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[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

### Solvent Effects in Infrared Spectroscopic Studies of Hydrogen Bonding<sup>1,2</sup>

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The effect of solvents on the stretching vibrations of hydrogen bonded systems has been studied. Contrary to previously held ideas, the frequencies of hydrogen bonded bands,  $\nu_{\text{OH}\dots\text{O}}$ , were found to be very solvent sensitive for many intramolecular or intermolecular hydrogen bonds. The solvent shifts of  $\text{OH}\dots\text{O}$  bands are proportional to  $\text{C}=\text{O}$  and other  $\text{X}=\text{O}$  solvent shifts, indicating a possible similarity of mode of interaction of solvents with these chromophoric groups. Existing theories of solvent shifts do not explain this behavior. An empirical linear free energy equation,  $(\nu^0 - \nu^s)/\nu^0 = aG$ , is proposed for the accurate prediction of the positions of a large number of solvent sensitive infrared bands. The limitations of this equation are discussed. For intermolecular hydrogen bonds involving the interaction of a proton donor ROH with a proton acceptor B in an "inert" solvent,  $\nu_{\text{OH}\dots\text{B}}$  is found to depend on the concentration of B, while  $\nu_{\text{OH}}$  (the "free" band) is practically independent. As a consequence  $\Delta\nu$ , the difference between the two bands, is concentration dependent, a result contrary to existing theories. Dielectric constants and refractive indexes were determined for several B + S solvent systems to test various "dielectric equations"; these do not explain the observed results. An empirical method is proposed for the prediction of the occurrence of such concentration dependence.

Infrared spectroscopy is a powerful method for the study of hydrogen bonding.<sup>5</sup> One of the most characteristic effects observed is the frequency shift due to hydrogen bonding,  $\Delta\nu$  (in  $\text{cm}^{-1}$ ), defined as the difference in position between a "free" stretching vibrational band, A-H, in a given environment and its bonded counterpart, A-H...B, displaced to lower frequencies in the same environment.<sup>6</sup> Most infrared spectroscopic studies of hydrogen bonding are conducted in the so-called "inert" solvents,  $\text{CCl}_4$ ,  $\text{CS}_2$ , etc., since vapor phase measurements pose experimental difficulties. Frequently comparisons of  $\Delta\nu$ , which is related to the strength of the hydrogen bond,<sup>5</sup> have to be made for several systems in which the solvent employed was not the same, either because of the unavailability of data or because of solubility problems. Despite the well known solvent sensitivity of many infrared absorption bands, such as carbonyl and sulfonyl<sup>7,8</sup> which vary as much as  $30 \text{ cm}^{-1}$  from solvent to solvent, the systematic study of the effect of liquid environment on "free" and hydrogen bonded stretching frequencies has been generally neglected.<sup>9,10</sup> We report here the results of such a study.

An early theoretical attempt to calculate infrared solvent shifts is the Kirkwood-Bauer-Magat equation.<sup>11,12</sup> Such attempts to correlate the effects of solvents on infrared spectra with bulk properties of the solvent—dielectric constant and refractive index—are sometimes referred to as dielectric theory.<sup>13</sup> On the other hand there have been attempts in recent years to explain spectral shifts qualitatively on the basis of specific solvent-solute interactions, dielectric effects being considered unimportant.<sup>10,15,16</sup> Also, a combination of non-specific (dielectric) and specific effects has been considered.<sup>16,17</sup> A more rigorous but mathematically involved approach has been proposed by Drickamer, Wiederkehr and Benson in which no use is made of the vague notions of "specific" and "non-specific" solvent interactions, rather a bond interaction model is used and consideration is given to both attractive and repulsive intermolecular interactions.<sup>14,18,19</sup>

An illustration will show differences in the predictions of some of these approaches. Consider a molecule A-H, capable of acting as proton donor toward

(1) Preliminary report: A. Allerhand and P. von R. Schleyer, Abstracts, Fourth Delaware Valley Regional Meeting, Am. Chem. Soc., Philadelphia, Pa., January, 1962, p. 99. This work was taken from the Ph.D. Thesis of A. A., Princeton University, 1962.

(2) Paper VII of a series on hydrogen bonding; IV, P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961); V, P. von R. Schleyer and A. Allerhand, *ibid.*, **84**, 1322 (1962); VI, R. West, D. L. Powell, L. S. Wheatley, M. K. T. Lee and P. von R. Schleyer, *ibid.*, **84**, 3221 (1962).

(3) Merck Foundation Fellow, 1960-1961; Esso Foundation Fellow, 1961-1962.

(4) Alfred P. Sloan Research Fellow.

(5) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Cal., 1960, Ch. 3, pp. 67-141.

(6) This is the definition to be used in this paper. The symbol " $\Delta\nu$ " is frequently used to designate the shift of an infrared frequency when passing from the gaseous state to a solvent, but we shall use  $\nu^0 - \nu^s$  for this latter purpose, to avoid confusion.

(7) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

(8) L. J. Bellamy, C. P. Conduit, R. J. Pace and R. L. Williams, *ibid.*, **55**, 1677 (1959).

(9) For studies of H-bonded systems in various solvents, see M.-L. Josien and N. Fuson, *J. Chem. Phys.*, **22**, 1169 (1954) and ref. 10.

(10) L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, **55**, 220 (1959).

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

(12) E. Bauer and M. Magat, *J. Phys. Radium*, **9**, 319 (1938).

(13) It is assumed, in this approach, that the solute molecule behaves like a polarizable point dipole at the center of a spherical cavity. The effect of the surrounding solvent molecules is taken as that of a continuous dielectric medium surrounding the cavity. An interesting discussion is given in ref. 14, pp. 30-34.

(14) R. R. Wiederkehr, Ph.D. Thesis, University of Illinois, 1957; *Disser. Abstr.*, **17**, 2542 (1957).

(15) L. J. Bellamy, H. E. Hallam and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958).

(16) L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc. (London)*, **A255**, 22 (1960).

(17) G. L. Caldow and H. W. Thompson, *ibid.*, **A254**, 1 (1960).

(18) R. R. Wiederkehr and H. G. Drickamer, *J. Chem. Phys.*, **28**, 311 (1958).

(19) A. M. Benson and H. G. Drickamer, *ibid.*, **27**, 1164 (1957).

proton acceptor B to give a hydrogen bonded complex A-H...B.  $\nu_{\text{AH}}^0$  is the gaseous A-H stretching frequency of the unassociated molecule, while  $\nu_{\text{AH}\cdots\text{B}}^0$  is the frequency for the associated gaseous complex. The symbols  $\nu_{\text{AH}}^{\text{S}}$  and  $\nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  are the corresponding frequencies in an "inert" solvent, S. Then in the gas phase  $\Delta\nu^0 = \nu_{\text{AH}}^0 - \nu_{\text{AH}\cdots\text{B}}^0$  (shift produced by H-bonding in the absence of environmental interactions) and in the solvent, S,  $\Delta\nu^{\text{S}} = \nu_{\text{AH}}^{\text{S}} - \nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  (shift produced by H-bonding in the presence of environmental interactions with S).

It has been suggested on the basis of the dielectric theory<sup>20</sup> that nonspecific effects should be the same for unassociated and associated species, so that  $\Delta\nu^{\text{S}}$  should be identical with  $\Delta\nu^0$  and be independent of solvent. Experimentally we will show that this is not generally so.

Adopting another point of view,<sup>10</sup> that all solvent shifts are mainly due to specific interactions,  $\nu_{\text{AH}}^{\text{S}}$  should differ from  $\nu_{\text{AH}}^0$  because of weak hydrogen bonding between A-H and the solvent S; consequently  $\nu_{\text{AH}}^{\text{S}}$  should vary with the "proton accepting power" of the solvent. Accordingly,<sup>10</sup>  $\nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  should be essentially independent of solvent, since A-H is already engaged in a hydrogen bond with B and  $\nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  would be expected to be close to  $\nu_{\text{AH}\cdots\text{B}}^0$ . Since  $\nu_{\text{AH}}^{\text{S}}$  would be solvent dependent and  $\nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  not, according to this viewpoint,<sup>10</sup>  $\Delta\nu^{\text{S}}$  would depend on the solvent in which the measurement was carried out. Although we will show that  $\Delta\nu^{\text{S}}$  does indeed depend upon the solvent, it will be demonstrated that this is due to variations in both  $\nu_{\text{AH}\cdots\text{B}}^{\text{S}}$  and  $\nu_{\text{AH}}^{\text{S}}$ .

In studying intermolecular hydrogen bonding it is possible to change the nature of the environment not only by changing the solvent but also by changing the concentration of proton acceptor, B. Again, if it is assumed that dielectric effects are the same for the free and associated absorption frequencies,<sup>20</sup> then  $\nu_{\text{AH}}$  and  $\nu_{\text{AH}\cdots\text{B}}$  but not  $\Delta\nu$  should vary with the concentration of B. On the other hand, if we assume the presence of specific interactions only,<sup>10</sup> neither  $\nu_{\text{AH}}$  nor  $\nu_{\text{AH}\cdots\text{B}}$  should vary with the concentration of B. Both assumptions will be shown to be incorrect. A few examples of the variation of  $\nu_{\text{AH}\cdots\text{B}}$  with concentration of proton acceptor B already have been reported.<sup>18, 21-23</sup> We will show that while  $\nu_{\text{AH}}$  is insensitive to the concentration of B,  $\nu_{\text{AH}\cdots\text{B}}$  and consequently  $\Delta\nu$  can change in complex ways, either increasing, decreasing or remaining constant. Rationalization for this behavior will be presented.

