Summary

1. The solubility of thallous chloride has been determined in alcohol-water mixtures of 10, 30, 40, 50 and 60% alcohol by weight, and with added potassium chloride. The densities of these solutions are given.

2. From these data, the activity coefficients of thallous chloride in each of the solvents have been calculated over a range of ionic strength. A correction for incomplete dissociation has been applied to the measurements.

3. The behavior of thallous chloride as a function of the dielectric constant has been compared with the predictions of the Born relation, and found to conform as to the order of magnitude, but shows deviations from the theory which increase as the dielectric constant decreases.

4. It is pointed out that these data permit the comparatively easy evaluation of the dissociation constant of a partially dissociated electrolyte.

COLUMBUS, OHIO RECEIVED OCTOBER 7, 1940

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, THE OHIO STATE UNIVERSITY]

Spectroscopic Evidence for Intermolecular Hydrogen Bonds between Phenylacetylene and Various Organic Solvents

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In 1935 Kumler[3] suggested that the association of hydrogen cyanide is due to a $—\mathrm{C}—\mathrm{H} \leftarrow \mathrm{N}$ bond. The known examples of hydrogen bonds involving the —C—H linkage have been extended during the past few years by molecular polarization,[4] solubility and heat of mixing studies,[5] as well as by measurements of infrared absorption spectra. It has been found that in the haloforms and some other halogenated hydrocarbons[5,6] the hydrogen bonded to carbon is sufficiently active to form hydrogen bonds with organic oxygen and nitrogen compounds such as ethers, ketones, esters, amines and amides. Infrared spectroscopic measurements[7] have verified these results in the case of the haloforms, chloroform and bromoform.

Recent solubility and heat of mixing experiments[8] provide evidence that acetylene and phenylacetylene may act as proton donors in the presence of the organic solvents mentioned previously. We have undertaken the researches reported here to ascertain whether electron-donor solvents such as amines and ethers produce in the acetylenic CH of phenylacetylene perturbations which may be attributed to hydrogen bonding. If any CH group in phenylacetylene should donate its proton, it would probably be the CH joined through the triple bond to the remainder of the molecule, as this is the CH group which has the strongest acid properties.[9] Fortunately the $\equiv\mathrm{C}—\mathrm{H}$ vibrational band occurs in a region sufficiently removed from that of the ordinary aromatic and aliphatic CH bands that it can be easily separated from them.

Experimental.—The instrument, cells and general technique used have been described.[10] The cell thickness was 0.002 cm.; the effective slit width was 0.01 μ. The instrument was calibrated before and after the determination of each band, and as an added precaution each band was checked at least twice. The shifts are accurate to 0.01 μ; the intensities may be somewhat in error due to the difficulty of reproducing the thickness of the very thin cells. One to one volume mixtures were used for all determinations.

Results and Discussion

The experimental data are plotted in Figs. 1–3. The solid lines represent the experimentally determined transmission curves; the broken lines represent the theoretical transmission curves which the mixtures should give if there were no interaction between the components of the mixture. The method of calculation of the theoretical curves has been described elsewhere.[11]

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(3) Kumler, THIS JOURNAL, **57**, 600 (1935).

(4) Earp and Glasstone, *J. Chem. Soc.*, 1709 (1935); Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).

(5) Zellhoeffer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938), and subsequent papers.

(6) Marvel, Copley and Ginsberg, *ibid.*, **62**, 3109 (1940).

(7) Gordy, *ibid.*, **60**, 605 (1938); *Nature*, **142**, 831 (1938); *J. Chem. Phys.*, **7**, 163 (1939); Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2528 (1938).

(8) Copley and Holley, *ibid.*, **61**, 1599 (1939).

(9) Conant and Wheland, *ibid.*, **54**, 1212 (1932).

(10) Gordy and Stanford, *ibid.*, **62**, 497 (1940).

(11) Gordy, *Phys. Rev.*, **50**, 1151 (1936).

