

## The Effect of Solvent Interaction with the Hydroxy Group of Saturated Monohydroxy Alcohols from Measurement of Hydroxy Stretching Vibrations

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The nature of the interaction of solvent molecules with the hydroxy group of saturated monohydroxy alcohols in specific rotamer conformations has been examined. For non-polar and nucleophilic-type solvents, the interaction centres at the OH proton, causing a decrease in the OH stretching frequency. Shielding of the hydroxy hydrogen by  $\beta$ -alkyl groups reduces the magnitude of the shift. In chloroform solution, evidence is given for an association of the solvent molecules with the oxygen lone-pair sites in conjunction with an association with the OH proton. The interaction of chloroform with the lone-pair sites causes an apparent increase in the OH stretching frequency which is counterbalanced by the decrease caused by association with the OH proton. Shielding of either the lone-pair sites or the OH proton by  $\beta$ -alkyl groups influences the accessibility of the solvent and consequently influences the OH stretching frequency.

The stability, and hence relative populations, of the hydroxy group rotamers of saturated monohydroxy alcohols are related to the infrared OH stretching vibrations of these rotamers. The OH stretching frequency of each rotamer has been rationalised<sup>1</sup> in terms of (i) structural factors in the vicinity of the OH; (ii) the accessibility of the OH proton to the solvent molecule; (iii) oxygen lone pair  $\cdots$   $\beta$ -alkyl repulsions. These three terms are not independent and the resultant effect determines the relative rotamer populations and affects the OH stretching frequencies. It has been shown that increased steric interactions through (i) decrease the OH stretching vibration of the hydroxy group.<sup>1</sup> Previous studies of the OH stretching vibration of saturated monohydroxy alcohols in different solvents have shown that the solvent may interact with the alcohol molecule in two ways,<sup>2</sup> (i) through a bulk effect with the molecule as a whole and (ii) through a local interaction with the hydroxy group.

The OH stretching frequency is highly sensitive to the nature of the solvent; the large frequency shifts that occur during the transition from the vapour phase to the solution phase in 'inert' solvents reflect the fact that association with the solvent occurs.<sup>3</sup> Even in a non-polar solvent such as  $\text{CCl}_4$  there is a bulk effect and a local effect. In principle, the local interaction of the solvent with the hydroxy group can occur in two ways, either through an association with the OH proton or through an association with the lone pairs of the oxygen. A solvent such as  $\text{CCl}_4$  which has no permanent dipole moment will have an induced dipole moment in the vicinity of the hydroxy group. The net effect of the dipole induction is to cause the solvent molecules to become polarised. In the case of  $\text{CCl}_4$  the solvent has an outer sphere of negatively polarised chlorine atoms surrounding the positively polarised carbon. In a local interaction the molecule therefore behaves as a nucleophile or proton acceptor and association with the hydroxy group therefore centres at the OH proton.<sup>2</sup>

Non-polar solvent molecules such as perfluorohexane (PFH) are expected to behave in a manner similar to  $\text{CCl}_4$ , although the much larger molecular volume of PFH is influenced to a much greater degree by the accessibility of the hydroxy group. Visser and van der Maas have shown that the  $\nu_{\text{OH}}$  frequency difference between the values measured in solution in  $\text{CCl}_4$  and  $\text{CS}_2$ ,  $\nu_{\text{diff}}$  ( $\text{CCl}_4 - \text{CS}_2$ ), can be related to the degree of accessibility of the hydroxy group by the solvent molecule.<sup>4</sup> Therefore, for large apolar molecules, such as PFH, access to the hydroxy group will be severely restricted.

