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A NEW METHOD FOR THE STUDY OF HYDROGEN BONDING IN SOLUTIONS OF VOLATILE COMPOUNDS IN NONVOLATILE, NONPOLAR SOLVENTS

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A NEW METHOD FOR THE STUDY OF HYDROGEN BONDING IN SOLUTIONS OF VOLATILE COMPOUNDS IN NONVOLATILE, NONPOLAR SOLVENTS

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A NEW METHOD FOR THE STUDY OF HYDROGEN BONDING IN SOLUTIONS OF VOLATILE COMPOUNDS IN NONVOLATILE, NONPOLAR SOLVENTS

CHAPTER I

INTRODUCTION

During the past few years numerous studies have been made of hydrogen bonding. The subject is important because of the widespread occurrence of hydrogen bonds in inorganic, organic and biological materials. An adequate theory of the hydrogen bonding will be necessary to explain the action of glues and adhesives, the behavior of many synthetic polymers and the properties and structure of proteins and other biochemical systems.

The hydrogen bond has an energy intermediate between that of primary chemical bonds and the weak van der Waals attractive forces between molecules. The hydrogen bond itself was first mentioned by Moore and Winmill,[1] then by Pfeiffer.[2] Pimentel and McClellan[3] in their book "The Hydrogen Bond" have presented the following operational definition for the hydrogen bond:

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

a) there is evidence of bond formation.

b) there is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A."

Cannon[4] cited three criteria for hydrogen bond formation drawn from the conclusion that the quantum contribution to hydrogen bonding is of major importance. These three criteria are:

1. partially ionic proton donor bond $-\overset{-\delta}{X}-\overset{+\delta}{H}-$.
2. asymmetric lone-pair orbitals on proton acceptor.
3. X-H bond and lone-pair orbital colinear.

From the chemical point of view, the concept of the hydrogen bond was first applied by Latimer and Rodebush[5] in discussing the abnormal physical behavior of such highly associated liquids as H_2O and HF. Since then, the effect of hydrogen bonding has been used to interpret deviations from ideality or normality of solutions, liquids and gases.

The existence and extent of hydrogen bonding can be detected by several methods which include electrical studies, vapor pressure and vapor density studies, spectroscopic methods, colligative properties, isopiestic and distribution studies of solutions, and others.

In solution studies, with which this work will be concerned, cryoscopic or freezing point depression measurements have been used to determine the extent of hydrogen bonding in a given solvent. From a knowledge of the freezing point lowering, which is proportional to the apparent molal concentration of the solute, the extent of association in solution can be calculated. Infrared and Raman spectroscopy, nuclear magnetic resonance and distribution experiments are among the most successful methods used in the recent years for the study of hydrogen bonding in solution. Vapor pressure studies of binary mixtures frequently

have been used for quantitative detection of hydrogen bonding in solution. Also, vapor pressure and vapor density techniques have been used extensively for the study of hydrogen bonding in the vapor phase.[6,7,8,9] Such studies have been extended to hetero-hydrogen bonding in several systems as shown by Christian[10] and by Lin.[11]

It was felt that by using a nonvolatile liquid as the solvent in a study of hydrogen bonding reactions of various volatile solutes, a versatile vapor pressure technique could be developed in which it would be possible to avoid the usual complications due to the solvent vapor pressure. Such a method should have the advantage over other solution methods of being fast, simple experimentally and free from difficulties of interpretations. It would be applicable not only to studies of homo-hydrogen bonding, but also to hetero-hydrogen bonding of different solutes in solution.

The work described here is a result of attempts to apply the vapor pressure technique to solutions of volatile solutes dissolved in diphenylmethane, a solvent which is nonvolatile at room temperature. A grease-free apparatus was constructed and used to study the homo-association of volatile carboxylic acids and alcohols, and the hetero-association of volatile-volatile and volatile-nonvolatile solute systems. This is, to the best of the knowledge of the author, the first time such a series of experiments has been performed.

CHAPTER II

OBJECTIVES

The primary objectives of this research were:

1. To develop a new method for the study of hydrogen bonding in solution, based on measurement of the total pressure of dilute solutions of volatile polar solutes in nonvolatile, nonpolar solvents.

2. To extend the method to the study of hetero-hydrogen bonding in solution.

3. To devise a total vapor pressure apparatus, combining the attributes of simplicity, accuracy and speed. It was anticipated that the apparatus should be grease-free and provide for the introduction of dry samples. It is well known that many organic solutions readily attack grease and are hygroscopic.

CHAPTER III

MATERIALS

All the reagents used in this research were either analytical reagents or C. P. grade reagents. Trifluoroacetic acid, acetic acid and methanol were further purified by double distillation through a 30 plate Oldershaw column at a reflux ratio in excess of 10-1. Diphenylmethane was purified by vacuum distillation. Benzoic acid and benzophenone were purified by double crystallization. After purification, all reagents, except acetic acid, were stored in desiccators containing a drying agent. Acetic acid was stored in an H-shaped tube containing anhydrous P_2O_5.

The boiling points ranges of the central fractions used in this work, corrected to 760 mm. were

Substance	Boiling Point (^{o}C)
Trifluoroacetic Acid	72.3 - 72.5
Acetic Acid	118.0 - 118.3
Methanol	64.0 - 64.3

All boiling points are within $\pm$ 0.3^{o}C of the best available literature values.

CHAPTER IV

EXPERIMENTAL

Apparatus

The apparatus constructed for this investigation shown in Figure 1 consists of a 100 ml. flat bottom flask (A) connected to a 28/15 ball joint attached to a glass cup (B). The ball joint leads to a tube plugged with a sintered glass disc (C), covered with mercury, at a distance of about 2.5 cm. from the open end. Branching from this tube at about 5 cm. below the disc is a horizontal tube leading to a closed end manometer (E). Also joined to this horizontal tube is a teflon stopcock (D) which leads to a vacuum pump through a two way stopcock and a vacuum trap. The solution is stirred by a glass-covered stirring bar (F) which is controlled by a magnetic stirrer (G) placed beneath the solution flask (A) and the thermostated water bath (H).

Procedure

Three different types of experiments were performed in this research. In the first type, vapor pressure measurements were related to the self-association of dilute solutions of volatile carboxylic acids or alcohols in nonvolatile solvents. The second type of experiment involved a study of cross-association of volatile carboxylic acids and nonvolatile carbonyl-containing compounds dissolved in nonvolatile

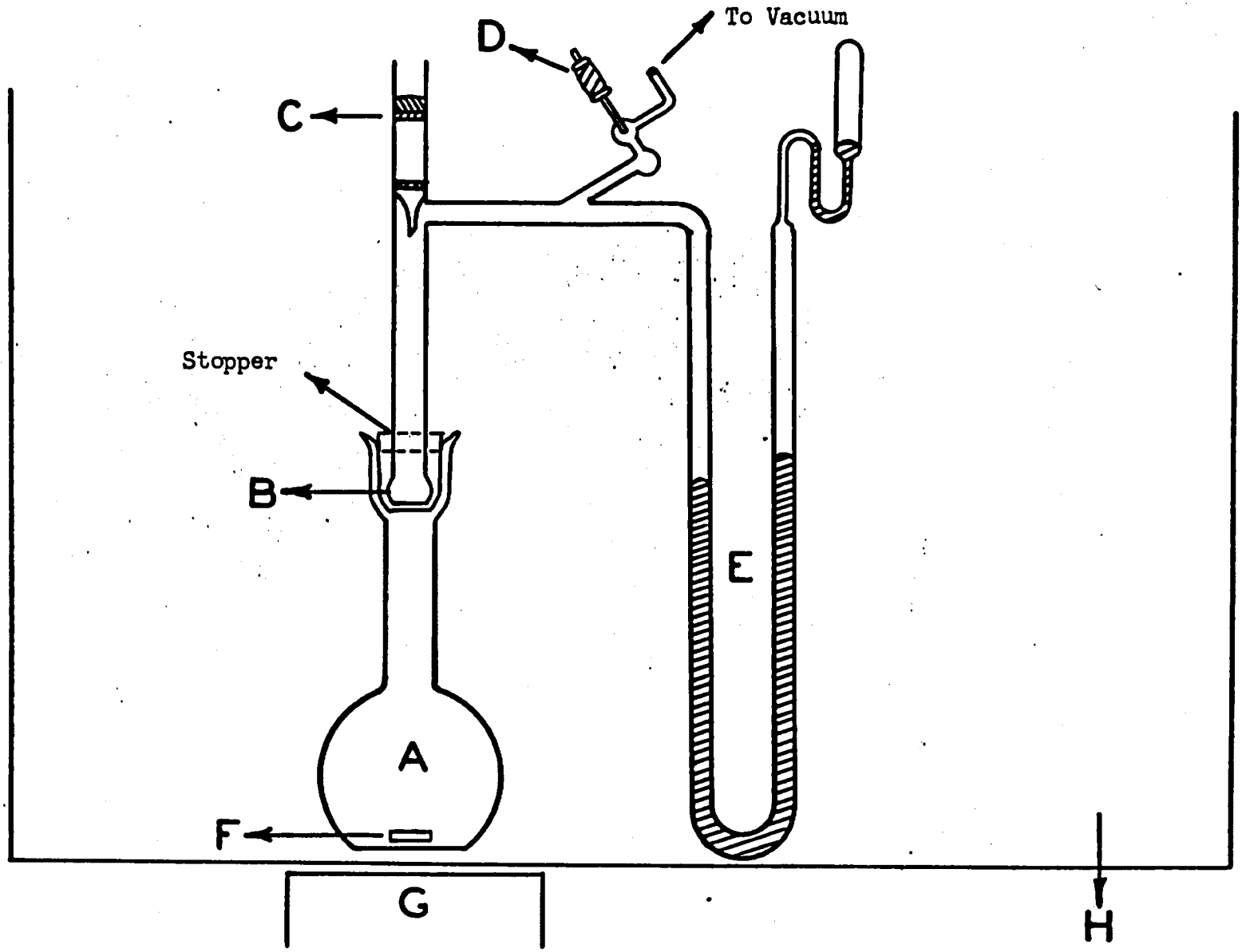


FIG. 1 -- Vapor Pressure Apparatus

solvents. In the third type, the cross-association of two volatile carboxylic acids in nonvolatile solvents was studied.

The first type of investigation was carried out in the following manner. An exactly measured amount of the nonvolatile solvent, 50 ml., was introduced into the solution flask (A). The ball joint was then connected, the cup above it was filled with mercury and the rubber stopper tightened in the glass cup. The system was evacuated through the teflon stopcock, with the magnetic stirrer running, to a pressure as close to zero as possible. The teflon stopcock made it possible to eliminate any interaction between the vapors and the grease of regular stopcocks. The system was brought to the desired temperature by adjusting the thermo-regulator. The pressure of the system was read on the manometer and recorded as the zero pressure. An increment of the sample was introduced through the mercury covering the sintered glass disc,[12] which has the function of eliminating any contact between the sample and the air. The sample was further protected from any contact with the air during its transfer from its container to the apparatus by using the "mercury sandwich" technique. This technique consists of placing some mercury at the bottom of the liquid sample container and drawing up the desired amount of the sample sandwiched between two layers of mercury in the pipette. The pipette is then discharged through the sintered glass disc as mentioned before. The increments added varied from 0.05 to 0.2 ml., depending on the system. A 0.2 ml. pipette graduated in 1/1000 ml. was used. After equilibrium had been established (usually about 10-15 minutes) the pressure was read on the manometer and recorded as the total pressure of that particular concentration of the

solute and the air dissolved in it. Another increment of the solute was then introduced and the pressure recorded as before. This was repeated until a reasonable concentration range had been covered. The entire run was repeated in each case to check reproducibility.

In the second kind of experiment, in which cross-association of a volatile acid with a nonvolatile carbonyl-containing compound was investigated, the latter compound was dissolved in the solvent before evacuating the system, then the volatile carboxylic acid was added in increments in the same manner described before. Several concentrations of the nonvolatile solute were studied; each run being repeated to ensure reproducibility as in the previous type of experiment.

The third type of study, in which the cross-association of two volatile carboxylic acids was investigated, was performed exactly as the first type, except that an increment of each acid was added each time, and the total pressure due to the combined effect of both species was recorded.

Since a fraction of the volatile solute will always be in the vapor phase, the amount of the solute added had to be corrected for this vapor concentration before calculating the formal solution concentration. To do this, theoretical values of P_A, the vapor pressure of the monomer species in the vapor phase, were assumed and theoretical curves of the total pressures vs. number of moles in the vapor phase were prepared for all the volatile solutes used. The curves were calculated using the equation $n = \frac{\pi V}{RT}$ where n is the number of moles in the vapor phase, π is the formal pressure,[11] which by analogy to the formal concentration is calculated as $\pi = P_A + 2K_2^V P_A^2$, where K_2^V is the self-

association constant in the vapor phase;[11,13] V is the volume occupied by the vapor phase, and was obtained by calibrating the apparatus using both carbon tetrachloride and benzene vapors;[12] R is the gas constant and T is the operating temperature. Also, the total pressure was calculated using the equation $P_T = P_A + K_2^v P_A^2$, where P_T is the total pressure.

Also, since all the liquids contained a certain amount of air dissolved in them, the pressure recorded after adding the sample was the sum of the pressures due to the organic solutes and that due to the air dissolved in them. The pressure due to air had to be subtracted before using the pressures in any further calculations. To make this correction, it was necessary to run two experiments, the first to determine how much air enters with the sample (for each solute) and the second to determine the pressure caused by a given quantity of air. The amount of air entering with the sample was determined by evacuating the apparatus with no solvent in it, adding increments of the pure sample and recording the corresponding pressures. This was repeated until the saturation pressure was reached, and beyond this point, four or five more increments were added. The pressure was plotted vs. the volume added, and from the difference between the experimental pressure after saturation and the horizontal line the number of mm. of air per ml. of liquid sample was calculated. This was converted by the use of the ideal gas law to a number of mls. of air, at an average atmospheric pressure of 740 mm. of mercury, per ml. of liquid sample.

The pressure caused by a given volume of air was determined in the following manner. The apparatus was evacuated with 50 ml. of the solvent in it. Several increments of air were added using the same

sandwich technique described before, and the corresponding pressures recorded. In this way, it was possible to correct for the small amount of air that dissolved in the nonvolatile solvent, by calculating the number of moles of air corresponding to the pressure recorded and subtracting it from the number of moles of air added. Thus, by using the two types of air corrections, a reduced total pressure, due to the solute only, was calculated.

The following systems were studied:

A. Self-association

1. Trifluoroacetic acid (TFA) at 30°C. and 40°C.
2. Acetic acid (HAc) at 30°C. and 40°C.
3. Methanol (MeOH) at 25°C., 30°C. and 40°C.

B. Cross-association of volatile-nonvolatile compounds

1. TFA -- benzophenone (ϕ_2CO) at 30°C. at 3 different concentrations of benzophenone.
2. TFA -- benzoic acid (BzOH) at 30°C. at 6 different concentrations of benzoic acid.

C. Cross-association of volatile-volatile compounds

1. TFA -- HAc at 30°C.

The preliminary studies made on the methanol system showed that the least squares values obtained for the association constants assuming monomer-dimer-trimer species in solution did not agree with the expected decreasing trend the constants should follow with changes in temperatures. Also, the root mean square deviations obtained assuming monomer-dimer or monomer-trimer species were nearly the same making it very difficult to prefer one type of fit to the other. Infrared spectroscopic studies

were made on solutions of methanol in diphenylmethane at concentrations in the same range as those used for the vapor pressure experiments. This was done to provide independent experimental evidence to use in deciding which combination of species is most likely to exist in this system. The absorbance of the methanol solutions was measured in 5 cm. cells at the monomer OH-stretching band in the overtone region at about 1.37 μ at 25°C.

CHAPTER V

METHODS OF CALCULATION

A--Self-Association

Data for dilute solutions of carboxylic acids and alcohols in nonvolatile, nonpolar solvents were analyzed by the method of this section. The equilibrium constant in solution for the association $nA = A_n$, where A stands for the carboxylic acid or alcohol, may be expressed in terms of the activities of the polymeric species A_n and the monomer A as

$$K_n^s = \frac{a_{A_n}}{a_A^n} \qquad .....(1)$$

In dilute solutions it is permissible to replace the respective activities by their concentrations. Pohl, Hobbs and Gross[14] have shown that in dilute solutions of carboxylic acids in nonpolar solvents the only equilibrium of importance is that which exists between monomer and dimer. For simplicity of calculations, methanol will be treated on the same basis, although it will be shown later that it exists in other polymeric forms.

The dimerization reaction can then be represented by

$$\begin{array}{ccc} & 2A & = A_2 \\ C_A, P_A & & C_{A_2}, P_{A_2} \end{array} \qquad .....(2)$$

where C_A and C_{A_2} are the molar concentrations of the monomer and dimer species in solution respectively. Also P_A and P_{A_2} are the partial vapor pressures of the monomer and the dimer respectively. The dimerization equilibrium constant in the vapor phase can be written

$$K_2^v = P_{A_2}/P_A^2 \quad ,$$

from which,

$$P_{A_2} = K_2^v P_A^2 \qquad \ldots\ldots(3)$$

The pressures recorded in any run are the vapor pressures of the solutes only, since the solvent has practically no vapor pressure. The calculated pressure, corrected for the air present, is that of all the volatile species of the acid or alcohol, and can be represented by

$$P_T = P_A + P_{A_2} + \ldots \qquad \ldots\ldots(4)$$

Substituting the value of P_{A_2} obtained from equation (3) into equation (4), we obtain

$$P_T = P_A + K_2^v P_A^2 \qquad \ldots\ldots(5)$$

The total or formal molar concentration, f_A, of the acid or alcohol A in solution may be written in terms of the molarities of the monomer and dimer species as

$$f_A = C_A + 2C_{A_2} \qquad \ldots\ldots(6)$$

The dimerization equilibrium constant in solution can be written as

$$K_2^s = C_{A_2}/C_A^2 \quad ,$$

from which

$$C_{A_2} = K_2^s C_A^2 \quad .$$

Substituting for the value of C_{A_2} into equation (6), we obtain

$$f_A = C_A + 2K_2^s C_A^2 \quad . \qquad .....(7)$$

From Henry's Law we have

$$P_A = K_A^H C_A$$

where K_A^H is Henry's Law constant in mm.l.mole^{-1}, which may be rearranged to give

$$C_A = P_A / K_A^H \quad . \qquad .....(8)$$

Substituting the value of C_A from equation (8) into equation (7), we may write

$$f_A = P_A/K_A^H + 2K_2^s \cdot P_A^2 / (K_A^H)^2$$

which may be rearranged to give

$$f_A / P_A = 1 / K_A^H + [2K_2^s / (K_A^H)^2] \cdot P_A \quad . \qquad .....(9)$$

P_A can be calculated from equation (5), by knowledge of P_T which is measured in the experiment, and by using literature values for K_2^v. For methanol, $P_T = P_A$ since only monomers exist in the vapor phase. For trifluoroacetic acid and acetic acid values for K_2^v obtained by Lin[11] and by Affsprung[13] were used. If values for f_A/P_A are plotted vs. P_A, the intercept will be equal to $1/K_A^H$ and the slope to $2K_2^s/(K_A^H)^2$. The value of K_A^H is therefore obtained from the intercept and substituted in the latter value to determine K_2^s.

Methanol is known to have the tendency to exist in polymers of greater molecular weight than the dimer, in solution. A computer program

was used to calculate possible least squares association constants for postulated systems containing monomer-dimer, monomer-trimer, or monomer-dimer-trimer species; and to calculate root mean square deviations for each system.

B--Cross-Association of Volatile-Nonvolatile Compounds

In the systems considered in this section, the nonvolatile solute has practically no vapor pressure. When both the volatile solute and the nonvolatile solute are present, equilibria of the following types may be established in solution:

$$nA + mB = A_nB_m$$

and $$2A = A_2$$

where B represents the monomer nonvolatile solute and A_nB_m represents the cross-polymer which is also assumed to be nonvolatile. The observed pressure will then be due only to the free volatile species in solution.

Trifluoroacetic acid was used as the volatile compound in the systems studied in this section. A plot was made for the values of the total pressures obtained for pure TFA in diphenylmethane in section A vs. the corresponding formal concentrations of TFA. The formal concentrations of the "free" TFA in the systems investigated in this section were obtained by matching the total pressures obtained in these systems with the corresponding formal concentrations from the plot mentioned above. The formal concentration of TFA tied up in the polymer A_nB_m can be obtained by subtracting the formal concentrations of free TFA, f_A^f, from the total formal concentration of TFA initially added to the system, f_A^t.

$$\Delta f_A = f_A^t - f_A^f \qquad \text{.....(10)}$$

C_A, the molar concentration of the monomer of TFA in solution can be obtained from f_A^f, since

$$f_A^f = C_A + 2K_2^s C_A^2 \qquad .....(11)$$

where K_2^s is the self-dimerization constant of TFA in solution, as obtained in section A.

For the system trifluoroacetic acid-benzophenone, a 1:1 dimer was postulated according to the equilibrium

$$A + B = AB \ .$$

The cross-association constant for this equilibrium can be represented by

$$K_{11}^s = \frac{C_{AB}}{C_A C_B} \qquad .....(12)$$

where C_{AB} is the molar concentration of the cross-dimer, C_A the molar concentration of the monomer of TFA in solution and C_B the molar concentration of the monomer of benzophenone in solution. C_{AB} is actually equal to Δf_A obtained in equation (10), C_A can be obtained from equation (11) and C_B can be obtained by subtracting C_{AB} from f_B, the total molar concentration of the added benzophenone, since it is all present as monomers.

