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GRADUATE COLLEGE

A SPECTROSCOPIC INVESTIGATION OF ASSOCIATION EQUILIBRIA IN CARBOXYLIC ACIDS

A DISSERTATION

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Norman, Oklahoma

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A SPECTROSCOPIC INVESTIGATION OF

ASSOCIATION EQUILIBRIA IN CARBOXYLIC ACIDS

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A SPECTROSCOPIC INVESTIGATION OF ASSOCIATION EQUILIBRIA OF CARBOXYLIC ACIDS

CHAPTER I

INTRODUCTION

During the last few years a great deal of work has been carried out in order to understand the properties and nature of the hydrogen bond. Between the two extremes of primary bonding between atoms and the usual van der Waals attractive forces between molecules there are interactions of intermediate energy which are known as hydrogen bonds. Hydrogen bonds may be considered to be primary links between atoms, but the relative weakness of the interaction gives these bonds distinctive properties. Pimentel and McClellan in their book "The Hydrogen Bond" have presented the following operational definition for the associative interaction known as the hydrogen bond.

"A hydrogen bond exists between a functional group A - H and an atom or group of atoms in the same or a different molecule when

a) there is evidence of bond formation

b) there is evidence that this new bond linking

A - H and B specifically involves the hydrogen atom already bonded to A. There are many types of physical measurements that give information relative to part a) of the definition, but only a very few relative to part b). It is in reality b) that distinguishes the hydrogen bond from most other types of Chemical Interaction."[29]

The importance of the hydrogen bond to the field of chemistry can hardly be overestimated. Hydrogen bonding can account for many of the properties of water and is of extreme importance in protein structure. Also deviations from ideality of solutes in non-polar solvents may often be traced to hydrogen bonding.

There are many methods available for determining the existence and extent of hydrogen bonding. These techniques may be conveniently arranged into the following general categories:

A) Electrical methods C) Solution studies

B) Vapor phase studies D) Spectroscopic methods

Two of the electrical methods in wide use for studying the hydrogen bond are dipole moment and conductance measurements. Since the hydrogen bond is polar, any tendency toward this type of bonding would increase the dipole moment of the A - H bond by the displacement of the hydrogen atom, leading to large changes in the dielectric constant. The very high dielectric constant of water is due to polymers formed through the mechanism of hydrogen bonding. Other molecules with dipole moments of the same order of magnitude, which however, do not have any tendency toward hydrogen bonding, have very much smaller dielectric constants. Davies[11] and Pimentel[30] give a review of the experimental techniques and findings using this type of measurement.

The conductance of systems where hydrogen bonding is known to occur which results in chain like polymers is usually much higher than in cases where hydrogen bonding is impossible. These observations can be rationalized if the mechanism of conductance includes the transfer of a proton along the hydrogen bonded polymer chain.

Vapor phase studies make use of the fact that hydrogen bonded substances show a larger deviation from the ideal gas law than do non-associating substances. Evaluation of the virial coefficients of the equation of state are used to measure the extent of association in gaseous systems. Vapor density methods can be used to determine apparent molecular weights which in turn can be used to calculate the degree of association in the gaseous state.

Cryoscopic or freezing point depression studies have been used to determine the amount of hydrogen bonding in a given solvent. The freezing point lowering is proportional to the apparent molal concentration of the solute. A knowledge of this quantity can be used to calculate the extent of association in solution. Vapor pressure studies of binary mixtures can also be used to yield data showing that hydrogen bonding is present in solution; however, in general this technique can only be applied for the qualitative detection of hydrogen bonding. Mixtures of hydrogen bonded substances show positive deviations from Raoult's law if the strength of the hydrogen bond between like molecules is stronger than the hydrogen bond between unlike species. Negative deviations occur when there is compound formation between unlike molecules. Ebullioscopic or boiling point elevation can be used to determine the amount of

hydrogen bonding. Azeotropic, solubility and partition methods are of lesser importance in hydrogen bond studies because of the difficulty of interpreting the experimental data.

Part b) of the operational definition of the hydrogen bond implies that methods such as infrared or Raman spectroscopy can give evidence that the new bond linking A - H and B specifically involves the proton already bonded to A.

"infrared and Raman spectroscopy provide:

a) a definite criterion for the detection and presence of the hydrogen bonds

b) direct evidence of the role of the proton in the association

c) a quantitative index of the physical and chemical properties of the hydrogen bonded system

d) a convenient tool in a wide variety of hydrogen bond studies."[31]

Near ultra-violet spectroscopy can also be used to detect hydrogen bonds; however, its utility is limited to those molecules whose chromophoric group is altered by the formation of the hydrogen bond. Nuclear magnetic resonance shows a great deal of promise as a tool in studying the properties of the hydrogen bond.

There have been many reviews published concerning the nature and theory of the hydrogen bond since 1920, when Latimer and Rodebush[25] first detected its existence in water. They recognized that the phenomenon is logically contained in the Lewis theory of valence. Some of the early reviews of the subject are by Sidgwick and Callow,[34]

Huggins,[22] Lassettre[24] and by Rodebush and Buswell.[33] The early work in Europe was reviewed by Freymann,[15,16] also by Batuev and Landsberg.[6] Pauling[27] gives many references about the theory of the hydrogen bond in his book, "The Nature of The Chemical Bond." Hadžĭ[18] has edited a collection of papers given at the Symposium on Hydrogen Bonding held at Ljubljana, Yugoslavia in 1957. Pimentel and McClellan[28] have written a very comprehensive survey of the theoretical and practical aspects of the subject of hydrogen bonding. Several workers[1,2,8,12] have written reviews that have dealt with the theory, detection and nature of the hydrogen bond.

Studies dealing with the association of carboxylic acids in carbon tetrachloride by infra-red absorption spectroscopy have been made by Buswell, Rodebush and Roy,[7] Davies and Sutherland,[12] Badger and Bauer,[3] Barrow and Yerger,[4] Spurr and Wenograd,[36] and Harris and Hobbs.[20]

Buswell, et al.,[7] studied the region 2.63 - 4.73 μ (3800-2100 cm^{-1}). A single absorption band at about 2.180μ (3500 cm^{-1}) was assigned to the unassociated hydroxyl bond. A very broad band at about 3.3μ was found to be characteristic of the H-bonded dimer. They measured the association of acetic acid, trichloroacetic acid, and benzoic acid in anhydrous carbon tetrachloride, using cell lengths of 0.64 and 10.18 cm., at concentrations of 0.008 molar and 0.0005 molar respectively. Also, the association of acetic acid vapor was studied in the 10.18 cm cell. Buswell, et al.,[7] state that acetic, trichloroacetic and benzoic acids are slightly associated at a concentration of about 0.0005 molar, while at 0.008 molar dimers are the

predominant species. No values of the association constants were obtained.

Davies and Sutherland[12] investigated the infra-red absorption spectra of solutions of acetic, trichloroacetic and benzoic acids as a function of concentration and temperature. Approximate values for the association constants were calculated from measurements of the absorption. The increase of the intensity of the 3μ band with increasing temperature was ascribed to changes in the equilibrium concentrations of monomer and dimer.

As the solutions were diluted the apparent absorbance at 3μ increased. This was considered to be caused by a shift in the equilibrium concentrations of the monomer and dimer. Measurements were made in cells of 1.3, 3.05, and 6.02 mm path lengths. The concentration of the acids in the carbon tetrachloride was always greater than 0.00565 molar. Davies and Sutherland evaluated the association constants of the acids by measuring the integrated intensities of the unassociated hydroxyl stretching and the carbonyl stretching frequencies in the 3μ and 6μ regions of the spectrum respectively as a function of concentration at different temperatures. From the dependence of the association constant on the temperature it was possible to calculate heats of dissociation for the dimer. The results for acetic acid gave a value of $\Delta H = 9{,}300 \pm 1000$ cal./g mole.[12] Allen and Caldin[1] quote a value of $7{,}600 \pm 1000$ cal. for the heat of dimerization of acetic acid in carbon tetrachloride.

Badger and Bauer[3] studied the association of water, alcohols, ketones and carboxylic acids in carbon tetrachloride using the

photographic region of the infrared spectrum (9000-11,000 Å). They discussed the alterations that take place in the hydroxyl stretching frequency absorption when hydrogen bonding occurs. They found that in many cases of intermolecular hydrogen bonding the hydroxyl stretching frequency was considerably decreased from what it would be if no association occurred and the characteristic bands due to the hydroxyl vibration were greatly broadened. A relationship between the energy of the hydrogen bond and the shift of the hydroxyl stretching frequency was derived. The frequency shifts caused by hydrogen bonding were shown to be semiquantitative measurements of heats of dimerization.

More recently Harris and Hobbs[20] investigated the association of unsubstituted, monochloro, dichloro, and trichloroacetic acids in carbon tetrachloride at 25°C. The absorbance of the hydroxyl stretching frequency at 2.8μ was determined in 1.000 and 10.000 cm. cells over the concentration range 10^{-1} - 10^{-5} molar. By combining Beer's law and the expression for the association constant it was possible to evaluate the molar absorptivities and dissociation constants for the acids. It was found that the apparent association constant changed with the length of the cell used. This effect was most pronounced in the case of acetic acid. Harris and Hobbs ascribe this variation to errors encountered in measuring the small amounts of monomer that were present. They found an average association constant to be $4 \times 10^{+3}$ for acetic acid and $5.5 \times 10^{+2}$ for trichloroacetic acid.

Barrow and Yerger[4] studied the association of acetic acid in carbon tetrachloride by measuring the absorption of the carbonyl group. The results for the association constant are somewhat lower than those

reported by Harris and Hobbs. Monomer and dimer concentrations were determined from the absorbancies of their respective carbonyl absorption bands. The molar absorbancy index of the acetic acid dimer was evaluated using the Beer-Lambert law with a cell of 0.034 mm light path. The results were extrapolated to higher concentrations and corrected for the small amount of monomer present by means of an approximate equilibrium constant. The molar absorbancy index of the monomer was calculated from the absorbancies and concentrations of the most dilute solutions. Using the 0.034 mm light path cell, Barrow and Yerger found the association constant of the acetic acid in anhydrous carbon tetrachloride to be $1 \times 10^{+3}$ at 25°C. In a 20.4 mm cell the association constant was found to be $2.17 \times 10^{+3}$.

Using a modification of the work of Harris and Hobbs,[20] Wenograd and Spurr[36] evaluated the association constants of a number of fatty acids in carbon tetrachloride, including acetic acid. Instead of using peak absorbances as Harris and Hobbs did, Wenograd and Spurr determined the "integrated absorbances" of the monomeric and dimeric hydroxyl stretching bands. From the stoichiometry and the "integrated absorbances" it was possible to calculate the association constants of the acids. The agreement between the work of Harris, et al, and Wenograd is quite good. Wenograd and Spurr also found that other saturated aliphatic acids, which were studied associated in carbon tetrachloride to the same extent as acetic acid.

Since carbon tetrachloride has a transmission cutoff at 280mμ, it is not possible to study the association of acetic acid in this solvent in the ultraviolet region of the spectrum.

From a study of Raman spectra, Batuev[5] found evidence of cyclic dimeric association in solutions of acetic acid in carbon tetrachloride. An intense sharp band occurs at 2.82μ in dilute solution. This wave length was ascribed to a monomeric hydroxyl stretching vibration. The intensity of this band was found to increase as the temperature increased. This behavior may be compared to that of the doublet at 2990 and 3028 cm^{-1} which Batuev ascribes to the hydroxyl stretching of the dimer ring. "With increasing temperature in dilute solution the doublet disappears."[5] No attempt was made in this work to determine the extent of dimerization.

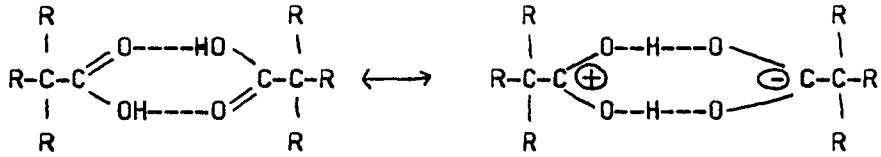
Huggins, Pimentel and Shoolery[21] studied the proton magnetic resonance of acetic acid in anhydrous carbon tetrachloride. It has been shown[17,26] that there is a significant "chemical shift" in the proton magnetic resonance spectrum of acetic acid when the acid is diluted with water. A corresponding hydrogen shift was not observed when pure acetic acid was diluted with anhydrous carbon tetrachloride. This behavior may be explained as follows: In carbon tetrachloride acetic acid forms dimers and at a mole fraction of 0.02 or 0.2 molar, the fraction of molecules present as monomers is very small. Proton magnetic resonance can detect the presence of molecular species down to a concentration of 0.05 moles/liter. In this system the amount of acetic acid monomer present was very much lower than this limit of detectability.[21]

There is quite a bit of uncertainty about the structure of carboxylic acid homo-dimers. Electron diffraction work on gaseous acetic acid indicates planar cyclic hydrogen bonded dimers. It is

usually assumed that the same structure applies to the liquid state either in solution or the pure compound. This planar form would be expected to have no net dipole moment. In contradiction to this expectation, finite values for the dipole moment have been found experimentally (0.8 - 2.0 D).[35]

Several suggestions have been made to explain this non-zero experimental value of the dipole moment.

a) Under the influence of an electric field there might be a shift of a proton of one hydrogen bond resulting in the formation of an ion pair as follows:



This behavior is termed atomic polarization by Pohl, Hobbs and Gross[32] and self ionization by Harris and Alder.[19]

b) The cyclic dimer may assume a non-planar configuration.

c) A portion of the dimeric units may be non-cyclic, or chains of molecules may be formed.

