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IN ORGANIC SOLVENTS

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THE SELF-ASSOCIATION OF TRIFLUOROACETIC ACID
IN ORGANIC SOLVENTS

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THE SELF-ASSOCIATION OF TRIFLUOROACETIC ACID
IN ORGANIC SOLVENTS

CHAPTER I

INTRODUCTION

The association of carboxylic acids by means of hydrogen bonding is a subject of long standing interest. The lower molecular weight aliphatic acids have been extensively studied in the vapor phase. Equilibrium constants, enthalpy and entropy terms have been evaluated by classical physical chemistry and spectroscopic methods. In general it has been found that in the vapor phase, $\Delta H = -14 \pm 1$ kcal/mole-dimer and $\Delta S = -35 \pm 3$ e.u./mole-dimer (based on standard states of one atmosphere) for the association reaction, regardless of carbon-chain length, extent of chain branching or degree of halogen substitution. Equilibrium constants do not show pronounced variation for saturated aliphatic acids but do exhibit a marked decrease when electronegative substituents are present or in the case of formic acid with only a single hydrogen adjacent to the carbonyl group.¹

Electron diffraction² and infrared spectral studies³ indicate that the vapor phase dimer is a cyclic, centro-symmetric structure. Both cyclic dimer structures, as in benzoic acid,⁴ and linear chain structures, as in acetic acid,⁵ have been found in the solid state by x-ray diffraction studies.

In the pure liquid phase and in solutions the nature of the structure of the associated species is not definitely established. It is, however, generally accepted that in dilute non-polar solution the cyclic dimer is the complex of primary importance, if not the only associated species.^{3,6} Both open dimers and chain polymers have been postulated as major species based on the interpretation of IR and NMR spectra.^{8,7} Recent low frequency Raman spectral work indicates that acetic acid is primarily (greater than 85%) in the form of cyclic dimers in the pure liquid and exclusively cyclic dimer in concentrated solution in pentane.⁹

A wide variety of acids, primarily halogen substituted acetic and benzoic acids, have been studied in solution and a considerable amount of data, both qualitative and quantitative, have been collected. However, there is rarely good agreement among thermodynamic data, especially equilibrium constants, reported by different investigators for the same system even using the same general experimental approach. Also, the influence of solvent character on the thermodynamics of an association reaction has seldom been studied systematically. The need for accurate and systematic studies of hydrogen bonding behaviour pointed out by Pimentel and McClellan in 1960 still exists.³

The hydrogen bonding properties of trifluoroacetic acid (TFA) have been of interest for several years. Because of the strong inductive effect of the trifluoromethyl group, TFA is a strong acid: pK_a of TFA is approximately 0.3 compared to $pK_a = 4.76$ for acetic acid,¹⁰ the parent compound. The electron withdrawing power of the perfluoromethyl group is also vividly shown in the carbonyl spectra: the

monomeric carbonyl stretching mode in the vapor phase is found at 1830 cm^{-1} in TFA,¹¹ while it is at 1791 cm^{-1} in acetic acid.¹² This frequency is among the highest known for carbonyl groups. On the basis of acid strength the TFA hydroxyl group would be expected to be quite polar and capable of strong interactions with even weak bases. TFA has been extensively studied in the vapor phase but little is known of its association thermodynamics in non-polar solution.

Thermodynamic functions for the self-association of TFA in the vapor phase, determined by several experimental methods, are given in the table below. Enthalpy and entropy values are, with one exception,

$K_2^{298^\circ\text{K}}, \text{ mm}^{-1}$	$-\Delta H, \text{ kcal/mole}$	$-\Delta S, \text{ e.u./mole}$	Method	Ref.
0.32	14.0		V.D.	13
0.27	$14.05 \pm .1$	36.5	PVT	14
	$13.7 \pm .4$		IR(OH)	15
0.30	14.0	36.2	VD, PVT	16
	17.7	$41.6 \pm .3$	IR(CO)	17

in the ranges $-14 \pm 1\text{ kcal/mole}$ and $-35 \pm 3\text{ e.u./mole}$ obtained for a wide variety of other carboxylic acids.

Hetero-association reactions in the vapor phase between TFA and various oxygen bases have been studied by Ling, utilizing vapor density and PVT measurements. With acetic acid (HAc), the hetero-dimer TFA-HAc was found to form preferentially, as expected, with ΔH and ΔS for the formation reaction being $-17.4 \pm .6\text{ kcal/mole}$ and $-53.8 \pm 2\text{ e.u./mole}$, respectively.¹⁶ By comparison with hydrogen bonding enthalpies for other carboxylic acids it was concluded that the bond between the TFA hydroxyl group and the acetic acid carbonyl has approximately a -11 kcal enthalpy

of formation. Equilibrium constants for the interaction of TFA with water and with 1,4-dioxane were obtained at only one temperature.¹⁸ The water system was best described by a 1:2 acid-water complex; a 1:1 complex was found with dioxane. Hetero-association reactions between TFA and acetone and TFA and cyclopentanone were studied over a range of temperature by a vapor density method.¹⁹ The hydrogen bond enthalpies determined for these complexes (-14.4 ± 1 kcal/mole for TFA-acetone and -11.7 ± 1 kcal/mole for TFA-cyclopentanone) are among the highest known for the $-O-H \cdots O=$ hydrogen bond.

A rather interesting microwave spectral study of the formation of carboxylic acid hetero-dimers was reported by Costain and Srivastava.²⁰ They observed the pure rotational spectra for vapor mixtures of TFA with formic, acetic, and monofluoroacetic acids. Spectra attributed to TFA-formic and TFA-acetic acid hetero-dimers were observed. Oxygen-oxygen bond distances in these complexes were found to be $2.69 \pm .02$ and $2.67 \pm .02$ Å, respectively. The enthalpy of formation of the TFA-formic acid complex, determined from the temperature dependence of the $J = 16 \leftarrow 15$ line, was reported as -15.9 ± 1.5 kcal/mole. The bond involving the TFA hydroxyl group is again probably several kcals stronger than the bond involving the TFA carbonyl.

There are only a few reports in the literature giving thermodynamic information about the association of TFA in non-polar solvents. Kagarise studied the infrared spectra of various halogen substituted acetic acids in carbon tetrachloride solution and reported an association enthalpy of -8.85 kcal/mole-dimer for TFA.¹⁵ This value was determined from the temperature dependence of the monomer and dimer

hydroxyl stretching bands. No systematic dependence of the association enthalpy upon extent of halogen substitution was found. Equilibrium constants were not reported.

Neparko⁵⁵ determined activities and partial pressures of the TFA-carbon tetrachloride system using a total pressure and vapor density method. Vapor phase association of TFA was accounted for. TFA was assumed to be completely dimerized in solution at concentrations above 0.1 mole fraction. The system was found to exhibit positive deviation from ideality. Pereira⁵⁶ studied heat of mixing for the binary system TFA-and HAc-carbon tetrachloride and for some concentration lines in the ternary system TFA-HAc-carbon tetrachloride. The maximum value of the heat of mixing was found to be more endothermic for the TFA system than for the HAc system. Heat effects in the ternary system were found to be strongly exothermic. It was inferred that the hetero-dimer, TFA-HAc, formed preferentially to either of the homo-dimers.

A classical vapor pressure method was used by Taha to study the association of a variety of compounds, including TFA, in the non-volatile solvent diphenylmethane.²¹ The association constant was reported to be 4.0 l/m at 30°C; $-\Delta H$ for the reaction was 9.0 ± 2 kcal/mole-dimer. Recent unpublished work indicates that this value may be too high. The interaction of TFA with the non-volatile solute benzophenone was also studied. The data were interpreted in terms of formation of a 1:1 and a 2:1 TFA-benzophenone complex. Equilibrium constants for the complexes were found to be 40 l/m and $275 (l/m)^2$, respectively, at 30°C. Similar complex stoichiometries were reported for the interaction of water with TFA in carbon tetrachloride solution

by Josien, et al.²¹ These results were based on the IR spectra of the free and bonded water species and on the carbonyl spectra of TFA.

From a dielectric constant study of TFA in cyclohexane, Thyriou and Decroocq reported a dimerization constant of 320 l/m at 25°C.²³

In order to obtain equilibrium constants for the association of TFA in a variety of non-polar solvents a new experimental technique, termed the vapor-solution method, has been developed. The vapor-solution method is strictly analogous to 'classical' vapor pressure methods where the vapor pressure of a volatile solute is measured manometrically as a function of its concentration in a suitable solvent. In such studies suitable implies non-volatile--for solvents with appreciable vapor pressure the problem of determining the vapor pressure of an association solute becomes quite unwieldy. The number of common non-volatile non-polar solvents is, however, rather limited. By utilizing a non-manometric means of measuring the pressure, the restriction of solvent volatility is removed. This method involves measuring the pressure of TFA indirectly by the vapor phase IR absorption of the monomeric hydroxyl stretching band.

A somewhat similar method was used by Denyer, et al.,²⁴ in studying complex formation between various amines and phenols. Their method involved the partitioning of a volatile solute (amine) between the vapor phase and a volatile solvent containing a non-volatile solute (phenol). They analyzed the vapor phase condensate obtained by sweeping the system with dry nitrogen. This involved a rather complex experimental set-up requiring flow-rate calibration and wet-chemical analysis of the condensate. In comparison, the vapor solution method developed here

requires a relatively simple experimental apparatus with the direct measurement of the spectra of the volatile solute over the solution providing a much simpler means of analysis.

