nevertheless, cyclohexane contains only CH_2-groups of higher interaction ability and the observation of these values is consistent with the higher values found with n-$C_{16}H_{34}$ ($\varrho = 0.7733\ \text{g} \cdot \text{cm}^{-3}$ and $\Delta\nu_{OH} = 46.6\ \text{cm}^{-1}$), a paraffin consisting mainly of CH_2-groups ($x(CH_2) = 0.88$). Taking into consideration also isomers of paraffins, a third kind of interaction of the OH-oscillators, OH ··· HC, should be possible. Consequently the observed $\Delta\nu_{OH}$ values of PFTB at 30 °C in the isomers n-hexane ($\Delta\nu_{OH} = 40.2\ \text{cm}^{-1}$), 2-methyl-pentane ($\Delta\nu_{OH} = 39.6\ \text{cm}^{-1}$) and 2,3-dimethyl-butane ($\Delta\nu_{OH} = 40.0\ \text{cm}^{-1}$) can be calculated with an equation equivalent to (1):

$$\Delta\nu_{OH} = x(CH) \cdot \Delta\nu(CH) + x(CH_2) \cdot \Delta\nu(CH_2) + x(CH_3) \cdot \Delta\nu(CH_3). \qquad (3)$$

The two isomers containing CH-groups give values for $\Delta\nu(CH)$ of 80 cm^{-1} and 81 cm^{-1}. This agreement demonstrates the usefulness of the assumption of different site group interactions. The series

$$\Delta\nu(CH) = 80.5\ \text{cm}^{-1},$$
$$\Delta\nu(CH_2) = 50.6\ \text{cm}^{-1},$$
$$\Delta\nu(CH_3) = 19.2\ \text{cm}^{-1}$$

reveals $\Delta\Delta\nu$-values of approximately 30 cm^{-1} for the substitution of an alkyl-group by a H-atom at the carbon-atom in an alcane. The values of these three "partial bands" are marked in Fig. 2 on the abscissa ($\nu(CH_3) = 3613.3\ \text{cm}^{-1}$, $\nu(CH_2) = 3581.9\ \text{cm}^{-1}$ and $\nu(CH) = 3552.0\ \text{cm}^{-1}$).

The spectra of PFTB in 2-methyl-pentane, which are shown in Fig. 5, could exhibit the three "partial bands" as band shoulders indicated at ~3615 cm^{-1} and ~3575 cm^{-1}. By lowering the temperature, the shoulder at ~3615 cm^{-1}, which we assign to OH ··· H_3C, seems to disappear. This observation can be explained by an increase of the probability for the OH-oscillators to undergo the stronger OH ··· H_2C-interactions.

In Table 1 are listed $d\nu/dT$-values for ν_{OH} of PFTB in paraffins. Unlike the experience that $d\nu/dT \sim \Delta\nu$ [3, 7], $d\nu/dT$ decreases a little the higher $\Delta\nu_{OH}$, i.e. the higher n of the paraffin (compare the values for $n = 5$, 6, 11, 15 in Table 1). This small deviation can be explained as indicated above: A preference of OH to undergo OH ··· H_2C-interactions may cause an additional T-dependence by T-dependent change of configurations from OH ··· H_3C to OH ··· H_2C. The superposition of this additional $d\nu/dT$ with the "usual" $d\nu/dT$-value of an absorption band [3, 7] could therefore induce the observed higher $d\nu/dT$-values for paraffins with higher contents of CH_3-groups.

