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STUDIES OF SOLUTE-SOLVENT
INTERACTIONS IN NON-AQUEOUS
SOLVENTS

MASTER

REPORT COVERING WORK FROM
July 1, 1968 through January 1, 1969

by

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SUMMARY

This report describes progress in the study of solute-solvent interactions in non-aqueous, aprotic solvents of low dielectric constant. This work was performed at the University of New Mexico, Department of Chemistry and is supported by the Sandia Corporation, Contract No. 53-8385 and is a continuation of Contract No. 53-6574. The work described was done in the time interval of July 1, 1968 to January 1, 1969.

The work proposes to gain a greater understanding into solvation in non-aqueous solvents by studying the kinetics and thermodynamics of association for several series of compounds in aprotic solvents. (See reports describing work completed, Contract No. 53-6574.) The kinetic parameters will be evaluated by analysis of ultrasonic absorption data. The thermodynamic properties of the association reactions will be investigated through the use of colligative solution properties and spectral data. Analysis of this data will permit a greater understanding of solution phenomena.

This report is divided into three sections which describe the majority of the work completed:

1. Association of Phenolic Compounds in Benzene Solution.
2. Design and Construction of an Ultrasonic Absorption Cell.
3. Extended Hückel Molecular Orbital Calculations on a Series of Phenols.

Extensive work has been completed collecting data (cryoscopic, differential vapor pressure, nuclear magnetic resonance spectroscopy) describing the association of phenol and substituted phenols, carboxylic acids (benzoic, acetic and the three chloroacetic acids), normal alkanes and aliphatic alcohols in the solvents benzene and cyclohexane. Although this report only describes the data analysis for phenol and a group of substituted phenols in the solvent benzene, considerable effort has been expended in the analysis of the remaining data.

These data analyses will be reported in the next progress report since some of the work is still in progress. Another apparatus for the measurement of differential vapor pressure has been designed, constructed and evaluated. This all-glass apparatus uses a triple-point bath for precise temperature control. Association of phenols in benzene is now being studied. The data and data interpretation will appear in the next report.

The second part of this progress report describes the design and construction of a new ultrasonic absorption cell. This cell has several quite convenient features and is unusually easy to use. Measurements have been made on a few selected phenol solutions as well as a series of neat solvents at several temperatures. This data will also appear in the final progress report.

In order to evaluate and interpret our experimental data more meaningfully we have undertaken a program of computer extended Hückel molecular orbital calculations. The initial part of this work is described in section 3 of this report. Work recently completed as well as that now in progress will attempt to evaluate the energies and configurations of selected models of the associated species.

A Cryoscopic Study of the Association of Phenolic Compounds in Benzene Solution

The measurement of colligative properties of liquid solutions, those properties which depend upon the number and not the type of dissolved species, has long been recognized as an important method for the study of molecular association. Of the several colligative property techniques, one of the most accurate and experimentally simple is the depression of the freezing point, cryoscopy. Early workers in this field soon discovered that many organic solutes, when used to depress the freezing points of aprotic solvents, showed smaller freezing point depressions than would be predicted on the basis of their formula weights. Since these solutes were then thought to be only slightly associated, if at all, several suggestions were made to explain this behavior.

The most commonly used explanations for this observed non-ideal behavior were the formation of solid solutions, changes in activity coefficients with concentration and molecular association. In this investigation we shall assume that the only causes of such deviations are due to association. Rationale for this assumption is circumstantial.

Solid solutions may be detected by careful chemical analysis or by the method of Van Bijlert (1). Several systems have been suspected of forming solid solutions or mixed crystals in benzene such as acetic acid (3,21,20) and phenol (10,13,7). In the above cases, careful analysis cast some doubt on this supposition. The usual method for correcting cryoscopic data for solid solution formation is to use an expression of the form (12)

$$\Delta T = K_f m(1-k)$$

where k is the partition coefficient for the solute between the solid and liquid phases. In the case of phenol, Bury and Jenkins (3) report $k = 0.47$ while Davison (7) reports a value of 0.41.

Even though the existence of solid solutions is suspected, it is not reasonable to interpret cryscopic data solely on this basis for systems which are known to contain other causes for deviations from ideal behavior. Solutions of phenols in benzene have infrared spectra characteristic of hydrogen bonded systems. The remarkable lack of experimental data on solid solutions in these systems remains a challenge for further work in this area.

Another explanation for deviations from ideal solution behavior lies in the concept of activity. Several theories for the determination of activity coefficients of non-electrolytes in non-aqueous media have been put forth, but the one derived from the normal theory of liquids (19) is, perhaps, the most common. These theories are generally unsatisfactory in explaining the deviations for ideal behavior since quite large activity corrections are necessary even in solvents with a low dielectric constant. For example, phenol has been reported to have an activity coefficient of less than 0.3 at 0.5 molal benzene solution (22).

The remaining cause for non-ideal behavior may be loosely classified as molecular association. The solute may associate with itself, the solvent or with impurities present. Infrared spectra of all solutes used in this investigation have been shown to exhibit hydrogen bonding (22); it is assumed that self association of the phenols is the cause of this spectral behavior. It is well known that hydrogen bonding phenomena are extremely sensitive to variables such as temperature, concentration, impurities present, and most importantly, to the nature of the solvent.

This paper is the first in a series which will evaluate the equilibrium constants of association for several phenols in various aprotic solvents. If all variables except the nature of the solvent are held constant, the differences observed between two different solvents should be due to only two factors; the temperature difference of the measurements and the effect of the solvent. It is possible to separate these two effects and gain information

about the nature and extent of solvation in these non-aqueous solvents. In this investigation, equilibrium constants for phenol (P), orthocresol (OC), metacresol (MC), paracresol (PC), orthochlorophenol (OCP), metachlorophenol (MCP), parachlorophenol (PCP), 2,5 dimethylphenol (25DMP), 2,6 dimethylphenol (26DMP), 3,4 dimethylphenol (34DMP), and 3,5 dimethylphenol (35DMP) are reported in the solvent benzene.