If assumption a) is valid, there should be a considerable frequency disturbance of some of the hydroxyl stretching mode overtones in the infra-red spectrum. Such a disturbance has not been reported.

With regard to noncyclic dimers or chain like association there are contradictory statements in the literature.[32,9]

On the other hand, it seems to be rather difficult to explain appreciable dipole moments (0.8 - 2.0 D) by assuming a non-planar configuration of the cyclic dimers (assumption C).

Except for the work of Christian[10] there is very little in the literature with reference to heterodimerization of carboxylic acids. He studied the systems acetic-trifluoroacetic and proplonic-pentafluoropropionic acid in the vapor phase. Marked homo and hetero (A+C = AC) dimerization was found in the two systems.

Christian[10] hypothesized that for the heterodimer the hydrogen bond between the proton of the perhalogenated acid and the carbonyl oxygen of the unhalogenated acid should be stronger than the hydrogen bonds forming the homo-dimers, because in the hetero-dimer case there is the linkage of an electrophilic proton and a nucleophilic oxygen atom. Arguing by analogy he concluded that the bond between the proton of the unhalogenated acid and the carbonyl oxygen of the perhalogenated acid should be weaker than the hydrogen bonds in either homo-dimer.

Consideration of the relative magnitudes of the homo and hetero-dimerization constants lead him to decide that the bond between the electrophilic proton and the nucleophilic oxygen overcomes any reduction in the strength of the bond between the proton of the unhalogenated acid and the carbonyl oxygen of the perhalogenated acid.

The situation with respect to hetero-dimerization of two carboxylic acids in anhydrous non-polar solvents such as carbon tetrachloride must be similar to that which occurs in the vapor phase. In dilute solutions there is no reason to assume that polymers other than homo and hetero-dimers are formed. Christian found that in the two systems studied, there were large negative deviations from Raoult's law.

Fowler and Guggenheim[14] derived a theoretical expression which relates homo and hetero-dimerization constants. If the symmetry numbers

of each of the homo-dimers are taken to be two and the symmetry number of the hetero dimer is one, then the ratio of the hetero-dimerization constant to the geometric mean of the two homo-dimerization constants is two. This derivation of Fowler and Guggenheim is of course statistical in nature and does not take into account the differing structures of the materials employed.

CHAPTER II

OBJECTIVES

The primary objectives of this research were:

1. To develop a method to determine the extent of association of fatty acids in anhydrous non-polar solvents.

2. To apply the method to obtain thermodynamic quantities for reactions of the type $2A \rightleftarrows A_2$, $2C \rightleftarrows C_2$, and $A + C \rightleftarrows AC$ in carbon tetrachloride where A and C are acid monomers, A_2 and C_2 are the respective homo-dimers and AC is the cross dimer between the two monomer species.

3. To investigate the effect of alpha halogen substituents on the dimerization of acetic acid.

CHAPTER III

EXPERIMENTAL

Reagents

a) Carbon tetrachloride

Spectroscopic grade carbon tetrachloride was prepared by refluxing the reagent several hours with a small amount of mercury to remove any sulfides that were present.[37] The carbon tetrachloride was then washed successively with portions of concentrated sulfuric acid, dilute potassium hydroxide solution, and distilled water. After the final wash with water the reagent was stored over anhydrous calcium chloride for several hours. A 30 plate Oldershaw column set at a reflux ratio of 10 : 1 was used to distill the carbon tetrachloride. Only the middle portion was taken for the preparation of solutions. The boiling point range corrected to 760 mm pressure was 76.3 - 76.6°C. The carbon tetrachloride was distilled directly into a delivery flask which contained anhydrous magnesium perchlorate. The magnesium perchlorate insured the removal of the last traces of water.

b) Acetic acid

Analytical reagent grade acetic acid was purified by a modification of the method of Pohl, Hobbs, and Gross.[32] A large quantity of acetic acid was frozen using an ice bath. When about half the acetic acid had frozen, the supernatant liquid remaining was discarded. This

process was repeated four times. The solidified acetic acid which remained after the successive freeze-thaw cycles was heated slightly above its melting point and then transferred to a flask which contained phosphorous pentoxide. A 30 plate Oldershaw column was used to distill the material and only the middle one third was collected. The boiling point range of the acetic acid, corrected to 760 mm pressure, was 117.5 - 117.9°C. Duplicate determinations of the equivalent weight of the acetic acid with standard potassium hydroxide solution gave a mean value of 60.03 grams/gram equivalent. The value obtained from the sum of the atomic weights is 60.05 grams/gram equivalent.

c) Trichloroacetic acid

Baker Analytical Reagent trichloroacetic acid was purified by the method of fractional freezing described above. The reagent was heated above its melting point. Upon cooling, when half the material present solidified, the supernatant liquid was discarded. The solidified trichloroacetic acid which remained after five successive freeze-thaw cycles was recrystallized six times from dry, freshly distilled benzene. Since trichloroacetic acid is very hygroscopic it was very difficult to take its melting point. Duplicate determinations of the equivalent weight with standard potassium hydroxide gave a mean value of 163.3 grams/gram equivalent. The value obtained from the sum of the atomic weights is 163.4 grams/gram equivalent.

d) Standard Potassium Hydroxide Solution

The potassium hydroxide solution was prepared by diluting a portion of a 50 per cent stock solution with freshly boiled distilled water. Dried potassium acid phthalate was used as the primary standard.

Replicate determinations of the standardization agreed to within 1 part of 1000.

Method of Handling and Preparing Solutions

a) Description of the Dry Box

Since the reagents used in the study sorb water very readily and take up a considerable amount during very short exposures to the atmosphere, it was necessary to work in a dry environment. A sheet-steel box with a volume of one cubic foot was used as a dry box. The container had ports to which gloves could be attached and petcocks to admit and remove air. Compressed air was passed in series through an expansion chamber, a manostat, a drying tower full of silica gel coated with cobalt chloride and a drying tower full of magnesium perchlorate before entering the dry box. The "tell tale" silica gel changed color when the reagent was spent indicating when the drying agent had to be changed. In addition approximately 3 pounds of silica gel was placed on the floor of the dry box to insure dry air within the enclosure.

b) Methods of Preparing Stock Solutions

To make certain the carbon tetrachloride was not exposed to the atmosphere, a short length of glass tubing containing a Teflon stop cock was sealed to a point 2 inches above the bottom of a 3 liter Erlenmeyer flask. A hole was bored in the wall of the dry box to allow the delivery tip of the dispensing flask to extend inside the dry box. Magnesium perchlorate was added to the flask so that the drying agent was always in contact with the carbon tetrachloride. Figure 1 is a picture of the apparatus.

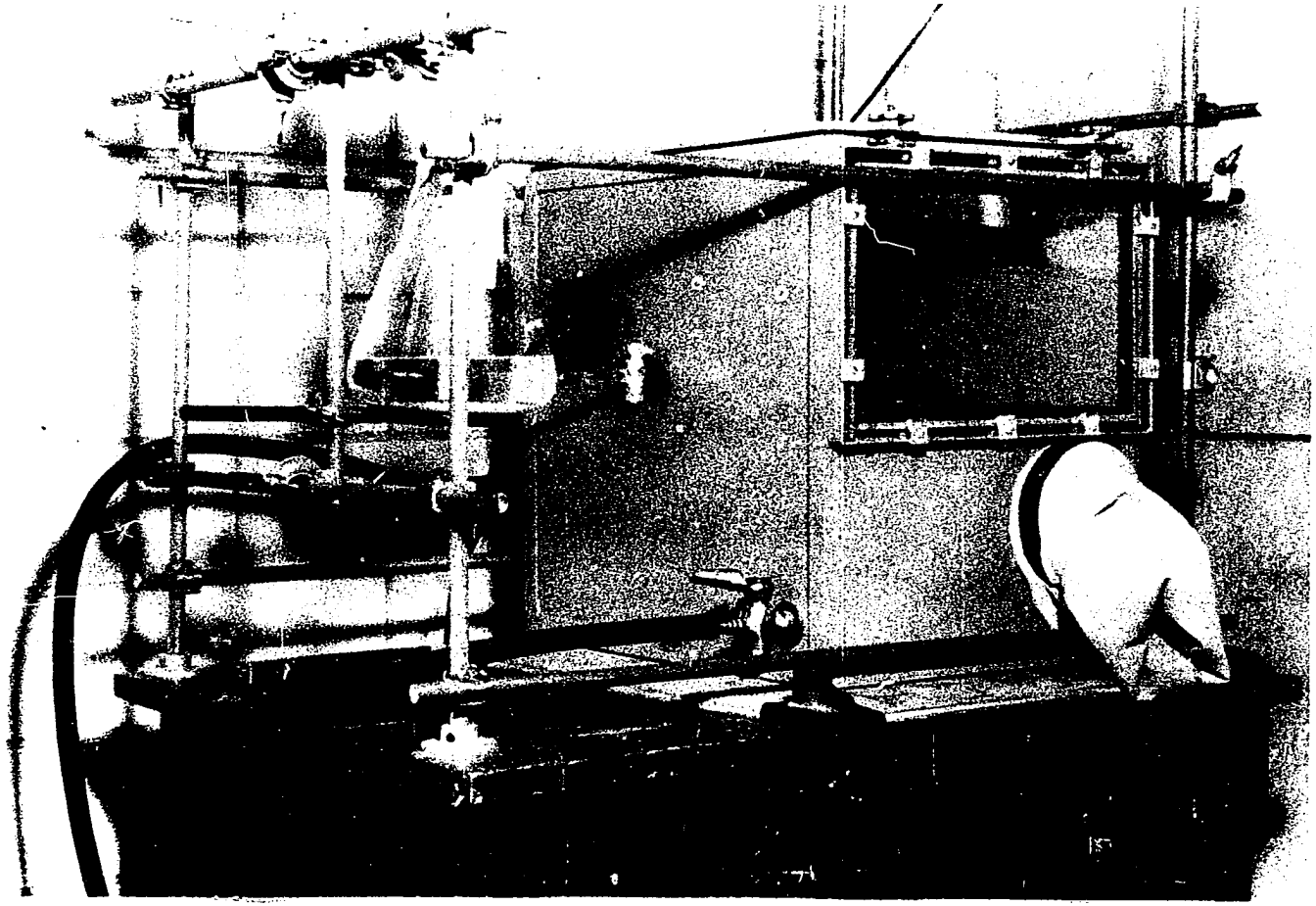


Figure 1. Dry Box Apparatus

Whenever the dry box was opened during the course of the work, it was flushed out, at a flow rate of one liter per minute for 10 minutes before further manipulations were made. A flow rate of one liter per minute was deemed adequate because of the small size of the dry box. The silica gel also helped to dry the air in the enclosure. As a check that a 10 minute flushing period was sufficient to prevent the sorbing of water by the solvent, carbon tetrachloride taken from the reservoir after an overnight flushing of the dry box was compared in the spectrophotometer versus carbon tetrachloride which was removed after a 10 minute purging of the enclosure. A scan of the near intra-red region of the spectrum where bands due to water occur showed that water was not present in the carbon tetrachloride removed after the 10 minute flushing period.

Stock solutions were prepared in the following way: A clean, dry milliliter volumetric flask was weighed to $\pm$0.1 mg. on a chain balance. A small amount of dry carbon tetrachloride was added to the flask in the dry box and the flask re-weighed. The desiccator containing the purified acid and the volumetric flask were again placed in the dry box. Enough acid was transferred to make up a solution of the proper concentration. The flask was weighed again to determine the amount of acid added. More carbon tetrachloride was added to the flask to make up approximately 50 milliliters of solution. The flask was re-weighed for the last time and shaken to insure good mixing.

The concentrations of the stock solutions were checked by withdrawing weighed aliquots in the dry box. After removing the aliquots from the dry box they were shaken with water and titrated with standard

potassium hydroxide using phenolphthalein as the indicator. The standardization of the stock solutions determined by titration agreed with the concentrations calculated by weight to within 2 parts in 1000.

The acetic-trichloroacetic acid stock solution was prepared in the same way as those of the individual acids except for the following change: after the addition of the small amount of dry carbon tetrachloride, enough trichloroacetic acid was transferred to the flask to make a solution of the proper concentration. From the difference in weights the number of gram-moles of trichloroacetic acid present was calculated. Using a calibrated hypodermic syringe graduated in 0.01 milliliter intervals enough acetic acid was added to give an equimolar acid mixture. After weighing the flask, carbon tetrachloride was added to make up 50 milliliters of stock solution. The flask was re-weighed and shaken to insure good mixing. The concentration was checked by withdrawing aliquots in the dry box. These samples were weighed, shaken with water then titrated with standard potassium hydroxide. Phenolphthalein was used as the indicator. The sum of the two acid molalities calculated by weight agreed with the total acid molality determined by titration to within 2 parts in 1000. The flasks containing stock solutions were stored in the dry box throughout the course of the work.

c) Methods of preparing solutions that were run in the spectrophotometer

The solutions whose transmittancies were to be determined were prepared in the following way: Empty, clean and dry 50 milliliter

volumetric flasks were weighed on a chain balance to ± 0.1 milligram. These were placed in the dry box which was flushed out for the usual 10 minute period. The flasks were filled with small amounts of dry carbon tetrachloride and re-weighed. After another 10 minute flushing in the dry box, aliquots of the acid stock solutions were quickly added to the flasks with a hypodermic syringe graduated in 0.01 milliliter intervals. The flasks were re-weighed and returned to the dry box. When the flushing period was complete more dry carbon tetrachloride was added to make up approximately 50 milliliters of solution. The flasks were weighed for the last time and the concentrations calculated. The concentrations were kept in a range which permitted the measured absorbancies to lie between values of 0.15 and 0.75.

