

HR PMR STUDY OF HYDROGEN BONDING IN ALCOHOLS

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The OH chemical shifts of methanol and ethanol dissolved in CCl_4 , CHCl_3 , C_6H_{12} , C_6H_6 and DMSO were measured as a function of temperature and concentration simultaneously. According to Van't Hoff's isobar formula the stronger hydrogen bonds are broken more easily by the temperature rise than the weaker ones. It was shown that the multimer equilibria are shifted by the temperature rise to favour open chain multimers and that the action of solvents is differentiated. CCl_4 forms hydrogen bonds with alcohols and cannot be regarded as an inert solvent. With Van't Hoff's isobar an unequivocal comparison of the average energy of intermolecular bonds is possible.

1. Introduction

An extensive literature has been collected on the studies of hydrogen bonding by proton magnetic resonance (PMR) and a review is given in the monographs [1]. PMR seems to be the most sensitive method for the detection and investigation of hydrogen bonds (HB) due to a great change of chemical shift of the protons engaged in HB. The chemical shifts were usually measured as a function of concentration or temperature but only a few works dealt with simultaneous measurements of concentration and temperature dependence.

The study presented here was stimulated by the results of Davis, Pitzer and Rao [2], who measured the chemical shifts of the OH proton of some alcohols diluted by CCl_4 at three temperatures in order to determine the equilibrium constants of dimerization. When considering the results presented in the tables of [2] we noticed a strange temperature behaviour of the chemical shift: with the dilution of the alcohols by CCl_4 , the temperature dependence became stronger but in the very dilute solutions it was again weak.

This work is an attempt to explain that observation. At first, our attention was directed at the equilibria of open chain and cyclic multimers and there arose the question of how they change by the action of a solvent and temperature rise, since it is obvious that the HB energy of open and cyclic multimers as well as their chemical shifts are different.

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2. Remarks on the thermodynamics of hydrogen bond equilibria

An increase of temperature brings about the breaking of hydrogen bonds. If we suppose that in the solution hydrogen bonds of different bond energies exist, the problem is to determine what bonds are broken "more easily" by the temperature rise. The answer is offered by Vant't Hoff's isobar formula

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, T is the absolute temperature, R is the gas constant and ΔH is the enthalpy of the HB formation which is identified with the HB energy and has a negative value for the bond formation.

The conclusion is that the equilibrium constant of the bonds with greater energy is more sensitive to the temperature change than that of the lower energy bonds. This means that, contrary to expectation, bonds with higher energy are broken more easily by the temperature rise.

The thermodynamic treatment is universal and must be valid for any kind of bonding.

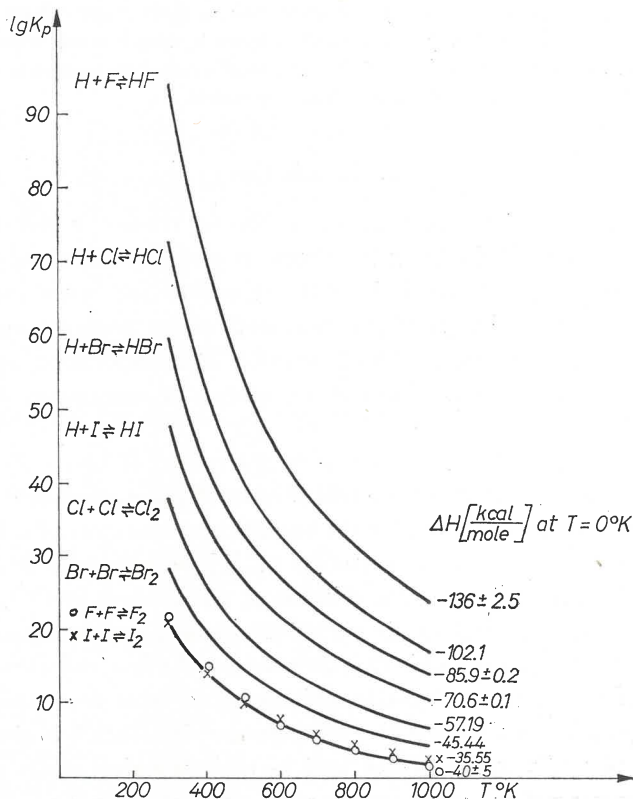


Fig. 1. The influence of temperature on the equilibria of chemical bond formation. The data for the curves are taken from [3]. The bond energy values taken from [4] are given at the right

An example of chemical bonding is shown in Fig. 1 according to data taken from the literature [3, 4]. It entirely confirms the above conclusion.