Experimental

Reagents: The chemicals used for this study as well as the method of purification and analyzed purity are shown in Table 1.

The apparatus used for these investigations was designed to measure the freezing points of solutions at millimolal and higher concentrations using a procedure designed to maximize accuracy and to minimize time spent in data collection. The test solution was maintained under an atmosphere of dried argon at all times. Stirring was accomplished by a Teflon disk stirrer driven at 600 rpm by a synchronous motor. The entire apparatus was sealed except when solution concentrations were changed. (See Figure I)

A Veco 51A1, 100,000 ohm nominal resistance, thermistor was used as the temperature sensing device associated with the measuring circuit shown in Figure II. The apparatus shown is capable of a recorder sensitivity of approximately 150 mv per degree and can detect 0.001°C . changes in temperature under the conditions used in this study. Use of the full sensitivity of this circuit would allow investigation of 2.5×10^{-4} molal solutions. Operating conditions were such that approximately a two degree temperature change corresponded to a full scale recorder response. Discussion of the measuring circuit may be found elsewhere (13).

TABLE 1

REAGENTS

<u>Reagent</u>	<u>Symbol</u>	<u>Method of Purification</u>	<u>Analysis of Purity</u>	
			rel. wt. % major	H ₂ O wt. %
benzene	B	1	99.6	0.025
napthalene	N	2	99.9+	not detectable
biphenyl	BP	3	99.9+	not detectable
phenol	P	1	99.7	0.055
<u>o</u> -cresol	OC	1	99.3	0.030
<u>m</u> -cresol	MC	1	99.3	0.030
<u>p</u> -cresol	PC	2	99.4	0.030
<u>o</u> -chlorophenol	OCP	1	99.6	0.029
<u>m</u> -chlorophenol	MCP	1	99.6	0.033
<u>p</u> -chlorophenol	PCP	3 and 2	99.8	0.019
2,5 dimethyl phenol	25DMP	2	99.1	0.041
2,6 dimethyl phenol	26DMP	2	99.1	0.048
3,4 dimethyl phenol	34DMP	2	99.3	0.043
3,5 dimethyl phenol	35DMP	2	99.2	0.047

1. Fractional distillation from Linde 4A molecular silver; system flushed with dried and purified argon.
2. Fractional crystallization from benzene, vacuum dried.
3. Sublimation.
4. GLC: 2 meter Silicone Oil DE-710 on firebrick; T = 190° for phenols, T = 80° for benzene.

Procedure: The apparatus was carefully cleaned and dried in a vacuum oven at 100° C. before use. A weighed charge of pure solvent was introduced into the chamber, the system flushed with dried argon and the freezing curve determined. A known volume of a solution of known composition of the solute in benzene was introduced, after melting the benzene frozen during the first determination, and the freezing curve for this solution determined. Repeated additions allowed the measurement of the cryoscopic behavior to be investigated throughout the desired concentration range. Using this procedure, it was possible to determine as many as twenty experimental points per hour.

Experimental Error: An error analysis of the method of concentration determination showed the concentrations to be accurate to 1%. Analysis of solutions made by successive addition verified this result. Error in temperature measurement was estimated on the basis of the minimum deflection observable and was found to be approximately 1%. The combination of these two errors leads to an overall 2% error in the freezing point depression and to a 3% error in the "observed concentration".

RESULTS:

Determination of the cryoscopic Constant of Benzene.

Cryoscopic techniques are only successful if a relationship is found between the observed freezing point lowering and the concentration of a species known to behave ideally in the solvent. If such ideal behavior has not been reported, a reference compound may be selected and then all concentrations can be related to this "standard". In this study, naphthalene and biphenyl were chosen as our nonassociated standards. Biphenyl is known to be nearly ideal in benzene solutions (18); positive deviations from Raoult's law for the liquid-vapor equilibrium are less than 5% at low concentrations. The freezing

points of a series of solutions of naphthalene and biphenyl were determined; the value of K_f determined was (for naphthalene) $5.112^\circ/\text{m}$ in good agreement with 5.070 reported by Kraus (1) and 5.492 of White and Kilpatrick (29) and 5.122 by Bury and Jenkins (3). Other reported values fall within this range and appear to vary slightly with the compound chosen as the standard.

In this investigation, the output of the temperature measuring circuit was compared with a NBS Calibrated Beckman thermometer. The data showed no temperature dependence, i. e., experimental plots of Δmv (the change of recorder output) versus concentration were linear to within 0.0091 sigma units with an intercept of 6×10^{-3} mv, or less than experimentally observable. This apparent linearity of data is due to a fortuitous cancellation of the non-linear response of the temperature sensing circuit used in this study with the change of K_f with temperature.

Interpretation of Experimental Data

In lieu of experimental data concerning solid solutions or a reliable theory of non-electrolyte activity, the non-ideal cryoscopic behavior of phenol and substituted phenol must be explained solely in terms of association. As pointed out succinctly by Rossitti and Rossitti (23), the data results in essentially two equations with n unknowns, a problem which may, in theory, be solved, but experimental error usually makes the set of equations ill conditioned. Attempts to increase the number of equations available results in essentially fixing some (arbitrary) relationship between successive equilibrium constants. Notable research on these lines is that of Lassettre (15,16), Dunken (8,27) and that of Bjerrum (2) as modified by Fronaeus (9). A second approach is based on the minimization of undetermined thermodynamic functions and on statistical curve fitting, which are reviewed by Rossitti and Rossitti (23) and by Zeleznik and Gordon (28).

