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Solvent and concentration dependence of the hydroxyl chemical shift of methanol

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Proton NMR chemical shift measurements of the hydroxyl proton in methanol were made as a function of concentration in six solvents: carbon tetrachloride, benzene, chloroform, acetonitrile, acetone and dimethyl sulphoxide. The hydroxyl proton peak shifts by approximately 5 ppm in carbon tetrachloride and benzene, and by lesser amounts in the other solvents. This behaviour is due to hydrogen bonding interactions of the methanol with other methanol molecules or with the solvent, and is correlated with *ab initio* estimates of solute–solvent hydrogen bond energies.

1. Introduction

It has been known for several decades that the isotropic chemical shift for the hydroxyl proton of alcohols in a relatively non-interacting solvent such as chloroform or carbon tetrachloride is concentration dependent [1–6]. This concentration dependence has been interpreted in terms of changing the equilibrium populations of various hydrogen-bonded clusters of the alcohol. The presence of hydrogen bonding generally causes a shift of the hydroxyl proton signal to higher frequency [7]. The stronger the hydrogen bond, the larger the shift in frequency. For hydroxyl protons which are not hydrogen bonded, the chemical shift values are observed near the TMS reference signal at 0·0 ppm. When the hydroxyl proton is strongly hydrogen bonded (as in the neat liquid), the chemical shift typically is >4 ppm. Since the hydrogen bond strength is different in each cluster, the chemical shift of the hydroxyl proton also is different; however, if the lifetime of these clusters is very short only a single resonance is observed. The observed chemical shift is given by

$$\delta_{\mathrm{obs}} = p_1\delta_1 + p_2\delta_2 + \cdots \qquad (1)$$

where p_i is the fraction of the molecules in cluster i, with chemical shift δ_i.

Early NMR work [4–6] investigated the concentration dependence of the chemical shift for the hydroxyl proton of alcohols in carbon tetrachloride. The thrust of these studies was to determine physical constants of the alcohol (i.e., enthalpy of dimerization, equilibrium constants for hydrogen bonded clusters, etc.). What was missing from these analyses was consideration of the alcohol–solvent interaction. Although this interaction probably is weak when the solvent is carbon tetrachloride or benzene, it becomes increasingly important when the solvent is chloroform, acetonitrile. acetone, or dimethyl sulphoxide (DMSO). Even when the interaction is weak, the solvent can have a profound effect on the distribution and structure of clusters present in the solution [8]. When the interaction is weak, formation of homogeneous clusters of the alcohol is favourable; when the interaction is very strong, homogeneous cluster formation of the alcohol is hindered.

In this paper we focus on the binding of the alcohol to the solvent, and present concentration dependent data for the methanol hydroxyl proton chemical shift in the solvents carbon tetrachloride, benzene, chloroform, acetonitrile, acetone and dimethyl sulphoxide. These data are compared with theoretical calculations for the alcohol–solvent interaction.

2. Experimental methods

The proton NMR spectra were recorded on a home-built spectrometer operating at 295·00 MHz using a 5 mm probe. All spectra were obtained at a constant temperature of 259 K. The magnet is an eighth-order corrected solenoid manufactured by Cryomagnet Systems. The magnet and its environment are sufficiently stable that no internal lock is necessary for periods up to several hours; when deuterated solvents were used, the spectrometer was locked to the solvent signal. All chemical shift references were made to an internal reference of less than 0·05% tetramethylsilane (TMS). The chemical shift measurements are accurate to about ±0·01 ppm. The concentrations below 0·1 mole fraction methanol are accurate to about 5%. The concentrations above 0·1 mole fraction are accurate to 1% or better. Since these uncertainties are so small, error bars have