### Experimental

Infrared spectroscopic measurements were carried out on a Perkin-Elmer Model 21 infrared spectrophotometer equipped with a lithium fluoride prism and a Reeder thermocouple detector. The following types of matched cells were used: 0.1, 0.2, 1 and 2-mm. sodium chloride cells; 1, 5, 10 and 20-mm. quartz cells, of a type transparent in the near infrared. Solvent absorption was excessive when cells thicker than 2 mm. were used with solvents containing C-H groups; hence, most of the measurements were carried out in 1-mm. cells. We believe our results to be accurate to within  $\pm 2$  cm.<sup>-1</sup> for the unassociated OH frequencies and to within  $\pm 4$  cm.<sup>-1</sup> for the broader absorption bands of the hydrogen bonded OH groups. All measurements were carried out at an average room temperature of 23°. The small variations of room temperature had no observable effect on the positions of the absorption frequencies.<sup>24</sup> All measurements were made at least twice and some were repeated later

(20) Referee's comments.

(21) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955).

(22) E. V. Shuvalova, *Optics and Spectroscopy*, **6**, 452 (1959).

(23) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962). This paper, which contains some observations similar to ours, appeared during final revisions of our manuscript.

(24) Small variations of temperature may have a considerable effect on hydrogen bonded equilibria but the effect on infrared frequencies is very small. See, e.g., E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

TABLE I

SOLVENT EFFECTS ON INTERMOLECULAR HYDROGEN BONDING<sup>a</sup>

Solvent	CH <sub>2</sub>   CH <sub>2</sub> O-CH-CH <sub>2</sub> CH <sub>2</sub> OH			CH <sub>2</sub> -CHOH-CH <sub>2</sub> -   CHOH-CH <sub>2</sub>		
	$\nu_{\text{OH}}$ free	$\nu_{\text{OH}}$ bonded	$\Delta\nu$	$\nu_{\text{OH}}$ free	$\nu_{\text{OH}}$ bonded	$\Delta\nu$
Hexane	3645	3554	91	3631	3556	75
Cyclohexane	3644	3552	92	3626	3554	72
Tetrachloroethylene	3639	3541	98	3623	3542	81
Carbon tetrachloride	3640	3536	104	3625	3537	88
Carbon disulfide	3624	3533	92	3611	3536	75
Toluene	3600	3528	72	..	..	..
Benzene	3604	3523	81	3590	3519	71
1,2-Dichloroethane	3608	3508	100	..	..	..
Dichloromethane	3619	3504	115	3607	3510	97
Chloroform	3624	3496	128	..	..	..
Bromoform	3609	3489	120	..	..	..

<sup>a</sup> All values are in cm.<sup>-1</sup>.

TABLE II

SOLVENT EFFECTS ON INTERMOLECULAR HYDROGEN BONDING<sup>a</sup>

Solvent	—Methanol-ether—			—Phenol-ether—		
	$\nu_{\text{OH}}$ free	$\nu_{\text{OH}}$ bonded	$\Delta\nu$	$\nu_{\text{OH}}$ free	$\nu_{\text{OH}}$ bonded	$\Delta\nu$
Gaseous phase	3682 <sup>b</sup>	3558 <sup>b</sup>	124	3654 <sup>c</sup>	..	..
Perfluoroöctane	3675	3530	145	3644	3374	270
Hexane	3654	3521	133	3621	3363	258
Cyclohexane	3649	3516	133	3617	3357	260
Tetrachloroethylene	3643	3502	141	3611	3343	268
Carbon tetrachloride	3643	3503	140	3611	3338	273
Carbon disulfide	3628	3496	132	3591	3330	261
Benzene	3612	3490	121	3557	3315	242
1,2-Dichloroethane	3618	3475	143	3564	3295	269
Dichloromethane	3627	3469	158	3584	3291	293
Chloroform	3634	3451	183	3599	3285	314
Bromoform	3616	3449	167	3579	3283	296
Diethyl ether	..	3506	..	..	3340	..

<sup>a</sup> All values are in cm.<sup>-1</sup>. <sup>b</sup> Ref. 26. <sup>c</sup> Ref. 27.

TABLE III

SOLVENT EFFECTS ON ALCOHOL DIMER HYDROGEN BONDING<sup>a</sup>

Solvent	—Methanol—		—Diphenylcarbinol—		
	$\nu_{\text{OH}}$ dimer <sup>b</sup>	$\Delta\nu$	$\nu_{\text{OH}}$ free	$\nu_{\text{OH}}$ bonded	$\Delta\nu$
Gaseous phase	3592 <sup>c</sup>	90	..	..	..
Perfluoroöctane	3565	110	Insoluble	..	..
Hexane	3551	103	3625	3494 <sup>d</sup>	131
Cyclohexane	3547	102	3623	3487	136
Tetrachloroethylene	3528	115	3616	3487	129
Carbon tetrachloride	3522	121	3616	3484 <sup>d</sup>	132
Carbon disulfide	3518	110	3605	3484	121
Toluene	..	..	3573	3471	102
Benzene	3505	107	3576	3470	106
1,2-Dichloroethane	..	..	..	..	..
Dichloromethane	3494	133	3594	3456	138
Chloroform	3482	152	3604	3464	140
Bromoform	..	..	3588	3446	142

<sup>a</sup> All values are in cm.<sup>-1</sup>. <sup>b</sup> Monomer band positions are given in Table II. <sup>c</sup> Ref. 28. <sup>d</sup> These values differ considerably from those reported in ref. 7. See text.

with freshly prepared samples. Excellent reproducibility was observed.

The measurements of static dielectric constants were carried out on a heterodyne beat apparatus<sup>25</sup> using a wave length of 575 m $\mu$ . The refractive indexes were measured on a Bausch and Lomb precision refractometer.

(25) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 209.

(26) R. G. Inskeep, F. E. Dickson and J. M. Kelliher, *J. Mol. Spectry.*, **4**, 477 (1960).

(27) L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc. (London)*, **A264**, 119 (1960).

(28) R. G. Inskeep, J. M. Kelliher, P. E. McMahon and B. G. Somers, *J. Chem. Phys.*, **28**, 1033 (1958).

TABLE IV  
THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL AND METHANOL IN SOLUTIONS OF DIETHYL ETHER IN CHLOROFORM<sup>a</sup>

Mole % dioxane	$\epsilon$	$\frac{\epsilon - 1}{2\epsilon + 1}$	Phenol-ether system			Methanol-dioxane system		
			$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$	$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$
0.0	4.78	0.358	3599	..	..	3634	..	..
2.3	4.92	.362	3599	3283	316	3634	3454	180
3.3	4.97	.363	3599	3285	314	3634	3451	183
7.4	5.17	.368	3598	3282	316	3634	3450	184
21.0	5.65	.378	3598	3292	306	3634	3453	181
35.4	5.93	.384	..	3308	(291)	3635	3461	174
79.3	5.14	.367	..	3333	(266)	..	3498	(136)
100.0	4.30	.344	..	3340	(259)	..	3506	(128)

<sup>a</sup> Dielectric constants at 20° obtained by interpolation from I. E. Coop, *Trans. Faraday Soc.*, **33**, 583 (1937). The dielectric constant of the ether-chloroform system has a maximum at about 45 mole % ether. For the chloroform-ether system, there is a linear variation of  $n_D^{20}$  with mole fraction, from 2.090 for pure chloroform to 1.822 for pure ether.

Commercially available compounds were purified by distillation or recrystallization and the melting points and boiling points were compared with literature values. Several compounds were prepared by known methods. "Spectroquality" and "Spectro Grade" solvents were used without further purification, except chloroform, which was shaken several times with concentrated sulfuric acid to remove ethanol preservative, then shaken with water and dried, first with anhydrous Na<sub>2</sub>SO<sub>4</sub> and then by distilling from P<sub>2</sub>O<sub>5</sub>. Chloroform so purified was used promptly to avoid decomposition.

The concentrations of R-OH were too small to produce any observable changes in the refractive indexes and dielectric constants of the solutions.

### Results

#### Variation of Infrared Frequencies with Solvent.—

Tables I-III summarize results on hydrogen bonded OH stretching frequencies in many solvents. The choice of solvents was limited to proton acceptors much weaker than the base B in the hydrogen bond being examined, ROH...B. Diethyl ether was used as solvent only in those systems in which the proton acceptor was diethyl ether itself. To avoid proton donor self association the lowest possible concentration of proton donor was used, except in alcohol dimer studies.

Table I lists data for cases of intramolecular hydrogen bonding of the OH...OCH<sub>3</sub> and OH...OH types. Table II gives examples of intermolecular association to diethyl ether as base. In alcohol dimer studies (Table III) interference from "polymer" bands at lower frequencies was serious in hexane, cyclohexane, CCl<sub>4</sub>, C<sub>2</sub>Cl<sub>4</sub> and CS<sub>2</sub> even for the sterically hindered alcohol, diphenylcarbinol. The position of the dimer band was difficult to determine with precision for this reason. Several concentrations and path lengths, within the limitations imposed by solvent absorptions, had to be used. At certain concentrations of alcohol the composite dimer-polymer band may happen to be nearly symmetrical and can be mistaken for the dimer band. For example, 0.44 M diphenylcarbinol in CCl<sub>4</sub> (0.2 mm. cells) shows a very broad band with an apparent maximum at 3410 cm.<sup>-1</sup>. On diluting this solution two broad bands become apparent; finally at 0.05 M concentration (10 mm. cells) there is no polymer band. The dimer band at 3484 cm.<sup>-1</sup> gradually disappears on further dilution. The previously reported "dimer" band of diphenylcarbinol at 3410 ± 20 cm.<sup>-1</sup> in CCl<sub>4</sub> and in hexane<sup>10</sup> corresponds to the fictitious maximum mentioned above. Systems of the type ROH...B presented no such difficulties, if the concentration of ROH was kept low.