The relationship of CO to CA is shown in Figures III, IV, V, and VI. Figures III and VI include the data of Davison and that of Bury and Jenkins for purposes of comparison. Table 2 lists equilibrium constants determined by curve fitting, those determined by Lassettre's method as well as those previously reported. Also shown in Table 2 is the function ∇ , the percent of association, evaluated at an analytical concentration of 0.50 molal:

$$\nabla = \frac{\text{concentration of all associated species} \times 100}{\text{concentration of all species}}$$

$$\nabla = \frac{(CO - C_{\text{Monomer}})100}{(CO)}$$

The equilibrium constants shown in Table 2 were determined by curve fitting. A series of CA-CO curves were generated using incremented values of overall equilibrium constants. The experimental data was then plotted and the resulting curves overlayed on the constructed curves to achieve a "best-fit". Criteria for "best fit" were that the deviations of the experimental points from the calculated curve are a minimum, of the same order of magnitude as the experimental error, and that the least number of equilibrium constants necessary to describe the data are used. This would lead to the simplest possible system required to describe the experimental data. To obtain a reasonable value of the initial dimerization constant, the data obtained for low values of CA were used since here the effects from higher order polymers should be small, less than experimental error, effects. Once the dimerization constant was determined in this manner, it was used to evaluate the trimerization equilibrium constant. This approach is generally similar to that used for the determination of successive formation constants of complex ions (23). In no case were association constants higher than the trimer necessary.

Table 2 also includes the results obtained by analysis of our data using the method described by Lassettre (15). This approach assumes three possible

TABLE 2

System	1 ∇	K_2^2	K_3^3	K_2^2	K_3^3	Previously reported	
						K_2^2	Ref
	%	Curve fit		Lassettre			
PB	84.75	125	450	.556	.190	.540	26
34DMP	21.81	.30	2.1	.653	.640		
35DMP	19.35	.20	2.0	.556	.464		
25DMP	31.95	.47	+	.309	.143		
26DMP	14.51	.17	+				
OC	16.27	.58	+	.18	.14	1.1 .28	21 8
MC	23.18	.50	1.80	.578	.955		
PC	18.96	.30	1.60	.675	.595	1.1 .42	21 8
OCP	9.09	.10	+	.006	.004		
MCP	31.51	.46	+	.168	.04		
PCP	35.49	.55	+	.242	.09		

+ less than 0.005

1 Defined in text.

2 Molal⁻¹

3 Molal⁻²

functional forms for the relationship between CO and CA, two of these describe a hyperbole and the third a quadratic. When the proper relationship has been selected, the maximum number of equilibrium constants is set by the degree of experimental error. Using the equilibrium constants obtained by this method, we attempted to reconstruct our experimental data. It was found that the reconstruction required a greater number of equilibrium constants than the experimental error indicated were significant. Sillén (25) and Rossitti and Rossitti (24) have pointed out that the precision of measurements as well as errors introduced computationally by smoothing of experimental error seldom justify more than three independent parameters. The errors introduced by forcing data to conform to a predetermined function may increase the overall error in the method. Sillén (25) introduced graphical curve fitting procedures which have been expanded in an attempt to reduce the error in similar data analysis. Rather than force the data to conform to a model, the data should be used to suggest a model.

Discussion of Results:

The extent of association of phenol is markedly greater than that of any of the substituted phenols investigated. This behavior is quite similar to that of the substituted benzoic acids (22) in that benzoic acid is associated to a larger extent than substituted acids.

The extent of association of chlorophenol isomers shows a trend that indicates that electron withdrawing groups, groups withdrawing electrons from the pi cloud of the ring, tend to diminish the extent of association and the more efficient the withdrawal, the greater is this effect. OCP shows less association than would be predicted on this basis; this might result from such factors as steric interference of the chloro-group with the formation of the hydrogen bond (4,5) or the interaction between the electronegative

chlorine and the phenolic hydrogen (6). Calculations and additional experiments are presently in progress to further define the nature and extent of these interactions.

The differences in the extent of association in the three cresols can also be correlated to the concept of varying electron density on the phenyl ring. As shown by the equilibrium constants, the order of association is ortho less than para less than meta. The methyl group is recognized as a weak electron donating group and hence might be expected to act opposite to that of the negative chloro substituent; the effect of a methyl substitution should be greatest when located either ortho or para to the hydroxyl group. As with OCP, the o-methyl substituent might interfere with the formation of the hydrogen bond. The inversion in the extent of association in the meta and para isomers from the chloro compounds is in accord with the idea that the methyl group should exert a smaller influence when located in the meta position than when in the para position. Although the association is less than that found for phenol, the trends found for meta and para substitution tend to indicate that electron donating groups serve to increase the extent of association.

Greater complexity is noted with the dimethyl substituted compounds. If the above assumption is correct, a dimeta (3,5) substitution should show the largest association followed in order of decreasing association by meta-para (3,4), ortho-meta (2,5 then 2,3), ortho-para (2,4) and finally, ortho-ortho (2,6) being the least associated. Furthermore, one would expect the 3,5 isomer to be approximately as associated as the meta isomer, the 3,5- to be similar in association to the para isomer and the 2,3- 2,5- compounds to correspond to the ortho isomer in extent of association. The 2,6- isomer, as would be expected, shows the smallest degree of association. These trends are verified by the data in Table II, however the results remain qualitative.

The behavior of phenol remains an enigma. Of all the compounds investigated, it is by far the most highly associated exhibiting association quite

similar to that found with the carboxylic acids (22). The dielectric constant, dipole moment, acid dissociation constant and absorption spectra of phenol do not show any properties unlike those of the other phenol compounds. One must, then, look for other explanations for this behavior. One such explanation that has been put forth is the formation of solid solutions (3,6,7,10,15). The criteria for the existence of a solid solution is that $R (= CA/CO)$ does not approach unity in dilute solutions. Our data indicates that the ratio does decrease in dilute solutions. Moreover, the data obtained can be regenerated (within experimental error) with the equilibrium constants shown in Figure II which describe a simple monomer-dimer-trimer equilibria. The existence of solid solutions of phenol in benzene is currently being investigated by analysis of the solid phase formed in these systems and will be reported in a subsequent communication.