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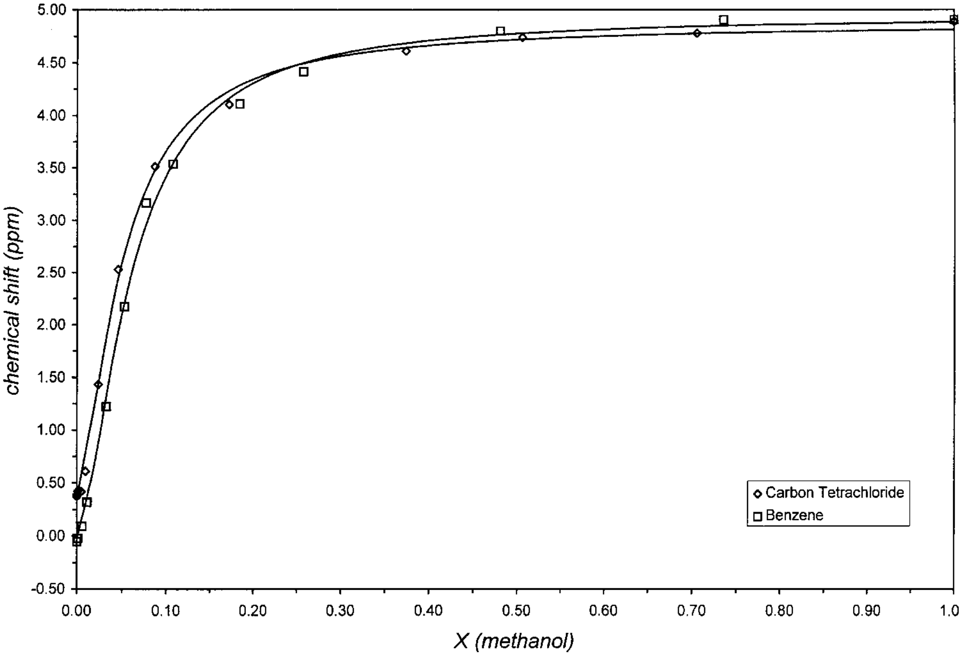

Figure 1. Concentration dependence of the chemical shift for methanol–carbon tetrachloride and methanol–benzene.

not been shown in the figures of chemical shift versus mole fraction methanol.

The methanol (99%, Aldrich) and deuterated solvents (Cambridge Isotope Laboratories) were used without further purification. All samples were dried over molecular sieves for at least 24 h to remove any trace amounts of water. All sample tubes were cleaned with nitric acid, rinsed with water, and then dried *in vacuo* for at least 24 h before use.

For samples more concentrated than 0·1 mol % methanol, a total amount of 0·50 ± 0·02 ml of solution was prepared in the same tube. For samples less concentrated than 0·1 mol % methanol, 1–5 ml of solution were prepared in a dry beaker. Aliquot of 0·50 ml was then transferred to each dry sample tube.

3. Results and discussion

3.1. *Concentration dependence of the chemical shift*

In the very dilute region, we assume the solutions consist of isolated methanol molecules surrounded only by solvent molecules. The chosen solvents lack either Lewis-acid or Lewis-base functionality for strong self-association and clustering, so their primary interactions will involve 1:1 dimer formation with available methanol molecules. Therefore, the chemical shift in this region is a measure of the relative strength of interaction between the methanol and the solvent. As the methanol concentration of a given solution increases, information can be obtained about preferences for hydrogen bonding, since methanol molecules can now interact with solvent molecules and/or with other methanol molecules.

The concentration dependence of the methanol–carbon tetrachloride and methanol–benzene systems is shown in figure 1. Both solvents show a similar concentration dependence: a low frequency chemical shift in the very dilute region with a sharp increase in frequency until a value close to that observed in the neat liquid is reached. This sharp increase in chemical shift is attributed to a strong preference for methanol molecules to hydrogen bond to other methanol molecules rather than solvent molecules.

It is commonly expected that carbon tetrachloride would be relatively non-interactive because it has no dipole moment. However, the presence of the chlorine lone pairs provides a means for an interaction with the methanol hydroxyl proton (small because the electronegative chlorine atom is a relatively weak Lewis base). In the very dilute region the chemical shift is 0·37 ppm. As the concentration of methanol increases, the chemical shift increases rapidly until the concentration reaches 25 mol % methanol, at which point the chemical shift is 4·5 ppm, which is close to the chemical shift observed in the neat liquid (4·9 ppm).

Benzene, like carbon tetrachloride, has no dipole moment; however, the aromatic ring provides a pi electron Lewis-base source for hydrogen bonding. In the very dilute region, the chemical shift is − 0·05 ppm, lower than the chemical shift measured in carbon tetrachloride. As in the carbon tetrachloride solution, the

Table 1. Mole fraction concentration and OH chemical shift values above which spin coupling is no longer observed.

