A Classification of Hydrogen-Bonding Solvents by Sonic Velocity Measurements

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Synopsis

The relative hydrogen-bonding capabilities (γ_w) of various solvents and mixtures were determined by measuring their effect upon a paper web using nondestructive sonic velocity techniques. Some exceptionally strong H-bonding solvents are identified.

INTRODUCTION

In previous papers, Craver and Taylor[1-3] have experimentally confirmed the relationship between the sonic velocity in paper and the elastic modulus and have shown that this nondestructive technique can be used to study paper anisotropy, moisture content, fiber bonding, fiber and molecular orientation under stress, and the effect of various saturating liquids.

Precise quantitative measurements reported here on the effect of a wide range of liquids on the velocity of sound in paper reveal that this technique provides a quick and sensitive method for ranking solvents according to their tendency to form hydrogen bonds. Solvents which do not swell or dissolve cellulose will interact with cellulosic fiber paper to reduce the velocity of sound through the paper in varying degrees. It appears that in measuring this effect of solvents on the interfiber bonding of paper, we are, in fact, measuring a hydrogen-bonding parameter of the liquids without introducing the complicating and obscuring effects of other intermolecular forces.

Solvent–paper interactions have been studied by other investigators, most of whom depended upon mechanically destructive tests for measuring the mechanical properties of paper saturated with various penetrating liquids. The excellent paper of Robertson[4] reviews previous work and should be consulted. The application of our nondestructive test to this area of investigation offers conveniences in speed, reproducibility, and in interpretation of the data.

BACKGROUND

In the field of polymer technology, there is a need for a method to predict the solubility of polymers in organic solvents.[5-9] A recent study[10] combines Hildebrand's solubility parameter δ with dipole moment and a value

A: Dilute Suspension   B: Partly Dried

Water

Fiber Cross-Section

Water

Fiber

C: Nearly Dry   D: Last Stage

Hydrogen
Bond

Water

Water Molecule

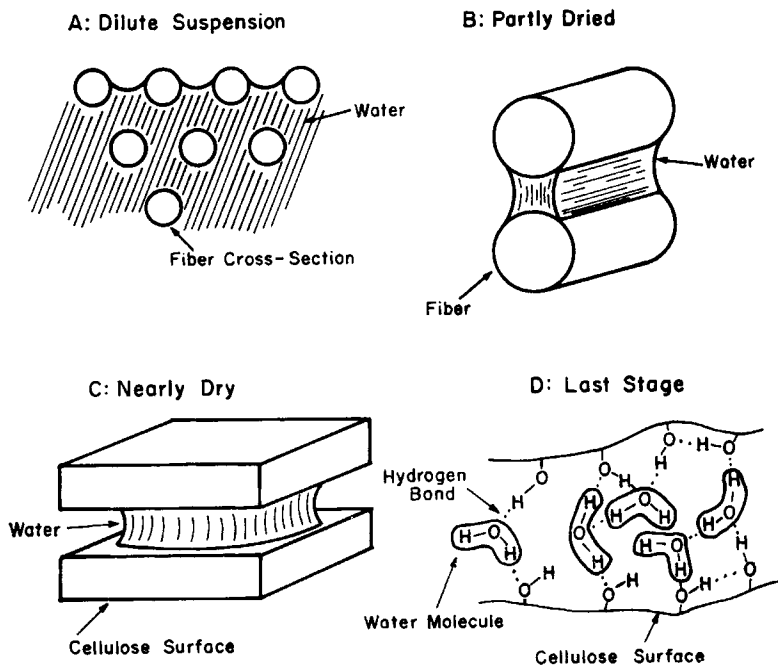Cellulose Surface   Cellulose Surface

Fig. 1. Cellulosic fiber-bonding process.

for the hydrogen bonding of a solvent into a three-dimensional plot, which predicts the solubility of polymers in organic solvents more reliably than had been possible before. The values for solubility parameters of most solvents are known with some accuracy, or can be calculated by Small's[5] empirical method. Dipole moments can be measured and are available for most solvents. Values for hydrogen bonding are not easily determined. Crowley et al.[10] used some hydrogen bonding parameters established by the infrared method of Gordy and determined others by a solvent dilution technique.