Summary:

The cryoscopic behavior of phenol, positional isomers of chlorophenol and cresol, and 2,5-, 2,6-, 3,4-, and 3,5-dimethyl phenol were studied in benzene, and equilibrium constants describing this behavior in terms of association were determined for the concentration range 0 to 0.8 molal.

The results indicate that substitution of a ring hydrogen of phenol by either chlorine or methyl decreases the amount of association of the parent phenol; chloro isomers having less association than methyl isomers. The degree of association is qualitatively related to the effects of the substituents on the pi electron cloud of the phenyl ring.

FIGURE 1

FIGURE II

E_{in} = 1.35 volt Mallory mercury battery

$R_1 = R_2 = R_3$ = 500,000 ohm cermet trimpot

R_t = 100,000 ohm Veco 51A1 thermistor

O_1 = Fairchild ADO-44 operational amplifier

FIGURE III
RELATIONSHIP OF CA TO CO FOR CHLOROPHENOLS

FIGURE IV
RELATIONSHIP OF CA TO CO FOR CRESOLS
AND PHENOL

FIGURE V
RELATIONSHIP OF CA TO CO FOR DIMETHYLPHENOLS

FIGURE VI
CA-CO DATA FOR COMPARISON

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Design and Construction of an Ultrasonic Absorption Cell

The measurement of ultrasonic absorption in solutions permits the evaluation of kinetic parameters as well as parameters describing the liquid state. In this paper we describe a variable path length cell for liquid and solution work. The cell is easy to use, simple to construct, and of moderate cost.

Although a single transducer may be used to both transmit and receive ultrasound, the construction of the necessary electronic gating is difficult. Many workers thus favor two transducer design, one to transmit, the other to receive. Andreae and his coworkers (1-3) have described several cells of the two-transducer design which have been used quite successfully to determine the ultrasonic absorption in a variety of liquids. Although these cells have several unique features, they are somewhat difficult to construct and use. All glass and quartz cells have been reported (1); most of the cells currently in use, however, are fabricated of stainless steel. Extended periods of contact between the solution and metal parts of the cell may lead to contamination. Since these effects have not been fully investigated, it is desirable to minimize metallic contact.

The temperature of test solution must be maintained to $\pm 0.1^\circ\text{C}$ to reduce density gradients which may cause a refraction of the ultrasonic beam. (1, 4-6) Edmonds (4) has designed a thermostated cell which allows stirring of the sample with only a small increase in the volume of the solution required for a measurement. It is, at times, necessary to control the atmosphere above the test solution, and cells which permit this have been described. An ultrasonic cell should be compatible with a wide variety of solvents, use a minimum amount of test solution and be relatively simple to assemble, align and clean.

Most liquid ultrasonic cells use a variable path length interferometric design, maintaining the upper and lower transducers parallel while the path length is varied. A change in the degree of parallelism as a function of

distance will introduce error in the measurement. It is assumed in making pulse-echo measurements that the power of the ultrasonic wave (P) is related to the path length (x) by the equation $P_x = P_{x_0} \exp(-ax)$ where the absorption coefficient, a , is only a function of the material in the path of the ultrasound. If the transducers are not exactly parallel, the path length, and hence the power, varies across the face of the receiving transducer and a signal with a large half-width will result. The maximum of the observed signal will then be a function of the area of the transducer as well as the distance separating the two transducers. It is essential that the orientation of the transducer faces remains fixed as the path length is changed.

The necessary precision of axial movement is usually accomplished by careful design and machining of the parts involved in the movement. The cell presently in use in this laboratory (Figure 1) is an adaptation of that reported by Andreae and coworkers (3). The precision axial movement is found in the fit of the plunger and barrel of a commercial individually ground glass 50 cm³ syringe, thus obtaining precise machining and all inert materials in construction.

Experimental Section

Fabrication of the Cell:

The plunger and barrel of a 50 cm³ syringe are clamped together (plaster block) and the tip of the syringe and end of the plunger simultaneously cut off with a glass saw. The end of the plunger and barrel are then simultaneously ground flat and parallel relative to each other using standard optical grinding techniques. The barrel and plunger are then separated from each other and a small hole is drilled into the lower part of the barrel for attachment of the side reservoir.

An optical flat is cemented to the lower part of the barrel. Onto the bottom of this flat the lower transducer is cemented. 0.50 inch, x-cut, overtone polished quartz transducers supplied "coaxially plated" by Valpey Corporation were found to be ideal. The upper transducer is cemented to the surface of an optical flat which had been lapped to 0.002 inch less than the bore of the syringe barrel. Micro coaxial cable is attached to the transducer, the optical flat is cemented to the flat end of the plunger. Assembly is facilitated by allowing the epoxy resin to harden while the upper assembly is held together in a close fitting teflon jig.

The optical flat cemented to the barrel may be of any desired thickness to insert necessary time delay in the ultrasonic pulse. Current cells use flats of 0.125 to 1.0 inches thick. After the optical flat and transducer have been cemented to the barrel, leads are connected and the transducer is covered with a machined aluminum cover. Finally, the solution reservoir is cemented to the side of the barrel allowing a path of solution from the reservoir to the cell. The cap for this reservoir is fitted with an opening which allows the introduction of an inert atmosphere.

Cell Holder:

In addition to the cell described above, additional apparatus is required to vary the cell path length in a precise manner. This movement must be precise enough for small, accurate path length changes to be effected and also allow for the measurement of those changes. The apparatus used for this is shown in Figure III.

