Monatshefte für Chemie 126, 889–895 (1995)

Monatshefte für Chemie
Chemical Monthly

An Infrared Spectroscopic Study on the Influence of Water on Alcohols

C. Kuttenberg, **E. Scheiber**, and **V. Gutmann**

Institute of Inorganic Chemistry, Technical University of Vienna, A-1060 Vienna, Austria

Summary: The influence of the water content on absorption bands in FTIR spectra of monohydric alcohols was studied and the effects were compared to changes in spectra of absolute solvents at various temperatures. The FTIR spectra were recorded by the ATR technique in order to distinguish the weak bands of the solvents from the intensive water bands more easily. By addition of water to anhydrous alcohols both OH stretching and bending bands increased in intensity and width. Similar changes in spectra of anhydrous alcohols can be obtained by decreasing the temperature. Addition of water to monohydric alcohols causes the lengthening of the intramolecular OH bonds to a smaller extent than the shortening of the intermolecular OH bonds. This contraction of the liquid structure is also reflected in other physical and chemical properties.

Keywords. FTIR spectroscopy; Influence of water on alcohols; Temperature study of IR spectra of alcohols; ATR.

Eine infrarotspektroskopische Untersuchung über den Einfluß von Wasser auf Alkohole

Zusammenfassung. Der Einfluß des Wassergehalts auf die Absorptionsbanden in den FTIR-Spektren einwertiger Alkohole wurde untersucht und die Effekte mit den Veränderungen der Spektren der absoluten Lösungsmittel bei Temperaturvariationen verglichen. Die FTIR-Spektren wurden mit Hilfe der ATR-Technik aufgenommen, um die meist nur schwachen Banden der Lösungsmittel neben den intensiven Wasserbanden besser erkennen zu können. Es zeigte sich, daß durch Zugabe von Wasser zu absoluten Alkoholen sowohl die OH-Streckschwingungs- als auch die Deformationsschwingungsbande an Intensität und Breite zunehmen. Ähnliche Veränderungen der Banden lassen sich auch in den Spektren von absoluten Alkoholen bei Temperaturerniedrigung feststellen. Diese spektroskopischen Veränderungen werden in folgender Weise interpretiert. Die Zugabe von Wasser zu einwertigen Alkoholen bewirkt die Verlängerung der intramolekularen O–H-Bindungen in schwächerem Ausmaß als die Verkürzung der Intermolekularen O···H-Bindungen, d.h. sie bewirkt eine Erhöhung der Symmetrie der H-Brückenbindungen und eine Verstärkung der O···O-Wechselwirkungen. Diese Verdichtung der Flüssigkeitsstruktur spiegelt sich auch in anderen physikalischen und chemischen Eigenschaften wider.

Introduction

Several spectroscopic studies on the changes of absorption bands in IR spectra of water caused by solutes have been made in order to learn about the influence of solutes on the water structure [1–11]. Since it is impossible to remove water completely from a liquid, the question of its influence is obvious. *Rosenholm* [12] found that "water diluted in 1-pentanol produces a structure characterized by hydrogen bonds stronger than in liquid water". *Bonner et al.* [13] studied changes in the spectra of alcohols by addition of water in the overtone range and concluded that "water appears to break up the alcohol structure".

In order to study the influence of water on monohydric alcohols, the comparative infrared spectroscopic examination was chosen, by which changes of the absorption bands of the IR spectra of alcohols depending on the water content are compared to changes in spectra of alcohols at different temperatures.

Results and Discussion

By addition of water to monohydric alcohols, both the OH stretching and bending bands increased in intensity and width as shown in Fig. 1 and Fig. 2.

Similar spectroscopic changes of anhydrous alcohols are found by decreasing the temperature. In addition, the maxima of the OH stretching bands shift to lower wave numbers by temperature decrease (Figs. 3–5) as summarized in Table 1.

Spectroscopic data are often interpreted by means of the concept of structure makers and structure breakers [6]. *Luck* [6] considers hydrophobic solutes as "structure makers" as they cause spectral changes in aqueous elektrolyte solutions in the same way as a decrease in temperature, and hydrophilic solutes as "structure breakers" as they cause spectral changes in the same way as increasing in temperature. Since addition of water to monohydric alcohols changes the spectra of alcohols in a similar way as a decrease in temperature, water should be considered as a structure maker in the case of alcohols.

