

Effect of Pressure on the Frequency of the O—H Band in Butanol Solutions*

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The infrared spectra of dilute solutions of normal butanol have been observed in the 3-micron region at pressures from 10 to 12 000 atmospheres. The sharp "monomeric" O—H band shifts toward lower frequencies as the pressure increases. If we define $\Delta\nu$ as the shift in frequency from its value at one atmosphere and 25°C in each solvent, $\Delta\nu$ at the maximum pressure varies from 11 cm⁻¹ in 2, 3 dimethyl butane to 41 cm⁻¹ in *n*-propyl iodide. The frequency shift is found to be a linear function of the square of the density and the polarizability of solvent bonds, though this latter relationship is not quantitative. The shifts are plausibly explained as due to van der Waals' forces between the O—H bond and the solvent. The pressure causes a large increase in the polymerization of the alcohol, from which the change of volume on polymerization is estimated to be -4.64 cm³/mole in the 1 to 5820 atmosphere range, and -2.47 cm³/mole in the 5820 to 11 330 atmosphere range.

TWO of the older problems of molecular spectroscopy are the shift in the infrared vibration band when a molecule is transferred from the vapor into solution and the effect of hydrogen bonding on the O—H band in solution. In our present study, the effect of pressure to 10 000 atmospheres on the O—H band of *n*-butanol in dilute solutions, we have sought results throwing light on both the foregoing problems.

Several papers¹⁻⁴ serve to define the problem. To summarize: It was observed that the O—H band in alcohols and acids consists of a very sharp peak at the fundamental frequency around 3600 cm⁻¹ and an extremely broad band centered around 3300 cm⁻¹. The relative intensities of the two bands is strongly dependent on concentration, temperature, and the nature of the solvent, as is their exact frequency. Chemical intuition has led to the assignment of the broad, low-frequency band to molecules associated by hydrogen bonding and the sharp band to the free molecules. Attempts to correlate the frequency shifts with macroscopic properties of the solvents have not been very convincing, at least from the standpoint of obtaining an exact mechanistic picture of the cause of the shift. West and Edwards⁵ correlated the frequency shift in HCl with the dielectric constant of the solvent in terms of a continuum theory (Appendix A). Gordy and Stanford⁶ showed that the frequency shift in CH₃OD was independent of the dipole moment of the solvent but correlated nicely with the "tendency of a solvent to acquire protons from a hydroxyl group" as measured by its basicity. Finally, Wulf, Liddel, and Hendricks,⁷ observed the effect of *ortho*-substituents of phenol on

the O—H frequency and noted good correlation with the polarizability of the *ortho*-group.

Our present study represents an effort to extend the scope of observations on the frequency shift in the hydroxyl group. We have compressed various alcohol solutions to 10 to 12 000 atmospheres pressure and have observed the effect of decreasing intermolecular distance on the O—H frequency at densities otherwise unobtainable and at constant temperature.

EXPERIMENTAL PROCEDURE

High-grade commercial compounds were used as solvents with no further purification other than drying over magnesium perchlorate. The alcohols were Eastman "White Label" brands, and these were used without purification.

The concentration of all solutions reported here was $\frac{3}{4}$ volume percent alcohol (with one exception). We chose this concentration for two reasons: (1) A $\frac{3}{4}$ % solution yielded a sharp, intense O—H band with a cell length of 1 to 2 mm. The window separation for all of our runs was in this range. (2) In CS₂ solution, the broad polymer band was plainly visible but not very intense at this concentration. These conditions therefore seemed suitable for making observations on the effect of pressure on the polymer band.

The following criteria governed our choice of solvents: (1) Transparency in the 3 μ region. (2) Ability to remain a liquid at 10 000 atmospheres pressure and room temperature. (3) Noncorrosiveness in contact with the steel bomb. Thus two of the best solvents as tested by conditions (1) and (3), benzene and carbon tetrachloride, were decisively ruled out by condition (2). Toluene represented a compromise, inasmuch as it froze at 8500 atmos. Our final choices were 2, 3, dimethyl butane (2, 3, DMB), CS₂, toluene, *n*-propyl bromide (*n*PrBr), and *n*-propyl iodide (*n*PrI). The objective was to vary the physical and chemical properties of the liquids as much as possible within the limits of our criteria.

The bomb was not thermostatted. The contents were assumed to be at room temperature throughout a run.

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