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KETONES IN ORGANIC SOLVENTS

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TABLE OF CONTENTS

LIST OF TABLES

Table   Page

LIST OF ILLUSTRATIONS

SELF-ASSOCIATION AND HYDRATION OF

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CHAPTER I

INTRODUCTION

Acetone has been widely used as a solvent, not only
for an enormous number of organic, but also for some inor-
ganic compounds. The complete miscibility of acetone with
water and the fact that mixtures of water and acetone have
higher densities and viscosities than ideal mixtures all in-
dicate that there is a relatively strong interaction between
the molecules of acetone and water. In this interaction,
water protons are associated with carbonyl groups of acetone,
which can act as a proton acceptor. The basicity of this
proton acceptor has long been recognized, but little work has
been done to determine its strength.

Infrared techniques have been employed to detect the
frequency shift of the carbonyl stretching vibration, and it
has been found that the shift arising from hydrogen-bonding
interaction is only a little larger than those attributed to
specific solvent effects. However, Josien, et al. (1), found
that the frequency shift of the carbonyl stretch for hydrogen-

bonding solvents cannot be directly correlated with the dielectric constants of organic solvents. He used a Kirkwood-Bauer-Magat plot (2, 3), i.e. $(n^2 - 1)/(2n^2 + 1)$ vs. $\delta\nu/\nu$, where n is refractive index of solvent, and showed that there were deviations whenever hydrogen-bonding occurred. Bayliss, et al. (4), and Tsubomura (5) found that hydrogen-bonding solvents cause an unusual enhancement of intensity, but no bandwidth increase. The blue and red shifts of acetone and other compounds in ultraviolet spectra in a variety of solvents were first discussed by Bayliss and ReRae (6). They attributed the frequency shifts to dipole-dipole, dipole-induced dipole and hydrogen-bonding interactions. Pimentel (7), using the Frank-Condon principle, noted a linear relation $\Delta\nu = \omega_b - \omega_1 + C$ where $\Delta\nu$ is the frequency shift, ω_b is the energy of the hydrogen bond in ground states, ω_1 is the energy of the hydrogen bond in excited states and a constant C required by Frank-Condon principle for $n \rightarrow \pi^*$ transition. In his argument, if the solvents are capable of hydrogen-bonding, the hydrogen-bonding effect on the frequency shift will dominate other effects.

During the last decade, NMR studies of hydrogen-bonding have attracted a great amount of interest. Arnold and Packard (8) first observed the concentration and temperature dependence of chemical shifts of the hydroxyl protons in ethanol. An interpretation of their results was given by Liddel and Ramsey (9), who attributed the variation of

chemical shifts to the rapid formation and dissociation of hydrogen bonded species. The hydrogen bond chemical shifts are generally very large, and undoubtedly as informative as infrared spectral effects. However, NMR has the disadvantage of averaging the effect of chemical shifts as the infrared has difficulty in identifying the absorption bands. Since ordinary oxygen does not have a nuclear magnetic moment, it is not possible to measure directly the effect of hydrogen-bonding on the carbonyl group unless oxygen isotope O^{17} is used. However, an alternative method is to determine the chemical shifts of protons which are affected by the carbonyl group.

Dielectric constant measurements of dilute solutions of polar solutes in polar or non-polar solvents provide an indication of interactions between solvent and solute. The effect of solvent on the dipole moment of a solute has been discussed theoretically in some detail by Weigle (10), Higas (11) and Frank (12, 13). In order to determine the geometric structures of complex species, some attempts (14, 15) have been made to determine the dipole moment of complex species from dielectric constant measurements. But no satisfactory result has been obtained, not only because of solvent effect, but also because of changes in the dipole moments of the donor and acceptor molecules when they interact to form the complex species. Dielectric dispersion techniques have become in-creasingly important in the studies of hydrogen bond. Basi-

cally, these methods involve the determination of dielectric constants over a range of frequency. The advance of experimental techniques permits the study of liquid samples in the microwave and short radio wavelength region, where dispersion behavior is very useful in elucidating molecular properties. Collie, Hasted and Ritson (16), using radar techniques, measured the dielectric dispersion behavior of water, and were led to conclusions of great value in interpretation of the nature of liquid water.

In addition to the infrared, ultraviolet, dielectric constant and dispersion techniques, there are several non-thermodynamic methods which can be utilized in hydrogen bond studies. These include Raman, ultrasonic flourescence, photo-tropism and optical rotation methods. Most of them have been used in relatively few studies.

The thermodynamic methods for studying complex formation include cryoscopy, boiling point elevation, viscosity, surface tension, partition and solubility methods. Among these, partition and solubility methods are new techniques developed in this laboratory (17, 18) for studying the hydration and self-association of polar molecules. The extent of hydration and self-association of polar molecules is determined by analyzing the partition and water solubility data. Partition data are obtained by measuring the distribution of a solute between an organic phase and water phase; water solubility data are obtained by analyzing the concentration

of water in the organic solvent phase in the presence of polar solutes at different activities of water. These techniques were employed by Taylor (19) to study the self-association and hydration of carboxylic acids. He found that water played an important role in the self-association of acetic and benzoic acids, an effect which had been neglected in previous distribution work. Johnson (20) also employed these techniques in his studies of the association and hydration of phenol, and showed that the partition and water solubility data are very useful in the interpretation of complex species in non-polar and slightly polar solvents.

A great deal of work has been done on the intermolecular forces in complexes which are stabilized by hydrogen bonds, dipole-dipole interactions and charge-transfer type interactions. The study of charge-transfer complexes is a relatively new field which has been expanding rapidly. The dipole-dipole interaction, although long recognized, has not attracted as much interest as hydrogen-bonding, because (1) the interactions are generally weak in comparison with the hydrogen bonds, and (2) the species are hard to detect spectroscopically. On the other hand, the hydrogen-bonded complex species, although stabilized in part by dipole-dipole interaction, can easily be detected spectroscopically. Since the forces of hydrogen bonds are relatively strong, hydrogen-bonding has a profound influence on the thermodynamic properties of solutions, a great deal of deviation from ideality

can be expected. The dipole-dipole interaction, on the other hand, exerts somewhat less influence on the thermodynamic properties of solutions.

Among the ketones, acetone is a simple molecule which should be studied intensively with respect to its hydration properties. Ultraviolet spectra show a remarkable blue shift of the acetone characteristic peak (at 265 mμ) in water relative to that of acetone in CCl_4 (at 280 mμ). Huggins (21) studied acetone and chloroform mixtures by NMR and concluded that in acetone-chloroform mixtures, the 1-1 complex is the major associated species. Mavel (22) has measured the chemical shifts of water protons in acetone-water mixtures and an interpretation was made of the effect of acetone on the dissociation of water complexes. Takahashi and Li (23) also measured the chemical shifts of water protons in the system acetone-water-cyclohexane. They have worked out a method of treating the NMR data to obtain the equilibrium constant of the association between 1-1 water-acetone complex and acetone. Recently, Wisdom and Philippe (24) have made a systematic study of the interaction of phenol with several ketones by means of infrared spectra. They showed that the basicity of ketones has the following order, acetone > methylethylketone > diethylketone > 4-heptanone > acetophenone. Fritzche and Dunken (25) measured the frequency shift of the OH stretch of phenol associated with different ketones and found that the enthalpy of association varies linearly with the frequency shifts.

Heinen (26) determined the association equilibrium constants
for the complexes between acetone and a number of alkylphenols.
A linear relationship was found between the logarithm of the
association equilibrium constants of the complexes and pK_a for
H^+ dissociation of the alkylphenol, except for 2,6-xylenol
which deviates from linearity, having a lower value for its
equilibrium constant due to a steric hindrance effects.

For the measurements of dielectric constants, Akerlof
(27) has used a resonance method at wavelength of 150 M to
measure the dielectric constants of acetone-water mixtures.
He found a linear relation between the molar polarization of
the mixture and the mole fraction of acetone, as predicted
by Clausius-Mossotti-Debye equation. Glasstone (28) measured
the dielectric constants of acetone-water mixtures and found
that the molar polarization of acetone calculated by using
Debye's equation decreases as the concentration of acetone
increases, indicating the "self-association" of acetone in
CCl_4. The second virial coefficient of acetone vapor meas-
ured by Lambert, et al. (29) agreed with the theoretical
values calculated by Rowlinson (30), assuming that the major
part of the observed deviation from ideality is due to the
dipole-dipole interaction of acetone molecules in the vapor
phase. Jakobson and Brash (31) found a broad peak in the far
infrared region (50 cm^{-1}) in pure acetone liquid. They ex-
plained the broad peak is due to the dipole-dipole interaction
of acetone. Bowen and Thompson (32) also found that in the

vapor phase at pressure less than a few mm, the characteristic broad acetone peak with maximum at 2800 $\overset{\circ}{A}$ splits up into four groups, each containing about 25 diffuse bands. This may indicate that the dipole-dipole interaction still persists at low pressures.

In the present investigation of the self-association and hydration of ketones, partition, water solubility, NMR, and dielectric constant methods were used. The ketones used in this investigation were acetone, 2,3-butanedione and acetylacetone. The solvents used were CCl_4, 1,2-dichloroethane and hexadecane.

CHAPTER II

OBJECTIVES

The objectives of this research are:

(1) To determine the basic strength of ketones through the determination of hydration parameters of ketones in several solvents.

(2) To determine the extent of self-association of ketones and reveal the physical properties of the dipole-dipole interactions.

(3) To reveal the influence of solvents on the thermodynamic and physical properties of complex species.

CHAPTER III

EXPERIMENTAL

(1) Purification of materials: Acetone was purified by distillation over anhydrous calcium sulfate in a 30-plate Oldershaw column; the middle portion of distillate was collected. The compound was further dried by means of vapor contact with anhydrous magnesium perchlorate. The reagent grade 2,3-butanedione is a yellow liquid purchased from Eastman Kodak Company and purified by distillation. Acetylacetone was purchased from Matheson Coleman & Bell Co. and was also distilled before use. The NMR spectrum of pure acetylacetone was found to be nearly identical with that reported in literature (33, 34, 37). The solvents carbon tetrachloride and 1,2-dichloroethane were purified by distillation through a 30-plate Oldershaw column, using 10:1 reflux ratio. The non-volatile solvent, hexadecane, was distilled at reduced pressure. Baker and Adamson C. P. Grade sulfuric acid was used to prepare the solvents of constant water activities. The relationships for different temperatures between water activities of sulfuric acid solution and their densities were obtained from the literature (35, 36).

(2) Partition and Isopiestic method: In the partition method, the ketones were allowed to distribute between a water phase and an organic solvent phase. The immiscible water phase and organic solvent phase were contained in 500 ml glass-stopped Erlenmeyer flasks supported in a constant temperature bath. After several days, both phases were sampled and the concentrations of ketones in the two phases were determined spectrophotometrically. Absorbances of ketones were measured at the maximum absorption wavelengths given in Table 1 for the different solvents. A Beckman D U Spectrophotometer was used for the absorbance measurements, using 1-cm silica cells with a mechanical slit width of 0.1 mm. Calibration curves of absorbances versus ketone concentrations were obtained by measuring the absorbance of solutions of ketone prepared by weight. In order to avoid systematic errors which might arise due to the change of instrument conditions, the calibration curves were obtained immediately before each set of measurements of sample solutions. In the case of absorbances greater than 1.0, the samples were diluted with pure solvent. The accuracy of the spectrophotometric method was estimated to be 1.2%. The calibration curves were found to obey Beer's law, except for the solutions acetone-water, and acetylacetone-water as indicated in Table 1. Since the absorptivity of acetylacetone is so large ($1600 \ ml^{-1}cm^{-1}$), it is impractical to determine the concentration of acetylacetone in CCl_4 by diluting with large quantities of CCl_4.

In order to avoid using excessive quantities of CCl_4, 2 c.c. samples of the acetylacetone-CCl_4 solutions were extracted with 2 liters of water. From absorbance measurements made on the aqueous phase, the corresponding concentrations of acetylacetone in the original CCl_4 phase could be calculated.

The isopiestic methods developed by Christian, Affsprung, and co-workers (17, 18) were used to determine the water solubility in the solvents in the presence of ketones. About 200 c.c. samples of ketone solution were contained in wide-mouth jars of approximately 1 liter capacity. Inside each jar was suspended or supported a 100 c.c. beaker containing 30 c.c. of sulfuric acid solution which acted as a constant water activity source. The system was closed from the atmosphere by a lid and layers of Saran Wrap. It was estimated that the transfer of water from the sulfuric acid solutions into ketone solution requires about two days to reach equilibrium. In order to demonstrate that equilibrium was attained, one of the jars was set up to contain only pure solvent, and the water solubility in this sample was determined and compared to the known solubility of water in the solvent at the given water activity. The concentrations of water in the solutions were determined by Karl Fisher titration with the Beckman KF-3 Aquameter. The composition of the Karl Fisher reagent used was: pyridine 269 ml, iodine 84.7 gr., methanol 667 ml, sulfur dioxide 45 ml. The titer of the Karl Fisher reagent was determined before each determination with

sodium tartrate dihydrate. The details of preparation of the
Karl Fisher reagent have been summarized by Johnson (20). In
the case of solutions containing acetone, the end point of
the titration was found to fade away, presumably because of
the reaction,

$$(CH_3)_2CO + 2CH_3OH \longrightarrow (CH_3)_2C(OCH_3)_2 + H_2O$$
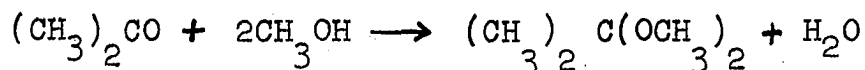
in which additional water is formed. In order to avoid the
fading end-point, the composition of the Karl Fisher reagent
was modified to: pyridine 961 ml, iodine 84.7 gr., methanol
100 ml, sulfur dioxide 45 ml (38). With the modified reagent,
the rate of the formation of water is relatively slow and may
be neglected during the titration. It was estimated that the
end-point of the titration can be obtained with an accuracy
of 2.0%. The concentration of ketones in the same solutions
were determined spectrophotometrically as described above.
Since acetone is quite volatile a small amount of acetone in
the organic phase undoubtedly transferred to the aqueous sul-
furic solution; hence, the activity of the aqueous solution
is lowered slightly. It was shown that the change of water
activity is so small that it can be neglected.

(3) NMR technique: The NMR method was used to deter-
mine the chemical shift of water protons in the presence of
acetone in 1,2-dichloroethane. The solvent CCl_4 could not be
used, because the water solubility in CCl_4 is too small
(0.0087 M at $25°$) to be detected by ordinary NMR methods.

The lowest concentration NMR is able to detect is about 0.02 M, which is much less than the solubility of water in 1,2-dichloroethane at 25° (0.125 M). Therefore, the NMR method is capable of detecting the water proton signal in 1,2-dichloroethane. After the concentration of water in 1,2-dichloroethane had been determined by Karl Fisher titration, the solution was partitioned into two parts. One part was then mixed with a known amount of distilled dry acetone; hence the concentration of acetone in this solution was known. Samples of different concentrations of acetone at the same formal concentration of water were made by mixing different ratios of these two solutions. The samples were then immediately run using the Varian A-60 NMR (magnetic field 14092 gauss) analytical spectrophotometer. The temperature of the sample was maintained within $\pm 1^\circ$ at 30° and $\pm 2^\circ$ at 45° by a Varian V-6057 high-low temperature control system. During each run, the samples were carefully capped to prevent possible evaporation. The error in chemical shift measurements was estimated to be about 0.2 cps. with 60 MC r. f. field. A long capillary filled with cyclohexane was inserted into the sample tube as an external reference. A sharp reference peak was observed, since the long capillary was held at the center of the sample tube by eddy currents of liquid during the sample spinning. In order to avoid saturation, the magnitude of the r. f. field was kept below 0.2 milligauss. The position of the peak was determined as the average of several

scannings and was read relative to the sharp reference peak of the spectrum chart. The percentage of enol and keto form in acetylacetone was determined by comparing the areas of the CH_3 peak of enol and keto form.

(4) Dielectric constant measurement: Dielectric constants of solutions were measured with the Dipolemeter DM01 which operates on the superposition (beat) method. Water-1,2-dichloroethane solutions were prepared by mixing 1,2-dichloroethane which is about 90% saturated with water, with dry 1,2-dichloroethane in different ratios. Acetone-1,2-dichloroethane solutions were also made up in the same way. Water-acetone-1,2-dichloroethane solutions were prepared by mixing in different ratios the dry acetone in 1,2-dichloro-ethane with wet solutions of acetone in 1,2-dichloroethane of the same concentration. MFL 2 cell (range from ϵ = 7 to 21) with a capacity of 45 ml was used for all the measurements. The constant temperature water was circulated through water jacket of the cell; the circulating water temperature was maintained at $25.00 \pm 0.03^\circ$. Once a series of measurements was started, the cell was not removed or turned in its connector in order to avoid the possibility of errors due to slight changes in the electric contact. The sample solutions were prepared in relatively large quantities in order to minimize the evaporation of volatile solute in the course of the measurements. After the dielectric constant of each sample solution was measured, the cell was drained and rinsed

with the new solution to be measured, and the new solution was introduced without moving the cell. A calibration curve was obtained by measuring the dielectric constant of water-dioxane mixture for which the dielectric constants versus mole fraction have been accurately measured and reported (39). The estimated error in the dielectric constant measurement was about 0.06%.

(5) Vapor pressure measurements: In order to determine the extent of self-association of acetone in non-polar solvents, the vapor pressures of acetone over the acetone-hexadecane solutions were measured. Since the vapor pressure of hexadecane is less than 0.1 mm, there is no complication arising from the presence of hexadecane in the vapor phase. The vapor pressure technique used is similar to methods described by Grigsby (40) and Taha (41). About 100 ml of hexadecane was placed in the apparatus which was immersed in a constant temperature bath. The liquid was stirred magnetically, using a magnet coated with Teflon, and the apparatus was evacuated to an initial pressure less than 0.3 mm. Acetone was added through a mercury-sealed, sintered-glass disc, using a microsyringe. After approximately 30 minutes, equilibrium was reached, and the vapor pressure of acetone was determined by measuring the mercury levels on the manometer with the aid of a cathetometer. The microsyringe was calibrated by delivering the acetone into an evacuated weighting bottle (42).

CHAPTER IV

THEORY

(1) Partition and Isopiestic method: The chemical potential of a species distributed between two phases in a thermodynamic system can be made equal by the partition and isopiestic methods. When equilibrium is reached, the chemical potential of one species in one phase can be determined from the known value of the chemical potential of the species in the other phase. For dilute solutions of polar solutes in organic solvents, if there is self-association of the solute, so that monomers, dimers, trimers, etc., are present, we can show thermodynamically that at equilibrium, the following equation is valid:

$$f_2 = \sum_{j \geq 1} j k_j a_2^j \qquad (1)$$

Where a_2 is the activity of the solute monomer and f_2 is the formal concentration of solute. To determine the equilibrium constants k_j, we must know the relation between f_2 and a_2 experimentally. Since it is usually impossible to measure a_2 directly, we must measure the activities of the solute in another phase in which there is no self-association of the solute. A vapor phase at low pressure, or liquid phase of

high dielectric constant can frequently be used as a second phase in which the self-association of solute is absent. We can show that the ratio of activity a_2 in one phase to the activity a_2' in the other phase is a constnat, i.e. $a_2/a_2' = k_c$. In dilute solutions, the activity coefficient is approximately unity, therefore, a_2, a_2' can be replaced by the concentration c_2, c_2', respectively. Using concentrations, we can rewrite equation (1) as

$$f_2 = k_c c_2' + 2k_2 k_c^2 c_2'^2 + 3k_3 k_c^3 c_2'^3 \text{------} \quad (2)$$

If there is no association in the second phase, the formal concentration of the solute is the same as the monomer concentration c_2' which can be measured directly. Once the experimental relations between f_2 and c_2' are known, the equilibrium constants can be obtained by a least squares analysis of the data. This is the basic principle of partition and isopiestic methods.

If the value of the equilibrium constant, k_c, k_1, k_2, k_3, etc., and their dependence on temperature are known, it is immediately possible to calculate the thermodynamic properties ΔH, ΔU, ΔF, ΔS for each complex species. ΔU should be, in principle, proportional to the strength of the intermolecular force; ΔH is equal to $\Delta U + \Delta PV$, a measure of heat change of the reaction at constant pressure, but in solution ΔPV is small so that $\Delta H = \Delta U$. ΔS is related to changes of randomness of a system. If a reaction occurs with an increase in entropy, there is more disorder possible among the products

than among the reactants--that is, there are more restrictions
to the motion of the reactant molecules than to the motion of
the product molecules. For example, the structures of complex
species stabilized by dipole-dipole interactions are not so
rigid as those of hydrogen bonded complexes; hence, it is ex-
pected that ΔS for the formation of this kind of species is
less negative than that for hydrogen-bonded complexes. ΔF is
related to the degree of spontaneous reaction--the more stable
and longer the mean life of a species, the more negative the
ΔF of the formation of that species.

By statistical thermodynamics, it is possible to re-
late the detailed molecular properties to the thermodynamic
properties of a macroscopic system. McMillan and Meyer (43)
have developed a dilute solution theory for osmotic equili-
brium, using the grand canonical ensemble. They can express
the osmotic pressure by a virial expansion which is similar
to Meyer's imperfect gas theory (44). Hill (45, 46) developed
a constant pressure solution theory which can be applied to
partition and isopiestic data obtained as described here. He
has derived an equation equivalent to equation (1) as follows,

$$M_2(P,T,a_2) = \sum_{j \geq 1} jQ_j(P,T)a_2^j$$

where $M_2 = N_2/N_1$, N_1 is the number of solvent molecules in
unit volume; N_2 is the number of solute molecules in unit
volume. a_2 is the activity of solute which is defined in
such a way that $a_2 \rightarrow M_2$ as $M_2 \rightarrow 0$. Q_j's are equivalent to
equilibrium constants, but are related to solute-solute, solute-

solvent interactions in a very complicated way. Another important alternative approach to solution theory is that due to Kirkwood and Buff (47). In principle, if the detailed information about all the intermolecular forces were known, by Hill's theory it would be possible to calculate all the parameters.

(2) NMR method: In the NMR techniques, the proton nuclei are used as a probe to detect the diamagnetic shielding of the surrounding electrons. There are three factors involved in the determination of a chemical shift of a proton in an isolated molecule (33): (a) Electronegativity of adjacent atomes. (b) The neighbor-anisotropic effect and (c) The ring current effect. When the molecule is hydrogen-bonded, a chemical shift arises because the magnetic field experienced by the proton nucleus is modified when a hydrogen bond XH----Y is formed, where Y is a proton acceptor. Three factors influence the magnitude of the hydrogen-bonding chemical shift: (a) The presence of Y has an electrostatic effect on the electronic structure of the XH bond and consequently changes its magnetic susceptivity (b) The presence of Y has a neighbor-anisotropic effect on the proton, and (c) If the association is of this type ----X----H', the chemical shift of H' moves to low field, because the axial symmetry of electron cloud in X--H bond is partially removed, and consequently the paramagnetic high field is removed. This so-called "quenching of the intramolecular paramagnetic effect" can be used to explain

the anomalously large association shift of hydrogen iodide. Among the three factors, the neighbor-anisotropic effect on protons is found to be the smallest one, since the H---Y hydrogen bond distance is usually large.

The average effect on the chemical shift arising from a rapid exchange between two proton environments was first described quantitatively by Gutowsky, McCall and Slichter (48, 49). When the mean life time before exchange is less than $\sqrt{2}/2\pi\Delta\nu$, where $\Delta\nu$ is the separation of chemical shift of the two sites, the two chemical shifts will coalesce, and the observed chemical shift is the weighted average of the individual chemical shifts: $\delta_{abs} = f_1\delta_1 + f_2\delta_2$ where f_1, f_2 are mole fractions of certain chemical sites with chemical shift δ_1, δ_2, respectively. If there are more than two average sites,

$$\delta_{abs} = \sum_1^N f_1\delta_1 \qquad (3)$$

In some simple cases, it is possible to obtain reasonable estimates of equilibrium constants and chemical shifts of species solely from NMR data by using equation (3) (50, 23). But in most cases, because too many parameters are involved, additional data from other sources such as infrared (51) are needed to obtain a useful result. If there are no complications of chemical shifts arising from the anisotropic and quenching effects, the chemical shifts of bonded protons are very helpful in interpreting hydrogen-bonding. The theoretical calculation of chemical shift differences between unbonded and bonded

protons has been discussed by Pople and others (52, 53). But no completely satisfactory result has been obtained up to the present time.