The effect of solvent properties on the association thermodynamics of carboxylic acids is well illustrated in a paper by Allen, et al.²⁵ They studied the association of benzoic acid in the vapor phase and in dilute cyclohexane, carbon tetrachloride, and benzene solutions. Association constants in solution were determined as a function of temperature by means of the carbonyl IR absorption of the free and bonded species. A summary of their results is given below. The thermodynamic functions given all decrease markedly in the order of increasing

solvent	K ₂ , l/m	-ΔH, kcal/mole	-ΔS, e.u./mole
vapor		16.2	
cyclohexane	7500	12.8	24.4
carbon tetra- chloride	3660	11.0	21.2
benzene	462	7.6	12.8

solvent interaction capability, i.e. cyclohexane < carbon tetrachloride < benzene. Allen, et al., discussed these results qualitatively in terms of solvation effects. Since both the monomer and dimer of benzoic acid will be solvated in solution, the experimentally determined enthalpy and entropy changes will contain contributions arising from the difference in extent of solvation. This is expressed by the equations

$$\Delta H = \Delta H_{\text{assoc}} + \Delta H_{\text{solv}} n$$

$$\Delta S = \Delta S_{\text{assoc}} + \Delta S_{\text{solv}} n$$

The association terms are negative, whereas the solvation terms are positive, since the monomer is more extensively solvated than the dimer. The solvation terms are evidently smaller than the association terms since the experimental terms are negative. However, the solvation terms will increase in magnitude as the solvating power of the solvent increases, because of increased solvation of the monomer relative to the dimer, leading to the observed decrease in the experimental values. While this discussion of solvation effects is qualitatively correct, Allen, et al., made no attempt quantitatively to correlate the observed effects with solvent properties.

Christian,²⁶ et al., have developed a method for quantitatively predicting the effects of solvation on the thermodynamics of hydrogen bonding association equilibria from a minimum amount of experimental data. Briefly, the method is based on the assumption

$$\Delta_{1 \rightarrow 2} F_{AB}^0 = \alpha \left(\Delta_{1 \rightarrow 2} F_A^0 + \Delta_{1 \rightarrow 2} F_B^0 \right) \quad (1)$$

where $\Delta_{1 \rightarrow 2} F_{AB}^0$ is the change in free energy of the associated complex AB upon transfer from medium 1 to 2, and $\Delta_{1 \rightarrow 2} F_A^0$ and $\Delta_{1 \rightarrow 2} F_B^0$ are the corresponding free energy changes for the monomers A and B. α is a parameter representing the fraction of free energy of solvation of the monomers that is retained in the associated complex. α is presumably less than unity and not strongly temperature or solvent dependent. The relationships 2 and 3

$$\frac{K_{AB}^2}{K_{AB}^1} = (K_{D,A} K_{D,B})^{-1} \quad (2)$$

$$\Delta H_2^0 - \Delta H_1^0 = (\alpha - 1) \left(\Delta_{1 \rightarrow 2} H_A^0 + \Delta_{1 \rightarrow 2} H_B^0 \right) \quad (3)$$

are obtained from equation 1 by application of the thermodynamic relationships $\Delta F^0 = -RT \ln K$ and $\frac{\partial \Delta F}{\partial T} = \Delta H$. K_{AB}^1 and K_{AB}^2 are the equilibrium constants for the association reaction $A + B = AB$ in two different media and $K_{D,A}$ and $K_{D,B}$ are the monomer distribution constants: the ΔH 's in equation 3 are the corresponding enthalpy changes. In order to compare vapor phase data directly with solution data, standard states of one mole/liter are used throughout.

This method has been used successfully in treating pyridine-water²⁷ and triethylamine-water²⁸ association data in several non-polar solvents. The TFA association data obtained in this research will be used to provide a further test of the method. Also a simple lattice theory of solutions will be used to provide an a priori means of obtaining the parameter α .

CHAPTER II

OBJECTIVES

The objectives of this research were:

1. To develop a method for obtaining equilibrium constants for the association of TFA in a variety of non-polar organic solvents.
2. To obtain as completely as possible the thermodynamic parameters describing the association of TFA in these solvents.
3. To examine the effect of solvation on the association of TFA in terms of the method of predicting solvation effects proposed by Christian,²⁶ et al.
4. To develop an a priori means of calculating the parameter α involved in the theory of solvation of Christian and co-workers.

CHAPTER III

EXPERIMENTAL

Chemicals

Trifluoroacetic acid, Matheson, Coleman and Bell Co. reagent grade, was distilled through a 30 plate Oldershaw column at a reflux ratio of 10:1. The middle portion of distillate (boiling point 72.0°C corrected to 760mm) was used. Distilled TFA was stored in a desiccator over calcium sulfate until needed.

Eastman Spectrograde carbon tetrachloride and benzene were used as received except for removal of water. Cyclohexane and 1,2-dichloroethane were distilled through a 30 plate Oldershaw column at a 10:1 ratio. Solvents were dried by storing them in vapor contact with P₂O₅ or CaSO₄.

Instrumentation

A Beckman DK-1a spectrophotometer was used in making measurements in the 2.8 - 3.4 micron region. The instrument is a direct recording, double-beam quartz prism spectrometer with a lead sulfide detector and automatic slit-width control. A germanium stray-light filter, having a 1.8 micron cut-off, was used at all times. All measurements were recorded directly in absorbance units.

Beckman near-infrared silica spectrophotometer cells were used. For vapor measurements cell path lengths were 10.0 cm; for dilute

solution work, 5.0 cm. A variable path-length cell with near-IR silica windows manufactured by Research and Industrial Instruments Co., London, England, was used to obtain qualitative spectra in concentrated solutions.

A water cooled cell holder was used in conjunction with a Haake Series F constant temperature bath for temperature control. This unit contains a circulating pump, mercury thermo-regulator, and high and low wattage heaters. A separate refrigeration unit provided cold water for cooling. With a coolant volume of approximately 1.5 liters, temperature changes of about 10°C could be achieved in roughly 10 minutes. Two thermometers were placed in the coolant flow stream, one before and one after the cell holder, to monitor temperature. Temperature control was better than $\pm 0.2^{\circ}\text{C}$.

A Perkin-Elmer 12C Model spectrophotometer, a single-beam instrument equipped with a CaF_2 prism, was used in measuring the TFA carbonyl absorption spectra in the 1800 cm^{-1} region. In order to study the carbonyl spectra as a function of temperature a Beckman VLT-2 variable temperature infrared cell having silver chloride windows was used. A cell path length of approximately 1.0mm was used in the carbon tetrachloride system; in cyclohexane and 1,2-dichloroethane a path length of 0.2mm was chosen. The cam number-frequency calibration chart was kindly furnished by Mr. E. E. Tucker. Frequency accuracy is about $\pm 3\text{ cm}^{-1}$. Temperature measurement was made by a Yellow Springs Instrument Co. Model 425C Tele-Thermometer. The thermistor probe was imbedded in one of the cell windows. These temperature measurements are believed to be accurate to within $\pm 0.5^{\circ}\text{C}$.

Auxillary Apparatus

Several pieces of equipment were used in the vapor phase and vapor-solution work. The device shown schematically in Figure 1 was used to dry and transfer TFA and could be connected to either the vapor or vapor-solution apparatus.

The vapor apparatus, shown schematically in Figure 2, is a modification of the single bulb vapor pressure apparatus developed by Christian,²⁹ et al. The only real modification is its adaptation for use in obtaining spectra as a function of pressure.

Figure 3 depicts the vapor-solution 'apparatus'. This is simply a device designed for forming dry TFA solutions. Its application will be further discussed in the procedure section.

Experimental Procedures

Dilute Carbon Tetrachloride Solution Study

Solutions were made up gravimetrically; aliquots of a dried TFA-carbon tetrachloride stock solution were added to weighed volumes of dry carbon tetrachloride in the five centimeter spectrophotometer cells. Drying was accomplished using the equilibrators caps developed by Christian,³⁰ et al., containing either P_2O_5 or $CaSO_4$. The cells were then stoppered and sealed with either Py-seal or polyethylene. Formal concentration of TFA was determined by titration of the stock solution with standard base.

Base-line absorptions of the solution cells were determined before adding the TFA solution by scanning against a reference cell

containing dry carbon tetrachloride. The DK-1 was standardized at the peak wavelength of the free OH stretching band, 2.847 micron. The mechanical slit-width was 0.12-0.13 mm over the peak.

Spectra of the TFA solutions were recorded after thermal equilibrium had been reached. This process was judged complete when a constant value of the hydroxyl peak absorbance was obtained. The free hydroxyl peak was then scanned three or four times and an average value of the peak absorbance was used.

Vapor Phase System

The TFA reservoir, Figure 1, containing TFA over CaSO_4 was connected to the single bulb apparatus, Figure 2, through a mercury-sealed ball joint.

Standardization of the DK - 1 was carried out at the free hydroxyl peak wavelength of 2.788 micron with the sample cell evacuated and the reference cell containing dry air. With the slit adjusted to 0.11 mm at 2.820 micron, a convenient checkpoint, a slit-width of 0.12 - 0.13 mm was obtained over the monomer peak. Base-line spectra were then recorded.

TFA in the reservoir was degassed by several cycles of freezing-thawing in the evacuated system. A small quantity, approximately 0.5 ml, of TFA was then frozen out into the second reservoir bulb. The system was then flushed several times with TFA vapor and re-evacuated.

Small increments of TFA vapor were admitted to the system from the reservoir. After each increment the pressure was measured manometrically and the spectra recorded. The peak absorbances recorded are an average of four scans. Measurements were made up to a total pressure

of 60 mm. Increments of TFA were then pumped from the system, each followed by pressure and absorbance measurements, until near zero pressure was obtained. About ten minutes between addition or removal of TFA samples was required for equilibrium to be established, as judged by cessation of drift in the peak absorbance reading. The spectrophotometer cell proper was thermostated at $25.0 \pm 0.2^{\circ}\text{C}$. Room temperature, ie., the temperature of the half-liter bulb, was $25.0 \pm 0.5^{\circ}\text{C}$.