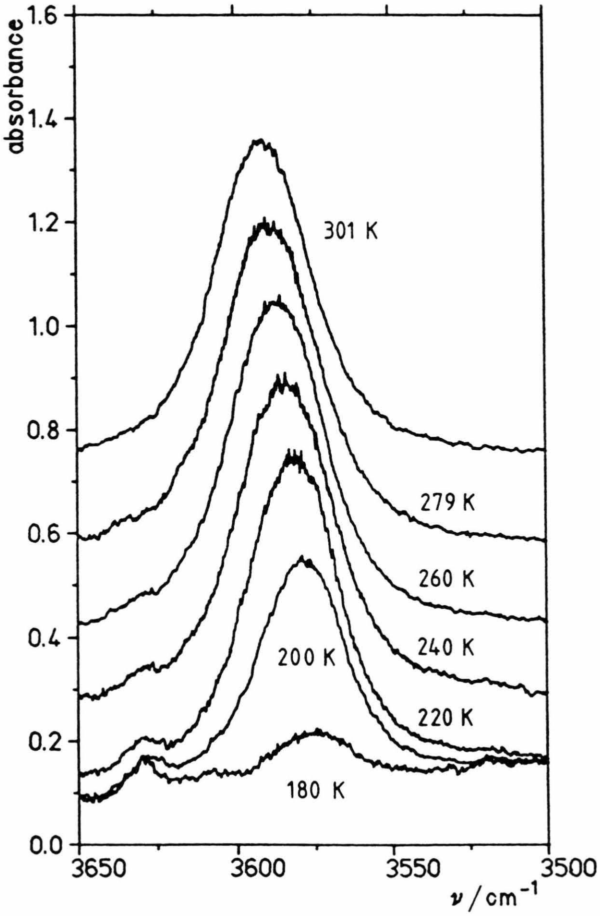

Fig. 5. The temperature dependence of the OH stretching band of 0.07 m PFTB in 2-methyl-pentane. The observed halfwidths of the bands may indicate the existence of an overlapping of bands on the high- and on the low-frequency side of the main band caused by OH ··· H_3C- (~3615 cm^{-1}) and OH ··· HC- (~3575 cm^{-1}) interactions.

Table 1. $\Delta\nu_{OH}$ (30 °C) in cm^{-1} and $d\nu/dT$ in $\text{cm}^{-1}\,\text{K}^{-1}$ (determined between 288 K and 322 K) of the OH band of 0.07 m PFTB in different n-paraffins and in the isomers 2-methyl-pentane (MP) and 2,3-dimethyl-butane (DMB).

	n-C_5H_{12}	MP	DMB	n-C_6H_{14}	n-$C_{11}H_{24}$	n-$C_{15}H_{32}$
$\Delta\nu_{OH}$	38.5	39.6	40.0	43.2	44.4	46.5
$d\nu/dT$	0.153	0.131	0.147	0.133	0.111	0.103

In the same way as the parameters used in (2) a volume contribution of $V(CH) = 0.05\ \text{cm}^3\,\text{g}^{-1}$ can be estimated for the CH-groups. With this $V(CH)$ calculations of V for the three isomers discussed above give values which correlate also with the observed shifts $\Delta\nu_{OH}$ of PFTB in these solvents. This supports our idea

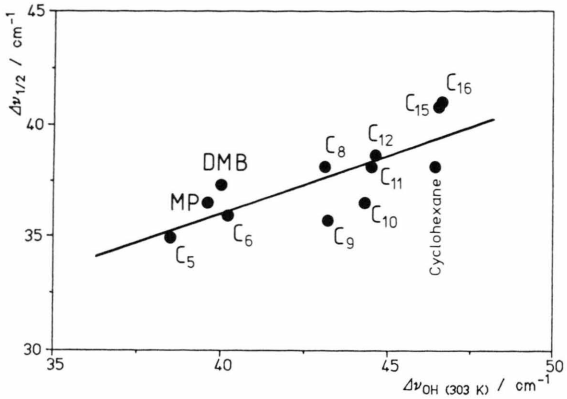

Fig. 6. Half width $\Delta\nu_{1/2}$ of the OH stretching band of PFTB in paraffins C_5H_{12} up to $C_{16}H_{34}$ and cyclohexane in dependence on $\Delta\nu_{OH}$ (30 °C), indicating a general linear dependence between $\Delta\nu_{1/2}$ and $\Delta\nu$. C_n is the abbreviation for C_nH_{2n+2}, MP = 2-methyl-pentane and DMB = 2,3-dimethyl-butane.

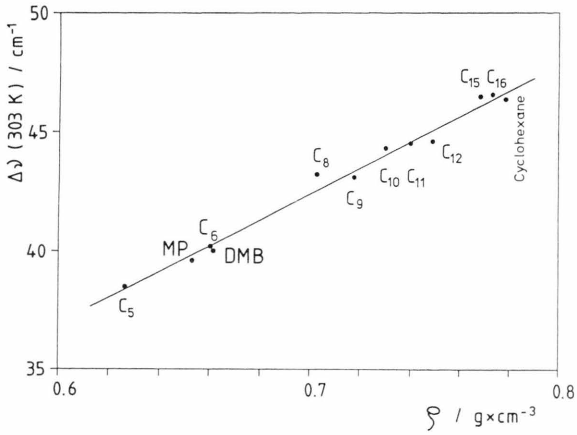

Fig. 7. $\Delta\nu_{OH}$ of PFTB in different n-paraffins as function of the density ϱ of the solvent at 30 °C. C_n is the abbreviation for C_nH_{2n+2}, MP = 2-methyl-pentane and DMB = 2,3-dimethyl-butane.

of summing up specific terms of different CH_x-groups to predict properties which are caused by intermolecular interactions.