Equation (12) can be rearranged to give

$$C_{AB} = K_{11}^s C_A C_B \qquad .....(13)$$

Plotting C_{AB} vs. $C_A C_B$ should give a straight line with an intercept equal to zero, and a slope equal to K_{11}^s, the cross-dimerization constant in solution.

The results obtained for this system did not entirely agree with this assumption, and it was necessary to assume the presence of an additional cross-polymer in the system; namely a 1 TFA : 1 ϕ_2CO dimer and a 2 TFA : 1 ϕ_2CO trimer, as will be shown in the Discussion. The two equilibria present in solution between TFA and benzophenone can then be represented by

$$A + B = AB$$

for which the cross-association constant K_{11}^s is given in equation (12),

and $$2A + B = A_2B \quad .$$

The cross-association constant for this equilibrium is given by

$$K_{21}^s = \frac{C_{A_2B}}{C_A^2 . C_B} \quad . \qquad \ldots\ldots(14)$$

The two constants can be calculated in the following way. We may write

$$f_B = C_B + C_{AB} + C_{A_2B}$$

and substituting for the values of C_{AB} and C_{A_2B} from equations (12) and (14) respectively, we obtain

$$f_B = C_B + K_{11}^s C_A . C_B + K_{21}^s C_A^2 . C_B$$

from which

$$C_B = f_B/(1 + K_{11}^s C_A + K_{21}^s C_A^2) \quad . \qquad \ldots\ldots(15)$$

The molar concentration of TFA taking part in the polymer formation, given by equation (10), is equal to

$$\Delta f_A = C_{AB} + 2 C_{A_2B} \quad .$$

Substituting for the values of C_{AB} and C_{A_2B} from equations (12) and

(14), we get

$$\Delta f_A = K^s_{11} C_A . C_B + 2K^s_{21} C^2_A . C_B \quad \ldots\ldots(16)$$

By inserting the value of C_B from equation (15) into equation (16), we obtain

$$\Delta f_A = K^s_{11} . C_A . f_B / (1 + K^s_{11} . C_A + K^s_{21} . C^2_A) + 2K^s_{21} . C^2_A . f_B / (1 + K^s_{11} . C_A + K^s_{21} . C^2_A) \quad \ldots\ldots(17)$$

Equation (17) may be rearranged to

$$\Delta f_A + K^s_{11} C_A (\Delta f_A - f_B) + K^s_{21} C^2_A (\Delta f_A - 2f_B) = 0$$

or

$$\Delta f_A / C_A (f_B - \Delta f_A) = K^s_{11} + K^s_{21} \left[C_A (\Delta f_A - 2f_B) / (\Delta f_A - f_B) \right] \quad \ldots\ldots(18)$$

If values of $\Delta f_A / C_A (f_B - \Delta f_A)$ are plotted vs. $C_A (\Delta f_A - 2f_B) / (\Delta f_A - f_B)$, we should obtain a straight line with an intercept equal to K^s_{11} and a slope equal to K^s_{21}.

No method of calculation will be included here for the system trifluoroacetic acid-benzoic acid, since no appropriate set of polymers could be postulated that would explain the anamolous data for that system. The results will be presented in the next chapter, and qualitatively treated in the Discussion.

C--Cross-Association of Volatile-Volatile Compounds

In the system to be treated in this section, both compounds are present in the vapor phase, as well as the cross-polymer formed by them. The two compounds used in the system investigated were acetic acid, and

trifluoroacetic acid. The equilibria assumed to occur in solution are:

$$2A = A_2 \qquad \text{for which} \quad K^s_{A_2} = C_{A_2}/C_A^2$$

$$2F = F_2 \qquad \text{for which} \quad K^s_{F_2} = C_{F_2}/C_F^2 \qquad \ldots\ldots(19)$$

$$\text{and} \quad A + F = AF \qquad \text{for which} \quad K^s_{AF} = C_{AF}/C_A C_F$$

where A represents the monomer of HAc, F the monomer of TFA, A_2 the homo-dimer of HAc, F_2 the homo-dimer of TFA and AF the hetero-dimer formed from both. The same species are assumed to be present in the vapor phase.

The corrected vapor pressure can then be represented by the following equation,

$$P_T = P_A + P_F + P_{A_2} + P_{F_2} + P_{AF} \qquad \ldots\ldots(20)$$

where P_A and P_F are the vapor pressures of the monomer of HAc and the monomer of TFA respectively, P_{A_2} and P_{F_2}, the vapor pressures of the dimer of HAc and the dimer of TFA respectively, and P_{AF} is the vapor pressure of the hetero-dimer. For the species in the vapor phase we have:

$$P_{A_2} = K^v_{A_2} P_A^2$$

$$P_{F_2} = K^v_{F_2} P_F^2 \qquad \ldots\ldots(21)$$

$$\text{and} \quad P_{AF} = K^v_{AF} P_A P_F$$

where $K^v_{A_2}$ and $K^v_{F_2}$ are the self-dimerization constants in the vapor phase of HAc and TFA respectively, and K^v_{AF} is the cross-dimerization constant in the vapor phase. We also have

$$P_A = K_A^H C_A$$

and $$P_F = K_F^H C_F \qquad \text{.....(22)}$$

where K_A^H and K_F^H are the Henry's Law constants of HAc and TFA respectively. Substituting for the values of P_{A_2}, P_{F_2} and P_{AF} from equation (21), and for the values of P_A and P_F from equation (22) into equation (20), we obtain

$$P_T = K_A^H C_A + K_F^H C_F + K_{A_2}^v (K_A^H C_A)^2 + K_{F_2}^v (K_F^H C_F)^2 + K_{AF}^v (K_A^H C_A)(K_F^H C_F) \quad \text{...(23)}$$

The formal molar concentrations of the added HAc and TFA, corrected for the amount of the acids present in the vapor phase, are given by:

$$f_A = C_A + 2C_{A_2} + C_{AF}$$

and $$f_F = C_F + 2C_{F_2} + C_{AF}$$

Substituting for the values of C_{A_2}, C_{F_2} and C_{AF} from (19), we obtain

$$f_A = C_A + 2K_{A_2}^s C_A^2 + K_{AF}^s C_A C_F$$

and $$f_F = C_F + 2K_{F_2}^s C_F^2 + K_{AF}^s C_A C_F \qquad \text{.....(24)}$$

The cross-dimerization constant, K_{AF}^s, of HAc and TFA in solution was calculated by the use of a curve fitting computer program adapted from a program used by Lin.[11]

A value for K_{AF}^s may be assumed and inserted in the expression for f_A and f_F in (24), thus allowing the calculation of trial values of C_A and C_F. The latter values are then used in equation (23) to give a calculated value for P_T. The root mean square deviation in the

total pressure is calculated from the experimental and calculated values of P_T. In equation (23), the Henry's Law constants were obtained from self-association studies done in this research, and the self- and cross-association constants in the vapor phase, $K^v_{A_2}$, $K^v_{F_2}$, and K^v_{AF}, were obtained from the work of Lin,[11] Affsprung[13] and Christian.[10]

The above procedure was repeated for several values of K^s_{AF}. A plot was made for the root mean square deviation in P_T vs. the corresponding values of assumed K^s_{AF} (Figure 22). The reported value of K^s_{AF} is the one which showed the minimum root mean square deviation.

D--Calculation for the Infrared Spectral Study of Methanol

The dimers and trimers of methanol were assumed to be largely linear, as will be explained in the Discussion; hence, the absorption due to the monomer and the H.....OH terminal groups was attributed to a single band. At infinite dilutions only monomers are assumed to exist, leading to a molar absorbance ϵ_M, that can be used to calculate an apparent monomer concentration, c_a, according to this equation

$$c_a = \frac{A}{1\,\epsilon_M} \qquad .....(1)$$

where A is the measured absorbancy, and 1 is the cell length. ϵ_M can in principle be obtained by plotting A/f_A vs. f_A, where ϵ_M will be the limiting value of A/f_A at $f_A = 0$, f_A is the formal concentration of methanol in solution.

The apparent concentration can be represented by

$$\begin{aligned} c_a &= C_M + C_{M_2} + C_{M_3} \\ &= C_M + K^s_2 C^2_M + K^s_3 C^3_M \end{aligned} \qquad .....(2)$$

where C_M, C_{M_2} and C_{M_3} are the molar concentrations of the monomer, dimer and trimer species in solution respectively. K_2^s and K_3^s are the dimerization and trimerization constants of methanol in solution respectively.

The formal molar concentration of methanol can be expressed by

$$f_A = C_M + 2K_2^s C_M^2 = 3K_3^s C_M^3 . \qquad .....(3)$$

Results of recent careful studies on the heat capacities,[15,16] P-V-T data[17] and association of ethanol in carbon tetrachloride[18] appeared to be best represented by the virial equation

$$PV = RT + BP + DP^3$$

the third virial coefficient C being very close to zero. Woolley[19] related the virial coefficients to the association constants for the formation of the different polymers from monomers as

$$B = -K_2RT; \quad C = (3K_2^2 - 2K_3)RT.....$$

Since $C \approx 0$, $K_3 \approx 3/2\ K_2^2$.

By analogy with the data for gaseous methanol, K_3^s, the trimerization constant in solution, was assumed to be equal to $3/2(K_2^s)^2$, where K_2^s is the dimerization constant in solution.

Substituting for the value of K_3^s in equations (2) and (3), and for the value of c_a from equation (1) into equation (2), one obtains

$$A/\epsilon_M = C_M + K_2^s C_M^2 + 1.5\ (K_2^s)^2\ C_M^3 \qquad .....(4)$$

$$\text{and} \quad f_A = C_M + 2K_2^s C_M^2 + 4.5\ (K_2^s)^2\ C_M^3 \qquad .....(5)$$

Multiplying equation (4) by 3.0 and subtracting equation (5) from the product, we get

$$\left[(3A/\epsilon_M) - f_A\right] = 2C_M + K_2^s C_M^2 \qquad .....(6)$$

Equation (6) is a quadratic equation which can be solved for C_M to give

$$C_M = \left[-2 + \sqrt{4 + 4K_2^s (3A/\epsilon_M - f_A)}\right] / 2K_2^s \qquad .....(7)$$

A computer program was written to calculate theoretical values of C_M based on assumed combinations of ϵ_M and K_2^s, and experimental values of f_A and A. The C_M values were then used to calculate theoretical values of A based on equation (4). Root mean square deviations in A were calculated for each combination of ϵ_M and K_2^s, and the best combination was obtained by plotting a line of minima of the root mean square deviations as a function of the ϵ_M and K_2^s values and calculating the lowest point on that line. Prior to applying the computer method, the approximate values of ϵ_M were obtained from the plot of A/f_A vs. f_A as explained earlier in this section. Also the magnitude of the assumed K_2^s values was obtained from preliminary calculations on the vapor pressure data, and a rough graphical treatment of the spectral data.

CHAPTER VI

RESULTS

The volume of the empty apparatus was found to be 196.5 ml. at zero pressure in the manometer. This volume was corrected for changes in the mercury levels in the manometer which occurred when samples were added. Figure 2 shows the change in pressure with added volumes of CCl_4, which was one of the liquids used to calibrate the apparatus.

Figure 3 relates total pressure to the volume of air (at an average atmospheric pressure of 740 mm. of mercury) added to the system containing only diphenylmethane. From this plot it was calculated that the pressure increment resulting from the addition of air was 4.8 mm. per ml. of air. It was found that, to within experimental error, all the air stays in the vapor phase; hence, this value was used for all the temperatures investigated.

Figures 4, 8, and 12 show the changes in the pressure with the volumes of the solutes added to the empty apparatus for TFA, HAc and MeOH respectively. From these graphs, the amount of air introduced with the samples was estimated. The total pressures used for calculations or for plotting the other graphs were first corrected for the pressure due to the air introduced with the samples.

In the graphs for the systems where theoretical values were computed, the solid lines represent calculated values and all the points are experimental.

Tables 5, 10, 11, and 22 include a summary of the results obtained in this research.

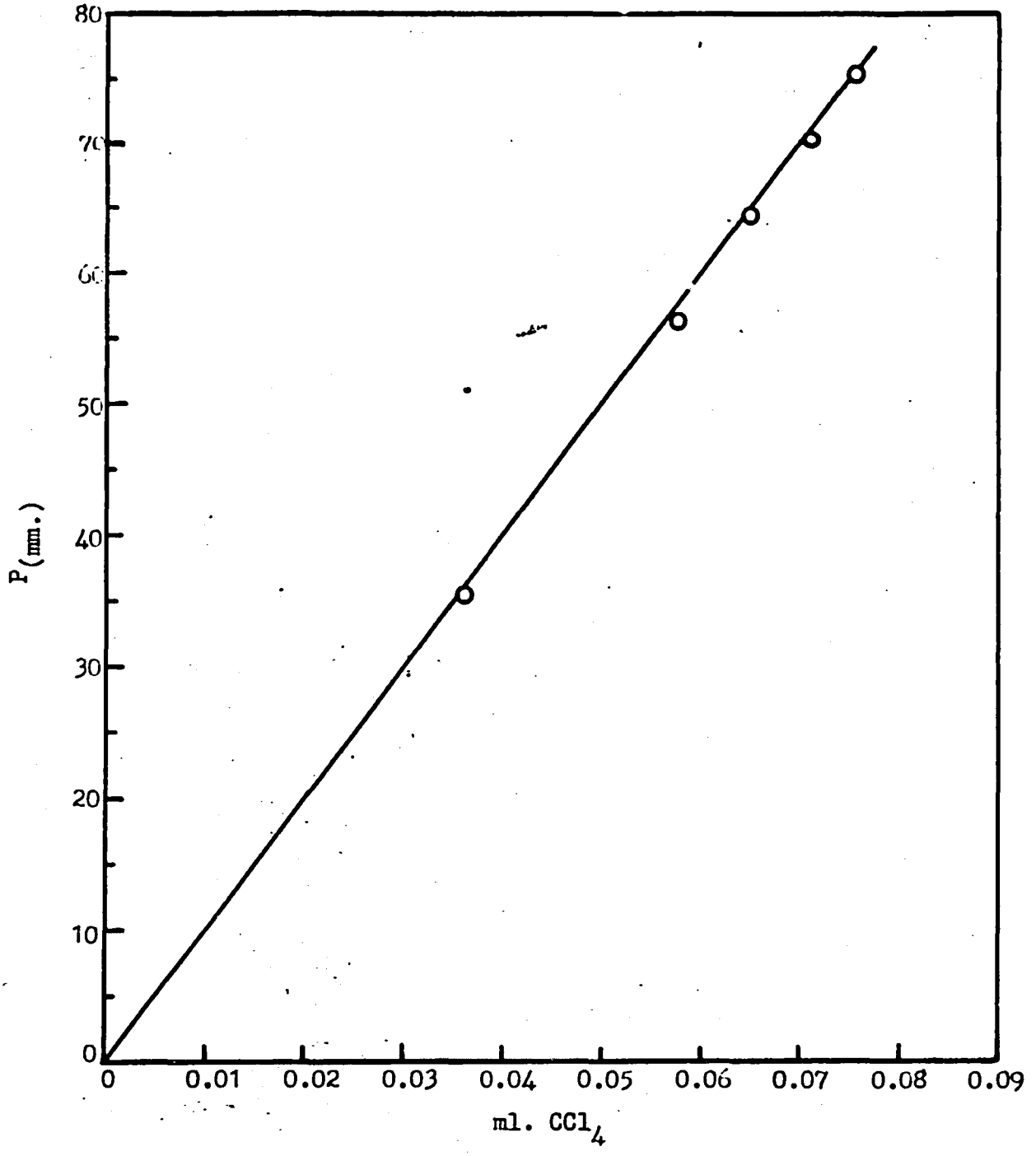


FIG. 2 — Calibration Curve. Variation of Vapor Pressure with Volume of Carbon Tetrachloride at 29.65°C.

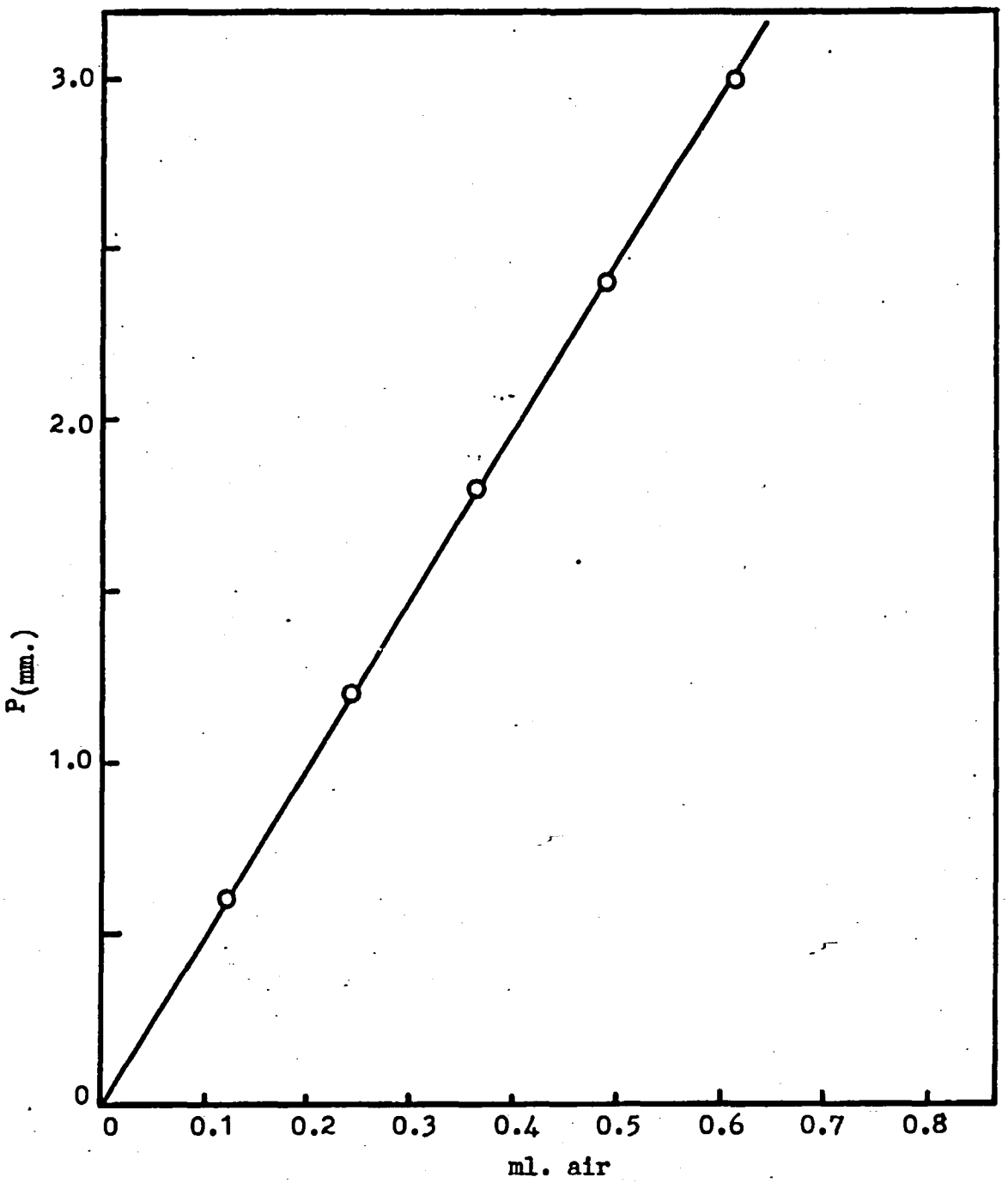


FIG. 3 -- Variation of Pressure with Volume of Air Added to Diphenylmethane at 30°C.

