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LETTER TO THE EDITOR

Hydration of methanol in aqueous solutions: a Raman spectroscopic study

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Abstract. High-resolution Raman spectroscopy was used to study methanol–water mixtures over the whole concentration range. We report a highly non-linear dependence of the carbon–oxygen and carbon–hydrogen stretching frequencies with composition. The difference between the polarized and depolarized frequencies of the carbon–oxygen stretching mode (non-coincidence effect) was also measured. Taken together, the data suggest a global picture of the progressive hydration of methanol: water first breaks up the molecular chains which exist in pure methanol, and then completely hydrates the hydroxyl groups before solvating the hydrophobic methyl groups.

1. Introduction

The importance of hydrogen-bonded liquids in physics, chemistry, biology and technology has kept them at the focus of experimental and theoretical attention for many decades. As prototype hydrogen-bonding molecules, water and methanol (CH₃OH, MeOH) both hold special status. MeOH has another claim to be at the focus of attention—it is one of the simplest amphiphile-like molecules. An *amphiphile* [1] is a bipolar molecule with solvent-loving and solvent-hating moieties, and they self-assemble to form superstructures (micelles, bilayers etc) in highly polar or highly non-polar solvents. Understanding the behaviour of amphiphiles is a central aim of soft-condensed-matter physics. Amphiphiles are also widespread in the chemical industry, e.g. as detergents, and are central to biology, most notably making up cell membranes. MeOH is the simplest amphiphile-like molecule capable of hydrogen bonding. The shortness of its alkyl chain means that MeOH probably does not show conventional self-assembly behaviour. Nevertheless, its clearly bipolar nature means that it can act as the starting point for a fundamental understanding of the solvation of amphiphiles.

There is a considerable literature on MeOH–water mixtures. A popular method of study is computer simulations (e.g. [2–6]). These are aimed at determining the detailed hydrogen-bond structure, but so far have produced conflicting results, partly because of the extreme sensitivity to the model potentials used as inputs. To deal with this problem, the empirical potential structure refinement method was invented in which the potentials themselves are refined against scattering data [7]. Its use on neutron scattering data from an $x = 0.1$ MeOH–water mixture [8] (where x is the mole fraction of methanol) and from neat methanol [9] has produced a picture of the local positional as well as orientational correlations with unprecedented detail.

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Simulations and neutron scattering investigations are both time-consuming methods, and have only been used on a very limited number of concentrations, mostly at high dilution ($x \lesssim 0.1$). Spectroscopy, however, has high throughput, and can easily cover the whole composition range ($0 < x \leq 1$). In particular, Raman spectroscopy has been used to monitor the carbon–hydrogen ($\nu_{\text{CH}} \approx 2836 \text{ cm}^{-1}$ at $x = 1$) and carbon–oxygen ($\nu_{\text{CO}} \approx 1036 \text{ cm}^{-1}$ at $x = 1$) stretching frequencies. Kabisch and Pollmer [10] found a non-linear dependence of ν_{CO} on x , and interpreted this (in the light of their data on other solute–solvent pairs) in terms of the participation of the MeOH hydroxyl group in donating and accepting hydrogen bonds. Kamogawa and Kitagawa [11] claimed that the shifts in ν_{CH} with x were too small to observe directly with any accuracy, and used an intensity-difference method to give, again, a non-linear dependence, interpreted in terms of intermolecular interactions. Zerda *et al* [12] reported, in a study otherwise devoted to high-pressure effects, that ν_{CO} is a *linear* function of x , contradicting Kabisch and Pollmer [10]. More recently, Kamogawa and Kitagawa reported *both* ν_{CH} and ν_{CO} [13], but did not comment on their correlation. None of these authors use the spectroscopic data to give a *global* picture of the progressive hydration of methanol, concentrating instead on the particulars of hydrogen bonding in special regimes (mostly at small x). Moreover, all of these studies predate two significant recent advances: the neutron scattering data already mentioned [8,9], and an infrared study of ν_{CH} in various MeOH complexes in the gas phase [14].