(3) Dielectric constants of dilute solutions: The dipole moment of a solute in solution calculated in terms of Clausius-Mossotti-Debye equation is always found to be different from the dipole moment of the solute in the gas phase. The difference observed between solution and gas phase values constitutes the so-called solvent effect. If we assume that the Clausius-Mossotti-Debye equation is essentially correct, an "apparent dipole moment" can be obtained from this treatment. Many workers such as Raman and Krishnan (54), Frank (12), Higasi (11, 55) and Weigle (10) have developed theoretical treatments of the solvent effect. Their theories all suggest that when the dipole axis of a solute is coincidental with the axis of maximum polarization of the solute molecule, the dipole moment of the solute should decrease with increasing dielectric constant of the solution; whereas if these axes are at right angles to one another, the dipole moment of solute molecule should increase with increasing dielectric constant of solution. None of the available theories can be satisfactorily applied to a wide variety of dilute solutions. In fact, the Clausius-Mossotti-Debye equation is only correct for nonpolar solvents, and if the solvent has a higher dielectric constant, the modified theories such as the one developed by Higasi (11, 55) should be used. One of the most versatile

of dielectric theories is that of Onsager. In his original
paper (56), Onsager developed, in addition to his well-known
equation for pure liquids, an expression which pertains to
solutions in which both solute and solvent have large dielec-
tric constants. His equation is

$$\epsilon = \text{constant} + \sum_i \frac{2\pi(n_i^2 + 2)^2 N_i \mu_i^2}{9kT}$$

Where n_i is refractive index, N_i is the concentration of com-
ponent i and μ_i is dipole moment of component i. If the di-
pole moment is small, the solvent term is small and ϵ should
have a linear relation with concentration of solute.

(4) Computer least squares method: The conventional
least squares method, first developed by Gauss, led to a set
of normal equations; and from the normal equations, the most
probable values of the parameters appearing in the observed
equations and their weights or standard deviations can be
calculated. A systematic way of calculating the parameters
and their weights has been introduced, but they involve te-
dious stepwise calculations which are not readily adaptable
to the computers. Mandel and Linnig (557) first introduced
a graphical least squares method for the two-parameter linear
case. Later Sillen (58, 59, 60) developed a general theorem
of least squares which is readily adaptable to the computers.
He showed that the standard deviation contour in p + 1-dimen-
sional hyperspace obeys the following relation,

$$S_b^2 = S_m^2(1 + \frac{1}{N-P})$$

Where S_m^2 is the square sum of residuals or deviations at the minimum point, S_b^2 is the square sum of residuals at the standard contour and P is the number of parameters. Christian, and co-workers (61, 62) have independently developed a similar graphical least squares method. In Sillen's original paper, a general proof of the p-parameter linear least squares solution has been given, but no rigorous proof of the p-parameter nonlinear least squares solution was presented. An alternative and rigorous proof for the nonlinear case is given in Appendix 1.

CHAPTER V

RESULTS AND CALCULATIONS

(1) Acetone-water-1,2-dichloroethane system: Partition data for acetone distributed between water and 1,2-dichloroethane are given in Table 2; these data are plotted in Figure 1 as concentration of acetone in water versus that in 1,2-dichloroethane. Based on the linearity of the plot, the data support the conclusion that there is no self-association of acetone in 1,2-dichloroethane up to 0.55 molar. The value of the distribution ratio is 2.36, indicating that acetone is more soluble in 1,2-dichloroethane than in water at a given acetone activity. Solubility data for water dissolved in 1,2-dichloroethane in the presence of acetone, determined by the solute isopiestic method, are given in Tables 3 ~~to 6~~ and Figures 2 to 3. From the solubility and distribution data, it is possible to determine what kind of complexes are present in these dilute systems. Since the systems studied are dilute solutions, highly polymerized species are unlikely to be present in significant concentrations and can be neglected. Accordingly, assuming no species larger than trimers present, the formal concentration of acetone, f_A, and that of water,

f_W, can be separately expressed as,

$$f_A = c_A + 2k_{20}c_A^2 + 3k_{30}c_A^3 + k_{11}c_A c_W + 2k_{21}c_A^2 c_W + k_{12}c_A c_W^2 \quad (1)$$

$$f_W = c_W + 2k_{02}c_W^2 + 3k_{03}c_W^3 + k_{11}c_A c_W + k_{21}c_A^2 c_W + 2k_{12}c_A c_W^2 \quad (2)$$

where c_A is the concentration of the acetone monomer, c_W is the concentration of water monomer and k_{ij} is the association equilibrium constant for the formation of complex species consisting of i acetone molecules and j water molecules. The terms which are larger than 4th power are neglected; therefore, only 7 complex species are postulated in the equations. The partition data indicate that there are no significant concentrations of associated acetone species in these systems. Hence, k_{20}, k_{30}, k_{21} can be set equal to zero. Johnson (20) has studied the system water-1,2-dichloroethane. They concluded that water primarily exists as monomers and trimers or tetramers in 1,2-dichloroethane, so that k_{02} can also be set to zero. After these simplifications, equation (1) and equation (2) can be rewritten as,

$$f_A = c_A + k_{11}c_A c_W + k_{12}c_A c_W^2 \quad (3)$$

$$\Delta f_W = f_W - c_W - 3k_{03}c_W^3 = k_{11}c_A c_W + 2k_{12}c_A c_W^2 \quad (4)$$

To test whether the term $2k_{12}c_A c_W^2$ in equation (4) ($2k_{12}c_A c_W^2$ is the term corresponding to the species acetone monomer dihydrate) contributes significantly or not, we can combine and rearrange (3) and (4), to obtain the relation

$$\frac{\Delta f_W}{f_A c_W - \Delta f_W c_W} = k_{11} + \frac{c_W(2f_A - \Delta f_W)}{f_A - \Delta f_W} \quad (5)$$

if k_{12} is zero, equation (5) can be rearranged as follows

$$\frac{\Delta f_W}{a_W} = c_W{}^O(f_A - \Delta f_W)k_{11}$$

where $c_W = c_W{}^O a_W$ and $c_W{}^O$ is the concentration of water monomer at water activity $a_W = 1.00$. $\frac{\Delta f_W}{a_W}$ vs. $f_A - \Delta f_W$ have been plotted for the 25° and 35° data. The plots appear to be straight lines passing through the origin; the calculated values of k_{11} by least squares analysis also appear to have no significant systematic change with water activity. Thus it appears that k_{12} is small and can be neglected. Values of $c_W{}^O$ obtained from water solubility data are 0.108 m/l at 25° (20) and 0.143 m/l at 35°. Values of the solubility of water in 1,2-dichloroethane at 35° are given in Table 4. By a linear least squares analysis, the equilibrium constant for the formation of the acetone monohydrate (k_{11}) was calculated to be 0.85 ± 0.05 1/m at 25° and 0.68 ± 0.04 1/m at 35°. Using these values, the theoretical values of Δf_W represented in Tables 3 to 6 were calculated by the equation,

$$\Delta f_W{}^{caled.} = k_{11}c_W{}^O a_W f_A / (1 + k_{11}c_W{}^O a_W) \tag{6}$$

It appears that the experimental values, Δf_W agree with theoretical values $\Delta f_W{}^{caled.}$ to within the expected errors in the water solubility determinations. Since the errors in the determination of the titer of Karl Fisher reagent will cause a systematic error in water solubility data, the theoretical lines will deviate systematically from experimental points.

In order to avoid this, the solid lines in Figures 4 and 5 are obtained by drawing straight lines through the experimental point at $f_A = 0.0$ but using the theoretical slopes. It is evident that the partition data and solubility data can be satisfactorily explained by assuming only two complex species, i.e. acetone monomer monohydrate and the water trimers ---in the dilute system acetone-water-1,2-dichloroethane.

NMR data have been obtained for the chemical shift of water protons in 1,2-dichloroethane; the resulting data are given in Table 5 and a plot of chemical shifts vs. f_W is shown in Figure 4. It is interesting to note that the NMR data can be shown to be consistent with the assumption of water trimers, but not water dimers. If we assume water exists as dimers, there are two possible complex structures, i.e.
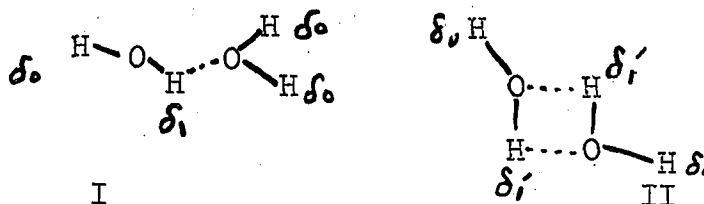
We assign the chemical shift of bonded proton by δ_1, and that of the unbonded proton by δ_0, which is assumed equal to the chemical shift of free water. Using the equation $\delta_{abs.} = \delta_0 f_1 + \delta_1 f_2$, we can derive the following equations for the structure I,

$$\delta_{abs.} \left(\frac{2 + 4k_2 c_W}{2 + 3k_2 c_W} \right) = \delta_0 + \frac{k_2 c_W}{2 + 3k_2 c_W} \delta_1 \qquad (7)$$

For the structure II

$$\delta_{abs.} \left(\frac{1 + 2k_2 c_W}{1 + k_2 c_W} \right) = \delta_0 + \frac{k_2 c_W}{1 + k_2 c_W} \delta_0' \qquad (8)$$

k_2 is the dimerization constant of water, estimated to be 0.78 1/m from water solubility data in 1,2-dichloroethane at several different temperatures with the assumption that only water monomer and water dimer exist in the solvent. In this equation, $\delta_{abs.}$ represents the observed chemical shift. The NMR data have been plotted in the form $Y = \delta_{abs.}(\frac{2 + 4 \ k_2 c_w}{2 + 3 \ k_2 c_w})$ vs. $X = \frac{k_2 c_w}{2 + 3 k_2 c_w}$ for the structure I and $Y = \delta_{abs.}(\frac{1 + 2k_2 c_w}{1 + k_2 c_w})$ vs. $X = \frac{k_2 c_w}{1 + k_2 c_w}$ for structure II. In both cases the X vs. Y plot is definitely non-linear, indicating that it is impossible to explain the NMR data by assuming only monomer-dimer equilibrium. By assuming water trimer, there is a variety of structures which can be constructed, but the cyclic trimer (63) seems to be a plausible species as follows,
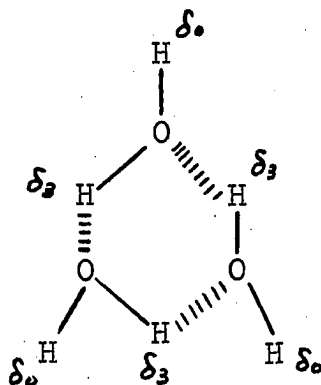
The chemical shift of the bonded proton is δ_3, the unbonded is assumed to be the same as free water. The observed chemical shift $\delta_{abs.}$ may be expressed as

$$\delta_{abs.} = \delta_0(\frac{2c_w + 3k_3 c_w^3}{2f_w}) + \delta_3(\frac{3k_3 c_w^3}{2f_w})$$

Rearranging, we obtain,

$$\delta_{abs.}\left(\frac{2 + 6k_3c_w^2}{2 + 3k_3c_w^2}\right) = \delta_o + \left(\frac{3k_3c_w^2}{2 + 3k_3c_w^2}\right)\delta_3$$

Data plotted in the form $Y = \delta_{abs.}\left(\frac{2 + 6k_3c_w^2}{2 + 3k_3c_w^2}\right)$ vs. $X = \frac{3k_3c_w^2}{2 + 3k_2c_w^2}$ are shown in Figure 5. The linearity of this plot

supports the assumption that the water trimer is the major

water aggregate present in 1,2-dichloroethane. Using least

squares analysis, δ_o is estimated to be 16.47 $\pm$ 0.06 cps,

and δ_3 is 99 $\pm$ 2 cps.

NMR data for the system acetone-water-1,2-dichloro-

ethane are given in Table 6 ~~to 12~~ and Figures 8 and 9. In

treating these data, in addition to cyclic water trimer, it

is assumed that the monomer monohydrate
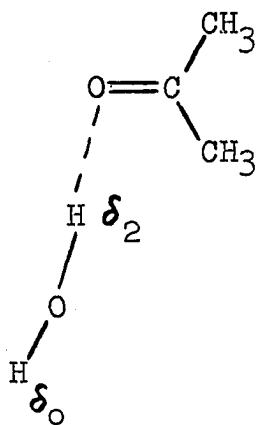
is present and that δ_2 is the chemical shift of proton bonded

to carbonyl group. It is possible to relate the chemical

shift $\delta_{abs.}$ to f_A and f_W through the equation

$$f_W(\delta_{abs.} - \delta_o) - \frac{3}{2}(\delta_3 - \delta_o)k_3c_w^3 = k_{11}c_w\left(\frac{f_A}{1 + k_{11}c_w}\right)\frac{\delta_1 - \delta_o}{2} \quad (9)$$

and

$$f_W = c_W + 3k_3c_W^3 + \frac{k_{11}c_Wf_A}{1 + k_{11}c_W} \qquad (10)$$

Values of c_W can be computed numerically from equation (10), using extrapolated and interpolated values of k_{11} and k_3 shown in Table 16. In order to obtain an unbiased least squares value of δ_1, data were plotted in the form $Y =$

$$f_W\left[(\delta - \delta') + (\delta' - \delta_0)\right] - \frac{3}{2}(\delta_3 - \delta_0)k_3c_W^3 \text{ vs. } X = k_{11}c_Wf_A/$$

$(1 + k_{11}c_W)$ in which δ' represents the chemical shift a solution would have at a given value of f_W, if f_A were zero. The results were analyzed by plotting Y vs. X for all NMR data obtained at 30° and 45°. Both sets of data appear to follow the same straight line. From the slope of the least squares straight line, the value $\delta_1 = 102 \pm 6$ cps was obtained.

Dielectric data of water in 1,2-dichloroethane and acetone in 1,2-dichloroethane are given in Table 7 and Table 8. These data appear to obey Onsager's equation,

$$\epsilon = a + \frac{2\pi(n^2 + 2)^2\mu^2}{9kT} f_A$$

If ϵ vs. f_A is plotted, the slope should be

$$\text{slope} = \frac{2\pi(n^2 + 2)^2\mu^2}{9kT} \qquad (11)$$

For the water-1,2-dichloroethane system, the slope was found to be 0.86 1/m at 25°, we calculate $\mu = 2.42$ D (n = 1.3325 for water). For the acetone-1,2-dichloroethane system, the slope was found to be 1.13 1/m at 25°, using equation (11), we calculate $\mu = 2.74$ D (n = 1.3584 for acetone). In treating

the system acetone-water-1,2-dichloroethane, the dielectric constant can be expressed as,

$$\epsilon = \epsilon_o + \alpha_W(f_W - k_{11}c_A c_W) + \alpha_A c_A + \alpha_{AW}k_{11}c_A c_W \qquad (12)$$

where ϵ is dielectric constant of pure 1,2-dichloroethane, α_W, α_{AW}, α_A are parameters which have the same values as those determined from equation (11) for each species. If $f_W = 0.0$, we get

$$\epsilon_{f_{W=0}} = \epsilon_o + \alpha_A f_A \qquad (13)$$

Since each set of measurement always has different apparent initial values of ϵ_o, in order to get an unbiased result, we subtract equation (13) from equation (12) to eliminate ϵ_o and obtain the expression,

$$\epsilon - \epsilon_{f_{W=0}} + \alpha_A f_A - \alpha_W(f_W - k_{11}c_A c_W) - \alpha_A c_A = \alpha_{AW}k_{11}c_A c_W$$

The results were analyzed by plotting $\epsilon - \epsilon_{f_{W=0}} + \alpha_A f_A - \alpha_W(f_W - k_{11}c_A c_W) - \alpha_A c_A$ vs. $k_{11}c_A c_W$, where the parameters $\alpha_A = 1.13$, $\alpha_W = 0.86$, and $k_{11} = 0.85$ 1/m have been used. A linear plot is obtained having the least squares slope $\alpha_{AW} = 1.7 \pm 0.2$. Using equation (10), and $n = (n_1 + n_2)/2 = 1.3355$, we obtain $\mu_{AW} = 3.4 \text{ D} \pm 0.2 \text{ D}$. The solid lines in Figure 8 have been calculated by using the three least square parameters, α_A, α_W and α_{AW}. A summary of all the results obtained are given in Table 10. Hence, all the NMR, dielectric constants and partition data are adequately explained by assuming the existence of the acetone monomer-monohydrate and the water trimer.

(2) Ketone-water-CCl$_4$ system: The partition data
and water solubility of the acetone-water-CCl$_4$ system are
given in Tables 11 to 12 and Figures 9 and 10; data for the
2,3-butanedione-water-CCl$_4$ system are given in Tables 13 to
16 and Figures 11 and 12. Data for the acetylacetone-water-
CCl$_4$ system are given in Tables 17 to 18 and Figures 13 and
14. It is to be expected that these systems involve more
complex species than the 1,2-dichloroethane system, conse-
quently, the data are more difficult to interpret.

Following the same argument as that of acetone-water-
1,2-dichloroethane system, we can neglect the species in-
volving more than three molecules per complex aggregate, and
also take advantage of the fact that the water monomer is
the primary form of water dissolved in pure CCl$_4$ (20, 64).
Also, the ketones apparently do not exist in species larger
than the dimers, which are stabilized by relatively weak
dipole-dipole interactions. We can then relate the data by
the expression:

$$f_A = c_A + 2k_{20}c_A^2 + k_{11}c_Ac_W + 2k_{21}c_A^2c_W \qquad (14)$$

$$\Delta f_W = f_W - c_W = k_{11}c_Ac_W + k_{21}c_A^2c_W \qquad (15)$$

$$c_A = k_c c_A^W \qquad (16)$$

It is impossible to eliminate additional species, because the
$k_{21}c_A^2c_W$ term in (15) is needed, since the solubility data
for all three ketones do not show linear relationship between
Δf_W vs. f_A. In fact, all the solubility curves tend to be

concave upward. A $2k_{20}c_A^2$ term in (14) is also needed for all three ketones, since if k_{20} were zero, the relation (14) and (16) would require that $(f_A - 2\Delta f_W)/c_A^W$ must be constant; but $(f_A - 2\Delta f_W)/c_A^W$ values are not approximately constant for any of the three systems. We conclude that in all three systems, three complex species must be assumed, i.e. ketone dimer, ketone monomer monohydrate and ketone dimer monohydrate.

Simple linear least squares analysis has been used to treat the data of the previous system. However, it cannot be used to deal with the ketone systems in CCl_4, since quadratic terms are involved in equations (14), (15), and (16). In order to handle this problem, the computer method for least squares analysis outlined in Appendix I was used to treat the data. The procedures for obtaining the statistically most probable values of the four parameters $(k_{20}, k_{11}, k_{21}, k_d)$ and their standard deviations are;

(a) Partition data are first treated by using the observed equation (14), to minimize the square sum of the residues of f_A, i.e.,

$$s_1^2 = \sum_i^{n_1} (f_{A_i}^{expt.} - \alpha c_{A_i}^W - \beta c_A^{W2})^2$$

where $\alpha = k_c + k_{11}c_w k_c$, $\beta = 2(k_c k_{20} + k_c k_{11}c_w)$ and n_1 is the number of experimental points. An optimum-seeking computer program is employed to obtain the minimum value of s^2 and the corresponding best values of α and β. Two optimum-seeking

methods have been used; one is a Partan method and the other is the elliptical-paraboloidal method (see Appendix I).

(b) Once α and β are known, the four unknown parameters can then be reduced to two independent unknown parameters, say, a and b, and the water solubility data can be optimized for $s_2{}^2$ as follows

$$s_2{}^2 = \sum_1^{n_2} (\Delta f_{W_i}^{expt.} - \Delta f_{W_i}^{calc.}(a, b))^2$$

Using the same optimum-seeking program as procedure 1, the best values of a, b can be obtained. Thus, when α, β, a, b are known, k_d, k_{11}, k_{21}, k_{20} can be calculated.

(c) This step is to obtain the standard deviations of these four parameters. By Sillen's theorem, the standard contour has the relation;

$$s_b{}^2 = s_m{}^2 (1 + \frac{1}{n-p})$$

where $s_m{}^2 = \frac{s_1^2}{s_{1m}^2} + \frac{s_2{}^2}{s_{2m}^2}$ and $n = n_1 + n_2$, s_{1m}^2 and s_{2m}^2 are the minimum values of s_1^2 and s_2^2 respectively. A computer program has been used to obtain the maximum value of the four parameters at the standard deviation contour in five-dimensional hyperspace. Using these procedures, the values of k_d, k_{11}, k_{12}, k_{20} and their standard deviations have been calculated; the derived values are given in Table 20.

(3) Acetone-hexadecane system: In the system ketone-water-CCl_4, we have shown that the ketone dimer is indispensable for the interpretation of its partition and water solu-

bility data. In order to support this conclusion, the system
acetone-hexadecane was chosen to demonstrate the existence of
acetone polymerization in an inert solvent such as hexadecane.
Hexadecane was used, primarily because its vapor pressure is
lower than 0.1 mm so that no complication would arise from
the presence of hexadecane in the vapor phase. The results
of the vapor pressure measurements are given in Table 21 ~~to~~
~~Table 32~~ and Figure 15 for several different temperatures.
In Table 21, the fugacities, as well as vapor pressures, are
given, corrected for air dissolved in the acetone. The reason
for using fugacities instead of measured vapor pressures is
that acetone deviates significantly from ideality at the ex-
perimental pressures and temperatures used in this study.
The relation between fugacity, vapor pressure and the second
virial coefficient B can be shown to be,

$$f(\text{fugacity}) = P\exp(BP/RT) = P(1 + PB/RT)$$

The values of B at different temperatures, given by Lambert
and Hobert (29), are given in Table 34, along with several
interpolated values (note that $B = -k_2$ in Table 23).

　　　　To treat the vapor pressure data, we expect that the
following equation is valid,

$$f_A = k_h f + 2k_2 k_h^2 f^2 + 3k_3 k_h^3 f^3 + 4k_4 k_h^4 f^4 + \text{-----}$$

It was found that only first three terms of above equation
are needed, i.e. terms corresponding to monomer, dimer,
trimer, to interpret the experimental data of the solubility
of acetone in hexadecane up to 0.3 molar. It is interesting

to note that if we assume that $k_3 = k_2^2$, $k_4 = k_3k_2 = k_2^3$, ------ $k_n = k_2^{n-1}$, we get,

$$f_A = k_nf(1 + 2k_2k_nf + 3(k_2k_nf)^2 + ----) = \frac{k_nf}{(1 - k_2k_n)^2}$$

After rearrangement, we get,

$$\sqrt{\frac{f_A}{f}} = \sqrt{k_n} + k_nk_2\sqrt{f_Af}$$

$\sqrt{\frac{f_A}{f}}$ has been plotted against $\sqrt{f_Af}$, and apparently straight lines are obtained. Henry's law constants were obtained for different temperatures from the intercept of these plots, and are given in Table 23. Although there is no assurance that the stepwise association constants will be equal, the assumption facilitates the calculation of the Henry's law constants. Using the equations $k_2 = k_2^o\exp(\frac{\Delta H_2}{RT} - \frac{\Delta H_2}{RT_o})$ $k_3 = k_3^o\exp(\frac{\Delta H_3}{RT} - \frac{\Delta H_3}{RT_o})$, and the values of k_2 and k_3 at 60° obtained by three parameter linear least square analysis, the whole data can be fitted with two adjustable parameters ΔH_2 and ΔH_3. The results of the non-linear least squares analysis are given in Table 23.