Tables I-III furnish ample proof that *stretching frequencies of OH groups already engaged in hydrogen bonding are solvent sensitive*. See Fig. 1 for a typical illustration. The OH...B stretching frequency of the methanol-ether complex is lowered by more than 50 cm.<sup>-1</sup> in going from the gaseous state to CCl<sub>4</sub> solution and by more than 100 cm.<sup>-1</sup> when the solvent is chloroform. The "free"  $\nu_{OH}$  also shifts, as expected, but the magnitude of the shift is different for the

"free" and "bonded" frequencies; as a consequence  $\Delta\nu$  varies with environment. The solvents employed can be divided into four groups. (1) Chloroform, bromoform and dichloromethane gave the largest  $\Delta\nu$ 's, in some cases as much as 50% larger than the gaseous state and 25% larger than CCl<sub>4</sub>. (2) Tetrachloroethylene, carbon tetrachloride, perfluorooctane and 1,2-dichloroethane gave  $\Delta\nu$ 's smaller than those of group 1 but larger than the gas phase values. For a given hydrogen bonded system the  $\Delta\nu$ 's are about the same for all these solvents of group 2 and we believe they may be used interchangeably for such measurements. (3) Carbon disulfide, hexane, cyclohexane

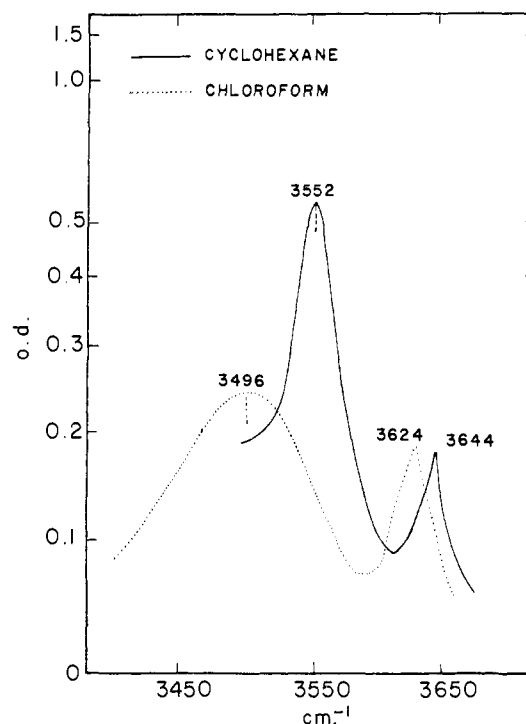


Fig. 1.—Solvent effect on the OH stretching frequencies of CH<sub>3</sub>-CH(OCH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>OH. Conc.: 7  $\mu$ l./ml.; 1-mm. cells.

and probably other saturated hydrocarbons gave  $\Delta\nu$ 's lower than solvents in the first two groups and only slightly higher than the gaseous state values. (4) Benzene, toluene and presumably other aromatic hydrocarbons gave the lowest  $\Delta\nu$ 's of all. Hydrogen bonding involving aromatic rings as proton acceptors is well established.<sup>29</sup> This produces a lowering of the "free" (actually H-bonded to the aromatic ring) OH stretching frequency and, consequently, low  $\Delta\nu$ 's.

**Effects of Variation of Proton Donor Concentration.**—Tables IV-IX show the effect of proton donor concentration on infrared spectra of hydrogen bonded systems.

(29) Ref. 5, p. 202, and references cited therein.

TABLE V

THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL AND METHANOL IN SOLUTIONS OF DIETHYL ETHER IN CARBON TETRACHLORIDE

Mole % ether	$\epsilon$	$\epsilon - 1$	$n^2 - 1$	Phenol-ether system			Methanol-ether system		
				$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$	$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$
0.0	2.234 <sup>a</sup>	0.226	1.463 <sup>b</sup>	3611	..	..	3643	..	..
0.4	2.246	.227	1.458	3610	3339	271	3642	3503	139
1.5	2.265	.229	1.457	3611	3337	274	3644	3498	146
4.6	2.329	.235	1.454	3611	3337	274	3643	3497	146
20.0	2.635	.261	1.437	3610	3337	273	3643	3498	145
40.6	3.061	.289	1.415	..	3337	(273)	3642	3500	142
63.7	3.528	.314	..	..	3338	(272)	..	3504	(138)
100.0	4.29 <sup>a</sup>	.343	1.350 <sup>c</sup>	..	3340	(270)	..	3506	(136)

<sup>a</sup> Obtained by extrapolation from ref. 37. <sup>b</sup> Refractive index at 15° (ref. 38). <sup>c</sup> Refractive index at 24.8° (ref. 38).

At high concentrations of proton acceptor the "free" bands gradually disappear so that the values for  $\Delta\nu$  have to be estimated. This is justifiable since the concentration dependence of the "free" bands is negligible up to the highest concentrations of proton donor at which they can be observed. The bonded peaks,  $\nu_{OH..B}$ , behave in peculiar ways; in some cases there is concentration dependence, in others none. Both the proton acceptor and the solvent are involved in this phenomenon.  $\nu_{OH..ether}$  varied with concentration of ether if chloroform was the solvent (Table IV) but did not change appreciably if the solvent was CCl<sub>4</sub> (Table V) and yet  $\nu_{OH..dioxane}$  varied with the concentration of dioxane in the latter solvent, CCl<sub>4</sub> (Table IV). An empirical method for predicting such concentration dependencies will be presented below.

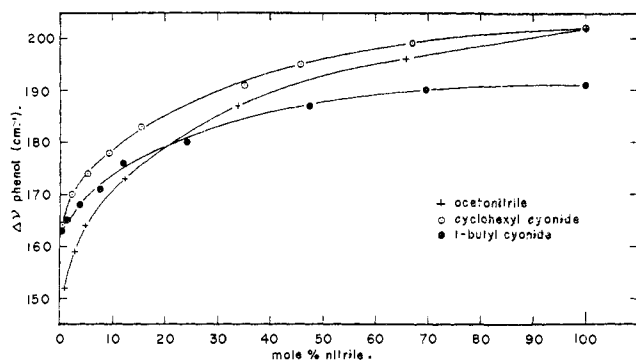


Fig. 2.—Effect of nitrile concentration on  $\Delta\nu$  of phenol in CCl<sub>4</sub> solution.

Because of the essential constancy of the positions of the "free" peaks and the frequent variation of the "bonded" peaks, the magnitudes of  $\Delta\nu$  will often depend upon the concentrations of proton acceptor chosen, even if the same solvent is used. Values of  $\Delta\nu$  from intermolecular hydrogen bonding studies are often of great interest for correlation with structure of proton donor or acceptor,<sup>30</sup> with "basicity"<sup>31</sup> or with the enthalpy of hydrogen bonding.<sup>32</sup> For these purposes  $\Delta\nu$ 's frequently have been measured in the literature<sup>33</sup> by the undesirable technique of using the proton acceptor as solvent. We should like to emphasize that  $\Delta\nu$  measurements should be made in an inert solvent with as low a concentration of proton acceptor as possible; extrapolation to infinite dilution is the preferable procedure.<sup>23</sup>

Figure 2 and Tables VIII and IX provide a graphic illustration of these difficulties. Nitriles, as proton acceptors in CCl<sub>4</sub> solution, show large concentration dependencies of  $\nu_{OH..N}$  and of  $\Delta\nu$ .<sup>34</sup> Binary solutions

(30) P. von R. Schleyer and A. Allerhand, *J. Am. Chem. Soc.*, **84**, 1322, (1962), and unpublished results.

(31) Cf. a review, J. Gordon, *J. Org. Chem.*, **26**, 738 (1961); also ref. 5.

(32) See ref. 5 and 23 and paper VI, ref. 2.

(33) For literature citations, see ref. 23.

(34) Despite such evidence to the contrary,<sup>31,32,33</sup> there is still a residual

TABLE VI

THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL IN SOLUTIONS OF DIOXANE IN CARBON TETRACHLORIDE<sup>a</sup>

Mole % dioxane	$\nu_{OH}$ "free"	$\nu_{OH}$ phenol-dioxane	$\Delta\nu$
0.0	3611	..	..
1.1	3612	3378	234
2.3	3612	3377	235
6.7	3611	3373	238
11.2	3610	3370	240
22.1	3610	3365	245
43.1	..	3357	(253)
72.5	..	3347	(263)
100.0	..	3338	(272)

<sup>a</sup>  $(\epsilon - 1)/(2\epsilon + 1)$  varies from 0.226 for CCl<sub>4</sub> to 0.224 for pure dioxane. There should be little variation of this function in the mixtures. Refractive indexes of CCl<sub>4</sub>-dioxane mixtures are given by B. Pesce and V. Lago, *Gazz. chim. Ital.*, **74**, 131 (1944).

of phenol in acetonitrile, cyclohexyl cyanide and *t*-butyl cyanide give the anomalous result that the latter compound appears to be the weakest base, contrary to the expected inductive effects of the substituent groups.<sup>30</sup> At lower nitrile concentrations in a CCl<sub>4</sub> solvent, the basicity orders change (Fig. 2); finally, at infinite dilution, the estimated  $\Delta\nu$  values of the three nitriles correspond to the anticipated order.<sup>30</sup>

For some other classes of compounds, e.g., ethers, there is much less dependence of  $\Delta\nu$  on proton acceptor concentration in CCl<sub>4</sub> solution. We will show how each type of behavior can be predicted.