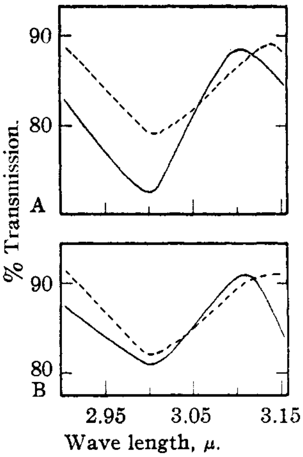

Fig. 1.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.002 cm.) of phenylacetylene with: A, carbon tetrachloride; B, monochlorobenzene.

Transmission curves for mixtures of phenylacetylene with carbon tetrachloride and with monochlorobenzene were measured to determine whether perturbations of the $\equiv$C—H band occur in solvents where hydrogen bonding with the phenylacetylene would not be expected. The results are plotted in Fig. 1. Inspection of the curves shows that no such perturbations occur with these solvents, since the minima for the experimental and theoretical curves all fall at the same wave length.

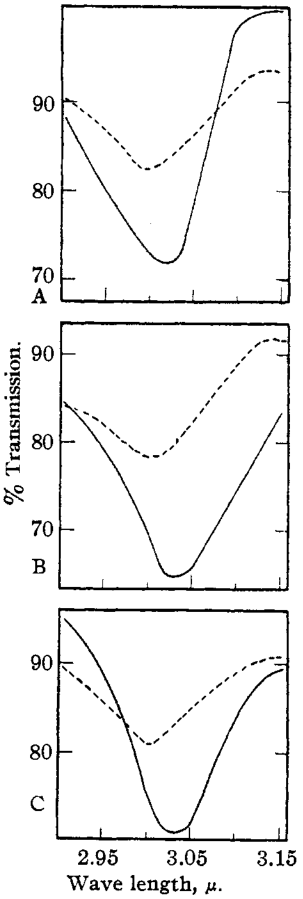

Fig. 2.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.002 cm.) of phenylacetylene with: A, acetone; B, triethyl phosphate; C, dioxane.

The results for mixtures of phenylacetylene with three oxygenated solvents, acetone, dioxane, and triethyl phosphate, are plotted in Fig. 2. The shifts for these compounds are listed in Table I. In all three cases the minimum in the band is shifted to slightly longer wave lengths, and the intensity of the band is increased. Although the shifts were small, they were reproducible. It is significant that shifts have been found in each case where hydrogen bonding could possibly occur and no shift where such bonding would not be predicted. Some, however, may not choose to define as hydrogen bonding these weak interactions between proton-donors and proton-acceptors.

The bands obtained for mixtures of phenylacetylene with six organic nitrogen compounds are plotted in Fig. 3. The shifts are listed in Table I. The minimum in the theoretical curve for the phenylacetylene–piperidine mixture is

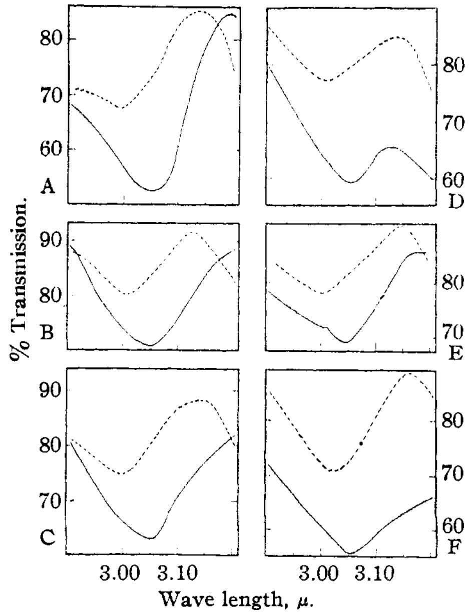

Fig. 3.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.002 cm.) of phenylacetylene with: A, N,N-dimethylacetamide; B, N,N-dimethylformamide; C, pyridine; D, dimethylcyclohexylamine; E, quinoline; F, piperidine.

shifted slightly (0.01_5 μ) from the position of the ≡C—H band of phenylacetylene (Figure 3F). This shift apparently is due to the fact that piperidine has a shallow band with its center at 3.04 μ. This band pulls the theoretical curve over to slightly longer wave lengths. However, the difference between the theoretical and experimental curves is sufficient to indicate hydrogen bonding.