TABLE 1

System TFA in Diphenylmethane--Dependence of Total Pressure on Acid Concentration at 30°C.

v_{TFA} (ml.)	$n^t_{TFA} \times 10^3$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{TFA} (mm.)	$n^v_{TFA} \times 10^5$ (moles)	$n^l_{TFA} \times 10^3$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A ($mole.l^{-1}.mm.^{-1}$)
0.098	1.3197	0.0762	3.2	0.3657	2.83	3.5	1.2847	0.0256	1.946	0.01318
0.100	1.3466	0.0774	3.4	0.3732	3.027	3.6	1.3106	0.0261	2.0456	0.0128
0.203	2.7336	0.1578	8.6	0.7575	7.84	9.5	2.6386	0.0526	4.0318	0.013
0.205	2.7605	0.1594	8.6	0.765	7.835	9.5	2.6655	0.0531	4.029	0.0132
0.301	4.0533	0.234	14.0	1.123	12.88	17.0	3.8833	0.0772	5.579	0.0138
0.303	4.0802	0.2356	14.2	1.1307	13.07	17.1	3.9092	0.0777	5.6323	0.0138
0.401	5.3999	0.312	19.8	1.496	18.404	25.0	5.1499	0.1022	6.9802	0.0146
0.403	5.4269	0.3133	19.9	1.504	18.396	25.1	5.1759	0.1027	6.9785	0.0147
0.500	6.7331	0.3887	25.2	1.866	23.33	32.3	6.4101	0.1269	8.0691	0.0157
0.512	6.8947	0.398	26.4	1.91	24.49	34.0	6.5547	0.1298	8.3077	0.0156
0.600	8.0797	0.466	31.4	2.24	29.16	41.0	7.6697	0.1516	9.222	0.0164
0.611	8.2278	0.475	31.8	2.28	29.52	41.5	7.8128	0.1544	9.2892	0.0166

TABLE 1 -- Continued

v_{TFA} (ml.)	$n^{t}_{TFA}x10^{3}$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{TFA} (mm.)	$n^{v}_{TFA}x10^{5}$ (moles)	$n^{l}_{TFA}x10^{3}$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole.l^{-1}.$mm.^{-1}$)
0.700	9.4263	0.544	37.9	2.612	35.288	50.5	8.9213	0.176	10.32	0.0171
0.715	9.6283	0.556	38.4	2.668	35.732	51.2	9.1163	0.1798	10.3956	0.0173
0.800	10.7729	0.622	44.7	2.985	41.715	59.8	10.1749	0.2003	11.376	0.0176
0.817	11.0018	0.635	45.0	3.049	41.951	60.4	10.3978	0.2046	11.413	0.0179
0.900	12.1195	0.700	51.0	3.358	47.642	68.5	11.4345	0.2246	12.281	0.0183
0.917	12.3485	0.713	50.8	3.422	47.378	68.2	11.6665	0.2291	12.242	0.0187
1.001	13.4796	0.778	56.5	3.735	52.765	76.3	12.7166	0.2492	13.0203	0.0191
1.027	13.8297	0.798	57.0	3.832	53.168	77.0	13.0597	0.2559	13.0767	0.0196

TABLE 2

System TFA in Diphenylmethane--Dependence of Total Pressure on Acid Concentration at 40°C.

v_{TFA} (ml.)	$n^t_{TFA} \times 10^3$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{Air} (mm.)	P_{TFA} (mm.)	$n^v_{TFA} \times 10^5$ (moles)	$n^l_{TFA} \times 10^3$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole.l.$^{-1}$mm.$^{-1}$)
0.099	1.333	0.077	4.6	0.369	4.231	4.0	1.293	0.02581	3.16	0.00817
0.101	1.360	0.0785	4.6	0.377	4.223	4.0	1.320	0.02635	3.156	0.00835
0.200	2.693	0.155	10.9	0.746	10.154	11.7	2.576	0.05131	6.128	0.00837
0.202	2.720	0.157	11.0	0.754	10.246	11.8	2.602	0.05183	6.168	0.00840
0.297	3.999	0.231	17.4	1.108	16.292	19.35	3.8055	0.07566	8.517	0.00888
0.300	4.040	0.233	17.4	1.119	16.281	19.35	3.8465	0.07647	8.513	0.00898
0.398	5.36	0.309	24.1	1.485	22.615	27.8	5.082	0.10084	10.59	0.00952
0.400	5.386	0.311	24.8	1.493	23.307	28.9	5.097	0.10113	10.80	0.00936
0.499	6.72	0.388	31.8	1.862	29.938	37.75	6.3425	0.1256	12.69	0.00990
0.501	6.747	0.389	32.3	1.869	30.431	38.4	6.3625	0.1260	12.82	0.00983
0.600	8.08	0.466	39.8	2.239	37.561	48.25	7.5975	0.15014	14.63	0.01027
0.601	8.09	0.467	39.6	2.242	37.358	47.8	7.612	0.15043	14.58	0.01032

TABLE 2 -- Continued

v_{TFA} (ml.)	$n^t_{TFA} \times 10^3$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{TFA} (mm.)	$n^v_{TFA} \times 10^5$ (moles)	$n^l_{TFA} \times 10^3$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole.l^{-1}mm.$^{-1}$)
0.700	9.426	0.544	46.6	2.612	43.988	57.25	8.8535	0.17462	16.12	0.01080
0.700	9.426	0.544	47.6	2.612	44.988	58.7	8.839	0.17434	16.35	0.01070
0.800	10.773	0.622	55.5	2.985	52.515	69.35	10.0795	0.19841	17.95	0.01105
0.800	10.773	0.622	55.5	2.985	52.515	69.35	10.0795	0.19841	17.95	0.01105
0.900	12.120	0.700	62.8	3.358	59.442	79.3	11.327	0.22253	19.34	0.01151

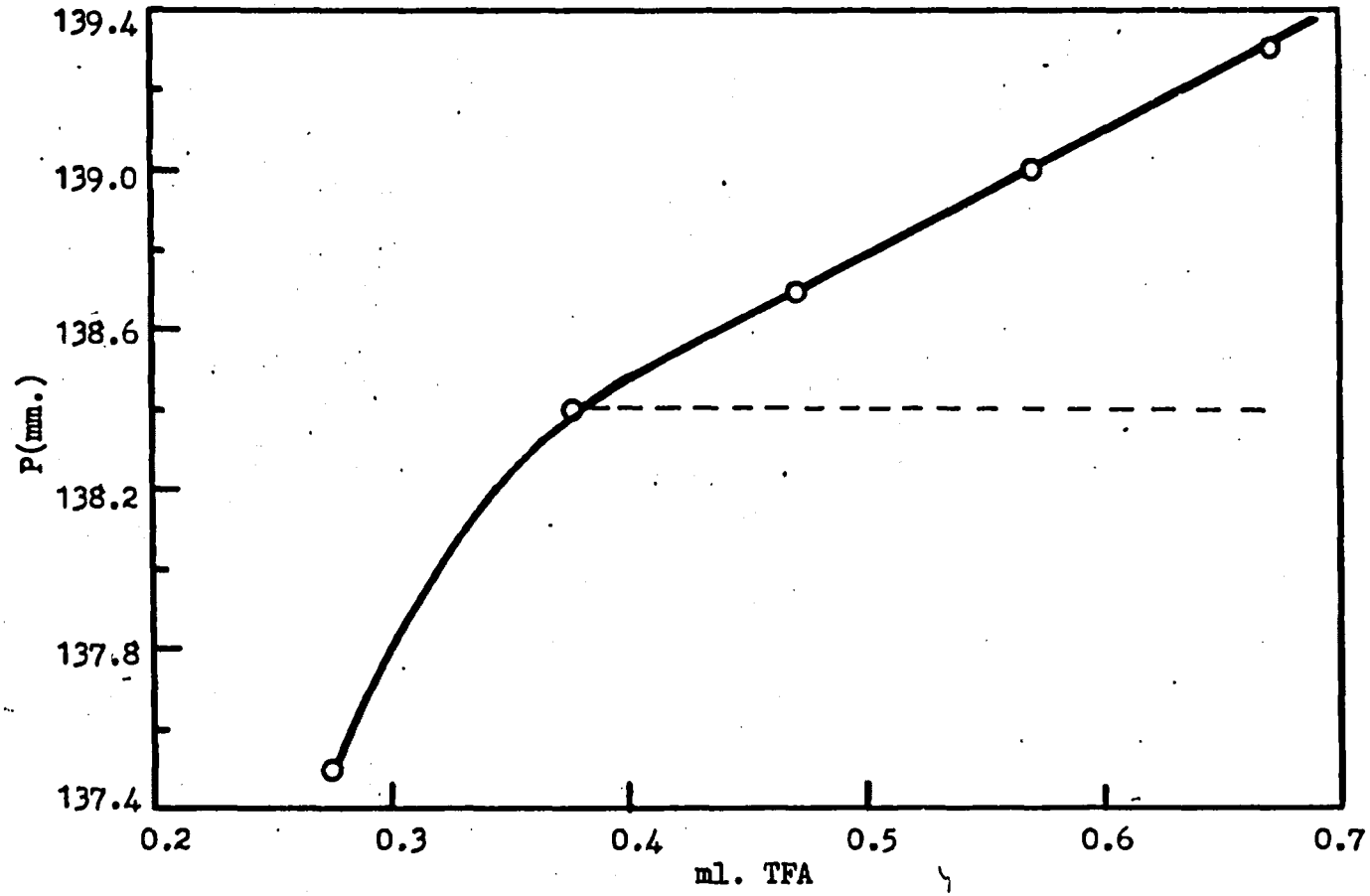


FIG. 4 -- Variation of Total Pressure with Volume of Pure Trifluoroacetic Acid at 30°C.

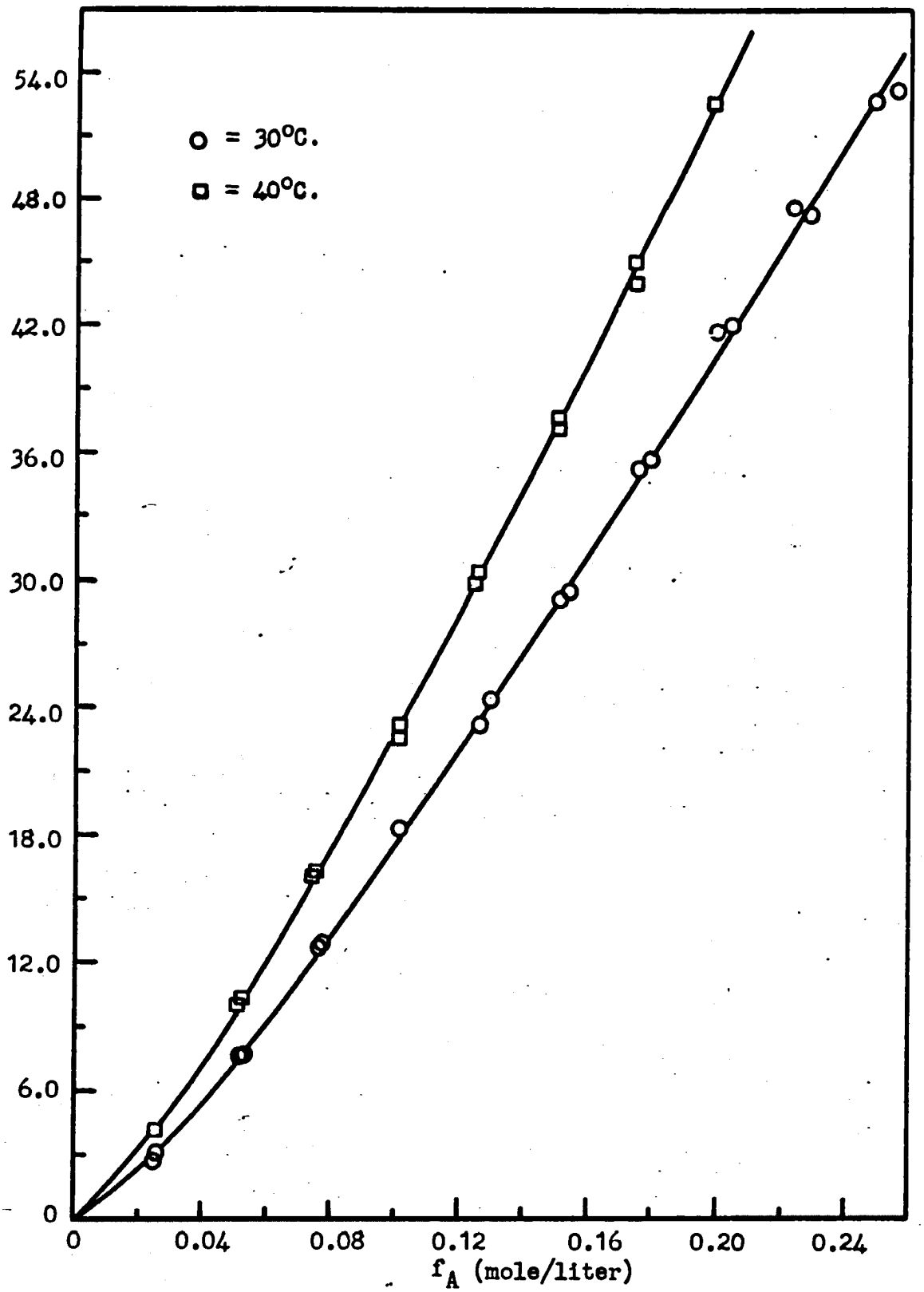


FIG. 5 -- Variation of Total Pressure with Formal Concentration of Trifluoroacetic Acid in Solution in Diphenylmethane at 30°C. and 40°C.

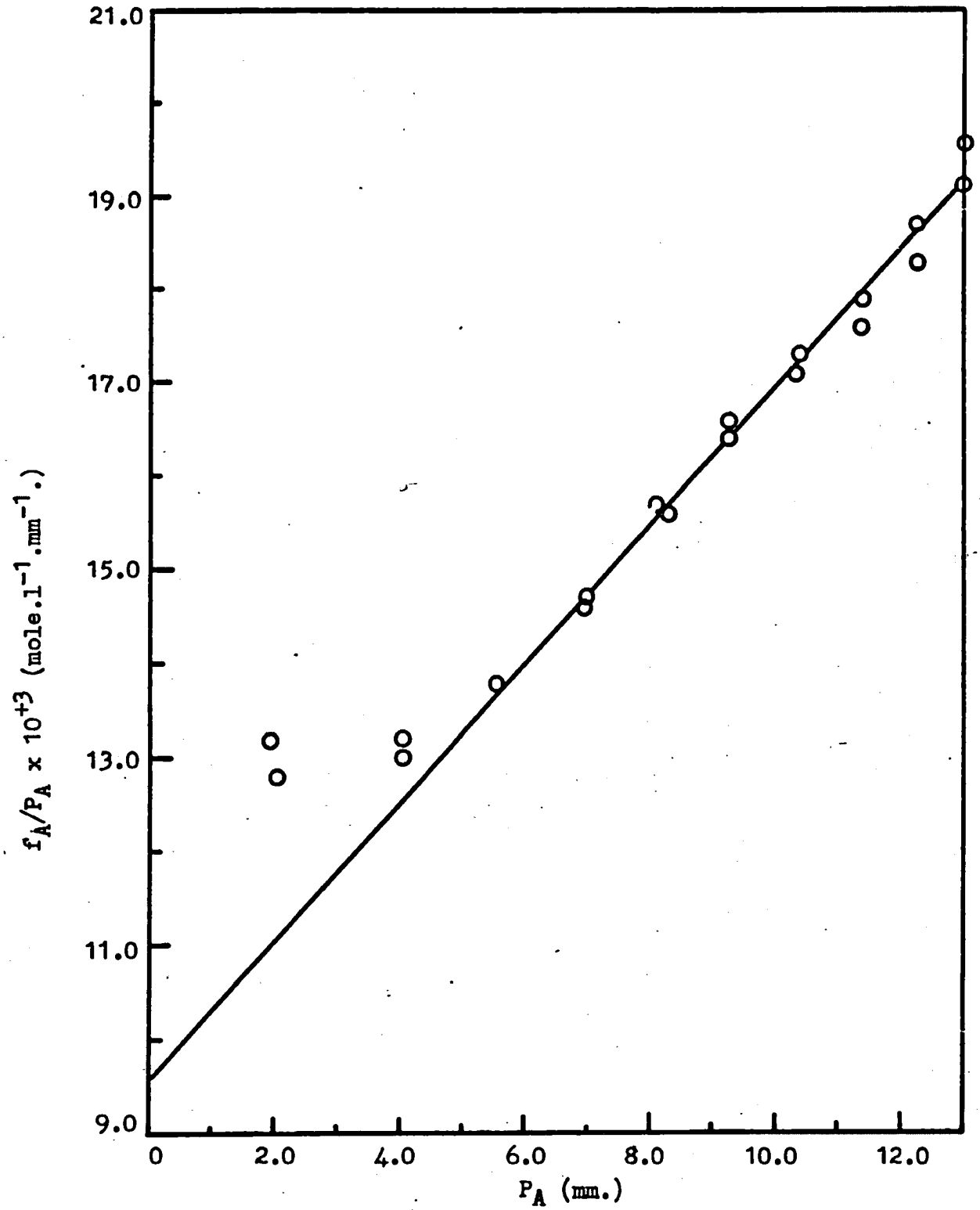


FIG. 6 — Variation of the Ratio of Formal Concentration of TFA to the Monomer Vapor Pressure with the Monomer Vapor Pressure of Trifluoroacetic Acid in Solution in Diphenylmethane at 30°C.

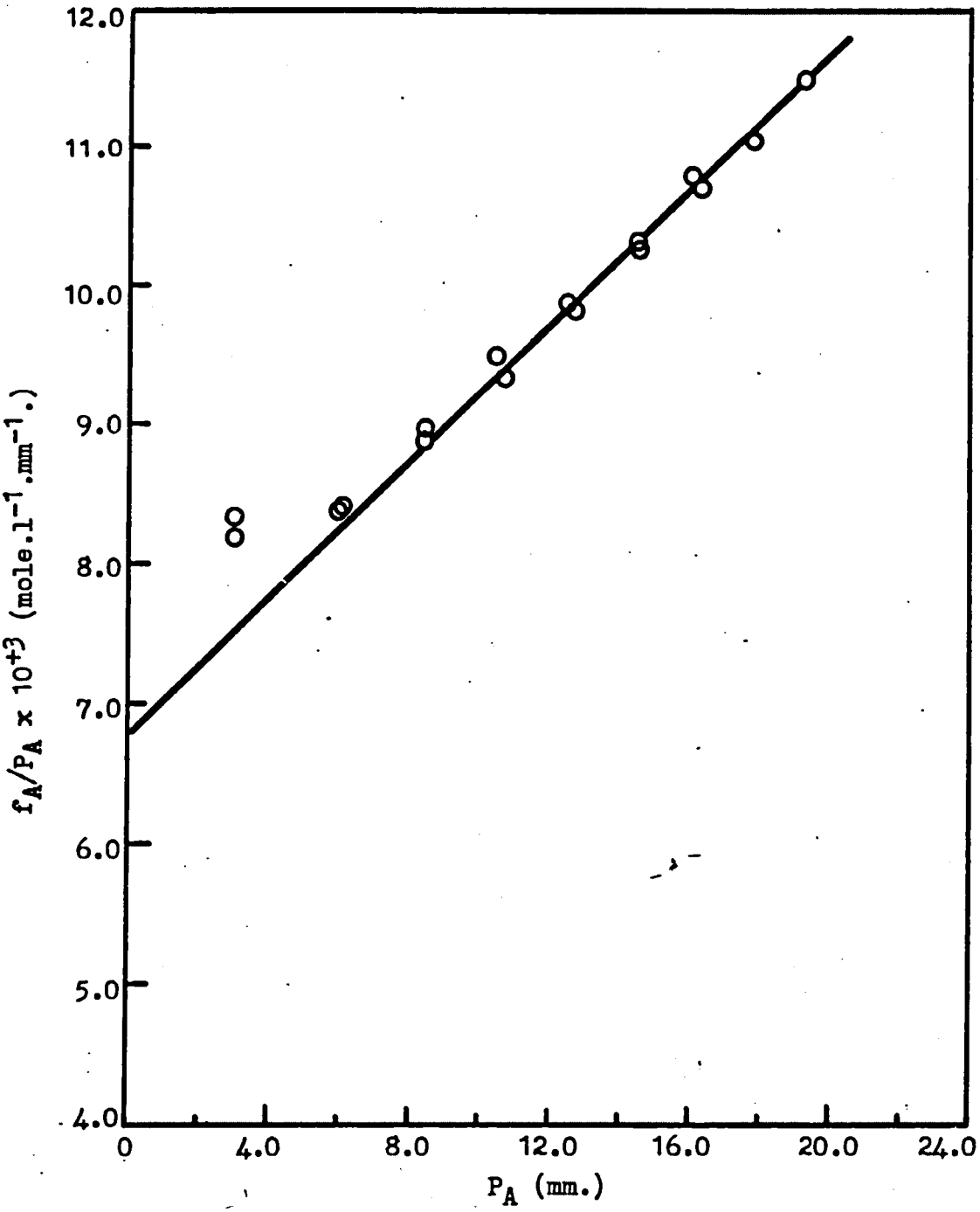


FIG. 7 — Variation of the Ratio of Formal Concentration of TFA to the Monomer Vapor Pressure with the Monomer Vapor Pressure of Trifluoroacetic Acid in Solution in Diphenylmethane at 40°C.