Below, we report a detailed study of ν_{CH} and ν_{CO} as functions of x . A closely spaced sequence of data points at $x \rightarrow 1$ and $x \rightarrow 0$ shows that ν_{CH} and ν_{CO} saturate at these two regimes respectively. We correlate the data from the hydrophobic and hydrophilic moieties, and show that they give a consistent overall picture of the progressive hydration of MeOH as x decreases. Our interpretation is corroborated by a measurement of the non-coincidence effect in ν_{CO} (the difference in frequency between the polarized and depolarized components of the mode), by recent neutron scattering data [8] and by the work of Gruenloh *et al* [14]. However, the suggestion that ν_{CH} reflects the hydrogen-bond environment of the hydroxyl group [14] is shown to be incomplete, at least for condensed phases.

2. Experimental procedure

MeOH from Sigma was used as purchased. Deionized water was boiled and passed through a 0.2 Millipore filter. Mixtures were used within 72 hours of being sealed in sample tubes. Raman spectra were excited at room temperature ($290 \pm 2 \text{ K}$) using 400 mW of the 514.5 nm line of an Ar⁺ laser, and analysed at 90° using a Coderg T800 triple-axis spectrometer to 1.2 cm⁻¹ resolution. To study the environment of the hydrophilic and hydrophobic ends of the molecule, we monitored ν_{CO} and ν_{CH} respectively†. The incident laser light was always polarized perpendicular to the scattering plane. The scattered light polarized parallel (VV) or perpendicular (VH) to the incident radiation was monitored for ν_{CO} . Only VV scattering was monitored for ν_{CH} . A neon emission line was used as an internal frequency standard. Peak frequencies were determined by inspection and the quoted error bars reflect the uncertainties in estimating the positions of peak maxima.

3. Results and discussion

Measured values of ν_{CO} in VV and VH polarizations and ν_{CH} in VV polarization are shown in figures 1 and 2. The x -dependence of ν_{CO} clearly separates into three regimes. Above

† The OH-stretch bands in MeOH overlap those in water and hence are not useful for studying the hydrophilic moiety of the former.

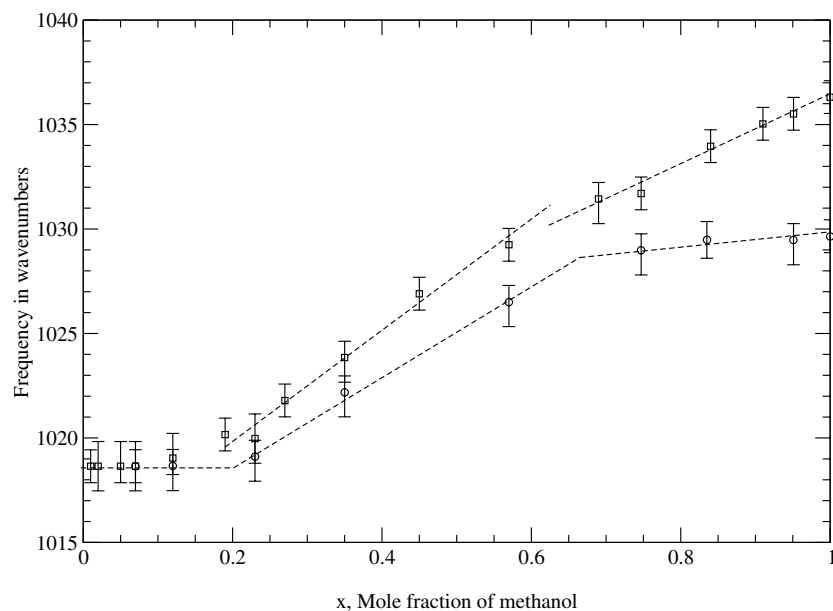


Figure 1. Variation of the C–O symmetric stretch frequencies (\square : VV; \circ : VH) of methanol as a function of concentration in water. Lines are guides to the eye.

