TABLE I. Experimental frequency shifts.

Pressure (atmos)	O−H abs maximum (cm^{-1})	Pressure (atmos)	O−H abs maximum (cm^{-1})
¾% *n*-BuOH in 2, 3 DMB		¾% *n*-BuOH in *n*PrBr	
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		
¾% *n*-BuOH in CS_2		¾% *n*-BuOH in *n*PrI	
1	3624	1	3594
2590	3618	2600	3582
5840	3609	5840	3563
8200	3603	8280	3558
11 330	3600	11 550	3553
¾% *n*-BuOH in toluene			
1	3606		
2250	3598		
5300	3592		
7150	3587		
8500	3584		
¾% MeOH in CS_2		¾% *t*-BuOH in CS_2	
1	3630	1	3607
2420	3621	2100	3602
5840	3615	5300	3597
8000	3609	8450	3593
10 900	3604		
2% *n*-BuOH in CS_2			
1	3616		
2350	3608		
5450	3603		
8500	3599		
10 200	3596		

Bridgman's compressibility data[11] 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 atmos 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 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[12] 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_2 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_2 solutions.) Other authors[13] 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

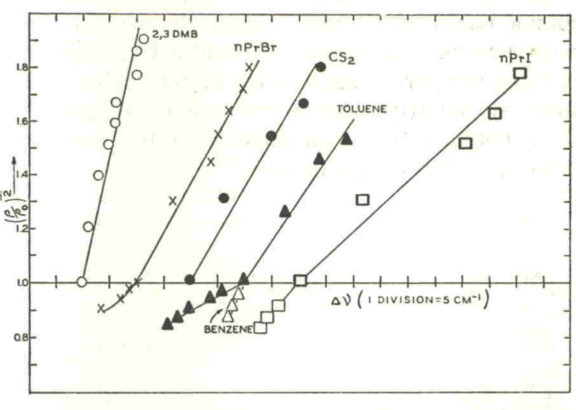

FIG. 2. Shift from atmospheric pressure frequency in monomer O−H Band ¾% *n*-BuOH Solutions *vs* $(\rho/\rho_0)^2$ of solvent. (Origin shifted for each solvent.)

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

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

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

the broad band very decidely away from the sharp band is consistent with the earlier interpretation.

The foregoing speculations have led us to attempt an estimate of the change in volume accompanying the polymerization of butanol. The equilibrium constant for the reaction

$$n\mathrm{BuOH} \rightleftharpoons (\mathrm{BuOH})_n$$

is defined as

$$K = \frac{[(\mathrm{BuOH})_n]}{[\mathrm{BuOH}]^n}$$

and, using the elementary thermodynamic relationship,

$$RT\left(\frac{\partial \ln K}{\partial p}\right)_T = -\Delta\bar{V}.$$

One can get a mean volume change, $\Delta\bar{V}$, from the value of K at two different pressures. Again assuming Beer's law to hold, in the form $\ln I/I_0 = -\epsilon CL$, where ϵ is the molar extinction coefficient, C the molar concentration, and L the cell length, we have estimated the ratio of the concentration of polymer at different pressures from the ratio of the optical densities. This assumes that ϵ and L do not change with pressure. Since the value of n in the polymerization reaction is unknown, and since the concentration of monomer does not change very much as seen from the near constancy of the intensity of the monomer band, we approximate the ratio of equilibrium constants at two different pressures by the ratio of polymer concentrations, or, in terms of observed data, the ratio of optical densities. There remains the question of the choice of wavelengths at which the comparison is made. We have chosen to compare the optical densities at the absorption maximum of the over-all polymer band at each pressure. The results are: $\langle\Delta V\rangle_{\mathrm{Av}} = -4.64$ cm^3/mole, in the range 1 to 5840 atmospheres, and $\langle\Delta V\rangle_{\mathrm{Av}} = -2.47$ cm^3/mole, in the range 5840 to 11 300 atmos. The percentage changes in volume based on the mean molar volume of n-butanol in the pressure ranges are 5.5% and 3.4%, respectively. The smaller percentage change in the higher pressure range can be attributed to the smaller compressibility of the polymer. These numbers are to be considered as order of magnitude estimates.

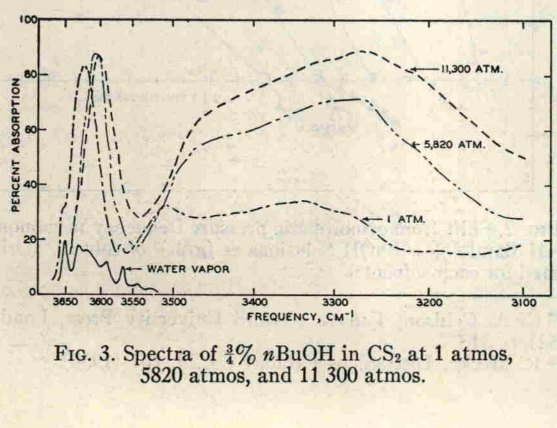

FIG. 3. Spectra of $\frac{3}{4}$% nBuOH in CS_2 at 1 atmos, 5820 atmos, and 11 300 atmos.

TABLE II. Temperature data.

Temp.	ν	Temp.	ν
$\frac{3}{4}$% in BuOH in nPrI		$\frac{3}{4}$% in BuOH in nPrBr	
25	3594	25	3602
44	3596	31	3603
64	3597	49	3605
82	3599	65	3609
94	3600		
$\frac{3}{4}$% in BuOH in toluene		$\frac{3}{4}$% in BuOH in benzene	
25	3606	25	3614
46	3600	42	3615
55	3610	61	3616
77	3614	74	3617
96	3616		
105	3618		

FREQUENCY SHIFT

The most significant feature of the frequency shifts reported is that the frequency moves toward the red as the pressure is increased. Thus, within the pressure range studied, the attractive forces tending to stretch the O−H bond have more influence on the results than do the repulsive forces.

The influence of any attractive force, F_{int}, on the frequency may be evaluated in a familiar manner by writing the energy change on stretching the O−H bond as

$$\Delta V = \frac{k}{2}(\Delta r)^2 + \frac{k'}{2}(\Delta r)^3 - F_{\mathrm{int}}\Delta r,$$

where k and k' are force constants and Δr is the change in O−H distance. Further terms could be included in this expression to increase the accuracy of the approximation. If now, $d\Delta V/d\Delta r$ is set equal to 0, a new equilibrium O−H distance is obtained, and a new harmonic force constant can be derived as the coefficient of the $(r_{\mathrm{equil}})^2$ term. As a first approximation, the new force constant and the frequency shift are linear in F_{int}.

Experimentally, the frequency shifts are found to be linear in ρ^2. The supposition that the density is proportional to R^{-3}, where R is the intermolecular distance, must be very nearly valid for liquids; thus, from our data, we observe that $\Delta\nu$ is linear in R^{-6}. A further observation is that $\Delta\nu$ depends more on the polarizability of the solvent than on its dipole moment. Since $\Delta\nu$ is linear in E_{int}, we seek a form of interaction energy which varies as the inverse sixth power of the intermolecular distance and the polarizability of interacting groups. Such force laws are indeed to be found under the heading of van der Waals' forces.[14] In particular, (1) the attraction between a dipole (the O−H bond) and an induced dipole in a neighboring molecule and (2) the attraction between two polarizable media (London

[14] J. A. A. Ketelaar, *Chemical Constitution* (Elsevier Publishing Company, Inc., New York, 1953), Chapter V.