TABLE 3

System HAc in Diphenylmethane -- Dependence of Total Pressure on Acid Concentration at 30°C.

v_{HAc} (ml.)	$n^{t}_{HAc} \times 10^{2}$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{HAc} (mm.)	$n^{v}_{HAc} \times 10^{5}$ (moles)	$n^{l}_{HAc} \times 10^{2}$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole/l.mm.)
0.2	0.3494	0.0259	1.345	0.124	1.221	1.5	0.3479	0.0693	0.658	0.1053
0.2	0.3494	0.0259	1.4	0.124	1.276	1.55	0.34785	0.06929	0.678	0.1022
0.4	0.6988	0.0581	2.25	0.249	2.001	2.43	0.6964	0.1382	0.914	0.1511
0.402	0.7022	0.0521	2.2	0.250	1.95	2.3	0.6999	0.1389	0.893	0.1554
0.6	1.0480	0.0778	2.688	0.373	2.315	2.84	1.0452	0.2066	1.004	0.2057
0.6	1.0480	0.0778	2.8	0.373	2.427	2.98	1.0450	0.2065	1.035	0.1996
0.8	1.3980	0.1037	3.178	0.498	2.68	3.28	1.3947	0.2746	1.102	0.2492
0.8	1.3980	0.1037	3.35	0.498	2.852	3.45	1.39455	0.2745	1.146	0.2396
1.0	1.7470	0.1296	3.862	0.622	3.24	4.0	1.743	0.3418	1.240	0.2756
1.0	1.7470	0.1296	4.05	0.622	3.428	4.23	1.7428	0.3417	1.284	0.2661
1.2	2.0960	0.1555	4.5	0.746	3.754	4.62	2.0914	0.4085	1.358	0.3009
1.2	2.0960	0.1555	4.501	0.746	3.755	4.62	2.0914	0.4085	1.358	0.3008

TABLE 3 -- Continued

v_{HAc} (ml.)	$n^t_{HAc} \times 10^2$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{HAc} (mm.)	$n^v_{HAc} \times 10^5$ (moles)	$n^l_{HAc} \times 10^2$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole/l.mm.)
1.4	2.4460	0.1814	4.95	0.871	4.079	5.08	2.4409	0.4749	1.428	0.3325
1.4	2.4460	0.1814	5.164	0.871	4.293	5.38	2.4406	0.4748	1.473	0.3224
1.6	2.795	0.2074	5.699	0.995	4.704	5.88	2.7891	0.5405	1.556	0.3474
1.602	2.799	0.2076	5.75	0.9965	4.7535	5.95	2.79305	0.5413	1.566	0.34566
1.801	3.146	0.2334	6.4	1.12	5.28	6.7	3.1393	0.606	1.667	0.36352
2.0	3.494	0.2592	7.0	1.244	5.756	7.25	3.4868	0.67053	1.754	0.3822

TABLE 4

System HAc in Diphenylmethane--Dependence of Total Pressure on Acid Concentration at 40°C.

v_{HAc} (ml.)	$n^t_{HAc} x10^2$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{HAc} (mm.)	$n^v_{HAc} x10^5$ (moles)	$n^l_{HAc} x10^2$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole/l.mm.)
0.201	0.3510	0.0260	1.802	0.1248	1.6772	1.85	0.34915	0.06955	0.960	0.07246
0.2	0.3494	0.0259	1.766	0.1244	1.6416	1.8	0.3476	0.06924	1.030	0.06719
0.401	0.7004	0.0520	2.954	0.2495	2.7045	2.98	0.69742	0.1384	1.467	0.09434
0.4	0.6988	0.0518	3.101	0.2488	2.8522	3.15	0.69565	0.13803	1.520	0.09747
0.601	1.0498	0.0779	4.232	0.374	3.858	4.28	1.04552	0.2066	1.860	0.11100
0.6	1.0480	0.0778	4.259	0.373	3.886	4.33	1.04367	0.2063	1.870	0.11020
0.801	1.399	0.1038	5.197	0.4982	4.6988	5.3	1.39370	0.2743	2.120	0.12950
0.8	1.398	0.1037	5.264	0.498	4.766	5.37	1.39263	0.27414	2.137	0.12826
1.0	1.747	0.1296	6.245	0.622	5.623	6.42	1.74058	0.3413	2.380	0.14366
1.0	1.747	0.1296	6.116	0.622	5.494	6.3	1.7407	0.3413	2.341	0.14580
1.2	2.096	0.1555	6.770	0.746	6.024	6.92	2.08908	0.4080	2.480	0.16444
1.2	2.096	0.1555	7.074	0.746	6.328	7.32	2.08868	0.4079	2.600	0.15942

TABLE 4 -- Continued

v_{HAc} (ml.)	$n^{t}_{HAc} \times 10^{2}$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{HAc} (mm.)	$n^{v}_{HAc} \times 10^{5}$ (moles)	$n^{l}_{HAc} \times 10^{2}$ (moles)	f_A (mole/l.)	P_A (mm.)	f_A/P_A (mole/l.mm.)
1.401	2.447	0.1816	7.844	0.8715	6.9725	8.08	2.43892	0.4745	2.720	0.17466
1.4	2.446	0.1814	7.992	0.871	7.121	8.28	2.43772	0.47426	2.750	0.17217
1.6	2.795	0.2074	8.363	0.995	7.368	8.55	2.78645	0.5400	2.810	0.19194
1.6	2.795	0.2074	8.585	0.995	7.59	8.88	2.78612	0.5399	2.870	0.18844
1.8	3.144	0.2333	9.438	1.12	8.319	9.77	3.13423	0.6050	3.030	0.19960
1.8	3.144	0.2333	9.441	1.12	8.322	9.78	3.13422	0.6050	3.030	0.19955
2.0	3.494	0.2592	10.141	1.244	8.897	10.50	3.4835	0.6699	3.158	0.21212

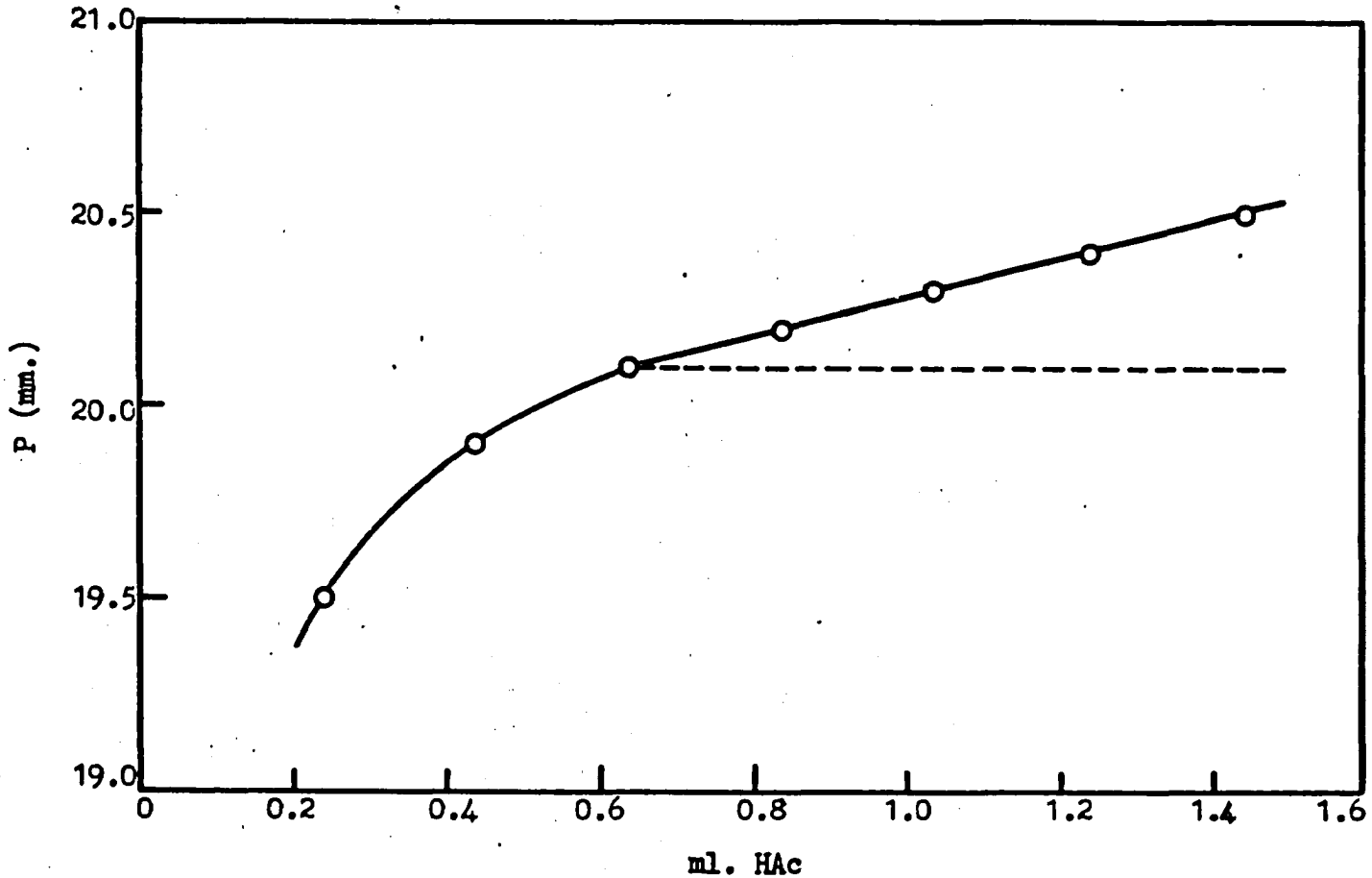


FIG. 8 -- Variation of Total Pressure with Volume of Pure Acetic Acid at 30°C.

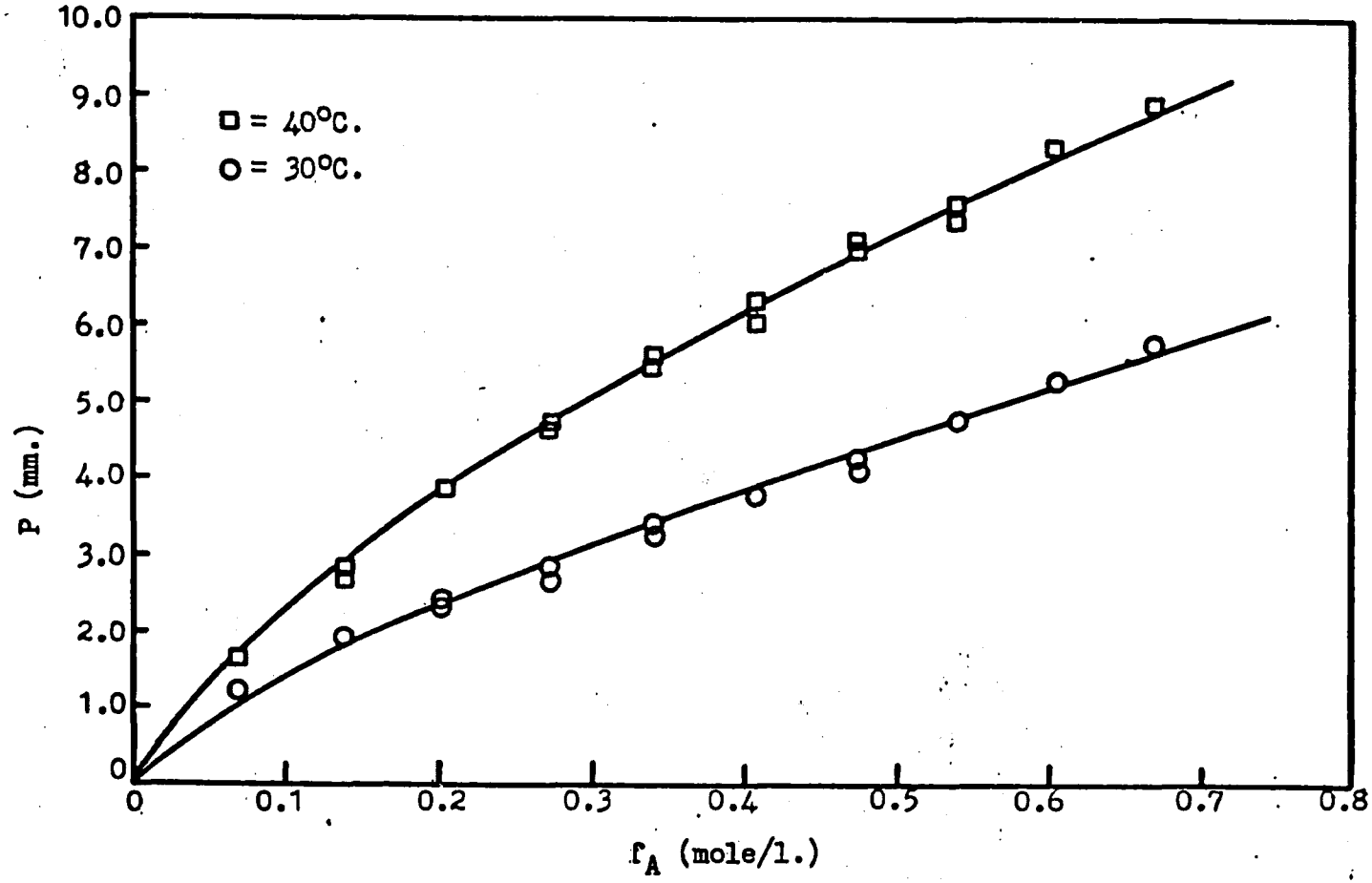


FIG. 9 -- Variation of Total Pressure with Formal Concentration of Acetic Acid in Solution in Diphenylmethane at 30°C. and 40°C.

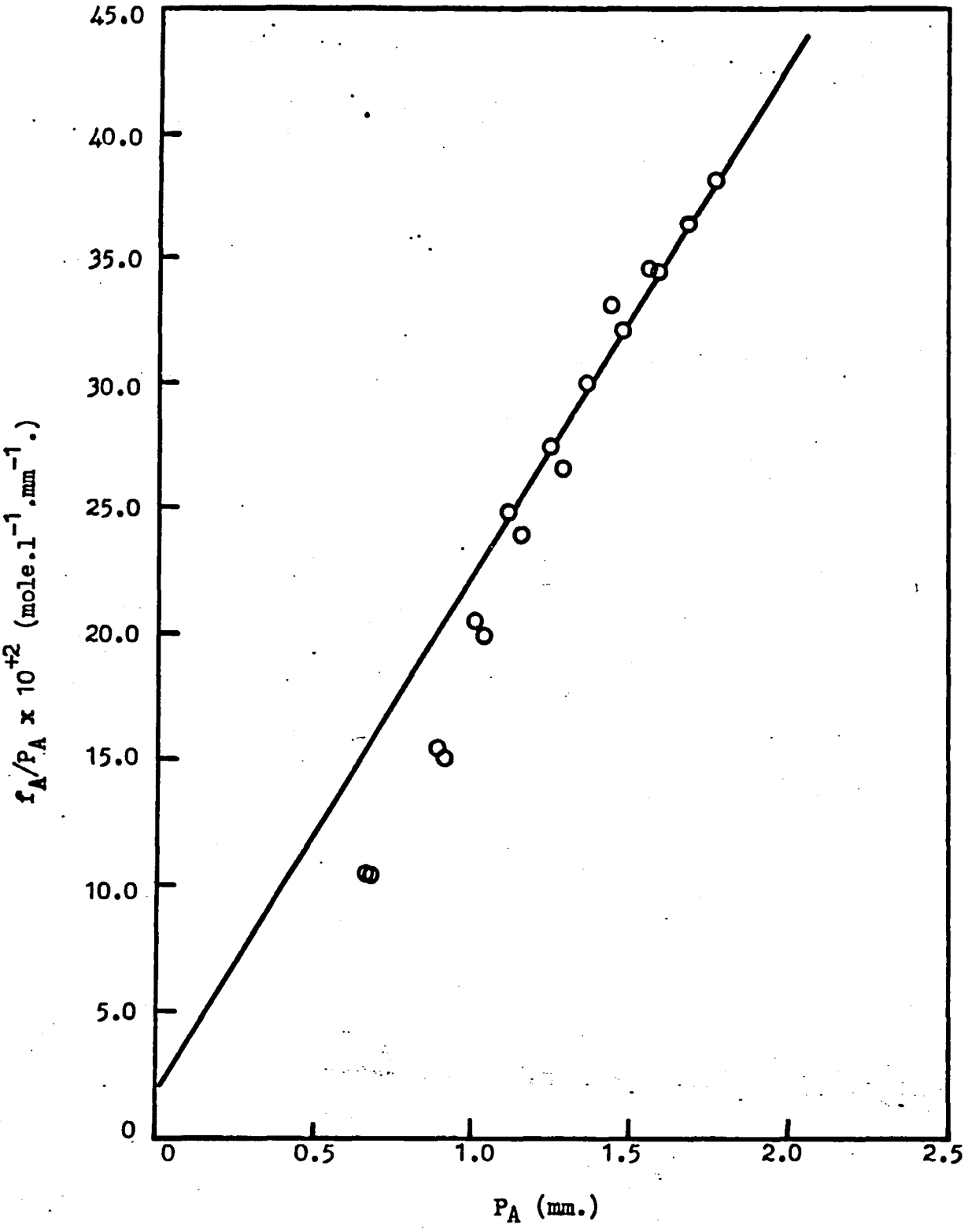


FIG. 10 -- Variation of the Ratio of Formal Concentration of HAc to the Monomer Vapor Pressure with the Monomer Vapor Pressure of Acetic Acid in Solution in Dimethane at 30°C.

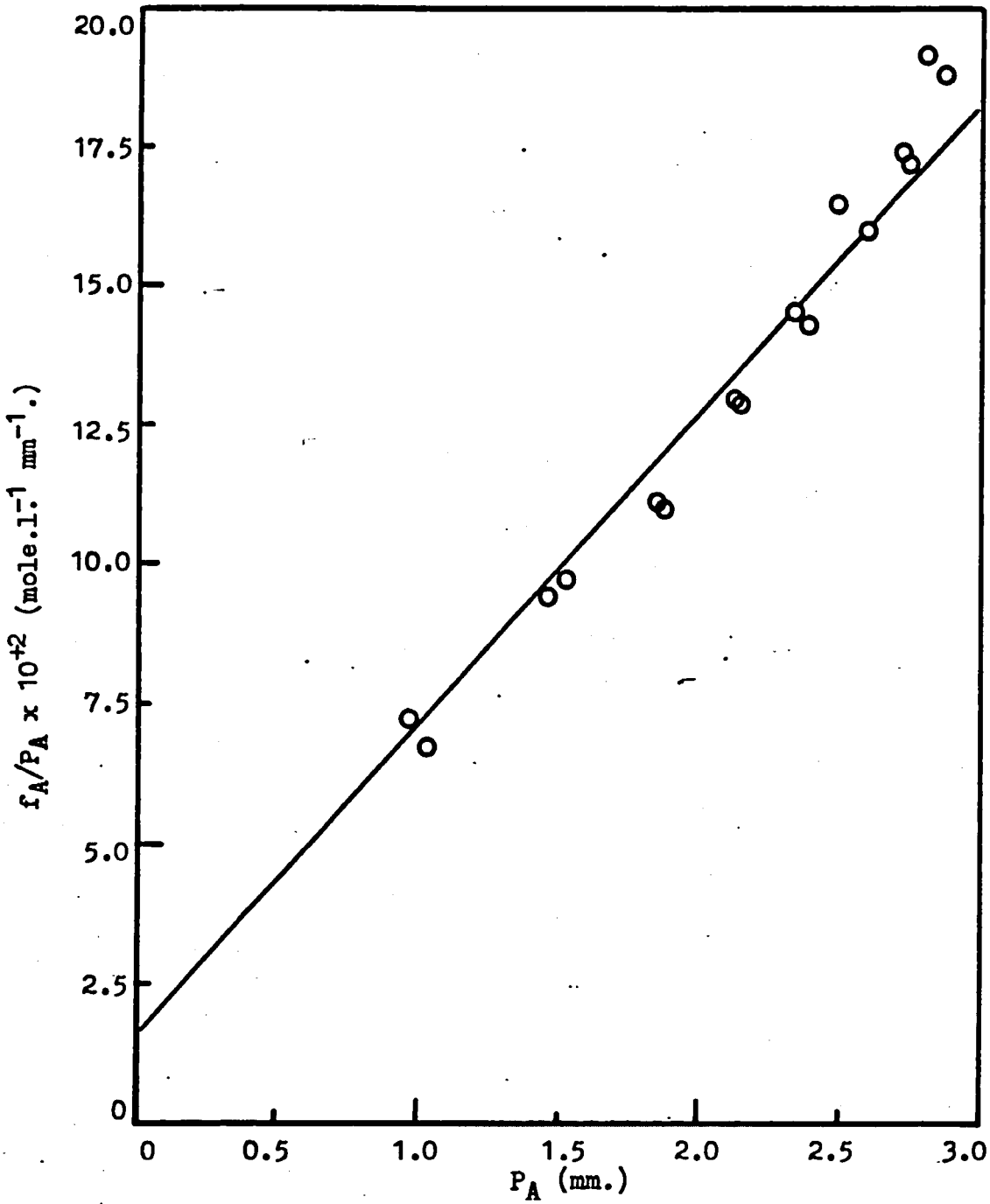


FIG. 11 -- Variation of the Ratio of Formal Concentration of HAc to the Monomer Vapor Pressure with the Monomer Vapor Pressure of Acetic Acid in Solution in Diphenylmethane at 40°C.

TABLE 5

Summary of Results for Trifluoroacetic Acid System and for Acetic Acid System At 30°C. and 40°C.

