

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

Solvent	$\alpha_2 \times 10^{25} \text{ cm}^3 \text{ a}$	K
2, 3 DMB	23.7 ^b	0.459
<i>n</i> PrBr	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
<i>n</i> PrI	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 CS₂ 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 CS₂ 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 CS₂ 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.

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APPENDIX A

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

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

has been tested by several authors¹⁶⁻¹⁸ 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

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

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

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

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 here¹⁰ 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.

¹⁰ Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 850.

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APPENDIX A

A formula first derived in the literature by Mason and Nagai¹¹

$$\Delta\nu = \frac{2\pi^2 N_A \rho^2 \mu^2}{3kT} \left(\frac{1}{D} - \frac{1}{D^2} \right)$$

has been tested by several authors^{12,13} observing frequency shifts in gases from the gas to liquid solution phase. Here ρ is the gas density, μ the dipole moment, N_A Avogadro's number, k the Boltzmann constant, and D the dielectric constant of the gas. The shift from the gas phase to liquid is $\Delta\nu$ in the shift from the gas phase to liquid. The physical model is that of a point dipole in a dielectric medium, since the Lorentz-Lorentz expression relating the density dependence of the refractive index to the static physical approximation can be used in our present context. The shift is given by the following expression in substitution of the Lorentz-Lorentz value for D from

$$D = \frac{4\pi N_A \mu^2}{3kT} \left(\frac{1}{D} - \frac{1}{D^2} \right) + 1$$

(Here ρ is the defined molar polarization, ρ the density, and M the molecular weight.) When this is done with the additional assumption that $\rho = \rho_0$ (constant), $\Delta\nu$ is the result for the density dependence of the shift.

¹¹ M. Mason and Y. Nagai, *J. Chem. Phys.*, **23**, 1197 (1955).
¹² J. T. Lewis and J. T. Lewis, *J. Chem. Phys.*, **23**, 1197 (1955).
¹³ J. T. Lewis and J. T. Lewis, *J. Chem. Phys.*, **23**, 1197 (1955).

where K is essentially constant and as is the polarity 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 electron energy of the electron, which however should not change much from solvent to solvent. This is a partial consistency of A from solvent to solvent is a partial measure of the correctness of our approach at the very simple level. Table III gives the results.

The correlation with the values of ρ seems fairly consistent, though it must be stated that there is considerable arbitrariness in the choice of ρ , 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 CS₂ solution "sees" two C-S bonds from a position perpendicular to the bonds, rather than the 2 way

$$\Delta\nu = A \rho^2 / D^2$$

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