Instrumentation

a) The spectrophotometer

The spectrophotometer used in this study was the Beckman "Custom" Ratio Recording Instrument Model DK-1. Its operating range lies between 175 mμ in the ultraviolet to 3500 mμ in the near infra-red region of the electromagnetic spectrum. Since this work was carried out in the near infra-red between 2,750 mμ and 3,100 mμ the details applicable to the instrument in this region will be discussed. The infra-red source used was a 6 volt incandescent tungsten bulb. The prism was cut from a single silica crystal and has a high dispersion in the near infra-red. A lead sulfide photo-conductive cell was the detector. The output of the detector was coupled to a recorder which gave the percent transmittancy directly. A germanium filter was placed in the light beam to remove stray light. The filter was opaque to light of a wavelength less than

1,900 mμ. Without the germanium filter or the filled 10.000 cm cells in the light path the mechanical slit width of the instrument at 2,847 mμ was 0.140 millimeters. The instrument was adjusted so that the minimum slit width was used at all times. With the 10.000 cm cells filled with carbon tetrachloride and no filter in the light path the mechanical slit width rose to 0.150 millimeters. When both the filter and filled cells were placed in the light path the mechanical slit width rose to 0.165 millimeters. This increase of the slit width indicated that the germanium filter removed some stray light present in the optical system. In all of the work carried out with the individual and mixed acids and mechanical slit width ranged from .155 - .165 millimeters.

b) The cells

Two matched glass cells of 10.000 cm path length were used in this study. The cylindrical portions of the cells were constructed of pyrex while the faces were composed of silica with a high transparency in the near infra-red portion of the spectrum.

c) Thermostatic Bath

The thermostatic bath consisted of a 6 gallon glass container filled with distilled water. Its auxiliary equipment included a cooling coil, a combination heating and stirring tower and a circulating pump. The temperature was controlled by a "Thermistemp" temperature regulator with a thermistor as the sensing element. The base heat required to keep the bath at an approximate temperature was supplied by the heating tower in the bath. Fine control at the desired temperature was achieved by two 125 watt knife edge heaters connected to the Thermistemp regulator. In this way it was possible to control the temperature to $\pm$ 0.1°C.

d) The thermostatic cell holder

The thermostatic cell holder shown in Figure 2 was used throughout this study.

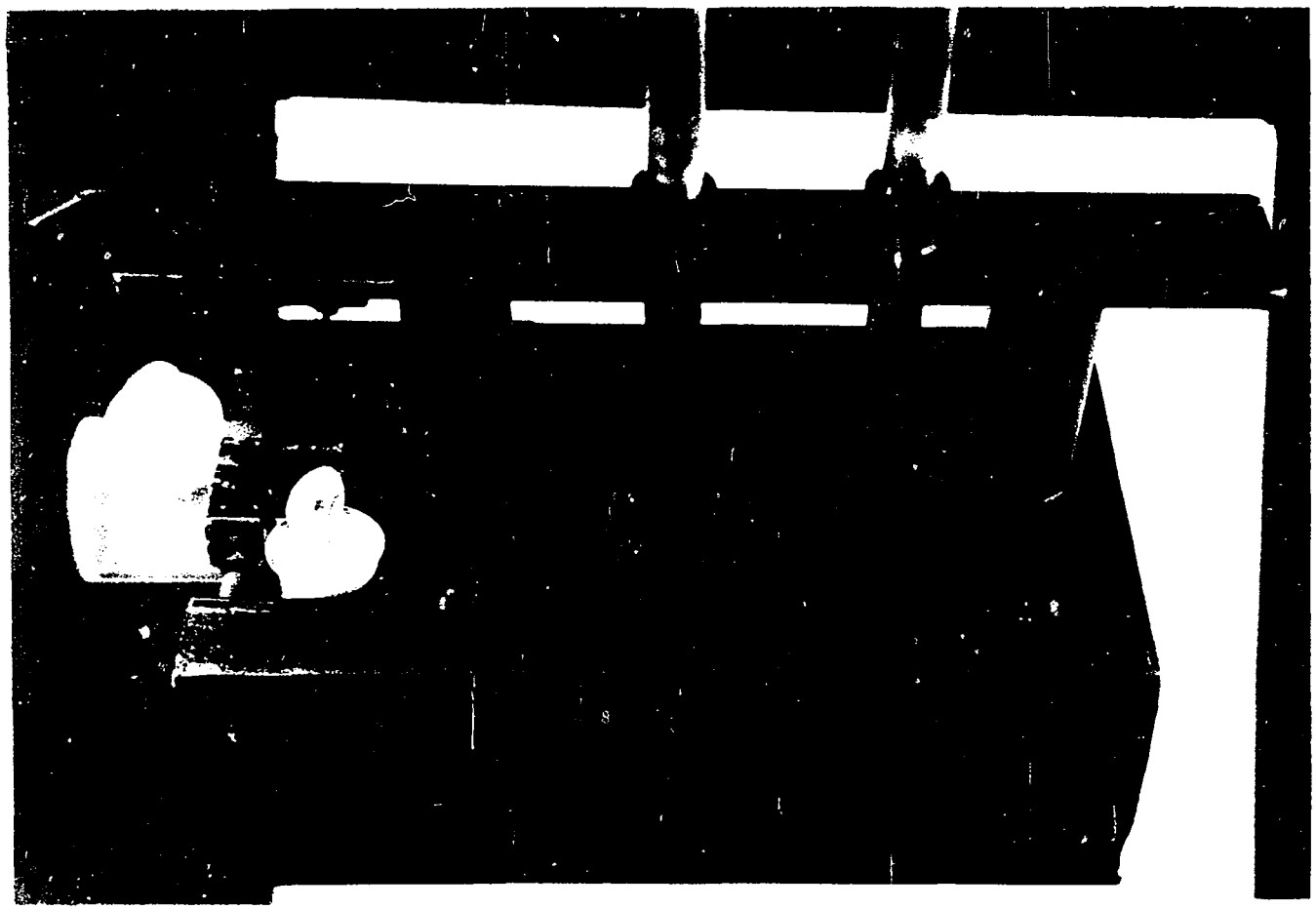


Figure 2. Thermostatic Cell Holder

It served the dual purpose of positioning the 10 cm cells in the light path of the spectrophotometer, and permitting water to be circulated around the cells at a given temperature. The holder was constructed of brass. Two tubes were built into the cell holder perpendicular to the spectrophotometer's light path to hold the cells in place. The glass cells fitted the tubes snugly so that there was good contact between the holder and the cells. In order to achieve good temperature equilibrium between the holder and the thermostatic fluid, baffles were constructed in the hollow portions of the cell holder. In addition 4 feet of channels were cut in the floor of the holder where the cells made contact. The cell holder could be used to accommodate glass cells up to a length of 11 cm.

Water was circulated through the cell holder at a high flow rate by means of a circulating pump. The temperature of the water entering and leaving was monitored by putting asbestos insulated side arm test tubes equipped with thermometers in series with the pump and the IN port of the cell holder and between the OUT port of the cell holder and the bath in the return line. The thermometers were read to within $\pm$0.1 degree °C. At no time was there a difference between the temperature of the water entering the cell holder and that leaving it when a scan was made. All temperatures noted in this work were obtained from the monitoring thermometers rather than the bath.

e) How the solutions were run in the DK-1

1) Setting the zero and 100% lines

The instrument was adjusted to read 100% transmittancy with pure dry carbon tetrachloride in both cells. Before any adjustments were

made on the controls of the spectrophotometer the carbon tetrachloride was permitted to come to the temperature at which the particular series of measurements was to be made. In the case of acetic and trichloroacetic acid the wavelength selector was set at the peak where the respective hydroxyl stretching frequencies occur, 2.822 and 2.847μ respectively. When setting the 100% line the desired wavelength was approached from the longer wavelength side of the spectrum. This was done to eliminate the effect of any backlashing of the gears in the instrument.

When the 100% line was set on the spectrophotometer for one of the acids, it was found to be the same with the wavelength selector on the peak wavelength of the other acid. As a matter of convenience the 100% line was set using the trichloroacetic acid wavelength when the measurements of transmittancy were made on the mixed acid solutions.

2) How the solutions were run in the spectrophotometer.

After the 100% line was set on the instrument the cell on the sample side of the compartment was removed and placed in the dry box. After a 10 minute flushing period the stopper was removed from the cell and the carbon tetrachloride poured out. The cell was rinsed three times with small portions of solution. It was then filled with the solution and placed in the spectrophotometer. To insure that there was temperature equilibrium between the cell plus contents and the circulating water from the bath, the wavelength selector was placed on the wavelength of the acetic or trichloroacetic acid peak and the action of the spectrophotometer recorder noted. If the temperature of the cell was less than that of the cell holder the recorder pen would start to

drift to the left (i.e. toward increasing transmittancy), until it reached a maximum. This maximum was usually reached in 10 minutes. If there was no change in the pen deflection within the succeeding 10 minutes the cells and the thermostatic fluid were considered to be at the same temperature. Conversely, if the temperature of the cell was greater than that of the cell holder the recorder pen would start to drift to the right (i.e. in the direction of decreasing transmittancy). The same time periods were alloted for equilibrium to be reached.

After temperature equilibrium was reached, the wavelength selector was turned up to 3.500μ then brought back to 3.100μ. This was done to eliminate gear backlash. At 3.100μ the recorder pen and a horizontal chart paper division marker were aligned and the scan started. The scan was considered complete when the wavelength indicator reached 2.750μ. The sample cell was then removed from the spectrophotometer compartment and placed in the dry box. After flushing for 10 minutes, the cell stopper was removed and the solution poured back into its flask.

The next solution studied was subjected to the same sequence of operations as outlined above. The base line was reset after two scans of solution. Very little change in the 100% line could be detected in this time. The base line never varied more than $\pm$ 1%.

Although there is provision for the direct measurement of the absorbancy built into the DK-1 spectrophotometer, all measurements were made with the selector on "Transmittance." Both the base line and the transmittancy of the cell + solution were measured from the chart of the scan in question.

CHAPTER IV

METHODS OF CALCULATION

Dimerization Constants of Organic Acids

The equilibrium constant for the association, $n\,A \rightleftarrows A_n$, of a carboxylic acid A in non-polar solvents may be defined in terms of the activities of the polymeric species A_n, and the monomer A.

$$K = \frac{a_{A_n}}{a_A^n} \qquad (1)$$

In dilute solutions it is permissible to replace the respective activities by their concentrations. Pohl, Hobbs and Gross[32] have shown that in dilute solutions of carboxylic acids in non-polar solvents the only equilibrium of importance is that which exists between monomer and dimer. Equation (1) may be written in terms of the molality of the monomer and dimer as shown in equation (2).

$$K = \frac{m_{A_2}}{m_A^2} \qquad (2)$$

The total acid or "formal" molality m_f of acid A may be written in terms of the molality of the monomer and dimer

$$m_f = m_A + 2m_{A_2} \qquad (3)$$

The Beer-Lambert law can be used to determine the concentration

of monomer at a wavelength where only the monomer absorbs radiation.

$$\log \frac{I_0}{I} = \log \frac{1}{T_s} = A = a_A m_A l \qquad (4)$$

I_0 and I are the transmitted intensities of pure solvent and acid solutions respectively.

T_s = the transmittancy of the solution =

$$\frac{\text{transmittance of the cell + solution}}{\text{transmittance of the cell + solvent}} = \frac{\text{I soln}/I_0}{\text{I solvent}/I_0}$$

A = the absorbancy of the solution

a_A = the absorptivity of the monomer in units of $\frac{1000 \text{ grams}}{\text{mole - cm}}$ of acid A

m_A = the concentration of monomer as moles of A per 1000 grams of solvent

l = the length of the absorbing layer of the solution expressed in centimeters.

If equation (2) is solved for the molality of the dimer and then substituted into equation (3)

$$m_f = m_A + 2Km_A^2 \qquad (5)$$

Equation (5) is obtained in terms of the total molality, the monomer molality and the dimerization constant.

Since

$$m_A = A/a_A l \qquad (6)$$

by substituting equation (6) into equation (5) there is obtained

$$m_f = \frac{A}{a_A l} + \frac{2KA^2}{(a_A l)^2} \qquad (7)$$

Dividing through by A gives the following:

$$\frac{m_f}{A} = \frac{1}{a_A\ 1} + \frac{2KA}{(a_A 1)^2} \qquad (8)$$

If m_f/A is plotted as the ordinate against A as the abscissa using rectangular coordinates a linear plot should result with an intercept equal to $\frac{1}{a_A\ 1}$ and a slope equal to $2K/(a_A 1)^2$.

The treatment given above shows that the K of equation (2) may be evaluated if m_f, the total acid molality, 1, the path length, and A the absorbancy of the monomer are known. The further assumptions are made that the Beer-Lambert Law may be applied to the measurement of the monomer concentration and that the equilibrium present involves only monomer and dimer.