Solvent	OH chemical shift	Mole fraction methanol
Carbon tetrachloride	0·54	0·01
Benzene	0·55	0·03
Chloroform	1·30	0·065
Acetonitrile	1·75	0·10
Acetone	2·50	0·095
Dimethyl sulphoxide	4·0	0·15

chemical shift reaches a value of 4·5 ppm at 25 mol % methanol.

The sharper increase in chemical shift combined with the lower initial chemical shift would seem to indicate superficially that benzene is less interacting than carbon tetrachloride. However, this observed chemical shift dependence needs to be analysed carefully. As described elsewhere [9], if hydrogen bonding occurs through the aromatic ring, the high electron density would shield the hydroxyl proton. Thus, the characteristic shift to higher frequency is not observed. The fact that benzene does interact with methanol is supported by the binding energy shown in table 1, which is discussed later.

The methanol–chloroform and methanol–acetonitrile systems have a similar concentration dependence, as shown in figure 2. The chemical shift increases rapidly with concentration until a value close to 4·9 ppm is reached. However, the chemical shifts in the very dilute region are 0·89 ppm and 2·13 ppm for chloroform and acetonitrile, respectively. Clearly this indicates the presence of hydrogen bonding between the methanol and the solvent. Here, again, the sharp increase in chemical shift with concentration shows a strong preference for methanol molecules to hydrogen bond with other methanol molecules rather than with solvent molecules.

The methanol–acetone system (figure 3) has a distinctly different concentration dependence. Rather than a rapidly increasing chemical shift, the dependence is nearly linear, increasing from a value of 3·1 ppm in the very dilute region to 4·9 ppm in the neat liquid. Because of the two lone pair electrons on the oxygen, it is expected that acetone would interact strongly with methanol. Thus, the high chemical shift in the very dilute region is expected; however, the rest of the dependence is surprising. The increase in the chemical shift suggests hydrogen bonding between methanol molecules, but the linearity of the dependence suggests very little preference for a methanol molecule to hydrogen bond preferentially with another methanol molecule rather than with an acetone molecule.

The concentration dependence for the methanol–dimethyl sulphoxide system is shown in figure 4. This dependence has two characteristics: (1) up to about 54 mol % methanol the chemical shift increases slowly and nearly linearly from 4·06 ppm to 4·20 ppm, and (2) at concentrations greater than 70 mol % methanol the chemical shift increases nearly linearly and much more rapidly from 4·37 ppm to 4·9 ppm. The two different

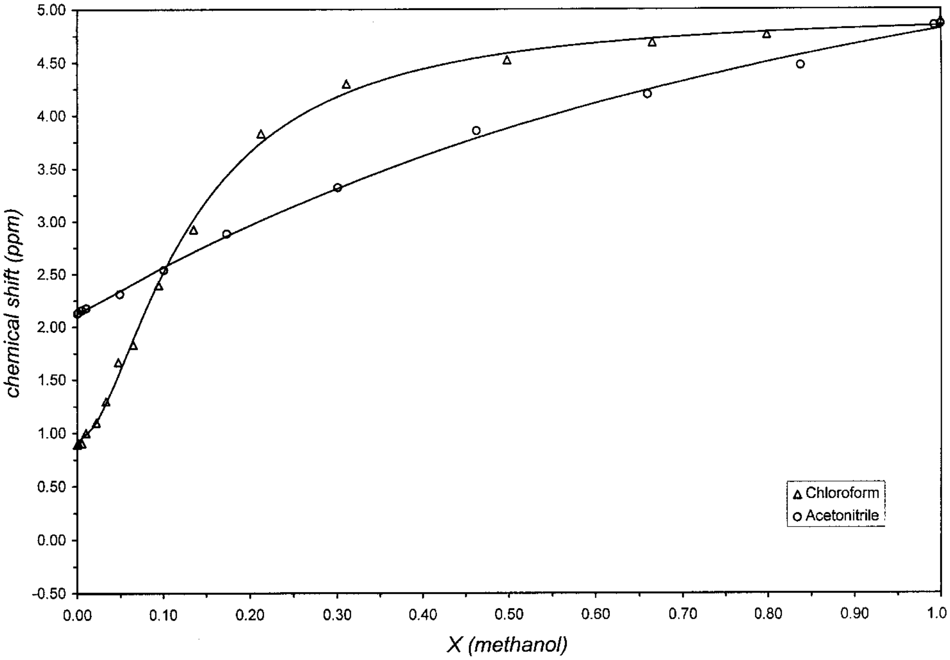

Figure 2. Concentration dependence of the chemical shift for methanol–chloroform and methanol–acetonitrile.