The presently described method is experimentally straightforward. It gives results generally in agreement with hydrogen-bonding values from other methods but shows significant differences for some solvents.

The dominance of hydrogen bonding between paper fibers as a main source of paper strength is well established. The process by which these hydrogen bonds are formed may be described as follows: Typical paper-making fibers prepared from wood by an appropriate pulping process are about 1.5 mm long and 20 microns in diameter and are, therefore, roughly 100 times longer than they are wide. Mechanical pretreatment in a water slurry causes fibrillation and swelling of the fibers. A very dilute suspension of such fibers, when poured upon a screen and allowed to drain, will form a wet web with very little physical strength. As water is removed through pressing and drying, surface tension forces arise because of the

water–air interfaces created within the fibrous mat. Fibers and fibrils are pressed together at crossing points by these very large surface tension forces, which can amount to 100 atm pressure or more, localized on small areas. Under these conditions, the cellulose surfaces come into intimate contact with a few molecules of water, forming a hydrogen-bonded bridge between the surfaces. These hydrogen-bonded fiber crossings are the "glue" that holds paper together (Fig. 1).

When paper is soaked in organic solvents, it loses some or most of its mechanical strength, depending upon whether the solvent in question is capable of displacing or disrupting the "hydrogen-bound water glue" which holds the fibers together. In many cases, if the organic solvent is allowed to evaporate, the paper recovers its original strength.

Preliminary data from infrared spectra using a transmitted beam technique show a partial displacement of water by organic solvents such as acetone and benzene.[11] Paper which was soaked in these liquids has a reduced water level that is restored only when the last traces of solvent have been removed. The spectra were obtained by the transmission and differential spectroscopy techniques of Smith and Wise.[14] This is in agreement with our belief that the decrease in sonic velocity that occurs when paper is saturated with a solvent corresponds to a displacement of the water involved in fiber–fiber bonding with consequent loss of structural physical properties.

EXPERIMENTAL

The paper used was Whatman No. 2 chromatography paper with a sonic velocity of 1.95 km/sec in the machine direction. This was cut into 5 $\times$ 50-cm strips and immersed in the appropriate solvent for 24 hr before testing. Except where indicated, the liquids were carefully dried, using conventional laboratory techniques. Excess liquid was removed by blotting lightly, and the sonic velocity was determined with a pulse propagation meter, Model 4, as described in detail in our earlier papers[1-3] and more recently in ASTM standard method F89–68.[12]

Briefly, a 10-kHz mechanical pulse is transmitted into the paper sample by a ceramic piezo-electric transducer and is detected by a similar transducer positioned a measured distance away. The time for the pulse to travel in the plane of the sample between transducers is recorded. The transit time and distance give the sonic velocity c. Sonic velocity is related to the sonic modulus E as follows:

$$E = \rho c^2 \tag{1}$$

where ρ = density of cellulose. (1.6)

By suitably positioning the transducers, the transmitted signal can be either the compressional or the shear mode. Since fluids cannot effectively transmit shear waves, a measurement of the shear wave velocity in saturated paper is a check on the presence or absence of a fiber–fiber bonded net-
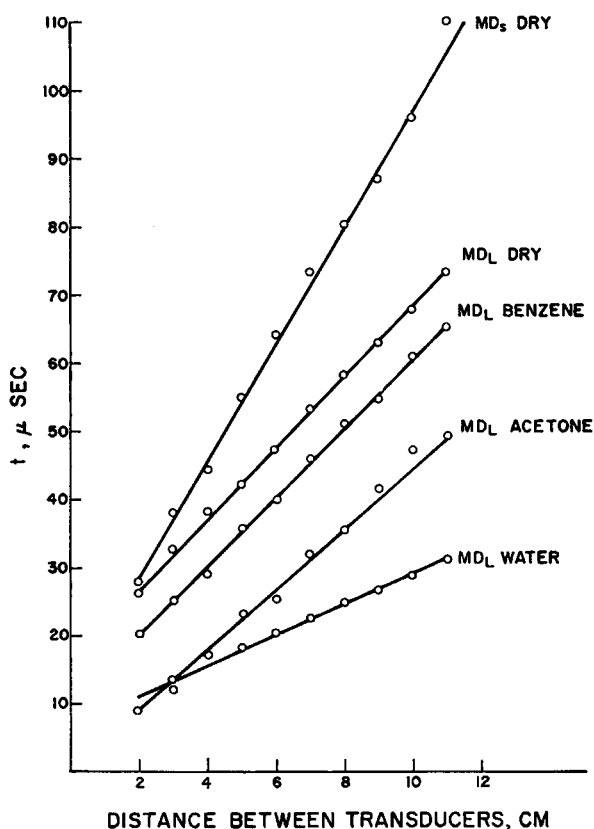
Fig. 2. MD_L = machine direction of paper, longitudinal mode of sound wave. MD_S = machine direction of paper, shear mode of sound wave.