SYSTEMS	ASSUMED REACTION	EQUILIBRIUM CONSTANTS ($molar^{-1}$)	HENRY'S LAW CONSTANTS ($mm.molar^{-1}$)
Trifluoroacetic Acid at 30°C.	$2TFA = (TFA)_2$	4.02 ± 0.48	104.44 ± 5.2
Trifluoroacetic Acid at 40°C.	$2TFA = (TFA)_2$	2.64 ± 0.28	148.00 ± 6.0
Acetic Acid at 30°C.	$2HAc = (HAc)_2$	300.00	54.17
Acetic Acid at 40°C.	$2HAc = (HAc)_2$	- - -	83.00

TABLE 6

System MeOH in Diphenylmethane
Dependence of Total Pressure on Alcohol Concentration at 25°C.

v_{MeOH} (ml.)	$n^t_{MeOH} \times 10^3$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{MeOH} (mm.)	$n^v_{MeOH} \times 10^5$ (moles)	$n^l_{MeOH} \times 10^3$ (moles)	f_A (mole/l.)
0.049	1.2082	0.0686	8.9	0.329	8.571	6.764	1.14056	0.02279
0.097	2.392	0.1358	16.7	0.652	16.048	12.657	2.26543	0.04522
0.152	3.748	0.2128	24.9	1.021	23.879	18.833	3.55967	0.07098
0.204	5.030	0.2856	31.8	1.371	30.429	23.999	4.79001	0.09541
0.250	6.164	0.3500	37.7	1.680	36.020	28.407	5.87991	0.11701
0.300	7.400	0.4200	43.8	2.016	41.784	32.955	7.07045	0.14057
0.353	8.704	0.4942	49.5	2.372	47.128	37.169	8.33231	0.16548
0.408	10.060	0.5712	54.8	2.742	52.058	41.058	9.64942	0.19142

TABLE 7

System MeOH in Diphenylmethane
Dependence of Total Pressure on Alcohol Concentration at 30°C.

v_{MeOH} (ml.)	$n^t_{MeOH} \times 10^3$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{MeOH} (mm.)	$n^v_{MeOH} \times 10^5$ (moles)	$n^l_{MeOH} \times 10^3$ (moles)	f_A (mole/l.)
0.05	1.233	0.07	10.2	0.336	9.864	7.672	1.1563	0.02310
0.10	2.466	0.14	19.7	0.672	19.028	14.800	2.3180	0.04627
0.10	2.466	0.14	19.7	0.672	19.028	14.800	2.3180	0.04627
0.15	3.699	0.21	28.4	1.008	27.392	21.306	3.4859	0.06951
0.15	3.699	0.21	28.3	1.008	27.392	21.305	3.4859	0.06951
0.20	4.931	0.28	36.4	1.344	35.056	27.267	4.6586	0.09280
0.20	4.931	0.28	36.4	1.344	35.056	27.267	4.6586	0.09280
0.249	6.140	0.349	43.9	1.673	42.227	32.844	5.8116	0.11566
0.25	6.164	0.35	44.4	1.680	42.720	33.228	5.8417	0.11625
0.297	7.323	0.419	50.65	1.996	48.654	37.843	6.9446	0.13807
0.30	7.400	0.42	51.4	2.016	49.384	38.411	7.0159	0.13948
0.352	8.680	0.493	58.0	2.365	55.635	43.273	8.2473	0.16380
0.35	8.630	0.49	57.8	2.352	55.448	43.128	8.1987	0.16280
0.403	9.937	0.564	64.0	2.708	61.292	47.673	9.4603	0.18770
0.40	9.863	0.56	63.6	2.688	60.912	47.377	9.3892	0.18630

TABLE 8

System MeOH in Diphenylmethane
Dependence of Total Pressure on Alcohol Concentration at 40°C.

v_{MeOH} (ml.)	$n^{t}_{MeOH} \times 10^{3}$ (moles)	v_{air} (ml.)	P_T (mm.)	P_{air} (mm.)	P_{MeOH} (mm.)	$n^{v}_{MeOH} \times 10^{5}$ (moles)	$n^{l}_{MeOH} \times 10^{3}$ (moles)	f_A (mole/l.)
0.049	1.208	0.067	13.5	0.329	13.171	9.917	1.1090	0.02216
0.050	1.233	0.070	13.6	0.336	13.264	9.987	1.1331	0.02264
0.099	2.441	0.139	26.0	0.665	25.335	19.076	2.2502	0.04492
0.100	2.466	0.140	26.2	0.672	25.528	19.221	2.2738	0.04538
0.149	3.674	0.209	37.7	1.001	36.699	27.632	3.3977	0.06775
0.151	3.723	0.211	37.9	1.015	36.885	27.772	3.4453	0.06870
0.198	4.882	0.277	49.5	1.331	48.169	36.269	4.5193	0.09003
0.198	4.882	0.277	49.3	1.331	47.969	36.118	4.5208	0.09006
0.249	6.140	0.349	60.1	1.673	58.427	43.992	5.7001	0.11344
0.250	6.164	0.350	60.3	1.680	58.620	44.137	5.7226	0.11388
0.299	7.372	0.419	70.2	2.009	68.191	51.344	6.8586	0.13630
0.300	7.400	0.420	70.6	2.016	68.584	51.640	6.8836	0.13680

TABLE 9

System MeOH in Diphenylmethane

Dependence of Absorbance on Alcohol Concentration at 25°C.
At the Peak Wavelength of Methanol ($\sim$ 1.37 μ).

f_A (mole/l.)	A (Absorbance in 5 cm cell)
0.2850	0.850
0.2850	0.840
0.1995	0.650
0.1995	0.645
0.1425	0.495
0.1425	0.485
0.1140	0.411
0.1140	0.4025
0.0570	0.209
0.0570	0.206

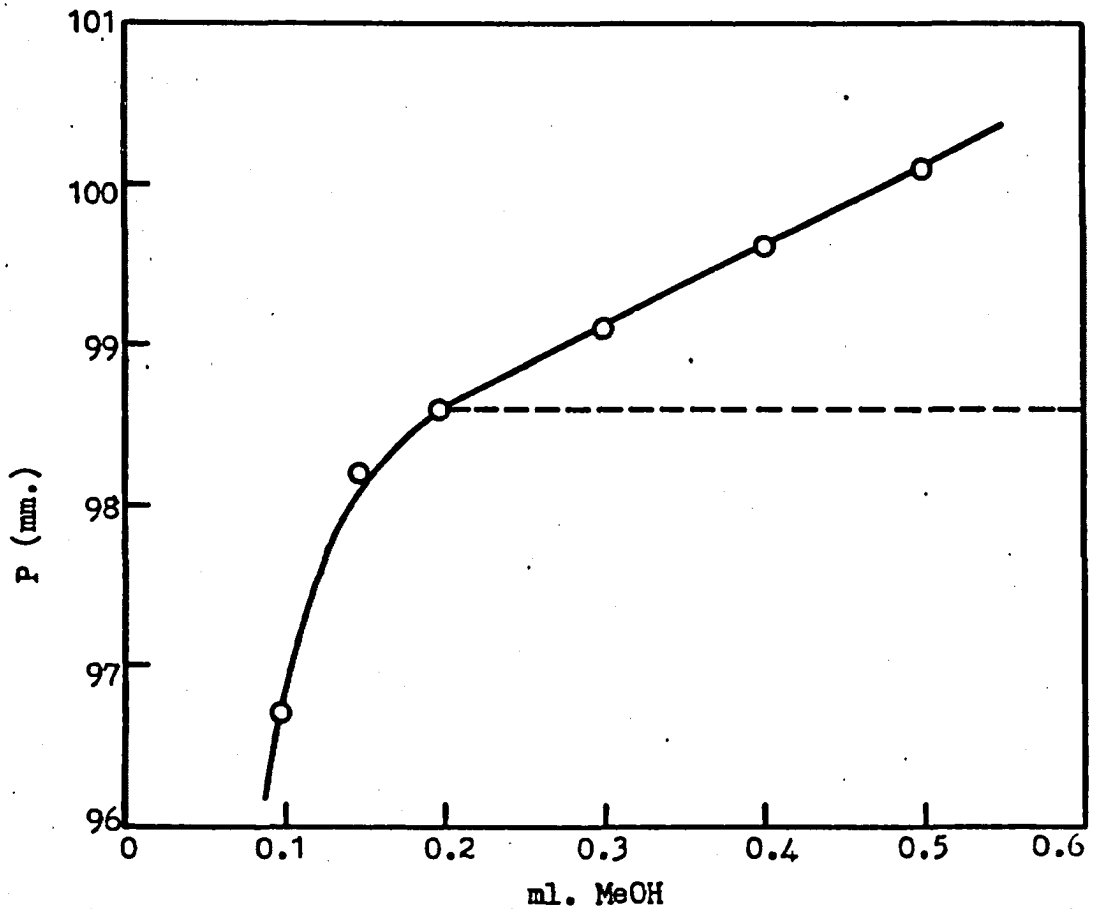


FIG. 12 — Variation of Total Pressure with Volume of Pure Methanol at 30°C.

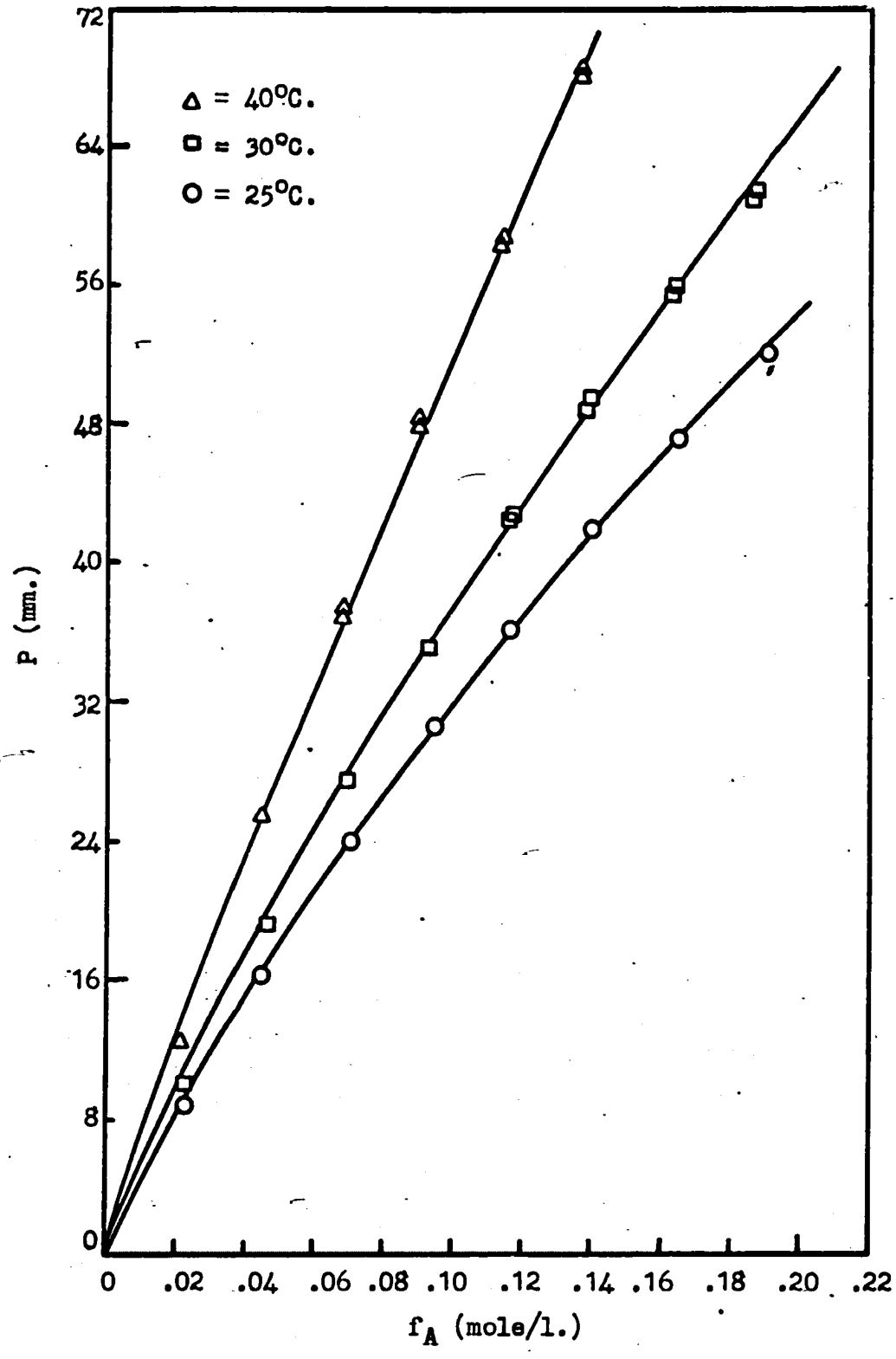


FIG. 13 — Variation of Total Pressure with Formal Concentration of Methanol in Solution in Diphenylmethane at 25°C., 30°C, and 40°C.

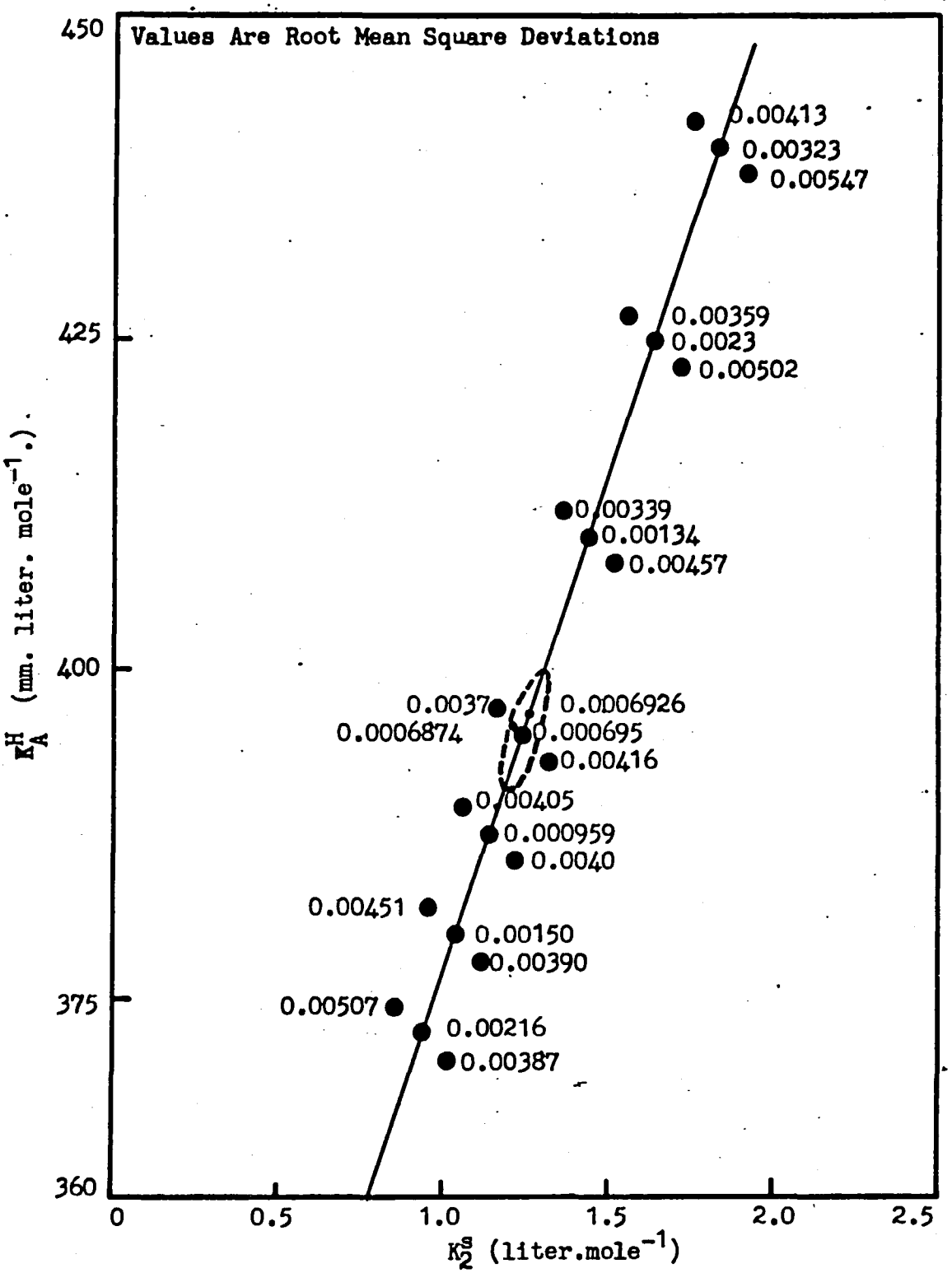


FIG. 14 -- Variation of Root Mean Square Deviation with Values of Henry's Law Constants and Dimerization Constants in Solution of Methanol in Diphenylmethane at 25°C.

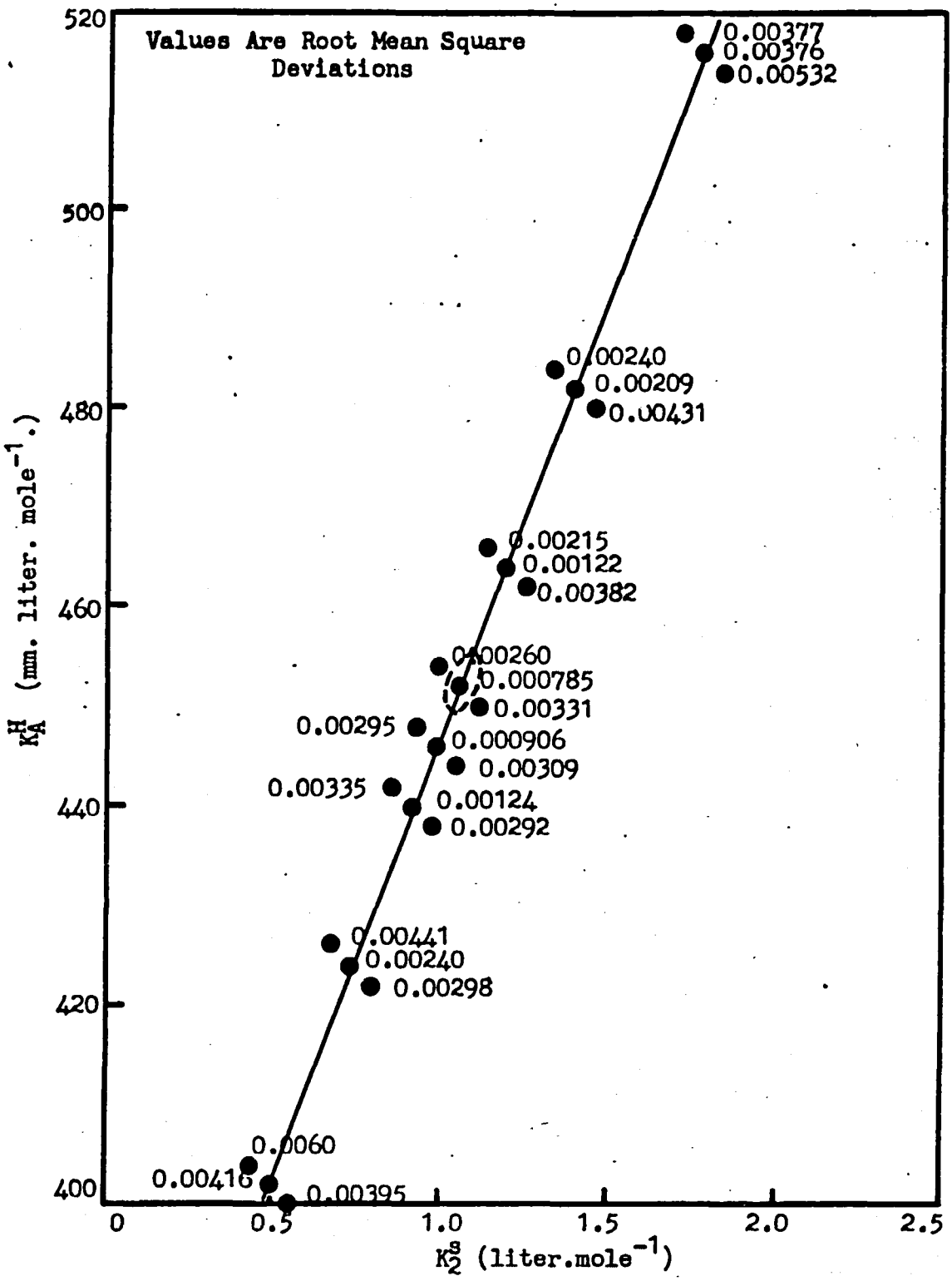


FIG. 15 -- Variation of Root Mean Square Deviation with Values of Henry's Law Constants and Dimerization Constants in Solution of Methanol in Diphenylmethane at 30°C.

