

Effect of Solvents and Temperature on O–H stretching Band of Methanol:

Measure of van der Waals Interactions

W. A. P. Luck and H. Y. Zheng *

Physikalische Chemie der Universität Marburg, Hans-Meerwein-Str. D-3550 Marburg (Lahn)

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The frequency shift of methanolic OH stretching bands by different nonpolar solvents at different temperatures can be described quantitatively by an equation proposed recently relating it to the temperature dependence of van der Waals interactions. The method shows that methanolic OH groups are surrounded by about 40% more solvent molecules than t-butanol OH groups.

Frequency shifts of CH₃OH by binary solvent mixtures demonstrate an averaged potential with small preference of the solvent with higher interaction.

1. Introduction

Recently [1] we have demonstrated that the frequency shift $\Delta\nu$ of the monomeric OH stretching vibration of t-butanol is proportional to the van der Waals interaction ΔU_{W12} between the OH group, 1, and the solvent, 2:

$$\Delta\nu \sim \Delta U_{W12}. \quad (1)$$

We relate the temperature dependence of $\Delta\nu$ to the temperature dependence of the heat of vaporization using our simple expression given in [2], the empirical rule [3, 4] that the pair potential U_{11} can be approximated as $U_{11} = f R T_c^{3/2}$ (T_c : critical temperature, f : a factor near unity), and the rule $U_{12} = (U_{11} U_{22})^{1/2}$. Thus we obtain for $T < T_B$ (T_B : boiling point)

$$\Delta\nu \sim \Delta U_{W12} = \frac{Z f R}{2} \left(\frac{3}{2} (T_{c1} T_{c2})^{1/2} - T \right), \quad (2)$$

where Z is the coordination number of the OH group.

Reprint requests to Prof. Dr. W. A. P. Luck, Institut für Physikalische Chemie der Universität Marburg, Hans-Meerweinstraße, D-3550 Marburg (Lahn).

* Permanent address: Chemistry Department, Hangzhou University, Hangzhou, Zhejiang, People's Republic of China.

In our previous paper [1] we found good agreement between the observed linear temperature dependence of $\Delta\nu$ and (2).

The aim of this paper is to test the validity of (2) with CH₃OH and to check the prediction that Z should be higher for CH₃OH than for t-butanol due to steric hinderance; we also like to test solvent mixtures for the possibility of the observation of a mixed potential.

2. Experimental

Infrared spectra were recorded on a Perkin Elmer 325 spectrometer for the fundamentals and on a Cary 17 I instrument for the first overtone.

The temperature measurements were made directly in the thermostatted cells (cell thickness 0.2 cm for fundamentals and 4 cm for the overtone). Methanol and the solvents (Fa. Merck, Darmstadt) were dried for a few days on 4 Å molecular sieves (Fa. Merck, Darmstadt).

The CH₃OH concentrations, determined by weighing, were kept (0.01 till 0.088 mol/l) with sufficient absorbance but low enough to assume that the environment of the OH groups is given by solvent molecules and not self association. The shifts of the band maximum $\Delta\nu = \nu_0$ (vapour) – ν (solvent) were calculated with ν_{01} (vapour) = 3687 cm⁻¹ and ν_{02} (vapour) = 7204.6 cm⁻¹. All solvents induce red shifts. The given spectra are directly recorded by a computer which is connected with the instruments.