The movable aluminum head rides on two one-inch stainless steel rods. Vertical movement is accomplished by a 32 turns per inch machined screw which has double bearings on the top support and a single bearing at the base. The screw turns in a brass sleeve which has a thread cleaning device located at both the top and bottom of the movable head. The base is an eight by eight by two inch aluminum plate. The screw is turned by an AC synchronous motor connected to the screw assembly by a short section of flexible cable. The movable head assembly holds a 0.75 inch brass rod which is connected to the top of the syringe plunger with a small universal joint. The syringe barrel is attached to one of the guide rods with a standard universal ring clamp.

Path length changes are measured with a Federal D8IS tubular dial gauge, with an precision of 0.001 inch. The dial gauge is attached to one of the guide rods; the plunger of the dial gauge rests on a bracket attached to the head piece. It is possible to reproduce path lengths to a greater degree of precision than can be read on the dial gauge, i.e., somewhat better than 0.001 inch.

Temperature Control:

Temperature control of the test solution is achieved by the immersion of the entire cell assembly into a silicone-oil bath. The temperature of this bath is maintained by pumping controlled temperature water from a Haake Model FJ water bath through a copper coil placed in the oil. A shielded AC induction motor and stirring apparatus helps to maintain homogeneity of temperature throughout the oil. Experience has shown that this type of temperature control is superior to a water jacket surrounding the cell. A thermistor temperature measuring apparatus capable of detecting

a change of 0.001°C. showed maximum deviations of 0.005 °C at 25°C in the temperature of the bath over a period of several hours.

Chemicals:

Epoxy Resins: Proper cementing is important to obtain good transmission and structural strength. We have found the Epon resins supplied by Shell Chemical Corporation to be most satisfactory although others might work as well. Depending upon the degree of rigidity of bond required, different amounts of resin, hardener and elasticizer were mixed, heated to 65-70°C, and degassed under vacuum. After cleaning with trichloroethylene, the two quartz surfaces are placed together using a minimum amount of the mixed resin, the joint subjected to two pounds dead weight and cured at 100°C for twenty-four hours. Omission of the elasticizer from the blending may formulate a resin that is quite rigid, so much so that surface ships in the quartz might result as the piece is cooled.

Test Solvents:

Water: The water used for the initial tests were first distilled, and then passed through two ion exchange beds. It was degassed under vacuum immediately before use and then transferred into the cell under Argon.

n-Hexane: n-Hexane was obtained from Signal oil and Gas Company and as supplied was 95% pure. It was fractionally distilled from Linde 4A Molecular Sieves twice before use. Gas-liquid chromatography (GLC) showed the purity to be 99.8 weight per cent.

Benzene: Eastman reagent grade benzene, thiophene free, was distilled three times from Linde 4A Molecular Sieves, the middle third being retained from each distillation. GLC indicated 99.6 weight percent purity.

Cyclohexane: Practical grade cyclohexane was fractionally distilled three times from Linde 4A Molecular Sieves. GLC analysis showed 98.7 weight percent purity. All of the organic liquids were stored and used under dried argon.

Apparatus:

The equipment used for generation and detection of the ultrasonic energy is shown schematically in Figure II. The pulsed oscillator, Arenberg Ultrasonic Laboratory, Model PG-650C, is operated in the pulsed mode with a 400 volt peak to peak pulse at a repetition frequency of 100 Hz with pulse length of approximately 10usec. Frequency drift was found to be less than 0.01% per hour after warm up. The frequency of the RF pulse was determined as indicated below and agreed within 1% of the dial settings. The matching network for the transmitting transducer is a standard π section with two continuously variable capacitors of 13.5 pfd to 320 pfd, Hammurlund type MC-325-M, and an air-coil inductor of approximately 32.5 microhenries (maximum). The coil was constructed from 30 turns of number 12 gauge tinned copper wire wound 8 turns per inch on a 2 3/4 inch diameter and is tapped every three turns to a ceramic cotary switch. The attenuated reference signal is obtained from a Hewlett Packard 608E VHF signal generator. This signal generator is capable of external pulse modulation from the time delay trigger of the AUL PG-650C. A precision attenuator built into the 608E is accurate to 0.2 db relative, 1.0 db absolute.

The signal from the receiving transducer is fed to the preamplifier, AUL, Model PA-620B, into a wide band amplifier, AUL, Model WA-600E, similar in design to that discussed in the MIT Radiation Laboratory Series (11) and finally is lead into a Tetranix 535 Oscilloscope equipped with a 53B amplifier. The sweep is triggered with a synchronizing pulse from the PG-650C.

Results and Discussion:

Measurement of Frequency:

For most accurate work, it is necessary to know the frequency of the RF pulse. This is relatively difficult to measure using standard frequency measuring techniques, since the pulse train is not sufficiently long to make a comparison with a known CW source. We have found it possible to estimate the frequency of the pulse train using the experimental arrangement shown in Figure IV. The pulsed r.f. is mixed with a c.w. source of approximately equal amplitude. The result of these signals will be the sum and difference frequencies within the output envelope. If the difference frequency is within the band pass of the detector and video circuits, sine waves will appear on the pulse envelope whose position is determined by the relative phase. At "zero beat", there will be one single straight line across the pulse whose amplitude is a function of phase. The random phase relation helps to emphasize any residual difference and limits the accuracy of the method.(12) Once this "zero beat" has been determined, the frequency of the c.w. source is determined using standard frequency measuring techniques.

The accuracy of this method is limited by the pulse length, the minimum slope of the line that can be detected along the top of the envelope and the frequency stability of the CW source. Frequency modulation within the pulse,

power supply variations, trigger jitter and transient effects will increase the lower limit of phase detection and hence the accuracy. Using this method, the frequencies used in this study have been measured to within 10KHz, over the range of 10MHz to 40MHz.