Dielectric constants and refractive indexes were measured for a number of the solvent mixtures employed (Tables IV, V, VII, VIII) for purposes of testing dielectric theories.

## Discussion

**Frequency Shifts in Different Solvents.**—Modifications of positions, shapes and intensities of spectral lines of emitting or absorbing species due to the presence of an environment have prompted much theoretical and experimental work in recent years.<sup>35</sup> The spectrum of a gaseous molecule is altered even by the presence of a noble gas such as argon in several ways; the theoretical treatment of such a system is far from

belief<sup>36</sup> that nitriles are very weak proton acceptors. It is true that the intramolecular hydrogen bond in *o*-cyanophenol is quite weak<sup>37</sup>; the interaction there is of the OH... $\pi$  type since the nitrogen atom, because of adverse geometry, cannot bond with the OH group. Nitriles form moderately strong intermolecular hydrogen bonds with alcohols and phenols.<sup>38,39,40</sup>

(35) Ref. 5, p. 471 and references therein cited, also see ref. 15 and 21.

(36) M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957); V. Prey and H. Berbak, *Monatsh. Chem.*, **82**, 990 (1951).

(37) NBS Circular 514, "Table of Dielectric Constants of Pure Liquids," U. S. Government Printing Office, Washington 25, D. C. (1951).

(38) "Handbook of Chemistry and Physics," 41st edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1959-1960.

(39) An excellent comprehensive review is available: (a) R. L. Williams, *Ann. Reports (Chem. Soc. London)*, **58**, 34 (1961). Also see (b) M. K. Wilson in E. A. Braude and W. D. Phillips, Ed., "Determination of Organic Structures by Physical Methods," Vol. II, 1962, pp. 203-206, 224-226; and (c) M. L. Josien, *Pure and Appl. Chem.*, **4**, 33 (1962).

TABLE VII  
THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL AND METHANOL IN SOLUTIONS OF DIOXANE IN CHLOROFORM<sup>a</sup>

Mole % dioxane	$\epsilon_{30}^{\circ}$	$\frac{\epsilon - 1}{2\epsilon + 1}$	Phenol-dioxane system			Methanol-dioxane system		
			$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$	$\nu_{OH}$ "free"	$\nu_{OH}$ bonded	$\Delta\nu$
0.0	4.806 <sup>b</sup>	0.359	3599	..	..	3634	..	..
1.8	4.68	.355	3600	3341	259	3634	3484	150
9.7	4.338	.345	3599	3340	259	3634	3485	149
19.6	4.049	.332	3597	3346	251	3634	3488	146
30.0	3.765	.324	(3593)	3342	(255) <sup>d</sup>	3633	3489	144
40.9	3.511	.313	..	3344	(253) <sup>d</sup>	(3631)	3494	(139) <sup>f</sup>
50.5	3.310	.303	..	3347	(250) <sup>d</sup>	*	3498	(135) <sup>f</sup>
60.2	3.111	.292	..	3343	(254) <sup>d</sup>	..	3501	(132) <sup>f</sup>
70.0	2.904	.280	..	3342	(255) <sup>d</sup>	..	3503	(130) <sup>f</sup>
80.2	2.683	.264	..	3340	(257) <sup>d</sup>	..	3504	(129) <sup>f</sup>
90.1	2.457	.246	..	3341	(256) <sup>d</sup>	..	3505	(128) <sup>f</sup>
100.0	2.217 <sup>c</sup>	.224	..	3338	(259) <sup>d</sup>	..	3504	(129) <sup>f</sup>

<sup>a</sup>  $n^{20D}$  varies linearly with mole fraction for this system. The total change from pure chloroform to pure dioxane is very small. The function  $(n^2 - 1)/(2n^2 + 1)$  is practically constant. <sup>b</sup> Ref. 37. <sup>c</sup> Ref. 37, by extrapolation. <sup>d</sup> Assuming  $\nu_{OH}$  "free" at 3597 cm.<sup>-1</sup>. <sup>e</sup> Shoulder. <sup>f</sup> Assuming  $\nu_{OH}$  "free" at 3633 cm.<sup>-1</sup>.

TABLE VIII  
THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL IN SOLUTIONS OF ACETONITRILE IN CARBON TETRACHLORIDE

Mole % aceto- nitrile	$\epsilon_{21.5}$	$n^{22.5D}$	$\frac{n^2 - 1}{2n^2 + 1}$		$\frac{\epsilon - 1}{2\epsilon + 1}$		$\nu_{OH}$ of phenol <sup>d</sup>		$\Delta\nu$
					"Free"	Bonded			
0.0	2.234 <sup>a</sup>	1.46305 <sup>c</sup>	0.216	0.226	3611	..	..	..	
1.0	2.386	1.45781	.2144	.240	3610	3458	152		
2.8	2.629	1.45667	.2143	.260	3610	3451	159		
4.9	2.916	1.45529	.2135	.280	3610	3446	164		
12.3	3.980	1.45024	.2120	.332	3607	3434	173		
33.8	7.74	1.43338	.2064	.408	..	3420	(187)		
65.9	18 <sup>b</sup>	1.39920	.195	.46	..	3411	(196)		
100	37 <sup>a</sup>	1.34596 <sup>d</sup>	.175	.480	..	3405	(202)		

<sup>a</sup> From ref. 37, by extrapolation. <sup>b</sup> Obtained by interpolation from F. Accascina, S. Petrucci and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1301 (1959). <sup>c</sup> Refractive index at 15°, from ref. 38. <sup>d</sup> Refractive index at 16.5°, from ref. 38.

TABLE IX

THE OH STRETCHING FREQUENCIES, IN CM.<sup>-1</sup>, OF PHENOL IN SOLUTIONS OF *tert*-BUTYL CYANIDE AND CYCLOHEXYL CYANIDE IN CARBON TETRACHLORIDE

Mole % <i>t</i> -butyl cyanide	$\nu_{OH}$ of phenol			Mole % cyclo- hexyl cyanide	$\nu_{OH}$ of phenol		
	"Free"	Bonded	$\Delta\nu$		"Free"	Bonded	$\Delta\nu$
0.0	3611	..	..	0.0	3611	..	..
0.5	3611	3448	163	0.4	3611	3447	164
1.4	3611	3446	165	2.3	3611	3441	170
3.8	3610	3442	168	5.2	3611	3437	174
7.6	3610	3439	171	9.4	3610	3432	178
12.0	3611	3435	176	15.5	3608	3425	183
24.2	3610	3430	180	35.1	(3605) <sup>a</sup>	3417	(191)
47.8	..	3423	(187)	45.7	..	3413	(195)
69.6	..	3420	(190)	66.9	..	3409	(199)
100	..	3419	(191)	100	..	3406	(202)

<sup>a</sup> Shoulder.

simple.<sup>40</sup> Hence, the effect of a liquid environment on spectra should be extremely difficult to treat quantitatively. The well-known Kirkwood-Bauer-Magat relationship<sup>11,12</sup> (eq. 1 and 2) has been found unsatisfactory to explain the observed medium shifts of X=O stretching frequencies,<sup>39,41,42</sup> the experimentally most extensively studied vibrations. Improved relationships, notably those of Pullin<sup>42</sup> (eq. 3) and of Buckingham<sup>43</sup> (eq. 4), have been proposed but these also are unsatisfactory.

(40) See, e.g., R. J. Breene, Jr., "The Shift and Shape of Spectral Lines," Pergamon Press, New York, N. Y., 1961; S. C. Ch'en and M. Takeo, *Rev. Mod. Phys.*, **29**, 20 (1957); A. D. Buckingham, *Trans. Faraday Soc.*, **58**, 449 (1962).

(41) R. B. Archibald and A. D. E. Pullin, *Spectrochim. Acta*, **12**, 34 (1958).

(42) A. D. E. Pullin, *ibid.*, **16**, 12 (1960).

(43) A. D. Buckingham, *Proc. Roy. Soc. (London)*, **A248**, 169 (1958).

$$\Delta\nu/\nu = C(\epsilon - 1)/(2\epsilon + 1) \quad \text{KBM relation} \quad (1)$$

$$\Delta\nu/\nu = C'(n^2 - 1)/(2n^2 + 1) \quad \text{Modified KBM relation} \quad (2)$$

$$\Delta\nu/\nu = C_0 + A \left\{ \frac{(n^2 - 1)/(2n^2 + 1)R}{B[(\epsilon - 1)/(2\epsilon + 1)R]} \right\} \quad \text{Pullin relation} \quad (3)$$

$$\Delta\nu/\nu = C_1 + C_2(\epsilon - 1)/(2\epsilon + 1) + C_3(n^2 - 1)/(2n^2 + 1) \quad \text{Buckingham relation} \quad (4)$$

Despite the insufficiencies of these theoretical treatments for practical predictive purposes, many regularities have been observed in solvent shifts of infrared bands. Empirical linear correlations have been established for the frequencies of different solutes in the same set of solvents; for example, X-H stretching vibrations of a number of compounds are said to shift proportionately in different solvents (*vide infra*).<sup>15,44,45</sup> Similar proportionalities of a more precise nature have been found for the C=O stretching frequencies of a wide variety of carbonyl compounds in different solvents<sup>7</sup>; S=O and P=O stretching frequency shifts are also proportional to C=O shifts,<sup>8</sup> but the solvent behavior of X=O absorptions is very different from that of X-H bands.<sup>7,41</sup> Strong proton acceptor solvents produce large X-H frequency shifts due to hydrogen bonding but affect X=O vibrations to a much smaller relative extent, e.g., O-H shifts are much larger than C=O shifts in ether, but the reverse is true in CH<sub>2</sub>Cl<sub>2</sub>. There is also little correlation between the effect of change of solvents upon the frequencies of "free" and hydrogen bonded OH stretching frequencies (Fig. 3),<sup>46</sup> contrary to expectations based on the simplified dielectric approach mentioned in the introduction.<sup>20</sup>

(44) W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941); W. Gordy and S. C. Stanford, *ibid.*, **9**, 204 (1941).