The acetone-nitrobenzene-hexadecane system was investigated in order to demonstrate the interaction between acetone and a second, highly polar solute. The experimental results are given in Table 22. Assuming the species involved in this system to be 1-1 acetone-nitrobenzene and 2-1 acetone-nitrobenzene complex, we can derive the equation,

$$\frac{\Delta f_A}{(f_N - \Delta f_A)k_nf} = k_{11} + \frac{k_{21}(2f_N - \Delta f_A)k_nf}{f_N - \Delta f_A}$$

Δf_A represents the concentration of bonded acetone; f_n is
the formal concentration of nitrobenzene. $\dfrac{\Delta f_A}{(f_N - \Delta f_A)k_h f}$ has

been plotted against $\dfrac{(2f_N - \Delta f_A)k_h f}{f_N - \Delta f_A}$ for $f_N = 0.0548$ m/l.

From the intercept of this plot, we get the equilibrium con-
stant for the 1-1 acetone-nitrobenzene complex as $k_{11} = 0.94$

1/m; and from the slope, we calculate the equilibrium con-
stant for the formation of 2-1 acetone-nitrobenzene complex

as $k_{21} = 4.76$ 1/m. The solid lines in Figure 16 are theo-
retical curves calculated by using these parameters. For

the higher concentration of nitrobenzene $f_N = 0.130$ m/l, the

theoretical line is systematically lower than that of experi-
mental values, probably indicating the existence of nitroben-
zene dimers.

TABLE 1

BEER'S LAW DATA FOR KETONES IN DIFFERENT SOLVENTS

Substances	Solvent	Wave Length of Maximum Absorption	Maximum Concentration	Absorptivity ($lm^{-1}cm^{-1}$)	Is Beer's Law Obeyed?
Acetone	CCl_4	280 mμ	0.12 mole/l	18.4	Yes
Acetone	1,2-Dichloroethane	274	0.12	15.8	Yes
Acetone	Water	265	0.12	16.0	Negative Deviation Above 0.06 mole/l
2,3-Butanedione	CCl_4	430	0.09	18.8	Yes
2,3-Butanedione	Water	420	0.40	3.8	Yes
Acetylacetone	Water	271	1.2×10^{-3}	1600.0	Negative Deviation Above 6×10^{-4} m/l

TABLE 2

PARTITION DATA OF THE SYSTEM ACETONE-WATER-1,2-DICHLOROETHANE AT 25°

	f_A^{water} (m/l)	$f_A^{1,2-Dichlor.}$ (m/l)	$f_A^{1,2-Dichlor.}$ (calcd.)
Run 1	0.010	0.015	0.024
	0.018	0.036	0.043
	0.035	0.074	0.083
	0.057	0.126	0.135
	0.074	0.165	0.175
	0.088	0.199	0.208
	0.103	0.236	0.243
Run 2	0.037	0.088	0.087
	0.062	0.150	0.146
	0.113	0.272	0.266
	0.137	0.327	0.324
	0.147	0.352	0.347
	0.196	0.456	0.463
	0.219	0.511	0.516
	0.238	0.556	0.561

TABLE 3

SOLUBILITY OF WATER IN 1,2-DICHLOROETHANE IN THE PRESENCE OF ACETONE AT VARIOUS WATER ACTIVITIES

f_A (m/l)	f_W (m/l)	Δf_W (m/l)	$\Delta f_W^{caled.}$ (m/l)
$a_W = 1.00$ at 25°			
0.000	0.1252	0.0000	0.0000
0.015	0.1273	0.0021	0.0012
0.037	0.1281	0.0029	0.0031
0.074	0.1312	0.0060	0.0062
0.126	0.1326	0.0110	0.0105
0.133	0.1360	0.0108	0.0111
0.165	0.1400	0.0148	0.0137
0.182	0.1400	0.0148	0.0151
0.199	0.1421	0.0169	0.0165
0.236	0.1468	0.0216	0.0196
0.260	0.1482	0.0230	0.0216
0.306	0.1522	0.0270	0.0254
0.408	0.1601	0.0351	0.0339
0.410	0.1620	0.0368	0.0340

TABLE 3--<u>Continued</u>

$f_A(m/l)$	$f_W(m/l)$	$\Delta f_W(m/l)$	$\Delta f_W^{caled.}(m/l)$
$a_W = 0.890$ at 25°			
0.000	0.1115	0.0000	0.0000
0.060	0.1150	0.0035	0.0045
0.069	0.1170	0.0055	0.0052
0.096	0.1200	0.0085	0.0072
0.098	0.1175	0.0060	0.0075
0.170	0.1260	0.0145	0.0128
0.271	0.1320	0.0205	0.0204
0.276	0.1350	0.0235	0.0208
0.388	0.1420	0.0305	0.0292
0.388	0.1400	0.0285	0.0292
$a_W = 0.616$ at 25°			
0.000	0.0722	0.0000	0.0000
0.025	0.0750	0.0028	0.0013
0.108	0.0780	0.0058	0.0058
0.171	0.0810	0.0088	0.0092
0.240	0.0849	0.0127	0.0128
0.296	0.0872	0.0150	0.0158
0.362	0.0894	0.0172	0.0193
0.422	0.0941	0.0219	0.0226

TABLE 3--Continued

f_A(m/l)	f_W(m/l)	Δf_W(m/l)	$\Delta f_W^{caled.}$(m/l)
a_W = 0.436 at 25°			
0.000	0.0500	0.0000	0.0000
0.051	0.0526	0.0026	0.0020
0.115	0.0540	0.0040	0.0046
0.175	0.0573	0.0073	0.0067
0.275	0.0602	0.0102	0.0105
0.358	0.0625	0.0125	0.0137
0.382	0.0633	0.0133	0.0146
0.408	0.0648	0.0148	0.0157
a_W = 1.00 at 35°			
0.000	0.1570	0.0000	0.0000
0.079	0.1645	0.0075	0.0067
0.142	0.1700	0.0130	0.0126
0.211	0.1780	0.0210	0.0187
0.281	0.1830	0.0260	0.0249
0.352	0.1910	0.0340	0.0312
0.409	0.1955	0.0385	0.0362
0.464	0.1980	0.0410	0.0411

TABLE 3--<u>Continued</u>

f_A(m/1)	f_W(m/1)	Δf_W(m/1)	$\Delta f_W^{caled.}$(m/1)
$a_W = 0.443$ at $35°$			
0.000	0.0655	0.0000	0.0000
0.059	0.0667	0.0012	0.0024
0.105	0.0676	0.0021	0.0043
0.163	0.0715	0.0060	0.0067
0.226	0.0736	0.0081	0.0093
0.272	0.0757	0.0102	0.0113
0.337	0.0786	0.0131	0.0139
0.366	0.0810	0.0155	0.0151
$a_W = 0.276$ at $35°$			
0.000	0.0395	0.0000	0.0000
0.092	0.0407	0.0012	0.0024
0.141	0.0426	0.0031	0.0037
0.252	0.0460	0.0065	0.0066
0.351	0.0478	0.0083	0.0092
0.468	0.0512	0.0117	0.0122
0.522	0.0546	0.0151	0.0144
0.629	0.0569	0.0174	0.0164
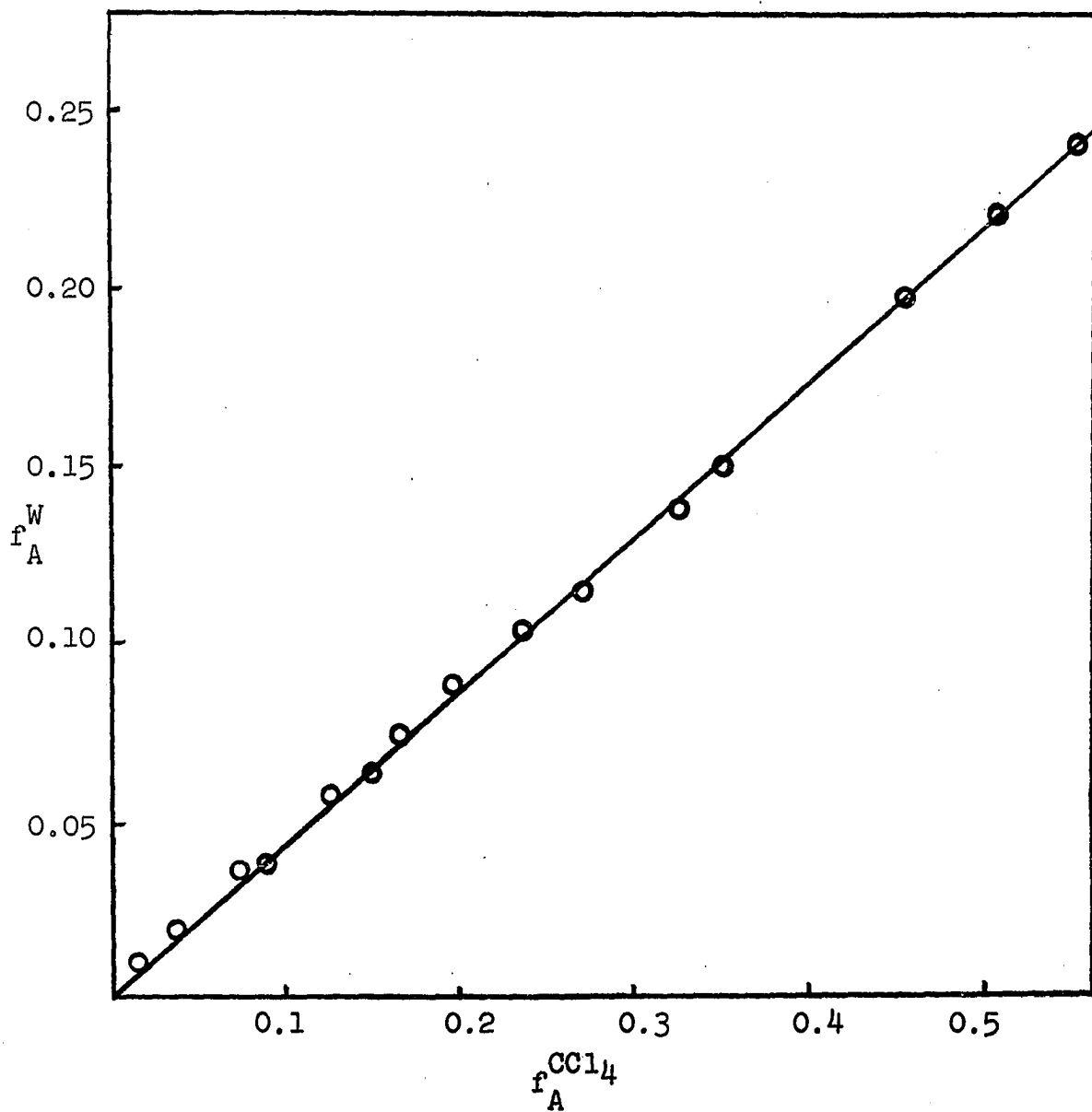
Fig. 1.   Partition Data for the System Acetone-Water-
1,2-Dichloroethane at 25°
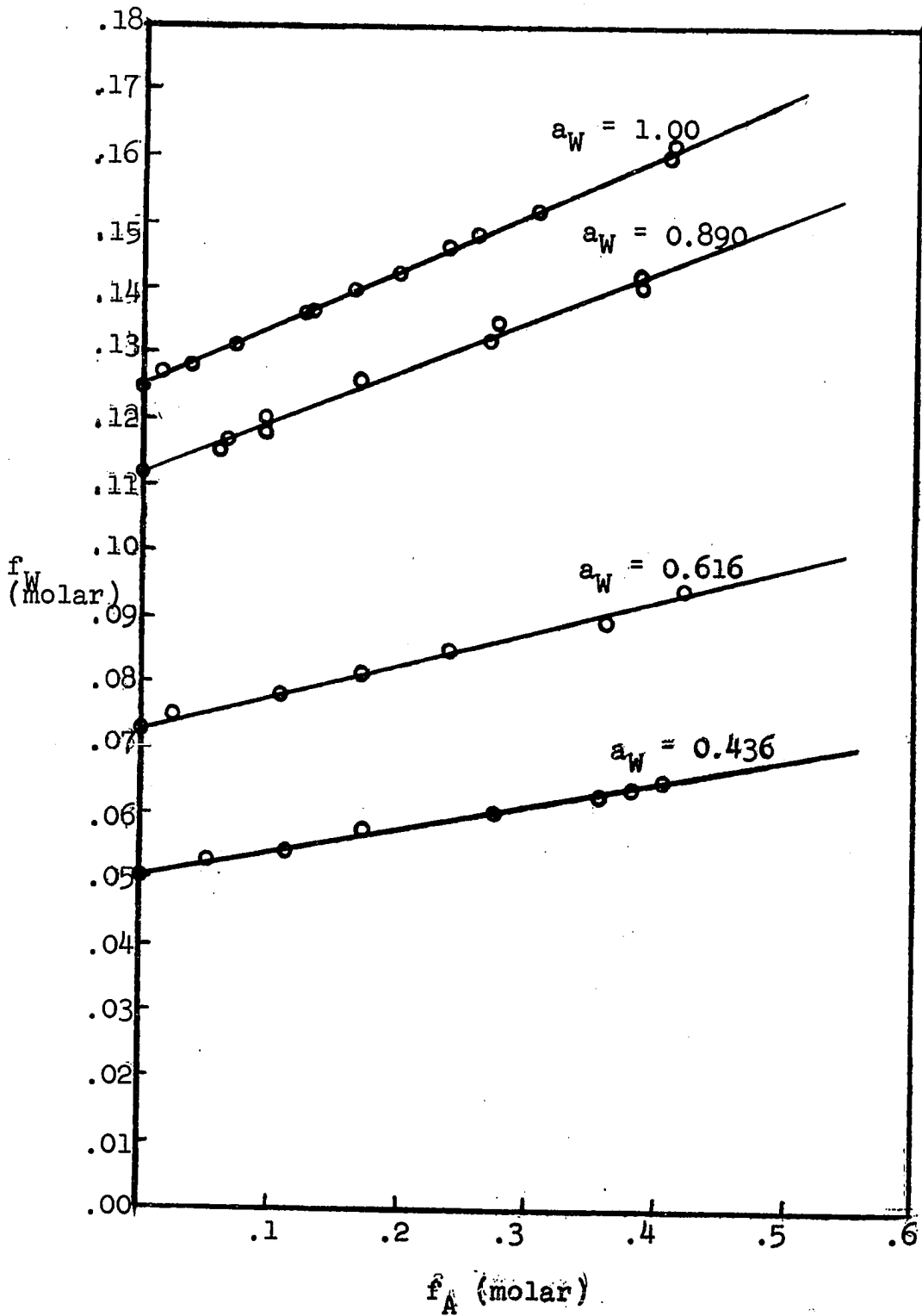
Fig. 2. Solubility of Water in 1,2-Dichloro-
ethane in Presence of Acetone at
Various Water Activities at 25°
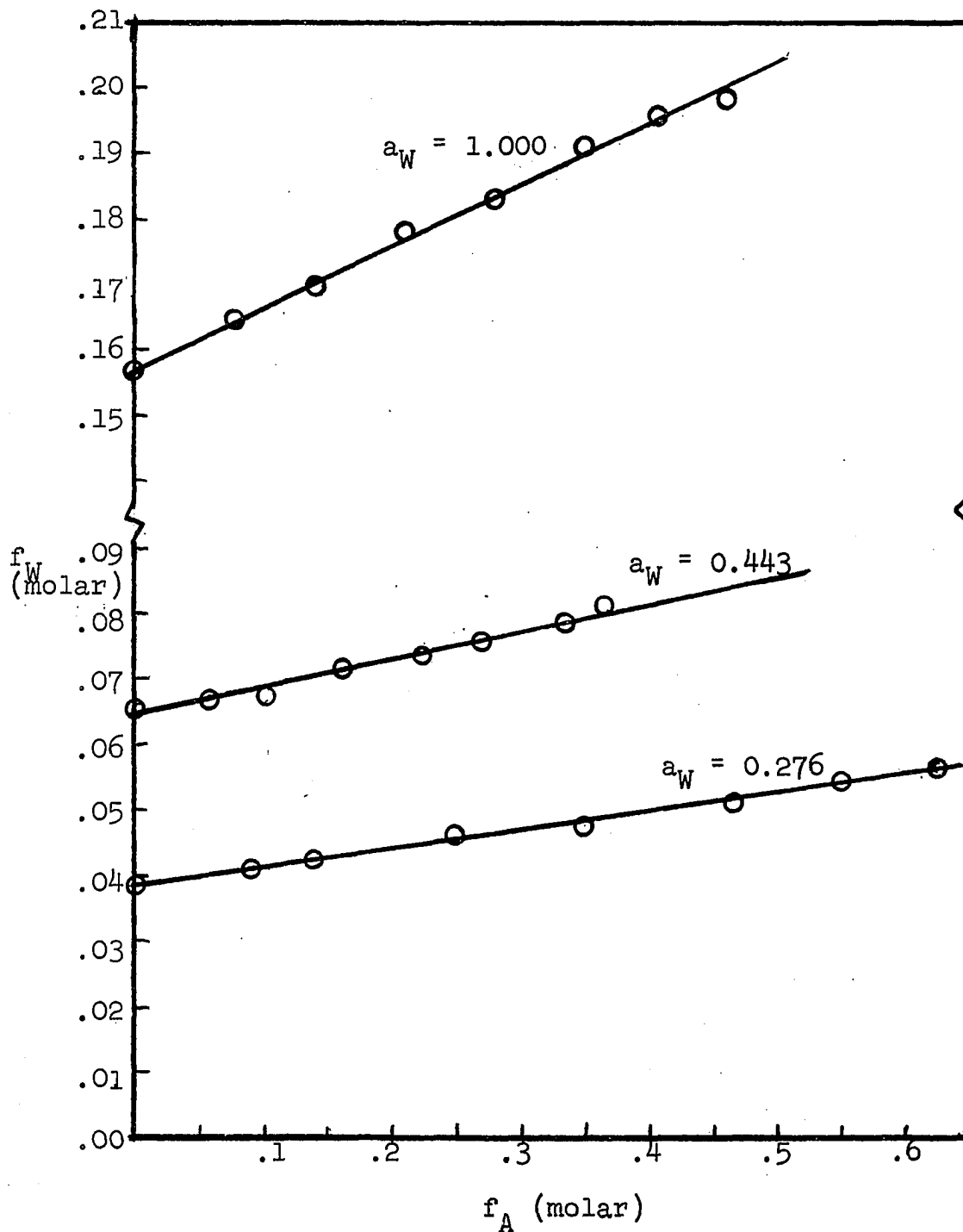
Fig. 3. Solubility of Water in 1,2-Dichloroethane in Presence of Acetone at Various Water Activities at 35°

TABLE 4

SOLUBILITY OF WATER IN 1,2-DICHLOROETHANE AT 35°

a_W	f_W(m/1)	$f_W^{caled.}$(m/1)
0.276	0.0402	0.0400
0.413	0.0594	0.0604
0.550	0.0849	0.0816
0.704	0.1085	0.1065
0.856	0.1348	0.1330
0.954	0.1492	0.1518

TABLE 5

CHEMICAL SHIFT OF WATER PROTONS AT 30°

f_W(m/1)	$-\delta$ (cps)	$-\delta^{caled.}$ (cps)
0.126	20.75	20.80
0.125	20.80	20.74
0.100	19.55	19.50
0.100	19.50	19.50
0.078	18.50	18.48
0.075	18.50	18.35
0.063	17.80	17.85
0.050	17.60	17.39
0.038	17.10	17.01
0.025	16.60	16.73
0.013	16.30	16.55
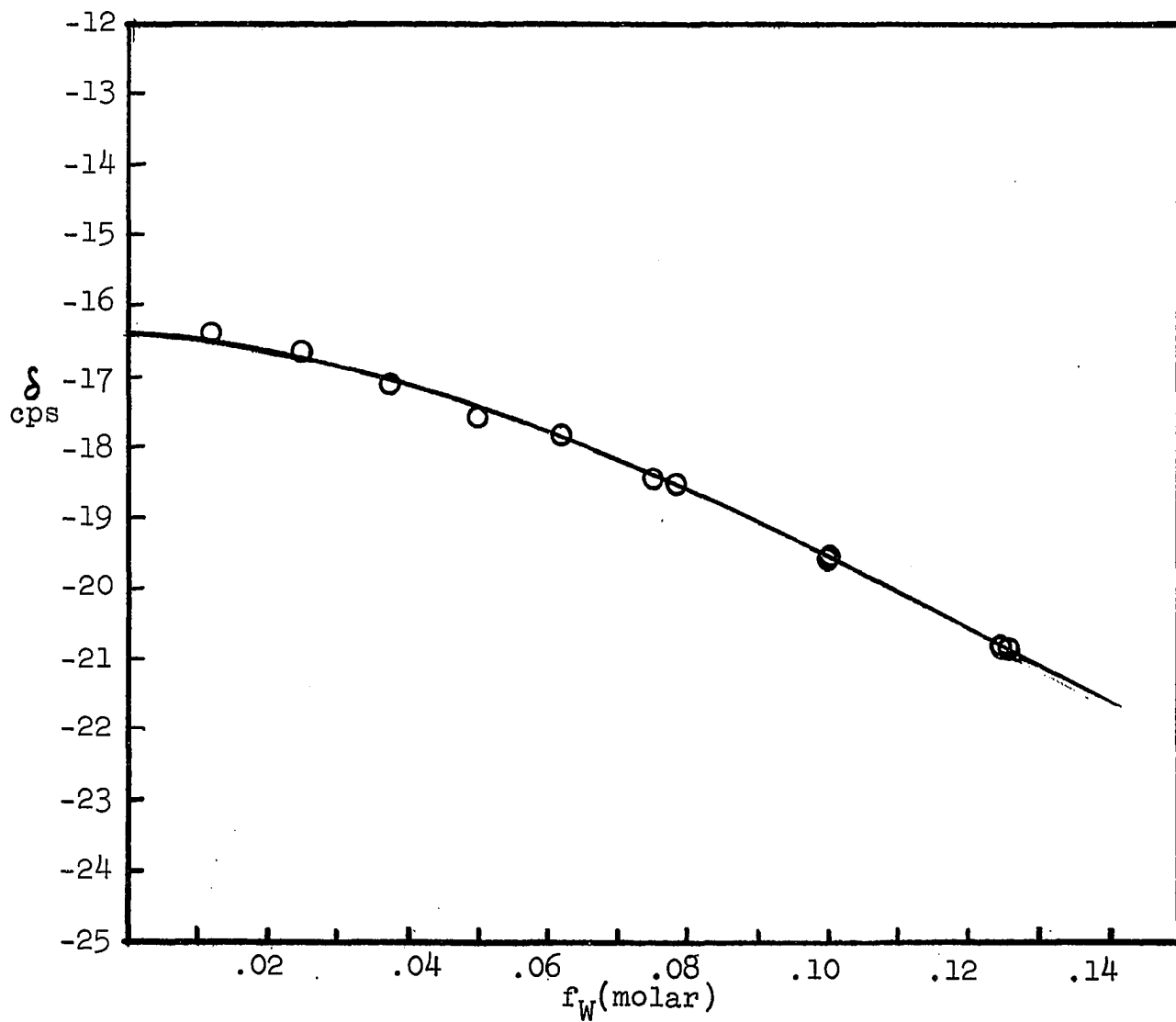
Fig. 4.   Chemical Shift of Water Protons in 1,2-Dichloro-
ethane at $30^{\circ}C$ (cyclohexane as external reference)
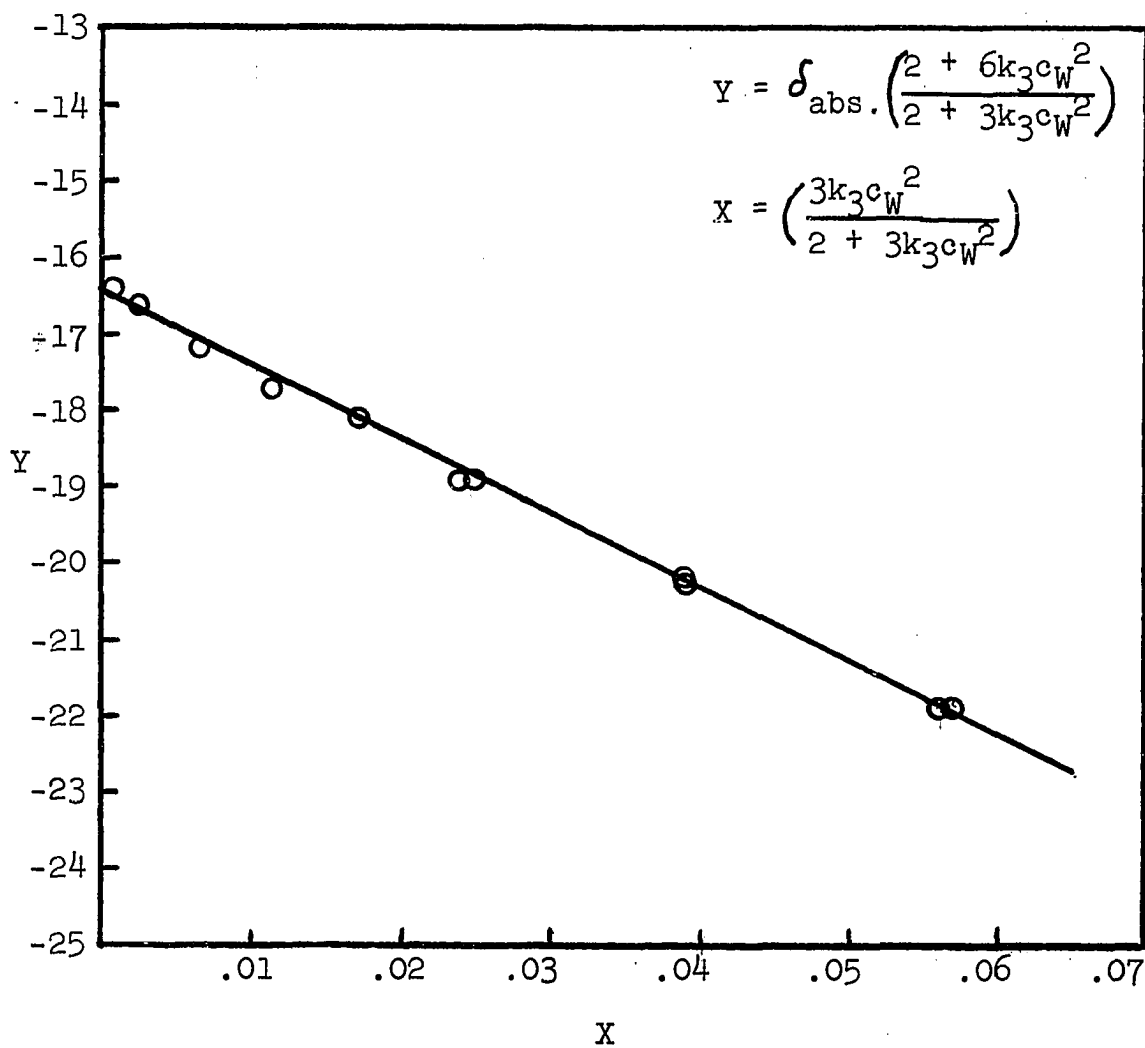
Fig. 5.   Y vs. X Plot for the Chemical Shifts of Water
in 1,2-Dichloroethane at 30°C