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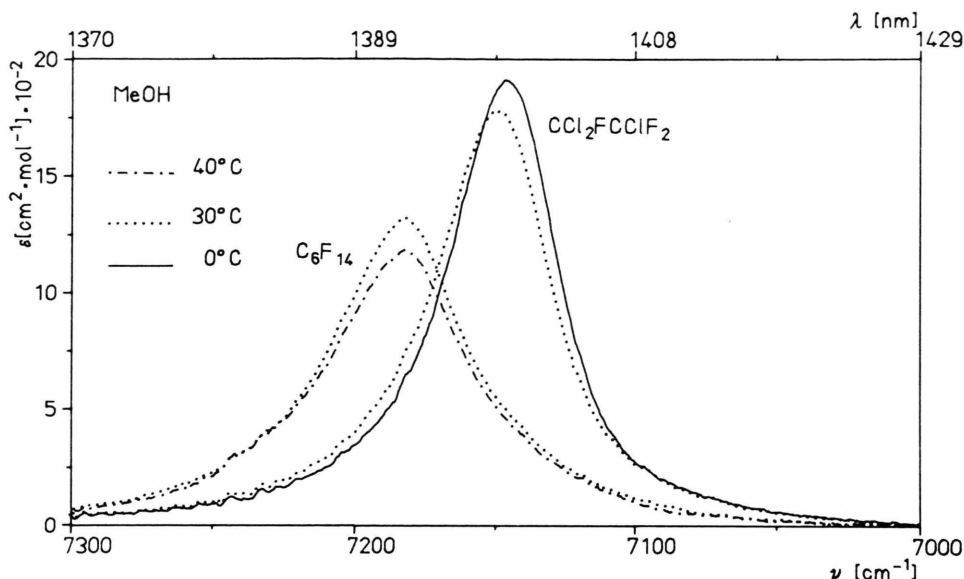


Fig. 1. Shift of the OH stretching band of monomeric methanol with solvent temperature. ϵ : Extinction-coefficients.

3. Results and Discussions

Figure 1 gives the OH overtone of methanol diluted in C_6F_{14} and in CCl_2FCClF_2 . The change of the solvent induces a band shift. CCl_2FCClF_2 induces a higher shift by higher intermolecular interactions. With decreasing temperature the shift enlarges because of smaller intermolecular distances leading to higher interactions.

a) Band Maximum Shifts $\Delta\nu_{OH}$

The band maxima shift with temperature because of the change in molecular distances and therefore in U_{W12} . As has been observed with t-butanol, this temperature dependence is strictly linear with methanol also (of Figure 2). It is found that (2) is also applicable to methanol.

The overtone shifts are double the fundamental shifts (hatched) lines in Figure 2. The correlation coefficients of the straight lines in Fig. 2 are better than 0.99.

The slopes of the straight lines, the $d(\Delta\nu)/dT$ -values, are 1.3 to 1.4 times larger than the corresponding slopes of t-butanol. In both cases the slopes of all solvents are similar, which means that with (2) we can assume a similar packing in all solvents (similar f Z-values). This observation together with (2) leads to the conclusion that the

methanolic OH group interacts with the solvent 30 to 40% more strongly than the t-butanolic OH group, due to its higher coordination number.

Similar results are obtained from the $\Delta\nu_0$ values, which are extrapolated to 0 K (Table 1). They are by a factor 1.3 to 1.5 bigger when compared with t-butanol.

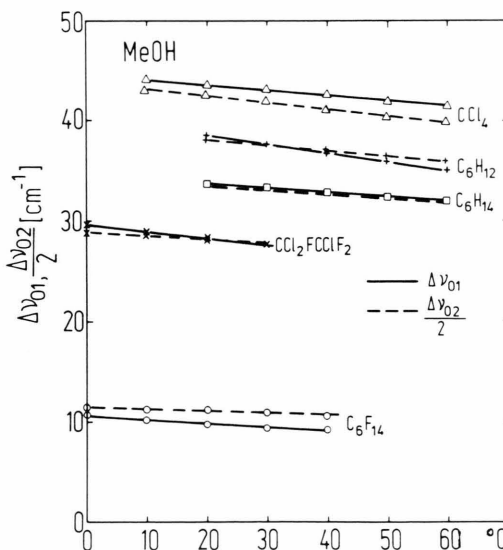


Fig. 2. The frequencies of band maxima decrease linearly with temperature. Full lines: fundamental band; hatched lines: 1st overtone.

Table 1. $\Delta\nu_0$ values of methanol in cm^{-1} .

	C_6F_{14}	$\text{CCl}_2\text{FCClF}_2$	$n\text{-C}_6\text{H}_{14}$	C_6H_{12}	CCl_4
$\Delta\nu_{0,01}$	22	47	48	64	64
$\Delta\nu_{0,02}$	18	41	48	55	62

Table 2. Comparison of the CCl_4 impact on different alcohols.