Now we must answer the question of why the temperature rise does not first break the chemical bonds, leaving the much weaker intermolecular bonds almost untouched. The answer becomes clear when we notice that the equilibrium constants of chemical bonds are of the order of 10^{10} – 10^{100} and those of HB are of the order of 1 – 10 . With the change of the chemical equilibrium constant by many orders of magnitude the dissociation products are still not detectable because of their negligible concentrations whereas the change of intermolecular equilibrium constants by a factor of 2 results in a fairly detectable change of concentrations.

The only approximation included in Van't Hoff's isobar formula is that the bond energy (ΔH) does not change with temperature. In fact it does change, but to a small extent. In Fig. 1 there is a crossing of the curves for F_2 and I_2 . Probably the bond energy of F_2 is in the low temperature region higher and in the high temperature region lower than the bond energy of I_2 .

In the isobaric reactions we can use the above treatment to compare unequivocally the relative bond energies. This is important in the case of hydrogen bonding since the absolute data of HB energies are often determined within rather broad error limits.

3. Experimental procedure

The PMR spectra were recorded at 60 MHz with a spectrometer of JEOL Co., type JNM-3H-60. The temperature of the samples was controlled by the variable temperature head of the JEOL Co., model JNM-NT, within the range of -20° to $+70^\circ\text{C}$ with an accuracy of $\pm 1^\circ$. The scale of chemical shift was calibrated by the side band technique. Chemical shifts were measured with respect to tetramethylsilane (TMS) as an internal standard. The results were averaged from 5–8 measurements and the error limits did not exceed ± 1 Hz in the extreme case of highly dilute solutions. The minus sign is for downfield shift with respect to the reference.

Methanol, analytical grade, was rectified on an efficient column, dehydrated with molecular sieves and distilled with a small amount of benzoic acid.

Ethanol, absolute, was rectified on an efficient column, dehydrated with $\text{Mg} + \text{I}_2$ and distilled.

Carbon tetrachloride, analytical grade, was treated with an aqueous 0.01 solution of NaOH and with water, dehydrated with CaCl_2 and distilled. It was protected against daylight during the experiment.

Chloroform, analytical grade, was treated with water, dehydrated with CaCl_2 and distilled.

Benzene, analytical grade, was dehydrated with molecular sieves and distilled.

Dimethylsulfoxide, analytical grade, was dehydrated with molecular sieves and distilled under low pressure at 65°C .

Cyclohexane, analytical grade, was treated with conc. H_2SO_4 , with KMnO_4 in 10% H_2SO_4 , with water, then dehydrated with CaCl_2 and distilled.

The concentrations of prepared solutions were determined by weighing.

The glass sample tubes were thoroughly cleaned to avoid the contamination of samples by any acidic or basic impurities. The cleaning procedure followed that described by Grunwald *et al.* [5].

4. Results and discussion

The solutions of methanol in chloroform, carbon tetrachloride, and of methanol and ethanol in cyclohexane, benzene and dimethylsulfoxide (DMSO) were investigated in a broad range of concentrations. For every solution the chemical shift of the OH proton was measured while changing the temperature by steps of about 5 degrees in the range of 22 to 70°C. For some solutions the study was extended to the temperature region of -20 to +22°C.

In all cases the function of OH chemical shift *vs* temperature was a straight line with positive slope showing the breaking of HB to be proportional to the temperature increase. This is illustrated in Fig. 2 with an example of the $\text{CH}_3\text{OH} + \text{CHCl}_3$ system.

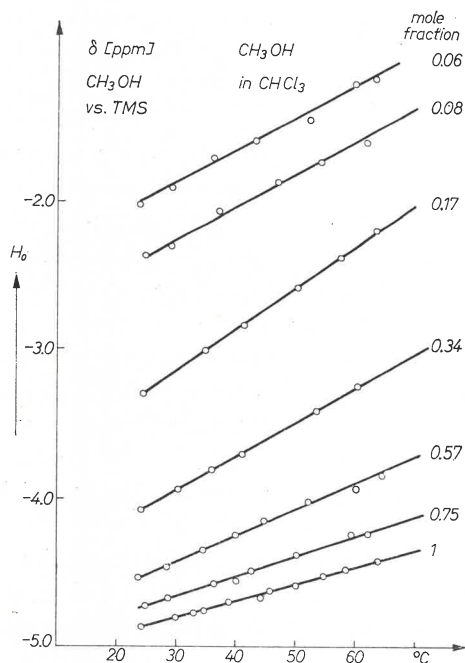


Fig. 2. The chemical shift of the OH group of methanol as a function of temperature and dilution with chloroform. The concentration of solutions is given on the right-hand side