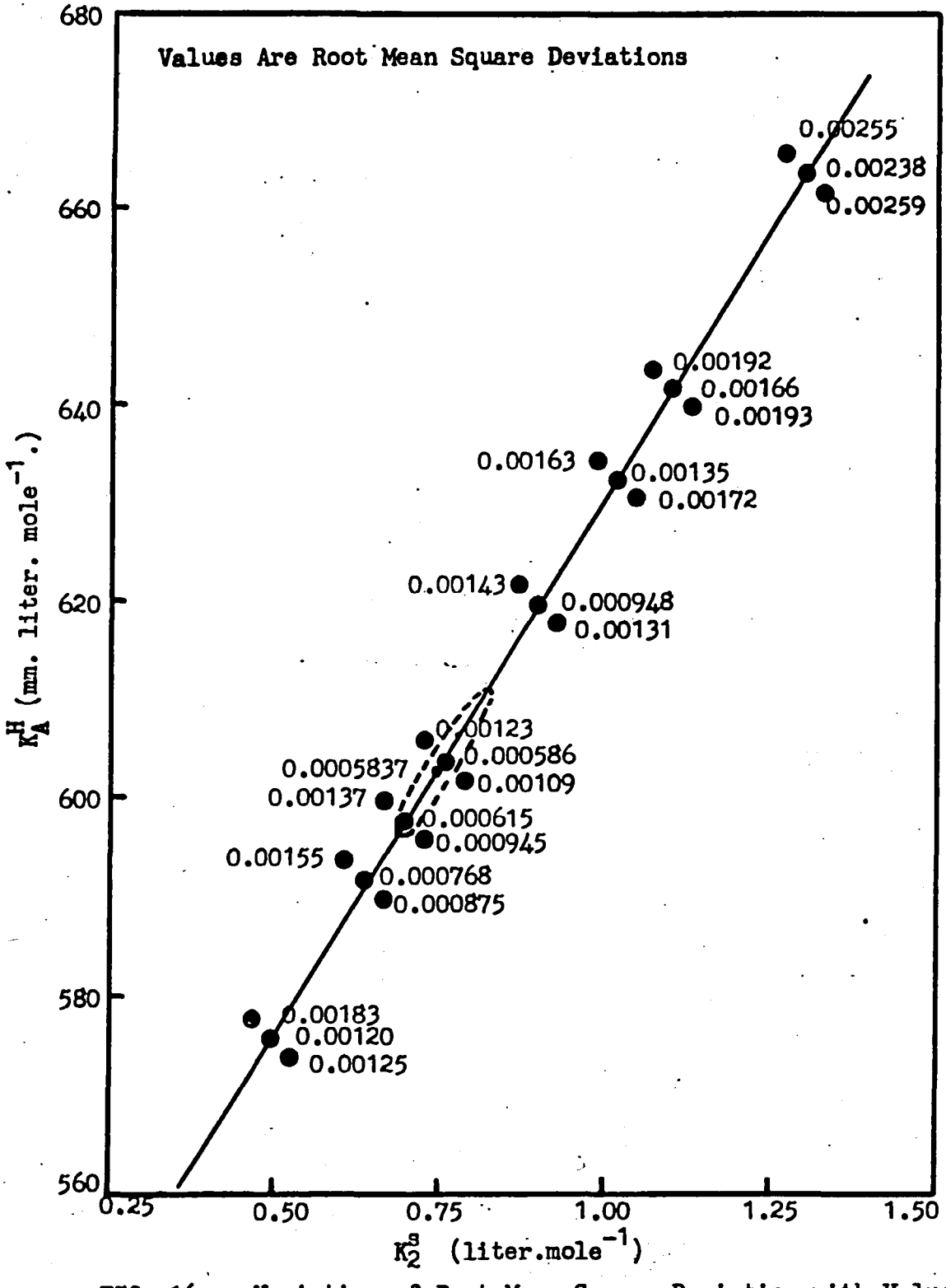


FIG. 16 — Variation of Root Mean Square Deviation with Values of Henry's Law Constants and Dimerization Constants in Solution of Methanol in Diphenylmethane at 40°C.

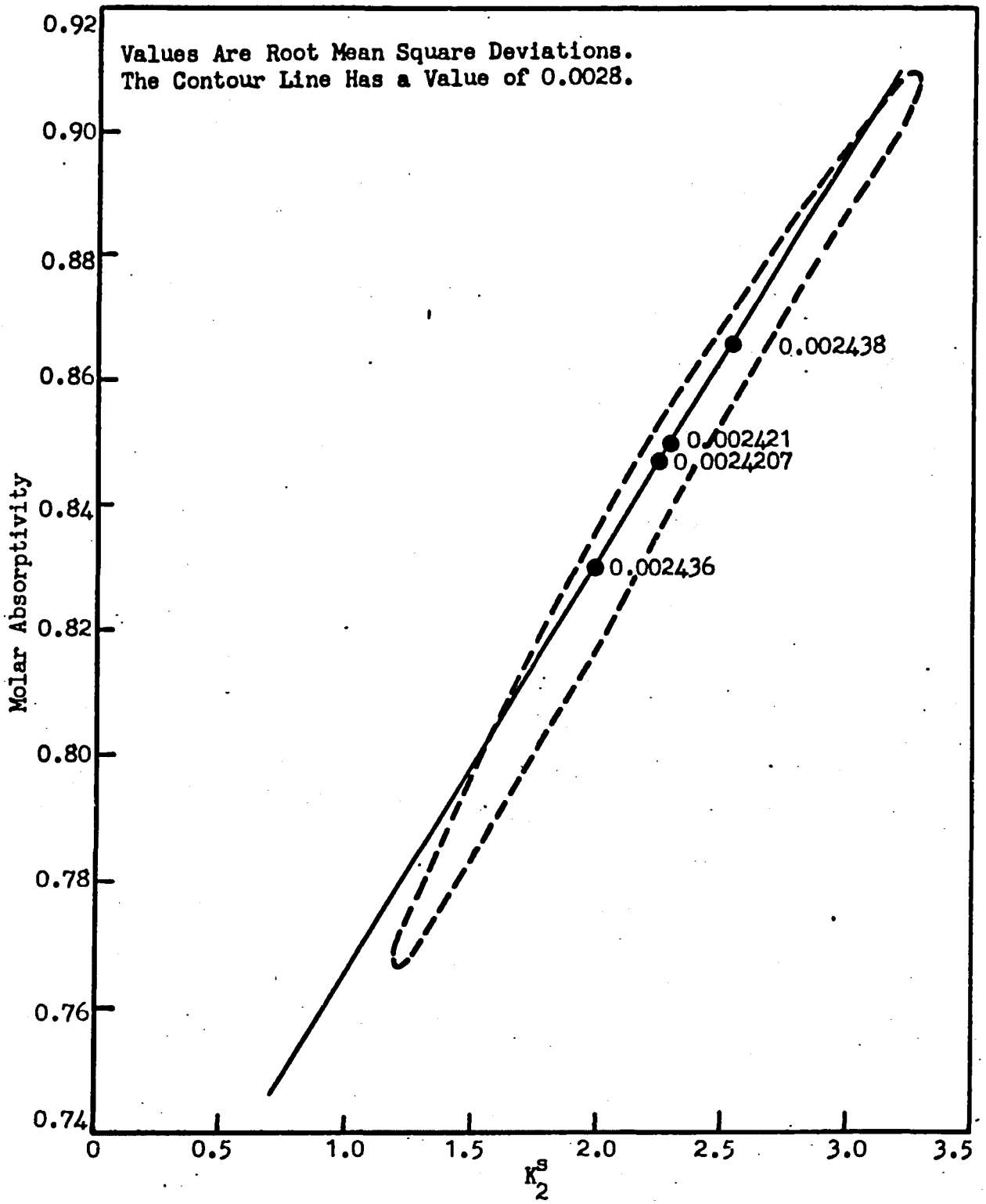


FIG. 17 -- Variation of Root Mean Square Deviation with Values of Molar Absorptivity and Dimerization Constants in Solution of Methanol in Diphenylmethane at 25°C.

TABLE 10

Summary of Results for Methanol System at 25°C., 30°C. and 40°C. Obtained from Vapor Pressure Data Assuming Different Species in Solution

SYSTEMS	ASSUMED SPECIES	EQUILIBRIUM CONSTANTS (reciprocal molar units)	HENRY'S LAW CONSTANTS ($mm.molar^{-1}$)	ROOT MEAN SQUARE DEVIATION (molar)
Methanol at 25°C.	1 - 2	$K_2^s = 2.137$	419.5	1.01×10^{-3}
	1 - 3	$K_3^s = 4.927$	357	0.964×10^{-3}
	1 - 2 - 3	$K_2^s = 0.871$	385.1	0.683×10^{-3}
		$K_3^s = 3.227$		
Methanol at 30°C.	1 - 2	$K_2^s = 1.738$	476	0.986×10^{-3}
	1 - 3	$K_3^s = 4.11$	414.5	0.63×10^{-3}
	1 - 2 - 3	$K_2^s = 0.422$	431.97	0.548×10^{-3}
		$K_3^s = 3.325$		
Methanol at 40°C.	1 - 2	$K_2^s = 0.945$	608	0.567×10^{-3}
	1 - 3	$K_3^s = 3.125$	568	0.704×10^{-3}
	1 - 2 - 3	$K_2^s = 0.729$	599	0.587×10^{-3}
		$K_3^s = 0.764$		

TABLE 11

Summary of Results for Methanol System at 25°C., 30°C. and 40°C. Obtained from Vapor Pressure Data and Spectral Data Assuming $K_3^s = 3/2\ (K_2^s)^2$. (Assumed Species for All Systems = 1 - 2 - 3).

SYSTEMS	EQUILIBRIUM CONSTANTS (reciprocal molar units)	HENRY'S LAW CONSTANTS ($mm.molar^{-1}$)	MOLAR ABSORPTIVITY ($l.mole^{-1}.cm^{-1}$)	ROOT MEAN SQUARE DEVIATION
Methanol at 25°C. (V.P. data)	K_2^s = 1.18-1.31 (1.235)* K_3^s = 2.082-2.562 (2.288)*	391-400 (395.2)*	-	0.687×10^{-3} molar
Methanol at 25°C. (spectral data)	K_2^s = 1.20-3.25 (2.250)* K_3^s = 2.16-15.84 (7.594)*	-	0.766-0.910 (0.8475)*	2.42×10^{-3} (absorbance units)
Methanol at 30°C. (V.P. data)	$K_2^s = 1.05 \pm 0.03$ $K_3^s = 1.654 \pm 0.099$	452.15 ± 3.0	-	0.785×10^{-3} molar
Methanol at 40°C. (V.P. data)	$K_2^s = 0.75 \pm 0.07$ $K_3^s = 0.844 \pm 0.157$	596-610.7 (602.7)*	-	0.584×10^{-3} molar

*Most Probable Values

TABLE 12

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.005 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	$\bar{P}_{TFA}$ (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.1	2.80	2.50	0.0263	0.0235	0.0028
0.1	2.80	2.50	0.0263	0.0235	0.0028
0.2	5.15	4.40	0.0526	0.0337	0.0189
0.2	5.15	4.40	0.0526	0.0337	0.0189
0.3	8.40	7.28	0.0785	0.0498	0.0287
0.3	9.10	8.00	0.0785	0.0535	0.0250
0.4	12.60	11.11	0.1040	0.0673	0.0367
0.4	12.60	11.11	0.1040	0.0673	0.0367
0.5	16.70	14.83	0.1297	0.0880	0.0417
0.5	16.45	14.60	0.1297	0.0868	0.0429
0.6	20.10	17.86	0.1552	0.1023	0.0529
0.6	19.85	18.40	0.1552	0.1048	0.0504

TABLE 12 - Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.7	24.60	22.00	0.1804	0.1213	0.0591
0.7	24.60	22.00	0.1804	0.1213	0.0591
0.8	28.40	25.40	0.2057	0.1366	0.0691
0.8	28.40	25.40	0.2057	0.1366	0.0691

TABLE 13

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.01 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.11	2.9	2.49	0.0289	0.0235	0.0054
0.10	2.6	2.23	0.0290	0.0215	0.0075
0.20	5.2	4.45	0.0525	0.0355	0.0170
0.20	5.0	4.25	0.0540	0.0340	0.0200
0.30	7.5	6.38	0.0787	0.0455	0.0332
0.38	10.3	8.88	0.0993	0.0575	0.0418
0.38	10.3	8.88	0.0993	0.0575	0.0418
0.50	13.3	11.43	0.1305	0.0677	0.0628
0.50	13.3	11.43	0.1305	0.0677	0.0628
0.60	16.1	13.86	0.1562	0.0814	0.0748
0.59	16.4	14.24	0.1556	0.0848	0.0708

TABLE 13 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.70	19.9	17.29	0.1816	0.0980	0.0836
0.70	19.9	17.29	0.1816	0.0980	0.0836
0.80	23.6	20.62	0.2069	0.1150	0.0919
0.81	23.4	20.45	0.2082	0.1142	0.0940

TABLE 14

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.0492 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.1	0.8	0.427	0.0267	0.0063	0.0204
0.1	0.8	0.427	0.0267	0.0063	0.0204
0.2	1.8	1.054	0.0533	0.0151	0.0382
0.2	1.9	1.154	0.0533	0.0160	0.0373
0.3	3.2	2.081	0.0798	0.0207	0.0591
0.3	3.1	1.981	0.0798	0.0200	0.0598
0.4	4.9	3.408	0.1060	0.0293	0.0767
0.4	4.7	3.208	0.1060	0.0280	0.0780
0.5	6.9	5.034	0.1320	0.0385	0.0935
0.5	6.8	4.934	0.1321	0.0380	0.0941
0.6	9.5	7.261	0.1579	0.0498	0.1081
0.6	9.6	7.361	0.1579	0.0502	0.1077

TABLE 14 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.7	12.4	9.788	0.1835	0.0617	0.1218
0.7	12.4	9.788	0.1835	0.0617	0.1218
0.8	14.9	11.915	0.2091	0.0708	0.1383
0.8	14.9	11.915	0.2091	0.0708	0.1383

TABLE 15

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.0983 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.1	0.7	0.327	0.0268	0.0050	0.0218
0.1	0.8	0.427	0.0267	0.0063	0.0204
0.2	1.5	0.754	0.0534	0.0098	0.0436
0.2	1.6	0.854	0.0534	0.0108	0.0426
0.3	2.6	1.481	0.0799	0.0161	0.0638
0.3	2.6	1.481	0.0799	0.0161	0.0638
0.4	4.0	2.508	0.1062	0.0235	0.0827
0.4	4.0	2.508	0.1062	0.0235	0.0827
0.5	5.6	3.734	0.1324	0.0313	0.1011
0.5	5.6	3.734	0.1324	0.0313	0.1011
0.6	7.4	5.161	0.1586	0.0392	0.1194
0.6	7.5	5.261	0.1585	0.0398	0.1187

TABLE 15 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.7	9.5	6.888	0.1842	0.0479	0.1363
0.7	9.5	6.888	0.1842	0.0479	0.1363
0.8	11.3	8.315	0.2100	0.0548	0.1552
0.8	11.3	8.315	0.2100	0.0548	0.1552

TABLE 16

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.1967 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.1	0.8	0.427	0.0267	0.0063	0.0204
0.1	0.8	0.427	0.0267	0.0063	0.0204
0.2	1.6	0.854	0.0534	0.0108	0.0426
0.2	1.6	0.854	0.0534	0.0108	0.0426
0.3	2.7	1.581	0.0799	0.0170	0.0629
0.3	2.7	1.581	0.0799	0.0170	0.0629
0.4	3.5	2.108	0.1063	0.0208	0.0855
0.4	3.4	2.008	0.1063	0.0202	0.0861
0.5	4.9	3.034	0.1326	0.0270	0.1056
0.5	5.0	3.134	0.1326	0.0277	0.1049
0.6	6.5	4.261	0.1586	0.0344	0.1242
0.6	6.5	4.261	0.1586	0.0344	0.1242

TABLE 16 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.7	8.0	5.388	0.1845	0.0405	0.1440
0.7	8.0	5.388	0.1845	0.0405	0.1440
0.8	9.9	6.915	0.2103	0.0480	0.1623
0.8	10.0	7.015	0.2103	0.0485	0.1618

TABLE 17

System TFA - BzOH in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.3933 mole/l. BzOH at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.1	0.80	0.427	0.0267	0.0063	0.0204
0.102	0.70	0.320	0.0273	0.0050	0.0223
0.2	1.30	0.554	0.0535	0.0080	0.0455
0.2	1.20	0.454	0.0535	0.0068	0.0467
0.3	2.00	0.881	0.0801	0.0110	0.0691
0.3	2.00	0.881	0.0801	0.0110	0.0691
0.4	2.80	1.307	0.1065	0.0148	0.0917
0.401	2.80	1.304	0.1068	0.0147	0.0921
0.5	3.80	1.934	0.1328	0.0194	0.1134
0.5	3.70	1.834	0.1328	0.0189	0.1139
0.6	5.05	2.811	0.1590	0.0254	0.1336
0.6	4.90	2.661	0.1590	0.0246	0.1344

TABLE 17 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected for air) (mm.)	f^t_{TFA} (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)
0.7	6.10	3.488	0.1850	0.0298	0.1552
0.7	6.00	3.388	0.1850	0.0292	0.1558
0.8	7.35	4.365	0.2110	0.0350	0.1760
0.8	7.20	4.215	0.2110	0.0342	0.1768

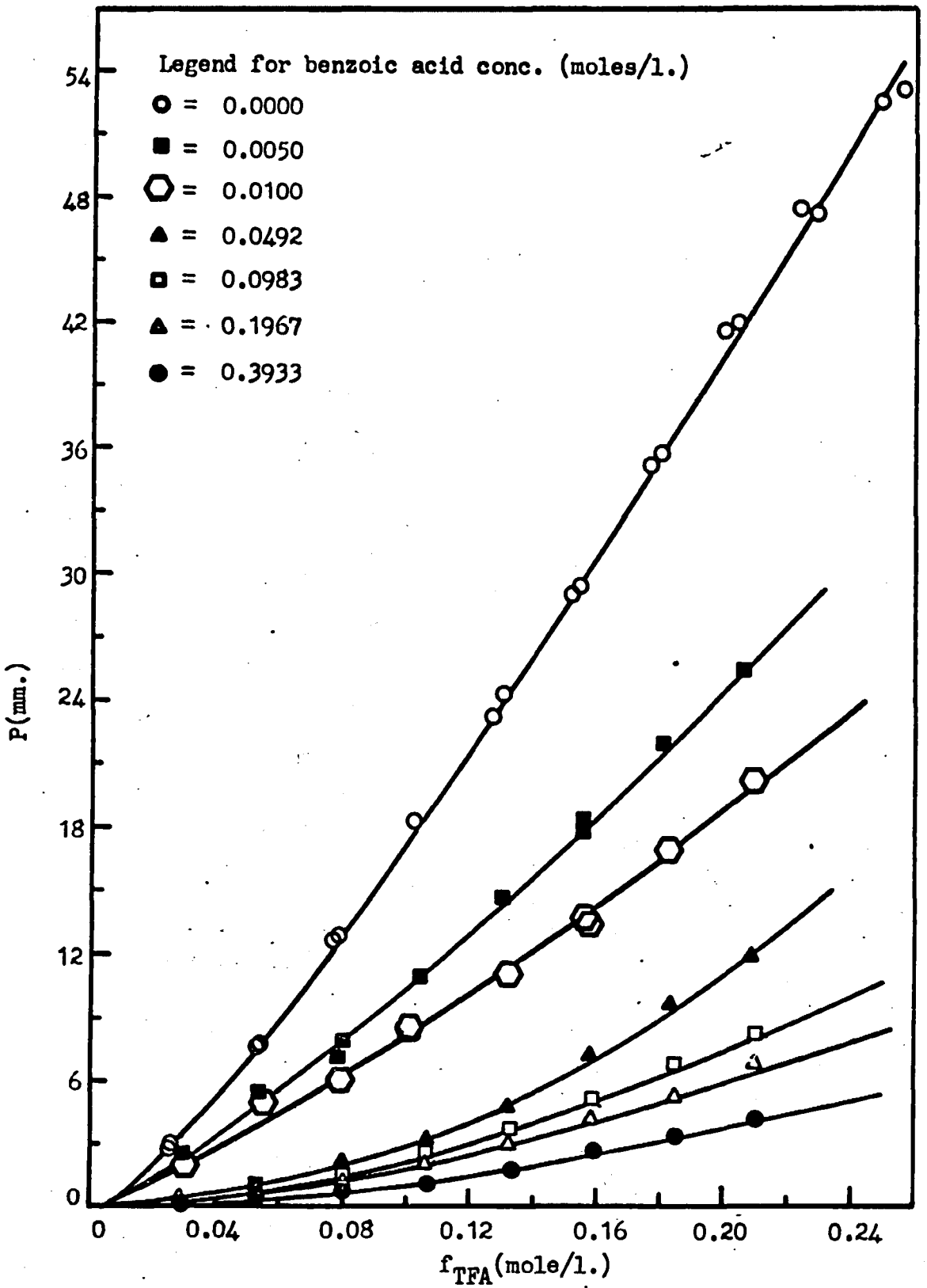


FIG. 18 — Variation of Total Pressure with Formal Concentration of Trifluoroacetic Acid at Different Concentrations of Benzoic Acid in Solution in Diphenylmethane at 30°C.

TABLE 18

System TFA - ϕ_2CO in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.02 mole/l. ϕ_2CO at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.100	2.3	1.927	0.0264	0.0195	0.0069	0.0171	0.0291
0.100	2.2	1.827	0.0264	0.0188	0.0076	0.0166	0.0289
0.200	5.7	4.954	0.0523	0.0382	0.0141	0.0307	0.0527
0.202	5.8	5.047	0.0529	0.0386	0.0143	0.0309	0.0527
0.300	10.1	8.981	0.0781	0.0580	0.0201	0.0431	0.0745
0.300	10.0	8.881	0.0781	0.0575	0.0206	0.0428	0.0744
0.400	14.8	13.308	0.1036	0.0790	0.0246	0.0548	0.1010
0.400	14.9	13.408	0.1035	0.0795	0.0240	0.0551	0.1011
0.500	20.3	18.434	0.1287	0.1035	0.0252	0.0672	0.1239
0.498	20.2	18.340	0.1283	0.1029	0.0254	0.0669	0.1238
0.600	25.4	23.161	0.1539	0.1247	0.0292	0.0770	0.1475
0.600	25.5	23.261	0.1539	0.1252	0.0287	0.0772	0.1475

TABLE 18 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.700	31.0	28.388	0.1787	0.1473	0.0314	0.0868	0.1706
0.700	31.1	28.488	0.1786	0.1477	0.0309	0.0869	0.1706
0.800	36.6	33.615	0.2033	0.1694	0.0339	0.0957	0.1938
0.800	36.7	33.715	0.2033	0.1697	0.0336	0.0958	0.1938

TABLE 19

System TFA - ϕ_2CO in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.10 mole/l. ϕ_2CO at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.1	1.0	0.627	0.0267	0.0085	0.0185	0.0080	0.0350
0.1	1.1	0.727	0.0266	0.0095	0.0171	0.0089	0.0352
0.2	2.5	1.754	0.0532	0.0185	0.0347	0.0164	0.0660
0.2	2.6	1.854	0.0517	0.0190	0.0327	0.0167	0.0661
0.3	4.2	3.081	0.0795	0.0273	0.0522	0.0230	0.0825
0.3	4.2	3.081	0.0795	0.0273	0.0522	0.0230	0.0825
0.4	6.8	5.308	0.1055	0.0400	0.0655	0.0318	0.1116
0.4	6.8	5.308	0.1055	0.0400	0.0655	0.0318	0.1116
0.5	9.8	7.934	0.1313	0.0530	0.0783	0.0401	0.1320
0.5	9.8	7.934	0.1313	0.0530	0.0783	0.0401	0.1320
0.6	13.2	10.961	0.1569	0.0664	0.0905	0.0479	0.1561
0.6	13.2	10.961	0.1569	0.0664	0.0905	0.0479	0.1561

TABLE 19 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.7	17.1	14.488	0.1823	0.0850	0.0973	0.0580	0.1830
0.7	17.0	14.388	0.1824	0.0844	0.0980	0.0577	0.1828
0.8	21.3	18.315	0.2075	0.1025	0.1050	0.0667	0.2068
0.8	21.2	18.215	0.2075	0.1022	0.1053	0.0666	0.2068

TABLE 20

System TFA - ϕ_2CO in Diphenylmethane -- Dependence of Total Pressure on TFA Concentration in 0.20 mole/l. ϕ_2CO at 30°C.