Solvent molecules which possess a permanent dipole moment

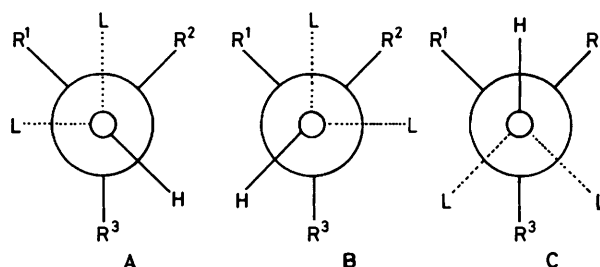


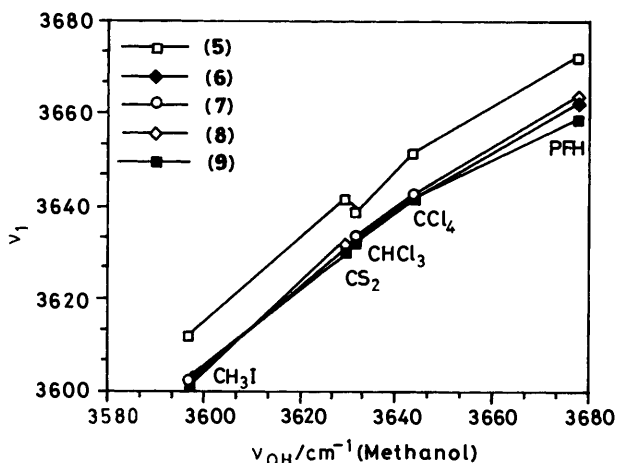
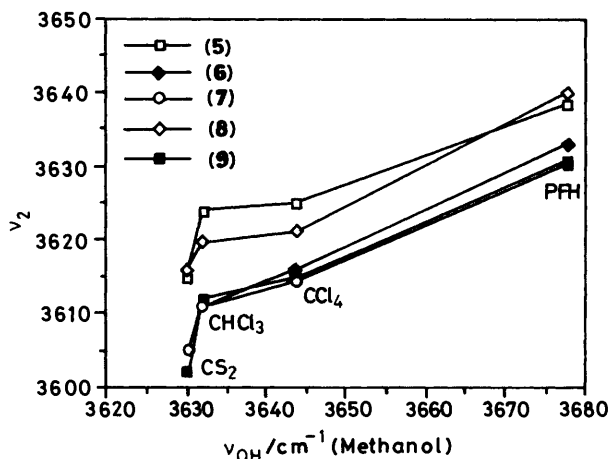
Figure 1. Newman projection along the C-O bonds, of rotamers showing the  $\beta$ -alkyl groups  $R^1$ ,  $R^2$ , and  $R^3$  present in each (from Table 1) and the direction of the lone pairs (L)

are much stronger proton acceptors or donors than solvent molecules in which the dipole is induced. Methyl iodide is a strong nucleophilic solvent, whilst in solvents such as  $\text{CHCl}_3$  the dipole moment gives the hydrogen a large charge density compared with the chlorine atoms. This makes  $\text{CHCl}_3$  a far better proton-donor solvent than a proton-acceptor solvent. In an association with the hydroxy group it would be expected that this solvent would associate with the hydroxy oxygen lone pairs in preference to the OH proton in a hydrogen-bonding-type interaction. However, the negatively charged chlorine atoms form a stronger nucleophilic centre than the induced dipole in  $\text{CCl}_4$ , therefore, relative to  $\text{CCl}_4$ , the affinity for the OH proton should be greater.

The solvents  $\text{CCl}_4$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{I}$  were chosen to investigate the nature of the interaction with the hydroxy group. The alcohols studied (Table 1) show distinct conformational preferences. The tertiary alcohols (1), (2), (3), and (4) are, by virtue of symmetry, monorotameric. These alcohols differ in the degree to which the hydroxy group is shielded by adjacent groups. Alcohols (5)–(9) show two peak maxima in the OH stretching region in  $\text{CCl}_4$  solution. The higher wavenumber band was attributed to the hydroxy rotamers which are less shielded (Figure 1, rotamer A or B) and the lower wavenumber band to the more shielded rotamer<sup>5,6</sup> (Figure 1 rotamer C). The alcohols (6) and (8) have three possible rotamers, A, B, and C since  $R^1$  and  $R^2$  are different. However, the bands of rotamers A and B are not resolved and the peak maxima of these compounds are assumed to correspond to the rotamers in which the OH proton is the

**Table 1.** The  $\beta$ -alkyl groups present in the alcohols (1)–(12)

Alcohol	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
(1) Methanol	H	H	He
(2) 2-Methylpropan-2-ol	Me	Me	Me
(3) Tri- <i>t</i> -butylmethanol	Bu <sup>t</sup>	Bu <sup>t</sup>	Bu <sup>t</sup>
(4) Adamantan-1-ol			
(5) 2,2,4,4-Tetramethylpentan-3-ol	Bu <sup>t</sup>	Bu <sup>t</sup>	H
(6) 2,2-Dimethylpentan-3-ol	Et	Bu <sup>t</sup>	H
(7) 2,4-Dimethylpentan-3-ol	Pr <sup>i</sup>	Pr <sup>i</sup>	H
(8) 2,2,4-Trimethylpentan-3-ol	Pr <sup>i</sup>	Bu <sup>t</sup>	H
(9) 3,5-Dimethylheptan-4-ol	Bu <sup>s</sup>	Bu <sup>s</sup>	H
(10) Propan-2-ol	Me	Me	H
(11) Ethanol	Me	H	H
(12) 2,2-Dimethylpropan-1-ol	Bu <sup>t</sup>	Me	H