TABLE 6

CHEMICAL SHIFT OF WATER PROTONS IN THE
SYSTEM WATER-ACETONE-1,2-DICHLOROETHANE
AT VARIOUS WATER CONCENTRATIONS

f_A (m/l)	$-\delta$ (cps)	$-\Delta\delta$ (cps)	$-\Delta\delta^{scaled.}$ (cps)
$f_W = 0.126$ m/l at $30°$			
0.0000	20.75	0.00	0.000
0.0053	20.85	0.08	0.110
0.0106	20.95	0.20	0.216
0.0242	21.20	0.45	0.487
0.0348	21.50	0.75	0.696
0.0526	21.80	1.05	1.044
0.0694	22.20	1.45	1.369
0.0888	22.55	1.80	1.739
0.1062	23.00	2.25	2.055
$f_W = 0.100$ m/l at $30°$			
0.0000	19.55	0.00	0.000
0.0106	19.80	0.25	0.245
0.0158	20.05	0.50	0.364
0.0346	20.50	0.95	0.787
0.0526	20.95	1.40	1.187
0.0732	21.40	1.85	1.636
0.0920	21.80	2.25	2.029
0.1125	22.30	2.75	2.459

TABLE 6--<u>Continued</u>

f_A (m/l)	$-\delta$ (cps)	$-\Delta\delta$ (cps)	$-\Delta\delta$ caled. (cps)
f_W = 0.078 m/l at 30°			
0.0000	18.50	0.00	0.000
0.0106	18.90	0.40	0.266
0.0252	19.20	0.70	0.632
0.0437	19.75	1.25	1.088
0.0650	20.20	1.70	1.602
0.0883	20.60	2.10	2.151
0.1125	21.40	2.90	2.718
f_W = 0.058 m/l at 30°			
0.0000	17.25	0.00	0.000
0.0087	17.70	0.45	0.243
0.0214	18.00	0.75	0.592
0.0375	18.45	1.20	1.028
0.0567	18.78	1.53	1.538
0.0815	19.50	2.25	2.171

TABLE 6--<u>Continued</u>

f_A(m/1)	$-\delta$ (cps)	$-\Delta\delta$(cps)	$-\Delta\delta^{\text{caled.}}$(cps)
f_W = 0.1425 m/1 at 45°			
0.0000	17.10	0.00	0.000
0.0252	17.75	0.65	0.454
0.0623	18.00	0.90	1.112
0.0955	18.50	1.40	1.691
0.1345	19.50	2.40	2.350
f_W = 0.1229 m/1 at 45°			
0.0000	16.50	0.00	0.000
0.0154	16.80	0.30	0.298
0.0347	17.10	0.60	0.659
0.0568	17.50	1.00	1.070
0.0808	17.80	1.30	1.507
f_W = 0.0744 m/1 at 45°			
0.0000	15.60	0.00	0.000
0.0131	15.95	0.35	0.277
0.0338	16.20	0.60	0.715
0.0645	16.70	1.10	1.345
0.1051	17.40	1.80	2.153

TABLE 6--Continued

f_A(m/l)	- (cps)	- (cps)	-	caled.(cps)
f_W = 0.0462 m/l at 45°				
0.0000	14.45	0.00		0.000
0.0088	14.75	0.30		0.197
0.0216	15.05	0.60		0.481
0.0378	15.40	0.95		0.834
0.0609	15.80	1.35		1.327
0.0890	16.25	1.80		1.919
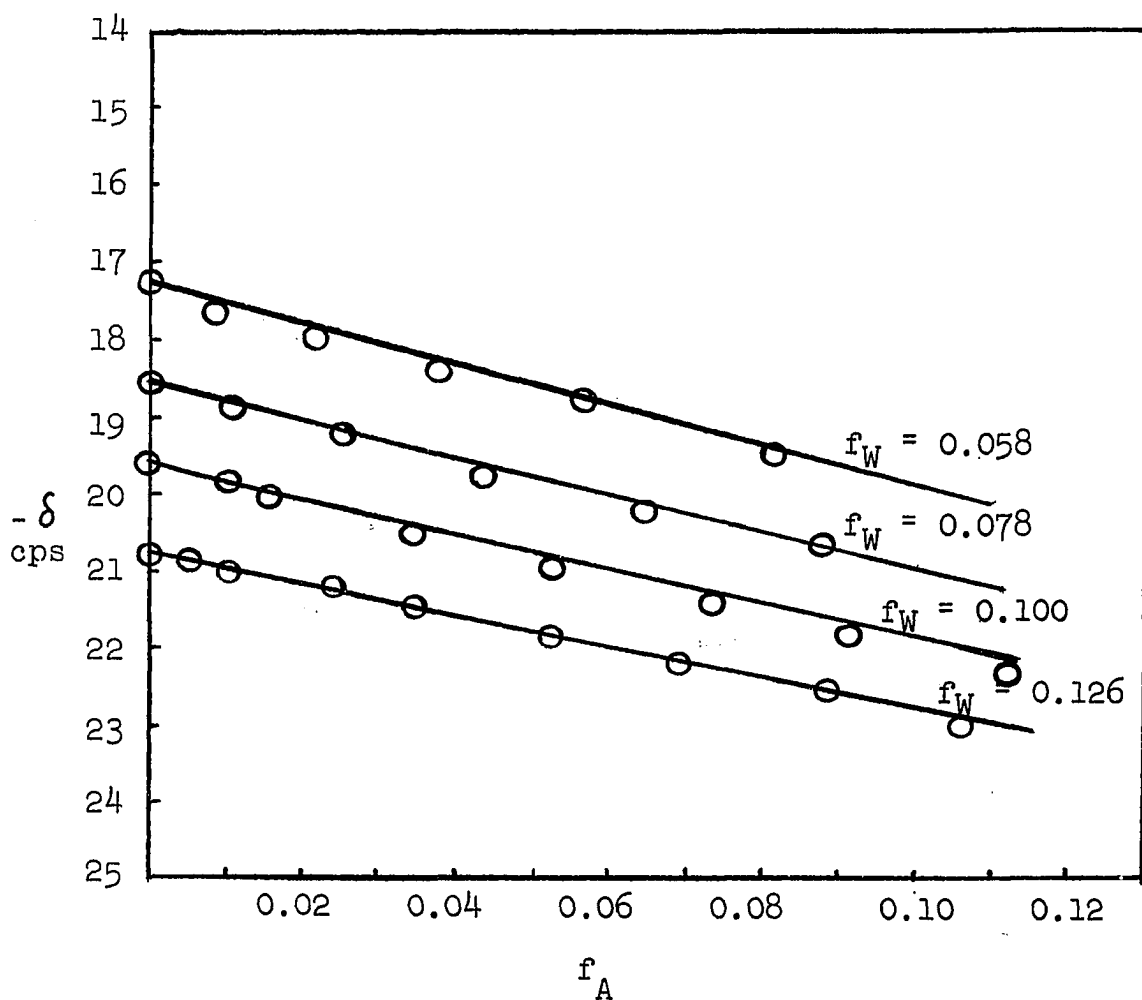
Fig. 6. Chemical Shifts of Water Protons in the
         System Acetone-Water-1,2-Dichloroethane
         at 30°
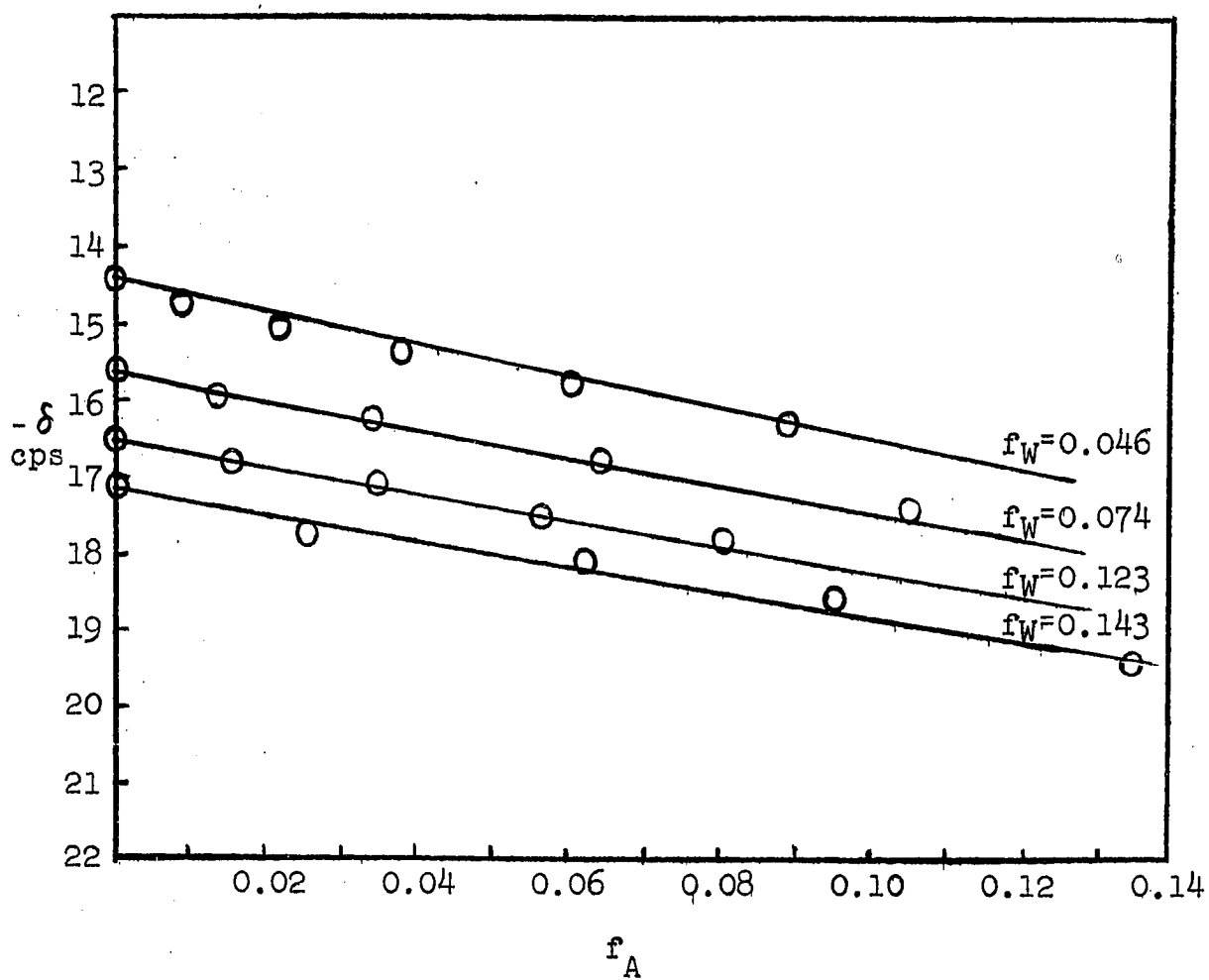
Fig. 7.   Chemical Shifts of Water Protons in the System
Acetone-Water-1,2-Dichloroethane at 45°

TABLE 7

DIELECTRIC CONSTANTS OF THE SYSTEM
WATER-1,2-DICHLOROETHANE AT 25°

	$f_W(m/1)$	ϵ	$\epsilon^{caled.}$
Run 1	0.0000	10.303	10.303
	0.0250	10.322	10.325
	0.0375	10.336	10.336
	0.0555	10.348	10.351
	0.0580	10.354	10.353
	0.0903	10.380	10.381
	0.1110	10.397	10.398
	0.1160	10.402	10.402
Run 2	0.0000	10.282	10.282
	0.0333	10.310	10.311
	0.0555	10.334	10.330
	0.0777	10.348	10.349
	0.0888	10.362	10.359
	0.1110	10.378	10.378
	0.1180	10.387	10.384

TABLE 8

DIELECTRIC CONSTANTS AND REFRACTIVE INDEXES FOR
THE SYSTEM ACETONE-1,2-DICHLOROETHANE AT 25°

f_A(m/l)	ϵ	$\epsilon^{caled.}$	f_A	$n^{25.8^{\circ}}$	$n^{25.0^{\circ}}$
0.0000	10.323	10.325	0.0000	1.4425	1.4430
0.0000	10.330	10.325	0.0613	1.4421	----
0.0217	10.347	10.350	0.0801	1.4420	----
0.0217	10.354	10.350	0.0948	1.4419	----
0.0869	10.425	10.422	0.1490	1.4415	1.4420
0.1086	10.445	10.447	0.2080	1.4412	----
0.1086	10.449	10.447	0.3480	1.4404	----
0.1521	10.495	10.496	0.5210	1.4394	1.4399
0.1956	10.537	10.546	0.6950	1.4384	----
0.2173	10.573	10.570	0.7820	1.4377	1.4380
			0.8340	1.4375	----
			1.0420	1.4362	1.4365

TABLE 9

DIELECTRIC CONSTANTS OF THE SYSTEM ACETONE-
WATER-1,2-DICHLOROETHANE AT 25°

	f_W(m/1)	ϵ	$\Delta\epsilon$	$\Delta\epsilon$ caled.
f_A = 0.108m/1	0.0000	10.433	0.000	0.000
	0.0226	10.450	0.017	0.019
	0.0454	10.468	0.035	0.035
	0.0680	10.485	0.052	0.057
	0.0906	10.502	0.069	0.076
	0.1022	10.513	0.080	0.086
	0.1133	10.525	0.091	0.096
f_A = 0.216 m/1	0.0000	10.570	0.000	0.000
	0.0234	10.588	0.018	0.019
	0.0468	10.608	0.038	0.039
	0.0702	10.622	0.052	0.058
	0.0935	10.640	0.070	0.077
	0.1052	10.655	0.085	0.087
	0.1170	10.665	0.095	0.097
f_A = 0.407 m/1	0.0000	10.758	0.000	0.000
	0.0271	10.778	0.020	0.022
	0.0542	10.802	0.044	0.044
	0.0678	10.816	0.058	0.055
	0.0813	10.824	0.066	0.066
	0.1083	10.848	0.090	0.088
	0.1220	10.863	0.105	0.099
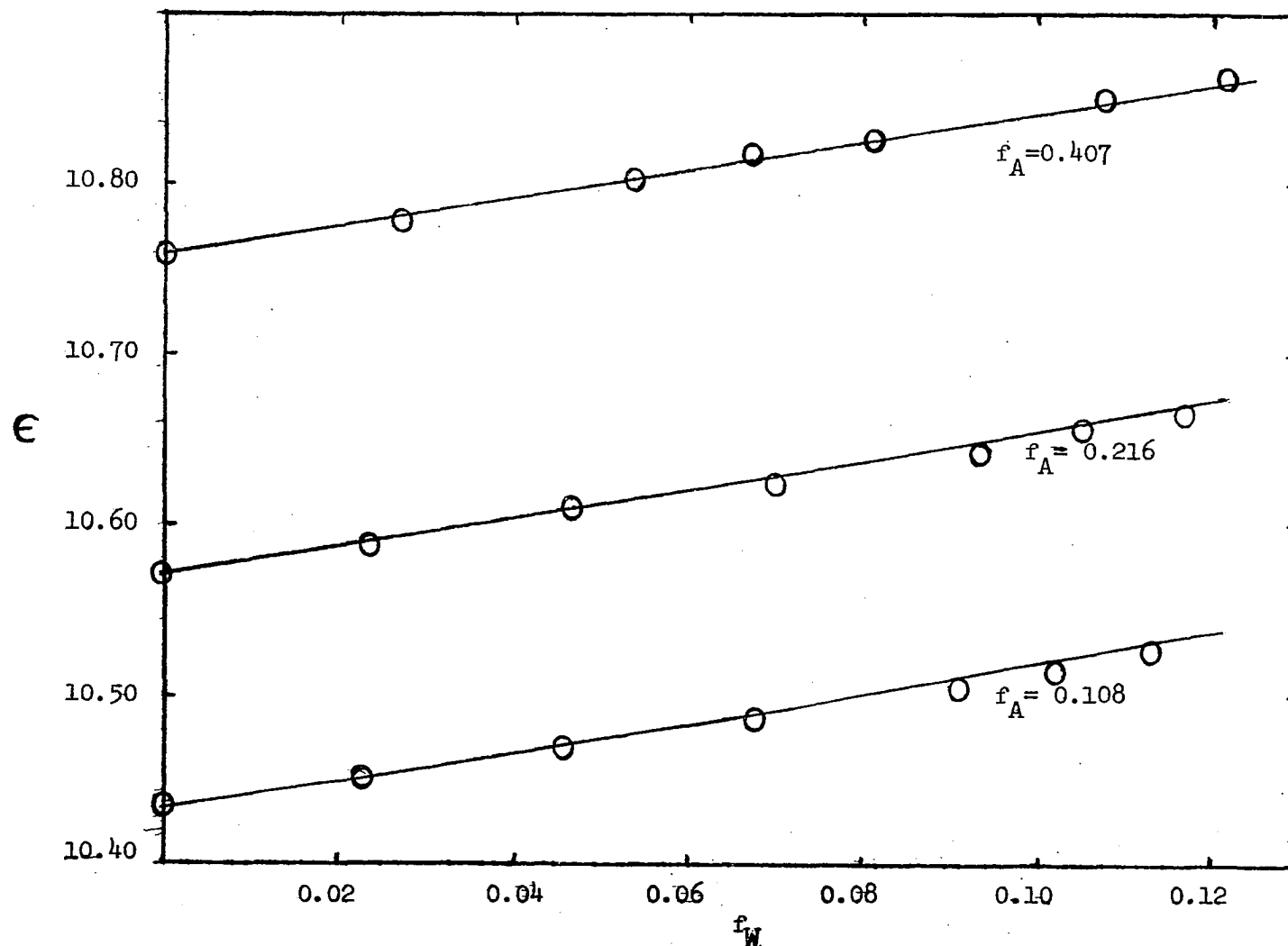
Fig. 8. Dielectric Constants of the System Acetone-Water-1,2-Dichloroethane at 25°.