Alcohol	$\Delta\nu_{0,01}$ (cm^{-1})	$d(\Delta\nu_{01})/dT$ ($\text{cm}^{-1} \text{K}^{-1}$)	Ref.
$\text{CH}_3\text{OH}/\text{CCl}_4$	64	-0.0708	this paper
phenol/ CCl_4	63.4	-0.0707	[4]
t-butanol/ CCl_4	42.3	-0.055	[1]

The observed values for $\text{CH}_3\text{OH}/\text{CCl}_4$ are very similar to the values which we calculated based on measurements by Juffenbruch and Perkampus [5] on the system phenol/ CCl_4 ($C=0.003 \text{ mol/l}$), cf. Table 2.

b) Half Widths

The term: $-ZfRT/2$ in (2) can be described as thermal population of the vibration levels of the intermolecular potential. By the statistics of this population we expect an increase in the half widths $\Delta\nu_{1/2}$ of the bands with increasing T . This has been observed with the fundamental and the overtone bands of t-butanol. We observe a similar trend with methanol (Figure 3). The half widths $(\Delta\nu_{1/2})_{02}$ obtained for the first overtone are nearly twice those of the fundamental bands; $(\Delta\nu_{1/2})_{02}/2$ and $(\Delta\nu_{1/2})_{01}$ increase with T very similarly.

With increasing T , $\Delta\nu$ decreases but the half widths increase.

The half widths at 20°C and the slopes $(d(\Delta\nu_{1/2})/dT)$ have been found to be higher for methanol than for t-butanol [1] for fundamentals as well as first overtones.

c) Solvent Mixtures

In solvent mixtures we expect two peaks in the case of selected solvation or local demixing of the solvents, or we expect an average potential of the different neighbours and one averaged peak. It would be of interest to study binary mixtures with

solvents of extremely different $\Delta\nu$ -values. Unfortunately, C_6F_{14} with the lowest $\Delta\nu$ does not mix with CCl_4 , $n\text{-C}_6\text{H}_{14}$ or C_6H_{12} . The interactions of C_6F_{14} seem to be too different from the other solvents. (Compare the excess molar enthalpies [6] of mixtures with SF_6 .) The binary mixtures $\text{CCl}_2\text{FCClF}_2/\text{C}_6\text{F}_{14}$ and $n\text{-C}_6\text{H}_{14}/(\text{C}_6\text{F}_{11})\text{CF}_3$ could be studied.

Figures 4–6 show averaged peaks near the ideal expected values

$$\Delta\nu = x_1 \Delta\nu_1 + x_2 \Delta\nu_2$$

($x_{1,2}$: mole fraction of solvent 1 and 2, $\Delta\nu_{1,2}$: shifts in pure solvents).

Small deviations from this ideal mixture rule are observed (Figures 7–8). The solvent environment with higher interactions and with higher $\Delta\nu_i$ is preferred. The half widths in the mixtures are bigger than in the pure solvents due to the statistics of the different coordination numbers Z_1 and Z_2 (Figure 9).

We could not observe two separate maxima in our mixtures like those observed by Allerhand and Schleyer [7] and Szczepaniak and Orville-Thomas [8] in the systems phenol/perfluorooctane/hexane and phenol/perfluoromethylcyclohexane/ CCl_4 . Our observation supports the conjecture of Allerhand and Schleyer [7] that in their systems a micro-demixing has happened with perfluorcompound-clusters of about 140 molecules.

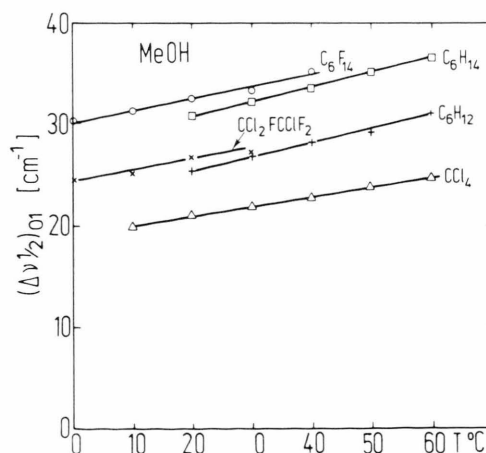


Fig. 3. The band half width $\Delta\nu_{1/2}$ of the methanolic OH stretching band increases linearly with temperature, indicating population of higher vibration levels in the intermolecular potential.