Cross Dimerization Constants of Organic Acids

When two carboxylic acids denoted by A and C are dissolved in a non-polar solvent three equilibrium expressions may be written:

$$A + A \rightleftarrows A_2$$

$$C + C \rightleftarrows C_2$$

$$A + C \rightleftarrows AC$$

The respective equilibrium constants in dilute solution are

$$K_A = \frac{m_{A_2}}{m_A^2} \qquad (9)$$

$$K_C = \frac{m_{C_2}}{m_C^2} \qquad (10)$$

$$K_{AC} = \frac{m_{AC}}{m_A m_C} \tag{11}$$

where m denotes the molality of each species.

If equations (9), (10) and (11) are solved for the dimer concentrations one obtains the following:

$$m_{A_2} = K_A m_A^2 \tag{12}$$

$$m_{C_2} = K_C m_C^2 \tag{13}$$

$$m_{AC} = K_{AC} m_A m_C \tag{14}$$

The total acid or "formal" concentration of A and C may be written as:

$$m_f^A = m_A + 2m_{A_2} + m_{AC} \tag{15}$$

$$m_f^C = m_C + 2m_{C_2} + m_{AC} \tag{16}$$

Substituting equations (12), (13) and (14) into (15) and (16) gives the total concentration of each acid in terms of the respective monomers and association constants.

$$m_f^A = m_A + 2K_A m_A^2 + K_{AC} m_A m_C \tag{17}$$

$$m_f^C = m_C + 2K_C m_C^2 + K_{AC} m_A m_C \tag{18}$$

The absorbancy A, in the region where only monomers absorb radiation, may be considered to be made up of a sum of two terms

$$A/1 = a_A m_A + a_C m_C \tag{19}$$

where 1 is the light path length

a_A = the molal absorptivity of the monomer of acid A

m_A = the molal concentration of the monomer of acid A

a_C = the molal absorptivity of the monomer of acid C

m_C = the molal concentration of the monomer of acid C

The absorptivities needed for the calculations can be determined at the peak wave lengths of acids A and C from a plot of equation (7). When these absorptivities are known it is then possible to calculate m_A and m_C. If equation (18) is written

$$m_f^C = m_C(1 + 2K_C m_C + K_{AC} m_A) \tag{20}$$

or

$$\frac{m_f^C}{m_C} - 2K_C m_C = 1 + K_{AC} m_A \tag{21}$$

then if $\frac{m_f^C}{m_C} - 2K_C m_C$ is plotted on the ordinate versus m_A as the abscissa a straight line should result whose slope is the cross dimerization constant K_{AC} and whose intercept is 1.

The dimerization constants of acetic and trichloroacetic acid were determined in the following way: From the values of m_f/A and A an intercept on the m_f/A axis was calculated by the method of least squares. This was done for each series of concentrations at every temperature studied for the acids. From the sets of values of the intercepts at the different temperatures a mean value $\bar{b}$ was calculated for each acid.

Using the mean intercept $\bar{b}$ the best slope m corresponding to it was calculated from the following relationship

$$m = \frac{\sum_i \left[\left(\frac{m_f}{A}\right)_i - \bar{b}\right] A_i}{\sum_i A_i^2} \qquad (22)$$

since $\bar{b} = \frac{1}{\bar{a}l}$ and $m = \frac{2K}{(\bar{a}l)^2}$ K could be evaluated. The dimerization constants calculated in this way were used in the plots of log K versus $\frac{1}{T}$ to determine the heats of dimerization.

Calculation of Cross Dimerization Constants

Equation (19) was used to evaluate the monomer concentrations of acetic (m_A) and trichloroacetic acids (m_C) used in this study. Inspection of the spectra shows that the molal absorptivities of trichloroacetic acid at the acetic acid peak wave length and of the acetic acid at the trichloroacetic acid peak wavelength had to be determined. In order to evaluate the monomer concentrations the absorbancies of trichloroacetic acid at the peak wavelength of acetic acid (2.822μ) and of acetic acid at the peak wavelength of trichloroacetic acid (2.847μ) were measured on the charts of the percent transmittancy versus wavelength obtained from the DK-1 spectrophotometer. From the values of m_f/A and A an intercept on the m_f/A axis was calculated by the method of least squares. This was done for each series of concentrations of acetic and trichloroacetic acid. At the different temperatures a mean value, $\bar{b}$, was determined. This mean intercept was then used to calculate the molal absorptivities at 2.822 and 2.847μ.

From a knowledge of the four absorptivities and the absorbancies at the acetic and trichloroacetic acid peak wavelengths, it is possible to determine m_A and m_C, the concentrations of the acetic and

trichloroacetic acid monomers. The simultaneous equations in two unknowns were solved by the method of determinants to give values of m_A and m_C.

The cross dimerization constant K_{AC} was evaluated using equation (21)

$$\frac{m_f^C}{m_C} - 2K_C m_C = 1 + K_{AC} m_A$$

There is less error in the value of the trichloroacetic acid association constant[20] because the larger amount of monomer of this acid present at all temperatures allows the molal absorptivity to be measured more accurately than that of the acetic acid. For this reason the expression relating trichloroacetic acid concentration and the cross dimerization constant was used instead of the one for acetic acid.

From values of $\frac{m_f^C}{m_C} - 2K_C m_C$ and m_A the best slope was determined by substituting the appropriate quantities into an equation similar to (22). From the form of the equation the fixed intercept is 1. The values of K_{AC} were utilized in the calculation of the heat of cross dimerization by means of the van't Hoff equation.

CHAPTER V

Results

Table I gives a comparison of the molalities of the different acid stock solutions as determined by weight and by titration with standard base. This table illustrates that the technique used in preparing the solutions was satisfactory. Any errors introduced by the procedure used were much smaller than the subsequent measurements of the absorbancy. The experimental data m_f, A and m_f/A for the system acetic acid-carbon tetrachloride at the indicated temperatures are given in Table II. Table IV lists m_f, A and m_f/A for the system trichloroacetic acid-carbon tetrachloride. The values of the absorbancy are the limiting measurements in this study, and although the values given for m_f/A are reported in some cases to four significant figures, the fourth figure is very uncertain since the absorbancy measurements are accurate to 0.5% and are known to three significant figures.

Tables III and V list the reciprocal of the molal absorptivity obtained at the different temperatures together with the association constants K at these temperatures calculated from the mean molal absorptivity of acetic and trichloroacetic acids respectively. The individual values of the reciprocal of the absorptivity are listed to illustrate the variation in these values. It should be observed that there is no

trend in the absorptivity coefficients indicating that the use of the mean produces a value for the association constant which is probably closer to the true value that the individual ones would have given. It also shows that within the errors of the measurements there is no variation of the absorptivity with the temperature. Figures 3 and 5 illustrate the linearity of the plots of m_f/A versus A at the temperatures noted for acetic and trichloroacetic acids at 2,822mμ and 2,847mμ respectively. The linearity of the plots also support the assumptions that a) the monomer is the only species absorbing at the particular wavelengths and b) there is a Beer's law obedience for the monomer peaks. The decrease in the slopes of the m_f/A versus A plots for each acid reflects an increase in the equilibrium amount of monomer.

The values of m_f, A and m_f/A for the system trichloroacetic acid-carbon tetrachloride at the peak wavelength of acetic acid and the values of m_f, A and m_f/A for the system acetic acid-carbon tetrachloride are given in Tables VI and VIII. The molal absorptivity of acetic acid at the peak wavelength of trichloroacetic acid and trichloroacetic acid at the acetic acid wavelength are listed in Tables VII and IX. Figures 7 and 8 represent plots of m_f/A versus A for the systems at the wavelengths of interest. As can be seen from the plots and data the values obtained for the absorptivities of acetic acid at 2,847mμ and trichloroacetic acid at 2,822mμ are quite uncertain because of the large scatter in the m_f/A versus A plots. However, since these absorptivities are relatively small and represent small correction terms to larger quantities the uncertainty in the correction does not introduce a corresponding uncertainty in the calculated association constants.

Table X lists the absorbancies at 2,847mμ and 2,822mμ, the calculated acid dimer concentrations and the cross dimerization constants K_{AC} at the indicated temperatures for the system acetic acid-trichloroacetic acid-carbon tetrachloride. Figure 9 illustrates the linearity of the plots $\frac{m_f^C}{m} - 2K_C m_C$ versus m_A at the indicated temperatures. The decrease in slope with increasing temperature reflects an increase in the equilibrium amounts of the two acid monomers. An increase in the scatter of the points at 40.8°C. reflects the difficulties encountered in making spectrophotometric measurements at elevated temperatures.

Log K versus $\frac{1}{T}$ values are plotted in Figures 4, 6 and 10 for the systems acetic acid-carbon tetrachloride, trichloroacetic acid-carbon tetrachloride and acetic acid-trichloroacetic acid-carbon tetrachloride, respectively. Because of the much greater uncertainty in K_{AC} caused by the need to solve simultaneous equations, a large amount of scatter is present in the log K versus $\frac{1}{T}$ plot. The value of ΔH_{AC} was obtained using the van't Hoff equation.

Table XI lists $\Delta H°$, $\Delta F°$ and $\Delta S°$ for the reactions

$2CH_3COOH \rightleftarrows (CH_3COOH)2$, $2CCl_3COOH \rightleftarrows (CCl_3COOH)_2$,

$CH_3COOH + CCl_3COOH \rightleftarrows CH_3COOH \cdot CCl_3COOH$ and

$\frac{1}{2}(CH_3COOH)_2 + \frac{1}{2}(CCl_3COOH)_2 \rightleftarrows CH_3COOH \cdot CCl_3COOH$.

TABLE I

The comparison of the molalities of the different acid stock solutions as determined by weight and by titration with standard base

Acid	The concentration calculated by weight in equivalents/1.0000 gram of stock solution	The concentration determined by titration in equivalents/1.0000 gram of stock solution
Acetic	1.546×10^{-5}	1.577×10^{-5} 1.580×10^{-5}
Acetic	5.643×10^{-5}	5.636×10^{-5} 5.640×10^{-5}
Acetic	1.610×10^{-5}	1.605×10^{-5} 1.606×10^{-5}
Trichloroacetic	3.307×10^{-5}	3.302×10^{-5} 3.304×10^{-5}
Acetic- Trichloroacetic	4.646×10^{-5}	4.649×10^{-5} 4.658×10^{-5}

TABLE II

The System Acetic Acid-Carbon Tetrachloride

Values of the molal concentrations, absorbancies, and temperatures at the peak wavelength of acetic acid (2.822μ)

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
4.5	2.035	.669	3.041	15.7	2.069	.844	2.451
	1.773	.575	3.083		1.788	.785	2.278
	.794	.398	1.995		1.400	.678	2.065
	.520	.298	1.745		.843	.500	1.686
	.447	.285	1.568		.429	.348	1.233
8.7	2.035	.710	2.866	19.7	1.422	.818	1.738
	1.773	.611	2.902		1.076	.694	1.550
	.794	.403	1.970		.879	.609	1.443
	.520	.323	1.610		.686	.550	1.247
	.447	.296	1.510		.464	.426	1.089
14.3	2.142	.745	2.875	20.1	1.275	.781	1.633
	1.452	.638	2.276		1.061	.728	1.457
	.988	.502	1.968		.850	.606	1.403
	.531	.316	1.680		.535	.473	1.131
	.229	.229	1.000		.275	.305	.902

TABLE II--Continued

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_fA \times 10^{+3}$
25.0	1.088	.770	1.413	34.5	.770	.777	.990
	.823	.708	1.175		.603	.625	.967
	.862	.703	1.226		.336	.439	.767
	.711	.612	1.162		.213	.307	.695
	.676	.590	1.146		.048	.127	.378
	.571	.545	1.048				
	.282	.351	.803	35.0	.760	.780	.974
	.169	.257	.657		.538	.609	.883
	.073	.131	.557		.385	.488	.789
	.031	.065	.476		.230	.319	.721
					.094	.160	.588
29.4	.780	.710	1.099				
	.609	.581	1.048	40.5	.790	.869	.909
	.448	.472	.949		.549	.697	.788
	.214	.333	.643		.310	.477	.650
	.107	.189	.566		.175	.301	.581
					.051	.131	.389
30.4	.770	.738	1.043				
	.603	.588	1.026	40.8	.760	.893	.851
	.336	.402	.836		.538	.689	.781
	.213	.286	.745		.385	.545	.706
	.048	.113	.425		.230	.380	.605
					.094	.202	.465