TABLE 10

SUMMARY OF THE SYSTEM WATER-ACETONE-1,2-DICHLOROETHANE

Equilibrium Constants and Henry's Law Constants of Water Trimers

Temperature	Equilibrium Constant	Henry's Law Constant
$10°$	$k_3 = 19.7 \pm 3.0 \, m^{-2}l^2$	$0.065 \pm 0.006 \, ml^{-1}$
$25°$	4.6 ± 0.3	0.108 ± 0.007
$35°$	2.0 ± 0.2	0.143 ± 0.009
$30°$	3.1 (Interpolated)	-----------
$45°$	0.90 (Interpolated)	-----------

Enthalpy Change for k_3, $\Delta H = 16.0 \, k \, cal/mole$

Equilibrium Constants of Acetone Monomer Monohydrate

Temperature	Equilibrium Constant
$25°$	$k_{11} = 0.85 \pm 0.05 \, m^{-1}l$
$35°$	0.68 ± 0.04
$30°$	0.76 (Interpolated)
$45°$	0.55 (Interpolated)

Enthalpy Change for k_{11}, $\Delta H = 4.1 \, k \, cal/mole$

TABLE 10--Continued

Chemical Shifts of Water Protons (Cyclohexane as External Reference)

Free Water $\qquad \delta_0 = 16.47 \pm 0.06$ cps

Bonded Protons in Water Trimers $\qquad \delta_2 = 99 \pm 2$ cps

Bonded Protons in Acetone Monomer Monohydrate $\qquad \delta_1 = 102 \pm 6$ cps

Apparent Dipole Moment of the Complex Species in 1,2-Dichloroethane

Water $\qquad \mu = 2.42 \pm 0.1D$

Acetone $\qquad \mu = 2.74 \pm 0.1D$

Acetone Monomer Monohydrate $\qquad \mu = 3.40 \pm 0.2D$

TABLE 11

PARTITION DATA OF THE SYSTEM ACETONE-WATER-CCl$_4$ AT 25°

	$f_A^{H_2O}$(m/l)	$f_A^{CCl_4}$(m/l)	$f_A^{CCl_4}$(calcd.)
Run 1	1.350	0.772	0.749
	1.130	0.596	0.600
	1.060	0.550	0.553
	0.802	0.398	0.395
	0.541	0.258	0.249
	0.289	0.127	0.125
Run 2	1.310	0.702	0.722
	1.035	0.517	0.538
	0.755	0.356	0.367
	0.451	0.197	0.203
	0.229	0.099	0.097
Run 3	1.114	0.609	0.593
	0.967	0.506	0.495
	0.840	0.428	0.417
	0.666	0.324	0.317
	0.592	0.281	0.276
	0.444	0.202	0.199
	0.295	0.130	0.127
	0.262	0.115	0.112
	0.017	0.005	0.007

TABLE 12

SOLUBILITY OF WATER IN CCl_4 IN THE PRESENCE OF
ACETONE AT VARIOUS WATER ACTIVITIES AT 25°

	$f_A^{CCl_4}$ (m/l)	$f_W^{CCl_4}$ (m/l)	$f_W^{CCl_4}$ (calcd.)
$a_W = 1.00$	0.609	0.0246	0.0246
	0.517	0.0220	0.0221
	0.510	0.0227	0.0218
	0.506	0.0219	0.0216
	0.428	0.0194	0.0195
	0.373	0.0186	0.0180
	0.356	0.0176	0.0176
	0.324	0.0167	0.0167
	0.281	0.0158	0.0156
	0.202	0.0139	0.0136
	0.197	0.0127	0.0135
	0.133	0.0122	0.0119
	0.115	0.0112	0.0114
	0.099	0.0103	0.0111
	0.000	0.0088	0.0088

TABLE 12--<u>Continued</u>

	$f_A^{CC14}(m/l)$	$f_W^{CC14}(m/l)$	$f_W^{CC14}(caled.)$
$a_W = 0.744$	0.552	0.0165	0.0170
	0.474	0.0155	0.0153
	0.388	0.0132	0.0136
	0.326	0.0122	0.0123
	0.236	0.0103	0.0106
	0.113	0.0082	0.0083
	0.079	0.0072	0.0077
	0.000	0.0065	0.0066
$a_W = 0.470$	0.533	0.0107	0.0106
	0.421	0.0097	0.0092
	0.415	0.0092	0.0091
	0.302	0.0074	0.0076
	0.301	0.0077	0.0076
	0.175	0.0059	0.0062
	0.080	0.0054	0.0050
	0.062	0.0048	0.0048
	0.000	0.0042	0.0041
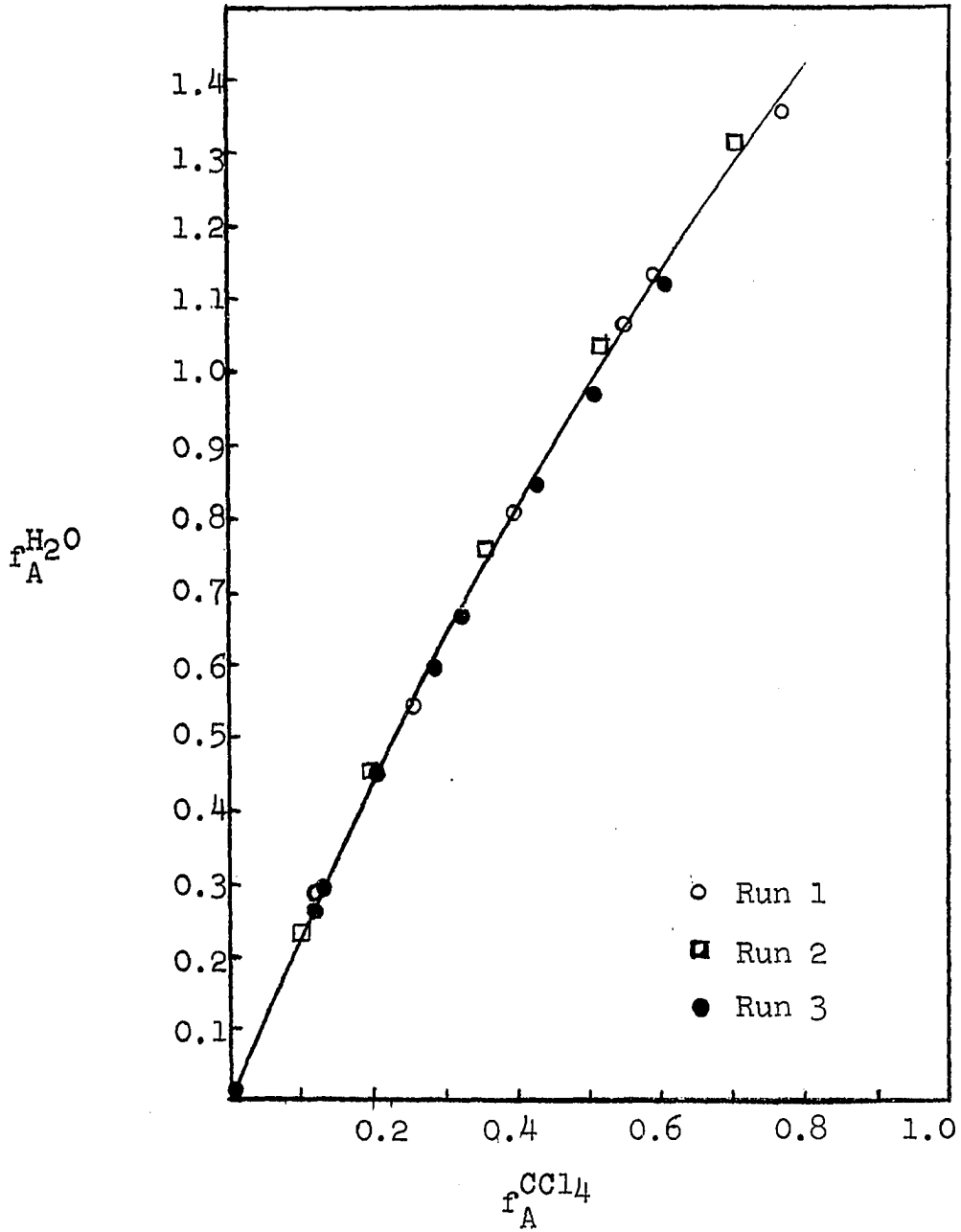
Fig. 9.   Partition Data for the System
Acetone-Water-CCl$_4$ at 25°
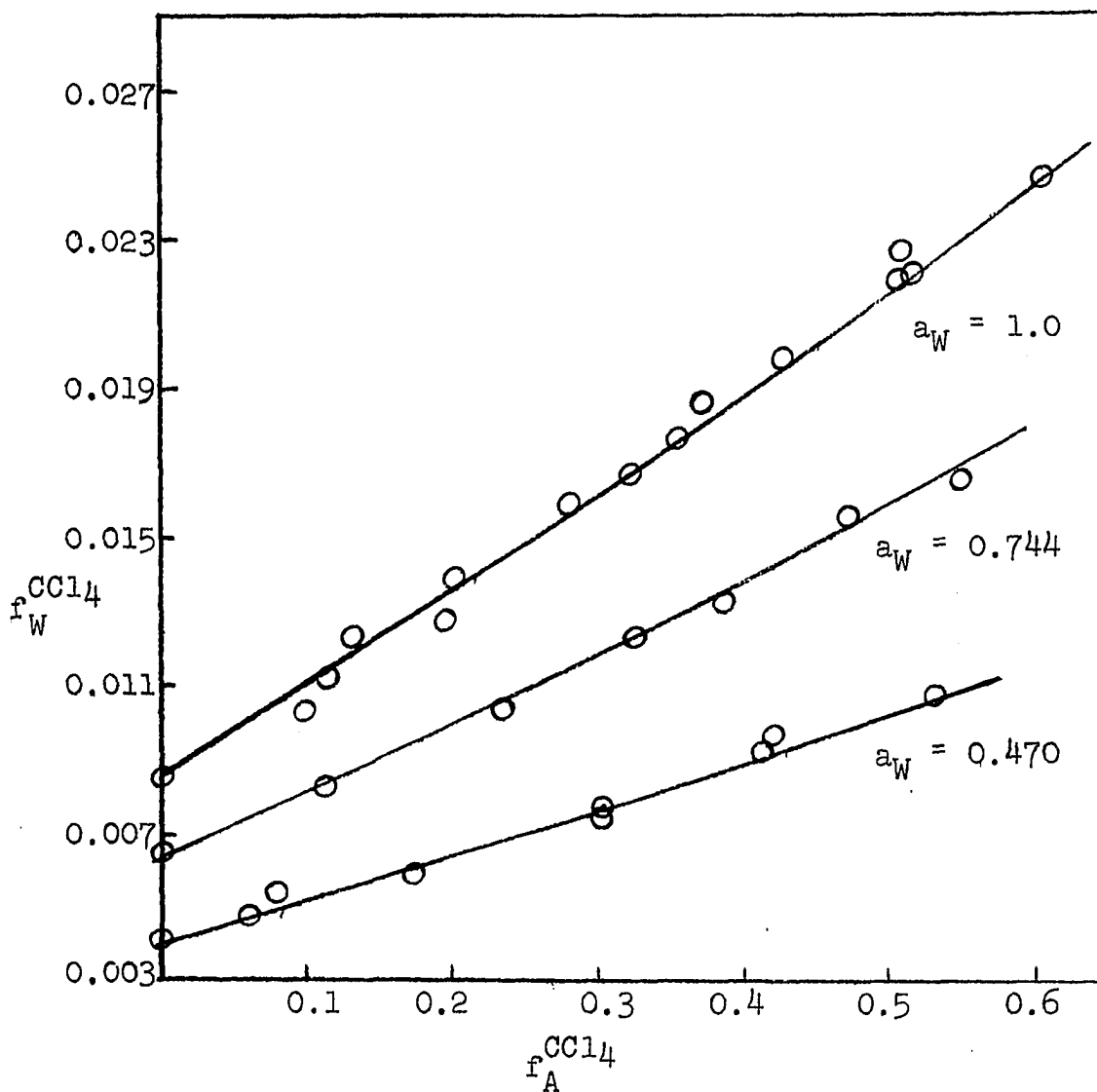
Fig. 10. Solubility of Water in CCl_4 in the Presence
of Acetone at Various Water Activities at
25°

TABLE 13

PARTITION DATA OF THE SYSTEM 2,3-BUTANEDIONE-
WATER-CCl$_4$ AT 25°C

	$f_D^{H_2O}$(m/l)	$f_D^{CCl_4}$(m/l)	$f_D^{CCl_4}$(caled.)(m/l)
Run 1	0.660	0.600	0.600
	0.601	0.522	0.515
	0.555	0.482	0.460
	0.541	0.441	0.443
	0.483	0.380	0.383
	0.372	0.298	0.278
	0.353	0.268	0.264
	0.321	0.244	0.236
	0.186	0.133	0.126
	0.092	0.063	0.058
Run 2	0.595	0.520	0.507
	0.532	0.455	0.432
	0.489	0.391	0.390
	0.380	0.292	0.287
	0.372	0.281	0.278
	0.325	0.248	0.240
	0.188	0.134	0.130
	0.100	0.064	0.065

TABLE 14

SOLUBILITY OF WATER IN $CC1_4$ IN THE PRESENCE OF 2,3-
BUTANEDIONE AT VARIOUS WATER ACTIVITIES AT 25°

	f_D^{CC14}(m/l)	f_W^{CC14}(m/l)	f_W^{CC14}(caled.)
a_W = 1.00	0.660	0.0167	0.0171
	0.520	0.0154	0.0151
	0.501	0.0152	0.0148
	0.455	0.0146	0.0141
	0.391	0.0137	0.0133
	0.358	0.0128	0.0129
	0.292	0.0125	0.0121
	0.281	0.0117	0.0120
	0.248	0.0117	0.0115
	0.226	0.0109	0.0113
	0.134	0.0102	0.0102
	0.073	0.0095	0.0095
	0.064	0.0096	0.0094
	0.000	0.0088	0.0088

TABLE 14--<u>Continued</u>

	$f_D^{CCl4}(m/l)$	$f_W^{CCl4}(m/l)$	$f_W^{CCl4}(caled.)$
$a_W = 0.842$	0.718	0.0146	0.0146
	0.584	0.0130	0.0130
	0.417	0.0112	0.0113
	0.279	0.0099	0.0100
	0.104	0.9983	0.0084
	0.000	0.0075	0.0074
$a_W = 0.687$	0.755	0.0129	0.0124
	0.594	0.0112	0.0109
	0.432	0.0099	0.0095
	0.252	0.0081	0.0080
	0.094	0.0069	0.0068
	0.000	0.0062	0.0061

TABLE 15

PARTITION DATA OF THE SYSTEM 2,3-
BUTANEDIONE-WATER-CCl_4 AT 15°

$f_D^{H_2O}$(m/l)	$f_D^{CCl_4}$(m/l)	$f_D^{CCl_4}$(calcd.)
0.770	0.535	0.515
0.760	0.513	0.505
0.687	0.437	0.438
0.629	0.400	0.414
0.628	0.391	0.414
0.550	0.331	0.327
0.525	0.313	0.310
0.476	0.274	0.274
0.421	0.236	0.235
0.364	0.198	0.198
0.364	0.199	0.198
0.199	0.103	0.100
0.196	0.103	0.098
0.063	0.030	0.030

TABLE 16

SOLUBILITY OF WATER IN CCl_4 IN THE PRESENCE OF 2,3-
BUTANEDIONE AT VARIOUS WATER ACTIVITIES AT 15^6

	$f_D^{CCl_4}$ (m/l)	$f_W^{CCl_4}$ (m/l)	$f_W^{CCl_4}$ (calcd.)
$a_W = 1.00$	0.437	0.0111	0.0111
	0.400	0.0101	0.0106
	0.391	0.0105	0.0104
	0.331	0.0099	0.0096
	0.313	0.0096	0.0094
	0.236	0.0083	0.0084
	0.198	0.0082	0.0080
	0.103	0.0070	0.0069
	0.030	0.0068	0.0066
	0.000	0.0059	0.0059
$a_W = 0.645$	0.526	0.0083	0.0080
	0.405	0.0067	0.0068
	0.221	0.0051	0.0053
	0.125	0.0044	0.0046
	0.010	0.0042	0.0044
	0.000	0.0038	0.0038
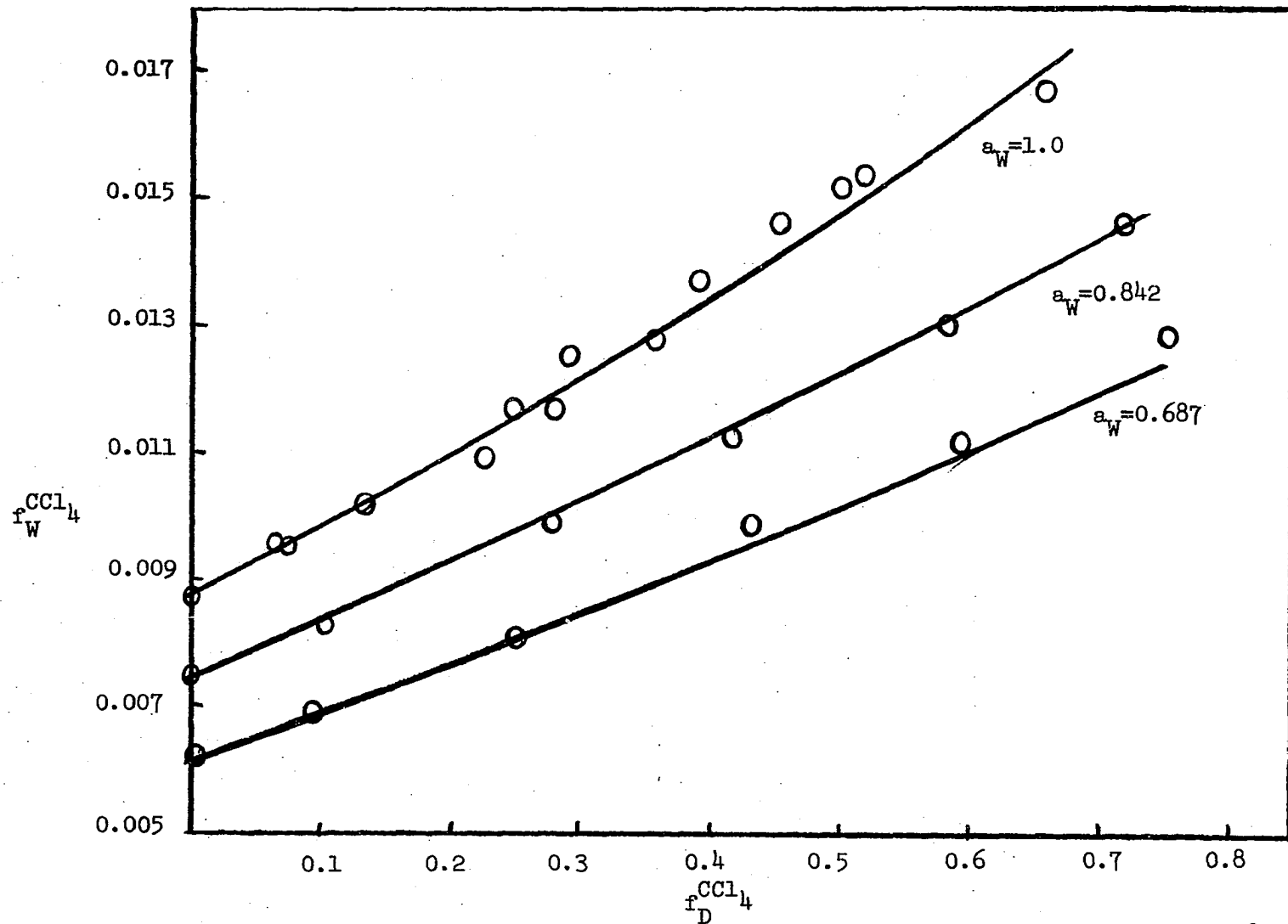
Fig. 11. Solubility of Water in CCl_4 in the Presence of 2,3-Butanediene at 25°.
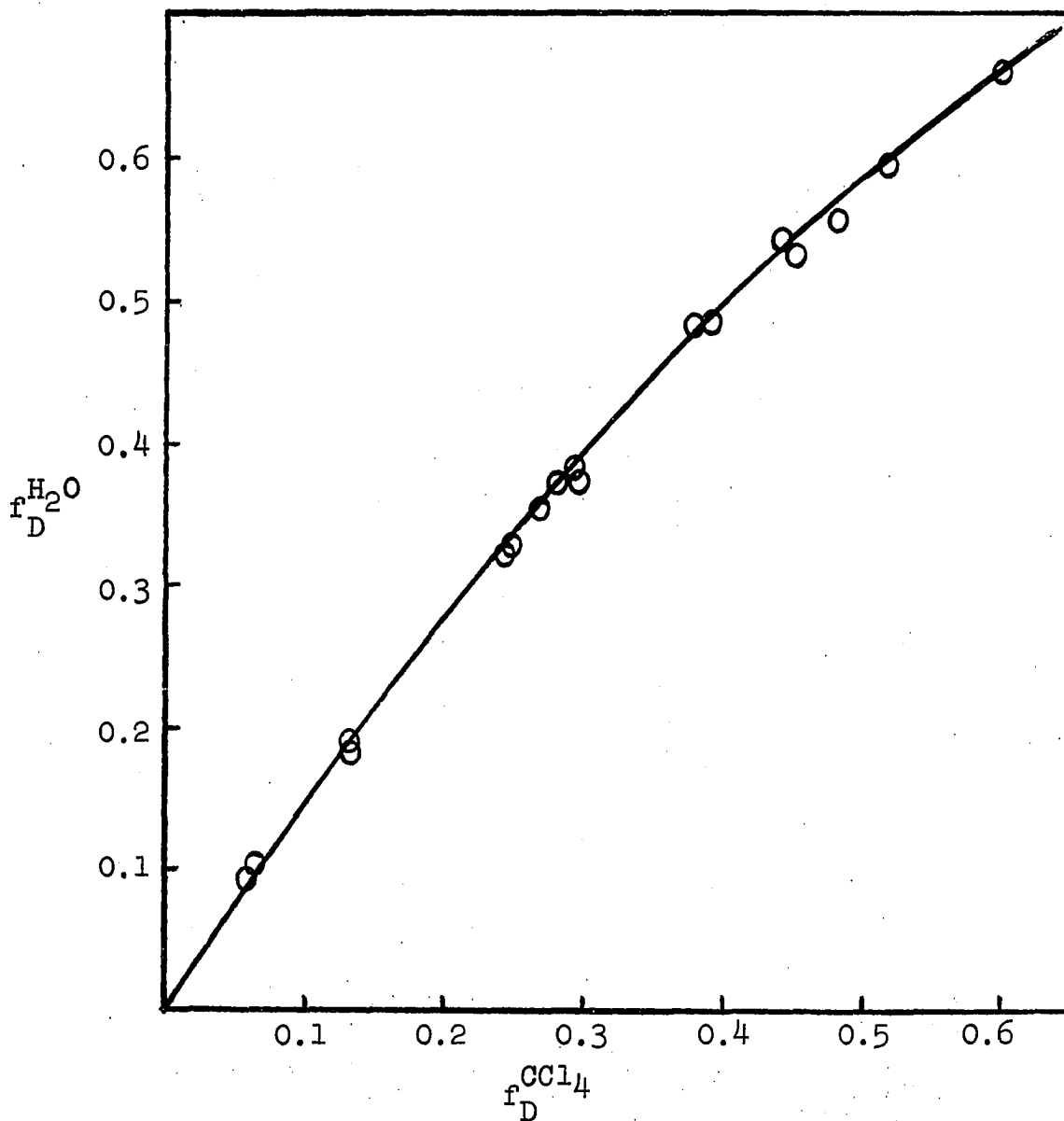
Fig. 12. Partition Data for the System 2,3-Butanedione-Water-CCl_4 at 25°

TABLE 17

PARTITION DATA OF THE SYSTEM ACETYLACETONE-
WATER-CCl$_4$ AT 25°

$f_{AA}^{H_2O}$ (m/l)	$f_{AA}^{CCl_4}$ (m/l)	$f_{AA}^{CCl_4}$(caled.)
0.303	1.302	1.251
0.279	1.091	1.132
0.250	0.971	0.990
0.212	0.828	0.814
0.183	0.676	0.687
0.155	0.571	0.569
0.129	0.466	0.462
0.097	0.350	0.338
0.069	0.224	0.235
0.028	0.093	0.091

TABLE 18

WATER SOLUBILITY IN CCl$_4$ IN THE PRESENCE
OF ACETYLACETONE AT VARIOUS
WATER ACTIVITIES AT 25°

	$f_{AA}^{CCl_4}$ (m/l)	$f_W^{CCl_4}$ (m/l)	$f_W^{CCl_4}$(caled.)
a_W = 0.470	1.110	0.0130	0.0135
	0.925	0.0109	0.0116
	0.745	0.0095	0.0099
	0.563	0.0083	0.0083
	0.372	0.0068	0.0071