Accuracy:

It is somewhat difficult to make statements about the accuracy of the measurements. The variation in previously published values makes the comparison of data as a criterium for accuracy impossible. The values of α/f^2 determined for the four neat liquids shown in Table I indicate good agreement within the range of literature values. The error in calibration of the electronic apparatus also limits the determination. Based on estimates, we feel that there is an average of $\pm 3\%$ uncertainty in α/f^2 . The accuracy of α/f^2 at low absorption values is limited by the total attenuation due to changing path length, Andrae (1-3) states that a 30dbm change is desirable, thus limiting the variety of liquids which may be used with this cell, since the path length available is only 10 cm. We feel that 30dbm is desirable, but not essential as witnessed by the values of α/f^2 determined in water using a total path length change of 5 cm.

The largest error in the measurement arises from the non-reproducibility of successive pulse trains, causing a rapid fluctuation in the pulse envelope and a corresponding inability to discern the true height of the pulse. This problem is most likely due to several instrumental factors, not originating in cell design, and should be reduced by signal averaging techniques; we are currently investigating this possibility. Other errors result from the combined effects of temperature instability, frequency measurement, and measurement of path length changes.

Discussion:

To precisely evaluate absorption coefficients of liquids it is necessary to achieve and maintain the alignment of the transducers while the path length is accurately incremented. If the plunger is maintained in the position, relative to the barrel, in which grinding was accomplished, the orientation should not vary during the measurement. It is desirable to achieve and maintain orientation to a small fraction of the acoustical wave length (1). Of primary importance is the maintenance of alignment provided initially the transducers are very nearly parallel. With cells in use in this laboratory, rotation of the plunger in the barrel brings about amplitude changes of approximately 0.01% indicating a high degree of relative parallelism. Due to the fit of the plunger in the barrel, it was impossible to obtain any lateral movement discernable as an amplitude change.

When the transit time of the ultrasound is approximately the same as the pulse length, it becomes necessary to insert time delay into the system. Time delay may also be necessary to allow the amplifier to recover from the cross talk pulse always present (1,4) before the actual pulse arrives at the receiving transducer. In either case, the time delay is experimentally introduced by means of a length of fused quartz rod, ground optically flat on both ends perpendicular to the main axis. In this cell, the necessary time delay may be inserted by either increasing the thickness of either flat, or by a delay line, coupled with silicone oil, placed on either flat. If either flat is thick enough to allow the oscilloscope to differentiate the peaks resulting from successive reflection within the flat either a peak broadening or a group of peaks of decreasing amplitude can be seen in the scope trace. Peak broadening is lessened by decreasing flat thickness. The normal experimental case is for the

transducers to be in direct contact with the solution, in which case only the decay in the transducer need be considered. If time delay is required, the transducer is isolated from the solution by a long, two to three inch, fused quartz delay rod. In the case of our cell with a 0.5 inch flat on the bottom, a chain of peaks were noticed; for a 0.25 inch thick flat, only a peak broadening was observed. Neither the peak broadening or the group of peaks varied with changing path length, and the absorption coefficient determined in either cell agreed to within 2%. If care is taken, no instrumental effects on the absorption coefficient will be introduced.

Summary:

This easily constructed ultrasonic absorption cell meets all the mechanical requirements of an absorption cell (1). The all glass and quartz construction allow the use of the cell with most liquids and solutions. Approximately 50 ml. of test solution are required. If 5dbm signal change is considered minimal the 10 cm path length available allows the cell to be used with liquids having absorption coefficients of 0.5dbm/cm or higher. The cell may be easily thermostated and atmospheric contamination controlled. Even though the cell is of low cost, easy to clean and fill and minimizes alignment problems, results obtained with this cell are in good agreement with those previously reported.

TABLE I

Solvent	T(°C)	f(MHz)	$\alpha/f^2 (\times 10^{-17} \text{ sec}^2/\text{cm})$	T(°C)	f(MHz)	$\alpha/f^2 (\times 10^{-17} \text{ sec}^2/\text{cm})$	Ref.
	This Investigation			Literature Values			
benzene	24.9	9.02	998	6	50	840	8
	25.0	13.00	941	* 25	50	920	8
	24.8	15.00	1019	24.4	104.0	849	9
	25.0	15.00	943	24.9	148.1	800	9
	25.0	17.00	946	25.0	192.5	775	9
n-hexane	24.9	9.02	55.8	22.7-24.9	32	70	2
	24.9	15.00	56.6	22.7-24.9	71	61	2
	24.9	20.75	56.0	25.0	107.5	60.4	9
	24.9	27.00	52.8	25.0	148.0	58.5	9
	24.9	33.20	50.6	25.0	191.5	56.7	9
	24.9	39.00	51.8				
Cyclohexane	25.0	9.00	317	20	20	153	7
	25.0	11.00	288	30	20	146	7
	25.0	13.00	276	25	107.5	192	9
	25.0	15.00	232	25	148.0	190	9
	25.0	17.00	216	24.8	192.3	182	9
	25.0	19.00	207				
	25.0	21.0	202				
	25.0	23.0	209				

$$* \alpha/f^2 (\times 10^{-17}) = \frac{940 \times 10^{-17}}{1 + (f/550\text{MHz})^2} + 50 \times 10^{-17}$$

** reports $f_R = 7.44 \text{ MHz}$

TABLE I

Solvent	T°C	f	$\alpha/f^2 \times 10^{17}$	T	$\alpha/f^2 \times 10^{17}$	Ref
Water	25.0	9.16	79.3			
	"	13.00	60.3	15	24.0	5
	"	15.01	35.0	20	25.3	5
	"	17.00	29.7	**15	29.6	10
	"	19.00	29.6			
	"	21.00	21.5			
	"	23.00	22.7			
	"	25.00	22.8			
	"	27.00	22.9			
	"	29.00	21.3			
	"	33.00	24.4			
	"	39.20	24.8			
	"	45.01	24.8			
	"	51.00	25.0			
	"	57.00	24.9			
	"	63.00	25.0			
	"	69.00	24.9			

FIGURE I

FIGURE II

FIGURE III

FIGURE IV

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Extended Hückel Molecular Orbital Calculations on a Series of Phenols

This communication reports preliminary results of an extended Hückel calculation on phenol, the chlorophenols, the cresols and four of the dimethylphenols. Data reported here consists of total energies of the molecules, net charge at each atomic center, the net charge dipole and the energy of the electronic transition from the highest filled molecular orbital to the lowest unfilled molecular orbital. Calculations have also been made on two possible forms of the phenol dimer; the results, however, require further verification before definite conclusion can be reached concerning the theoretically most stable configuration of the dimeric species.

