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# A novel high pressure tool: the solvation pressure of liquids

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**Abstract**

Co-solvents were studied to determine if the change in the cohesive energy density (CED) generates an effective solvation pressure equivalent to the application of an external hydrostatic pressure. Raman modes of chloroform under hydrostatic pressure with co-solvents (chloroform–ethanol, chloroform–acetone) and in the vapour phase were recorded. In some cases the Raman frequency shifts indicate that the solvation pressure behaves as a true hydrostatic pressure. The pressure-induced gelation of starch grains was studied in aqueous media. A higher co-solvent concentration is postulated to put the grains under effective negative pressure, and indeed an increase in the external pressure needed for gelation was seen after the introduction of solvents. The quantitative agreement between the change of solvation pressure and hydrostatic pressure is very good over a wide range of solvent concentration.

## 1. Introduction

Much chemistry and all biochemistry takes place in aqueous solution. The aqueous medium may be very far from pure, particularly *in vivo*, and much attention has been paid to the specific effects of impurities. Some impurities may act as anti-freeze or anti-pressure agents, protecting specific or general biological processes (Wohrmann *et al* 1997, Sebert 2002). For example, ethanol has a general effect on animal brains (inebriation and anaesthesia) and glycerol is generally a stabilizer of proteins (Gekko and Timasheff 1981).

The aqueous medium exerts an internal pressure on structures, such as proteins, contained therein, and the magnitude of this pressure may be characterized by the cohesive energy density (CED) (Hildebrand and Scott 1950). We call this the solvation pressure. It is also known that the application of an external hydrostatic pressure has general effects on biological systems, for example, leading to the unfolding of proteins (Gross and Jaenicke 1994) or as an antagonist

  

to many forms of anaesthesia. Johnson and Flagler (1950) anaesthetized tadpoles with a few per cent ethanol in their water and reversed the effect by the application of a few hundred bar of hydrostatic pressure. It is natural, therefore, to conclude that solvation pressure may also affect biological systems by the same physical process.

Water has a high CED and hence a high solvation pressure. The solvation pressure can be controlled by the addition of a second solvent with, most certainly, a lower CED. In this paper, the relationship between the solvation pressure of co-solvents and hydrostatic pressure is explored. In previous work we have found that the effects of a reduced solvation pressure can be reversed by the application of hydrostatic pressure and that there are quantitative relationships (van Uden *et al* 2003). However, rarely will a co-solvent have no specific interactions with the subject of study, and such specific interactions will often mask the general effect of changed internal pressure.

In this paper, we show that such phenomena can also occur in non-aqueous systems and we report data in ethanol–chloroform mixtures showing that ethanol increases the effective pressure on chloroform molecules. The effective pressure on chloroform molecules is interrogated by measuring the change in particular Raman frequencies. We also report data on starch in aqueous solution, in which the internal pressure is reduced by the presence of ethanol and glycerol and the effective pressure is determined by the onset of gelation.

## 2. Experimental methods

Chloroform–ethanol and chloroform–acetone mixtures were prepared in increments of 15 vol% in the co-solvent concentration. The mixtures were placed in small glass sample tubes, which were sealed and placed under a Renishaw Raman microscope system. Raman spectra of the vibrational modes of chloroform, in the 300–3000 $cm^{-1}$ region, were recorded at room temperature and ambient pressure for each co-solvent concentration. The excitation source was a 632.8 nm He–Ne laser (60 mW); the signal was collected in the backscattering geometry. In order to eliminate any drift in the spectrometer, each spectrum was calibrated against the emission lines of a neon lamp. The absolute peak positions are accurate to within 0.15 $cm^{-1}$.

Raman spectra of pure chloroform were taken under increasing hydrostatic pressure up to 800 MPa. A single sided (van Uden and Dunstan 2000) diamond-anvil cell (DAC) was used to increase the control of the pressure in this relatively low pressure region. The pressure inside the DAC was determined by using the photoluminescence (PL) of ruby. The PL of a chip of ruby which was placed inside the cell was compared with the spectrum of an external piece subjected to ambient pressure. The uncertainty in the deduced pressure values is 40 MPa.

Chloroform in the vapour phase was also studied under Raman. A vertical hole was drilled in a stainless-steel cube. Along the top a small channel was milled, which had a dead end on one side and merged with the hole on the other side. Liquid chloroform was poured into the cube to half fill the hole. The top was then covered with a thin glass cover slide. Several hours were allowed for some of the chloroform to evaporate and to fill the channel with saturated vapour. The cube was placed under the microscope so that the focus lay within the channel but no scattered light from the liquid chloroform could reach the objective. The acquisition time for a single spectrum was about 2 h.