(45) M. L. Josien and G. Sourisseau in D. Hadzi, ed., "Hydrogen Bonding," Pergamon Press, London, 1959, p. 129.

(46) Generally in the literature comparisons are made of the quantities  $(\nu^b - \nu^v)/\nu^v$ , where  $\nu^v$  is the vapor phase frequency and  $\nu^b$  is the frequency in solvent S. We prefer to use the frequencies directly, since  $\nu^v$  is unknown

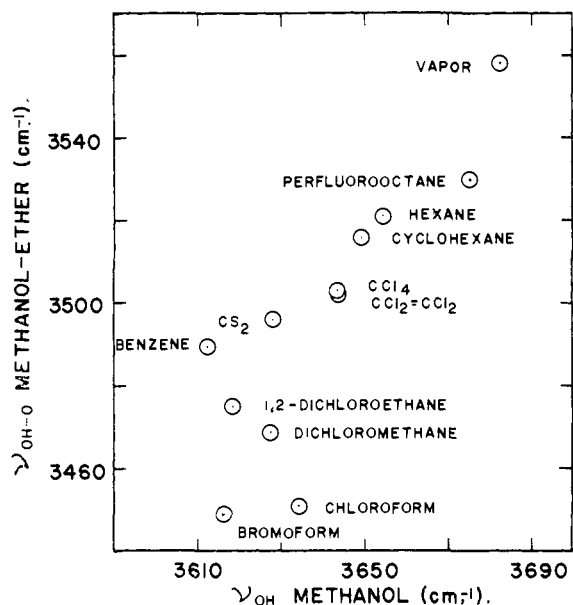


Fig. 3.—Solvent effects on "free" and hydrogen bonded OH stretching frequencies.

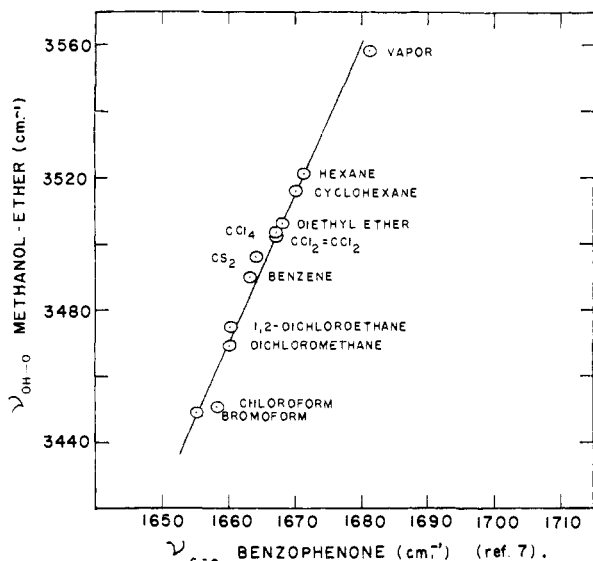


Fig. 4.—Correlation between  $\nu_{\text{OH-O}}$  of methanol-ether and  $\nu_{\text{C=O}}$  of benzophenone in various solvents.

We find that solvent shifts of  $X=O$  stretching frequencies are proportional to solvent shifts of  $X-H\cdots B$  stretching frequencies, i.e., of proton donor groups already engaged in intermolecular or intramolecular hydrogen bonding. An example is given in Fig. 4. All other  $X-H\cdots B$  frequencies in Tables I-III behave similarly. This proportionality implies that solvents interact in a similar manner with  $X=O$  and with  $X-H\cdots B$  stretching frequencies. These results cannot be reconciled with the "specific-interactions-only" approach advocated chiefly by Bellamy and his school.<sup>10,15,16</sup> It is hard to see how the "specific interactions" of solvents with  $X=O$  and  $X-H\cdots B$  groups could be similar.

We propose an empirical linear free energy relationship (5) for the correlation of solvent sensitive infrared vibrations

$$(\nu^0 - \nu^s)/\nu^s = aG \quad (5)$$

$\nu^0$  is the stretching vibration in the vapor phase; for hydrogen bonded  $X-H\cdots B$  vibrations it refers to the vapor

for many OH vibrations. For any given species  $\nu^0$  is a constant, so that only a scale change is involved. The two types of plots are equivalent for showing linearity relationships for different spectral shifts.

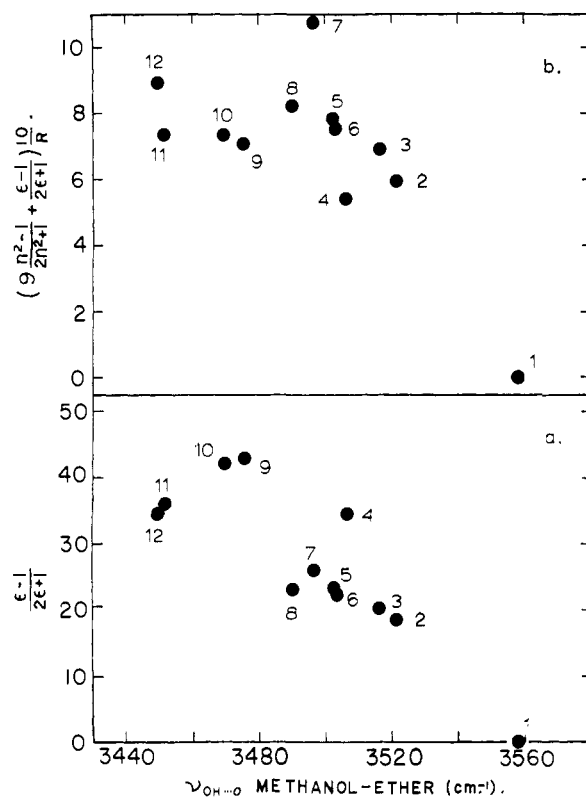


Fig. 5.—Correlation of hydrogen bonded OH stretching frequencies with dielectric equations: (a) Kirkwood-Bauer-Magat function (eq. 1); (b) Pullin function (eq. 6 of ref. 42). Solvents are: 1, gaseous phase; 2, hexane; 3, cyclohexane; 4, diethyl ether; 5, tetrachloroethylene; 6, carbon tetrachloride; 7, carbon disulfide; 8, benzene; 9, 1,2-dichloroethane; 10, dichloromethane; 11, chloroform; 12, bromoform.

phase value for the H-bonded complex and *not* the free  $X-H$  molecule.  $\nu^s$  is the observed frequency in a solution.  $a$  is a function of the particular infrared vibration of a given molecule and is a measure of its solvent sensitivity.  $G$  is a function of the solvent only.<sup>47</sup> Values of  $G$  are compiled in Table X; they were determined from the best fit of solvent shifts given in the literature for the carbonyl bands of dimethylformamide<sup>7</sup> and of benzophenone<sup>7</sup> and the sulfonyl band of dimethyl

TABLE X

SOLVENT SHIFT PARAMETERS			
Solvent	$G$	Solvent	$G$
Vacuum	00	Benzene	80
Perfluorooctane	36 <sup>a</sup>	Dioxane	86
Hexane	44	Methyl iodide	89
Cyclohexane	49	Acetonitrile	93
Dibutyl ether	61	Pyridine	94
Triethylamine	62	1,2-Dichloroethane	95
Diethyl ether	64	Nitromethane	99
Tetrachloroethylene	64	Dichloromethane	100
Carbon tetrachloride	69	Chloroform	106
Carbon disulfide	74	Dibromomethane	108
Toluene	74	Bromoform	118

<sup>a</sup> Based on methanol-ether and phenol-ether ROH...B solvent shifts (Table I and Fig. 6 and 7).

(47) Equation 5 is similar in form and intent to that proposed by S. Brownstein (*Can. J. Chem.*, **38**, 1590 (1960)),  $\log(k'/\text{solv}/k/\text{ethanol}) = SR$  for the correlation of the effects of solvents upon equilibria, spectra and reaction rates. The  $G$  constants (Table X) are related to Brownstein's  $S$  values, but there are discrepancies. Hence, eq. 5 is much more accurate for the prediction of infrared spectral shifts. The  $a$  constants are related to the slopes of "BHW" plots,<sup>15</sup> termed " $S$ " constants by Hallam.<sup>48,49</sup>

(48) E. A. Cutmore and H. E. Hallam, *Trans. Faraday Soc.*, **58**, 40 (1962).

(49) H. E. Hallam and T. C. Ray, *ibid.*, **58**, 1299 (1962).

