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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 cm^3/mole in the 1 to 5820 atmosphere range, and -2.47 cm^3/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 papers[1–4] 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 lead 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 Edwards[5] correlated the frequency shift in HCl with the dielectric constant of the solvent in terms of a continuum theory (Appendix A). Gordy and Stanford[6] showed that the frequency shift in CH_3OD 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 CS_2 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 3μ 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), CS_2, 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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* This work was supported in part by the U. S. Atomic Energy Commission.

[1] R. M. Badger and S. H. Bauer, J. Chem. Phys. 5, 605, 839 (1937).

[2] J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) A162, 419 (1937).

[3] Errera, Gaspart, and Sack, J. Chem. Phys. 8, 63 (1940).

[4] W. Gordy, J. Chem. Phys. 7, 93 (1939); 9, 215 (1941).

[5] W. West and R. T. Edwards, J. Chem. Phys. 5, 14 (1937).

[6] W. Gordy and S. C. Stanford, J. Chem. Phys. 8, 170 (1940).

[7] Wulf, Liddel, and Hendricks, J. Am. Chem. Soc. 58, 2287 (1936).

Since the band position was independent of the time after compression, this condition was at least practically fulfilled. Furthermore, the experiments were carried out in an air conditioned room, in which the day-to-day temperature variation was small.

The details of the high-pressure apparatus are described elsewhere.[8] We present a schematic drawing, Fig. 1, to show the arrangement of low- and high-pressure ends, ring seals, and windows. The windows are similar to those used previously for high-pressure scintillation counting.[9] The use of sapphire windows limits this bomb to the spectral region between 4μ and 0.2μ. The high-pressure end was calibrated against the readings on a Bourdon gauge in the low-pressure end by means of a Manganin gauge. The gauge, not in place during spectroscopic runs, was inserted through the bottom plug. The pressures reported are considered accurate to ±25 atmos.

The spectrometer used was a Perkin-Elmer Model 112. The external optics were replaced by an arrangement of two spherical mirrors allowing an image of the globar source to be focused on the sample in the bomb. Because of the $\frac{1}{4}$-inch hole at the end of the window plugs, there was still a considerable loss of radiation and it was found necessary to work at a fairly large slitwidth for this region (0.10 mm) and high gain. The resulting high noise level was partially smoothed by using a slow amplifier response and slow sweeping speed. Since we were interested in a small spectral region containing a single, intense band, no important errors were introduced by this procedure.

Most of the radiation path was swept clear of water vapor by a rapid flow of air from the laboratory supply line. The air was dried by $CaCl_2$ and a liquid nitrogen trap. However, the 20 cm of exposed path in our present set up caused considerable absorption by the intense rotation-vibration band of water vapor in this region. Since we determined frequencies from the position of the absorption maximum, some error in the absolute values and in the frequency shifts was undoubtedly caused by the water vapor. In one case we performed a point-by-point subtraction of the water vapor band from the alcohol O−H band and found one or two wave number changes in ν and in $\Delta\nu$. It was our feeling that the errors introduced by the subtraction procedure outweighed any gain in accuracy so obtained.

A LiF prism was used, calibrated by the rotational lines of the water vapor. Our estimate of the accuracy of frequency determinations, based on repeated observations, is ±2 cm^{-1} in the value of ν and ±1 cm^{-1} in $\Delta\nu$.

EXPERIMENTAL RESULTS AND DISCUSSION

The data which we obtained are all presented in Table I. The results on *t*-butanol, 2% *n*-butanol, and methanol were obtained to determine the importance of the alkyl radical of the alcohol and the concentration on the frequency shifts. Comparison of these results with the *n*BuOH in the same solvent show the existence of some effects due to the alkyl radial; however, they are not large and will be considered outside the scope of subsequent discussion.

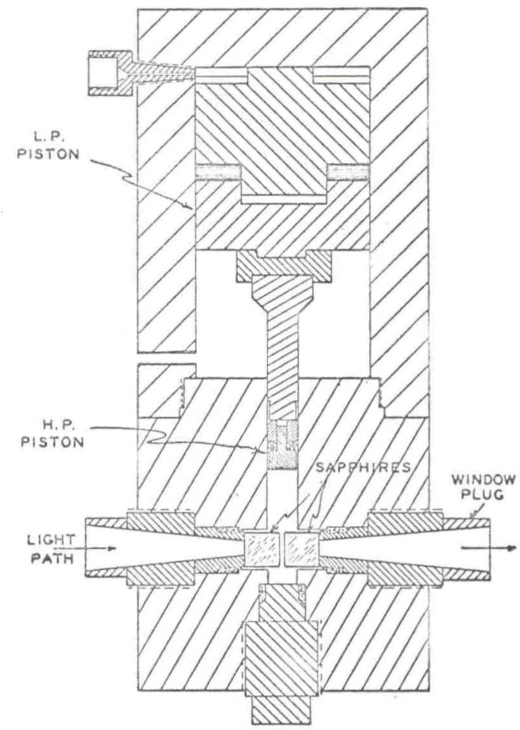

FIG. 1. Cross section of spectroscopic bomb.