Vapor-Solution Method

Base-line spectra were recorded with the vapor cell evacuated, as previously described and under the same instrument operating conditions. The TFA reservoir was then connected to the cell, again through a mercury-sealed ball joint. After degassing of TFA in the reservoir, a small quantity--approximately 0.002 - 0.01 grams, or a sufficient quantity to give an initial monomer absorbance of 0.2 to 0.7 depending upon the solvent used--of TFA was frozen out into the cell. The cell was then disconnected from the reservoir and placed in the spectrophotometer. After thermal equilibrium had been reached the monomer absorption peak was scanned six times and the average reading recorded. This value was used in calculating the initial formal pressure of TFA in the system. A 0.2 ml micro-buret, manufactured by Roger Gilmont Industries (no. S-1200A), was used to add small increments of dry solvent to the system through the mercury-sealed sintered-glass disc. After each addition a period of 10-15 minutes was allowed for equilibrium to be attained. The free hydroxyl peak of the vapor phase TFA was then scanned and an

average of four readings taken. Solvent was added up to a maximum volume of 4 or 5 ml. Temperature control was the same as described in the vapor phase system section.

Carbonyl Spectra Measurements

In order to remove interfering water vapor absorption bands, the 12C was flushed with dry air from a Puregas Manufacturing Co. Heatless Dryer purging unit. The cell container (vacuum jacket) and cell were oriented to obtain maximum transmission. Dry solvent base-lines were set to 90-95%T. The base-lines exhibited negligible change at the extremes of the temperature ranges used. At temperatures below ambient, temperature control was maintained by balancing the electrical input to the cell heater (50 watt maximum), adjusted with a variable transformer against the ice-bath heat-sink. The vacuum jacket salt windows were also heated to prevent fogging. Temperatures above ambient were maintained with the cell heater alone. A period of five to ten minutes was allowed for equilibrium to be re-established after changing temperature.

A slow scanning speed, 25 seconds/10 cm^{-1} , was used with high pen response suppression. At the gain setting used this provided a low-noise spectra. The mechanical slit-width was 0.180 - 0.190 mm over the carbonyl doublet.

The spectra, recorded in %T units, were converted to absorbance units point-by-point.

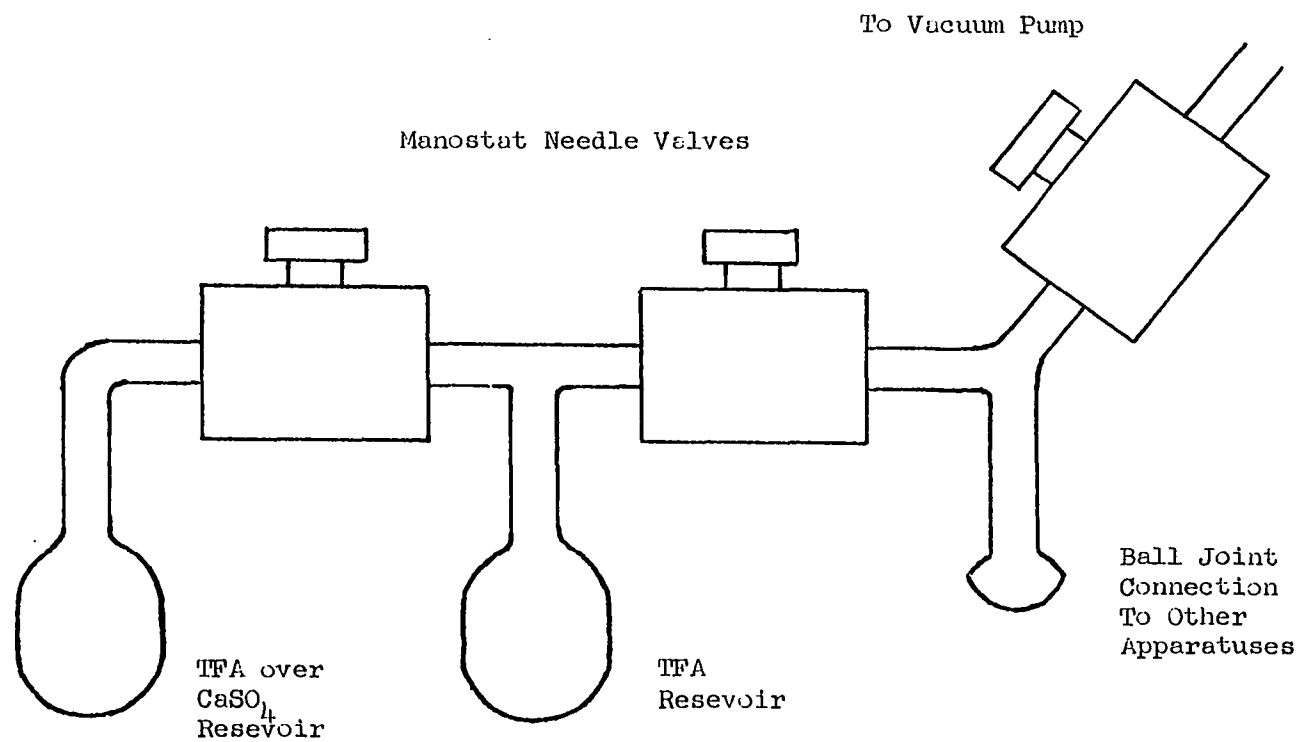


Figure 1. TFA Drying and Transfer Apparatus.

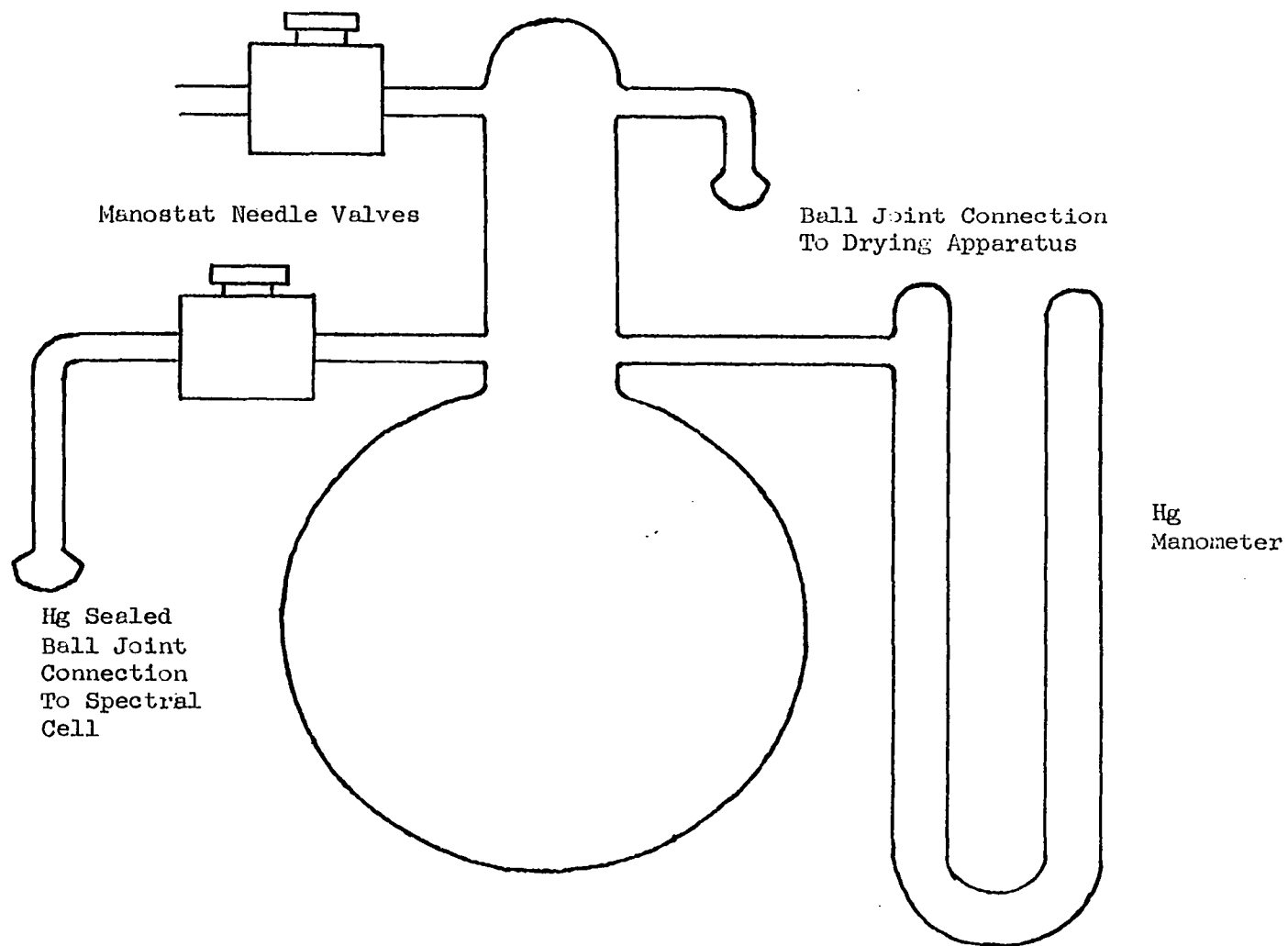


Figure 2. Modified Vapor Apparatus.