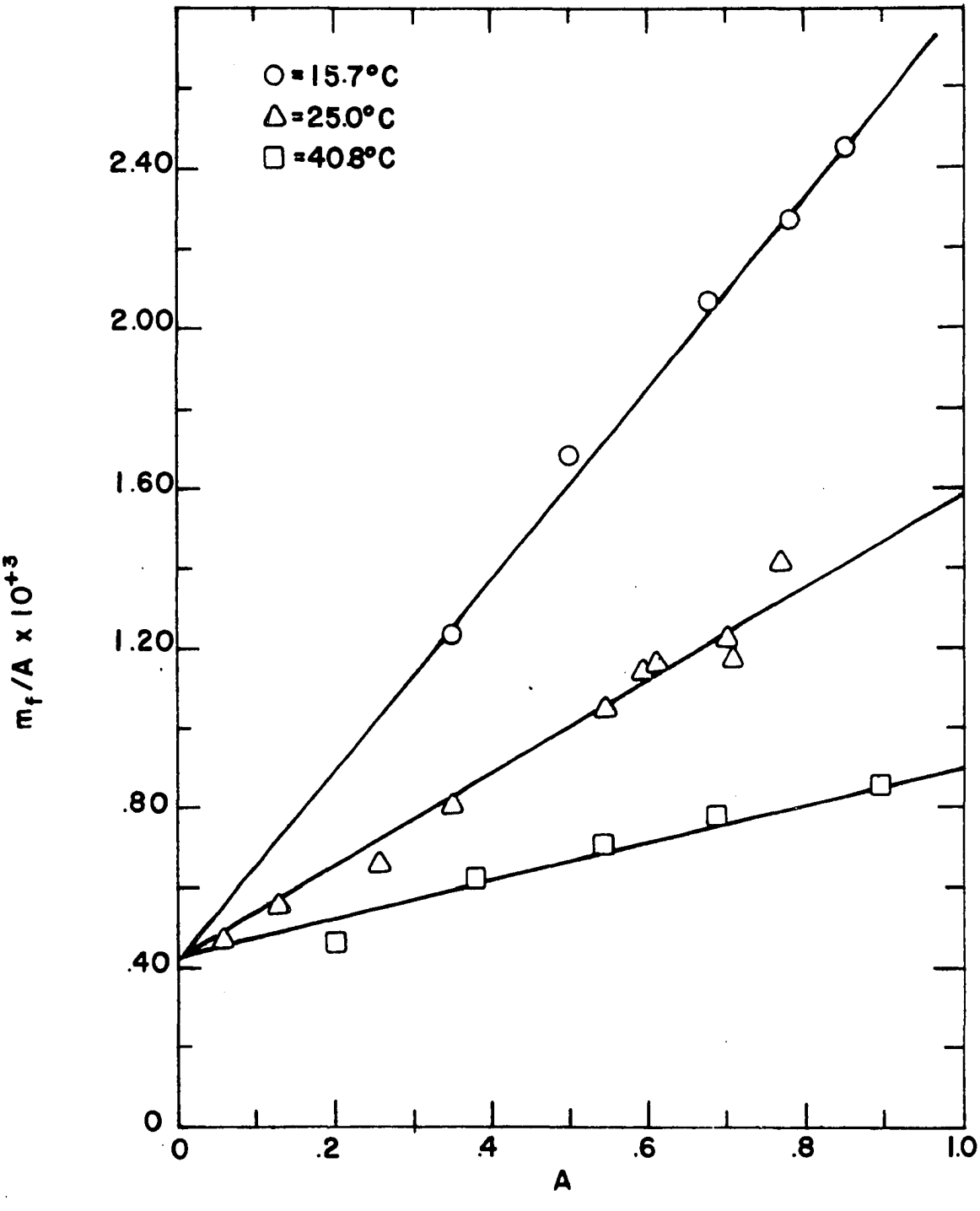


FIG. 3-- Relation of the ratio m_f/A of the total acid concentration to the absorbancy A and the absorbancy for acetic acid at 2822 mμ. at the temperatures indicated.

TABLE III

The System Acetic Acid–Carbon Tetrachloride

The reciprocal of molal absorptivity of acetic acid and the association constants calculated from the mean absorptivity for the temperature indicated

t°C.	$\frac{1}{a_m} \times 10^{+2}$ $\frac{1000\ grams}{cm\text{-}mole}^{-1}$	$K_{association}$	t°C.	$\frac{1}{a_m} \times 10^{+2}$ $\frac{1000\ grams}{cm\text{-}mole}^{-1}$	$K_{association}$
4.5	.439	$1.15 \times 10^{+4}$	25.0	.341	$3.21 \times 10^{+3}$
8.7	.488	$1.02 \times 10^{+4}$	29.4	.385	$2.70 \times 10^{+3}$
14.3	.440	$8.70 \times 10^{+3}$	30.4	.433	$2.56 \times 10^{+3}$
15.7	.445	$6.63 \times 10^{+3}$	34.5	.334	$2.14 \times 10^{+3}$
19.7	.558	$4.46 \times 10^{+3}$	35.0	.503	$2.06 \times 10^{+3}$
20.1	.457	$4.35 \times 10^{+3}$	40.5	.335	$1.46 \times 10^{+3}$
			40.8	.378	$1.34 \times 10^{+3}$

Average value of $\frac{1}{a_m} = .426 \times 10^{-2}$

$a_m = 235$

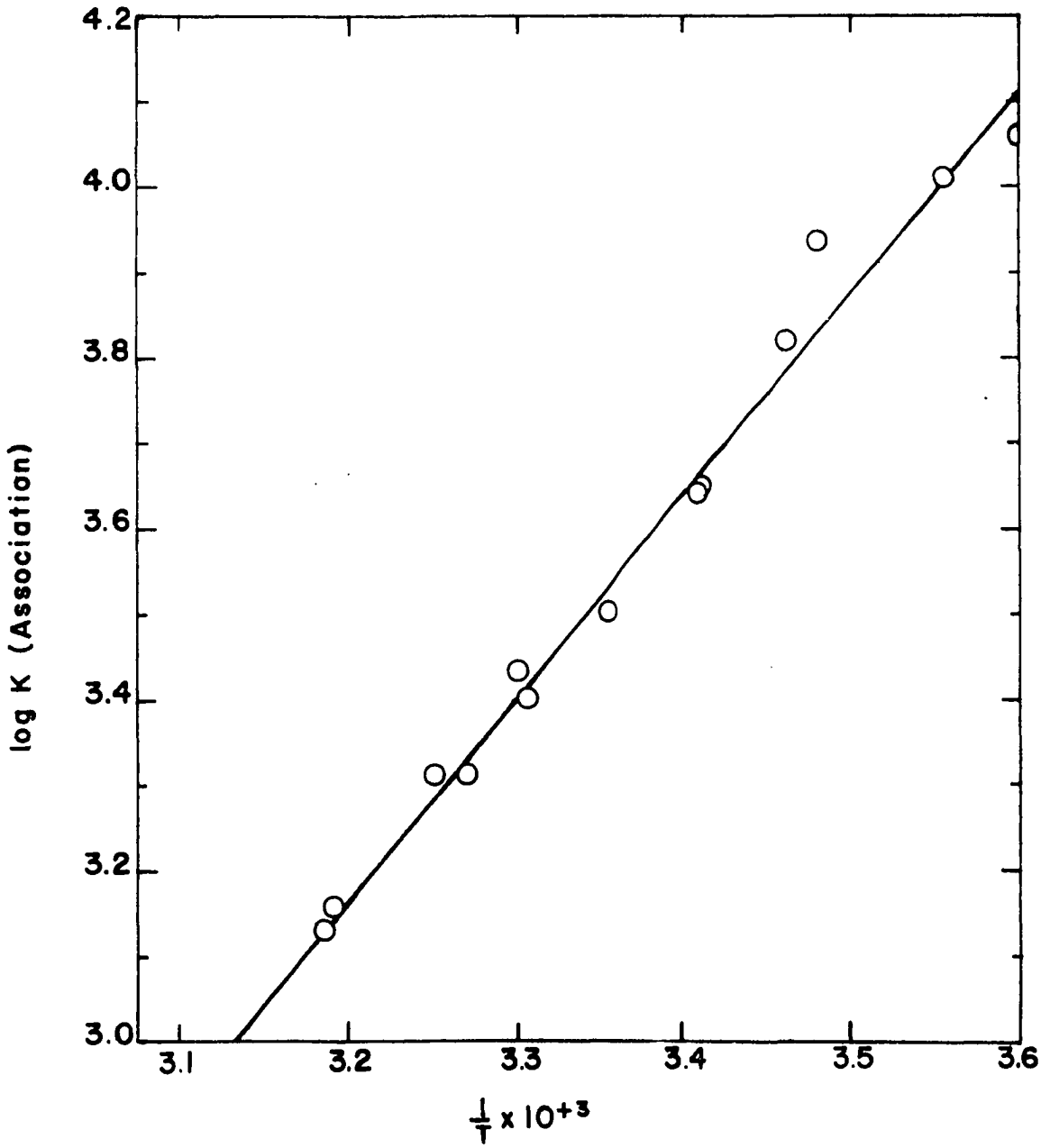


FIG. 4 -- Variation of logK (Association) with $\frac{1}{T}$ for acetic acid in carbon tetrachloride.

TABLE IV

The System Trichloroacetic Acid-Carbon Tetrachloride

Values of the molal concentrations, absorbancies, and temperatures at the peak wavelength of trichloroacetic acid (2.847μ)

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
15.5	.360	.607	.594	21.4	.383	.664	.577
	.272	.462	.588		.279	.519	.537
	.168	.321	.523		.191	.373	.511
	.087	.183	.473		.108	.218	.494
	.068	.141	.483		.065	.136	.480
15.5	.408	.688	.593	24.6	.395	.698	.567
	.337	.568	.594		.297	.564	.527
	.205	.434	.471		.182	.369	.494
	.175	.323	.542		.120	.256	.468
	.066	.138	.479		.094	.207	.456
20.0	.395	.654	.604	25.5	.383	.698	.549
	.297	.532	.558		.279	.533	.523
	.182	.350	.520		.191	.395	.483
	.120	.236	.507		.108	.233	.462
	.094	.194	.486		.065	.145	.448

TABLE IV--Continued

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
30.1	.348	.682	.510	35.9	.353	.697	.506
	.247	.491	.503		.235	.491	.479
	.139	.292	.476		.145	.308	.470
	.082	.174	.470		.104	.234	.444
	.065	.139	.467		.053	.127	.417
30.4	.353	.670	.526	36.7	.348	.695	.501
	.235	.470	.500		.247	.503	.491
	.145	.304	.477		.139	.295	.472
	.104	.227	.458		.082	.179	.456
	.053	.122	.433		.065	.142	.457
30.8	.383	.730	.525	41.2	.348	.714	.487
	.279	.561	.497		.247	.520	.475
	.191	.403	.473		.139	.301	.462
	.108	.234	.461		.082	.179	.456
	.065	.149	.436		.065	.145	.448
				42.3	.353	.728	.485
					.235	.502	.468
					.145	.312	.465
					.104	.231	.452
					.053	.121	.433

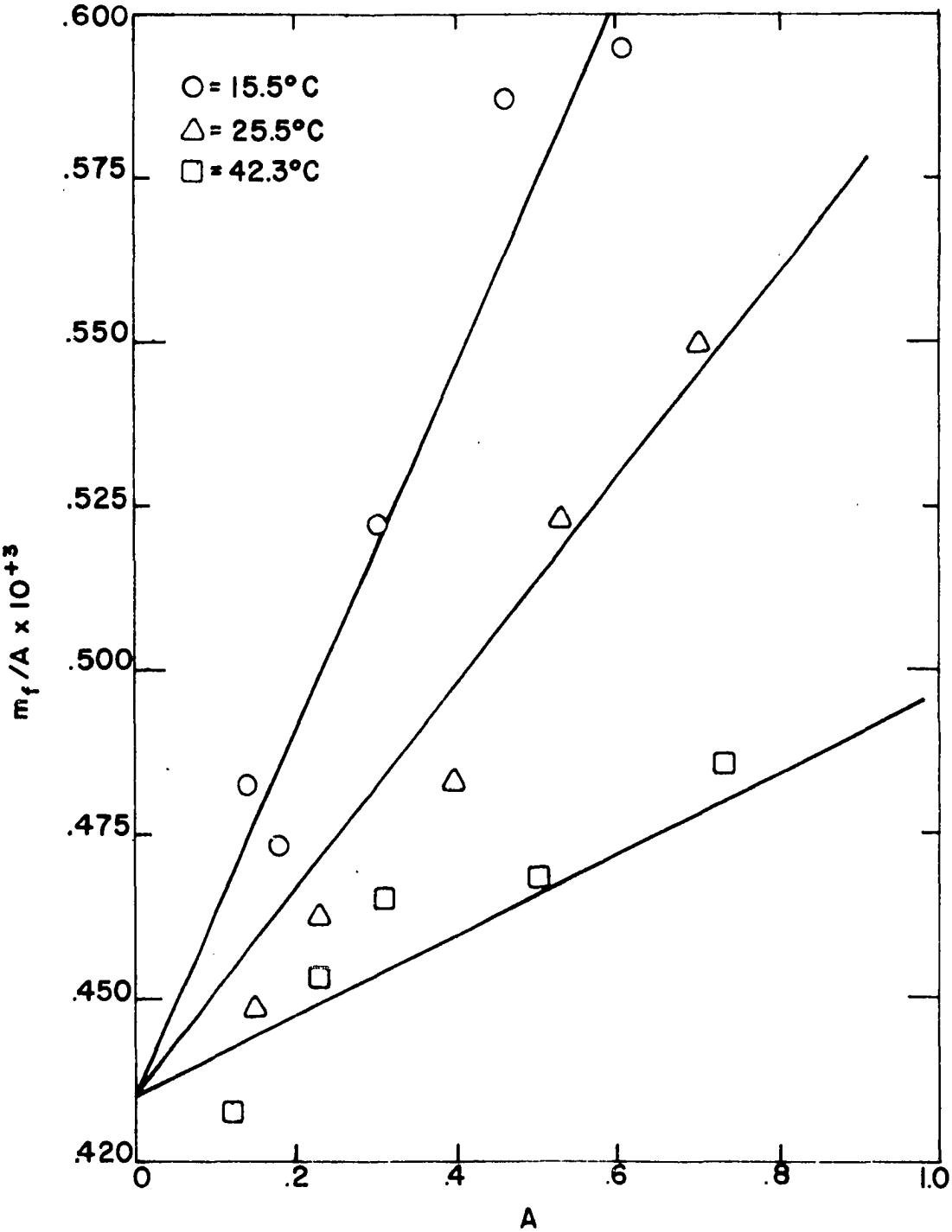


FIG. 5--Relation of the ratio m_f/A of the total acid concentration to the absorbancy A and the absorbancy for trichloroacetic acid at 2847mμ. at the temperatures indicated.