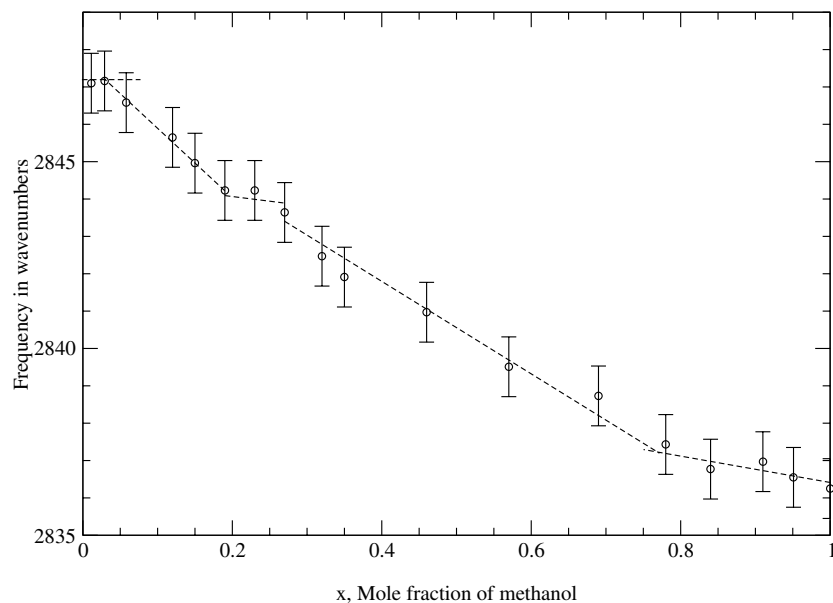


Figure 2. Variation of the C–H stretch frequency (VV) as a function of methanol concentration in water. Lines are guides to the eye

$x \sim 0.7$, $\nu_{\text{CO}}^{(\text{VH})}$ is approximately constant while $\nu_{\text{CO}}^{(\text{VV})}$ red-shifts at $\sim 2 \text{ cm}^{-1}$ per 0.1 decrease in x . Below $x \sim 0.7$, $\nu_{\text{CO}}^{(\text{VH})}$ starts to red-shift, and the rate of red-shifting of $\nu_{\text{CO}}^{(\text{VV})}$ increases by nearly 50%. Finally, below $x \sim 0.25$, there is no difference between $\nu_{\text{CO}}^{(\text{VV})}$ and $\nu_{\text{CO}}^{(\text{VH})}$ within

experimental error, and both remain constant down to $x = 0$. The x -dependence of ν_{CH} is consistent with this picture. ν_{CH} is nearly constant down to $x \sim 0.7$, whereupon significant blue-shift begins. The blue-shift somewhat saturates at $x \sim 0.25$, but starts to rise again below $x \sim 0.15$ until $x \sim 0.05$, below which it again saturates.

We propose that these trends can be interpreted as follows. It has long been suggested that molecules in pure MeOH (i.e. $x = 1$) hydrogen bond with each other to form chains. A recent scattering and simulation study [9] confirms this, giving an average chain length of five or so molecules at 25 °C; see figure 3(a). The existence of these chains implies non-zero average orientational correlation between molecules, which is reflected in the measured non-coincidence effect, $\nu_{\text{CO}}^{(\text{VV})} - \nu_{\text{CO}}^{(\text{VH})} \neq 0$ [15, 16]. We suggest that in the first hydration regime, $1 > x \gtrsim 0.7$, water molecules participate in hydrogen bonding to chain ends [10]; see figure 3(b). Chain-end hydration in this concentration regime has also been suggested very recently by Sato *et al* [17] on the basis of reorientation relaxation time measurements using dielectric spectroscopy. The fact that $\nu_{\text{CO}}^{(\text{VV})}$ red-shifts suggests that the chain-end methanols act preferentially as H-bond acceptors[†] [10]. The reason for this preference is unclear.