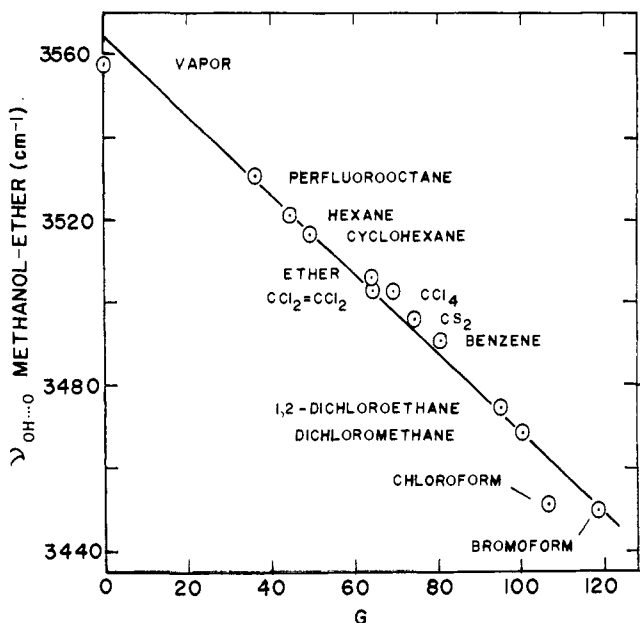


Fig. 6.—Correlation of the OH stretching frequency of the methanol-diethyl ether complex with  $G$  of the solvents.

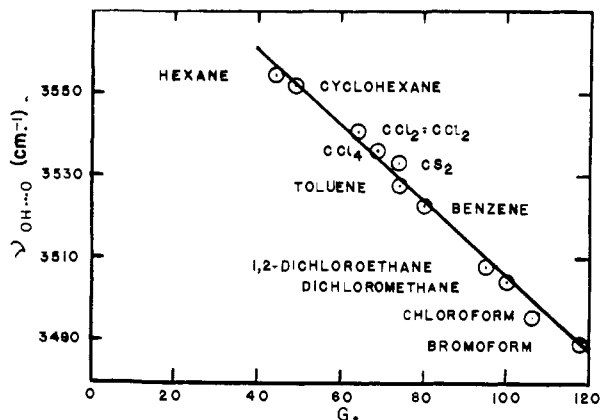


Fig. 7.—Correlation of the OH stretching frequency of the intramolecularly hydrogen bonded complex of  $\text{CH}_3\text{-CH}(\text{OCH}_3)\text{-CH}_2\text{CH}_2\text{OH}$  with  $G$  of the solvents.

sulfoxide.<sup>8</sup> An arbitrary value of 100 was assigned to dichloromethane to fix the scale.<sup>50</sup> To use eq. 5 it is not necessary to know  $\nu^0$ , rather this value can be estimated easily. Equation 5 is used in the form  $\nu^s = \nu^0 - aG\nu^0$ ;  $\nu^s$  is plotted against  $G$ . The intercept at  $G = 0$  gives  $\nu^0$  and the slope  $-a\nu^0$ , from which  $a$  can be calculated.  $\nu^0$  values, estimated in this manner, come within 8 cm.<sup>-1</sup> or better of the experimental values, where these are available.

Equation 5 is just a modified Kirkwood-Bauer-Magat relationship in which the dielectric constant function  $(\epsilon - 1)/(2\epsilon + 1)$  has been replaced by the empirical parameter  $G$ , obtained from infrared spectroscopic data on  $\text{X}=\text{O}$  stretching frequencies. A comparison of Figs. 5 and 6 shows the advantage of  $G$  over  $(\epsilon - 1)/(2\epsilon + 1)$  for predictive purposes. Equation 5 also gives more accurate results than the relationships

(50) Much work has been published on solvent effects on  $\text{X}=\text{O}$  stretching frequencies, especially  $\text{C}=\text{O}$  bands.<sup>7,41,42,51</sup> However, there are large discrepancies between the results reported by different workers. Table X will need to be revised when more accurate values are available.

(51) (a) N. S. Bayliss, A. R. H. Cole and H. Little, *Australian J. Chem.*, **8**, 26 (1955); (b) M. L. Josien and J. Lascombe, *J. Chim. Phys.*, **52**, 162 (1955); (c) T. V. Yakovleva, A. G. Maslennikova and A. A. Petrov, *Optics and Spectr.*, **7**, 383 (1959); (d) K. Inuzuka, M. Ito and S. Imanishi, *Bull. Chem. Soc. Japan*, **34**, 467 (1961); (e) R. E. Kagarise and K. B. Whetsel, *Spectrochim. Acta*, **17**, 869 (1961); **18**, 341 (1962); (f) H. W. Thompson and D. J. Jewell, *ibid.*, **13**, 254 (1958).

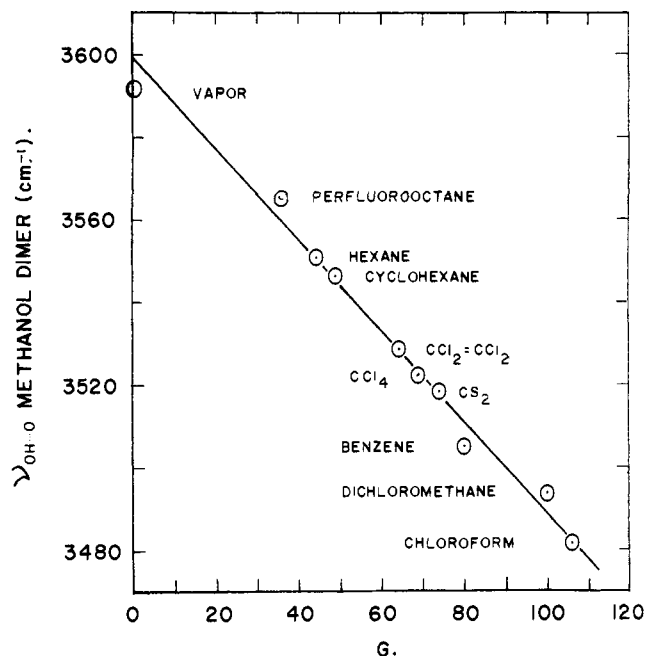


Fig. 8.—Correlation of the OH stretching frequency of the methanol dimer with  $G$  of the solvents.

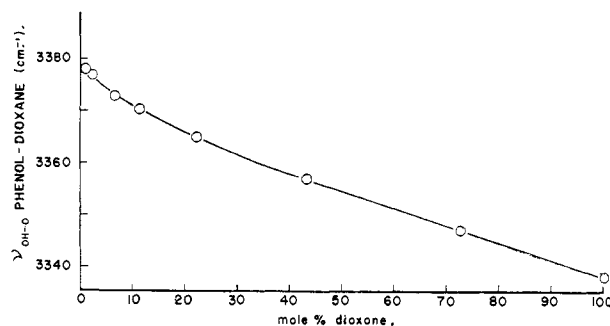


Fig. 9.—Effect of dioxane concentration on the OH stretching frequency of the phenol-dioxane complex in  $\text{CCl}_4$  solution.

proposed by Pullin (3)<sup>42</sup> and by Buckingham (4)<sup>43</sup> and is simpler to use.

It follows from its definition and from the literature that eq. 5 holds for  $\text{C}=\text{O}$ ,  $\text{S}=\text{O}$  and  $\text{P}=\text{O}$  bands, and to a lesser degree  $\text{N}=\text{O}$  bands.<sup>7,8,16</sup> Our results indicate that it also applies to hydrogen bonded  $\text{X}-\text{H}\cdots\text{B}$  stretching frequencies; Fig. 6-8 show excellent linear plots of intermolecular and intramolecular hydrogen bonded O-H stretching frequencies against  $G$  for the hydrogen bonded complexes we have studied (Tables I-III). Equation 5 also holds but less satisfactorily for some reported carbon-halogen,<sup>49,52</sup>  $\text{C}\equiv\text{C}$ <sup>53</sup> and other stretching frequency solvent shifts; Table XI lists values of  $a$  for a number of infrared bands which are correlated by eq. 5.

Possible interpretations of the magnitude of the solvent sensitivity of infrared vibrations, measured here by  $a$  constants, have been commented on by Bellamy and his collaborators.<sup>7,8,16</sup> Among other factors, steric hindrance by substituent groups seems to decrease the solvent sensitivity in some cases, possibly by diminishing access of the solvent to the chromophoric group. Hydrogen bonded vibrations,  $\text{XH}\cdots\text{B}$ , are particularly sensitive to changes in solvent, but for very strong hydrogen bonds this solvent sensitivity tends to disappear.<sup>10</sup>

(52) (a) D. H. Whiffen, *Trans. Faraday Soc.*, **49**, 878 (1953); (b) G. Chirudoglu and J. Reisse, *Bull. Soc. Chim. Belg.*, **70**, 472 (1961).

(53) P. V. Huang, J. Lascombe and M.-L. Josien, *J. Chim. Phys.*, **58**, 694 (1961).