TABLE V

The System Trichloroacetic Acid-Carbon Tetrachloride

The reciprocal of molal absorptivity of trichloroacetic acid and the association constants calculated from the mean absorptivity for the temperatures indicated

t°C.	$\frac{1}{a_m} \times 10^{+2}$ $\frac{1000 \text{ grams}^{-1}}{\text{cm-mole}}$	$K_{association}$	t°C.	$\frac{1}{a_m} \times 10^{+2}$ $\frac{1000 \text{ grams}^{-1}}{\text{cm-mole}}$	$K_{association}$
15.5	0.419	$5.31 \times 10^{+2}$	30.4	0.418	$3.48 \times 10^{+2}$
15.5	0.432	$7.47 \times 10^{+2}$	30.8	0.420	$2.97 \times 10^{+2}$
20.0	0.443	$6.68 \times 10^{+2}$	35.9	0.409	$2.57 \times 10^{+2}$
21.4	0.453	$5.62 \times 10^{+2}$	36.7	0.447	$2.98 \times 10^{+2}$
24.6	0.472	$4.50 \times 10^{+2}$	41.2	0.442	$2.05 \times 10^{+2}$
25.5	0.419	$4.06 \times 10^{+2}$	42.3	0.422	$1.63 \times 10^{+2}$
30.1	0.455	$3.37 \times 10^{+2}$			

Average value of $\frac{1}{a_m} = .435 \times 10^{-2}$

$a_m = 230$

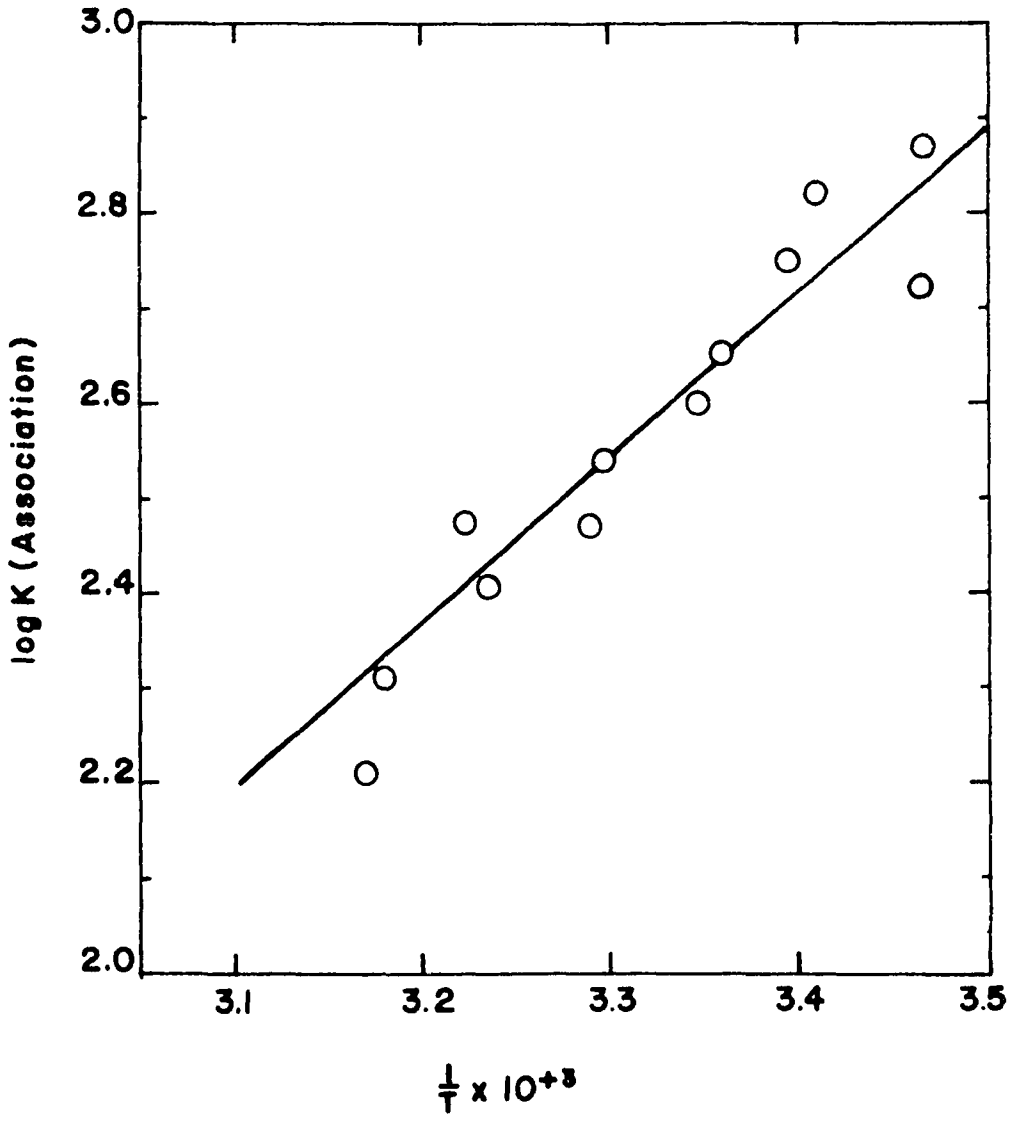


FIG. 6 -- Variation of log K (Association) with $\frac{1}{T}$ for trichloroacetic acid in carbon tetrachloride.

TABLE VI

The System Acetic Acid–Carbon Tetrachloride

Values of the molal concentrations, absorbancies and temperatures at the peak wavelength of trichloroacetic acid (2.847μ)

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
4.5	2.035	.196	10.382	15.7	2.069	.212	9.760
	1.773	.158	11.222		1.788	.188	9.511
	.794	.122	6.508		1.400	.173	8.092
	.520	.074	7.027		.843	.109	7.733
	.447	.080	5.587		.429	.082	5.231
8.7	2.035	.194	10.489	19.7	1.422	.182	7.813
	1.773	.174	10.190		1.076	.143	7.524
	.794	.108	7.352		.879	.122	7.205
	.520	.073	7.123		.686	.113	6.071
	.447	.072	6.208		.464	.102	4.549
14.3	2.142	.161	13.304	20.1	1.275	.270	4.722
	1.452	.144	10.083		1.061	.197	5.386
	.988	.117	8.444		.850	.155	5.484
	.531	.073	7.274		.535	.092	5.815
	.229	.055	4.163		.275	.058	4.741

TABLE VI--Continued

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
25.0	1.088	.161	6.757	34.5	.770	.150	5.135
	.832	.133	6.255		.603	.113	5.327
	.862	.131	6.580		.336	.074	4.551
	.711	.121	5.876		.213	.065	3.280
	.676	.115	5.878		.048	.026	1.845
	.571	.108	5.287				
	.282	.073	3.863	35.0	.760	.129	5.891
	.169	.048	3.520		.538	.113	4.761
	.073	.024	3.042		.385	.076	5.065
	.031	.008	3.875		.230	.060	3.833
					.094	.021	4.476
29.4	.780	.144	5.416				
	.609	.131	4.643	40.5	.790	.167	4.730
	.448	.103	4.349		.549	.143	3.839
	.214	.094	2.276		.310	.094	3.298
	.107	.042	2.547		.175	.068	2.573
					.051	.030	1.700
30.4	.770	.107	7.196				
	.603	.088	6.852	40.8	.760	.173	4.393
	.336	.063	5.333		.538	.161	3.342
	.213	.048	4.437		.385	.163	2.362
	.048	.018	2.666		.230	.093	2.473
					.094	.065	1.446

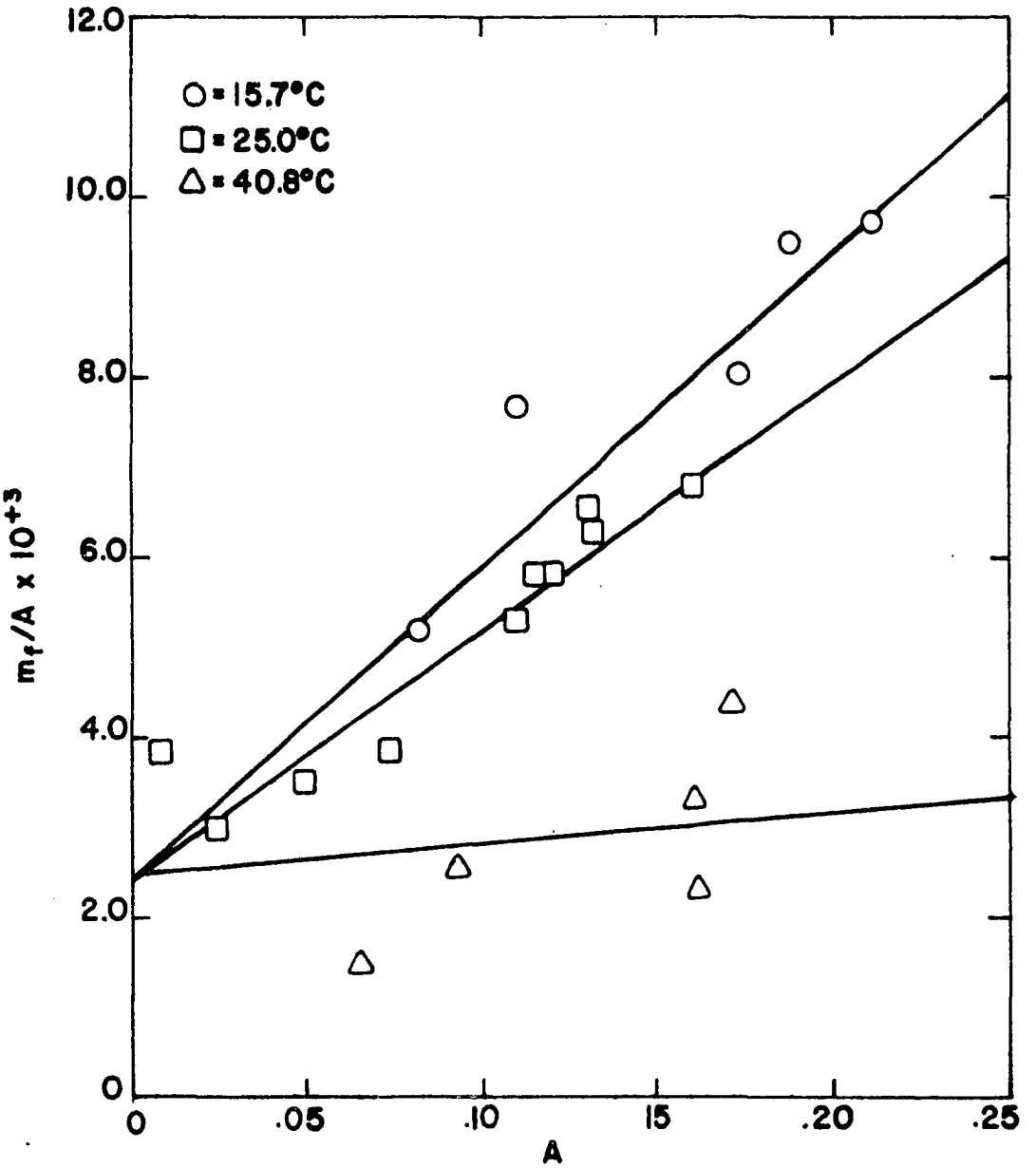


FIG. 7 -- Relation of ratio m_f/A of the total acid concentration to the absorbancy A and the absorbancy for acetic acid at 2847 mμ at the temperatures indicated.

