

TABLE I. Experimental frequency shifts.

Pressure (atmos)	O-H abs maximum (cm <sup>-1</sup> )	Pressure (atmos)	O-H abs maximum (cm <sup>-1</sup> )
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		
1% n-BuOH in CS <sub>2</sub>		1% n-BuOH in nPrI	
1	3624	1	3594
2590	3618	2600	3582
5840	3609	5840	3563
8200	3603	8280	3558
11 330	3600	11 550	3553
1% n-BuOH in toluene		1% t-BuOH in CS <sub>2</sub>	
1	3606	1	3607
2250	3598	2100	3602
5300	3592	5300	3597
7150	3587	8450	3593
8500	3584		
1% MeOH in CS <sub>2</sub>		2% n-BuOH in CS <sub>2</sub>	
1	3630	1	3616
2420	3621	2350	3608
5840	3615	5450	3603
8000	3609	8500	3599
10 900	3604	10 200	3596

Bridgman's compressibility data<sup>11</sup> for the pure solvents we have plotted the frequency shifts against the relative density squared  $(\rho/\rho_0)^2$  in Fig. 2. Here  $\rho_0$  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

<sup>11</sup> 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. Coulson<sup>12</sup> 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 CS<sub>2</sub> 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 CS<sub>2</sub> solutions.) Other authors<sup>13</sup> 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

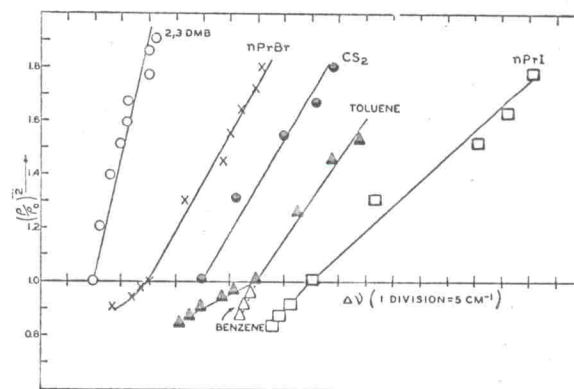


FIG. 2. Shift from atmospheric pressure frequency in monomer O-H Band 1% *n*-BuOH Solutions vs  $(\rho/\rho_0)^2$  of solvent. (Origin shifted for each solvent.)

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

<sup>13</sup> R. Mecke, *Discussions Faraday Soc.* 9, 161 (1950).