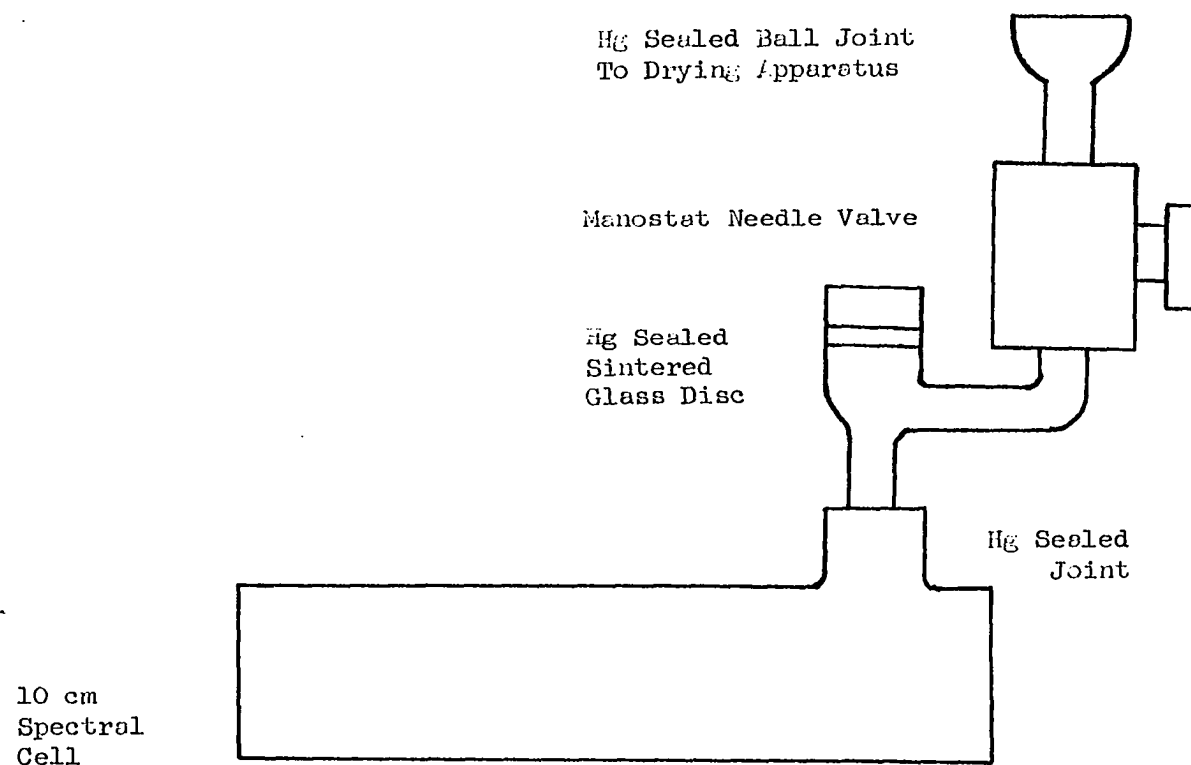


Figure 3. Vapor-Solution Apparatus.

CHAPTER IV

CALCULATIONS AND RESULTS

Dilute Carbon Tetrachloride Solution

In order to have a means of comparing results obtained from the vapor-solution method, the association of TFA in dilute carbon tetrachloride solution at several temperatures was first studied using a conventional infrared method. Data treatment is similar to that of Harris and Hobbs.³¹

If only dimerization occurs, the association reaction may be written $2\text{TFA} = (\text{TFA})_2$ and is governed by the equilibrium constant

$$K_2 = \frac{C_D}{C_M^2} \quad (1)$$

where C_D and C_M are the dimer and monomer concentrations. It is assumed that the individual species concentrations are sufficiently low so that activities may be replaced by concentrations; that is, it is assumed that each species obeys Henry's law. The formal concentration, an observable, is given by

$$f_A = C_M + 2C_D \quad (2)$$

or, substituting from the equilibrium expression

$$f_A = C_M + 2K_2C_M^2 \quad (3)$$

Assuming that the free hydroxyl-stretching band at 2.848 micron is a

function of monomer concentration only, and that Beer's law is obeyed, the equation

$$A_M = \epsilon_M b C_M \quad (4)$$

is obtained. A_M is the peak absorbance, ϵ_M the peak absorptivity and b is the cell path length. Combining equations 3 and 4 gives the equation

$$f_A = \frac{A_M}{\epsilon_M b} + \frac{2K_2}{(\epsilon_M b)^2} A_M^2 \quad (5)$$

or the linear equation

$$\frac{f_A}{A_M} = \frac{1}{\epsilon_M b} + \frac{2K_2}{(\epsilon_M b)^2} A_M \quad (6)$$

If the assumptions made in obtaining equation 6 are valid, then a plot of f_A/A_M vs. A_M should be linear; the dimerization constant and monomer hydroxyl absorptivity may be evaluated from the slope and intercept. Positive curvature in this type plot would result if associated species other than the cyclic dimer were formed in significant concentrations.

Data for this dilute solution investigation, over a concentration range of approximately $1.6(10^{-4})$ to $1.7(10^{-3})$ molal, at 15, 25, and 40°C are given in Table 1. Figure 4 is the ratio plot, f_A/A_M vs. A_M of the data. While there is some scatter in the data, a not uncommon occurrence in spectrophotometric studies, there is no trend indicating positive curvature. The apparent linearity of the data supports the initial assumptions. Equilibrium constants and monomer hydroxyl peak absorptivities given in Table 2 were obtained by least squares analysis of the data at each temperature. The RMSD--defined as the square root of the sum of deviations, calculated minus observed, squared, divided by

T = 288°K			T = 298°K			T = 313°K	
$f_A \times 10^4$	A_M	$f_A/A_M \times 10^3$	A_M	$f_A/A_M \times 10^3$	A_M	$f_A/A_M \times 10^3$	
3.62 molal	.338	1.071	.363	.998	.371	.976	
1.64	.165	.994	.168	.976	.170	.965	
11.95	.880	1.358	.982	1.217	1.088	1.098	
6.49	.544	1.193	.593	1.094	.625	1.039	
7.18	.587	1.223	.634	1.132	.683	1.051	
11.74	.866	1.357	.973	1.206	1.071	1.096	
13.83	.971	1.424	1.082	1.278	1.480	1.173	
15.38	1.036	1.484	1.173	1.311	--	--	
17.36	1.150	1.510	1.303	1.332	--	--	
7.34	.590	1.244	.649	1.131	.695	1.056	

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Dilute TFA-CCl₄ Solution Data

Table 1

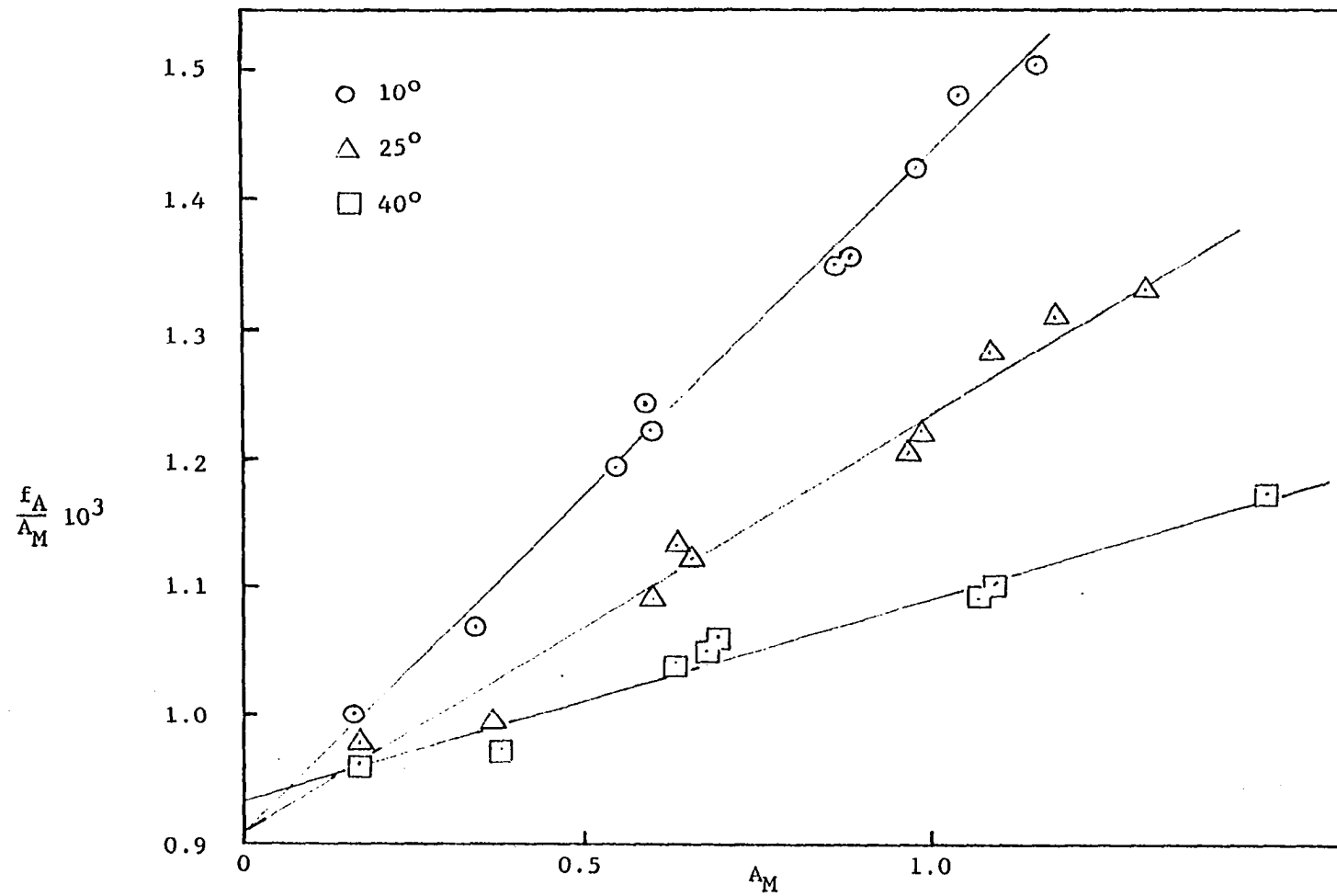


Figure 4. Ratio Plot, f_A/A_M vs. A_M , for Dilute TFA-CCl₄ Solution Data.