work in saturated paper.   For experimental reasons, the compressional mode was chosen for most of the experiments reported here.   At least ten separate measurements were made on each sample, with the distance between the probes varying from 2 to 12 cm, by 1-cm intervals.

A plot of distance versus time should be linear to show that local random discontinuities in the paper are not affecting the results.   Typical data are shown in Table I and plotted in Figure 2.   Once this test of linearity is made, the results are averaged and expressed as c in km/sec.

Water itself is the most commonly used solvent for disrupting fiber–fiber bonds in paper, as, for example, in repulping dry lap or recovering waste paper for reuse.   It may be also considered as the most thoroughly hydrogen-bonded solvent of all.   It was, therefore, chosen as a reference standard for this study.   The relative effects of other solvents may be defined by the following:

$$\gamma_w = \frac{C_1 MD \text{ water-soaked paper}}{C_1 MD \text{ solvent-soaked paper}} \times 100.$$

TABLE I

| | | t, microsec | | |
| | | Saturated with | | |
d, cm	Dry paper	acetone	benzene	water
2	26	8	20	11
3	32.5	11.5	25	13.5
4	38	17	29	16
5	42	23	36	18
6	47	25	40	20
7	53	32	46	22.5
8	58	35	51	24.5
9	62.5	42.5	54.5	26.5
10	67.5	47	61	28
11	72.5	49	65	31
C_LMD, km/sec	1.95	1.56	1.64	0.46

RESULTS AND DISCUSSION

The organic solvents examined behave as predictable on the basis of their hydrogen-bonding classification given by Pimentel and McClellan[13]:

a.   Proton donors: chloroform.

b.   Proton acceptors: ketones, aldehydes, ethers, esters, *tert*-amines, olefins, and perhaps aromatic hydrocarbons.

c.   Simultaneous proton acceptors and donors: water, alcohols, carboxylic acids, and primary and secondary amines.

d.   Nonhydrogen-bonding: paraffins, carbon disulfide, and carbon tetrachloride.

The aliphatic alcohols behave as both proton acceptors and donors (Table II).   The effect of the increasing molecular weight of the homologous series of normal alcohols is shown in Figure 3.   This clearly shows that methanol behaves more like water in disrupting fiber–fiber bonds than do the other

TABLE II

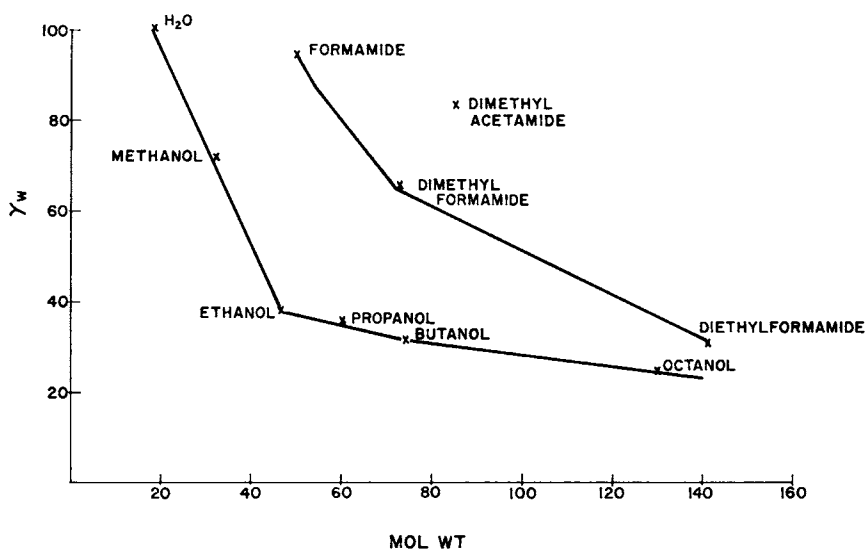| Alcohols	C_LMD, km/sec	γ_w
Water	0.46	100
Methanol	0.64	72
Ethanol	1.21	38
n-Propanol	1.33	34.5
iso-Propanol	1.60	29
n-Butanol	1.41	32.6
iso-Butanol	1.61	28.6
sec-Butanol	1.66	28
Cyclohexanol	1.56	29.5
1-Octanol	1.82	25
2-Octanol	1.59	28
2-Ethylhexanol	1.45	32