**Figure 2.****Figure 3.**

least shielded by the  $\beta$ -alkyl groups. Alcohols (10), (11), and (12) show only one OH stretching band, a reflection that either a particular rotamer is predominant or that the individual rotamer bands are unresolved. In either case, the peak maximum is assumed to correspond to the rotamer which has the higher population.

### Experimental

Infrared spectra of the alcohols in PFH, CH<sub>3</sub>I, and CCl<sub>4</sub> were recorded on a Perkin-Elmer 1710 FT-IR spectrometer. For

PFH solutions, 1-cm Infracil quartz cells were used, resolution 1.0 cm<sup>-1</sup>, number of scans 10; for CHCl<sub>3</sub> and CH<sub>3</sub>I, 1-mm NaCl cells were used, resolution 4.0 cm<sup>-1</sup>, number of scans 50. The spectra in CCl<sub>4</sub> and CS<sub>2</sub> solutions were recorded on a Perkin-Elmer 1800 FT-IR spectrometer, number of scans 16, 1-cm Infracil quartz cells, resolution 1 cm<sup>-1</sup>. Accuracy is believed to be  $\pm 0.5$  cm<sup>-1</sup>.

The solvents CH<sub>3</sub>I (Aldrich), CCl<sub>4</sub> (Merck), CS<sub>2</sub> (Aldrich), and PFH (Aldrich) were dried for several days over molecular sieves (type 3A). The trace water and stabiliser (ethanol) in the CHCl<sub>3</sub> (Aldrich) were removed by allowing the chloroform to stand over molecular sieves (type 4A) for 7 days.

### Results and Discussion

The OH stretching frequencies of the observed bands of the rotamers of the alcohols (1)–(12) in the above solvents are given in Tables 2 and 3.

The observed bands  $\nu_1$  and  $\nu_2$  in Tables 2 and 3 correspond to the rotamers A/B and C, respectively.

In Table 2 gas-phase measurements are included for the alcohols (1)–(5). Comparison of the frequencies in PFH and in the gas phase shows that, in the former, the solvent interaction with the hydroxy group is small. The largest difference between PFH and the gas phase occurs in the alcohols with the more shielded rotamers, strongly suggesting that solvent interaction involving PFH is primarily a bulk effect *i.e.* solvation of the  $\beta$ -alkyl groups. The lack of any appreciable local interaction with the hydroxy group makes PFH a good reference solvent.

Methanol (1) symmetrically is monorotameric and there is very little shielding of the hydroxy group by the three  $\alpha$  protons. Therefore, in this alcohol there is little steric influence on the solvent approach to the hydroxy group. The OH stretching frequencies of this rotamer in each solvent can therefore be used as a standard for the system under investigation.

Similarly, tri-*t*-butylmethanol (3) is monorotameric; however, the hydroxy experiences the most shielding from the solvent of all the above alcohols and is therefore used as a standard in which solvent approach to the hydroxy group is severely restricted.

For each alcohol, the observed rotamer bands in each solvent were compared with those of the rotamers of methanol and tri-*t*-butylmethanol by plotting the OH stretching frequencies of the alcohols against the two standards (Figures 2–7). Of the plots referenced to methanol, the A/B rotamers of alcohols (5)–(9) (Figure 2) show a remarkable similarity in their behaviour toward the different solvents. The approximate linearity of the plots suggests that the accessibility of the solvents to the hydroxy group is proportional to that in methanol, *i.e.* the shielding of the hydroxy group by the  $\beta$ -alkyl groups is similar for each of the solvents. However, for alcohol (5), in chloroform there is a slight negative deviation from linearity.

The rotamer type C plots (Figure 3) all show a positive deviation from linearity in chloroform. In methanol, both the OH proton and the lone-pair sites of the hydroxy oxygen are, relative to the above alcohols, unshielded from the solvents. Type C rotamers all have the OH proton shielded by  $\beta$ -alkyl groups and consequently the lone-pair site contribution becomes more important. It follows, therefore, that the shielding of the OH proton causes an increase in the OH stretching frequency in chloroform.