From the functions $\delta = f(T)$ the slopes, *i. e.* the derivatives $d\delta/dT$ were measured and displayed in the following figures as functions of concentration. Fig. 3 shows such a function of $d\delta/dT$ *vs* mole fraction of methanol in chloroform. With the dilution of

methanol there is an increase in the breaking of the HB by temperature increase up to a certain concentration where a maximum occurs. According to Van't Hoff's isobar formula this can be interpreted as an increase of the average HB energy with dilution, followed by a decrease of the HB energy in the region of small concentration. We find the explanation for these effects in the equilibria of open chain \rightleftharpoons cyclic multimers. The entire HB energy of a cyclic multimer is higher than that of the open chain multimer of the same multiplicity because of one additional bond in the cycle. If by dilution the open chain multimers

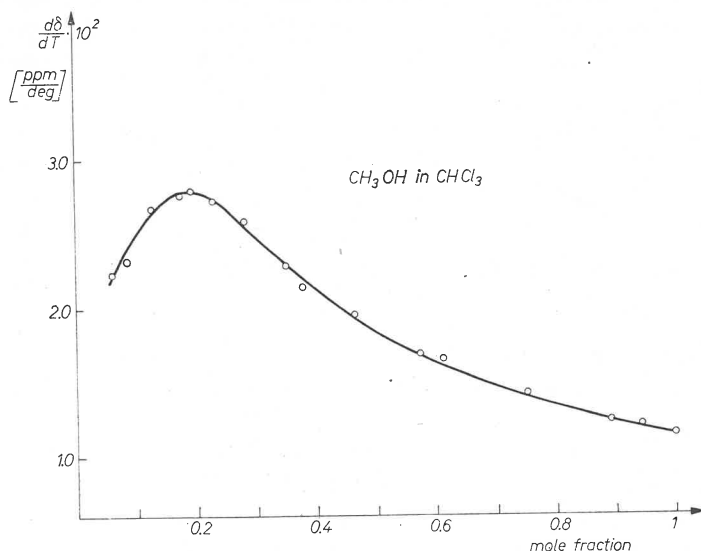


Fig. 3. The dependence of the chemical shift derivative with respect to temperature on the concentration of methanol in chloroform

are broken more easily, then the average HB energy of the whole system increases and more of the cyclic multimers are left for breaking by the temperature rise. On the other hand, upon dilution, new HB are formed between the alcohol and chloroform molecules, their energy being much smaller than that of O—H...O—H bonds and this explains the decrease of $d\delta/dT$ with dilution in the region of small concentrations where the amount of methanol-chloroform complexes prevails.

As mentioned above, a similar effect is observed with the solutions of alcohols in CCl_4 . We repeated the measurements for methanol in CCl_4 and obtained similar results as in the work of Davis, Pitzer and Rao [2]. In Fig. 4 a comparison is made between the systems of methanol in CCl_4 and in CHCl_3 . The increase of $d\delta/dT$ with dilution in CCl_4 is steeper, showing that the existence of cyclic multimers is more favourable in CCl_4 than in CHCl_3 . The maximum on the CCl_4 curve is, consequently, an argument for hydrogen bonding of methanol with CCl_4 . This supports the conclusion of Fletcher [6] who proved with IR spectra the formation of hydrogen bonds between 1-octanol and CCl_4 and questioned the accuracy of HB energy measurements carried out by other authors in CCl_4 as an "inert" solvent. The maximum on the curve for CCl_4 in Fig. 4 occurs at smaller concen-

trations and the decrease with further dilution is steeper than for CHCl_3 , showing the HB energy of CCl_4 with methanol to be lower.

In order to prove the above conclusions we made a comparison study of solutions of methanol and ethanol in cyclohexane, the latter being a solvent rather unable to form

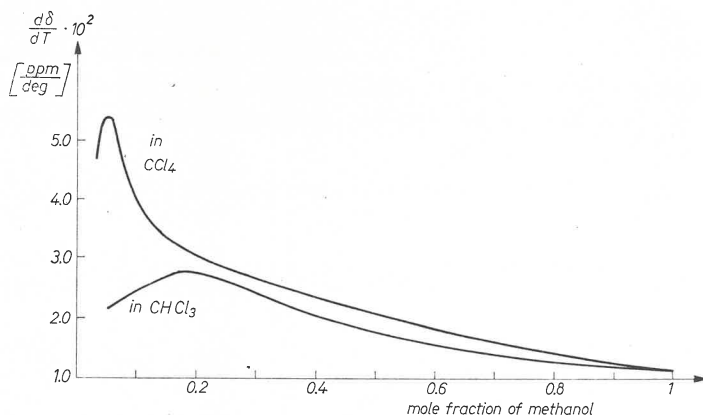


Fig. 4. The dependence of the chemical shift derivative with respect to temperature on the concentration of methanol in carbon tetrachloride and chloroform

HB with alcohols. The results are displayed in Fig. 5. There is no maximum on the curves in the whole concentration range we could reach with the sensitivity of our instrument. This can be considered as a proof that the maxima of the $d\delta/dT$ as functions of concentration are caused by the HB formation between the alcohol and solvent molecules.