TABLE XI  
 CORRELATION OF SOLVENT SENSITIVITY OF INFRARED BANDS

Compound	Chromophore	$\nu$ , cm. <sup>-1</sup>	$a \times 10^4$	Degree of correlation	Ref.
X=O Bands					
Acetone	C=O	1738	1.3	Very good	51a
Acetophenone	C=O	1709	1.3	Excellent	7
Benzophenone	C=O	1716	1.2	Excellent	7
Diisopropyl ketone	C=O	1730	1.3	Excellent	51a
Acetaldehyde	C=O	1747	1.3	Very good	51a
Methyl acetate	C=O	1770	1.8	Very good	7
Dimethylformamide	C=O	1681	2.3	Excellent	7
Acetone	C=O overtone	3456	1.2	Very good	51a
Diisopropyl ketone	C=O overtone	3443	1.2	Good	51a
Acetaldehyde	C=O overtone	3472	1.3	Very good	51a
Dimethyl sulfoxide	S=O	1103	4.2	Excellent	8
Diphenyl sulfoxide	S=O	1059	1.6	Good	8
Phosphoryl chloride	P=O	1324	2.1	Excellent	8
Methyl nitrite	N=O <i>cis</i>	1620	0.7	Fair	8
	N=O <i>trans</i>	1678	1.6	Fair	8
X-H Bands					
Propyne	C-H (free)	..	0.8	Good	54
Pyrrole	N-H	3530	..	Poor	15
Aniline	N-H asym.	3502	..	Poor	15
	N-H sym.	3419	..	Poor	15
<i>p</i> -Toluidine	N-H asym.	3475	..	Very poor	48
	N-H sym.	3387	..	Very poor	48
<i>p</i> -Chloroaniline	N-H asym.	3497	..	Very poor	48
	N-H sym.	3412	..	Very poor	48
Methanol	O-H	3682	..	Very poor	Here
Phenol	O-H	3654	..	Very poor	Here, 27
X-H...B Bands					
Methanol dimer	O-H...O	3592	3.1	Very good	Here
Benzhydrol dimer	O-H...O	(3524)	1.8	Good	Here
Diisopropyl carbinol dimer	O-H...O	(3560)	1.9	Very good	1
Methanol-ether	O-H...O	3558	2.7	Very good	Here
Phenol-ether	O-H...O	(3412)	3.4	Very good	Here
CH <sub>3</sub> CH(OCH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	O-H...O intra.	(3598)	2.6	Excellent	Here
2,4-Dihydroxypentane	O-H...O intra.	(3594)	2.3	Very good	Here
N-( $\beta$ -hydroxyethyl)piperidine)	O-H...N intra.	(3552)	2.8	Very good	1
Methanol-R <sub>4</sub> N <sup>+</sup> X <sup>-</sup>	O-H...X <sup>-</sup>	..	ca. 0	...	1
<i>o</i> -Nitrophenol	O-H...O intra.	(3240)	ca. 0	...	10
8-Hydroxyquinoline	O-H...N intra.	(3431)	0.7	4 points only	10
C≡X Bands					
1-Heptyne	C≡C	2127	0.5	Good	53
N-Cyanodimethylamine	C≡N	2235	1.2	Good	55
C-X Bands					
Chloroform	C-Cl asym.	773	1.8	Good	49, 52a
Methyl chloride	C-Cl	732	3.1	Fair	49
<i>cis</i> -Dichloroethylene	C-Cl	857	1.6	Fair	49
Acetonitrile	C-C	919	ca. 0	..	51a
Cyclohexanol	C-O axial	(ca. 1065)	..	Poor	56

All solvent sensitive infrared vibrations would not be expected to vary linearly with the  $G$  values of the solvents; a number of chromophores give poor correlations (Table XI). The theoretical treatment of Drickamer and Wiederkehr<sup>14,18</sup> resolves the total interaction energy between a molecule and its surroundings into four contributions: electrostatic, inductive, dispersive, and repulsion interaction energies; the frequency shifts depend upon the derivatives of these interaction energies.<sup>14</sup> If the inductive energy contributions are much larger than the other factors, the dielectric approach, of which eq. 5 is an empirical modification, may prove useful. For C=O bond vibrations of several carbonyl compounds (which give very good

correlations), the inductive interactions accounted for 65% of the observed shifts.<sup>14</sup> For the C≡N stretching frequency of acetonitrile (which correlates only moderately well), dispersion and repulsion contributions to the solvent shifts are large,<sup>14,18</sup> and eq. 5 is less satisfactory in this case. Other poor correlations may be due to similar factors.

The behavior of "free" XH bonds with a change in solvent is particularly important. As expected from Fig. 3, there is no general correlation of XH stretching vibrations with eq. 5 because most of the solvents listed in Table X, e.g., the aromatic compounds, the mono and dihalogenated hydrocarbons and especially the solvents containing O and N atoms, are capable of forming weak to strong hydrogen bonds with proton donors. Hydrogen bonding of XH groups with these solvents will give rise to frequency shifts in excess of those expected

(54) P. V. Huong and J. Lascombe, *Compt. rend.*, **254**, 2543 (1962).(55) J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958).(56) G. Chirudoglu and W. Masschelein, *Bull. Soc. Chim. Belg.*, **70**, 307 (1961).



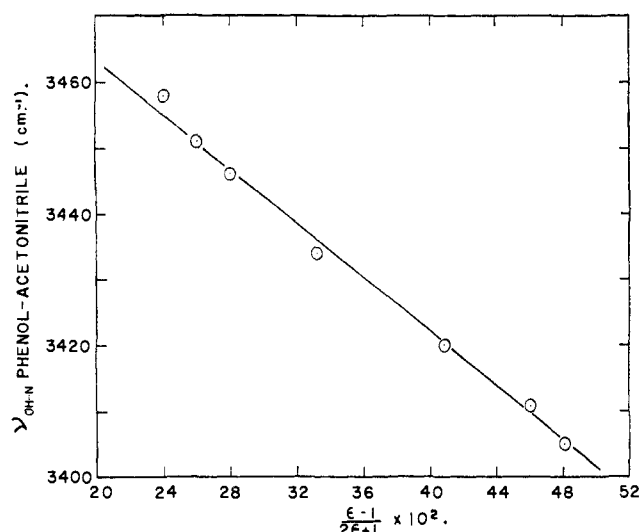


Fig. 10.—Kirkwood-Bauer-Magat plot for  $\nu_{\text{OH..N}}$  of the phenol-acetonitrile complex in  $\text{CCl}_4$  solutions.

merely on the basis of bulk property effects, empirically measured by  $G$  constants. At best, the "free" OH stretching frequencies in Tables I-III might correlate with  $G$  constants only for the truly "inert" solvents, *i.e.*, those incapable of acting as proton acceptors. These solvents include: perfluoroöctane, hexane, cyclohexane, tetrachloroethylene, carbon tetrachloride and perhaps chloroform (a proton donor). Even with this limited list of solvents poor correlation of XH frequency shifts with eq. 5 are obtained (Table XI). A critical examination of the correlations of various XH stretching vibrations in different solvents with each other reveals that agreements are generally less satisfactory<sup>57</sup> than often assumed<sup>15,39a,b,44-45</sup> especially for the "inert" solvents. Lines often do not pass through the origin. A convincing rationalization for the solvent dependence of XH frequencies appears not yet to have been offered.

There is no direct relationship between the  $G$  values in Table X and the "basicities" or proton accepting ability of the various solvents. Triethylamine, diethyl ether and tetrachloroethylene all have similar  $G$  values. Nor is there any straightforward relationship between these  $G$  values and the functions  $(n^2 - 1)/(2n^2 + 1)$  or  $(\epsilon - 1)/(2\epsilon + 1)$  or a combination of them. Solvents with high refractive indexes or dielectric constants generally have high  $G$  constants, but not all solvents with high  $G$  values have high refractive indexes or dielectric constants. A theoretical basis for these empirical  $G$  parameters is yet to be found.

**Changes in Solvent Concentrations.**—Both from the point of view of the simplified dielectric approach<sup>20</sup> and the "specific-interactions-only" hypothesis, the results of Tables IV, VI-IX are unexpected, since both  $\nu_{\text{ROH..B}}$  and  $\Delta\nu$  vary with concentration of proton acceptor in an "inert" solvent. The variation of  $\nu_{\text{ROH..B}}$  is greatest at low concentrations of B (Fig. 2 and 9). A comparison of Tables IV and V shows that the variation or constancy of  $\nu_{\text{ROH..B}}$  with concentration of proton acceptor depends both on the nature of proton acceptor B and the "inert" solvent. It appears impossible to explain the observed results using equations 1-4, with one exception. The  $\nu_{\text{OH..N}}$  frequency of phenol-acetonitrile in  $\text{CCl}_4$  solution varies linearly with  $(\epsilon - 1)/(2\epsilon + 1)$  (Fig. 10). This quantitative agreement is in accord with suggestions in the literature<sup>15,23</sup> that such frequency shifts with concentration are due

(57) See Fig. 7 and 8 of ref. 39c; similar behavior is exhibited by the data of Table II.

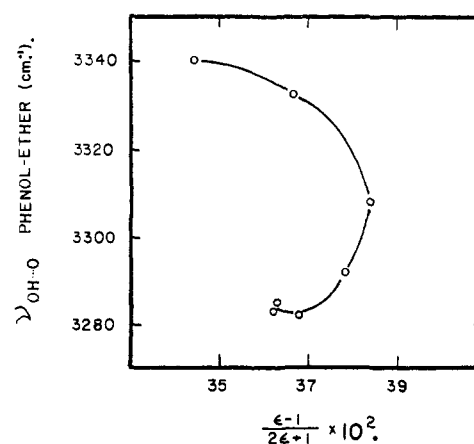


Fig. 11.—Kirkwood-Bauer-Magat plot for  $\nu_{\text{OH..O}}$  of the phenol-diethyl ether complex in chloroform solutions.

to the large difference in dielectric constants between the two solvents,  $\text{CH}_3\text{CN}$  and  $\text{CCl}_4$ . *This is not general behavior.* Both dioxane and  $\text{CCl}_4$  have low dielectric constants yet there are large concentration frequency shifts (Table VI and Fig. 9). The failure of eq. 1 is further emphasized in a plot of the phenol-ether system in chloroform solvent (Fig. 11 and Table IV).