Comparing the solvent shifts for the above alcohols with tri-*t*-butylmethanol, the rotamers A/B (Figure 5) all show a small positive deviation for chloroform, whilst the rotamers C (Figure 6) all show a large positive deviation. In tri-*t*-butylmethanol, both the OH proton and the lone-pair sites of the oxygen are highly shielded from the solvent. The much reduced shielding of

**Table 2.** OH-Stretching frequencies/cm<sup>-1</sup> of monohydroxy alcohols in various solvents

Alcohol	Gas	PFH	CCl <sub>4</sub>	CHCl <sub>3</sub>	CS <sub>2</sub>	CH <sub>3</sub> I
(1)	3 681.4	3 678.0	3 644.0	3 632.0	3 630.0	3 597.0
(2)	3 643.0	3 640.0	3 617.0	3 608.0	3 606.5	3 579.0
(3)	3 651.0	3 643.0	3 629.5	3 617.0	3 623.5	3 599.5
(4)	3 634.0	3 632.0	3 607.0	3 598.0	3 596.0	3 568.0
(5) $\nu_1$	3 678.0	3 672.0	3 651.5	3 639.0	3 641.5	3 612.0 <sup>a</sup>
$\nu_2$	3 647.0	3 638.5	3 625.0	3 624.0	3 615.0	

<sup>a</sup> The frequencies measured in CH<sub>3</sub>I show only one peak maximum, which corresponds to  $\nu_1$ .

**Table 3.** OH-Stretching frequencies/cm<sup>-1</sup> of monohydroxy alcohols in various solvents

Alcohol	PFH		CCl <sub>4</sub>		CHCl <sub>3</sub>		CS <sub>2</sub>		CH <sub>3</sub> I $\nu_1^a$
	$\nu_1$	$\nu_2$	$\nu_1$	$\nu_2$	$\nu_1$	$\nu_2$	$\nu_1$	$\nu_2$	
(6)	3 662.5	3 633.0	3 641.0	3 616.0	3 633.0	3 611.0	3 631.0	3 605.0	3 601.0
(7)	3 663.0	3 630.5	3 642.5	3 614.5	3 633.5	3 611.0	3 631.0	3 605.0	3 603.0
(8)	3 664.0	3 640.0	3 642.0	3 621.0	3 632.0	3 619.5	3 632.0	3 616.0	3 602.0
(9)	3 659.0	3 631.0	3 641.5	3 615.0	3 632.0	3 612.0	3 630.0	3 602.0	3 601.5
(10)	3 652.0		3 627.0		3 614.0		3 616.0		3 587.0
(11)	3 668.0		3 636.5		3 621.0		3 623.0		3 590.0
(12)	3 664.0		3 641.0		3 630.0		3 630.0		3 601.0

<sup>a</sup> The frequencies measured in CH<sub>3</sub>I show only one peak maximum which corresponds to  $\nu_1$ .

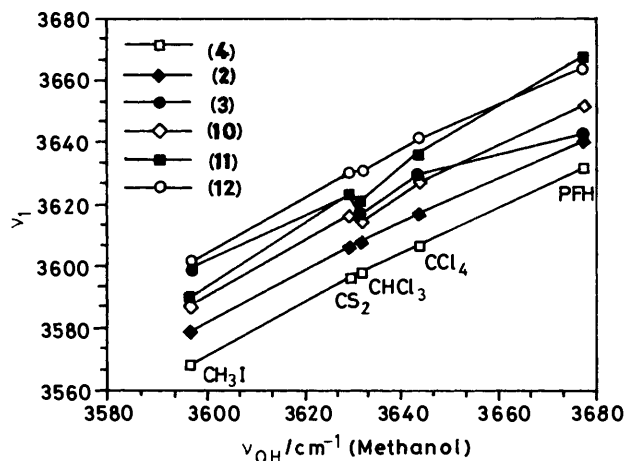


Figure 4.