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.1	0.60	0.227	0.0268	0.0035	0.0233	0.0034	0.0288
0.1	0.60	0.227	0.0268	0.0035	0.0233	0.0034	0.0288
0.2	1.25	0.504	0.0535	0.0073	0.0462	0.0069	0.0475
0.2	1.15	0.404	0.0535	0.0061	0.0474	0.0058	0.0466
0.3	2.00	0.881	0.0801	0.0110	0.0691	0.0102	0.0720
0.3	1.90	0.781	0.0801	0.0101	0.0700	0.0094	0.0706
0.4	3.00	1.508	0.1064	0.0163	0.0901	0.0146	0.1052
0.4	2.95	1.458	0.1065	0.0162	0.0903	0.0145	0.1052
0.5	4.20	2.334	0.1327	0.0224	0.1103	0.0193	0.1265
0.5	4.20	2.334	0.1327	0.0224	0.1103	0.0193	0.1265
0.6	5.70	3.461	0.1588	0.0296	0.1292	0.0247	0.1570
0.6	5.60	3.361	0.1588	0.0290	0.1298	0.0243	0.1569

TABLE 20 -- Continued

v_{TFA} (ml.)	P_T (mm.)	P_{TFA} (corrected) (mm.)	f^t_{TFA} (exper.) (mole/l.)	f^{free}_{TFA} (mole/l.)	Δf_{TFA} (mole/l.)	C_A (mole/l.)	f^t_{TFA} (calc.) (mole/l.)
0.7	7.50	4.888	0.1847	0.0378	0.1469	0.0304	0.1774
0.7	7.50	4.888	0.1847	0.0378	0.1469	0.0304	0.1774
0.8	9.50	6.515	0.2105	0.0462	0.1643	0.0359	0.1980
0.8	9.35	6.365	0.2105	0.0454	0.1651	0.0353	0.1976

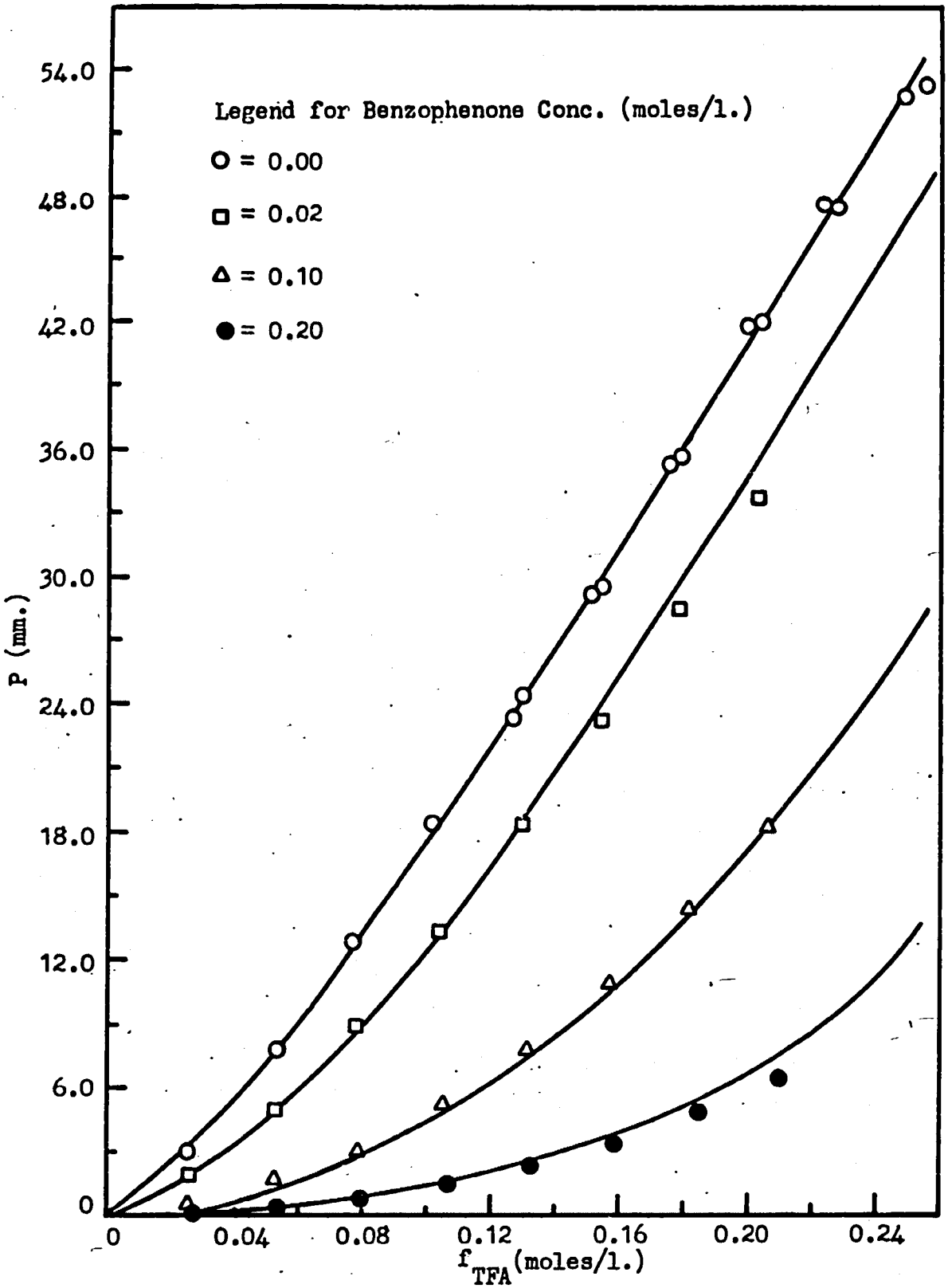


FIG. 19 -- Variation of Total Pressure with Formal Concentration of Trifluoroacetic Acid at Different Concentrations of Benzophenone in Solution in Diphenylmethane at 30°C.

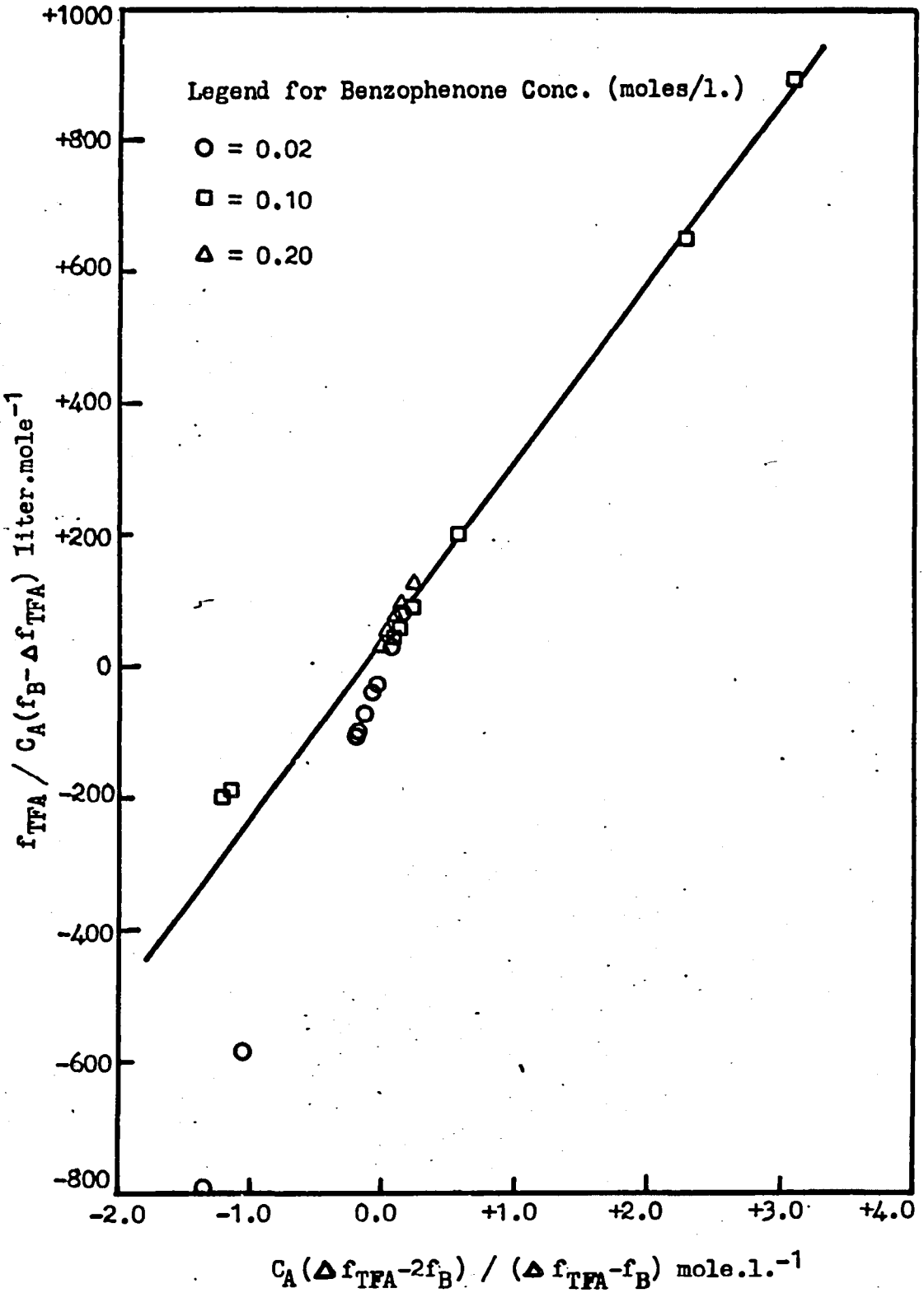


FIG. 20 -- Determination of the Hetero-association Constants of Trifluoroacetic Acid and Benzophenone in Solution in Diphenylmethane at 30°C.

TABLE 21

System TFA - HAc in Diphenylmethane
Dependence of Total Pressure on Combined Acid Concentration at 30°C.

Constants Used in the Calculations:

$K^v_{F_2} = 0.234\ mm^{-1}$, $K^s_{F_2} = 4.02\ l.mole^{-1}$, $K^H_F = 104.44\ mm.l.mole^{-1}$

$K^v_{A_2} = 1.300\ mm^{-1}$, $K^s_{A_2} = 300.0\ l.mole^{-1}$, $K^H_A = 54.17\ mm.l.mole^{-1}$

$K^v_{AF} = 4.546\ mm^{-1}$

v_{TFA} (ml.)	v_{HAc} (ml.)	P_T (exper.) (mm.)	P_T (exper.,) (corrected) (mm.)	f_{TFA} (mole/l.)	f_{TFA} (calc.) (mole/l.)	f_{HAc} (mole/l.)	f_{HAc} (calc.) (mole/l.)	P_T (calc.) (mm.)
0.1	0.1	1.8	1.365	0.02657	0.02653	0.0348	0.0347	1.982
0.1	0.1	1.9	1.465	0.02657	0.02653	0.0348	0.0347	1.982
0.2	0.2	3.5	2.630	0.05278	0.05290	0.0693	0.0691	3.649
0.2	0.2	3.6	2.730	0.05278	0.05290	0.0693	0.0691	3.649
0.3	0.3	5.8	4.494	0.07852	0.07903	0.1036	0.1031	5.217
0.3	0.3	5.9	4.594	0.07852	0.07903	0.1036	0.1031	5.217
0.4	0.4	8.0	6.258	0.1045	0.1050	0.1376	0.1369	6.778

TABLE 21 - Continued

v_{TFA} (ml.)	v_{HAc} (ml.)	P_T (exper.) (mm.)	P_T (exper.,) (corrected) (mm.)	f_{TFA} (mole/l.)	f_{TFA} (calc.) (mole/l.)	f_{HAc} (mole/l.)	f_{HAc} (calc.) (mole/l.)	P_T (calc.) (mm.)
0.4	0.4	7.9	6.158	0.1045	0.1050	0.1376	0.1369	6.778
0.5	0.5	10.1	7.923	0.1301	0.1307	0.1713	0.1705	8.294
0.5	0.5	10.0	7.823	0.1301	0.1307	0.1713	0.1705	8.294
0.6	0.6	12.2	9.588	0.1555	0.1562	0.2047	0.2037	9.786
0.6	0.6	12.2	9.588	0.1555	0.1562	0.2047	0.2037	9.786
0.7	0.7	14.5	11.453	0.1808	0.1815	0.2379	0.2367	11.263
0.7	0.7	14.5	11.453	0.1808	0.1815	0.2379	0.2367	11.263
0.8	0.8	17.3	13.817	0.2059	0.2065	0.2709	0.2694	12.719
0.8	0.8	17.3	13.817	0.2059	0.2065	0.2709	0.2694	12.719

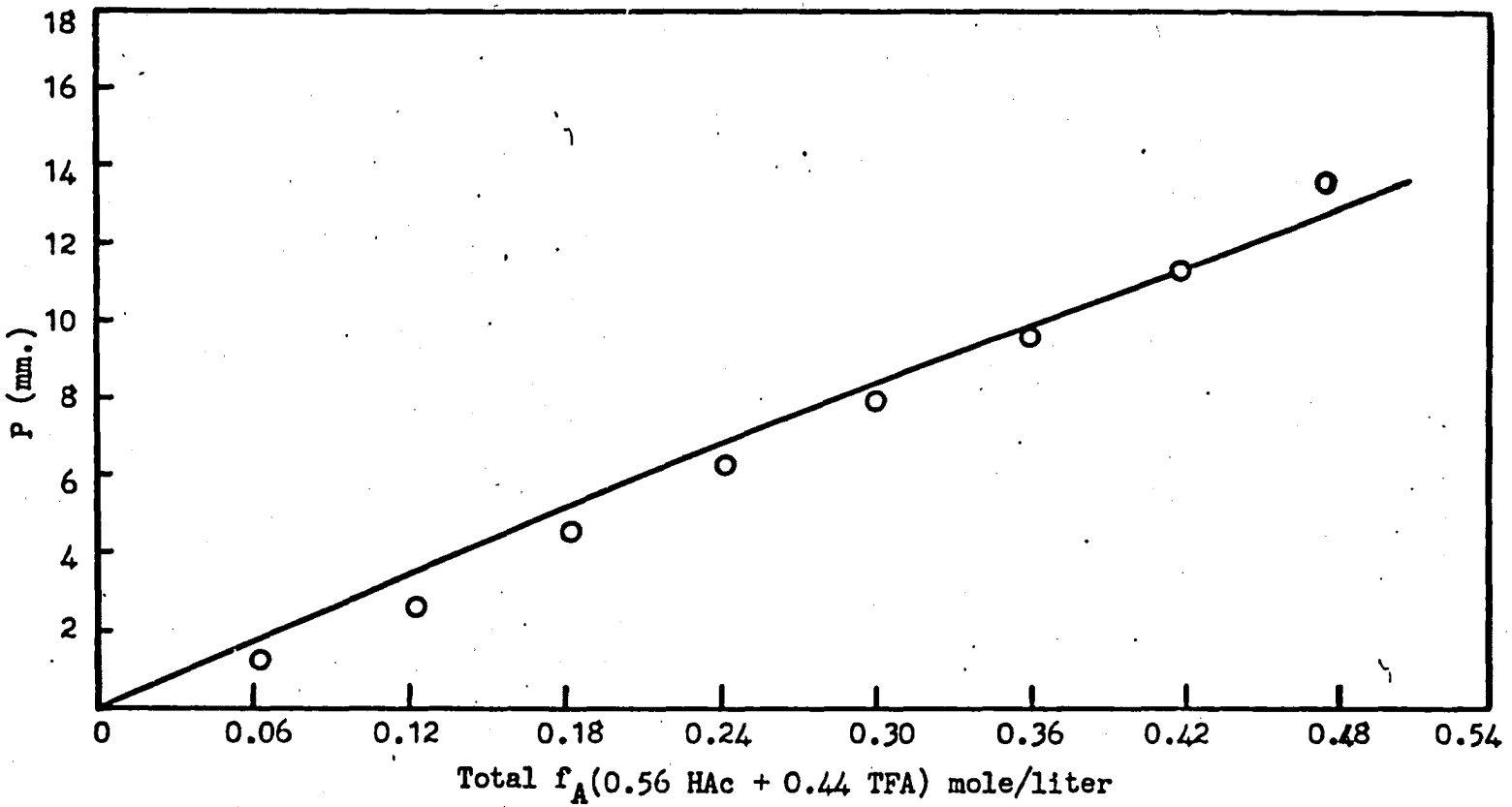


FIG. 21 -- Variation of Total Pressure with Combined Formal Concentration of Trifluoroacetic Acid and Acetic Acid in Solution in Diphenylmethane at 30°C.

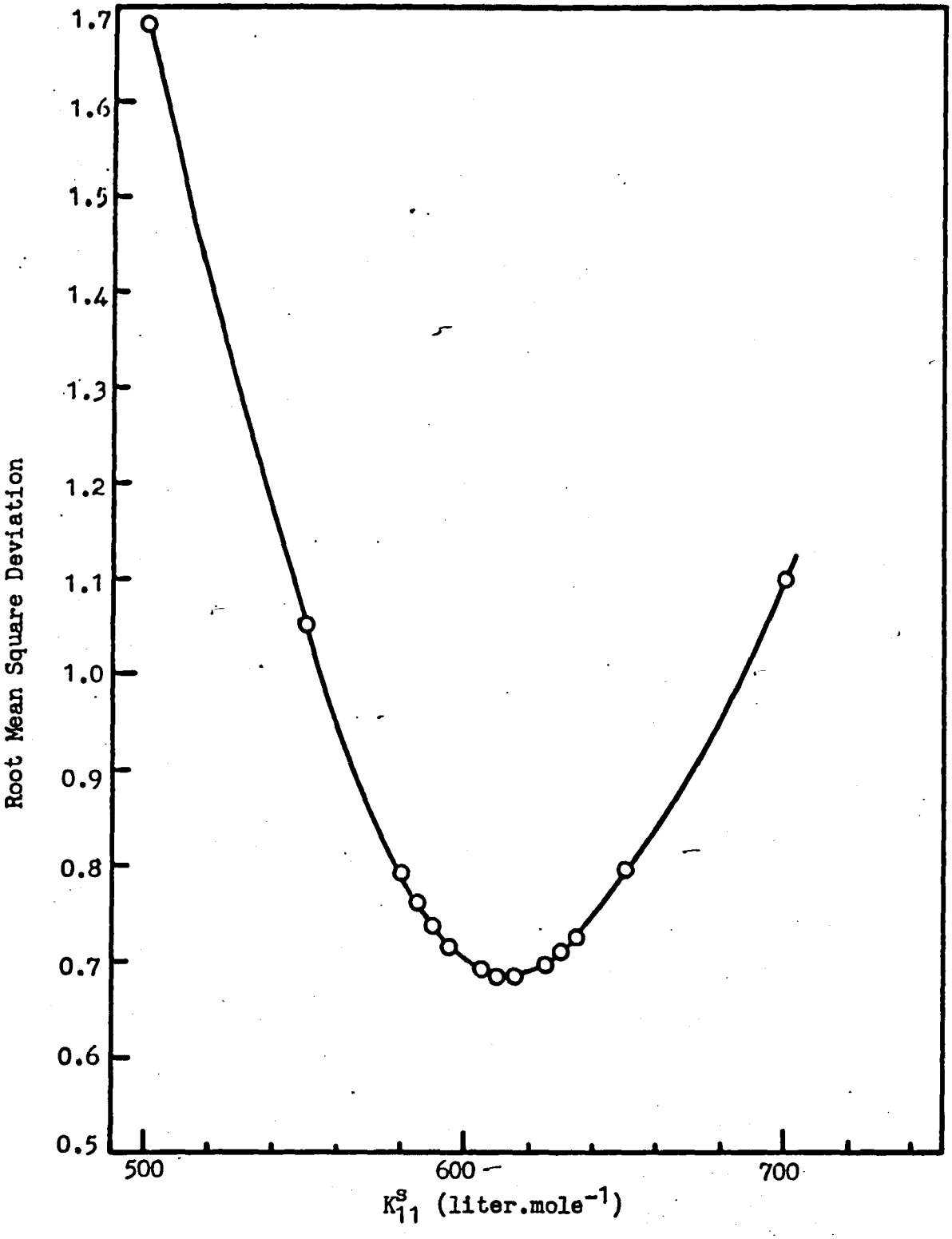


FIG. 22 -- Variation of Root Mean Square Deviation with Values of Hetero-dimerization Constants for the System Trifluoroacetic Acid-Acetic Acid in Solution in Diphenylmethane at 30°C.