Table 2

Results of Dilute TFA-CCl₄ Solution Study

RMSD (f_A/A_M)	T°K	K ₂ , M ⁻¹	ϵ_M , cm ⁻¹ M ⁻¹
1.2 x 10 ⁻⁵	288	205 ± 8	138 ± 2
1.8 x 10 ⁻⁵	298	128 ± 7	139 ± 2
1.1 x 10 ⁻⁵	313	58 ± 4	137 ± 2

$$\Delta H = -9.0 \pm .4 \text{ kcal/mole}$$

$$\Delta S^\circ = -20.6 \pm 1.4 \text{ e.u./mole}$$

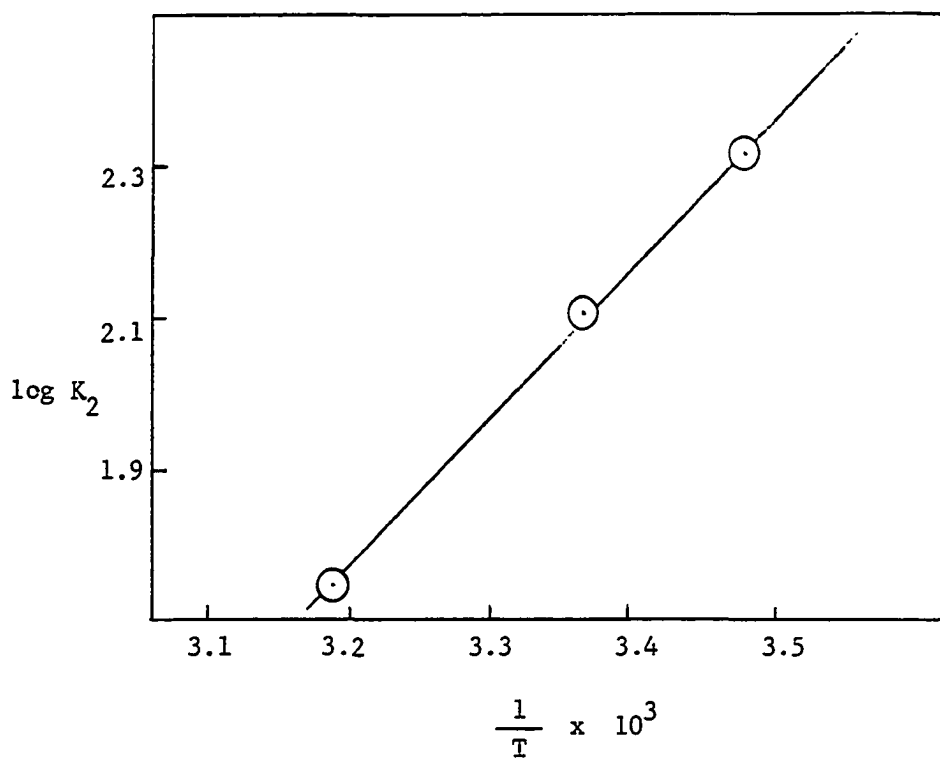


Figure 5. $\log K_2$ vs. $1/T$ Plot for Dilute TFA-CCl₄ Solution Dimerization Constants.

the number of data points less the number of parameters--of each fit is somewhat better than the expected maximum uncertainty of approximately 3% f_A/A_M . Uncertainties given for derived quantities are standard errors obtained from the least squares treatment. While molal concentration units were used for convenience in the experimental work the thermodynamic parameters are based on molar units for later correlations. The enthalpy change for the association reaction was found to be $-9.0 \pm .4$ kcal/mole from the $\log K_2$ vs. $1/T$ plot, Figure 5. This is in good agreement with the value -8.85 kcal/mole found by Kagarise.¹⁵

Vapor Phase System

The vapor-solution method requires knowing the vapor phase absorptivity, ϵ_M^v , of the free hydroxyl peak and the vapor phase association constant K_2^v . K_2^v is available from several sources. Both K_2^v and ϵ_M^v may be determined through the following considerations. The equilibrium constant for the vapor phase association reaction $2TFA = (TFA)_2$ is

$$K_2^v = \frac{p_D}{p_M^2} \quad (7)$$

where p_D and p_M are dimer and monomer partial pressures. Total pressure of the system is

$$p_T = p_M + p_D \quad (8)$$

or

$$p_T = p_M + K_2^v p_M^2 \quad (9)$$

Again, assuming that the monomer hydroxyl stretching peak is a function of monomer pressure only and that Beer's law is obeyed, the equation

$$A_M^v = \epsilon_M^v b p_M \quad (10)$$

is obtained. Combining equations 9 and 10 gives the equation

$$P_T = \frac{A_M^v}{\epsilon_{Mb}^v} + \frac{K_2^v}{(\epsilon_{Mb}^v)^2} A_M^{v^2} \quad (11)$$

or, in linear form

$$\frac{P_T}{A_M^v} = \frac{1}{\epsilon_{Mb}^v} + \frac{K_2^v}{(\epsilon_{Mb}^v)^2} A_M^v \quad (12)$$

Thus, by following monomer absorbance as a function of total TFA pressure the vapor phase absorptivity and association constant may be obtained.

Data for the vapor phase association of TFA at 25.0°C up to approximately 50 mm total pressure are given in Table 3. The data are plotted in the form P_T/A_M^v vs. A_M^v in Figure 6. Again there is some scatter but the plot appears linear within experimental error. Least squares fitting of the data in this form gave an equilibrium constant of $0.30 \pm .02 \text{ mm}^{-1}$, in good agreement with the value 0.30 mm^{-1} obtained by Chii Ling.¹⁶ Evaluation of the vapor phase monomer absorptivity was the main objective of this experiment. This quantity was found to be $(7.73 \pm .30) \times 10^{-3} \text{ cm}^{-1} \text{ mm}^{-1}$, or, in more familiar units, $143 \pm 5 \text{ cm}^{-1} \text{ l/m}$. It is interesting to note that there is little change in the monomer absorptivity on going from dilute carbon tetrachloride solution to the vapor phase.

Vapor-Solution Method

Calculations involved in the vapor-solution method are formally quite similar to those required in usual methods for inferring association constants from solution spectral data. In the vapor-solution method, the solution concentration of TFA is calculated from the decrease in

Table 3

TFA Vapor Phase System Data

T = 298°K

A_M^V	P_t	P_t/A_M^V
.188	4.2	22.4
.291	8.3	28.5
.409	14.3	35.0
.522	21.1	40.4
.633	29.5	45.6
.736	37.8	51.4
.808	44.5	55.5
.880	51.1	58.1
.845	48.4	57.2
.742	38.6	52.0
.676	33.0	48.8
.584	25.2	43.2
.502	19.6	39.0
.439	15.6	35.5
.377	12.3	32.6
.307	8.9	29.0
.257	6.8	26.4
.204	4.8	23.5
.132	2.6	19.7
.085	1.5	17.6
.091	1.5	16.5

Table 3 (Continued)

A_M^V	P_t	P_t/A_M^V
.152	3.0	19.7
.195	4.3	22.0
.261	6.9	26.4
.319	9.3	31.2
.369	11.5	31.2
.413	13.8	33.4
.475	17.5	36.8
.530	20.9	39.4
.576	24.1	41.6
.638	28.6	44.8
.695	31.9	45.9
.753	37.5	49.8
.798	41.9	52.6
.842	46.1	54.7
.911	52.5	57.6

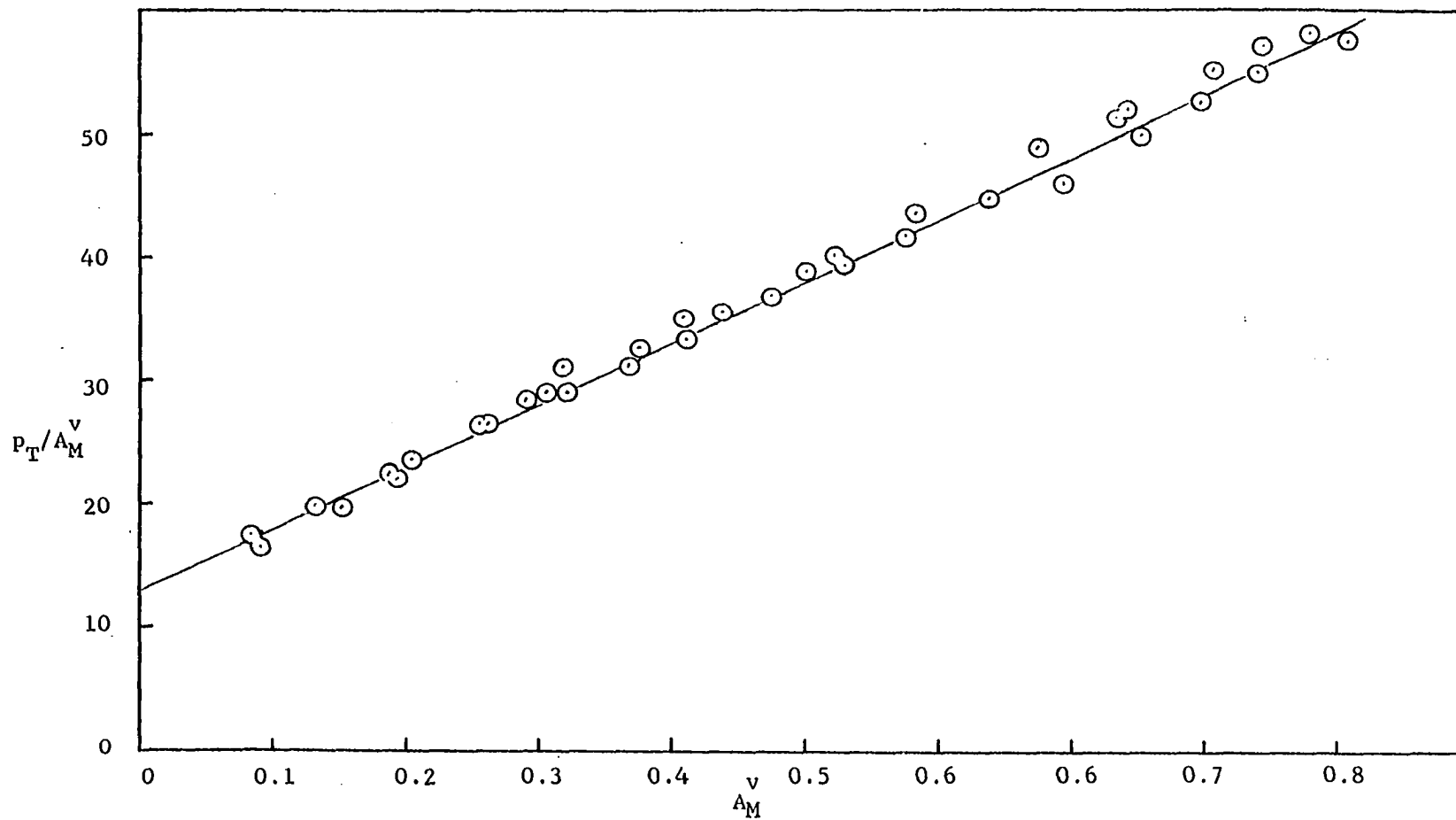


Figure 6. Ratio Plot, p_T/A_M^v vs. A_M^v , of Vapor Phase TFA Data.