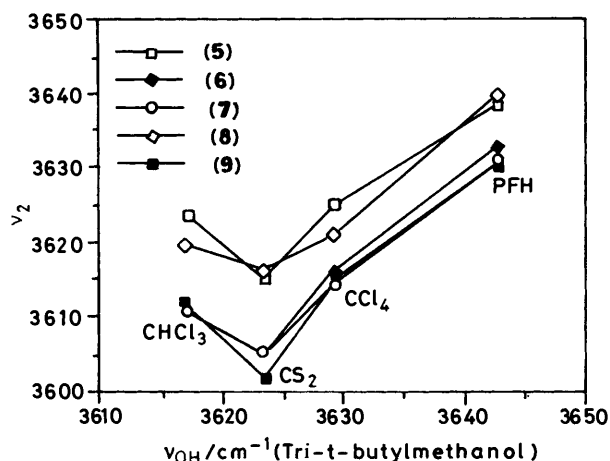


Figure 6.

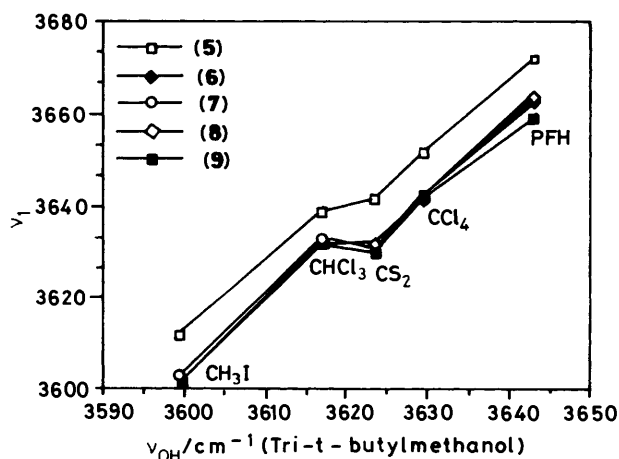


Figure 5.

the lone-pair sites in rotamer C must be responsible for the large positive deviation in chloroform, *i.e.* solvation of the lone-pair sites by chloroform causes an increase in the OH stretching frequency. The slight positive deviation in chloroform for rotamers A/B reflects the fact that some solvation of the lone-pair site must occur even in the most extreme cases of shielding. For comparison, the alcohols, (1)–(4) and (10)–(12) are shown in Figures 4 and 7. Adamantan-1-ol is comparable with methanol in that the hydroxy group is relatively unshielded from the solvent. For *t*-butyl alcohol (2), the extent of hydroxy group shielding is mid-way between methanol and tri-*t*-butylmethanol. Compared with methanol, the alcohols (2)–(4) and (10)–(12) show a linear relationship with a slight negative deviation for chloroform solutions of alcohols (3), (10), and (4). Compared with tri-*t*-butylmethanol, the alcohols (1), (2), (4), (10), (11), and (12) show a linear relationship with a positive deviation for chloroform. The plots of these alcohols are comparable with the type A/B rotamers, *i.e.* the measured peak maxima correspond to the rotamers in which the OH proton is less shielded from the solvent than are the lone-pair sites.

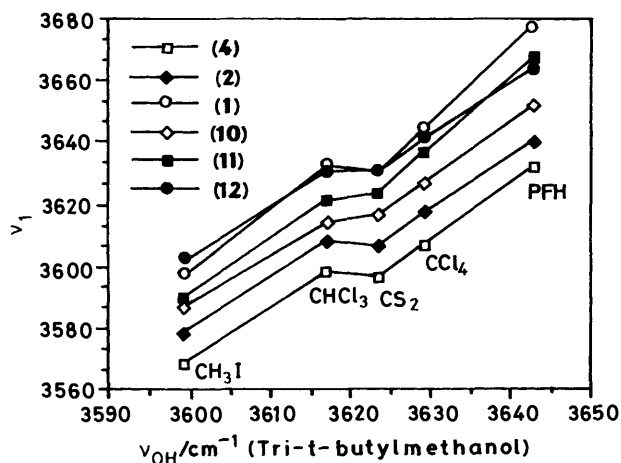


Figure 7.

In general, the solvents PFH,  $\text{CCl}_4$ ,  $\text{CS}_2$ , and  $\text{CH}_3\text{I}$  behave as nucleophilic solvents with respect to the hydroxy group. The association or solvation phenomena in the non-polar solvents may be merely a van der Waals effect, whilst in  $\text{CH}_3\text{I}$ , the association may be strong enough to be called hydrogen bonding. The nomenclature of the association is unimportant since it has been demonstrated that van der Waals forces influence OH stretching vibrations in a similar but weaker way than hydrogen bonds.<sup>7</sup> The predominant feature of each of these solvents is that they have a local interaction with the hydroxy group which centres at the OH proton. Association of the hydroxy group with chloroform must therefore occur by association with the OH proton and also with the lone-pair sites. This amphoteric nature of chloroform with regard to the hydroxy group arises from the fact that it possesses both highly electronegative and electropositive substituents. Compared with the polar  $\text{CH}_3\text{I}$  molecule, the positive dipole of the proton of  $\text{CHCl}_3$  is far more electropositive than the three protons of  $\text{CH}_3\text{I}$  owing to the charge-density distribution.