TABLE 18--<u>Continued</u>

	$f_{AA}^{CCl_4}$(m/1)	$f_{W}^{CCl_4}$(m/1)	$f_{W}^{CCl_4}$(caled.)
	0.242	0.0054	0.0057
	0.107	0.0049	0.0048
	0.000	0.0042	0.0041
a_W = 1.00	1.110	0.0284	0.0283
	0.971	0.0264	0.0259
	0.971	0.0256	0.0259
	0.775	0.0211	0.0220
	0.695	0.0201	0.0203
	0.570	0.0184	0.0179
	0.445	0.0163	0.0158
	0.320	0.0135	0.0136
	0.190	0.0119	0.0115
	0.060	0.0099	0.0096
	0.000	0.0090	0.0088
a_W = 0.0744	1.120	0.0224	0.0215
	0.955	0.0193	0.0189
	0.760	0.0161	0.0160
	0.580	0.0132	0.0134
	0.381	0.0107	0.0108
	0.245	0.0087	0.0091
	0.107	0.0079	0.0076
	0.000	0.0066	0.0065
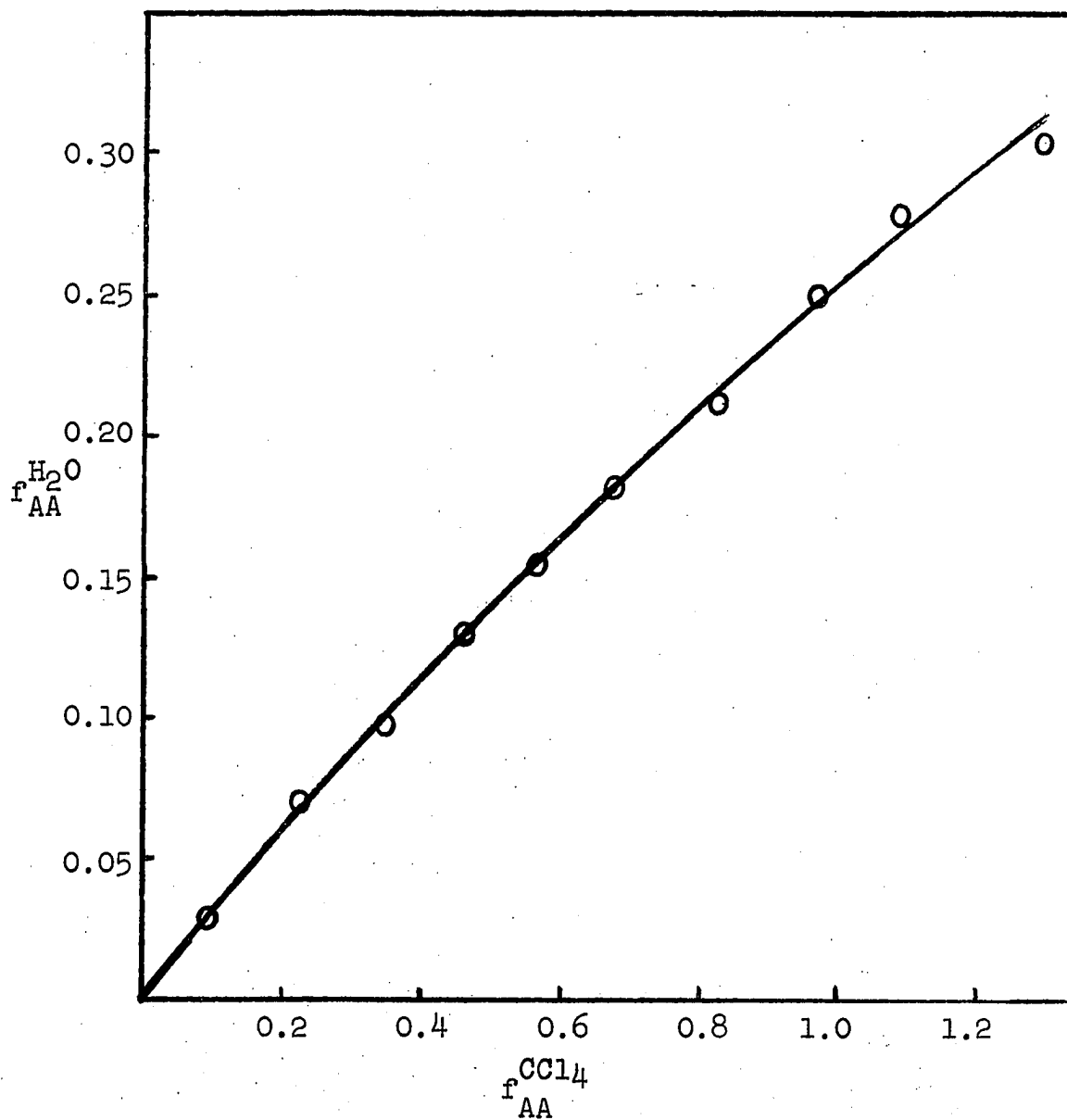
Fig. 13.   Partition Data for the System Acetylacetone-
Water-CCl_4 at 25°
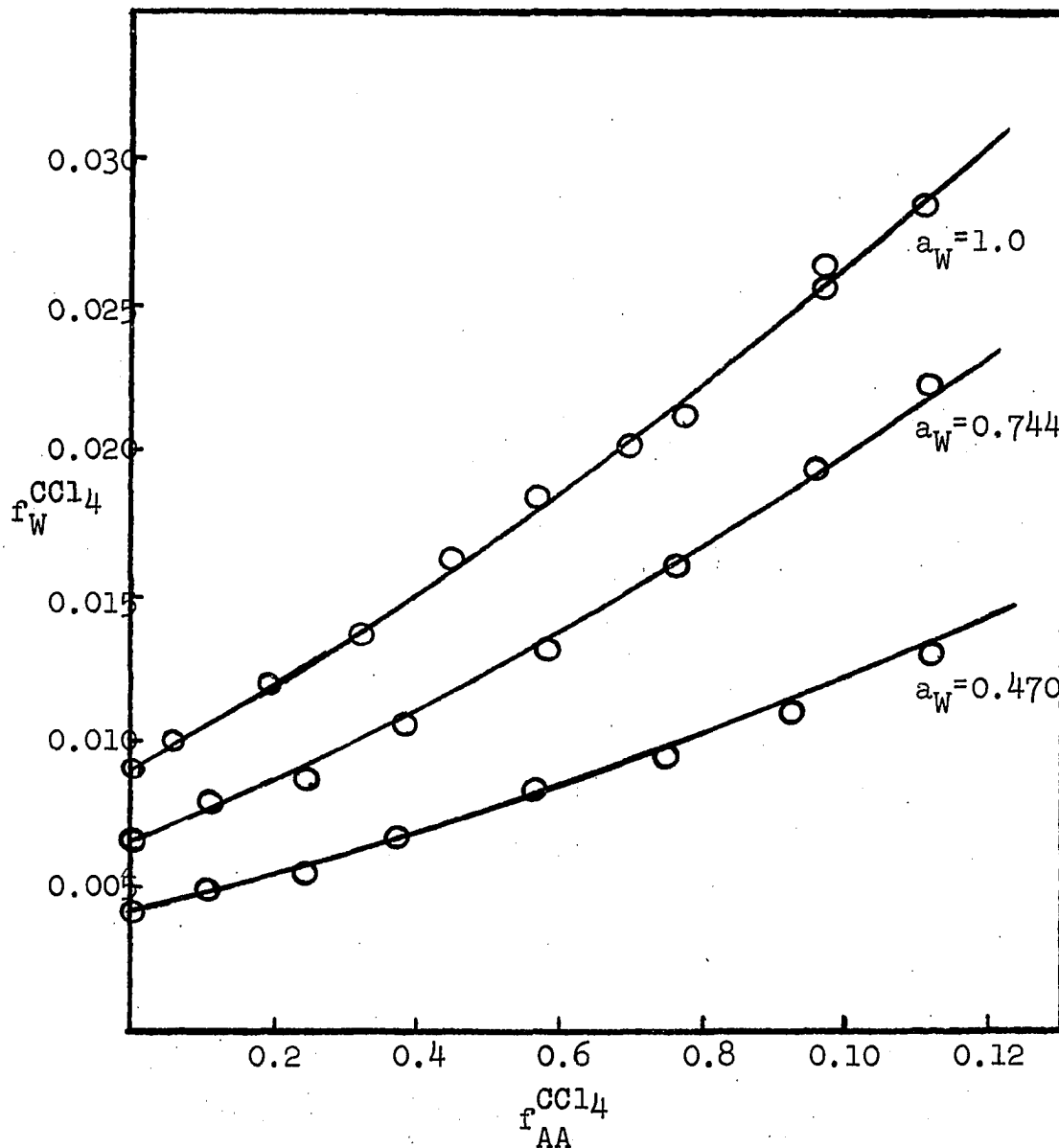
Fig. 14. Solubility of Water in CCl$_4$ in the Presence of Acetylacetone at 25°

TABLE 19

KETO PERCENTAGE OF ACETYLACETONE IN CCl_4 AT $25°$

	$f_{AA}(m/l)$	Keto(%)		$f_{AA}(m/l)$	Keto(%)
Run 1	0.79	4.7	Run 2	1.06	5.1
a_W = 1.0	0.73	5.0	a_W = 1.0	0.85	4.9
	0.59	4.3		0.64	5.0
	0.46	4.1		0.43	4.2
	0.33	3.5		0.21	3.9
	0.20	3.8		0.11	3.0
	0.07	3.4		----	---
Run 1	0.93	5.9	Run 2	1.05	5.0
a_W = 0.0	0.75	5.7	a_W = 0.0	0.84	5.0
	0.56	5.7		0.63	4.3
	0.28	5.3		0.42	3.6
	0.09	5.9		0.21	3.9
	----	---		0.11	3.0

TABLE 20

EQUILIBRIUM CONSTANTS OF THE SYSTEM KETONE-WATER-CCl_4

Substance	k_c	$k_{11}(m^{-1}l)$	$k_{21}(m^{-2}l^2)$	$k_{20}(m^{-1}l)$
Acetone at 25°	0.388 ± 0.004	2.45 ± 0.13	3.89 ± 0.31	0.39 ± 0.03
2,3-Butane-dione at 25°	0.604 ± 0.006	1.17 ± 0.11	2.41 ± 0.26	0.57 ± 0.04
2,3-Butane-dione at 15°	0.430 ± 0.005	1.24 ± 0.13	6.12 ± 0.40	0.78 ± 0.05
Acetyl-acetone at 25°	3.143 ± 0.005	1.48 ± 0.10	1.33 ± 0.20	0.146 ± 0.005

Enthalpy change for k_{20} is $\Delta H = -5.4$ Kcal/mole for 2,3-Butanedione

TABLE 21

SOLUBILITY OF ACETONE IN HEXADECANE
AT VARIOUS TEMPERATURES

	p(mm)	f(Fugacity mm)	$f_A^{Hexadecane}$(m/l)	$f_A^{Hexadecane}$(caled.)
at 20°	8.67	8.66	0.026	0.025
	16.39	16.35	0.053	0.051
	24.27	24.19	0.079	0.076
	31.54	31.42	0.106	0.103
	38.47	38.28	0.133	0.131
	44.74	44.49	0.159	0.158
	50.92	50.59	0.186	0.181
	56.30	55.91	0.213	0.212
	61.73	61.26	0.240	0.241
	66.41	65.86	0.266	0.267
	71.44	70.80	0.293	0.296
	76.03	75.30	0.320	0.324
	8.67	8.66	0.026	0.025
	23.87	23.79	0.079	0.074
	31.09	30.97	0.106	0.103
	37.73	37.54	0.133	0.128
	44.24	44.00	0.159	0.157
	50.47	50.15	0.186	0.184
	56.05	55.66	0.213	0.211
	61.68	61.21	0.240	0.240
	66.51	65.96	0.266	0.264
	71.59	70.95	0.293	0.297
at 25°	10.40	10.39	0.026	0.026
	20.07	20.01	0.053	0.051
	29.27	29.17	0.079	0.078
	37.64	37.46	0.105	0.103
	45.65	45.40	0.132	0.130
	53.11	52.79	0.158	0.157
	63.93	63.47	0.199	0.199
	70.55	69.99	0.226	0.226
	76.62	75.96	0.253	0.253
	82.50	87.73	0.280	0.281
	88.02	87.14	0.307	0.307
at 30°	11.98	11.96	0.026	0.026
	22.98	22.92	0.052	0.052
	33.44	33.33	0.078	0.078
	42.82	42.63	0.105	0.104
	47.46	47.24	0.118	0.117
	56.20	55.88	0.144	0.143
	64.30	63.89	0.171	0.169
	72.40	71.88	0.197	0.196
	80.11	79.47	0.224	0.223

TABLE 21--Continued

p(mm)	f(Fugacity mm)	Hexadecane f_A(m/1)	Hexadecane f_A(caled.)
90.99	90.16	0.264	0.264
11.98	11.97	0.026	0.026
22.99	22.92	0.052	0.052
33.49	33.38	0.078	0.078
43.31	43.12	0.105	0.105
52.69	52.41	0.131	0.132
61.29	60.91	0.158	0.159
69.58	69.10	0.184	0.186
77.44	76.80	0.211	0.214
84.51	83.79	0.237	0.240
91.38	90.55	0.264	0.266

at 40°

p(mm)	f(Fugacity mm)	Hexadecane f_A(m/1)	Hexadecane f_A(caled.)
15.74	15.72	0.026	0.026
29.94	29.86	0.051	0.051
37.02	36.90	0.064	0.064
43.90	43.73	0.077	0.077
56.85	56.57	0.103	0.103
63.24	62.89	0.116	0.117
69.17	68.75	0.129	0.129
75.34	74.85	0.142	0.143
80.88	80.31	0.155	0.156
85.98	85.34	0.168	0.168
91.41	90.68	0.181	0.181
97.29	96.47	0.194	0.195
102.33	101.42	0.208	0.208

at 60°

| p(mm)	f(Fugacity mm)	Hexadecane f_A(m/1)	Hexadecane f_A(caled.)
23.65	23.61	0.026	0.025
44.88	44.75	0.050	0.049
66.40	63.54	0.076	0.074
87.22	86.73	0.101	0.100
107.51	106.76	0.127	0.126
126.46	125.42	0.152	0.152
142.73	141.41	0.178	0.175
12.05	12.03	0.012	0.013
23.94	23.90	0.025	0.026
34.95	34.87	0.038	0.038
46.56	46.42	0.050	0.051
57.22	57.01	0.063	0.063
68.08	67.78	0.075	0.076
78.65	78.25	0.088	0.089
88.02	87.58	0.100	0.100
97.49	96.86	0.113	0.113
107.36	106.61	0.126	0.126
117.08	116.19	0.139	0.139
126.06	125.03	0.151	0.152
135.69	134.49	0.164	0.165
144.92	143.56	0.177	0.179
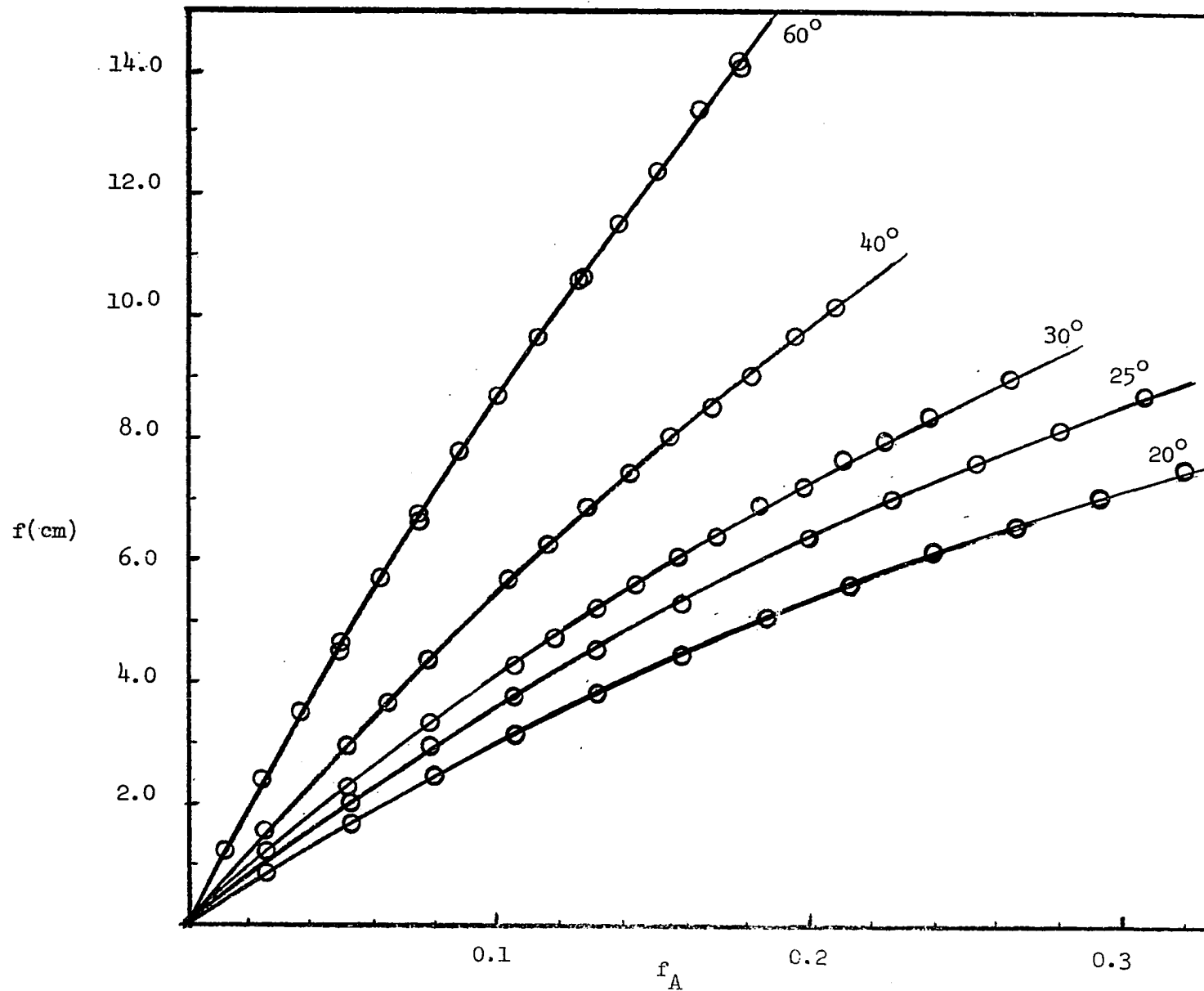
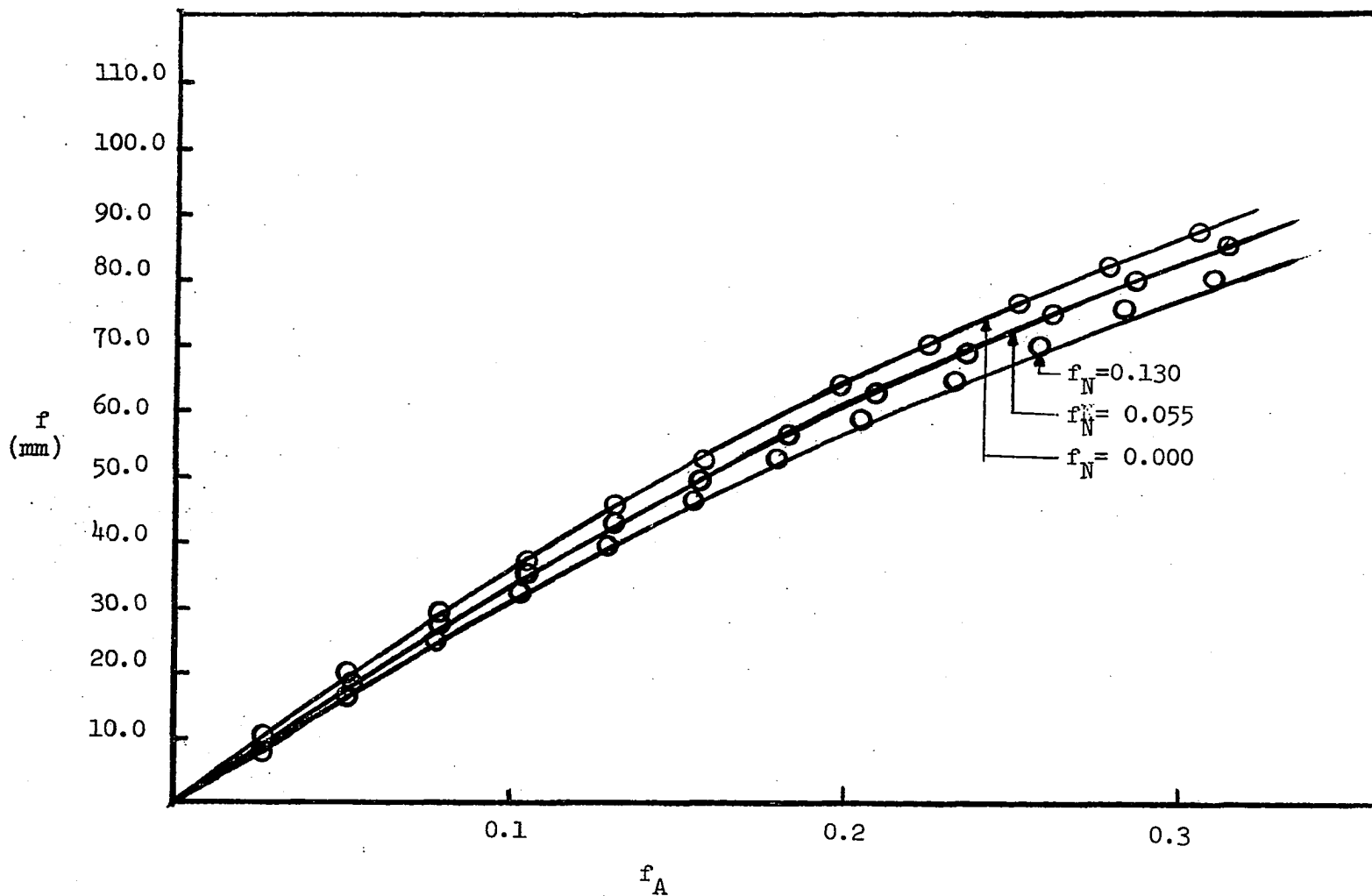Fig. 15. Solubility of Acetone in Hexadecane at Various Acetone Fugacities.

Fig. 16. Solubility of Acetone in Hexadecane in the Presence of Nitrobenzene at Various Acetone Fugacities.

TABLE 22

SOLUBILITY OF ACETONE IN HEXADECANE
IN THE PRESENCE OF NITROBENZENE

at 25°	f(Fuga-city mm)	$f_A^{Hexadecane}$ (m/l)	f(Fuga-city mm)	$f_A^{Hexadecane}$
f_N=0.0548 m/l	0.00	0.0000	f_N=0.130 m/l 0.00	0.0000
	9.65	0.0258	8.20	0.0256
	18.76	0.0521	16.53	0.0514
	27.27	0.0789	24.75	0.0770
	35.31	0.1055	32.29	0.1035
	42.65	0.1310	39.49	0.1287
	49.87	0.1570	46.32	0.1545
	56.53	0.1835	52.70	0.1800
	62.84	0.2082	58.87	0.2050
	68.84	0.2360	64.77	0.2330
	74.69	0.2620	70.19	0.2580
	79.95	0.2870	75.69	0.2840
	84.93	0.3150	80.41	0.3100

TABLE 23

THE EQUILIBRIUM HENRY'S LAW CONSTANTS OF
THE SYSTEM ACETONE-HEXADECANE

$$f_A = k_h f + 2\ k_h{}^2 k_2 f^2 + 3\ k_h{}^3 k_3 f^3$$

	20°	25°	30°	40°	60°
$k_h \times 10^3$ $(ml^{-1}{}_{mm}{}^{-1})$	2.74	2.34	2.09	1.60	1.04
$k_2 (m^{-1}l)$	0.94	0.84	0.79	0.66	0.52
$k_3 (m^{-2}l^2)$	1.43	1.32	0.97	0.82	0.64
$k_2 (m^{-1}l)$	2.29	2.10	1.90	1.70	1.35

(Vapor phase)(29)

TABLE 24

THERMODYNAMIC PARAMETERS OF ACETONE SELF-ASSOCIATION

	$\Delta H^{25^{\circ}}$ (kcal/mole)	$\Delta F^{25^{\circ}}$ (kcal/mole)	$\Delta S^{25^{\circ}}$ (e.u.)	Standard State
k_h	-4.8 ± 0.3	-2.25	-8.6	1 mole/l
k_2	-2.8 ± 0.3	0.10	-9.7	1 mole/l
k_3	-3.4 ± 0.4	-0.17	-10.8	1 mole/l
k_2 (Vapor phase)	-3.0 ± 0.3	-0.44	-8.1	1 mole/l

CHAPTER VI

DISCUSSION AND CONCLUSIONS

In addition to the assumption that the only aggregate of water molecules present in 1,2-dichloroethane is the cyclic trimer, which is supported by NMR data, it has been postulated that acetone forms the acetone monomer monohydrate in this solvent. Using the calculated equilibrium constants of the postulated species from partition and solubility data, it has been possible to make a satisfactory interpretation of NMR as well as dielectric constant data with some additional assumptions about the structure of the complex species.