formal pressure of TFA in the vapor phase after addition of each increment of solvent. Formal pressure is analogous to formal or analytical concentration used in solution studies and is given the symbol π . Thus, initially, with no solvent present the formal pressure of TFA is

$$\pi_o = p_M + 2p_D \quad (13)$$

From the equilibrium expression, equation 7, the formal pressure may be written in terms of monomer pressure

$$\pi_o = p_M + 2K_2^v p_M^2 \quad (14)$$

Monomer pressure is calculated from the vapor phase Beer's law expression, equation 10. When solvent is added to the system an amount of TFA dissolves. Monomer concentration in solution is then related to monomer pressure in the vapor phase by Henry's law

$$p_M = K_H C_M \quad (15)$$

where K_H is the Henry's law constant. The decrease in TFA formal pressure which occurs when solvent is added is related to the number of moles of TFA that dissolve by the ideal gas law. Thus, $\Delta(\pi V) = \Delta n RT$ or

$$\Delta n_i = \frac{(\pi_o V_o - \pi_i V_i)}{RT} \quad (16)$$

π_i is the calculated formal pressure after the i^{th} addition of solvent; V_i is the vapor volume of the system. The formal concentration of TFA in the solution, in molal units, is then

$$f_A = \frac{\Delta n}{g_s} \cdot 10^3 = \frac{(\pi_o V_o - \pi_i V_i) 10^3}{g_s RT} \quad (17)$$

where g_s is the weight of solvent. g_s is obtained by applying a Raoult's

law correction to g_t , the total weight of solvent added to the system. Simply, $g_s = g_t - g_v$, where g_v is the weight of solvent in the vapor phase. V_1 is a variable and is determined from the total vapor volume of the empty system less the volume of solvent added (g_t / d to an adequate approximation, where d is the density of the solvent).

Once the formal concentration is obtained the formulation is quite similar in form to the equation obtained in the dilute solution work. The formal TFA concentration is related to monomer and dimer concentrations by equation 3. Combination of Beer's law and Henry's law equations gives

$$A_M^v = \epsilon_M^v K_H b C_M \quad (18)$$

Substitution in equation 3 yields

$$f_A = \frac{A_M^v}{\epsilon_M^v K_H b} + \frac{2K_2^S}{(\epsilon_M^v K_H b)^2} A_M^{v^2} \quad (19)$$

or the linear equation

$$\frac{f_A}{A_M^v} = \frac{1}{\epsilon_M^v b K_H} + \frac{2K_2^S}{(\epsilon_M^v K_H b)^2} A_M^v \quad (20)$$

This equation relates vapor phase monomer absorbance and formal TFA concentration to the solution association constant and the monomer Henry's law constant.

Data for the systems TFA-cyclohexane, TFA-carbon tetrachloride, TFA-benzene, and TFA-1,2-dichloroethane, all at 25°C, are given in Tables 4 through 7. With the exception of the benzene system the ratio plots f_A/A_M^v vs. A_M^v Figures 7 through 10, are linear to within experimental error. The benzene system shows pronounced curvature at the higher

V	m1	g _t	g _s	A _M ^V	P _M	π	$\Delta(\pi V)$	f _A	f _A /A _M ^V
34.66	0			.654	8.45	52.12			
34.16	.50	.387	.372	.532	6.89	35.77	586	.0845	.1588
33.96	.70	.542	.527	.492	6.36	31.08	751	.0766	.1557
33.56	1.10	.851	.836	.434	5.61	24.84	973	.0626	.1442
33.16	1.50	1.161	1.146	.395	5.11	21.04	1109	.0520	.1317
32.76	1.90	1.470	1.456	.358	4.64	17.72	1226	.0453	.1265
32.16	2.50	1.934	1.920	.322	4.16	14.75	1332	.0373	.1158
31.36	3.30	2.554	2.540	.286	3.70	12.05	1429	.0302	.1057
34.66	0			.516	6.68	33.85			
34.36	.30	.232	.217	.457	5.91	27.23	238	.0589	.1288
33.86	.80	.619	.604	.380	4.91	19.66	508	.0452	.1189
33.36	1.30	1.006	.991	.328	4.24	15.23	665	.0361	.1100
32.86	1.80	1.393	1.378	.287	3.71	12.12	775	.0302	.1054
32.16	2.50	1.934	1.920	.252	3.26	9.74	860	.0241	.0956
31.26	3.40	2.631	2.619	.221	2.86	7.84	928	.0191	.0862
30.26	4.40	3.405	3.392	.193	2.50	6.20	983	.0156	.0807

TFA-C₆H₁₂ System Data

Table 4

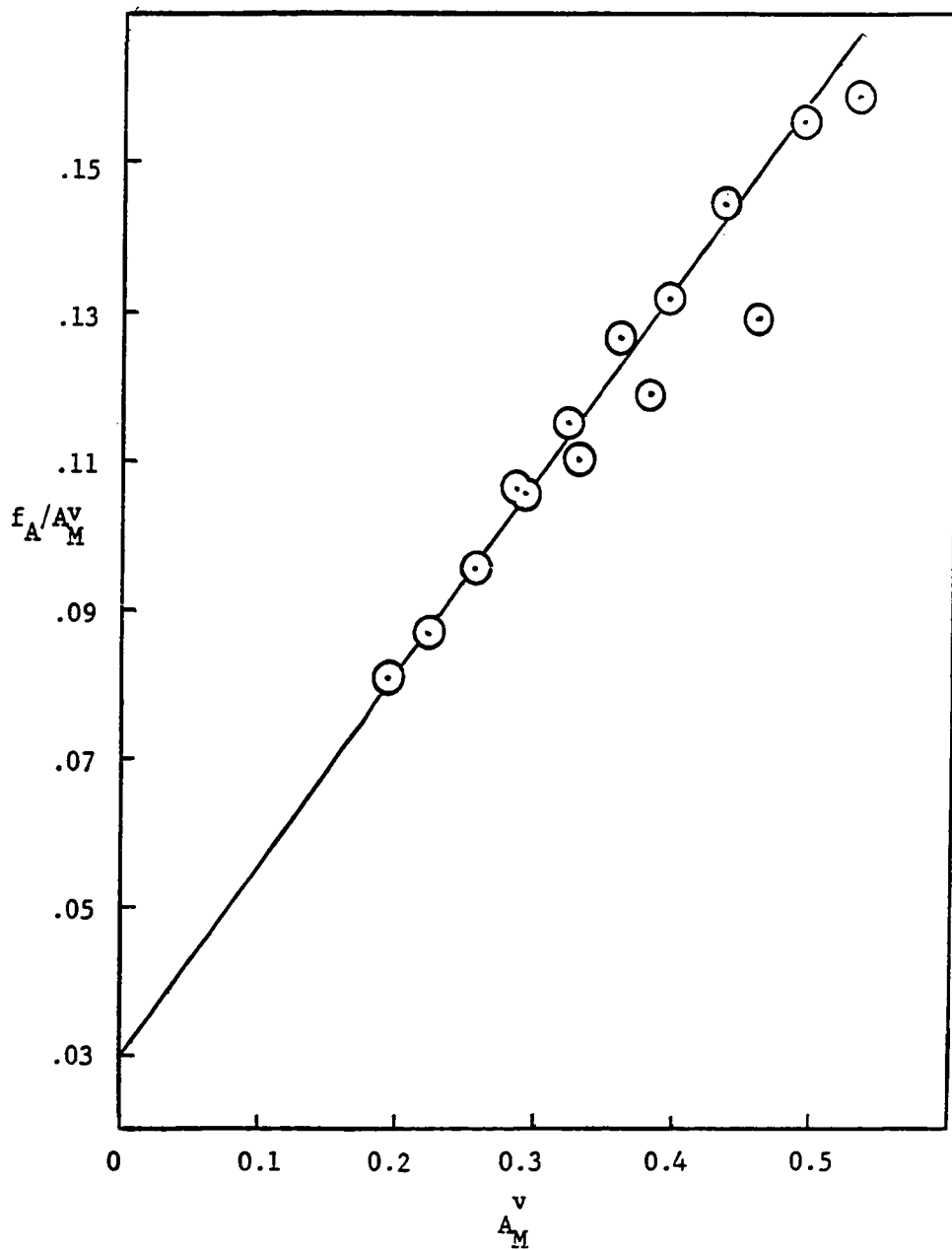


Figure 7. Ratio Plot, f_A/A_M^v vs. A_M^v , of TFA-C₆H₁₂ System Data.