TABLE VII

The System Acetic Acid–Carbon Tetrachloride

Values of the molal absorptivity at the peak wavelength of trichloroacetic acid (2.847)

t°C.	a_m $\frac{1000 \text{ grams}}{\text{cm–mole}}$	t°C.	a_m $\frac{1000 \text{ grams}}{\text{cm–mole}}$
4.5	33	29.4	66
8.7	42	30.4	34
14.3	110	34.5	43
15.7	28	35.0	29
19.7	48	40.5	37
20.1	187	40.8	41
25.0	107		

The Median Value of a_m is 42

TABLE VIII

The System Trichloroacetic Acid-Carbon Tetrachloride

Values of the molal concentrations, absorbancies and temperatures at the peak wavelength of acetic acid (2.822μ)

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
15.5	.361	.316	1.141	21.4	.383	.348	1.101
	.272	.244	1.113		.297	.263	1.129
	.168	.173	.970		.191	.185	1.030
	.087	.099	.878		.108	.114	.947
	.068	.079	.860		.065	.069	.942
15.5	.408	.356	1.147	24.6	.395	.353	1.120
	.337	.303	1.113		.297	.271	1.097
	.205	.216	.947		.182	.182	1.000
	.175	.166	1.054		.120	.141	.849
	.066	.074	.893		.094	.119	.792
20.0	.395	.315	1.255	25.5	.383	.350	1.095
	.297	.267	1.113		.279	.279	1.000
	.182	.184	.990		.191	.197	.968
	.120	.120	1.000		.108	.134	.806
	.094	.105	.898		.065	.082	.793

TABLE VIII--Continued

t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$	t°C.	$m_f \times 10^{+3}$ in moles/1000g CCl_4	A	$m_f/A \times 10^{+3}$
30.1	.348	.347	1.003	35.9	.353	.362	.974
	.247	.250	.988		.235	.251	.937
	.139	.161	.864		.145	.177	.819
	.082	.097	.845		.104	.140	.742
	.065	.074	.877		.053	.087	.609
30.4	.353	.359	.983	36.7	.348	.354	.983
	.235	.252	.933		.247	.254	.973
	.146	.173	.844		.139	.155	.897
	.104	.140	.742		.082	.093	.882
	.053	.082	.646		.065	.077	.844
30.8	.383	.410	.935	41.2	.348	.340	1.023
	.279	.305	.914		.247	.263	.940
	.191	.224	.851		.139	.157	.886
	.108	.148	.728		.082	.097	.845
	.065	.094	.691		.065	.073	.889
				42.3	.353	.350	1.007
					.235	.269	.874
					.145	.169	.855
					.104	.124	.838
					.053	.069	.768

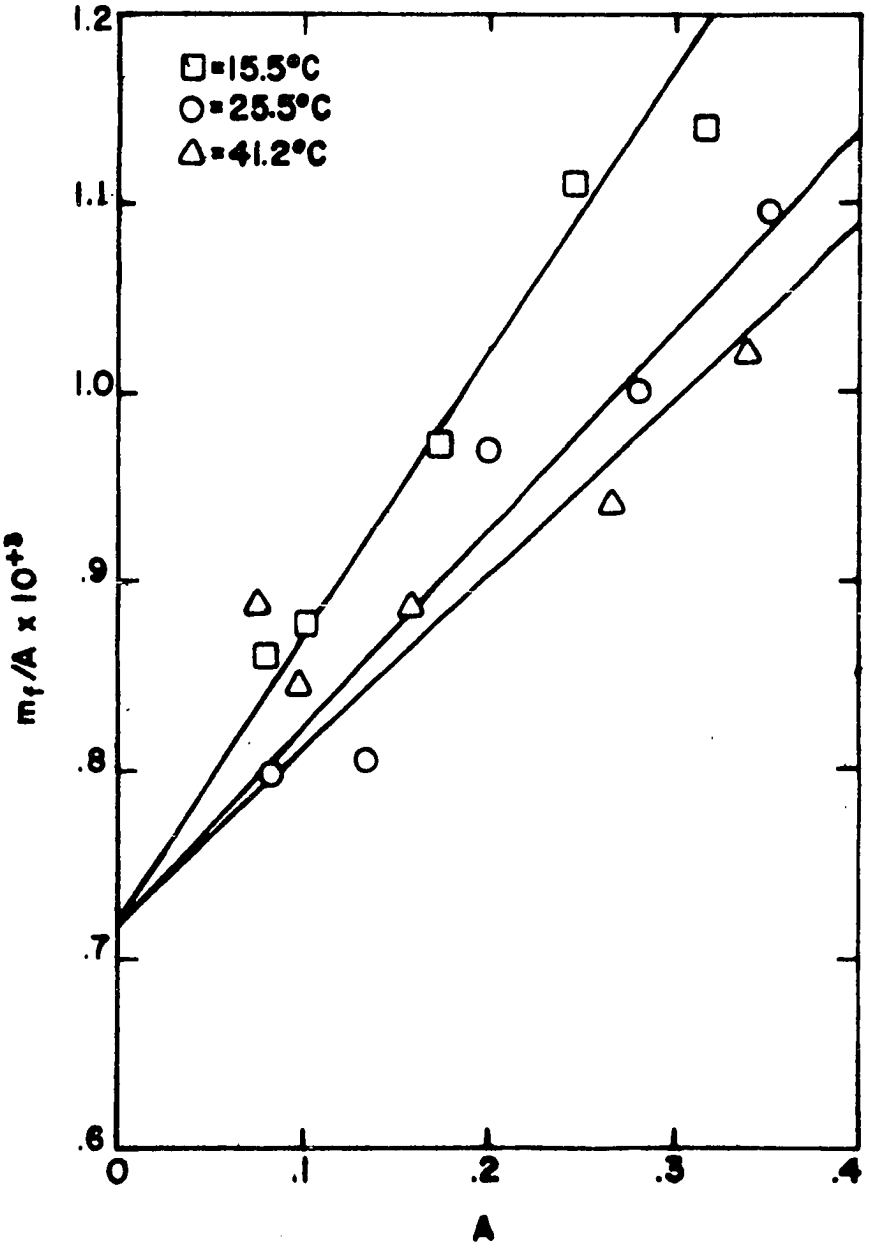


FIG. 8--Relation of ratio m_f/A of the total acid concentration to the absorbancy A and the absorbancy for trichloroacetic acid at 2822 mμ. at the temperatures indicated.

TABLE IX

The System Trichloroacetic Acid–Carbon Tetrachloride

Values of the molal absorptivity at the peak wavelength of acetic acid (2.822μ)

t°C.	a_m $\frac{1000 \text{ grams}}{\text{cm–mole}}$	t°C.	a_m $\frac{1000 \text{ grams}}{\text{cm–mole}}$
15.5	133	30.4	172
15.5	119	30.8	158
20.0	130	35.9	182
21.4	122	36.7	122
24.6	148	41.2	123
25.5	145	42.3	138
30.1	124		

The Average Value of a_m is 140

TABLE X

The System Acetic Acid–Trichloroacetic Acid–Carbon Tetrachloride

The absorbancies at 2.847μ and 2.822μ, the calculated acid monomer concentrations and the cross dimerization constant K_{AC}

t°C.	$\frac{A^{2.847\mu}}{10}$	$\frac{A^{2.822\mu}}{10}$	$m_A \times 10^{+4}$	$m_C \times 10^{+4}$	$m_f^c \times 10^{+4}$	K_{AC}
15.8	.0466	.0450	.792	1.885	4.033	
	.0361	.0389	.806	1.426	2.909	
	.0256	.0290	.639	.999	1.690	$9.22 \times 10^{+3}$
	.0153	.0194	.480	.580	.855	
	.0132	.0176	.455	.493	.650	
15.9	.0450	.0465	.910	1.799	4.096	
	.0359	.0395	.840	1.411	3.217	
	.0304	.0334	.709	1.195	2.436	$1.16 \times 10^{+4}$
	.0223	.0244	.515	.878	1.530	
	.0180	.0219	.521	.690	1.145	
19.9	.0469	.0502	1.031	1.856	4.096	
	.0394	.0435	.929	1.548	3.217	
	.0323	.0368	.816	1.259	2.436	$9.03 \times 10^{+3}$
	.0233	.0276	.639	.899	1.530	
	.0192	.0233	.553	.736	1.145	

TABLE X--Continued

t°C.	$\frac{A^{2\cdot847}\rho}{10}$	$\frac{A^{2\cdot822}\rho}{10}$	$m_A \times 10^{+4}$	$m_C \times 10^{+4}$	$m_f^c \times 10^{+4}$	K_{AC}
20.8	.0488	.0456	.757	1.987	4.033	
	.0395	.0377	.650	1.602	2.909	
	.0276	.0292	.590	1.095	1.690	$7.75 \times 10^{+3}$
	.0171	.0194	.428	.667	.855	
	.0144	.0185	.464	.544	.650	
24.7	.0513	.0561	1.184	2.019	4.096	
	.0428	.0475	1.021	1.679	3.217	
	.0353	.0397	.869	1.380	2.436	$7.25 \times 10^{+3}$
	.0254	.0292	.654	.988	1.530	
	.0204	.0242	.560	.787	1.145	
25.5	.0519	.0564	1.181	2.046	4.033	
	.0434	.0403	.661	1.769	2.909	
	.0294	.0314	.643	1.164	1.690	$5.90 \times 10^{+3}$
	.0171	.0194	.428	.667	.855	
	.0147	.0178	.421	.564	.650	
30.3	.0504	.0520	1.015	2.010	3.857	
	.0394	.0378	.658	1.596	2.765	
	.0263	.0273	.538	1.048	1.622	$9.03 \times 10^{+3}$
	.0138	.0113	.138	.575	.886	
	.0105	.0110	.219	.415	.638	

TABLE X--Continued

t°C.	$\frac{A^{2\cdot847}\rho}{10}$	$\frac{A^{2\cdot822}\rho}{10}$	$m_A \times 10^{+4}$	$m_C \times 10^{+4}$	$m_f^c \times 10^{+4}$	K_{AC}
30.5	.0504	.0545	1.134	1.989	3.684	
	.0384	.0439	.977	1.496	2.601	
	.0257	.0288	.626	1.006	1.541	$6.97 \times 10^{+3}$
	.0175	.0189	.393	.691	.949	
	.0077	.0111	.305	.349	.531	
35.2	.0547	.0577	1.162	2.171	3.684	
	.0426	.0456	.937	1.685	2.601	
	.0280	.0314	.684	1.096	1.541	$5.40 \times 10^{+3}$
	.0189	.0213	.466	.739	.949	
	.0095	.0134	.363	.348	.531	
36.7	.0593	.0638	1.319	2.343	3.857	
	.0461	.0495	1.021	1.822	2.765	
	.0299	.0352	.809	1.156	1.622	$4.34 \times 10^{+3}$
	.0175	.0206	.474	.677	.886	
	.0128	.0146	.324	.486	.638	
40.0	.0593	.0684	1.538	2.304	3.684	
	.0452	.0542	1.271	1.739	2.601	
	.0300	.0376	.921	1.140	1.541	$3.42 \times 10^{+3}$
	.0206	.0281	.741	.764	.949	
	.0111	.0171	.492	.395	.531	

TABLE X--Continued

t°C.	$\frac{A^{2.847\mu}}{10}$	$\frac{A^{2.822\mu}}{10}$	$m_A \times 10^{+4}$	$m_C \times 10^{+4}$	$m_f^c \times 10^{+4}$	K_{AC}
40.8	.0588	.0638	1.334	2.319	3.857	
	.0462	.0517	1.123	1.809	2.765	
	.0326	.0371	.822	1.271	1.622	$3.93 \times 10^{+3}$
	.0184	.0224	.533	.705	.886	
	.0147	.0172	.393	.569	.638	

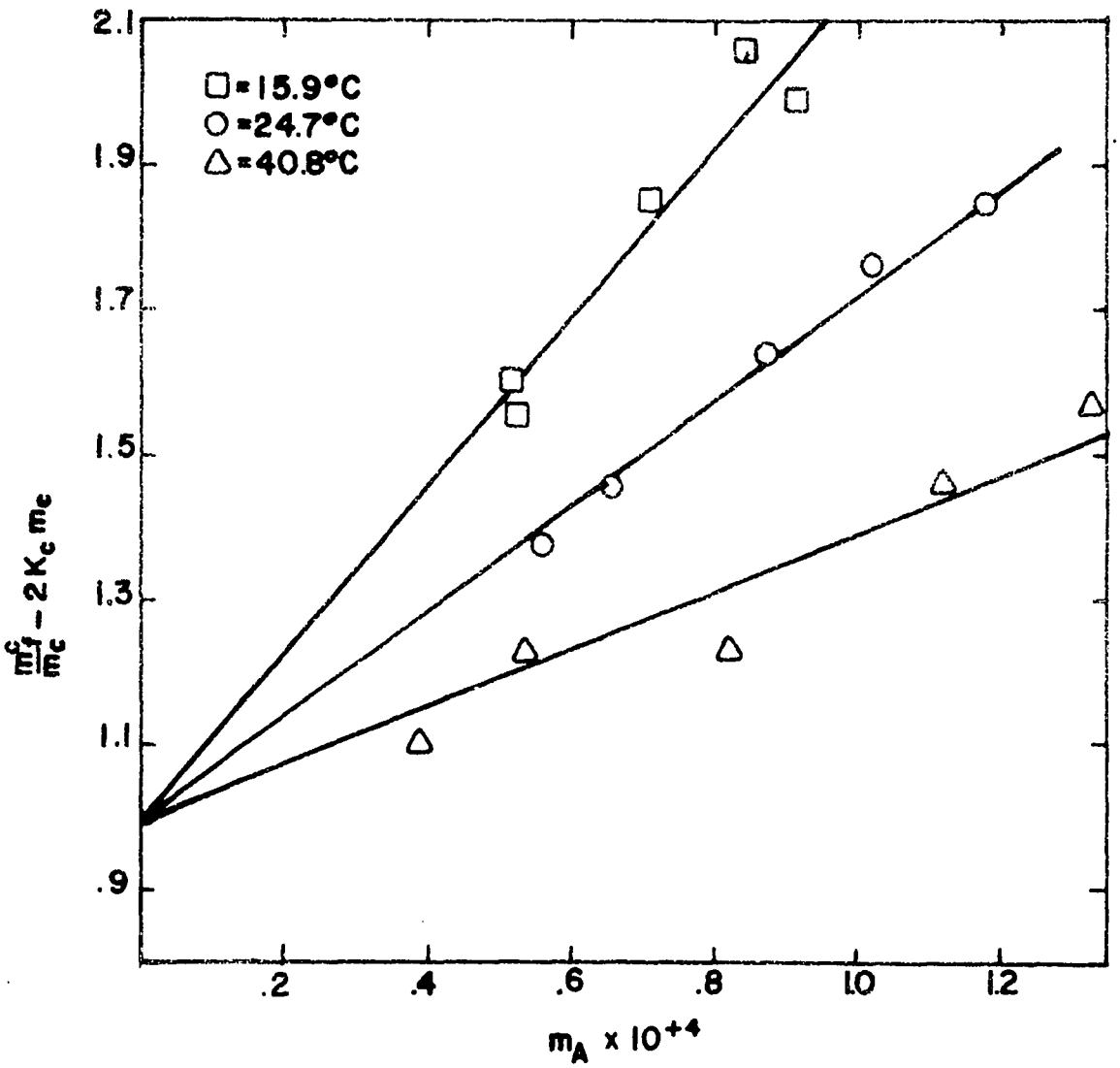


FIG.9 -- Relation of $\frac{m^c_f}{m_c} - 2K_c\, m_c$ and m_A at the temperatures indicated.