There does not appear to be a record of the vapor phase spectrum of *n*BuOH in the 3-micron region. The vapor phase spectrum of ethanol was reported with a central frequency of the O−H band at 3640 cm^{-1},[10] which ought to be close to the value for butanol. We find a frequency of 3648 cm^{-1} in 2, 3, DMB solution and this represents our best estimate of the O−H frequency in the unperturbed alcohol molecule. From the data in Table I, it is apparent that the greater the displacement of the O−H band from 3648 cm^{-1} at one atmos in a particular solvent, the greater is the pressure-induced shift. For subsequent discussion we define $\Delta\nu$ as the shift in frequency from its value at 1 atmosphere and 25°C for each solvent; therefore the values of $\Delta\nu$ only indirectly reflect the difference in frequency in going from solvent to solvent, as indicated.

Since pressures of the order of 50 000 atmos are probably required to bring about significant compression of ordinary chemical bonds, it is clear that the frequency shifts reported are brought about by intermolecular effects, not by deformation of the molecules. Using

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[8] E. Fishman and H. G. Drickamer, Ind. and Eng. Chem. (to be published).

[9] R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

[10] J. Errera and P. Mollet, Compt. rend. 204, 259 (1937).

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

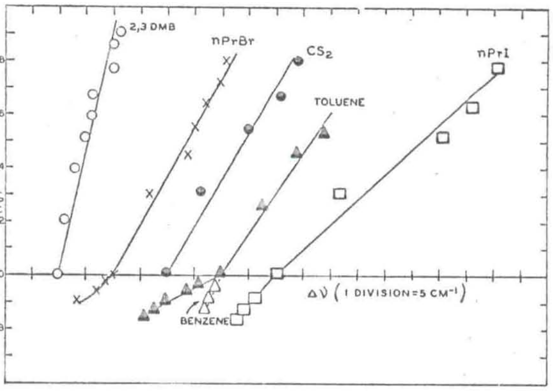

FIG. 2. Shift from atmospheric pressure frequency in monomer O−H Band ¾% *n*-BuOH Solutions *vs* $(\rho/\rho_0)^2$ of solvent. (Origin shifted for each solvent.)

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[11] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 49, 1 (1913); 66, 185 (1931); 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.

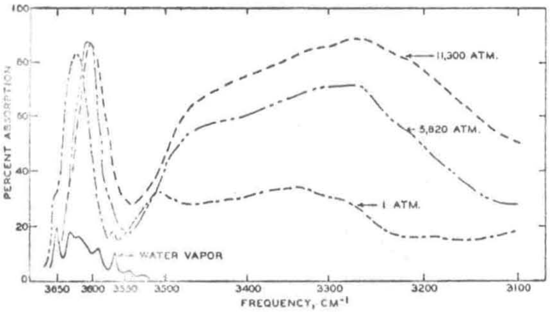

FIG. 3. Spectra of $\frac{3}{4}$% nBuOH in CS$_2$ at 1 atmos, 5820 atmos, and 11 300 atmos.

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

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

TABLE III. Value of constant in dispersion formula for frequency shifts.

Solvent	$\alpha_2 \times 10^{25}$ cm^3 [a]	K
2, 3 DMB	23.7[b]	0.459
nPrBr	50.4[c]	0.551
CS_2	75.7	0.395
CS_2	55.4[d]	0.539
Toluene	20.5[e]	1.65
Toluene	63.5[f]	0.534
nPrI	75.5[g]	0.714

[a] Taken from Landolt-Bornstein Tables, sixth edition, 1950, Volume I, part 3, pp. 509–511.
[b] Sum of three C−H bonds in methyl group.
[c] C−Br bond.
[d] Two C=S bonds, perpendicular.
[e] Aromatic C−H bond.
[f] Two aromatic C−H bonds plus a C−C aromatic bond.
[g] Estimated from values for C−Cl and C−Br.

dispersion forces) are appropriate, though we have no means of distinguishing between them. The average dipole-dipole interaction energy is also linear in R^{-6} and it is temperature dependent, thus the discrepancy between the temperature and pressure data in toluene may be due to the importance of this form of E_{int} for the particular case of n-butanol-toluene interaction.