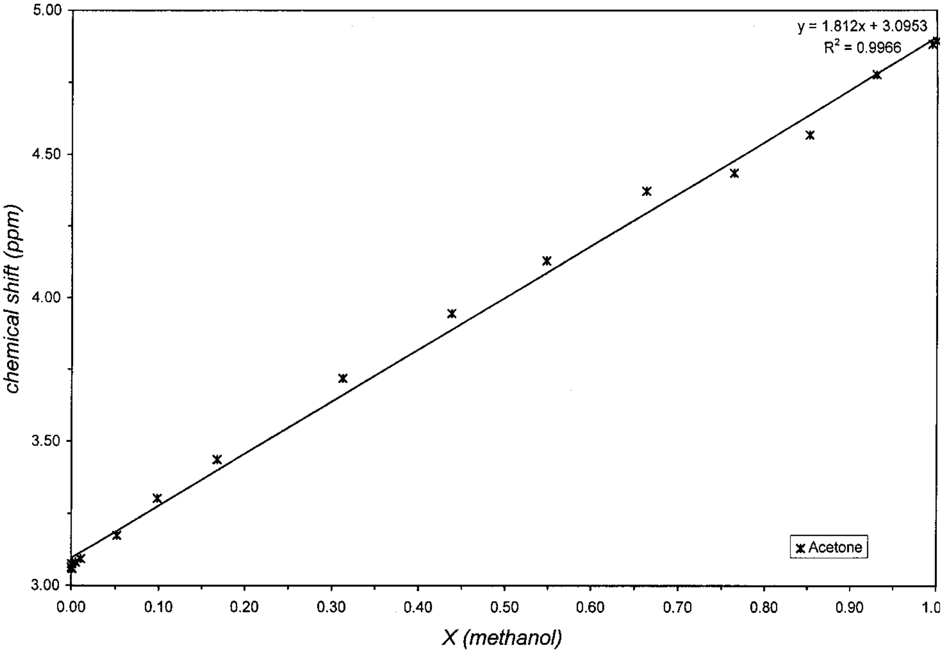

Figure 3. Concentration dependence of the chemical shift for methanol–acetone.

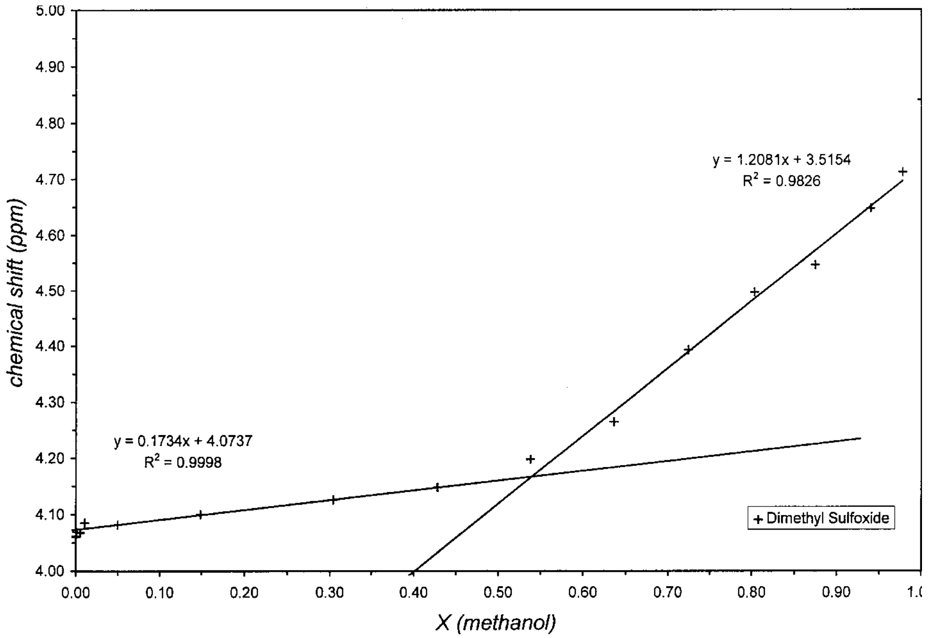

Figure 4. Concentration dependence of the chemical shift for methanol–dimethyl sulphoxide.

regions reveal a clear preference for a methanol molecule to hydrogen bond to a dimethyl sulphoxide molecule until half of the DMSO Lewis-base sites have been used.