Relatively little research has been done previously on the basicity of the carbonyl group. However, some attempts (24, 25) have been made to determine the extent of interaction between phenol and several bases. Fritzch and Dunken (25) have made an extensive study of these interactions by infrared techniques. Part of their reported values of frequency shifts of the phenol OH strength and related thermodynamic properties of the interactions of phenol and some bases in CCl_4 are the following:

	$\Delta \nu \text{cm}^{-1}$	$-\Delta H$(kcal/mole)	$-\Delta S^{20^{o}}$ e.u.	$-\Delta G^{20^{o}}$(kcal/mole)
Acetonitrile	160	4.35±0.35	11.0±1.27	1.07
Benzophenone	195	4.37±0.2	11.0±0.7	1.14
Fluorenone	215	4.65±0.4	11.4±1.4	1.33
Acetophenone	225	5.05±0.35	12.6±1.2	1.37
Acetone	235	4.7 ±0.3	10.8±1.0	1.52
Pyridine	230	0.5 ±0.4	14.4±1.3	2.30

(ΔS, ΔG are calculated for the standard state 1 mole/liter)

From the present investigation, the thermodynamic properties of formation of the acetone monomer monohydrate is calculated to be $\Delta H = -4.1$ kcal/m which is slightly lower than Fritzche and Dunken's value of ΔH for the acetone-phenol complex. In order to compare the entropy and free energy change of the formation of acetone monomer monohydrate with Fritzche and Dunken's value, we use $\Delta H = -4.1$ kcal/mole and $k_{11} = 2.45$ at 25° to calculate the k_{11} at 20°; thus, k_{11} was calculated to be 2.76 1/m in CCl_4. Using this value, $\Delta F^{20^{o}}$ is calculated to be -0.593 kcal/mole (standard state is 1 mole/liter) and $\Delta S^{20^{o}}$ is -11.8 e.u. The enthalpy change ΔH and free energy change ΔG were found to be slightly less in magnitude than Fritzche and Dunken's value, probably due to the greater acidity of the hydrogen of the OH group of phenol. The change of entropy occurring on formation of both complex species is about the same, indicating that the relative ordering effects of the two types of hydrogen bond are approximately the same. Pimentel and McClellan (65) have

tabulated values of ΔH for the self-association of water and some alkylalcohols (such as methanol, ethanol, propanol, isopropanol). The enthalpy changes of the formation of these compounds are approximately around 4.3 kcal/mole for the $=$O---H$\longrightarrow$O- type hydrogen bonding. The enthalpy change for forming the acetone monomer monohydrate is about the same as that for attaching a hydroxylic hydrogen to oxygen in water and alkylalcohols. Therefore, the basic strength of carbonyl group of acetone is about the same as the basicity of hydroxyl group in water and alkylalcohols.

The question of whether the NMR hydrogen bond shift may give a relative measure of hydrogen bond strength was first discussed by Korinek and Schneider (66). They showed that a rough correction between NMR hydrogen bond shifts and their strengths can be made. No significant anomalous magnetic effects such as an anisotropic and quenching effect of the proton acceptor have been found for triethylamine, acetone, propionitrile, diethyl ether and propyl fluoride. Therefore, the hydrogen bond shifts of water proton interacting with acetone are mostly dictated by the electronegativity of the carbonyl group. In the present experiment, the chemical shift of the bonded proton in the acetone monomer monohydrate is found to be 102 cps or 1.66 ppm in comparison with the chemical shift of the bonded water proton, 99 cps or 1.65 ppm. The near equality of the chemical shift of these two complexes further supports the conclusion that the basicity

of the acetone carbonyl group is about the same as the basicity of oxygen in the hydroxyl group of water and alkyl-alcohols.

The apparent dipole moment of the acetone monomer monohydrate is calculated to be 3.4 D, which is less than the sum of dipole moment of water (1.8 D) and that of acetone (2.8 D). Consequently, the structure of the complex species probably does not consist of two parallel dipoles arranged in a head-to-tail fashion. The structures of cystalline formic and acetic acid have been reported (67). The angle between OH bond and C=O bond was found to be 122° for formic acid and 144° for acetic acid. A portion of the formic acid crystal structure is as follows,
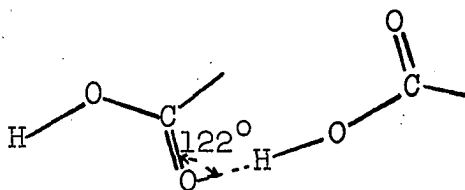
By this geometric structure, the acidic hydrogen of hydroxyl group can attach to one electron pair in the oxygen of the carbonyl group, and a hydrogen bond which is partially co-valent and partially electrostatic can be formed in the same way as the tetrahydral structure of oxygen in the ice crystal. The acetone molecule carbonyl group presumably should be similar to the carbonyl group of formic acid, and it is reasonable to assume that the acetone monomer monohydrate has the following structure, (this is one of the structures suggested by Fritzche (68) for the ketone-phenol complex).

$$O = C \begin{array}{c} CH_3 \\ \\ CH_3 \end{array}$$

H 120°

O

H
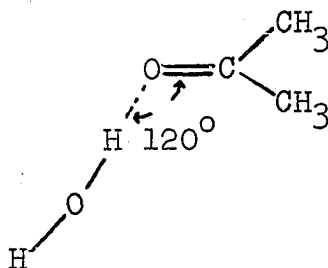
The water molecule in this structure is assumed capable of rotation about —H----O hydrogen bond. If this model and the dipole moment of water (1.85 D) and that of acetone (2.8 D) are used, the dipole moment of the complex species can be calculated to be 3.5 D, which is in good agreement with the experimental value 3.4 D.

The system acetone-water-1,2-dichloroethane is of interest because the data obtained enable the calculation of an accurate value of ΔH for particular species as well as their structures. Interpretation of results is simplified by the fact that relatively few species are involved and water is sufficiently soluble in 1,2-dichloroethane to permit the use of NMR and dielectric constant techniques. On the other hand, investigation of the system acetone-water-CCl₄ makes it possible to obtain more information about several complex species and equilibrium constants in a relatively inert solvent. The solvent effect on equilibrium constants can be roughly estimated from an equation derived by Kirkwood (69,70). The free energy (ΔF) required to transfer a dipole from a medium of dielectric constant D to a vacuum can be expressed as

$$\Delta F = \frac{\mu^2}{r^3} \frac{D - 1}{2D + 1}$$

Where μ is dipole moment of a molecule with radius r. Using this equation, we can relate the equilibrium constant and dielectric constant of the solvent by the expression,

$$\log k = A \frac{D - 1}{2D + 1} + B$$

where A and B are constants at a fixed temperature. If the values of the acetone dimerization constant in the vapor phase, 2.09 l/m, and 0.39 l/m in CCl_4 are used, we can calculate that the dimerization constant of acetone in 1,2-dichloroethane should be about 0.09 l/m, and in water about 0.06 l/m at 25°. The dimerization constants will be even smaller if specific hydrogen bond effects between solvent and solute are important. Owing to the small values expected for the dimerization constants of acetone in 1,2-dichloroethane and water, it has been assumed that there are no significant concentrations of dimer in these solutions.

The basicity of ketones which were used in this investigation has been found to have the following order, acetone > acetylacetone > 2,3-butanedione. It is apparent that the presence of the conjugated system in 2,3-butanedione largely decreases the basicity of the two adjacent carbonyl groups. Unfortunately, the effect of various factors on the basicity of acetylacetone are complicated by the tautomeric behavior of acetylacetone. Acetylacetone is one of the ring-chain tautomers which have two forms, the keto and enol forms.

The enol form is further stabilized by intramolecular hydrogen bonding having an enthalpy of about -2.4 kcal/mole (71) and a free energy of about -1.3 kcal/mole (71) at 25° in the gas phase. There are two possible structures for the enol form,
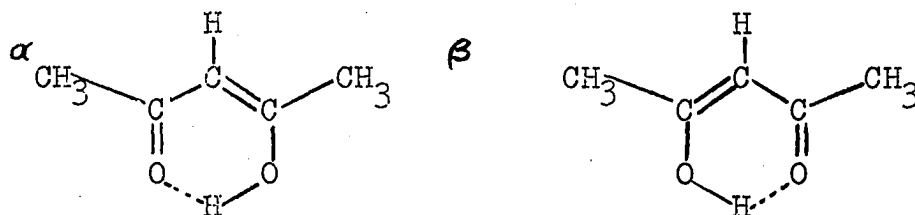

which are believed to be equivalent (72). One indication of the equivalence of these two resonance structures of the enol form is that the chemical shifts of the α-methyl and β-methyl group as indicated by the above structures are equal (73). The intramolecular hydrogen bonding not only leads to a chemical shift of the acidic hydrogen at the lowest field ever found for protons (13.6 ppm low field from its methyl group) (73), but also the OH strength does not appear in its usual region (71, 75, 76). It has been observed that strong bases such as trimethylamine or dimethylamine can convert all the acetylacetone molecules into the enol form. In the nonpolar solvents the enol form is favored, since it can be stabilized by intramolecular hydrogen bonding. With the increase of dielectric constant of solvent, the content of the keto form increases (73).

The keto-enol ratios of β-diketones and similar compounds were first determined with a bromination method reported by Meyer (83). Later IR (71, 77), UV (78, 79) and NMR (73,

80, 81, 74) were employed to determine the keto-enol equili-
brium ratios. So far the most reliable method is the NMR
method which simply measures the intensity of the appropriate
peaks of the NMR spectrum. In the present experiment, the
enol percentage of acetylacetone in CCl_4 in the dry system
(a_W = 0.0) and wet system (a_W = 1.0) were found to be nearly
the same--95% enol form (Table 28). It was also found that
in 1,2-dichloroethane 80% of the acetylacetone molecules are
in the enol form and in water 21%. The higher percentage
of the keto form in water indicates that the keto form is
slightly more basic than the enol form.

By kinetic arguments, the equilibrium constant of
acetone monomer monohydrate should be approximately related
to the equilibrium constant of the acetone dimer monohydrate
by the expression $k_{21} = k_{11}^2/4$ (62). However, the values given
in Table 29 indicate that k_{21} is greater than $k_{11}^2/4$ for all
three ketones. A reasonable explanation of the large value
of k_{21} is that the acetone dimer monohydrate is not only
stabilized by the interactions of the carbonyl groups with
hydrogen of water, but also by the dipole-dipole interaction
as shown in the following structure,
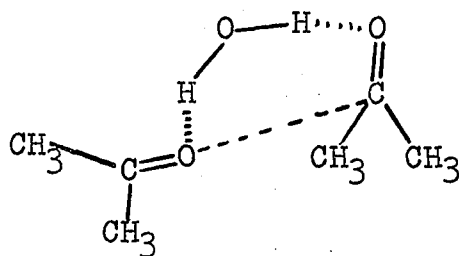
This picture only represents the idea of triple interactions,

i.e. 2 oxygen-hydrogen interactions and one dipole-dipole interaction between the carbonyl groups. In fact, a more plausible structure can be constructed by using three dimensional models, and undoubtedly many variations from the most favored structure are possible due to the weakness of the dipole-dipole interaction.
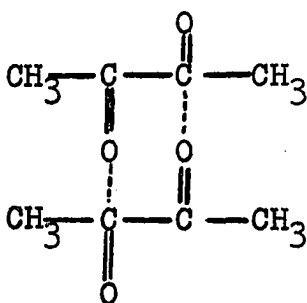
Acetone dimers were found to be present in CCl_4 and hexadecane. The change of enthalpy for the formation of acetone dimers in hexadecane was found to be -2.8 kcal/m, which is significantly less than that of ordinary hydrogen bonding. Let us calculate the interacting energy of an anti-parallel dipole pair as

$$\leftarrow 1.23\text{Å} \rightarrow$$

$$O \overset{O}{=\!=\!=} C \overset{CH_3}{\underset{CH_3}{\diagdown}}$$

$$3.2\text{Å}$$

$$\overset{CH_3}{\underset{CH_3}{\diagup}} C \overset{O}{=\!=\!=} O$$
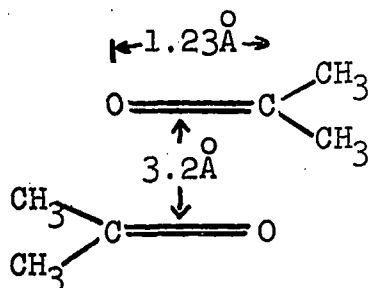
If the dipole moment of acetone 2.8 D and the bond distance of $C\!=\!\!=\!O$, 1.23 Å are used, the net charge on either end of the carbonyl group was calculated to be 2.28×10^{-10} stat-coulombs. The minimum distance between two parallel carbonyl groups is assumed to be 3.2 Å, which is the sum of Van der Waals' radii of carbon and oxygen. Using these values, the total electric energy calculated by adding all the point-charge interaction energy is -3 kcal/mole, which is close to the experimental value $\Delta H = \Delta U = -2.8$ kcal/mole. The actual geometric structure is not strictly an anti-parallel

alignment of two dipoles, and undoubtedly many variations from the anti-parallel alignment are possible. Owing to the relatively weak dipole-dipole interaction, the species stabilized by this interaction would be less rigid than hydrogen-bonded species. This kind of dimer was appropriately called a "random dipole pair" by Saum (82). The less rigid structure of a random dipole pair should result in a less negative entropy change than that found for hydrogen bonded complexes. This is illustrated by the entropy change of acetone dimer in hexadecane, which is $\Delta S = -9.7$ e.u., in comparison with -12.0 e.u. for the formation of the acetone monomer monohydrate in CCl_4.

The large value of k_2 for 2,3-butanedione can be explained by a double interaction of two local dipoles. This explanation is supported by the large enthalpy change (5.4 kcal/mole) for the formation of the 2,3-butanedione dimer, which is about twice that of the acetone dimer. The dimer may exist as,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-CH_3$$

In the case of acetylacetone, the extent of dimerization is the smallest among the three ketones, which may be rationalized by noting that 95% of the acetylacetone molecules are in the enol form, which is not so capable of self-association.

For further studies of the basicity of ketones, it is very valuable to investigate the possible complex species in which there are two water molecules attaching to one carbonyl group as

$$CH_3 \\\\ CH_3 \diagdown C=O \diagup^{O}_{\diagdown} \begin{matrix} H-O \diagdown H \\ H-O \diagup H \end{matrix}$$
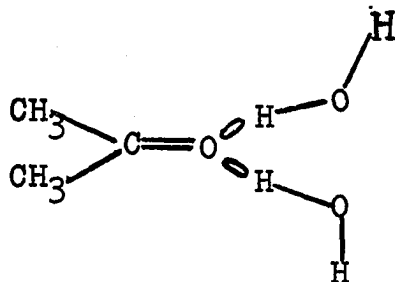
Since the partition and solubility method cannot distinguish the above structure from the following structure,

$$CH_3 \\\\ CH_3 \diagdown C=O \cdots H-O \diagup^{H} \cdots H-O \diagdown H$$
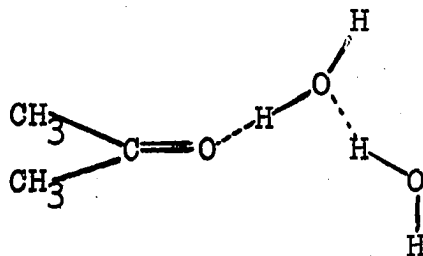
we must resort to spectroscopic methods. One possible method is the NMR technique by which we can determine chemical shifts of oxygen isotope O^{17} of the carbonyl group in pure water and compares this to the chemical shift of oxygen isotope O^{17} of carbonyl group in acetone monomer monohydrate obtained by the same method used in the determination of the chemical shift of water proton of the same complex species in acetone-water-1,2-dichloroethane system. If the chemical shift of oxygen isotope O^{17} of the carbonyl group in pure water is found to be at a significantly lower field than that of the acetone monomer monohydrate, it probably indicates the existence of the species in which two water molecules are attached

to one carbonyl in aqueous solutions of ketone.

Little work has been done on dipole-dipole interactions in the liquid phase. In the present experiment, acetone polymerization due to this interaction was demonstrated by showing the large deviation from Henry's law through the measurement of acetone vapor pressure. It would be interesting to determine the extent of dipole-dipole interaction of a homologous series of ketones or alkylnitriles in order to reveal the influence of geometric structure and the magnitude of the dipole moments of molecules on the dipole-dipole interactions. Also some theoretical calculations can be made on these relatively simple dipole-dipole interactions by the existing dilute solution theories.

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APPENDIX I

COMPUTER METHOD FOR LEAST SQUARES ANALYSIS

<u>Introduction</u>:

Least squares analysis is a method for adjusting data to conform to specified functional or geometric conditions. By minimizing the sum of the weighted squares of the residuals, it is possible to obtain the most probable values of the parameters appearing in the given functional relations. A complete least squares treatment must yield not only the most probable values of the parameters but also the probable error or standard deviation of each parameter. The conventional least squares method, first developed by Gauss, leads to a set of normal equations derived from the observation equations; from the normal equations, both the parameters and the weights of the parameters can be calculated (1-6). Unfortunately, in any but the simplest cases, the derivation and solution of the normal equations are time-consuming, particularly when the functions chosen to represent the data are non-linear and cannot readily be reduced to linear form.

This article describes a simple, convenient method

-104-

for obtaining the complete least squares solution without setting up the normal equations. The method is applicable to non-linear as well as linear problems, and is readily adaptable to the computer.

Theory and Method:

Consider the function $f(a_1, a_2, \ldots a_P, x_1, x_2, \ldots x_n)$ which has been selected to represent y, an observed variable subject to error, where $a_1, a_2 \ldots \ldots a_P$ represent the P parameters to be adjusted and $x_1, x_2, \ldots x_n$ are observed variables assumed free from error. For convenience in notation, let $f_i(a_1, a_2, \ldots a_P)$ represent the value of f corresponding to the ith set of values of $x_1, x_2, \ldots x_n$. Assuming equal weights for all the values of y_i, the root mean square deviation of y for the P-parameter case is defined by

$$s = \sqrt{\frac{\sum_{i=1}^{N} [y_i - f_i(a_1, \ldots a_P)]^2}{N - P}} \tag{1}$$

where N is the number of measured values of y. Note that when the least squares values of $a_1, a_2, \ldots$ are substituted into equation (1), the value of s obtained is the best estimate of σy, the standard deviation of y.

A. One-parameter case.

For simplicity, consider first the problem of calculating the least squares value of a, a single parameter to be obtained by minimizing

$$s = \sqrt{\frac{\sum_i [y_i - f_i(a)]^2}{N - 1}} \tag{2}$$

Regardless of the form of the function $f_i(a)$, the minimum value of s can readily be obtained with the aid of the computer, using an appropriate optimum-seeking method (7). In the vicinity of the minimum, a plot of either s or s^2 vs. a will be parabolic, as shown in Figure 1. It will be demonstrated that the standard deviation of a can be estimated from the points of intersection of the horizontal line,

$s^2_\sigma = s^2_m(1 + \frac{1}{N-1})$, with the s^2 vs. a curve; where s^2_m is the minimum value of s^2, corresponding to a_m, the best value of a. The difference between a at the intersection points and a_m will be shown to be approximately equal to $\pm\sigma_a$. In the limit, as $N \to \infty$, the true value of σ_a can be calculated by this procedure.

Let $v_i = y_i - f_i(a)$ be the residual corresponding to each observation. The normal equation, which may be obtained by equating the derivative of equation (2) with respect to a equal to zero, may be written

$$\Sigma[y_i - f_i(a_m)]f_i'(a_m) = 0 \qquad (3)$$

From the equation of propagation of error, assuming normal distribution of the errors in y_i,

$$\sigma^2_a = \sum_j (\partial a_m/\partial y_j)^2 \sigma^2_y \qquad (4)$$

If equation (3) is differentiated with respect to any one of the y values, say y_j, and rearranged, the expression

$$(\partial a_m/\partial y_j) = -f_j'(a_m)/\{\Sigma[y_i - f_i(a_m)]f_i''(a_m) - \Sigma f_i'^2(a_m)\}$$

is obtained. This expression may be substituted into equation

(4) to give the result

$$\sigma_a^2 = \frac{\Sigma f_i'^2(a_m)}{\{\Sigma[y_i - f_i(a_m)]f_i''(a_m) - \Sigma f_i'^2(a_m)\}^2} \sigma_y^2 \qquad (5)$$

Since the observed y_i values are assumed to be subject only to random error, $y_i - f_u(a_m)$ fluctuates in sign, whereas $f_i''(a_m)$ is a smoothly varying function. Therefore, the expression $\Sigma[y_i - f_i(a_m)]f_i''(a_m)$ can be neglected in comparison with $\Sigma f_i'^2(a_m)$, for N sufficiently large. Hence, we set the first term in the denominator of equation (5) equal to zero to obtain

$$\sigma_a^2 = \sigma_y^2/\Sigma f_i'^2(a_m) \qquad (6)$$

Next, we seek the value of s^2 at the point $a = a_m + \sigma_a$; denoting this value by s_σ^2, we can rearrange equation (2) to yield

$$(N - 1)s_\sigma^2 = \Sigma[y_i - f_i(a_m + \sigma_a)]^2$$

By Taylor's expansion to second order terms,

$$(N - 1)s_\sigma^2 = \Sigma[y_i - f_i(a_m)]^2 - 2\Sigma[y_i - f_i(a_m)]f_i'(a_m)\sigma_a$$
$$- 2\Sigma[y_i - f_i(a_m)]f_i''(a_m)\sigma_a^2/2 + \Sigma f_i'^2(a_m)\sigma_a^2$$

However, $\Sigma[y_i - f_i(a_m)]f_i'(a_m)$ is zero from the normal equation and we set $\Sigma[y_i - f_i(a_m)]f_i''(a_m) = 0$ as in the derivation of equation (6). Thus,

$$(N - 1)(s_\sigma^2 - s_m^2) = \Sigma f_i'^2(a_m)\sigma_a^2 \qquad (7)$$

If σ_a^2 is eliminated between equations (6) and (7) the expression

$$(N - 1)(s_\sigma^2 - s_m^2) = \sigma_y^2$$

results. Since, for large N, σ_y^2 is equal to s_m^2, we obtain $s^2 = s_m^2 (1 + \frac{1}{N-1})$. This is a remarkable and useful result, since it implies that the value of s^2 at the points $a_m + \sigma_a$ and $a_m - \sigma_a$ is independent of the functional form $f(a,x_1,x_2, . . . x_n)$ but depends solely on s_m^2 and the number of observations, N. The method for estimating σ_a, illustrated in Figure 1, is thus justified.

B. Two-parameter case.

A more useful case is the two-parameter problem, in which

$$s = \sqrt{\frac{\Sigma[y_i - f_i (a,b)]^2}{N-2}}$$

must be minimized with respect to both a and b. As in the one-parameter problem, a minimum in s or s^2 can be found with the aid of the computer. Figure 2 illustrates a contour curve of constant s^2 and the point corresponding to a minimum in s^2 for a typical two-parameter problem. It will be shown that if the standard error contour, $s_\sigma^2 = s_m^2(1 + \frac{1}{N-2})$, is represented in the figure, σ_a and σ_b can be deduced from the location of the vertical and horizontal tangents to this curve. The difference between the a coordinate of the vertical tangent and a_m is $\pm \sigma_a$; the difference between the b coordinate of the horizontal tangent and b_m is $\pm \sigma_b$.