The extended Hückel method (EHMOM) was initiated by Hoffmann (1,2,3,4) and consists of approximating the total electronic wave function as an inner-shell nonbonding fraction and a valence-shell fraction. A Löwdin basis set of Slater-type orbitals are used to form the molecular orbitals. The matrix elements of the Hartree-Fock operator are all assigned explicit non-zero values, the diagonal elements being the negative of the valence state ionization potentials associated with the proper basis atomic orbitals; off-diagonal elements were approximated by appropriate methods. Input data required were the geometry of the molecule, orbital coefficients for the valence-state orbitals and ionization potentials (experimental) for the valence state orbitals. The geometry of the hydrogen bond in dimeric phenol was taken from the work of Wehrhahn and Stackelberg (5). All other geometries were the "standard geometries" reported by Pople and Gordon (6). Hoffman and Grimison (7) give indications of the accuracy and reliability of the predictions based upon the results of similar calculations. It is their opinion that trends may be correctly inferred from the results; however, the results often seem quantitative incorrect.

The results of these calculations have been used to estimate net charge densities, net charge dipole moment vectors and magnitudes of the dipoles, electronic transition energies and total molecular energies. These data are tabulated (Table 1) and illustrated on the accompanying figures. Included in Table 1 are previously reported experimental values for the same parameters.

Dipole moments were calculated by the method of Daudel, Lefebvre and Moser (8); however, no mixing polarization of pi polarization was considered. Methods for including these terms have been described (8,9) but have not been completed for all molecules investigated. Net charge densities for each atom are shown on the accompanying figures as well as the magnitude and orientation of the net dipole moment vector which is represented on a relative basis.

Acid dissociation constants for the phenol molecules were calculated on the basis of the modified Hammett equation (10). It should be noted that these values were obtained using Hammett sigma constants which were estimated in protic media.

Discussion:

A cursory examination of the results shown in Table 1 indicates that EHMOM calculations do not allow for prediction of experimentally determined dipole moments. Inclusion of the electronic polarization terms in the Daudel treatment may yield more valid results. However, it has been reported (6,7,9,16,17) that pi electron density calculations seldom give meaningful dipole moments even when the electronic configuration of the core structure is included. Methods recently introduced by Pople and Segal (9) which use complete neglect of differential overlap (CNDO) seem to give values of dipole moments which are in reasonable agreement with experiment but even these methods, like the EHMOM, predict only trends and not quantitative results. Several workers (15,18,19,20) have suggested correlations between acid strengths or dipole moments and degree

of association and it is hoped that the results of these calculations will lead to a clarification of these theories.

The EHMOM gives a more reliable measure of pi electron distribution in these systems than the CNDO method and will be used in an attempt to strengthen the ideas put forth in the cryoscopic section of this report. In essence, the data indicates the main stabilizing factor in hydrogen bonding in phenols is the pi-pi interactions of the phenyl rings. Substituents on the ring will vary the amount of distortion in the pi electron cloud in a manner that depends upon the degree of interaction between pi orbitals of the substituent and the pi electrons of the ring. That is, the degree of association will depend on the location of the substituent and the ability of the substituent to add to or to diminish the pi electron cloud of the phenol.

Although the interaction of the electronegative oxygen and the hydrogen of a second phenol may remain important, a more complete explanation of associative behavior might be gained through this explanation. Infrared spectral changes, cryoscopic behavior and ultraviolet spectral properties can all be explained as changes in the pi electron distribution of the benzene ring. Cryoscopic data collected in this laboratory bear out these ideas, at least in a qualitative fashion.

Preliminary calculations have been made for two possible geometries of the phenol dimer. Indications are that EHMOM calculations should be quite successful for the prediction of that form of the dimer that is most energetically favored.

Acknowledgement:

The calculations reported in this communication were done at The Computing Center of Colorado State University (CDC 6400 computer) with the valuable assistance of Professor C. M. O'Donnell. We would like to thank Professor O'Donnell for his stimulating discussions.

TABLE 1

Name	% association	$\hat{\mu}_Q$ calc Debye	$\hat{\mu}$ found Debye	References	$\Delta\epsilon$ calc (ev)	E_T calc (ev)	pKa calc	pKa found	References	dielectric const of pure liquid	References
phenol	84.75	4.54	1.36 1.45 1.7*	15 11 12	2.784	613.179	9.92	10.00	14	9.78 ₆₀	11
34DMP	21.81	3.38			2.831	804.88	10.46	10.32	10		
35DMP	19.35	6.64			3.133	805.263	10.23	10.15	10		
25DMP	31.95	5.26			3.801	804.52	10.37				
26DMP	14.51	7.30			3.249	803.86	10.50	10.59	10		
OC	16.27	5.65	1.41 1.4	15 13	2.882	708.68	10.21			11.5 ₂₅	11
MC	23.78	3.50			2.935	709.22	10.08	10.09	10	11.8 ₂₅	11
PC	18.56	3.50	1.57 1.6	15 13	2.558	708.94	10.30	10.26	10	9.9 ₅₈	11
OCP $\theta=0$		4.57			2.815	722.20					
OCP $\theta=90$	9.09	5.29	1.24	11	3.058	721.86	11.44			6.31 ₂₅	11
OCP $\theta=180$		4.88			2.815	722.14					
MCP	31.51	4.50			2.953	723.96	9.09	9.02	10		
PCP	35.49	4.34	2.11	11	2.446	723.84	9.41	9.38	10	9.47 ₅₅	11