If the contribution to E_{int} of 2nd, 3rd, 4th, etc., nearest neighbors is summed to get the total interaction energy, then the result is an over-all R^{-3} dependence; however, for a force which falls off as rapidly as the van der Waals' force, it seems reasonable to include only nearest neighbors in the total interactions.

We have fitted the straight lines of Fig. 2 to the equation

$$\Delta\nu = K\alpha^2(\rho/\rho_0)^2,$$

where K is essentially constant and α_2 is the polarizability of the most polarizable solvent bond, parallel to the bond. K contains the polarizability of the O−H bond and a combination of terms involving the excitation energies of the electrons, which however should not change much from solvent to solvent. Thus the constancy of K from solvent to solvent is a partial measure of the correctness of our approach at this very simple level. Table III gives the results.

The correlation with the values of α_2 seems fairly consistent, though it must be stated that there is considerable arbitrariness in the choice of α_2, as explained in the reference to Table III. However, there are hidden factors in K involving the packing of the molecules and their orientation, for which the present theory of liquids cannot provide an answer. For example one might multiply the polarizability by a factor depending on the number of nearest neighbors to the O−H bond, or a certain weighted average of parallel and perpendicular polarizabilities might be involved depending on average orientations. Thus our data are more consistent if one assumes that the O−H bond in CS_2 solution "sees" two C=S bonds from a position perpendicular to the bonds, rather than the S atom head on. This implies a structure of CS_2 involving long chains of S=C=S S=C=S S=C=S molecules, with alcohol molecules fitting between the chains. The high molar density of CS_2 also indicates such an efficient packing.

In conclusion, the polarizabilities of solvent groups predict, qualitatively, the grouping of solvents into those causing small or large frequency shifts. A quantitative theory must await more knowledge of the structure of liquids. Conversely, it may be hoped that experimental results of this nature can help to solve these theoretical problems.

ACKNOWLEDGMENTS

The authors wish to thank Professor Donald F. Hornig of Brown University for a most informative discussion of the frequency shifts.

APPENDIX A

A formula first derived in the literature by Bauer and Magat,[15]

$$\frac{\Delta\nu'}{\nu_0} = -\frac{D-1}{2D+1}\cdot\frac{1}{a^3}E,$$

has been tested by several authors[16–18] observing frequency shifts in going from the gas to liquid solution phase. Here ν_0 is the gas phase frequency, D the dielectric constant (static value?), a the radius of the spherical cavity in the dielectric medium containing the radiating dipole, and E is a group of terms involving the solute which should be constant from solution to solution. ($\Delta\nu'$ is the shift from the gas phase frequency.) The physical model is that of a point dipole radiating in a spherical cavity surrounded by a continuous dielectric medium. Since the Clausius-Mosotti expression giving the density dependence of the molar polarization is true to the same physical approximation, one can test our pressure-induced shifts against the Bauer-Magat expression by substitution of the Clausius-Mosotti value for D from

$$P = \frac{m}{\rho}\frac{D-1}{D+2}.$$

(Here P is the defined molar polarization, ρ the density and, M the molecular weight.) When this is done, with the additional assumption that $a^3 =$ (constant) $\times M/\rho$ the result for the density dependence of the shift is

$$\frac{\Delta\nu'}{\nu_0} = (\text{constant})\frac{(\rho/M)^2}{(\rho/M)+(1/P)}.$$

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[15] E. Bauer and M. Magat, J. phys. radium 9, 319 (1938).
[16] L. H. Jones and R. M. Badger, J. Am. Chem. Soc. 73, 3132 (1932).
[17] M. L. Josien and N. Fuson, J. Chem. Phys. 22, 1169 (1954).
[18] P. Tuomikoski, Suomen Kemistilehti 23, 44 (1950).

According to this, the shift should be nearly linear in ρ^2 for a low value of P, but for high P the shift should be more nearly linear in ρ. This does not agree with our observations since all substances maintain the ρ^2 dependence within experimental error as shown in Fig. 2. Two of the main difficulties seem to be that the approximation of point dipoles for dipole-dipole interaction breaks down drastically at the intermolecular distances involved here[19] and the inclusion of the permanent dipole contribution to P ought to depend on the ability of the solvent dipoles to keep up with the librating and/or rotating alcohol molecules.

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[19] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 850.