Fig. 3.

aliphatic alcohols. Ethanol and the higher alcohols form a series whose γ_w varies little with increasing molecular weight.

The polyhydric alcohols give results intermediate between those of methanol and ethanol. Ethylene glycol and glycerin give practically identical results (Table III).

Some observations on the effect of structure upon the γ_w of ethers can be deduced from Table IV. To be noted is that tetrahydrofuran and ether are of about the same molecular weight, but the oxygen in the cyclic struc-

TABLE III

Glycols	C_LMD	γ_w
Ethylene glycol	0.71	65
Propylene glycol	0.95	48.5
Diethylene glycol	0.85	54.5
Glycerin	0.70	65.6

TABLE IV

	C_LMD	γ_w
Ethers		
Diethyl ether	1.9	24.4
Tetrahydrofuran	1.43	31.2
Dioxane	1.0	46.0
Ether-Alcohols		
Ethyl Cellosolve	1.05	44.0
Butyl Cellosolve	1.52	30
Hexyl Cellosolve	1.47	31

TABLE V

Esters	C_LMD	γ_w
Ethyl acetate	1.61	28.6
Propyl formate	1.72	26.8
Methyl propionate	1.75	26.2
γ-Butyrolactone	1.44	32
Dimethyl phthalate	1.51	30.5

ture of tetrahydrofuran is apparently a better proton acceptor than that in the linear ether. This same effect can be seen in the series of esters and cyclic esters (γ-butyrolactone) (Table V). The normal esters, ethyl acetate, propyl formate, and methyl propionate, have identical molecular weights and similar hydrogen bond parameters. The γ_w for butyrolactone is appreciably higher than that for normal esters and even higher than that for the diester dimethyl phthalate, but the differential effect is not as pronounced as in the case of diethyl ether and tetrahydrofuran.

TABLE VI

Phosphorus-Containing Esters	C_LMD	γ_w
Trimethyl phosphate	1.11	41.5
Tributyl phosphate	1.32	35
Trioctyl phosphate	1.82	25
Trioctyl phosphite	1.75	26
Triphenyl phosphite	1.56	29.5
Dimethyl acid phosphite	0.59	78

The phosphorus-containing esters behave about as one would predict, with the exception of dimethyl acid phosphite (Table VI). This dialkyl phosphite is a neutral liquid with the probable formula $(CH_3O)_2HP = O$. Considering that DMAP has a molecular weight of 132, it has a surprisingly high γ_w. It should be classed as a strong proton acceptor and donor.

The data on some amines are given in Table VII. Formamide and its n-dialkyl derivatives form a series which resembles the aliphatic alcohols in the variation of γ_w with molecular weight (Fig. 3). There are too few members of the series which are still liquids at room temperature to draw many conclusions, however.

The primary aliphatic amines ethylenediamine and diethylenetriamine are known to affect the crystalline structure of cellulose under the proper conditions. Thus, the values for sonic velocity could be affected both by a change in fiber–fiber bonding and by a change in the elastic modulus of the cellulose itself due to adsorption of solvent into the fine structure of the fiber. The values for γ_w for these primary amines should be considered suspect on this count.

