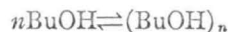


the broad band very decidedly away from the sharp band is consistent with the earlier interpretation.

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



is defined as

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

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: $\langle \Delta V \rangle_n = -4.64 \text{ cm}^3/\text{mole}$, in the range 1 to 5840 atmospheres, and $\langle \Delta V \rangle_n = -2.47 \text{ cm}^3/\text{mole}$, 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.

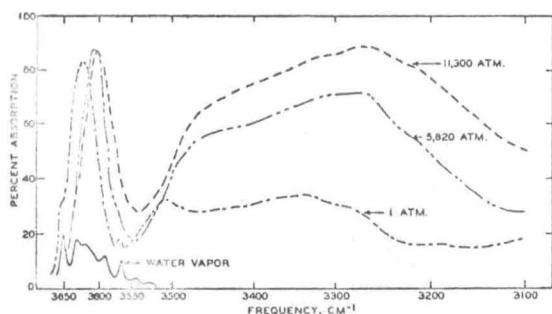


Fig. 3. Spectra of 1% *n*BuOH in CS_2 at 1 atmos, 5820 atmos, and 11 300 atmos.

TABLE II. Temperature data.

Temp. 1% in BuOH in <i>n</i> PrI	ν	Temp. 1% in BuOH in <i>n</i> PrBr	ν
25	3594	25	3602
44	3596	31	3603
64	3597	49	3605
82	3599	65	3609
94	3600		
1% in BuOH in toluene		1% 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

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

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 $(r_{\text{equil}})^2$ 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.