Finally, the gelation of potato starch in a solution of distilled water was observed as a function of applied hydrostatic pressure, following the work of Rubens *et al* (1999). The range of solutions was extended to binary water–ethanol and water–glycerol and tertiary water–ethanol–glycerol mixtures. Several potato starch grains ($\sim$20) were loaded in a double sided DAC with a thick gasket. This was done in order to achieve back illumination to observe the grains and to have the ability to increase the pressure in small increments. A small ruby chip

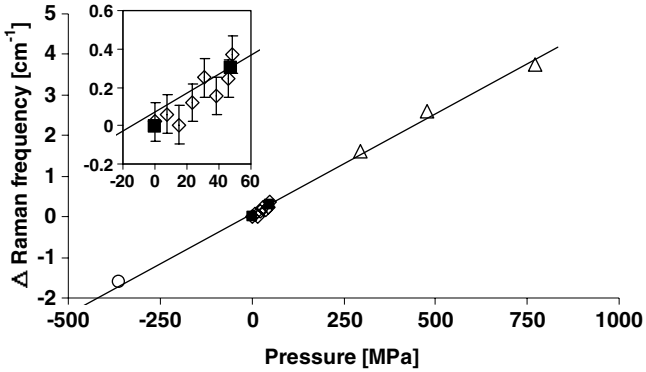


**Figure 1.** Raman shifts of the symmetric CCl deformation in chloroform as a function of hydrostatic pressure (△) and solvation pressure: chloroform–acetone (◊), chloroform–ethanol (■) and chloroform vapour (○). Shifts are relative to the Raman frequency of liquid chloroform at ambient pressure (366.1 $cm^{-1}$). The solid line is a guide to the eye through the hydrostatic pressure data.

was also placed inside the cell to monitor the pressure. After each pressure increment the pressure inside the cell was recorded and the starch grains were examined under an optical microscope to see whether gelation has taken place or not. The steps were repeated until gelation occurred.

## 3. Results and discussion

The Raman frequency shift of the 366 $cm^{-1}$ CCl symmetric deformation mode (umbrella) in pure chloroform is plotted as a function of hydrostatic pressure in the DAC in figure 1. The data from the liquid mixtures are plotted on the pressure axis by taking the cohesive energy density of the mixture as a measure of pressure. The CED is a standard quantity, energy of vaporization per unit volume, which may be found in data-books (Grulke 1998). The products of CED and volume fraction for each component in a mixture were summed together to give the average CED of the mixture; we define this quantity as the solvation pressure.

Figure 1 shows a solid line as the expected dependence of the Raman frequency of the CCl symmetric deformation mode. This trend line is extrapolated from the Raman shifts under hydrostatic pressure in the DAC (△). Both acetone and ethanol have a CED which is higher (412 and 676 MPa, respectively) than chloroform (361 MPa). Consequently, the chloroform–acetone (◊) and chloroform–ethanol (■) mixtures have a higher solvation pressure than pure chloroform and therefore their respective data points are found on the positive pressure side. The inset in figure 1 shows an enlargement of the region in which the mixtures are found. The Raman frequency shifts in both mixtures are in good quantitative agreement with the rate projected by the DAC data. This agreement holds for all acetone concentrations but is only valid for ethanol concentrations up to 20%. At higher concentrations there is no further shift in the chloroform Raman frequency. By definition the CED of the vapour phase is zero, hence the chloroform vapour data (○) is plotted on the negative pressure axis at −361 MPa. Again the Raman frequency is in excellent agreement with the expected value.

The data for the 668 $cm^{-1}$ CCl symmetric stretch mode (breathing) of chloroform are shown in figure 2. For this mode the Raman shifts due to solvation pressure do not have the same pressure dependence as seen under hydrostatic pressure. It might possibly, but not necessarily, be the case that the effect of solvation pressure is masked by specific interactions.

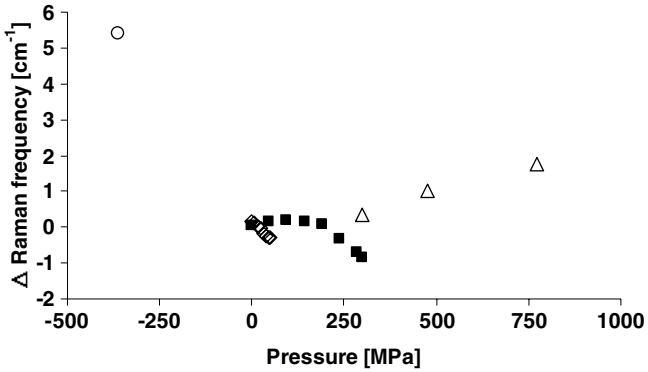


**Figure 2.** Raman shifts of the symmetric CCl stretch in chloroform as a function of hydrostatic pressure (△) and solvation pressure: chloroform–acetone (◇), chloroform–ethanol (■) and chloroform vapour (○). Shifts are relative to the Raman frequency of liquid chloroform at ambient pressure (667.7 $cm^{-1}$).