Association with the OH proton causes a decrease in the OH stretching frequency, a phenomenon common to all the above solvents. Association with the lone pairs causes an increase in the OH stretching frequency. The OH stretching vibration in chloroform is therefore dependent upon the rotameric composition although in a different way from that in nucleophilic type solvents. Since  $\beta$ -alkyl group shielding of the lone pairs causes significant changes in the OH stretching frequency in chloroform, there is no simple relationship between changes in frequency between e.g.  $\text{CCl}_4$  and  $\text{CHCl}_3$ , since the overall shift is a composite effect caused by two different associations. Qualitatively, the magnitude of the shift in  $\text{CHCl}_3$  may be used as indication of the extent of shielding of the lone-pair sites by  $\beta$ -alkyl groups and consequently a preferred conformation may be identified. However, measurements of peak intensities suggest that the relative populations of type C rotamers is greater in  $\text{CHCl}_3$  than in the non-polar solvents. This may be due to the fact that the solvent is a stronger electrophile than it is a nucleophile and consequently the enthalpy of the association with the lone pairs may be greater than that with the OH proton.

### Conclusions

The general linearity of the relationships shows that the non-polar solvents associate with the hydroxy group predominantly

via the hydroxy hydrogen, although there may be a slight lone-pair interaction. Shielding of the hydroxy hydrogen by  $\beta$ -alkyl groups influences the accessibility of the solvent molecules. This effect is pronounced for PFH because of its larger steric volume, although the low polarisability of C-F bonds may also be a contributing factor.

For solutions in chloroform, two types of association are possible, an interaction with the lone-pair sites and an interaction with the OH proton. In both cases, the solvent causes a shift in the OH stretching frequency. Association with the lone-pair sites causes an increase, whilst association with the OH proton causes a decrease. Shielding of either the lone-pair sites or the OH proton by  $\beta$ -alkyl groups decreases the magnitude of the shifts.

Additional evidence for a greater degree of association in  $\text{CHCl}_3$  solution compared with solutions in  $\text{CCl}_4$  and  $\text{CS}_2$  comes from the halfband widths (HBW). Alcohol (2) has HBWs of 16.9 and 18.5  $\text{cm}^{-1}$  in  $\text{CCl}_4$  and  $\text{CS}_2$ , respectively, whilst in  $\text{CHCl}_3$  the HBW is 25.0  $\text{cm}^{-1}$ . Similarly, for alcohol (3), the HBWs are 14.3 and 16.6  $\text{cm}^{-1}$  in  $\text{CCl}_4$  and  $\text{CS}_2$ , whilst in  $\text{CHCl}_3$ , the HBW is 26.0  $\text{cm}^{-1}$ . This increase in HBW in chloroform is also shown by the monorotameric alcohols (1) and (4). The increased band area reflects the fact that two types of association with the hydroxy group exist.

The associative behaviour of the OH group in an 'amphoteric' solvent such as chloroform advances the understanding of the solvation of alcohols. Previously, it had been assumed that association effects and the change in the OH stretching vibration accompanying a change in the solvent resulted solely from changes in the basic character of the solvent or the solvent-acceptor site.<sup>8</sup> It is now apparent that the OH stretching frequency and consequently the OH group-solvent interaction is dependent upon the nature of both the donor and acceptor sites of the solvent molecule.

It is expected that amphoteric solvents such as chloroform will behave in a similar manner; the effectiveness of the solvent as either a proton-donor or -acceptor will depend upon the relative charge densities of the positive and negative dipoles. Highly halogenated protic solvents show typically high charge densities and these types of molecules should show similar solvation effects to chloroform.

The study of composite rotameric bands of alcohols in chloroform-type solvents are of potential use for the evaluation of the relative repulsive forces between the hydroxy hydrogen and  $\beta$ -alkyl groups and lone pairs and  $\beta$ -alkyl groups.

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