Jackson et al. [22] and *Franks* [23] pointed out, however, that the characterization as structure makers and structure breakers based on the exclusive consideration of spectroscopic data can lead to wrong conclusions. It is well known [24] that

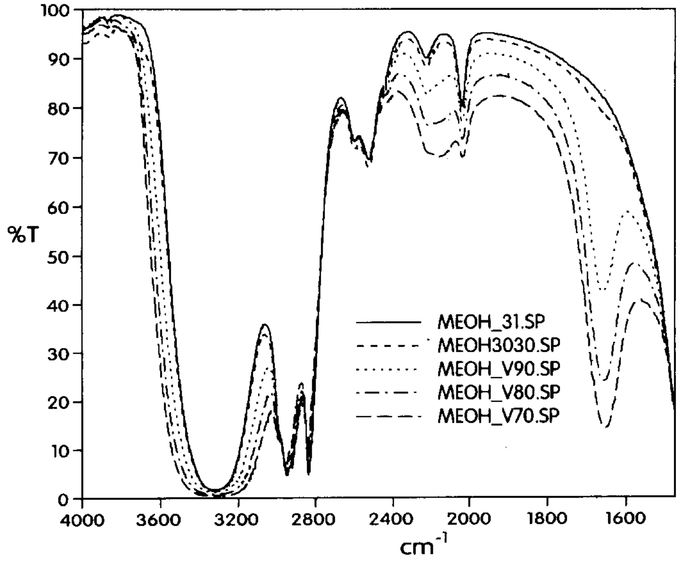

Fig. 1. FTIR spectra of methanol (MEOH_31 = 31 mg H_2O/l; MEOH3030 = 3030 mg H_2O/l; MEOH_V90 = 88% (w/w); MEOH_V80 = 76% (w/w); MEOH_V70 = 65% (w/w)

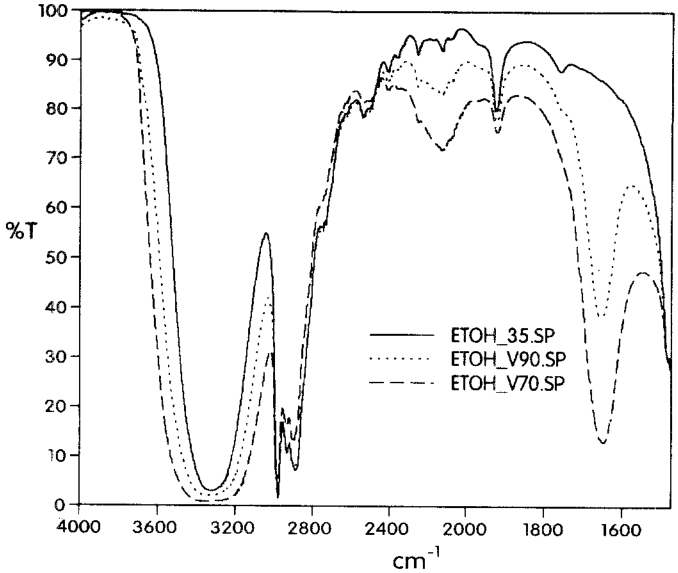

Fig. 2. FTIR spectra of ethanol ETOH_35 = 35 mg H_2O/l; ETOH_V90 = 88% (w/w); MEOH_V70 = 65% (w/w)