This system has been studied by Romanowski, Kinart and Kinart [10]. Their results show similar behaviour: two regions with a linear increase. However, the concentration at which the slope changes in their study is 67 mol % methanol, compared with about 54 mol % methanol observed in this study. Their interpretation of the results is that two methanol molecules preferentially hydrogen bond with one DMSO molecule to form a hydrogen bonded cluster of the sort DMSO–2MeOH. When the concentration is greater than 67 mol % methanol, hydrogen bonding between methanol molecules commences. The results in this present study, however, show that the slope of the concentration dependence changes at about 50 mol % methanol.

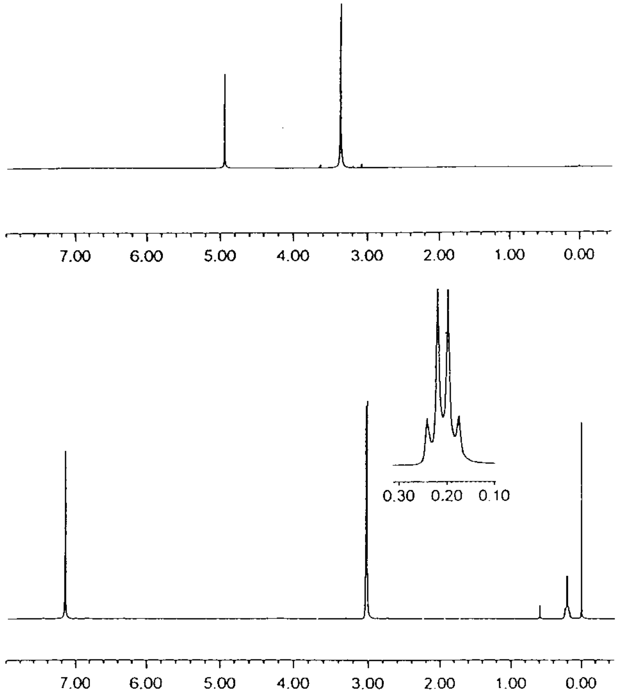

Figure 5. Upper trace, spectrum of neat, liquid methanol; and lower trace, spectrum of 0·6 mol % methanol in benzene (with 0·05 mol % water impurity). The inset shows the methanol OH peak.

Thus, it is likely that other methanol–DMSO or methanol–methanol clusters are present at concentrations less than 67 mol % methanol. The presence of other clusters at a concentration as low as 15 mol % is suggested by the disappearance of the fine structure; this is discussed in more detail below.

3.2. *Spin coupling interactions*

The upper trace of figure 5 shows a spectrum of neat methanol. In methanol, the three methyl protons are *J*-coupled to the OH proton, so the methyl group should be observed as a doublet and the OH proton should be observed as a quartet; however, in the neat liquid both proton signals are relatively sharp singlets at room temperature. The spin coupling can be observed in the neat liquid only when it is cooled to less than 223 K; however, in the very dilute solutions studied here, the fine structure is resolved provided that the solutions are very dry. The lower trace of figure 5 shows the spectrum for a 0·6 mol % methanol in benzene-d_6 solution.

This loss of spin coupling fine structure arises from exchange of the methanol hydroxyl proton. Since the dry solvents used do not have any exchangeable protons, this exchange can occur only between methanol molecules. Thus, the concentration at which the fine structure is lost is an indication of the concentration at which methanol molecules start to hydrogen bond to and/or to exchange OH protons with other methanol molecules. The last concentration data point at which the fine structure was observed for each solvent is shown in table 1. As expected, this concentration point increases as the strength of interaction between the methanol and the solvent increases. It is important to note that for methanol–dimethyl sulphoxide solutions the fine structure is lost at 15 mol % methanol, which suggests that hydrogen bonds between methanol molecules are formed well before the change in slope of the concentration dependence near 50 mol % methanol.