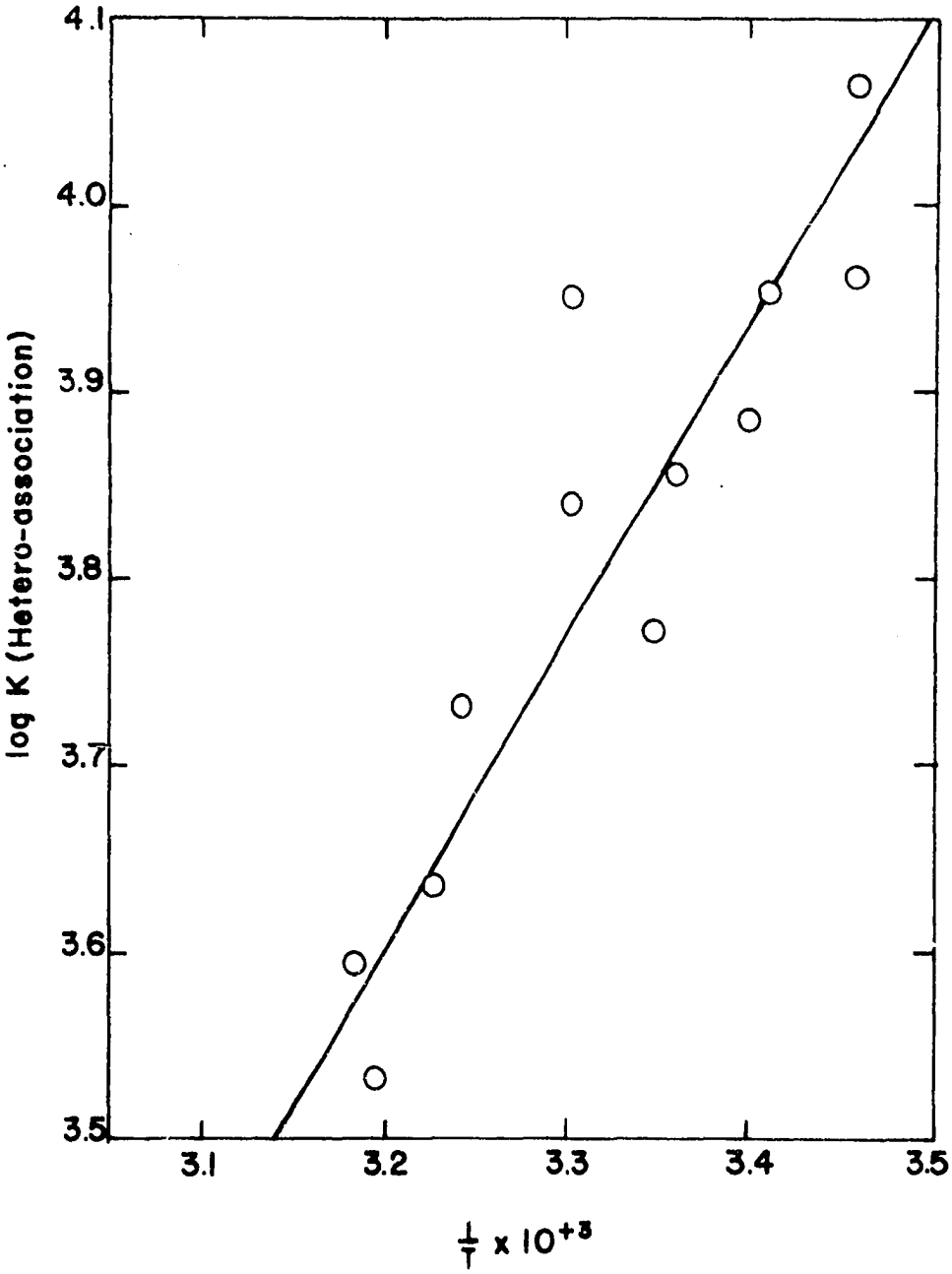


FIG. 10-- Variation of log K(Hetero-association) with $\frac{1}{T}$ for acetic acid + trichloroacetic acid in carbon tetrachloride.

TABLE XI

Thermodynamic Functions of the Association Reactions

Values of the Thermodynamic Functions $\Delta H°$, $\Delta F°$ and $\Delta S°$ at 25°C.

Reaction	K	$\Delta H° \frac{kcal}{mole}$	$\Delta F° \frac{kcal}{mole}$ (1)	$\Delta S° \frac{EU}{mole}$
$2CH_3COOH \rightleftarrows (CH_3COOH)_2$	$3.21 \times 10^{+3}$ molal^{-1}	-10.7	-4.78	-19.9
$2CCl_3COOH \rightleftarrows (CCl_3COOH)_2$	$4.28 \times 10^{+2}$ molal^{-1}	-7.9	-3.59	-14.5
$CH_3COOH + CCl_3COOH \rightleftarrows CH_3COOH \cdot CCl_3COOH$	$7.17 \times 10^{+3}$ molal^{-1}	-7.7	-5.26	-8.2
$\frac{1}{2}(CH_3COOH)_2 + \frac{1}{2}(CCl_3COOH)_2 \rightleftarrows CH_3COOH \cdot CCl_3COOH$	6.12	+1.6	-1.07	+9.0

(1) The units of K are molal^{-1} for the first three reactions. K is unitless for the fourth reaction.

CHAPTER VI

Discussion

In the systems acetic acid-carbon tetrachloride and trichloroacetic acid-carbon tetrachloride both acetic and trichloroacetic acids dimerize, with the former showing more extensive association. The association constant of acetic acid in anhydrous carbon tetrachloride was experimentally determined to be $3.21 \pm 0.43 \times 10^{+3}$ molal^{-1} at 25.0°C. Harris and Hobbs[20] obtained a value of $3.21 \times 10^{+3}$ at the same temperature. The constant of Spurr and Wenograd[36] is somewhat lower than the value obtained here. With a 6.0 cm. cell their measurements gave a value for the association constant of $2.4 \times 10^{+3}$. The mean molal absorptivity of acetic acid in carbon tetrachloride was 235 $\frac{1000 \text{ grams}}{\text{mole-cm}}$ with a standard deviation of 39. Conversion of this mean molal absorptivity to units of $\frac{\text{liter}}{\text{mole-cm}}$ gave a value of 147 which exceeds the value reported by Harris and Hobbs[20] by 45. In the case of trichloroacetic acid the association constant was found to be $4.06 \pm 0.39 \times 10^{+2}$ molal^{-1} at 25.5°C. This value is lower than that reported by Harris and Hobbs of $5.8 \times 10^{+2}$ at 25.0°C. The calculation of the molal absorptivity gave a value of 230 $\frac{1000 \text{ grams}}{\text{mole-cm}}$ with a standard deviation of 9. Conversion of this mean molal absorptivity into units of $\frac{\text{liter}}{\text{mole-cm}}$ gave a value of 144 compared to 130 reported by Harris and Hobbs.[20]

The heats of dimerization of acetic and trichloroacetic acids were determined from plots of log K (association) versus $\frac{1}{T}$ (Figures 4 and 6). The slopes were evaluated by the method of least squares.

Heats of dimerization were assumed to be independent of temperature in the interval of temperature studied. For acetic acid the heat of dimerization was -10.7 ± 1.2 kcal. per mole of dimer (2 hydrogen bonds). Kagarise[23] obtained an average heat of dimerization of -10.7 kcal. per mole of dimer using association constants evaluated at 3 different frequencies in the temperature interval 20-60°C. In the case of trichloroacetic acid the heat of dimerization was -7.9 ± 1.2 kcal. per mole of dimer. This result is lower than the value quoted by Kagarise of -10.3 kcal. per mole of dimer for the temperature interval 20-60°C. Allen and Caldin[1] have concluded that heats of dimerization derived from spectroscopic measurements have an experimental uncertainty of $\pm$ 1 kcal. per mole of dimer.

For the system acetic acid-trichloroacetic acid-carbon tetrachloride the hetero dimerization constant was experimentally determined to be $7.25 \pm 0.91 \times 10^{+3}$ at 24.7°C. Examination of the relative magnitudes of K (association) shows that there is extensive hetero dimerization. These results are in accord with the findings of Christian[10] for the systems acetic acid + trifluoroacetic acid and propionic acid + perfluoropropionic acid in the gas phase.

Values of the molal absorptivity of trichloroacetic acid at 2,822 mμ and of acetic acid at 2,847 mμ were required to calculate m_A and m_C, the two monomer concentrations. Any error in the evaluation of these quantities would affect the calculated monomer concentrations

to a marked degree. The molal absorptivity of trichloroacetic acid was 140 $\frac{1000 \text{ grams}}{\text{liter-cm}}$ with a standard deviation of 22. Plots of m_f/A versus A were linear with some scattering of the points. In the case of the molal absorptivity of acetic acid at 2,847 mμ plots of m_f/A versus A gave values of the intercepts that scattered widely. At that wavelength the measured absorbancies of acetic acid ranged from 0.02 to about 0.2 with most of the readings below A = 0.125. This meant that in the measurement of the heterodimerization the contribution of acetic acid monomer at 2,847 mμ was relatively small. If the mean molal absorptivity were used the very high and very low results would be weighed too heavily. Since most of the values were between 25 and 65 it was felt that the median of 42 was an adequate correction factor at that wavelength with most of the absorbancy being due to the trichloroacetic acid monomer. The effect of using the mean molal absorptivity of acetic acid at 2,847 mμ instead of the median value is demonstrated by the calculation of K_{AC} at 24.7°C. Monomer concentrations were evaluated from the appropriate absorbancies and mean absorptivities. With the median value of $a^{2,847m}_{HOAc} = 41$, $K_{AC} = 7.25 \times 10^{+3}$ while $\bar{a}^{2,847m}_{HOAc} = 65$, increased K_{AC} to $8.57 \times 10^{+3}$.

From the plot of Log K (hetero-association) versus $\frac{1}{T}$ (Figure 10) the heat of hetero-dimerization was calculated from the best straight line by the method of least squares. In the temperature interval studied the heat of dimerization was assumed to be independent of the temperature. For this system the heat of hetero dimerization was -7.7 ± 1.5 kcal. per mole of cross dimer (2 hydrogen bonds).

The theoretical value of the ratio $K_{AC}/\sqrt{K_A K_C}$ is 2 according

to Fowler and Guggenheim.[14] Their derivation assumes that the average heat of dimerization of the two individual acids equals the heat of hetero dimerization. The further assumption is made that the entropy change of the hetero dimerization reaction is Rln2, i.e. ΔS results from the difference between the symmetry numbers of the hetero and homo dimers. At 25°C. the calculated ratio in this work is 6.12. Christian[10] found ratios of 5.20 and 7.25 for the gas phase hetero dimerization of the acetic acid and propionic acid systems respectively. The fact that the ratio was found to be 3.06 times greater than the theoretical value must be a result of the inductive effect of the trichloromethyl group.

The thermodynamic constants in Table XI imply that the entropy factor is the major one inducing the formation of hetero-dimers at the expense of homo-dimers. It is likely, however, that the enthalpy of the reaction $CH_3COOH + CCl_3COOH \rightleftarrows CH_3COOH \cdot CCl_3COOH$ is more negative than the value calculated. If this is the case both $\Delta F°$ and $\Delta S°$ should be more negative for the reaction $\frac{1}{2}(CH_3COOH)_2 + \frac{1}{2}(CCl_3COOH)_2 \rightleftarrows CH_3COOH \cdot CCl_3COOH$. In any event, there is no doubt that the reaction, $\frac{1}{2}(CH_3COOH)_2 + \frac{1}{2}(CCl_3COOH)_2 \rightleftarrows CH_3COOH \cdot CCl_3COOH$, does occur spontaneously even though it is not possible at present to assess accurately the relative importance of $\Delta H°$ and $T\Delta S°$ as driving forces. Throughout the range of temperature studied the concentration of the hetero-dimeric species was several times that of each type of homo-dimer, while the two homo-dimers are present in approximately equal concentrations.

This work has contributed association data and thermodynamic functions for acetic acid, trichloroacetic acid, and mixtures of the

two acids in anhydrous carbon tetrachloride. The objections raised to studies of association equilibria by spectrophotometry were overcome by using very dilute solutions, discrete monomer absorption bands, improved infra-red instrumentation, good temperature control and by employing a solvent which gives a minimal solute-solvent interaction.

Suggestions for further work would include a study of the systems acetic acid + monochloroacetic acid and acetic acid + dichloroacetic acid in anhydrous carbon tetrachloride. Although K_{AC} was shown to be greater than either K_A or K_C for the acetic acid + trichloroacetic acid system, it would be of value to determine the effect of halogen substitution on the hetero-dimerization.

An important question raised by this work concerns the problem of elucidating the geometry of the hetero dimeric species, such as was dealt with here. Are the two hydrogen bonds forming the dimer equivalent to each other? What are the bond lengths and angles in the cross dimer? Nuclear magnetic resonance and dipole moment studies may prove useful in this respect.

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