

TABLE I. Experimental frequency shifts.

| Pressure (atmos) | O-H abs maximum (cm ⁻¹) | Pressure (atmos) | O-H abs maximum (cm ⁻¹) |
|------------------------------|-------------------------------------|------------------------------|-------------------------------------|
| ½% n-BuOH in 2, 3 DMB | | | |
| 1 | 3648 | 1 | 3602 |
| 1050 | 3646 | 2100 | 3594 |
| 2100 | 3645 | 3700 | 3588 |
| 3200 | 3643 | 5300 | 3587 |
| 4250 | 3642 | 7000 | 3585 |
| 5300 | 3639 | 8600 | 3582 |
| 7000 | 3638 | 10 500 | 3581 |
| 8700 | 3638 | | |
| 9525 | 3637 | | |
| ½% n-BuOH in CS ₂ | | | |
| 1 | 3624 | ½% n-BuOH in nPrI | |
| 2590 | 3618 | 1 | 3594 |
| 5840 | 3609 | 2600 | 3582 |
| 8200 | 3603 | 5840 | 3563 |
| 11 330 | 3600 | 8280 | 3558 |
| | | 11 550 | 3553 |
| ½% n-BuOH in toluene | | | |
| 1 | 3606 | | |
| 2250 | 3598 | | |
| 5300 | 3592 | | |
| 7150 | 3587 | | |
| 8500 | 3584 | | |
| ½% MeOH in CS ₂ | | | |
| 1 | 3630 | ½% t-BuOH in CS ₂ | |
| 2420 | 3621 | 1 | 3607 |
| 5840 | 3615 | 2100 | 3602 |
| 8000 | 3609 | 5300 | 3597 |
| 10 900 | 3604 | 8450 | 3593 |
| 2% n-BuOH in CS ₂ | | | |
| 1 | 3616 | | |
| 2350 | 3608 | | |
| 5450 | 3603 | | |
| 8500 | 3599 | | |
| 10 200 | 3596 | | |

Bridgman's compressibility data¹¹ for the pure solvents we have plotted the frequency shifts against the relative density squared $(\rho/\rho_0)^2$ in Fig. 2. Here ρ_0 is the density at 1 atm and 25°C. The linearity of these plots strongly suggests that the interaction energy of solute and solvent follows a $1/R^6$ law, where R is the intermolecular distance. In order to corroborate this finding about the density dependence some experiments were run at atmospheric pressure and varying temperature. In the low-temperature runs we observed that the formation of polymeric alcohol rapidly decreased the intensity of the monomer band in favor of the broad polymer band. When the temperature had been lowered to 0°C, the monomer band was completely obscured in the atmospheric water background and the slight frequency shift predicted could not be accurately found. On the high-temperature side, only the higher-boiling solvents could be run and the observations obtained are included in Fig. 2 and Table II as extensions below the $(\rho/\rho_0)^2 = 1$ line.

In the first place the change in temperature varies the

¹¹ P. W. Bridgman, Proc. Am. Acad. Arts. Sci. 49, 1 (1913); 66, 185 (1930); 68, 1 (1933).

density. One would anticipate additional orientation effects of temperature, however the *n*PrBr and *n*PrI curves are seen to extend the pressure data fairly well. The toluene curve on the other hand, breaks sharply in a direction indicating decreased coupling with the alcohol molecules as the temperature is raised. It is interesting to note that an extension of the high-pressure toluene data was obtained by raising the temperature of a benzene solution. This possibly indicates a specific interaction between the toluene and the butanol. The relatively small effect with the benzene indicates that the interaction may possibly be with the methyl group in addition to that with the ring. Coulson¹² reports a slight electron deficiency on the methyl group, which could account for this special effect. Unfortunately pressure data with benzene were unobtainable due to its low freezing pressure.

The spectrophotometer traces of the CS₂ solution at three different pressures and the atmospheric water vapor are presented in Fig. 3. The high-pressure curves have been corrected for the increased amount of solution in the light path resulting from the density increase using Beer's law correction. It is possible that an additional correction should be included for the increased window separation due to the expansion of the bomb; however this would be a small effect whose exact magnitude it would be difficult to determine. The shift in the position of the absorption maximum of the sharp peak is the one which we have tabulated and will discuss subsequently, but there is a notable change in the shape, intensity, and position of the polymer peak. (This band is only clearly observable in the CS₂ solutions.) Other authors¹³ have attempted to divide this band into regions attributable to dimer, trimer, tetramer, etc. Since each higher *n*-mer would involve a lower molar volume, high pressures would favor the higher polymers; thus the shift in the peak of

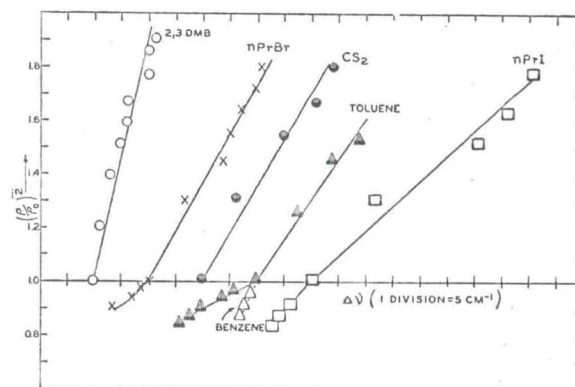


FIG. 2. Shift from atmospheric pressure frequency in monomer O-H Band ½% n-BuOH Solutions vs $(\rho/\rho_0)^2$ of solvent. (Origin shifted for each solvent.)

¹² C. A. Coulson, *Valence* (Oxford University Press, London, 1952), p. 313.

¹³ R. Mecke, *Discussions Faraday Soc.* 9, 161 (1950).