V	ml	g_t	g_s	A_M^V	P_M	π	$\Delta(\pi V)$	f_A	f_A/A_M^V
34.66	0			.675	8.73	55.25			
34.46	.20	.317	.284	.538	6.96	36.51	657	.1244	.2313
34.36	.30	.476	.443	.485	6.28	30.29	877	.1065	.2196
34.26	.40	.634	.602	.439	5.69	25.35	1045	.0935	.2130
34.16	.50	.792	.760	.409	5.30	22.37	1151	.0815	.1992
33.86	.80	1.268	1.236	.337	4.36	15.95	1375	.0598	.1776
33.26	1.40	2.219	2.187	.264	3.42	10.53	1565	.0385	.1458
34.66	0			.615	7.96	46.61			
34.36	.30	.476	.443	.442	5.72	25.66	734	.0891	.2016
34.06	.60	.951	.919	.354	4.58	17.37	1024	.0599	.1693
33.76	.90	1.426	1.394	.302	3.91	13.22	1169	.0451	.1494
33.46	1.20	1.902	1.870	.268	3.47	10.80	1254	.0361	.1364
33.06	1.60	2.536	2.505	.237	3.07	8.80	1325	.0285	.1200
32.46	2.20	3.487	3.456	.203	2.62	6.83	1394	.0217	.1069
31.86	2.80	4.438	4.401	.181	2.34	5.69	1434	.0175	.0969

TFA-CCl₄ System Data

Table 5

V	ml	g_t	g_s	A_M^V	p_m	$\overline{TT}$	$\Delta (\overline{TT} V)$	f_A	f_A/A_M^V
34.66	0			.686	8.87	56.92			
34.46	.20	.317	.284	.537	6.95	36.38	719	.1362	.2537
34.26	.40	.634	.602	.443	5.73	25.76	1090	.0974	.2200
34.06	.60	.951	.919	.385	4.98	20.11	1288	.0754	.1958
33.76	.90	1.426	1.394	.328	4.25	15.23	1459	.0563	.1716
33.16	1.50	2.377	2.346	.261	3.38	10.33	1630	.0374	.1432
32.26	2.40	3.802	3.774	.205	2.66	6.94	1749	.0249	.1216
31.36	3.30	5.230	5.200	.174	2.25	5.34	1805	.0187	.1073
34.66	0			.284	3.67	11.91			
34.46	.20	.317	.284	.214	2.77	7.44	156	.0296	.1385
34.26	.40	.634	.602	.182	2.36	5.74	216	.0193	.1061
33.96	.70	1.109	1.077	.150	1.94	4.24	269	.0134	.0895
33.66	1.00	1.584	1.553	.130	1.68	3.41	298	.0103	.0794
33.16	1.50	2.377	2.346	.108	1.40	2.59	327	.0075	.0694
32.26	2.40	3.804	3.774	.086	1.11	1.87	352	.0050	.0584
31.36	3.30	5.230	5.200	.068	.88	1.35	370	.0038	.0564

TFA-CCl₄ System Data

Table 5 (Continued)

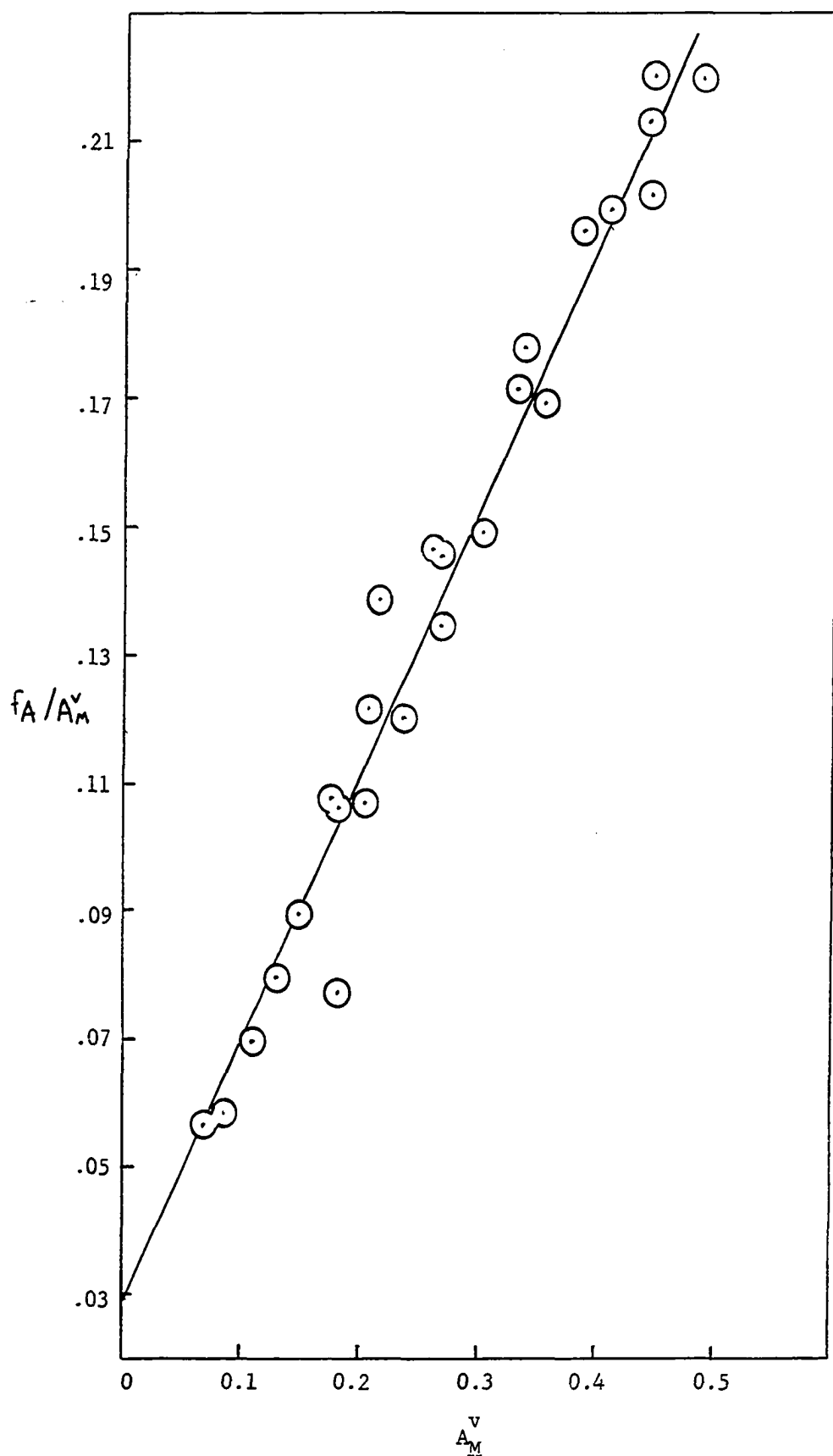


Figure 8. Ratio Plot, f_A / A_M^v vs. A_M^v , of TFA-CCl₄ System Data.

V	m1	g_t	g_B	A_M	p_m	Π	$\Delta (\Pi V)$	f_A	f_A/A_M^V
34.66	0			.296	3.83	12.77			
34.56	.10	.087	.070	.216	2.80	7.56	181	.1394	.645
34.46	.20	.175	.157	.163	2.11	4.82	276	.0947	.581
34.36	.30	.262	.245	.125	1.62	3.21	333	.0730	.584
34.26	.40	.349	.332	.105	1.36	2.48	358	.0579	.552
34.06	.60	.494	.477	.081	1.05	1.72	384	.0433	.535
34.66	0			.862	11.16	90.13			
34.46	.20	.175	.157	.528	6.83	35.29	1908	.654	1.238
34.36	.30	.262	.245	.462	5.98	27.79	2169	.476	1.031
34.26	.40	.349	.332	.413	5.34	22.76	2345	.380	.920
34.16	.50	.437	.420	.367	4.75	18.50	2492	.319	.870
33.96	.70	.612	.594	.312	4.04	13.97	2649	.240	.769
33.76	.90	.787	.769	.271	3.51	11.00	2752	.192	.710
33.36	1.30	1.136	1.119	.212	2.74	7.33	2879	.138	.653
32.96	1.70	1.485	1.468	.176	2.28	5.44	2945	.108	.613
32.56	2.10	1.845	1.818	.150	1.94	4.29	2984	.088	.589
32.06	2.60	2.272	2.255	.120	1.56	3.02	3027	.072	.600