TABLE 22

Summary of Results for Trifluoroacetic Acid -- Benzophenone System, and for Trifluoroacetic Acid-Acetic Acid System at 30°C.

SYSTEM	ASSUMED REACTION	EQUILIBRIUM CONSTANTS (Molar^{-1} units)	ROOT MEAN SQUARE DEVIATION (mm.)
Trifluoroacetic Acid-Benzophenone	TFA + $\emptyset_2CO$ = TFA.$\emptyset_2CO$	40.0 ± 4.0	
	2TFA + $\emptyset_2CO$ = $(TFA)_2.\emptyset_2CO$	275.0 ± 28.0	
Trifluoroacetic Acid-Acetic Acid	TFA + HAc = TFA.HAc	614.0 ± 30.0	0.684

CHAPTER VII

DISCUSSION AND CONCLUSIONS

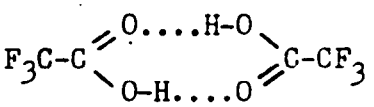
A. Systems

1--Trifluoroacetic Acid System

The only polymer believed present in the solution of this acid in diphenylmethane is the dimer formed by the reaction

$$TFA + TFA = TFA.TFA$$

The homo-dimerization constant that gave the best fit with the vapor pressure data was found to be 4.02 ± 0.48 liter.mole^{-1} at 30°C. and 2.64 ± 0.28 liter.mole^{-1} at 40°C. The structure of this complex is very likely to be the cyclic form



The magnitude of errors was obtained from probable values of the errors of parameters of the straight lines in Figures 6 and 7.

From the temperature dependence of these self-association constants it is possible to estimate an approximate enthalpy of the association reaction of TFA. In the case of the formation of $(TFA)_2$ from monomers, ΔH is approximately 4.5 ± 2.1 K.cal.

The values of the dimerization constants show that trifluoroacetic acid does not dimerize to a large extent in diphenylmethane. Preliminary

studies on the association of TFA in CCl_4, being done by Stevens,[20] show that the value of the homo-dimerization constant of TFA at 25°C. is about 200 $molal^{-1}$.

In general, self-association constants of carboxylic acids in benzene are of the order of 1/10 to 1/50 of the values in CCl_4. It is not surprising that self-association constants in diphenylmethane are in the same range as those in benzene, due to the presence of the benzene ring in both.

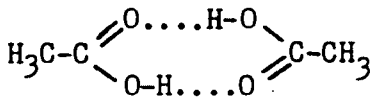
2--Acetic Acid System

The dimer was also believed to be the only polymer present in the solution of acetic acid in diphenylmethane according to the reaction

$$HAc + HAc = HAc.HAc$$

The very low vapor pressure and consequently the low monomer pressure of acetic acid, together with its high degree of association, made it very difficult to estimate a reliable value for the homo-dimerization constant of the above reaction. A very small shift in the parameters of the straight line on the curves in Figures 10 and 11 leads to a large change in the Henry's Law constants, which in turn leads to a large uncertainty in the association constants. The value of the self-association constant at 30°C. was needed later for the calculation of the hetero-association constant of the TFA-HAc system. Several possible values of the homo-dimerization constant obtained from the data for the HAc system were used to fit the hetero-association data, and the value that gave the minimum root mean square deviation, 300 $liter.mole^{-1}$ at 30°C., is reported in Table 5 as the homo-dimerization constant of HAc.

The reported Henry's Law constant at 30°C. was calculated from data for the HAc system using the value of the self-association constant for HAc mentioned above. Since the hetero-association of HAc-TFA was not investigated at 40°C., the Henry's Law constant at 40°C. was calculated from an estimated self-association constant for HAc at 40°C., obtained by assuming that the ratio of the two constants at 30°C. and 40°C. for HAc is the same as that for TFA. The cyclic form is also believed to be the most likely structure for this polymer



The value of the dimerization constant shows that HAc dimerizes to a much greater extent than TFA in diphenylmethane, but is itself dimerized to a much lesser degree than in CCl_4, where the value of the dimerization constant was found by Affsprung, et.al.,[21] and by Harris and Hobbs[22] to be about 3.21×10^3 $molal^{-1}$ at 25°C. This again shows the resemblence of diphenylmethane to benzene, where the ratio of the dimerization constant of HAc in benzene to that in CCl_4 is about 1/10.

3--Methanol System

Regarding the structure of the methanol polymers in solution, the linear structure of the dimer is generally accepted;[23,24] accordingly, higher polymers than the dimers are very likely to exist. At the concentration limits at which methanol was studied in this research, the largest polymer believed to be present is the trimer. The evidence regarding the structure of the trimer is conflicting. Hoffmann[25] suggested the cyclic form for the trimer based on his infrared studies, but he

pointed out some discrepancies between his data and data from non-spectroscopic studies. Coburn and Grunwald[18] supported the linear structure for the trimer, based on experimental results of the heats of association of ethanol. They also considered the steric requirements of the hydrogen bond. The bond is most stable if the covalent O-H donor bond is colinear with the orbital occupied by the acceptor electron pair.[23,26,27] Coburn and Grunwald[18] used a model analogous to that developed by Pople[27] for liquid water in which the bonding and non-bonding electrons in ROH are assumed to occupy approximately tetrahedral orbitals and the most stable bond directions are as shown in Figure 23a. Based on these structures, if the trimer were cyclic, the strain angle θ would have a value of 49°28',

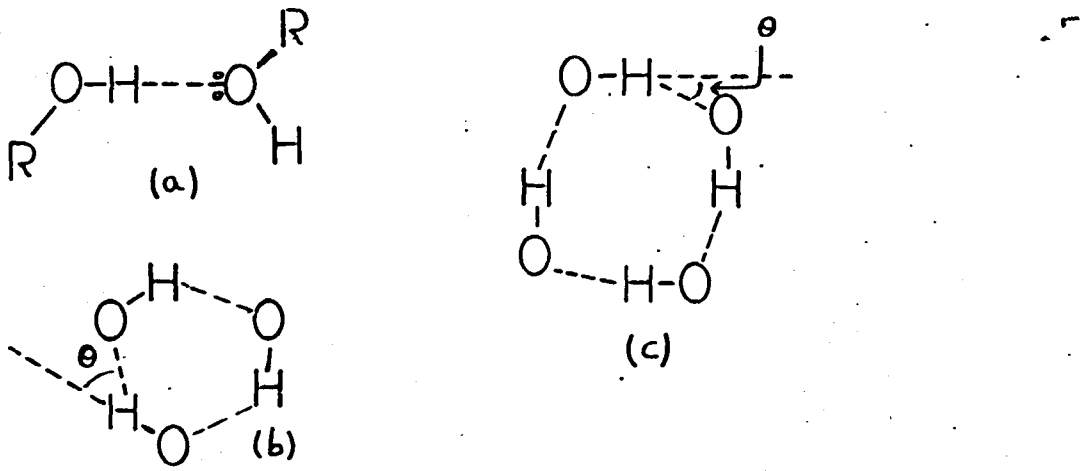


FIG. 23. -- Strain Angles in Cyclic ROH Complexes. (a) Preferred Linear Orientation (b) Planar Cyclic Trimer, θ = 49°28' (c) Planar Cyclic Tetramer, θ = 19°28'.

whereas in the tetramer it would be only 19°28'. Pople[27] has estimated the force constant for O-H....O bending in liquid water and has concluded that the average value of θ is about 26° at room temperature; thus the observation that a cyclic trimer is not formed appears reasonable. In

the present study, it has been assumed that both the dimer and the trimer of methanol in diphenylmethane are linear.

The vapor pressure data were first analyzed assuming the monomer and dimer, the monomer and trimer or the monomer, dimer and trimer as three possible combinations of associated species present in solution. On the basis of the root mean square deviations and progressions of values of the constants for the three sets of assumed species (Table 10), it was not possible to select one species as being superior to the other two.

Since it is most likely that all three species, monomers, dimers and trimers, are present in the solution, K_3^s, the trimerization constant in solution, was set equal to $3/2\ (K_2^s)^2$ using the assumption of Coburn and Grunwald[18] (see the Chapter on Calculations), and a computer program was designed for the calculation in each system of the combination of K_2^s and the Henry's Law constant that will give the minimum root mean square deviation in the formal concentrations (Figures 14, 15, and 16). The homo-dimerization constant was found to be 1.18-1.31 with a most probable value of 1.235 at 25°C., 1.05 ± 0.03 at 30°C. and 0.75 ± 0.07 at 40°C., all in molar^{-1} units. Accordingly, the homo-trimerization constant is 2.082-2.562 with a most probable value of 2.288 at 25°C., 1.654 ± 0.099 at 30°C. and 0.844 ± 0.157 at 40°C., all in molar^{-2} units. From the temperature dependence of the homo-association constants it is possible to estimate an approximate enthalpy of the association reaction of methanol. In the case of the formation of the linear dimer $(MeOH)_2$ from monomers, ΔH is approximately 6.2 ± 1.7 K.cal. The errors in the constants were estimated by setting a probable discrepancy between the minimum root mean square deviations and the true standard deviations of the experimental values to

be equal to $\Delta\sigma = \pm 0.477\,\sigma/(n-p)^{\frac{1}{2}}$, where σ is the minimum root mean square deviation, n is the number of experimental points and p the number of parameters used in fitting the data.[11,28] The limits of the errors were obtained by finding the contour line that encircles the values of the association constants and Henry's Law constants corresponding to the limits of the true values of standard deviations obtained by the above method. The homo-dimerization constant obtained from the spectral data was found to be 1.20-3.25 with a most probable value of 2.25 molar^{-1} at 25°C., and accordingly, the homo-trimerization constant is 2.16-15.84 with a most probable value of 7.59 molar^{-2}. The errors were obtained in the same way described above.

The advantage of the vapor pressure method over the spectral method in this case is illustrated by the magnitude of the values of the root mean square deviations of the reported constants, and also by the shape of the line of minima of the root mean square deviations. For example, for the vapor pressure data at 25°C. (Figure 14) there is a very apparent dip in the parabola of the root mean square deviations that might be estimated from the line of minima; whereas, for the spectral data at 25°C. (Figure 17) such a parabola will be very flat, leading to a great deal of uncertainty. The uncertainty in the spectral method is traceable to the difficulty of obtaining the molar absorptivity.

4--Trifluoroacetic Acid-Benzoic Acid System

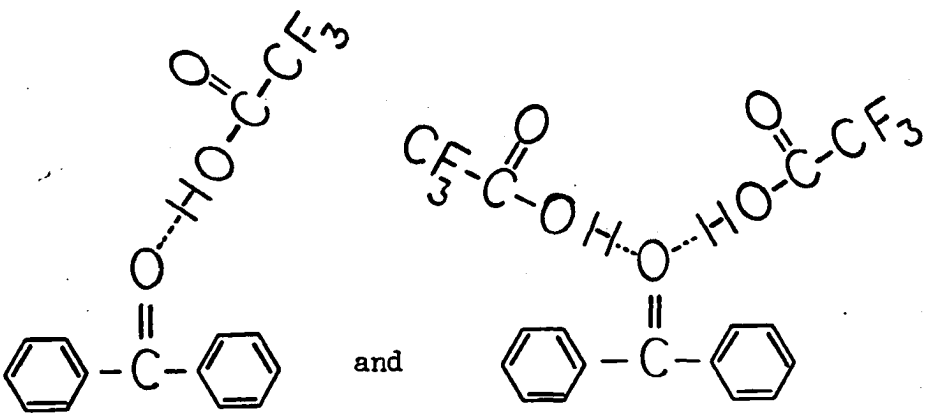
No hetero-association constants in solution were obtained from the study of this system. This is due to the fact that the experimental results obtained showed an apparent 12-14 moles of TFA tied to each mole of BzOH in solution, which cannot be explained at present.

To be sure that there is no non-reversible reaction taking place when the three compounds, TFA, BzOH and diphenylmethane, come in contact, the following experiment was made. An experiment was run exactly in the same manner as the experiments described in Chapter IV, with diphenylmethane in the flask and TFA added in increments. After a period of time to allow for equilibrium, the system was evacuated and the TFA was collected in the vacuum trap over distilled water which was kept frozen by dry ice surrounding the trap. The TFA was titrated against standard NaOH solution, and this showed that 90% of the TFA was recovered in the trap. Undoubtedly some TFA was lost during the process, probably being absorbed by the rubber tubing used in the apparatus. This value, however, served as a blank for the following experiment. A 0.1 molar solution of benzoic acid in diphenylmethane was placed in the flask and TFA added in increments as before. A period of time was allowed to establish equilibrium and the system was then evacuated for a longer time; the TFA was collected as before. Titration of the TFA showed that 89% of the added TFA was recovered in this case; titration of the benzoic acid in the flask accounted for the full amount of the acid added. This is partial evidence that there is no non-reversible reaction taking place between the three compounds in solution, or between any combination of them.

5--Trifluoroacetic Acid-Benzophenone System

Two hetero-polymers were assumed to be the most likely species present in this system; namely, $(TFA).(\emptyset_2CO)$ and $(TFA)_2.(\emptyset_2CO)$, and this assumption led to the best fit of the experimental data obtained. The two TFA moles in the trimer are believed to be bonded to the two lone pairs of electrons on the carbonyl-oxygen of the benzophenone, which will have

an extra amount of electronegativity due to the -I,-R effects of the two phenyl groups. The structure of the two complexes is very likely



The hetero-association constants that gave the best fit of the experimental data at 30°C. were found to be K^s_{11} = 40±4 liter.mole^{-1} and K^s_{21} = 275±28 liter^2.mole^{-2}.

If the two sites for hydrogen bond formation are assumed to be equivalent, and if there is no influence of one of the hydrogen bonds on the formation of a second hydrogen bond, a relation between the two equilibrium constants K^s_{11} and K^s_{21} can be predicted theoretically as[11]

$$K^s_{21} = (K^s_{11})^2 / 4 \quad .$$

This relation is obtained assuming a sequential hydrogen bond formation according to the following reactions:

$$CF_3COOH + OC\phi_2 = CF_3COOH...OC\phi_2$$

$$CF_3COOH + CF_3COOH...OC\phi_2 = (CF_3COOH)_2...OC\phi_2 \quad .$$

The difference between the value of K^s_{21} obtained from the experimental data, 275 molar^{-2}, and that obtained from the above relation, 400 molar^{-2}, can be attributed in part to the fact that the first hydrogen bond formed

might have some hindering effect on the second lone pair of electrons on the carbonyl-oxygen in the benzophenone.

6--Trifluoroacetic Acid-Acetic Acid System

The hetero-hydrogen bonded species is believed to be the one to one complex. The experimental data could best be fitted by assuming a value of 614±30 molar^{-1} for the equilibrium constant of the following reaction in a solution of the two acids in diphenylmethane at 30°C.

$$CF_3COOH + CH_3COOH = CF_3COOH.CH_3COOH \quad .$$

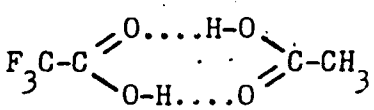
An explanation of the rather high value of the root mean square deviation is that one of the constants used in the calculations, the hetero-association constant of TFA and HAc in the vapor phase at 30°C., was obtained using two different sources, the work of Christian[10] and that of Lin.[11] It is also apparent from the curve fit (Figure 22) that the experimental point at the highest concentration has the highest deviation. This might be due to the presence of another species at this concentration, or that the system started deviating from Henry's Law.

The fact that the value obtained for the cross-association constant, 614 molar^{-1}, is very much higher than either of the values for the homo-dimerization constants, 4.02 molar^{-1} for TFA and 300 molar^{-1} for HAc, indicates that the cross-dimer TFA.HAc is very much favored over either of the homo-dimers. This result supports previous work done on hetero-association of carboxylic acids both in the vapor phase and in solution. Lin[11] studied the hetero-association of TFA and HAc in the vapor phase, and Christian and Hansen[29] studied the hetero-association of different organic acids and the corresponding perfluorinated acids

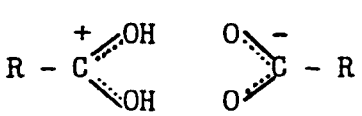
in the vapor phase. They all reported that the hetero-dimers are much favored over either of the homo-dimers in the vapor phase. Affsprung, et. al.[21] noted this same effect in studying the hetero-dimerization of acetic acid and trichloroacetic acid in CCl_4 solution. Kohler, et.al.[30] determined calorimetrically that the mixing of liquid TFA and HAc is strongly exothermic. They also postulated that the following reaction occurs exothermically in dilute CCl_4 solution

$$\tfrac{1}{2}\,(HAc)_2 + \tfrac{1}{2}\,(TFA)_2 = HAc.TFA \quad .$$

The structure of the cross-dimer of TFA and HAc in diphenylmethane is very likely the cyclic form



Statistically, one might predict that the hetero-dimerization constant would be greater than the geometric mean of the homo-dimerization constants by a factor of two, according to Fowler and Guggenhein,[31] since the symmetry number of the hetero-dimer is unity and the symmetry number of each of the homo-dimers is two. However, this assumption was made with no reference to the nature of the end groups of the two species in the hetero-dimer. The value of the hetero-dimerization constant is about nine times the value predicted by this assumption. Harris and Alder[32] attributed part of the stability of the dimer to the existence of an assumed zwitterion structure in which the dimer forms an ion-pair by transfer of a proton from one molecule to the other.



Kohler[33] suggested that on the basis of the zwitterion structure, the hetero-dimer TFA.HAc should be more stable, due to the inductive effect of the CF_3 group, and hence form preferentially to either of the homo-dimers. Affsprung, et.al.[21] suggested that the increased tendency for formation of hetero-dimers in systems of aliphatic and perhalo-aliphatic acids results from a cooperative interaction between the electric moment of the perhalogenated methyl or methylene group and the -COOH group belonging to the aliphatic member of the hetero-dimer. In homo-dimers of the perhalogenated acids, the effect of this interaction would be at least partially opposed by an unfavorable interaction between the perhalogenated methyl or methylene groups in the two molecules in the dimer. Costain and Srivastava[34] attributed the stability of the TFA.HAc hetero-dimer to the fact that the hydrogen atoms in the hydrogen bonds are exchanged very rapidly between the two partners.

B. Experimental Method

No reference was found in the literature which used this method, or this type of solvent for similar studies; therefore, the basic work represented here opens a new area in research which can be utilized in many fields of self- as well as cross-association studies.

The dependability of the apparatus was illustrated by the fact that, in duplicate runs, the experimental values agreed to within expected uncertainties in the measured pressures.

From this study it appears that the results obtained are quite reliable with highly volatile solutes having a relatively low degree of association in solution. On the other hand, in the system acetic acid-

diphenylmethane, the solute has a very low vapor pressure and is highly associated in solution, with the result that a small absolute error in the measured pressure will lead to a large deviation in the calculated constants. It is therefore recommended that this method not be applied to systems of this kind, except for qualitative purposes.

The results of this study illustrate that the nonvolatile, nonpolar solvent used, diphenylmethane, is similar in properties to benzene, a volatile, nonpolar solvent which is used extensively in solution studies. It was also shown that the degree of self-association of different solutes is less in this type of solvent than, for example, in CCl_4, a volatile, nonpolar solvent. This effect is generally attributed to an interaction between the polar solute and the π bonds of the phenyl groups of the solvent.

C. Summary and Suggestions for Further Work

A new method, which is rather fast and simple, has been developed in which vapor pressure data have been determined and analyzed for the study of self-association of trifluoroacetic acid, acetic acid and methanol in solution; and of cross-association of trifluoroacetic acid-benzoic acid, trifluoroacetic acid-benzophenone and trifluoroacetic acid-acetic acid in solution. A nonvolatile, nonpolar solvent, diphenylmethane, was used in all solutions. Self-association constants and Henry's Law constants have been determined from the self-association studies, and hetero-association constants from the cross-association studies, with most plausible structures being proposed for all the systems except the TFA-BzOH system. Hydrogen bond enthalpies were only roughly determined since the experiments were limited to a narrow range of temperatures.

It is suggested that detailed studies be done in the future on the association of the same solute in different nonpolar, nonvolatile solvents to note the effect of the nature of the solvent on the degree of association. In particular, nonpolar, nonvolatile aliphatic solvents should be used in studying solvent effects similar to those of CCl_4, since the type of solvent used in this research gave similar effects to those of benzene. Hydration studies can also be a very important application of the method represented in this work. Another suggestion for future work is the study of the association of solutes throughout a wider range of temperatures to allow for the accurate determination of the enthalpies of the hydrogen bonds.

The TFA-benzoic acid system, for which the results could not be satisfactorily explained, should be further investigated by different experimental methods. Spectral studies of the same system in different solvents including diphenylmethane should be helpful. Also the system could be studied by the present method, but using a different nonvolatile, nonpolar solvent.

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