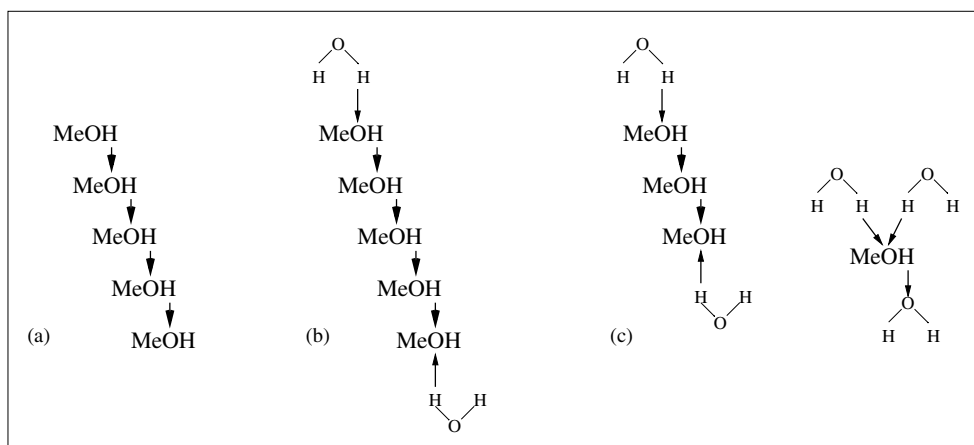


Figure 3. A schematic picture of progressive methanol hydration. (a) An average chain in pure methanol. (b) Water molecules donating hydrogen bonds to chain ends. The proposed mode of hydration in the regime $1 \gtrsim x \gtrsim 0.7$. (c) Water molecules breaking chains; on the right is a single MeOH molecule with ‘AAD’ hydrogen bonds round its hydroxyl group. The proposed hydration mechanism for $0.7 \gtrsim x \gtrsim 0.25$.

Given that the two ends of a chain can accept up to three hydrogen bonds, we can estimate that this effect saturates (for chains of average length five) at $x \sim 5/(3 + 5) \gtrsim 0.6$, which is not far from the crossover at $x \sim 0.7$ to the second regime of behaviour. Once the chain ends are saturated, further hydration proceeds by the water molecules progressively breaking up chains of MeOH and solvating the molecules individually; see figure 3(c). Recently Gruenloh *et al* [14] have measured ν_{CH} in MeOH in which the hydroxyl group is hydrogen bonded to other species in the gas phase. They found that ν_{CH} is sensitive to the *configuration* of hydrogen bonds at the polar moiety, but not to the kind of complexing species giving rise to a particular hydrogen-bond configuration. A single MeOH molecule can maximally accept two and donate one hydrogen bond; see figure 3(c). For such an ‘AAD’ configuration, Gruenloh *et al* always found ν_{CH} blue-shifting, as indeed we observe in MeOH in the regime $0.7 \gtrsim x \gtrsim 0.15$. We mention in passing that in the previous concentration regime, $1 > x \gtrsim 0.7$, ν_{CH} is essentially

[†] The oxygen atom on an *acceptor* molecule forms a hydrogen bond with a hydrogen atom on a *donor* molecule.

constant, indicating that there is as yet no significant ‘AAD’ hydrogen bonding, supporting our earlier conclusion of chain-end hydration.

When all direct MeOH–MeOH hydrogen bonds are broken by this process, we expect little or no average alignment of intermolecular dipoles, i.e. the non-coincidence effect should decrease to zero. This we do observe at $x \sim 0.25$, which corresponds to three waters per MeOH, $1/(1+3) = 0.25$. Moreover, at $x \sim 0.25$, the blue-shift in ν_{CH} appears to saturate, suggesting that the hydrogen-bond configuration round the hydroxyl groups in MeOH has stabilized.

Blue-shift in ν_{CH} starts again at $x \sim 0.15$. By this stage, the primary ‘AAD’ hydration shell of the hydroxyl group is associated with a further three or so water molecules. When this process of hydroxyl solvation is complete, further increase in water content takes the form of water molecules forming structure round the methyl groups. This we propose as the hydration process below $x \sim 0.15$. Indeed, very recent neutron scattering and simulation work by Finney and Soper [8] reports a more or less complete shell of water molecules surrounding each MeOH at $x = 0.1$. Interestingly, even though the average hydrogen-bonding configuration of the hydroxyl group is not expected to change in this regime, ν_{CH} continues to blue-shift. The conclusion of Gruenloh *et al* [14] from gas-phase work, that ν_{CH} in MeOH is sensitive to the hydrogen-bond configuration at the polar moiety, therefore needs supplementing in the condensed phase, where ν_{CH} clearly also responds to the immediate environment of the non-polar moiety.