Another feature of absorption bands, the half-width $\Delta\nu_{1/2}$, is shown in Fig. 6 in dependence on the frequency shift $\Delta\nu_{OH}$ of the band maximum. The roughly found correlation between $\Delta\nu_{1/2}$ and $\Delta\nu_{OH}$ agrees with the general experience that $\Delta\nu_{1/2}$ depends linearly on $\Delta\nu$ [3]. This can be explained theoretically with a distribution function of T-dependent intermolecular distances and is discussed in detail in a separate paper [19].

In Fig. 7 is shown the linear dependence between the experimental $\Delta\nu_{OH}$-values and the densities ϱ of the paraffins. The correlation reminds one of the relation between $\Delta\nu$ and Hildebrandt's cohesion energy. It can be understood in a way that all the specific groups of the solvents exhibit similar interaction energies with the OH-oscillators and may be induced mainly by the carbon-atoms of the groups but modified by different intermolecular distances to CH_2 resp. CH_3 as discussed in this article.

Conclusions

IR spectra of solutions of an alcohol in different n-paraffins reveal frequency shifts $\Delta\nu_{OH}$ as a measure of mean interaction energies which can be described in the same way as the densities of the solvents by a sum of contributions of specific interacting CH_3-, CH_2- and CH-groups. A method for the calculation of densities by adding group increments has already been given by Edwards et al. [8]. Based on direct spectroscopic evidence such a method is favoured too to describe intermolecular interaction energies by a sum of different interaction abilities of groups in larger molecules. This description seems to be easier and more intuitive than non-central force models [15] as e.g. the calculations of Pitzer et al. with acentric factors ω (Table 2) [9, 10] or calculations with mean radii contributions of groups given by Altenburg [13].

Table 2. Acentric factors ω of paraffins by Pitzer et al. [9, 10].

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_7H_{16}
ω	0.013	0.105	0.152	0.201	0.252	0.352

From our point of view represented in this article the designation of the chemical reactivity of solvents by donor numbers (DN) and acceptor numbers (AN) should be applied reservedly: A standard dye, used in general to determine AN-values, could interact preferentially with a certain group of a solvent molecule which is not necessarily the group where a chemical reaction starts.

Spectroscopic studies of H-bonded liquids as e.g. water with an equilibrium between H-bonded and non H-bonded OH-groups [16] reveal that water interacts temperature dependently with different parts of its molecules:

1. H-bond interaction (proton ··· lone pair),
2. "H-bond repulsion" (proton ··· proton, lone pair ··· lone pair) and
3. van-der-Waals-interactions between the O-atoms with sites between the lone pairs and the substituted protons.

This is indicated also by the spectrum of water dissolved in diethylamine shown in Fig. 1, revealing an absorption band at $\sim 5300\ \mathrm{cm}^{-1}$ which has to be assigned to non H-bonded OH-groups.

The different shapes of such absorption bands in the liquids water, methanol and ethanol (see Fig. 6 in [17]) may be caused by different van-der-Waals interactions: Interactions between the protons of the OH-groups with specific parts of the oxygen atoms in water and in addition with CH_3-groups in methanol resp. CH_2-groups in ethanol.

The small differences in the shapes of these absorption bands can be explained in this way. The occasionally made statement that water exhibits only H-bonded OH-groups in contrast to alcohols containing also non H-bonded OH-groups [18] referring to these small differences is therefore a weak argument, taking into account the knowledge of disturbances of the vibration spectra by van-der-Waals interactions.

In the meantime appeared a paper by Bartagnolli and Schulz [21]. The authors have calculated the Lennard-Jones parameter ε of different site group interactions of liquid ethyliodide based on x-ray scattering experiments:

	$I \cdots CH_2$	$I \cdots CH_3$
$\varepsilon/\mathrm{kJ \cdot mol^{-1}}$	0.05	0.02

This result with the ratio $\varepsilon(I \cdots CH_2) : \varepsilon(I \cdots CH_3) = 0.05 : 0.02$ is in excellent agreement with our conclusion $\Delta\nu(OH \cdots CH_2) : \Delta\nu(OH \cdots CH_3) = 50 : 20$ and with our recent spectroscopic result [20] that the interaction parameter of OH is similar to that of HI, $OH_{PFTB} : HI = 486 : 423$.

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