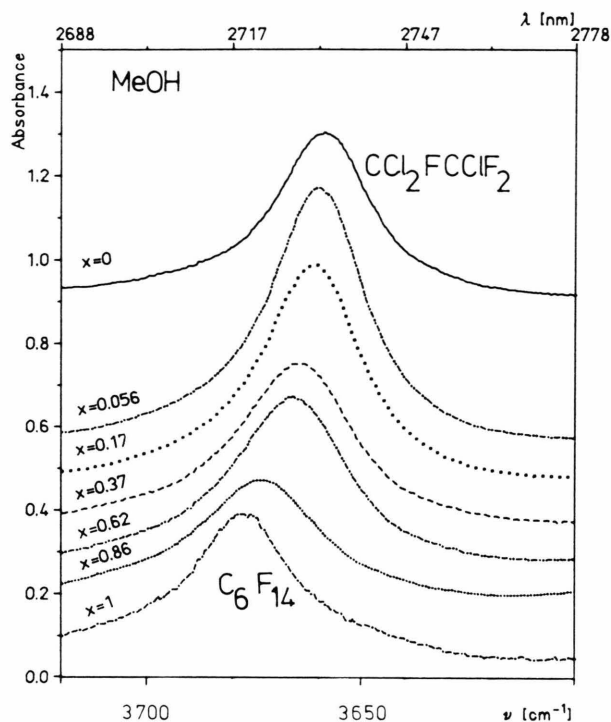


Fig. 4. The OH fundamental band of monomeric methanol at 20 °C in $\text{CCl}_2\text{FCClF}_2/\text{C}_6\text{F}_{14}$ mixtures; parameter: mole fraction of C_6F_{14} .

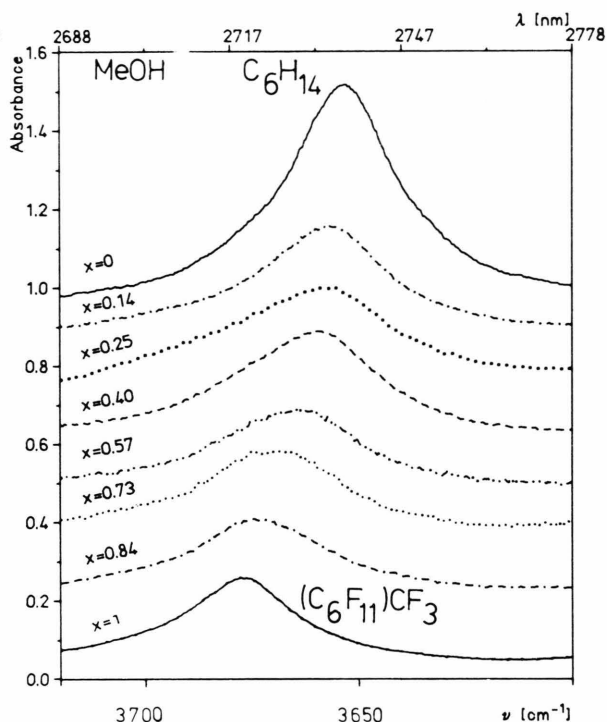


Fig. 5. Fundamental OH band of monomeric methanol at 20 °C in $n\text{-C}_6\text{H}_{14}/(\text{C}_6\text{F}_{11})\text{CF}_3$ mixtures; parameter: mole fraction of $(\text{C}_6\text{F}_{11})\text{CF}_3$.