3.3. *Calculated binding energies*

Current *ab initio* methods can calculate the binding energy for a methanol–solvent dimer with reasonable accuracy. Knowing the binding energies for these dimers should allow for approximate prediction of the concentration dependence of the chemical shift at low concentrations, assuming that entropic effects are small compared with enthalpic dependence. Table 2 summarizes the calculated binding energies for two theoretical treatments, using uncorrelated Hartree–Fock (RHF) and hybrid density functional (BLYP) methods with the extended 6-31 + G^* basis set in each case. All calculations were performed using Gaussian 94 [11]. The two methods agree rather well in all qualitative respects; for simplicity we refer to B3LYP values (which incorporate electron correlation effects) in the ensuing discussion. The B3LYP/6-31 + G^* dimer geometries are shown in figure 6. As shown at the bottom of table 2, the calculated methanol–methanol binding energy is 6·25 kcal mol^{-1}.

Carbon tetrachloride, benzene, chloroform, and acetonitrile all have significantly lower calculated

Table 2. *Ab initio* M···X binding energies of methanol (M) with various solvent molecules (X), calculated at fully optimized Hartree–Fock (RHF/6-31 + G^*) and hybrid density functional (B3LYP/6-31 + G^*) levels.

	Binding energy kcal mol^{-1}	
Complex	RHF	B3LYP
M···CCl_4	0·62	0·68
M(a)···C_6H_3	1·94	2·16
M(b)···C_6H_6	1·18	0·99
M···$HCCl_3$	4·13	4·39
M···$NCCH_3$	4·26	4·89
M···$O{=}C(CH_3)_2$	5·51	6·33
M···$OS(CH_3)_2$	8·87	8·28
M···CH_3OH	5·32	6·25

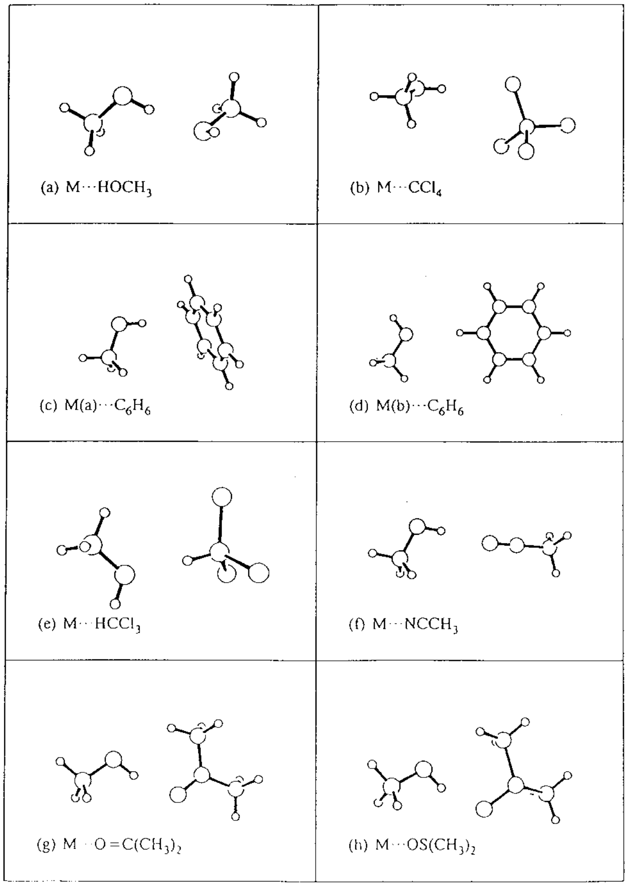

Figure 6. Optimized dimer geometries for methanol with the solvents benzene, carbon tetrachloride, chloroform, acetonitrile, acetone and dimethyl sulphoxide.