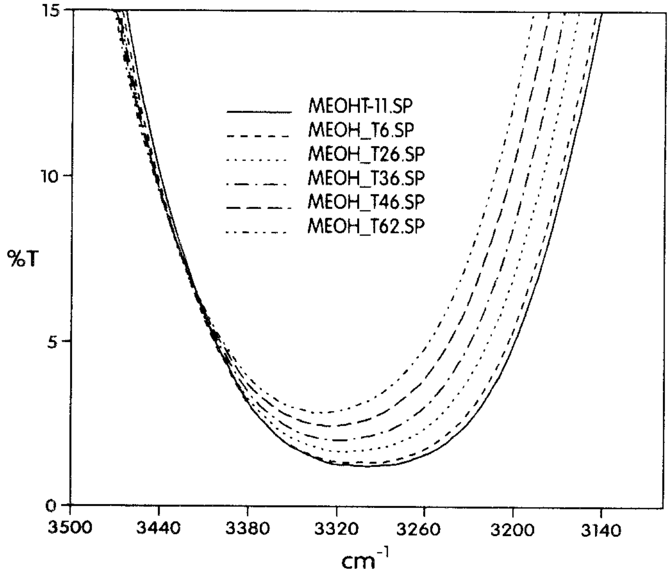

Fig. 3. Shift of the maxima of the OH stretching bands of methanol by variation of the temperature (MEOHT-11 = −7.5 °C; MEOH_T6 = 7.6 °C; MEOH_T26 = 24.9 °C; MEOH_T36 = 34.7 °C; MEOH_T46 = 44.2 °C; MEOH_T62 = 58.7 °C)

addition of structure breakers and structure makers leads to different changes in macroscopic properties as shown in Table 2.

Table 3 shows that the changes in macroscopic properties of alcohols by addition of water and by decrease in temperature occur in the same direction as by addition of structure breakers.

According to these changes, water in alcohols should be considered as a structure breaker, *i.e.* water molecules are well integrated in the structural framework of alcohols.

The spectroscopic changes due to the addition of water to monohydric alcohols, namely the increase in intensity and width of the OH stretching and bending bands can be interpreted in the following way: The intramolecular OH bands are lengthened whereas the intermolecular OH bands are shortened. The H-bridges are

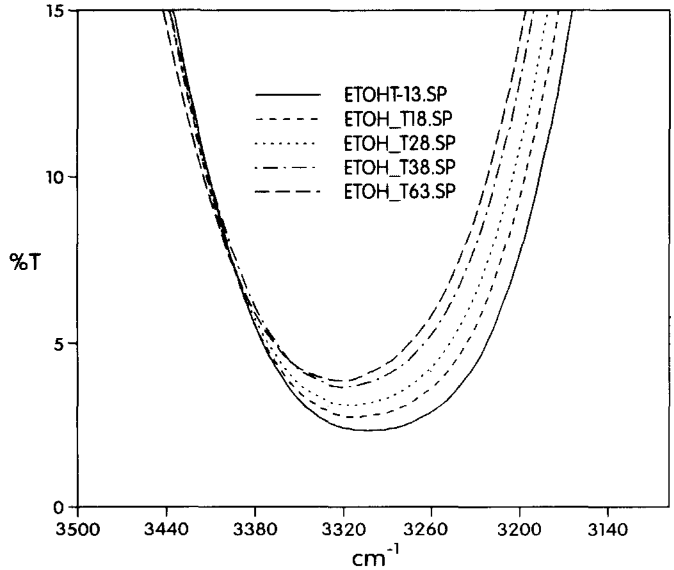

Fig. 4. Shift of the maxima of the OH stretching bands of ethanol by variation of the temperature (ETOHT-13 = −5 °C; ETOH_T18 = 18.7 °C; ETOH_T28 = 24.9 °C; ETOH_T38 = 34.6 °C; ETOH_T63 = 58.7 °C)

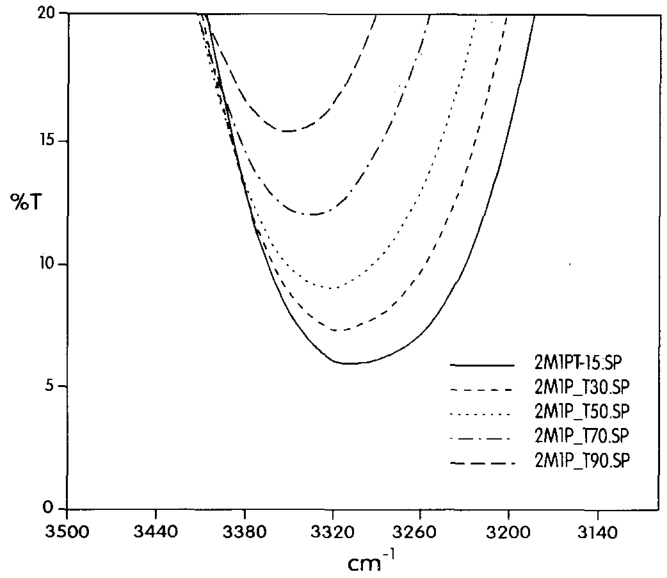

Fig. 5. Shift of the maxima of the OH stretching bands of 2-methyl-1-propanol by variation of the temperature (2M1PT-15 = −12.2 °C; 2M1P_T30 = 29.5 °C; 2M1P_T50 = 48.9 °C; 2M1P_T70 = 68.5 °C; 2M1P_T90 = 87.7 °C)