A comparison of the aromatic amines aniline and pyridine with their hydrogenated derivatives cyclohexylamine and piperidine presents an

TABLE VII

Amides and Amines	C_LMD	γ_w
Formamide	0.49	94
Dimethyl formamide	0.68	68
Diethyl formamide	1.50	31
Dimethyl acetamide	0.53	87
Ethylenediamine	0.19	240
Diethylenetriamine	0.23	200
Aniline	0.96	94
Cyclohexylamine	1.67	27.6
Pyridine	0.58	80
Piperidine	0.52	88.5
Morpholine	0.23	200

interesting case. Aniline, which ranks with formamide as far as γ_w is concerned, becomes only a moderate hydrogen-bonding solvent when hydrogenated to cyclohexylamine. On the other hand, hydrogenation of pyridine definitely increases the hydrogen-bond parameter.

The ketones are proton acceptors and have about the same γ_w values as the aliphatic esters (Table VIII). Here again, a cyclic aliphatic structure appears to improve γ_w.

Glacial acetic acid has a surprisingly poor γ_w, possibly because it is already self-bonded to form a dimer. Dilution with a few percent water gives some improvement, but not a significant one.

Mixtures of dimethyl sulfoxide and water show a synergistic effect with a maximum at 50–50% wt-% (Fig. 4). (The 60% DMSO–40% H_2O mixture

TABLE VIII

	C_LMD	γ_w
Ketones		
Acetone	1.56	29
Methyl ethyl ketone	1.48	30.5
Cyclohexanone	1.20	37.5
Acids		
Glacial acetic	1.10	41
Glacial acetic + 7% H_2O	0.88	51.5
Misc.		
Carbon disulfide	1.35	33
Dimethyl sulfoxide	0.57	79

TABLE IX

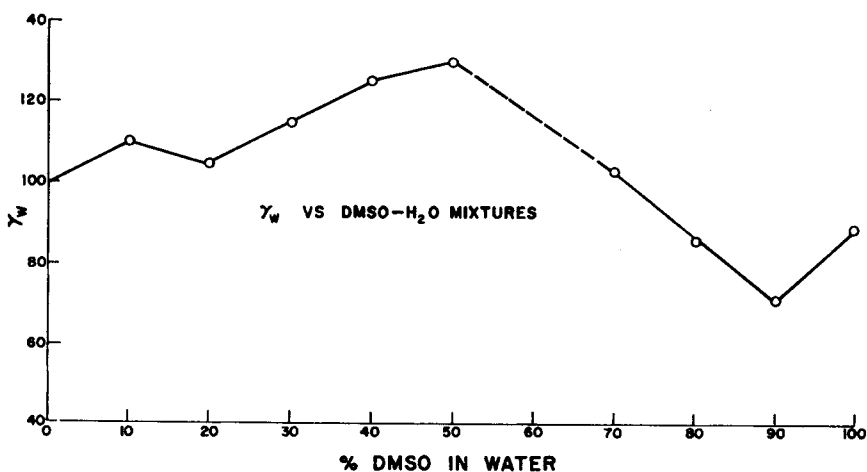| Water solutions	C_LMD	γ_w
10% LiCl	0.46	100
10% KCl	0.46	100
10% NaCl	0.46	100
10% Urea	0.48	95
10% Sucrose	0.44	105

Fig. 4.

separated into two phases during the paper-soaking period and was discarded.) Similar synergisms are indicated for urea, trimethyl phosphate, and glacial acetic acid solutions in DMSO (Table X). The urea–DMSO mixture has the highest γ_w of any of the solvents tested, excepting only the polyamines and morpholine (Table VII), which are suspected of being swelling agents.

The activity of water is not affected by the addition of the neutral salts, as shown in Table IX.

As would be expected, the normal hydrocarbons have no effect upon the fiber bond as measured by sonic velocity and have the same γ_w (23.6) as the

TABLE X

DMSO solutions	C_LMD	γ_w
50% Trimethyl phosphate	0.41	112
50% Methanol	0.86	54
50% Ethanol	1.07	43
10% Urea	0.26	173
10% Glacial acetic acid	0.33	139
10% Phenol	0.62	73.5

TABLE XI

Hydrocarbons	C_LMD	γ_w
n-Hexane	1.95	23.6
n-Pentane	1.95	23.6
n-Octane	1.95	23.6
Benzene	1.64	28
Toluene	1.70	27
Diphenyl methane	1.31	35