binding energies to methanol (by more than kT) compared with the methanol–methanol value. Hence methanol molecules should bind preferentially to one another, rather than form solute–solvent heterodimers. The calculated binding energies are fully consistent with the relative order inferred from NMR measurements (section 3). Two distinct methanol–benzene complexes were investigated: (a) a 'pi complex' (figure 6(*c*)) in which methanol acts as the Lewis acid in an out-of-plane $\pi\cdots$H—bond ($\pi_{CC} \rightarrow \sigma^*_{OH}$ delocalization), and (b) a 'sigma complex' (figure 6(*d*)) in which methanol acts at the Lewis base in an in-plane O··H—C bond ($n_O \rightarrow \sigma^*_{CH}$ delocalization). Although the pi complex appears slightly stronger as an isolated dimer (~ 2 versus ~ 1 kcal mol^{-1}), the sigma complex evidently can form without disrupting the presumed face-to-face interactions of benzene molecules in the liquid phase, and therefore may be the thermodynamically favoured isomer in dilute methanol–benzene solutions. (The latter complex also is more consistent with the measured shieldings and concentration dependence, planned for discussion in a forthcoming paper.) No matter which benzene complex is present, it is clear from table 2 that CCl_4, C_6H_6, $HCCl_3$ and CH_3CN solvents belong to the 'weak interaction' limit in which solute–solute aggregation is favoured over solute–solvent interactions, leading to characteristic concentration dependence manifested as an 'early' sharp increase in chemical shift up to the value observed in the neat liquid.

Acetone is different in that its calculated binding energy to methanol (6·33 kcal mol^{-1}) is comparable with the methanol–methanol interaction (6·25 kcal mol^{-1}). Therefore, methanol molecules should show little preference for binding to solute or solvent molecules, and the concentration dependence should be nearly linear (as observed, figure 3).

Finally, dimethyl sulphoxide represents the other extreme, with calculated binding to methanol (8·28 kcal mol^{-1}) significantly greater than the methanol–methanol interactions. Hence, methanol molecules should show a very strong preference for binding to a solvent DMSO molecule. Binding a second methanol molecule to a methanol–DMSO dimer results in a drop of the binding energy to 7 kcal mol^{-1} for each methanol molecule. This is observed in the concentration dependence as a very slight change in the chemical shift over a large concentration range (figure 4), until solute methanols are no longer able to find 'free' DMSO molecules. Thus, in each case the calculated binding energies are in excellent agreement with the experimentally measured concentration dependence.

4. Conclusion

Concentration dependent NMR proton chemical shift measurements are in excellent agreement with *ab initio* calculations for the chemical shifts and binding energies of methanol–solvent dimers. At this point it seems clear that although simple alcohols preferentially hydrogen bond with stronger hydrogen bonding solvents such as DMSO, other methanol–methanol interactions also are present, even at rather dilute concentrations. More detailed experimental and theoretical studies are in progress.

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References

[1] Pimental, G. C., and McClellan, A. L., 1959, *The Hydrogen Bond* (San Francisco: Freeman).

[2] Pople, J. A., Schneider, W. G., and Bernstein, H. J., 1959, *High-resolution Nuclear Magnetic Resonance* (New York: McGraw-Hill), chap. 15.

[3] Gutowsky, H. S., and Saika, A., 1953, *J. chem. Phys.*, **21,** 1688.

[4] Becker, E. D., Liddel, U., and Shoolery, J. N., 1958, *J. molec. Spectrosc.*, **2,** 1.

[5] Saunders, M., and Hyne, J. B., 1958, *J. chem. Phys.*, **29,** 1319.

[6] Davis Jr., J. C., Pitzer, K. S., and Rao, C. N. R., 1960, *J. chem. Phys.*, **64,** 1744.

[7] Becker, E. D., 1996, *Encyclopedia of Nuclear Magnetic Resonance* (New York: Wiley), p. 2409.

[8] Zwier, T. S., 1996, *Annu. Rev. phys. Chem.*, **47,** 205.

[9] Becker, E. D., and Liddel, U., 1957, *Spectrochim. Acta*, **10,** 70; and references cited therein.

[10] Romanowski, S. J., Kinart, C. M., and Kinart, W. J., 1995, *J. chem. Soc. Faraday Trans*, **91,** 65.

[11] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W. Andres, J. L., Replogle, E. S., Gomerts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., and Pople, J. A., 1995, Gaussian 94, Revision C.2 (Pittsburgh, PA: Gaussian, Inc.).