enhanced in symmetry, the O···O interactions are strengthened, and the O–H–O bond angles are increased. These variations of the bond length leads to a contraction of the liquid structure. This is reflected in increasing values for density [14], viscosity [15], and surface tension [16] as well as the decreasing values in compressibility [17], gas solubility [18–20], and heat capacity [21]. All these changes are analogous to those produced by lowering the temperature. It may, therefore, be concluded that water acts as a structure breaker in alcohols.

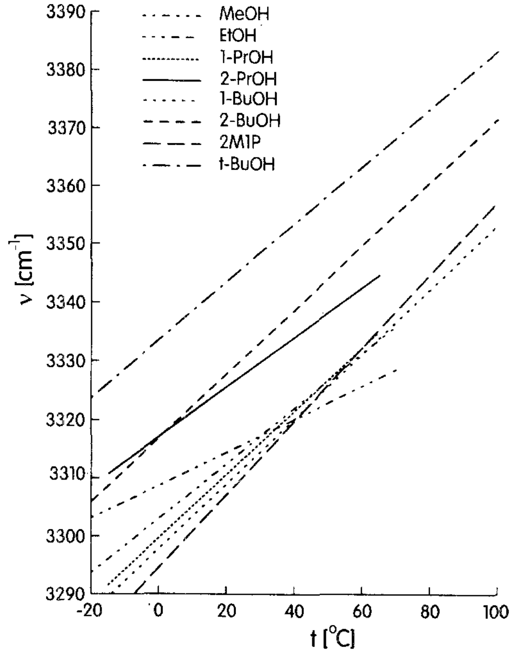

Fig. 6. Shift of the maxima of the OH stretching bands *vs.* temperature

Table 1. Shift ($\Delta\nu$) of the maxima of the OH stretching bands (in cm^{-1}); the relationship between ν and T is linear as shown in Fig. 6

Methanol	3303–3331 (−2.6 °C)(58.7 °C)	1-Pentanol	3305–3334 (−7.5 °C)(58.7 °C)
Ethanol	3306–3325 (−5 °C)(58.7 °C)	2-Pentanol	3321–3376 (−12.2 °C)(87.7 °C)
1-Propanol	3299–3334 (−7.5 °C)(58.7 °C)	3-Pentanol	3327–3388 (−12.2 °C)(87.7 °C)
2-Propanol	3318–3343 (−2.6 °C)(58.7 °C)	2-Methyl-1-butanol	3305–3358 (−12.2 °C)(87.7 °C)
1-Butanol	3300–3331 (−5 °C)(58.7 °C)	2-Methyl-2-butanol	3352–3412 (−12.2 °C)(87.7 °C)
2-Butanol	3318–3340 (5 °C)(44.2 °C)	3-Methyl-1-butanol	3308–3352 (−12.2 °C)(87.7 °C)
2-Methyl-1-propanol	3305–3353 (−12.2 °C)(87.7 °C)	3-Methyl-2-butanol	3340–3398 (−12.2 °C)(87.7 °C)
t-Butanol	3347–3378 (25 °C)(78.3 °C)		

Experimental

Instrumentation

IR spectra were recorded on a Perkin Elmer 16 PC FTIR in the spectral region of 4400–600 cm^{-1} (resolution: 4 cm^{-1}; weak apodization and 100 scans for each spectrum). In order to obtain FTIR spectra of liquids, the ATR technique was used. Measurements at room temperature were carried out

Table 2. Action of solutes on solution properties

Property	Addition of hydrophilic solutes causes	Addition of hydrophobic solutes causes
Vapor pressure	Decrease	Increase
Surface tension	Increase	Decrease
Density	Increase	Decrease
Solubility of gases	Decrease	Increase
Heat Capacity	Decrease	Increase
Compressibility	Decrease	Increase

Table 3. Changes of properties of alcohols caused by addition of water, by decrease in temperature, and of solutions by addition of structure breakers