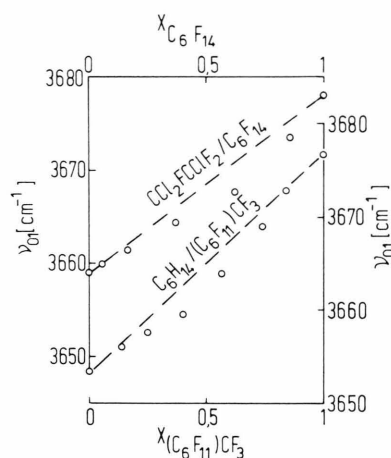
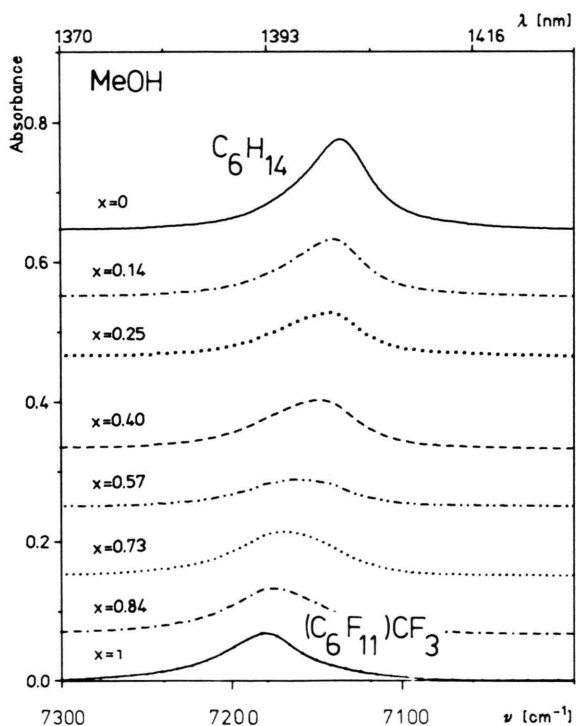


Fig. 7. Band maxima of the spectra in Figs. 4 and 5 (straight lines ideal mixtures).

Fig. 6. First overtone of OH stretching of monomeric methanol at 20 °C in $n\text{-C}_6\text{H}_{14}/(\text{C}_6\text{F}_{11})\text{CF}_3$ mixtures; parameter: mole fraction of $(\text{C}_6\text{F}_{11})\text{CF}_3$.

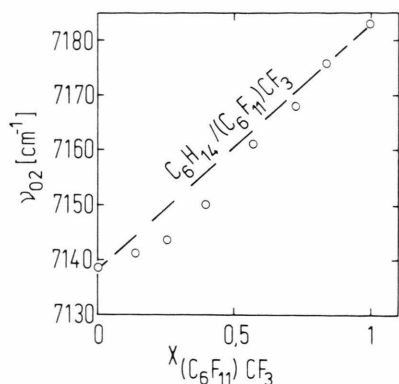


Fig. 8. Band maxima of spectra Fig. 6 (straight lines ideal mixtures).

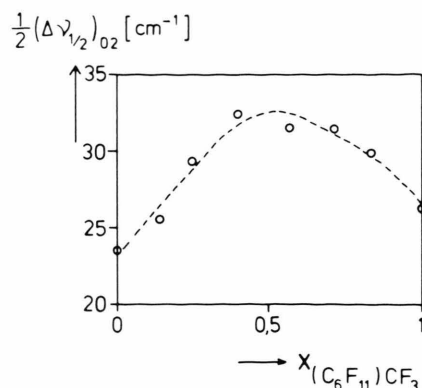


Fig. 9. The half widths of overtone spectra Fig. 6 as function of the mole fraction.

Conclusions

The comparison of the solvent and temperature dependence of the OH stretching band of methanol t-butanol demonstrates that the OH group of methanol is more sensitive to the environment. This result shows that the old method to describe solvent effects by the refraction index and/or dielectric constant is not sufficient. These corrections are only a measure of the interacting properties of the

solvent. The vibration bands depend on the interaction OH/solvent, that means on the interacting ability of both.

Last not least this paper demonstrates that the solvent effect on vibration bands is a useful tool to study van der Waals interactions and that the recently given formula for nonpolar interactions seems to be very efficient.

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