For the two-parameter case, the normal equations are

$$\sum_i [y_i - f_i(a_m,b_m)] \partial f_i(a_m,b_m)/\partial a = 0 \qquad (8)$$

and

$$\sum_1 \left[y_1 - f_1(a_m, b_m) \right] \partial f_1(a_m, b_m) / \partial b = 0 \tag{9}$$

When these relations are differentiated implicitly with respect to y_j and the assumptions are made that

$$\sum_1 \left[y_1 - f_1(a_m, b_m) \right] \partial^2 f_1(a_m, b_m) / \partial a^2 = 0 \tag{10-a}$$

$$\sum_1 \left[y_1 - f_1(a_m, b_m) \right] \partial^2 f_1(a_m, b_m) / \partial a \partial b = 0 \tag{10-b}$$

$$\sum_1 \left[y_1 - f_1(a_m, b_m) \right] \partial^2 f_1(a_m, b_m) / \partial b^2 = 0 \tag{10-c}$$

the expressions

$$\partial a_m / \partial y_j = \frac{f_a \sum f_b^2 - f_b \sum f_a f_b}{\sum f_a^2 \sum f_b^2 - (\sum f_a f_b)^2}$$

and

$$\partial b_m / \partial y_j = \frac{f_b \sum f_a^2 - f_a \sum f_a f_b}{\sum f_a^2 \sum f_b^2 - (\sum f_a f_b)^2}$$

result, where f_a represents $\partial f_1 / \partial a$ and f_b represents $\partial f_1 / \partial b$, evaluated at a_m, b_m. From the propagation of error formula,

$$\sigma_a^2 = \frac{\sum f_b^2}{\sum f_a^2 \sum f_b^2 - (\sum f_a f_b)^2} \sigma_y^2 \tag{11}$$

and

$$\sigma_b^2 = \frac{\sum f_a^2}{\sum f_a^2 \sum f_b^2 - (\sum f_a f_b)^2} \sigma_y^2 \tag{12}$$

Applying Taylor's expansion to the equation

$$(N - 2)s^2 = \sum \left[y_1 - f_1(a_m + \Delta a, b_m + \Delta b) \right]^2$$

and neglecting terms equivalent to equations (10), one obtains

$$(s^2 - s_m^2)(N - 2) = \sum f_a^2 (\Delta a)^2 + \sum f_b^2 (\Delta b)^2 + 2 \sum f_a f_b \Delta a \Delta b \tag{13}$$

where $\Delta a = a - a_m$ and $\Delta b = b - b_m$. From equation (13) it is

evident that contours of constant s^2 are elliptical in the vicinity of a_m, b_m, since $\Sigma f_a^2 \, \Sigma f_b^2 \geqslant (\Sigma f_a f_b)^2$. The maximum value of Δa on the surface of constant s^2 is given by

$$(\Delta a)^2 = \frac{(s^2 - s_m^2)(N - 2)\Sigma f_b^2}{\Sigma f_a^2 \, \Sigma f_b^2 - (\Sigma f_a f_b)^2} \qquad (14)$$

If $(\Delta a)^2$ in equation (14) is set equal to σ_a^2, equations (11) and (14) may be equated. Then, it follows that

$$s^2 = s_m^2(1 + \frac{1}{N - 2}) = s_\sigma^2$$

This equation denotes the standard error contour on which the maximum value of a is $a_m + \sigma_a$ and the maximum value of b is $b_m + \sigma_b$. Hence, the construction illustrated in Figure 2 may be used to calculate both σ_a and σ_b.

C. General P-parameter case:

Although the simple graphical methods for obtaining σ values cannot be used in solving problems involving more than two parameters, it is possible to prove a general theorem which allows the computation of standard deviations from the equation for the standard error surface. Note that the equation for a hyper-surface of constant s^2 in the vicinity of the minimum can be expressed in the general elliptical-paraboloid form:

$$s^2 - s_m^2 = A_1(\Delta a_1)^2 + A_2(\Delta a_2)^2 + \ldots + A_P(\Delta a_P)^2 +$$
$$B_{12}\Delta a_1 \Delta a_2 + \ldots + B_{(P-1)P}\Delta a_{P-1}\Delta a_P$$

If we select the particular surface $s^2 = s_m^2(1 + \frac{1}{N - P})$,

which we shall term the standard error surface in P + 1 dimensions, it can be shown that the maximum value of each of the parameters a_1, a_2, . . a_P on the surface will occur at $a_{1_m} + a_1$, $a_{2_m} + a_2$, ... $a_{P_m} + a_P$, respectively, where a_{1_m}, a_{2_m}, . . a_{P_m} are the values of the parameters minimizing s^2.

Proof: The relation between s^2 and the parameters in the P dimensional case can be obtained by Taylor's expansion for points in the vicinity of the minimum. To second order terms, the equation is

$$(s^2 - s_m^2)(N - P) = \sum f_{a_1}^2 (\Delta a_1)^2 + \sum f_{a_2}^2 (\Delta a_2)^2 + \ldots + \sum f_{a_P}^2 (\Delta a_P)^2$$

$$+ 2\sum f_{a_1} f_{a_2} \Delta a_1 \Delta a_2 + 2\sum f_{a_1} f_{a_3} \Delta a_1 \Delta a_3 + \ldots \qquad (15)$$

This expression includes $(P^2 - P)/2$ cross-terms in $\Delta a_1 \Delta a_2$, $\Delta a_1 \Delta a_3$, etc., which may be eliminated by performing a linear transformation of the type

$$a_1 = \alpha_{11} b_1 + \alpha_{12} b_2 + \ldots . + \alpha_{1P} b_P$$

$$a_2 = \alpha_{21} b_1 + \alpha_{22} b_2 + \ldots . + \alpha_{2P} b_P$$

$$. . . . .$$

$$a_P = \alpha_{P1} b_1 + \alpha_{P2} b_2 + \ldots . + \alpha_{PP} b_P \qquad (16)$$

In the new parameters, b_1, ... , b_P, the function chosen to represent y becomes

$$F(b_1, b_2, \ldots . b_P) = f(a_1, a_2, \ldots . a_P)$$

Again, by Taylor's expansion

$$(s^2 - s_m^2)(N - P) = \sum F_{b_1}^2 (\Delta b_1)^2 + \sum F_{b_2}^2 (\Delta b_2)^2 + \ldots \ldots$$

$$+ 2\sum F_{b_1} F_{b_2} \Delta b_1 \Delta b_2 + 2\sum F_{b_1} F_{b_3} \Delta b_1 \Delta b_3 + \ldots \qquad (17)$$

The coefficients of the cross-terms will all vanish for proper choice of $\alpha_{11}, \ldots, \alpha_{PP}$ in equations (16), since there are P^2 coefficients to adjust in the linear transformation equations, but only $(P^2 - P)/2$ cross-terms. Thus, equation (17) reduces to

$$(s^2 - s_m^2)(N - P) = \sum F_{b_1}^2 (\Delta b_1)^2 + \ldots + \sum F_{b_P}^2 (\Delta b_P)^2 \qquad (18)$$

The maximum value of $(\Delta b_1)^2$ on any surface of constant s^2 is given by

$$(\Delta b_1)_{max}^2 = \frac{(s^2 - s_m^2)(N - P)}{\sum F_{b_1}^2} \qquad (19)$$

and similarly,

$$(\Delta b_2)_{max}^2 = \frac{(s^2 - s_m^2)(N - P)}{\sum F_{b_2}^2}, \text{ etc.}$$

Using equation (18), the normal equations are

$$\sum [y_i - F_i(b_{1_m}, b_{2_m}, \ldots b_{P_m})] \, F_{b_1}(b_{1_m}, \ldots b_{P_m}) = 0$$

$$\vdots \qquad \qquad \vdots \qquad \qquad \vdots \qquad \qquad \vdots \qquad (20)$$

$$\sum [y_i - F_i(b_{1_m}, b_{2_m}, \ldots b_{P_m})] \, F_{b_P}(b_{1_m}, \ldots b_{P_m}) = 0$$

When the first of equations (20) is differentiated implicitly with respect to y_j, the expression

$$\sum [y_i - F_i(b_{1_m}, \ldots b_{P_m})][F_{b_1 b_1}(\partial b_1/\partial y_j) +$$

$$F_{b_1 b_2}(\partial b_2/\partial y_j) + \ldots] + F_{b_1} - \sum F_{b_1}^2 (\partial b_1/\partial y_j)$$

$$- \sum F_{b_1} F_{b_2}(\partial b_2/\partial y_j) - \ldots = 0 \qquad (21)$$

results, where it is understood that all the derivatives are evaluated at b_{1_m}, b_{2_m}, ... , b_{P_m}. But, since the first terms in brackets are negligible, and since $\sum F_{b_1} F_{b_2} = \sum F_{b_1} F_{b_3} = \ldots = 0$, equation (21) simplifies to

$$(\partial b_1/\partial y_j) = F_{b_1}/\sum F_{b_1}^2$$

Hence, $\sigma_{b_1}^2 = \sigma_y^2 \sum (\partial b_1/\partial y_j)^2 = \sigma_y^2/\sum F_{b_1}^2$

and similarly $\sigma_{b_2}^2 = \sigma_y^2/\sum F_{b_2}^2$, etc. (22)

Equating (22) and (19) for $(\Delta b_1)_{max}^2 = \sigma_{b_1}^2$, we observe that

$$s^2 = s_m^2 (1 + \frac{1}{N - P}) = s_\sigma^2.$$ The standard

error surface is therefore the contour for which the maximum value of b_1 equals $b_{1_m} + \sigma_{b_1}$. Similarly, the maximum value of each of the other parameters on the standard error surface is given by the value of the parameter at the minimum plus the standard deviation of the parameter. In other words, we have proved the theorem for the case in which all the cross-terms in equation (17) are zero.

To prove the theorem in the general case, we can make use of the Lagrange multiplier technique to maximize the values of a_1, a_2, ..., etc., on a surface of constant s^2. Since $a_1 = \alpha_{11} b_1 + \alpha_{12} b_2 + \ldots . + \alpha_{1P} b_P$, at the maximum value of a_1

$$da_1 = 0 = \alpha_{11} db_1 + \ldots . + \alpha_{1P} db_P \tag{24}$$

Upon differentiating equation (18), for constant s^2, we obtain

$$0 = \sum F_{b_1}^2 \Delta b_1 db + \sum F_{b_2}^2 \Delta b_2 db_2 + \ldots + \sum F_{b_P}^2 \Delta b_P db_P \quad (25)$$

If equation (25) is multiplied by the undetermined multiplier, λ, and added to equation (24), the coefficients of db_1, db_2, . . db_P may be set simultaneously equal to zero to give

$$\lambda \Delta b_1 = -\alpha_{11}/\sum F_{b_1}^2, \ldots . \lambda \Delta b_P = -\alpha_{1P}/\sum F_{b_P}^2 \quad (26)$$

These expressions may be substituted into equation (18) to yield

$$\lambda^2 (s^2 - s_m^2)(N - P) = \alpha_{11}^2/\sum F_{b_1}^2 + \alpha_{12}^2/\sum F_{b_2}^2 + . + \alpha_{1P}^2/\sum F_{b_P}^2 \quad (27)$$

From (16), $\Delta a_1 = \alpha_{11}\Delta b_1 + \alpha_{12}\Delta b_2 + . + \alpha_{1P}\Delta b_P$ \quad (28)

where $\Delta a_1 = a_1 - a_{1_m}, \Delta b_1 = b_1 - b_{1_m}$, etc.

Substituting equations (26) into (28)

$$-\lambda \Delta a_1 = \alpha_{11}^2/\sum F_{b_1}^2 + \alpha_{12}^2/\sum F_{b_2}^2 + \ldots + \alpha_{1P}^2/\sum F_{b_P}^2 \quad (29)$$

By eliminating λ between equations (27) and (29) we obtain

$$(\Delta a_1)_{max}^2 = (s^2 - s_m^2)(N - P)[(\alpha_{11}^2/\sum F_{b_1}^2 + \alpha_{12}^2/\sum F_{b_2}^2$$
$$+ \ldots + \alpha_{1P}^2/\sum F_{b_P}^2] \qquad \text{From relation (19)}$$

$$(\Delta a_1)_{max}^2 = \alpha_{11}^2 (\Delta b_1)_{max}^2 + \alpha_{12}^2 (\Delta b_2)_{max}^2 + . . + \alpha_{1P}^2 (\Delta b_P)_{max}^2$$

This is the expression for the maximum value of $(\Delta a_1)^2$ on the standard error contour; however, from our previous results, it is obvious that $(\Delta b_1)_{max}^2 = \sigma_{b_1}^2, (\Delta b_2)_{max}^2 = \sigma_{b_2}^2$, etc., for this contour.

Thus

$$(\Delta a_1)_{max}^2 = \alpha_{11}^2 \sigma_{b_1}^2 + \alpha_{12}^2 \sigma_{b_2}^2 + \ldots + \alpha_{1P}^2 \sigma_{b_P}^2 \quad (30)$$

On the other hand, by applying the propagation of error rule directly to the first of equations (16), it is observed that

$$\sigma_{a_1}^2 = \alpha_{11}^2 \sigma_{b_1}^2 + \ldots \ldots + \alpha_{1P}^2 \sigma_{b_P}^2 \qquad (31)$$

The identity of the right hand sides of equations (30) and (31) proves that the maximum value of a_1 on the standard error contour is $a_{1_m} + \sigma_{a_1}$; similarly each of the other parameters has a maximum on this surface equal to its value at the minimum point plus the standard deviation of that parameter. The proof is thus complete for the general P-parameter case.

Application:

Graphical methods have been described for calculating standard deviations for one- and two-parameter problems. However, it is necessary to develop numerical methods to solve problems involving three or more parameters.

To calculate $\sigma_{a_1}, \sigma_{a_2}, \ldots \sigma_{a_P}$ from $y, x_1, \ldots$ x_n measurements, it is first necessary to find the absolute minimum in s^2 by numerical methods and to compute $A_1, A_2, \ldots A_P, B_{12}, \ldots B_{(P-1)P}$ in the expression

$$s^2 - s_m^2 = A_1(\Delta a_1)^2 + A_2(\Delta a_2)^2 + \ldots + A_P(\Delta a_P)^2$$
$$+ B_{12}\Delta a_1 \Delta a_2 + \ldots + B_{(P-1)P}\Delta a_{P-1}\Delta a_P \qquad (32)$$

The coefficients may be calculated from the relations

$$A_1 = \frac{s^2(a_{1_m} + \delta a_1, a_{2_m}, \ldots a_{P_m}) - 2s_m^2 + s^2(a_{1_m} - \delta a_1, a_{2_m}, \ldots a_{P_m})}{2(\delta a_1)^2}$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$A_P = \frac{s^2(a_{1_m}, \ldots a_{P_m} + \delta a_P) - 2s_m^2 + s^2(a_{1_m}, \ldots a_{P_m} - \delta a_P)}{2(\delta a_P)^2}$$

$$B_{12} = [s_m^2 + s^2(a_{1_m} + \delta a_1, a_{2_m} + \delta a_2, a_{3_m}, \ldots a_{P_m})$$

$$-s^2(a_{1_m} + \delta a_1, a_{2_m}, \ldots a_{P_m}) - s^2(a_{1_m}, a_{2_m} + \delta a_2, \ldots a_{P_m})]/\delta a_1 \delta a_2$$

$$\vdots$$

etc. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (33)

where $\delta a_1, \delta a_2, \ldots \delta a_P$ are suitably chosen small increments in each of the parameters. In general, there will be $(P^2 + P)/2$ coefficients to calculate in equation (32) and it will be necessary to compute s^2 at $(P^2 + 3P + 2)/2$ points in the vicinity of the minimum. Note that a small error in location of the absolute minimum will not lead to a corresponding error in the calculated values of the coefficients $A_1, A_2, \ldots$ $A_P, B_{12}, \ldots B_{(P-1)P}$, provided equation (32) is valid throughout the region selected for applying equations (33).

Once the coefficients have been calculated, Δa_1 can be maximized, using the Lagrange method or numerical techniques, for the particular hyper-surface $s^2 - s_m^2 = s_m^2(\frac{1}{N - P})$. Similarly, maximum values of $\Delta a_2, \ldots, \Delta a_P$ can be located on the standard error surface; these values are, of course, the calculated values of the standard deviations of the para-

meters.

Discussion:

The results of the previous sections indicate that a complete least squares solution may be obtained for any function, linear or nonlinear, provided detailed information about the behavior of $s^2(a_1, \ldots a_P)$ in the vicinity of the minimum is available. Practically, this means that one can avoid the difficulty of formulating and solving the very cumbersome normal equations which frequently arise in least squares problems. It is quite feasible to develop general computer programs for minimizing s^2, in which it is only necessary to modify a small section each time a new functional relation, $f(a_1, \ldots, a_P, x_1, \ldots x_n)$, is selected for the adjustment of data. We have successfully applied this approach in solving numerous parameter calculation problems (8). A related least squares method has been developed by Sillén and co-workers (9-11).

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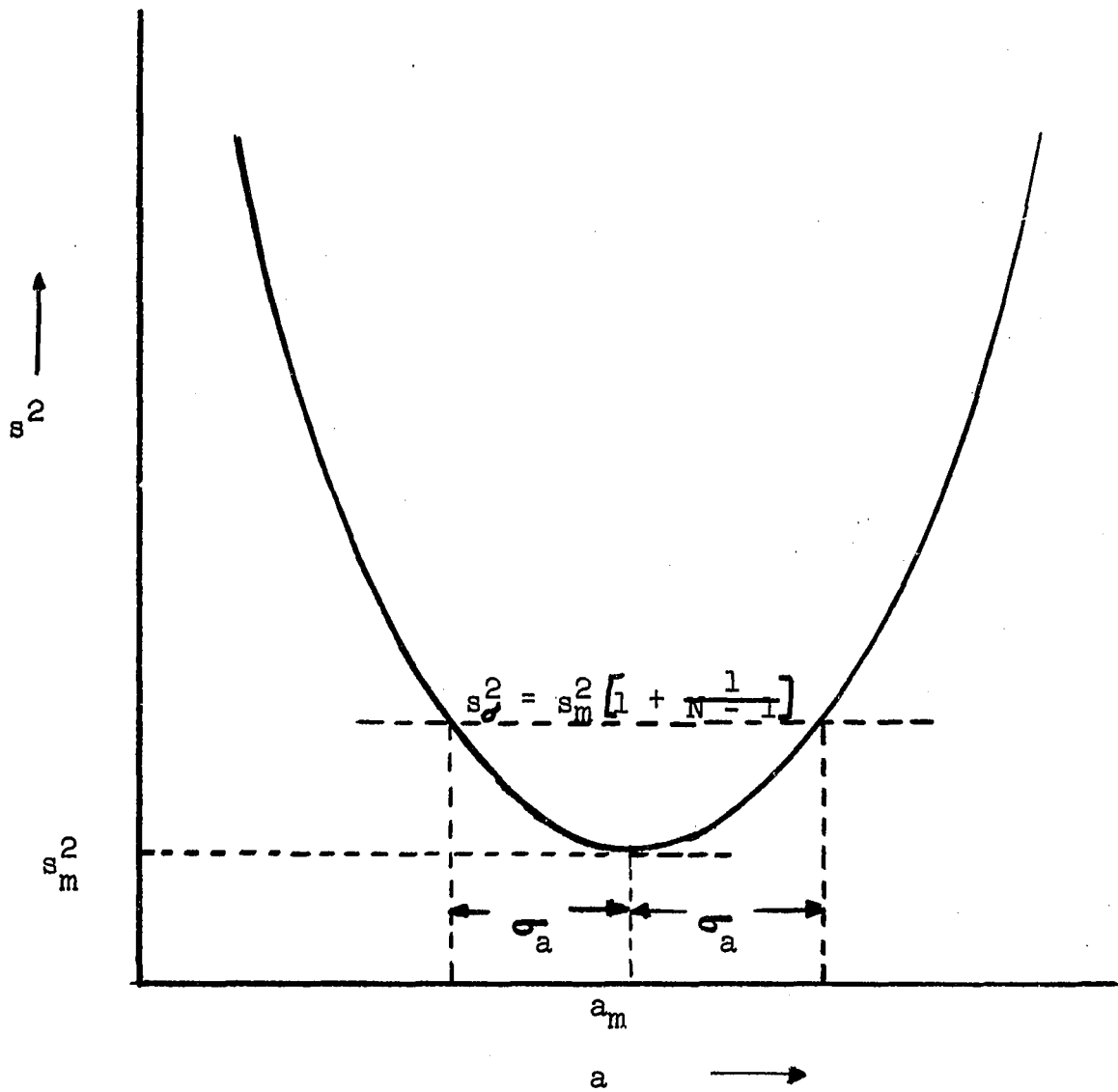11. L. G. Sillen, Acta Chem. Scand., 16, 159 (1962).

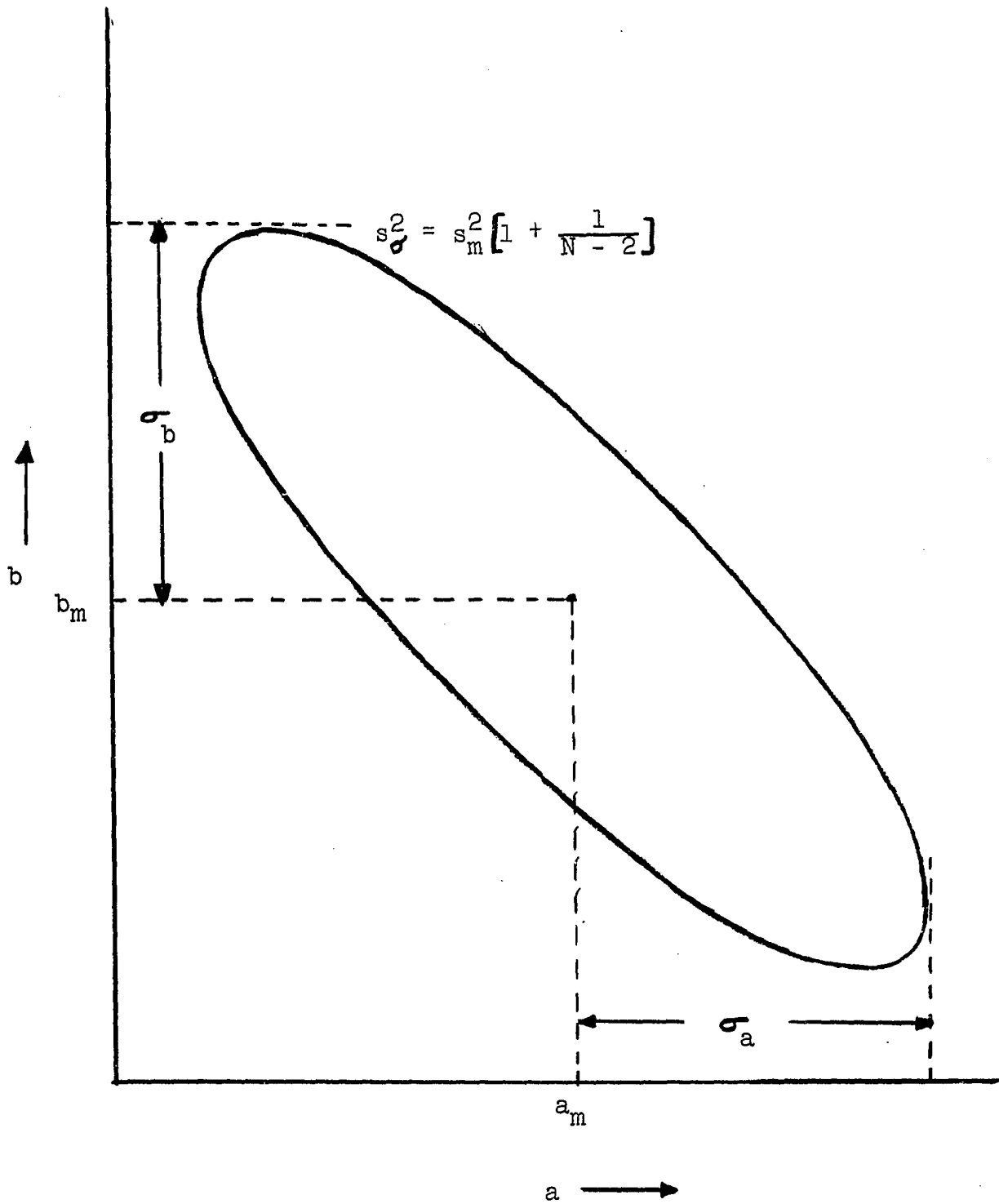Fig. 1. Standard Error Curve for the 1-parameter Case

Fig. 2. Standard Error Contour for the 2-parameter Case