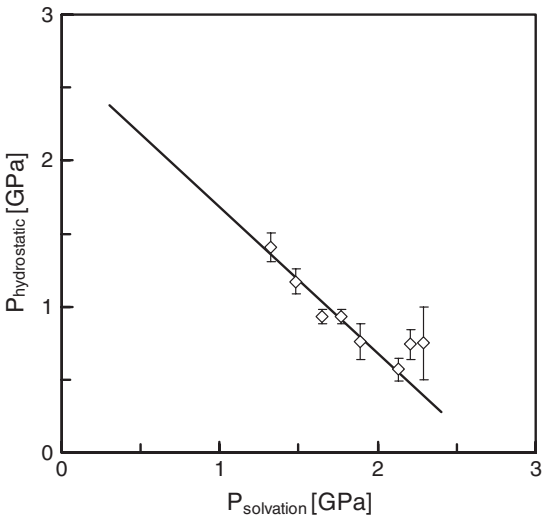


**Figure 3.** The externally applied hydrostatic pressure needed to induce gelation in starch grains is plotted against the solvation pressure of the water–ethanol solution (◇) containing the grains. The solid line of slope −1 shows the phase boundary expected if solvation pressure acts truly as a hydrostatic pressure.

The gelation pressure of the starch grains was determined by taking the average between the highest pressure at which the grains have not 'popped' and the pressure at which more than half of the grains went through the phase transition. The error bars indicate the range between the two pressures. In figure 3, the hydrostatic pressure needed for gelation is plotted against the solvation pressure of the water–ethanol solutions (◇). The ethanol content varies from zero in the rightmost point to 60% on the left. As water has one of the highest CED values (∼2.3 GPa), any addition of ethanol or glycerol decreases the solvation pressure considerably. The data show that an increase in applied hydrostatic pressure is then needed for gelation to occur. Our model predicts that the popping of the starch occurs at constant overall pressure represented by a straight line with a slope of −1 (the solid line drawn in figure 3). The ethanol

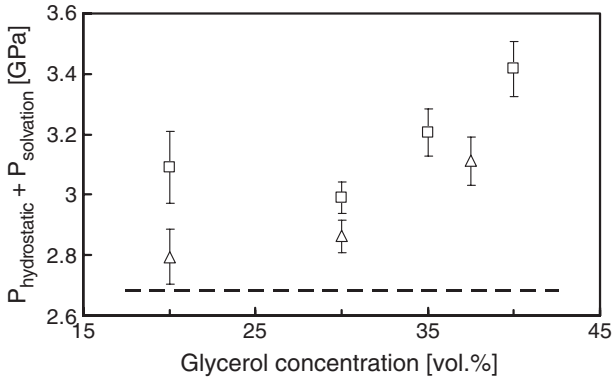


**Figure 4.** The sum of hydrostatic and solvation pressure during starch gelation as a function of glycerol concentration. A binary water–glycerol (□) and a tertiary water–ethanol–glycerol mixture (△) are shown. The horizontal dashed line is the phase boundary from figure 3.

seems to increase the susceptibility of the starch to pressure slightly since the data points for all but the very low ethanol concentrations (<10%) fall slightly below the pure water point. However, this effect seems to be independent of the ethanol concentration as the slope is still −1 as predicted.

Figure 4 presents the water–glycerol (□) and water–ethanol–glycerol (△) data in which the total pressure (applied hydrostatic + solvent) is plotted against the glycerol concentration. Here our model predicts a horizontal line. The water–glycerol data (□) agree reasonably well with the prediction of a constant total pressure. The data points lie on an approximately horizontal line but are shifted vertically upwards when compared to the water–ethanol data. The dashed line in figure 4 is the solid line from figure 3 transformed into the new set of axes to give a reference. The glycerol might have an additional stabilizing effect on the starch and therefore a higher external pressure is needed. The data of the tertiary water–ethanol–glycerol mixture (△) also display the reality of the solvation pressure with the points falling on an approximately horizontal line and lying in between the two binary mixtures, indicating, again, the opposing specific effects of ethanol and glycerol. Only at high glycerol concentrations (>30%) do the data start to deviate from the model. But for all mixtures a good agreement is seen over a wide range of co-solvent concentrations.

## 4. Conclusions

The data presented here go as far as experimental work can towards showing the existence of a general solvation pressure (positive and negative), given the inevitable presence of masking due to specific interactions. It remains possible, of course, to interpret all of our data in terms of specific interactions only, with the quantitative agreement of the solvation pressure model being due to chance.

This cannot be resolved by future experiments. Theory, however, and a better understanding of solvation, may offer a way forward. For example, in molecular dynamics, specific interactions can be chosen, controlled, or even be switched off.

We have reported some MD of ethanol (van Uden *et al* 2003) which supports the experimental results presented here on chloroform vapour. However, future MD work is needed and other theoretical techniques may also be relevant.

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