* solution value

PHENOL

3,5- DIMETHYLPHENOL

3,4-DIMETHYLPHENOL

2,4-DIMETHYLPHENOL

2,6-DIMETHYLPHENOL

ORTHOCRESOL

METACRESOL

PARACRESOL

ORTHOCHLOROPHENOL

$\theta = 90$

ORTHOCHLOROPHENOL

$\theta = 180$

METACHLOROPHENOL

PARACHLOROPHENOL

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The following additional apparatus has been purchased:

1. Two "stub lines" at \$30.00. These will be used for variable termination of the RF field in order to minimize reflection losses at the transducer-RF cable interfaces.
2. Ten operational amplifiers (\$200); used for the construction of three additional temperature measuring circuits.
3. Two constant temperature baths (\$800), Haake, Model FJ, used for temperature control on the ultrasonic apparatus and on the vapor pressure assembly.
4. Various integrated circuits and associated apparatus for ultrasonic velocity apparatus.

Plans for Future Work:

Thermodynamic Association Studies:

Effort will be directed along four lines:

1. The complete analysis of all cryoscopic data previously collected will be completed. Cryoscopic measurements have been extended to the solvent cyclohexane; the series of compounds that have been studied are shown in Table 1. The n-aliphatic compounds will be used in a comparison study of the relative strengths of various groups involved in hydrogen bonding. When completed, this series will include all aliphatic hydrocarbons from C_6 to C_{12} , all alcohols of the type $R-OH$ from C_6 through C_{12} , all normal aliphatic acids from C_6 through C_{12} . A series of compounds are being studied in an attempt to clarify the relationship between dipole moment and association. These compounds were selected on the basis of having no hydrogen attached to any atom other than carbon, i.e., no "acidic" hydrogen to become involved in hydrogen bonding. In this way, we hope to be able to clearly see the effects of dipole-dipole interactions. This investigation will include the compounds sulfolane and dimethylsulfate, already studied, and cyclic ketones such as cyclopentanone and cyclohexanone, and several of the cyclic ethers, dioxane, diethyl ether and diphenyl ether. In addition to these studies, it is planned to commence a study of cryoscopic behavior of carboxylic acids; several series of these compounds have been studied such as acetic acid and its three chloro-derivatives as well as a series of compounds related to benzoic acid.

Several other solvents will also be studied. At present, another cryoscopic assembly is being fabricated to study association behavior in cyclohexane (m.p. -45), n-hexane (m.p. -95) and carbontetrachloride

(m.p. -22.9). Almost no cryoscopic studies have been reported in these solvents and the results would indeed be significant. Once the compounds reported above have been studied, work on this phase of the investigation will commence.

Currently data is being collected on the formation of solid solutions utilizing GLC analysis. Initial indications verify the assumption made in the cryoscopic section; phenol appears not to form solid solutions under the conditions that our measurements are made.

TABLE 1

Compounds Studied Cryoscopically to Estimate Association

Solvent	<u>Benzene</u>	<u>Cyclohexane</u>
	acetic acid	<u>o</u> -chlorophenol
	chloroacetic acid	<u>m</u> -chlorophenol
	dichloroacetic acid	<u>p</u> -chlorophenol
	trichloroacetic acid	<u>o</u> -cresol
	benzoic acid	<u>m</u> -cresol
	cis-cinnamic acid	<u>p</u> -cresol
	cyclohexane	phenol
	<u>p</u> -methoxyphenol	acetic acid
	<u>o</u> -methoxy phenol	dichloroacetic acid
	<u>o</u> -phenylphenol	trichloroacetic acid
	<u>p</u> -phenyl phenol	dodecane
	sulfolane	dodecanol
	hexane	hexane
	dimethylsulfate	heptane
	octane	octanoic acid
	octanoic acid	
	dodecane	
	dodecanol	
	aniline	
	<u>o</u> -methylaniline	

Note: Data analysis will appear in the next progress report.

Differential vapor pressure measurements will be completed at several temperatures in the solvents benzene and cyclohexane. The same series of compounds as reported in the cryoscopic section are now under investigation. These measurements have been slowed by a lack of personnel to operate the instrument. A recently acquired undergraduate problem student will assist during the latter half of this contract as well as in the summer of 1969.

Ultrasonic Studies:

The ultrasonic absorption apparatus has been in operation for several months. Initial studies complete the ultrasonic absorption of sulfolane over the frequency range of 10 to 75 MHz at several different temperatures. The interesting results will probably be explained on the basis of relaxation in viscous media. Aqueous solutions of MnSO_4 and MgSO_4 have been studied at three different concentrations and a single temperature. The relaxations observed in these well characterized systems will be used to determine the applicability of computer analysis of relaxing systems IN ANTICIPATION OF MORE COMPLETE RESULTS FROM THE PHENOL SYSTEMS.

Due to the extremely high absorption of benzene solutions, the initial solvent used for the phenol systems has been either cyclohexane or chlorobenzene. These investigations will be extended to benzene solutions, however the frequency range will be considerably smaller in benzene than in the other solvents.

During the remainder of this contract, a major portion of the effort will be expended to extend these ultrasonic studies. Further automation of the system will be attempted in an effort to speed data collection.

Work has begun again on the direct ranging apparatus for velocity measurements. Preliminary data should be included in the next portion of the report.