At very low concentration, $x \lesssim 0.05$, ν_{CH} again saturates. This may be taken as evidence that the primary hydration around methyl groups is complete. This suggestion has also been made very recently on the basis of dielectric spectroscopy relaxation data [17]. Note that the saturation of ν_{CH} was *not* observed by Kamogawa and Kitagawa [11]; but these authors used a highly complex procedure to analyse their ‘Raman difference spectra’, so direct comparison is not straightforward.

Before summarizing the global picture of MeOH hydration to emerge from our findings, we return to a feature of our data on which we have not yet commented. In the regime $1 > x \gtrsim 0.7$, $\nu_{\text{CO}}^{(\text{VH})}$ remains constant while $\nu_{\text{CO}}^{(\text{VV})}$ red-shifts. Perhaps surprisingly, this behaviour is almost identical to that observed in pure MeOH under pressure from 1 bar to 4 kbar [12]. Detailed modelling of the non-coincidence effect in pure MeOH based on the model of McHale [18] has been carried out by Torii and Tasumi [15]. They suggest that the initial increase in density on application of pressure is largely absorbed by closer packing of methyl groups, leaving the hydrogen-bonding structure at the methyl moieties (and therefore the chain structure) little affected. That there is little change in the chain structure is consistent with our interpretation of what happens in the regime $1 > x \gtrsim 0.7$; see figure 3(b). Furthermore, thermodynamic measurements on MeOH–water mixtures have yielded a *decrease* in the MeOH partial molar volume for all concentrations down to $x \sim 0.1$ [19]. The partial molar volume at $x \sim 0.7$ is equivalent to an effective MeOH density of $\rho \sim 0.8 \text{ g cm}^{-3}$. This is equivalent to pure bulk MeOH at ~ 0.5 kbar [20]. It is therefore at least plausible that the behaviour of the non-coincidence effect in ν_{CO} in the concentration range $1 > x \gtrsim 0.7$ basically reflects an increase in MeOH packing density due to the presence of water, and is an example of a ‘solvation pressure’ effect [21].

4. Summary and conclusions

The behaviour of ν_{CO} and ν_{CH} in MeOH–water mixtures suggests three regimes of hydration. At $1 > x \gtrsim 0.7$, the addition of water leaves the chain structure of pure MeOH substantially

intact; hydration takes place at the chain ends, where the MeOH molecules act principally as H-bond acceptors. For intermediate concentrations, $0.7 \gtrsim x \gtrsim 0.25$, water progressively breaks up MeOH chains; individually molecules become hydrated, accepting two and donating one H bond with water. Below $x \sim 0.15$, when the hydroxyl groups are completely surrounded by water, hydration of the methyl groups take place, resulting in their complete primary solvation by $x \sim 0.05$. The naive picture of water hydrating an amphiphile-like molecule, namely, that it solvates the polar moiety before the non-polar moiety, is therefore seen to be essentially correct.

Corroboration for our proposed picture has come from a number of sources, including dielectric spectroscopy, thermodynamic measurements [22] and neutron scattering and simulations. Further use of the last two techniques, in the form of the empirical potential structure refinement method, at key concentrations ($x \sim 0.7$ and ~ 0.05) should provide direct confirmation. Work in this direction is under way. The comparison of the effect of dilution with water and hydrostatic pressure is intriguing. High-pressure spectroscopic data on MeOH–water mixtures will be published elsewhere, where the comparison will be taken further. We conclude with a general remark. This work shows how careful spectroscopy at high frequency and concentration resolutions can be a powerful tool in the study of liquid mixtures. In particular, it provides a guide to the choice of parameters for studies using more time-consuming techniques, such as direct structural investigations using scattering and simulation methods.

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