Property	Addition of water to alcohols causes	Decrease in temperature causes	Addition of structure breakers causes
Vapor pressure	Decrease	Decrease	Decrease
Surface tension	Increase	Increase	Increase
Density	Increase	Increase	Increase
Viscosity	Increase	Increase	Increase
Solubility of gases	Decrease	Decrease	Decrease
Heat capacity	Decrease	Decrease	Decrease
Compressibility	Decrease	Decrease	Decrease

in an open-boat circle cell with a sample volume of 0.5 ml equipped with a zinc selenide cylindrical internal reflection crystal. To record spectra at different temperatures, the circle cell was fitted in a heating/cooling jacket combined with an external circulating cryostat.

Chemicals

Methanol (Merck, *p.a.* 99,5%), Ethanol (Mautner Markhof, *p.a.* 99,8%), 1-Propanol (Riedel-de Haen, *p.a.* 99,5%), 2-Propanol (Riedel-de Haen, *p.a.* 99,8%), 1-Butanol (Riedel-de Haen, *p.a.* 99,5%), 2-Butanol (Aldrich, 99%), 2-Methyl-1-propanol (Aldrich 99,5%), 2-Methyl-2-propanol (Riedel-de Haen, *p.a.* 99,5%), 2-Pentanol (Aldrich 98%), 3-Pentanol (Aldrich 98%), 2-Methyl-1-butanol (Aldrich 99%), 2-Methyl-2-butanol (Aldrich 99%), and 3-Methyl-2-butanol (Aldrich 98%) were absoluted with Mg and I_2 (or CCl_4) by a *Grignard* reaction and then distilled. 1-Pentanol (Aldrich, 99%) was purified from water by pressing in sodium and subsequent vaccum distillation. 3-Methyl-1-butanol (Aldrich 98,5%) was dehydrated with BaO and then distilled. The alcohols were stored over molecular sieve. The anhydrous alcohols were mixed with distilled and ion exchanged water. The water content was measured by *Karl Fischer* titration with an accuracy of ± 2 mg H_2O/l.

Acknowledgements

We thank the "*Österreichische Nationalbank*" for their generous financial support.

References

[1] Böhm L, Smith DL, Angell CA (1987) J Mol Liq **36**: 153

[2] Covington AK, Jones P (1986) Hydrogen-Bonded Solvent Systems. Taylor and Francis, London

[3] Draegert DA, Williams D (1968) J Chem Phys **48**: 401

[4] Ganz E (1937) Ann Phy **28**: 445

[5] Kecki Z (1973) Adv Mol Relax Processes **5**: 137

[6] Luck WAP (1974) Structure of Water and Aqueous Solutions. Luck WP (ed) Verlag Chemie, Weinheim

[7] Busing WR, Horing DF (1961) J Phys Chem **65**: 284

[8] Suhrmann R, Breyer F (1933) Z Phys Chem **B20**: 17

[9] Collins JR (1925) Phys Rev **26**: 771

[10] Walrafen GE (1962) J Chem Phys **36**: 1035

[11] Weston RE (1962) Spectrochim Acta **18**: 1257

[12] Rosenholm JB (1987) Ber Bunsenges Phys Chem **91**: 106

[13] Bonner OD, Choi YS (1975) J Sol Chem **4**: 457

[14] Sorensen CM (1983) J Chem Phys **79**: 1455

[15] Halfpap BL, Sorensen CM (1982) J Chem Phys **77**: 466

[16] Seemann FW (1981) PTB-Mitt **91**(2): 95

[17] Conde O, Teixeira J, Papon P (1982) J Chem Phys **76**: 3747

[18] Tokunaga J (1975) J Chem Eng Data **20**: 41

[19] Cargill RW (1978) J Chem Soc, Faraday Trans **I74**: 1444

[20] Cargill RW, Morrison TJ (1975) J Chem Soc Faraday Trans **I71**: 618

[21] Knight WS, Princeton University, July 1962 (Diss Abs 1963, 24, 993)

[22] Franks F (1973) Water-A Comprehensive Treatise, vol II. Plenum Press, New York London

[23] Jackson SE, Symons MCR (1976) Chem Phys Lett **37**: 551

[24] Gutmann V, Scheiber E, Resch G (1989) Monatsh Chem **120**: 671

Received February 10, 1995. Accepted February 20, 1995