It seemed worthwhile to take next into consideration those solvents which do form

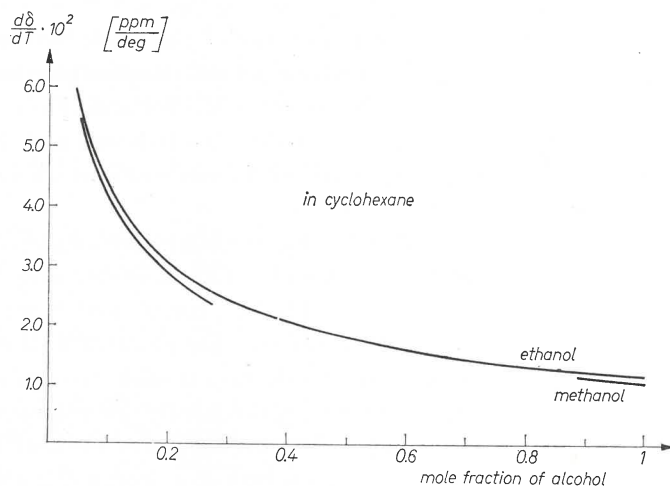


Fig. 5. The dependence of the chemical shift derivative with respect to temperature on the concentration of methanol and ethanol in cyclohexane

HB-s with alcohols and we took benzene and DMSO. The HB-s of methanol with benzene were described in the work of Barańska [7]. Drinkard and Kivelson [8] stated that the HB-s between DMSO and methanol are a little weaker than those of methanol-methanol. Our results are shown in Fig. 6. In benzene the $d\delta/dT$ functions are similar to those in CCl_4 and CHCl_3 , but the maxima are shifted to higher concentrations, probably because of higher HB energy for benzene.

We get a very different picture with DMSO. There is a decrease of $d\delta/dT$ on dilution, without any extrema. In terms of our considerations above, this means that the HB-s of DMSO and alcohol are weaker than those of alcohol-alcohol but, moreover, the destruc-

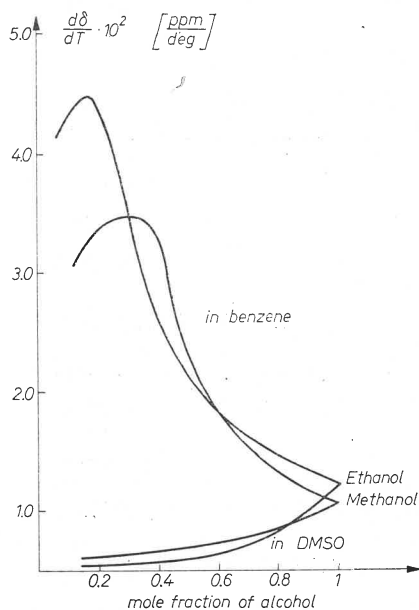


Fig. 6. The dependence of the chemical shift derivative with respect to temperature on the concentration of methanol and ethanol in benzene and DMSO

tive action of DMSO is directed mainly at the cyclic multimers of alcohol. The reason for this action is that DMSO molecules with the dipole moment of 3.9 D [9] are highly polar and they do not favour resisting the cyclic multimers of low polarity.

We refrain from comparing the HB energies in the investigated systems in a more detailed manner because of the low accuracy of our $d\delta/dT$ results, their estimated error being $0.1 \cdot 10^{-2}$ ppm/deg. In any case, we think that with an increased accuracy it should be quite possible to compare unequivocally the average energies of intermolecular bonds in this way. For instance, our $d\delta/dT$ results for pure water, methanol and ethanol are $0.98 \cdot 10^{-2}$, $1.05 \cdot 10^{-2}$ and $1.17 \cdot 10^{-2}$ ppm/deg, respectively. This would suggest an increasing average HB energy from water to ethanol if the data were accurate enough. The average energy here is meant as a statistical result of the equilibrium states of various multimers with their individual HB energies.

5. Conclusions

The temperature rise brings about a preferential breaking of HB-s in cyclic multimers of alcohols and in this way causes a shifting of the equilibria to the advantage of open chain multimers. The behaviour of solvents in breaking the HB-s is differentiated. The unpolar solvents with small molecules break more easily the open chain multimers. The temperature and solvent both affect the average HB energy and it is highly probable that the wide discrepancy of the HB energy values determined by various authors is caused by these effects.

Carbon tetrachloride, widely used for HB energy determinations, is by no means an "inert" solvent and the results obtained with this solvent should be revised.

The thermodynamic treatment of parameters, depending on equilibrium state and temperature through Van't Hoff's isobar formula is proposed for an unequivocal comparison of the average energy of intermolecular bonds influencing these parameters.

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