TABLE XII

Solvent	γ_w	γ Crowley et al.[10]	γ Lieberman[7]	Robertson[4] Breaking strength, kg
Water	100	—	2.89	0.52
Formamide	94	—	—	0.78
Aniline	94	18.1	0.49	9.19
Piperidine	89	24.2	—	—
Dimethyl acetamide	87	12.3	—	—
Pyridine	80	18.1	2.89	2.74
Dimethyl sulfoxide	79	7.7	—	—
Dimethyl acid phosphite	78	—	—	—
Methanol	72	18.7	2.89	2.35
Dimethyl formamide	68	11.7	2.89	1.13
Glycerin	66	—	2.89	—
Ethylene glycol	65	20.6	2.89	1.35
Diethylene glycol	55	—	1.96	2.39
Propylene glycol	49	—	—	—
Dioxane	46	9.7	0.64	8.31
Ethyl Cellosolve	44	13.0	1.69	5.17
Trimethyl phosphate	42	—	—	—
Glacial acetic acid	41	—	—	—
Ethanol	38	18.7	2.89	4.05
Cyclohexanone	38	11.7	0.49	—
Diphenyl methane	35	—	—	—
Tributyl phosphate	35	—	—	—
n-Propanol	35	18.7	2.89	—
Carbon disulfide	33	0	0.09	—
Butanol	33	18.7	2.89	8.25
γ-Butyrolactone	32	9.7	1.0	7.69
2-Ethylhexanol	32	18.7	2.89	—
Tetrahydrofuran	31	—	—	—
Diethyl formamide	31	11.7	2.89	—
Hexyl Cellosolve	31	—	—	—
Dimethyl phthalate	31	—	1.0	—
Methyl ethyl ketone	31	7.7	0.64	7.75
Triphenyl phosphite	30	—	—	—
Butyl Cellosolve	30	13.0	—	8.38
Cyclohexanol	30	18.7	2.89	—
Acetone	29	9.7	1.0	6.70
iso-Propanol	29	—	2.89	—
iso-Butanol	29	—	—	—
Ethyl acetate	29	8.4	1.0	8.31
sec-Butanol	28	—	2.89	—
sec-Octanol	28	—	—	—
Benzene	28	0	0.09	10.60
Cyclohexylamine	28	—	—	—
Toluene	27	4.5	0.09	10.20
Propyl formate	27	—	1.0	—
Methyl propionate	26	8.4	—	—
Trioctyl phosphite	26	—	—	—
Trioctyl phosphate	25	—	—	—
n-Octanol	25	18.7	2.89	—
Diethyl ether	24	13.0	1.0	—
n-Hexane	24	0	0.0	—
n-Pentane	24	0	0.09	—
n-Octane	24	—	0.09	—
Dry	24	—	—	12.00

air-dried paper (Table XI).   Both benzene and toluene, though, do have an appreciable effect and diphenylmethane has an even higher value.   These aromatic hydrocarbons certainly should be classed as proton acceptors.

The hydrogen-bonding values for the solvents investigated (except for those of the primary amines) are given in decreasing order in Table XII. A comparison of these values with those given by Crowley et al.[10] and Lieberman[7] shows no clearly definable correlations.   The hydrogen-bonding values given by Crowley et al.[10] do not distinguish among the primary alcohols or between diethyl and dimethyl formamide.   The values given by Lieberman[7] are even more closely aggregated and might be said to represent only a sorting of solvents into high, medium, and low hydrogen-bonding values.   I have not attempted to convert the data of Robertson[4] into comparable hydrogen-bonding values, but his results (expressed as the breaking strength in kilograms of paper which has been saturated with the appropriate solvent) show some relationship to γ_w along with some inexplicable contradictions.   For example, the values for aniline and for dioxane seem to be out of line.

In summary, a hydrogen-bonded fiber network—paper—was used to classify organic liquids and solutions as to their hydrogen-bonding capabilities by sonic modulus techniques.   DMSO–water mixtures show synergistic effects with a maximum at about equal parts by weight of each. Dimethyl acid phosphite has been shown to be a surprisingly strong hydrogen-bonding solvent, comparable to well-known solvents such as dimethyl sulfoxide and methanol.   A solution of urea in dimethyl sulfoxide has an unusually high hydrogen-bonding value.   These mixtures should be useful as solvents for highly hydrogen-bonded polymers such as starches, proteins, polyamides, and poly(vinyl alcohol).

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