TABLE I

Phenylacetylene plus	Position of CH band (μ)	Shift (μ)	Shift in —OD band[a] (μ)
Carbon tetrachloride	3.00_0		
Monochlorobenzene	3.00_0	0.00_0	0.02
Acetone	3.02_0	$.02_0$	.14
Dioxane	3.02_7	$.02_7$	.14
Triethyl phosphate	3.03_0	$.03_0$	.17
N,N-Dimethylacetamide	3.04_3	$.04_3$	.18
N,N-Dimethylformamide	3.04_0	$.04_0$	.17
Pyridine	3.04_0	$.04_0$	.27
Dimethylcyclohexylamine	3.05_0	$.05_0$	.28
Quinoline	3.04_3	$.04_3$	.29
Piperidine	3.04_7	$.04_7$	.37

[a] Gordy, *J. Chem. Phys.*, **7**, 93 (1939); Gordy and Stanford, *ibid.*, **8**, 170 (1940); *ibid.*, paper in press.

The experimental curve for the quinoline–phenylacetylene mixture shows two minima, one at 3.00 μ; the second at 3.04 μ. From this behavior it is evident that in a one to one volume mixture of these substances, sufficient phenylacetylene remains in the unbonded condition to give a definite minimum in the transmission curve. The curves for mixtures of phenylacetylene with pyridine, dimethylcyclohexylamine, N,N-dimethylacetamide, and N,N-dimethylformamide indicate hydrogen bonding because they are shifted to longer wave lengths and their intensities are considerably increased. The shifts for the nitrogen compounds are, on the average, about twice as great as those for the oxygen compounds, indicating that the bonds formed to nitrogen are stronger than those to oxygen.

The infrared investigation therefore supports the work of Copley and Holley.[8] It is unfortunate that more heat of mixing data are not available for comparison. Two solvents, acetone and N,N-dimethylacetamide, were used in both researches. Acetone with a heat of mixing of 200 cal./mole at a mole fraction of 0.5 shifts the ≡C—H band of phenylacetylene 0.02 μ; N,N-dimethylacetamide with a heat of mixing of 644 cal./mole at a mole fraction of 0.5 gives a shift of 0.04 μ; hence it is seen that the same order of strengths of hydrogen bonding is indicated by both methods.

The shifts in the ≡C—H band follow essentially the same order as shifts in the —OD band of CH_3OD in these solvents. The shifts for the —OD band are given in Column 3, Table I. The discrepancies are no greater than would be expected from a consideration of the great differences in strength of the bonds and the magnitude of the possible experimental error. It should be remembered that when the shifts are small, slight variations in the electron–donor power may cause differences in shift which are not detectable due to the error involved in the method. Variations which would be detected with CH_3OD (shifts of the order of 0.1 μ) may not be detected with phenylacetylene (shifts of the order of 0.01 μ).

The authors wish to express their appreciation to Dr. H. H. Nielson and Dr. Alpheus W. Smith for the use of their equipment and for their constant interest in the work, and to Dr. M. J. Copley for suggesting the problem.

Summary

1. Infrared absorption measurements have been made on mixtures of phenylacetylene with carbon tetrachloride, monochlorobenzene, acetone, dioxane, triethyl phosphate, pyridine, piperidine, quinoline, dimethylcyclohexylamine, N,N-dimethylacetamide, and N,N-dimethylformamide.

2. It has been found that the acetylenic hydrogen of phenylacetylene forms weak intermolecular hydrogen bonds with the organic oxygen and nitrogen compounds studied.

3. The magnitude of the shifts shows that the hydrogen bonds to nitrogen are stronger than those to oxygen.

4. It was found that the shifts for the various solvents are in essentially the same order for both the —OD band of CH_3OD and the ≡C—H band of phenylacetylene.

COLUMBUS, OHIO RECEIVED DECEMBER 31, 1940