The solvent shift parameters  $G$  are helpful in predicting when  $\nu_{\text{ROH..B}}$  will depend on the concentration of B and when not. Carbon tetrachloride and ether have similar  $G$  values; when ether is used as the proton acceptor and  $\text{CCl}_4$  the solvent there is practically no variation of  $\Delta\nu$  with ether concentration (Table V). Chloroform and ether have very different  $G$  values and  $\nu_{\text{OH..B}}$  is concentration dependent; in this case  $\Delta\nu$  decreases with increasing proton donor concentration because ether has a lower  $G$  value than  $\text{CHCl}_3$  (Table IV). The opposite behavior is observed in Tables VI, VIII and IX where  $\Delta\nu$  increases with increasing proton donor concentrations; in these cases  $G$  for the proton donors exceeds that of the solvents. *When the inert solvent S and the proton acceptor B have similar G values, we conclude that  $\nu_{\text{ROH..B}}$  will be solvent concentration independent; when the two G values are very different,  $\nu_{\text{ROH..B}}$  will be solvent concentration dependent.* Of the systems we have examined, only the phenol-dioxane-chloroform system in Table VII fails to conform to this generalization. Actually,  $G$  values could be determined for each mixed solvent as well as for the pure solvents themselves.

A test of these ideas is illustrated by the following example.  $\nu_{\text{SO}}$  for dimethyl sulfoxide in  $\text{CCl}_4$  and in the pure liquid are reported to be identical.<sup>8</sup> Consequently the  $G$  values of  $\text{CCl}_4$  and dimethyl sulfoxide should be similar. According to the above generalization  $\nu_{\text{CH}_3\text{OH..OC}(\text{CH}_3)_2}$  should be the same in  $\text{CCl}_4$  solvent and in pure dimethyl sulfoxide, despite the vast difference between the dielectric constants for these two compounds, 2.2 vs. 49,<sup>58</sup> respectively. Experimentally, however, the  $\nu_{\text{CH}_3\text{OH..OC}(\text{CH}_3)_2}$  values were found to be much lower in pure dimethylsulfoxide (3369  $\text{cm}^{-1}$ ) than in 1 molar  $\text{CCl}_4$  solution (3406  $\text{cm}^{-1}$ ). This behavior was found not to be due to a failure in the generalization concerning  $G$  values and solvent shift variations in mixed solvents, but rather due to an incorrect reported value for  $\nu_{\text{SO}}$  of dimethyl sulfoxide (1071  $\text{cm}^{-1}$ )<sup>8</sup> (pure liquid) upon which our  $G$  estimates were based. Using the correct value (1055  $\text{cm}^{-1}$ ), a  $G$  value of about 108 can be estimated for dimethyl sulfoxide.

**Behavior in Mixed "Inert" Solvents.**—Many spectroscopic measurements have been carried out in mixed

(58) H. L. Schlafer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).

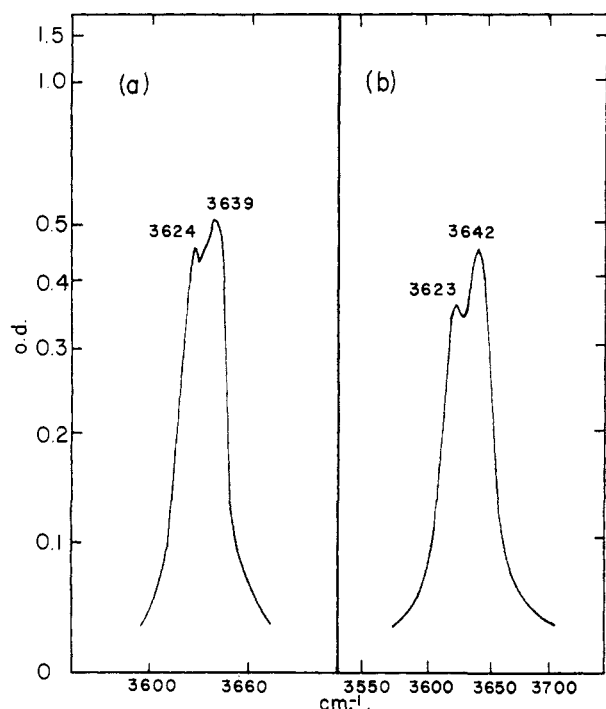


Fig. 12.—The appearance of the OH band of dilute phenol in (a) perfluorooctane + hexane (8:1 w./w.); (b) perfluorooctane +  $\text{CCl}_4$  (7:1 w./w.); concn. of phenol  $<0.02$  molar; 1-mm. cells.

solvents and the presence of more than one band or of an asymmetry in the observed band have been taken as evidence for specific interactions, *e.g.*, hydrogen bonding, between one of the solvents in the mixture and the solute.<sup>5</sup> This type of evidence should be taken with caution, since it does not take into account the possible presence of non-equivalent sites in the solvent mixture. This is illustrated by the behavior of phenol in mixtures of hexane and perfluorooctane. The OH stretching frequency of phenol is  $3654\text{ cm}^{-1}$  in the vapor phase,<sup>27</sup>  $3644\text{ cm}^{-1}$  in perfluorooctane and  $3621\text{ cm}^{-1}$  in hexane. The spectrum of phenol in a mixture of hexane and perfluorooctane shows two partially overlapped but well defined bands with apparent

Solvent mixtures	$\nu_{\text{OH}}$ phenol, $\text{cm}^{-1}$ (max.)
Cyclohexane + $\text{CCl}_4$ (20:17 v./v.)	3614 (symmetrical)
$\text{CCl}_4$ + $\text{CS}_2$ (3:2 v./v.)	3606 (slight asymmetry on low freq. side)
Cyclohexane + $\text{CS}_2$ (1:1 v./v.)	3608 (definite asymmetry on low freq. side)
Hexane + $\text{CS}_2$ (10:7 v./v.)	3614 (definite asymmetry on low freq. side)
Perfluorooctane + hexane (8:1 w./w.)	3639, 3624 (see text and Fig. 12a)
Perfluorooctane + $\text{CCl}_4$ (7:1 w./w.)	3642, 3623 (see Fig. 12b)
FC-75 <sup>a</sup> satd. with $\text{CCl}_4$	3640, 3623 (similar to above)
FC-75 <sup>a</sup> satd. with cyclohexane	3640 (slight asymmetry on low freq. side)

<sup>a</sup> FC-75 is a mixture of perfluorocyclic ethers (Minnesota Mining and Mfg. Co.). Its behavior is very much like that of perfluorooctane, and it is much more readily available. The free band of phenol in FC-75 is at  $3645\text{ cm}^{-1}$ ; there is no tendency to hydrogen bond to the oxygen atom in this solvent. Perfluorotributylamine (FC-47) behaves similarly in these respects, but solubilities are lower in this solvent.

maxima at  $3639$  and  $3624\text{ cm}^{-1}$  (Fig. 12a). It is hardly possible to attribute the lower frequency band to the presence of a hydrogen bonded complex, phenol..hexane; the prevalence of this effect in mixtures of presumed "inert" solvents (Table XII) suggests that another cause may be responsible. The system perfluoroheptane-isooctane has been studied by small angle X-ray measurements<sup>58</sup>; evidence of clusters up to 140 perfluoroheptane molecules has been found. It is possible that such clustering in solvent mixtures such as perfluorooctane-hexane gives sites essentially similar to the pure solvents and this is responsible for the behavior reported in Table XII.

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## Proton Spin-Spin Coupling in Aromatic Molecules. *p*-Disubstituted Benzenes

BY P. F. COX

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Nuclear magnetic resonance spectra of several *p*-disubstituted benzene derivatives have been obtained at 60 Mc./sec. The aromatic proton spectra were analyzed in terms of the relative chemical shift of the two aromatic proton types and the spin coupling constants between proton pairs. It was possible to obtain these solutions of the spin Hamiltonian without the use of numerical or iterative techniques. While the coupling constant did not vary greatly in the compounds studied, a definite relationship was found between the coupling constants and the electronegativity of the atoms attached to the aromatic ring.

The *p*-disubstituted benzene derivatives are a fruitful class of compounds to study by nuclear resonance. Because of symmetry of the spin coupling Hamiltonian, the spectra are relatively simple and may be easily analyzed in terms of chemical shift and spin coupling parameters. Richards and Schaefer<sup>1</sup> have examined the spectra of several *p*-disubstituted benzene derivatives and noted qualitative correlation between chemical shift and the substituent groups. Small differences

in spin coupling constants were reported, but no attempt was made to correlate their magnitude with the substituent group. Schaefer and Schneider<sup>2</sup> have reported the effect of solvent on the chemical shift of aromatic protons in *p*-substituted toluenes and fluoro-benzenes.

McConnell has examined the mechanism for spin coupling of aromatic protons.<sup>3</sup> The observed coupling constant between proton N and N' is composed of con-

(1) R. E. Richards and T. P. Schaefer, *Trans. Faraday Soc.*, **54**, 1280 (1958).

(2) T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

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