TFA-C₆H₆ System Data

Table 6

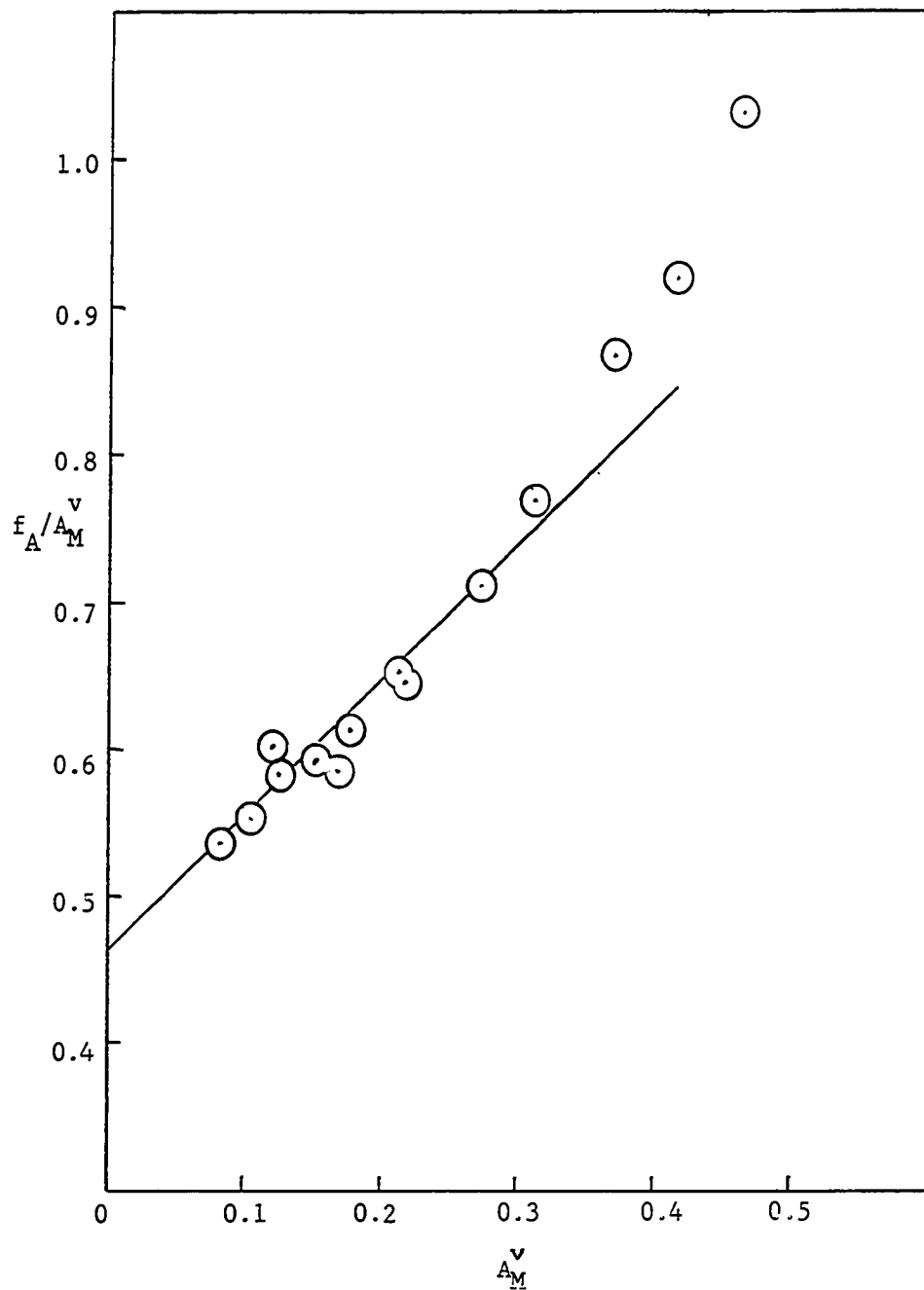


Figure 9. Ratio Plot, f_A/A_M^v vs. A_M^v , of TFA-C₆H₆ System Data.

V	ml	g_t	g_s	A_M^V	P_M	Π	$\Delta(\Pi V)$	f_A	f_A/A_M^V
34.66	0			.550	7.12	38.00			
34.56	.10	.124	.109	.400	5.18	21.51	574	.283	.707
34.46	.20	.249	.236	.308	3.98	13.67	846	.193	.626
34.36	.30	.374	.361	.244	3.16	9.23	1000	.149	.611
34.26	.40	.498	.485	.204	2.64	6.89	1081	.120	.588
34.16	.50	.623	.610	.180	2.32	5.64	1124	.099	.551
34.06	.60	.747	.734	.158	2.04	4.59	1162	.085	.528
33.86	.80	.996	.984	.130	1.68	3.41	1202	.066	.505
33.56	1.10	1.370	1.357	.099	1.28	2.28	1241	.049	.497
33.36	1.30	1.619	1.606	.086	1.11	1.87	1255	.042	.489
33.16	1.50	1.868	1.856	.076	0.98	1.57	1265	.037	.482
32.76	1.90	2.366	2.354	.061	0.79	1.17	1277	.029	.479
32.16	2.50	3.114	3.102	.048	0.62	0.86	1289	.022	.466
31.56	3.10	3.861	3.849	.041	0.54	0.70	1295	.018	.441

TFA-C₂H₄Cl₂ System Data

Table 7

V	ml	g_t	g_s	A_M^V	P_M	π	$\Delta(\pi V)$	f_A	f_A/A_M^V
34.66	0			.587	7.59	42.77			
34.46	.20	.249	.236	.329	4.25	15.26	956	.218	.661
34.36	.30	.374	.361	.265	3.43	10.60	1118	.167	.629
34.26	.40	.498	.485	.217	2.81	7.61	1222	.136	.624
34.16	.50	.623	.610	.184	2.38	5.84	1283	.113	.615
34.06	.60	.747	.734	.162	2.10	4.77	1320	.097	.597
33.86	.80	.996	.984	.130	1.68	3.41	1367	.075	.575
33.66	1.00	1.245	1.233	.113	1.46	2.76	1389	.061	.536
33.26	1.40	1.744	1.731	.086	1.11	1.87	1420	.044	.513

TFA-C₂H₄Cl₂ System Data

Table 7 (Continued)

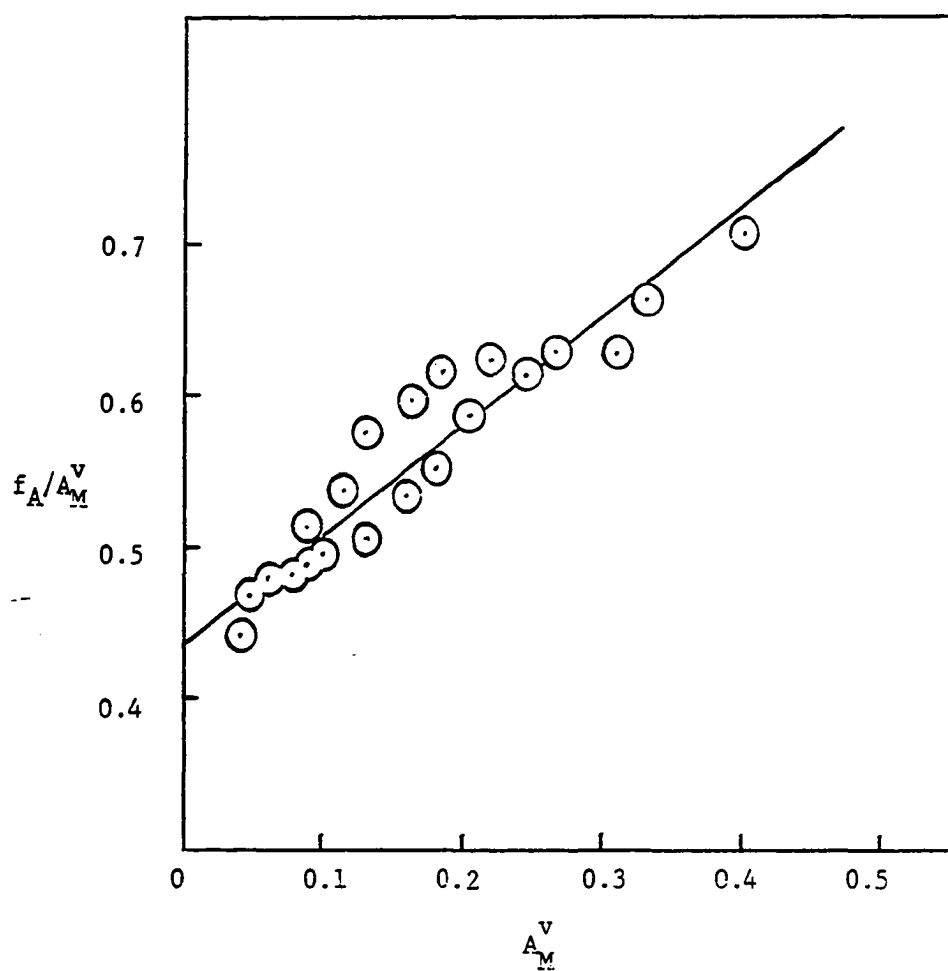


Figure 10. Ratio Plot, f_A/A_M^V vs. A_M^V , of TFA-C₂H₄Cl₂ System Data.

concentrations; data points above a concentration of approximately 0.3 molal were not included in the data fitting. Taha, working with TFA in the aromatic solvent diphenylmethane, observed similar curvature at concentrations above 0.3 molal.²¹ Least squares fitting was used to obtain the dimerization equilibrium constants and the monomer Henry's law constants.

The formal acid concentration ranges were from approximately 0.01 to 0.08 molal in cyclohexane; 0.005 to 0.15 molal in carbon tetrachloride; 0.04 to 0.3 molal in benzene; 0.02 to 0.2 molal in 1,2-dichloroethane. These concentration ranges are considerably higher than normally encountered in 'dilute' solution studies. The linearity of the ratio plots justifies the assumed monomer-dimer equilibrium.

The results of this study are given in Table 8.

Table 8

TFA Dimerization and Henry's Law Constants

System	From the Vapor-Solution Method		
	K_2, M^{-1}	$K_H, \text{mm } M^{-1}$	RMSD (f_A/A_M^V)
TFA-C ₆ H ₁₂	192 $\pm$ 36	592 $\pm$ 110	.0052
TFA-CCl ₄	149 $\pm$ 19	275 $\pm$ 35	.076
TFA-C ₆ H ₆	2.6 $\pm$ 9	32.5 $\pm$ 3.5	.018
TFA-C ₂ H ₄ Cl ₂	1.5 $\pm$.4	23.8 $\pm$ 4.2	.084

In conjunction with the solution study by the vapor-solution method, the TFA free and associated hydroxyl stretching mode spectra in the near-IR region were examined in the four solvents used. Peak frequencies and monomer half-peak-height band widths are given below.

Table 9

TFA Hydroxyl Peak Frequencies			
Solvent	ν_{OH}^M	$\Delta \nu_{\frac{1}{2}}^M$	ν_{OH}^D
C ₆ H ₁₂	3519	46 $\pm$ 6	3109
CCl ₄	3508	65 $\pm$ 6	3115
C ₆ H ₆	3390	105 $\pm$ 10	3120 ^a
C ₂ H ₄ Cl ₂	3381	183 $\pm$ 10	3110 ^a
Vapor ¹⁵	3589	28 $\pm$ 3	3138

^aThese values are rather approximate because of overlapping by the monomer and broadness of the peak.

Enthalpy Calculations

The enthalpy change in an association reaction may be calculated from the general thermodynamic relationship

$$\frac{\partial \ln K}{\partial \left(\frac{1}{T}\right)} = \frac{-\Delta H}{R} \quad (21)$$

or the integrated form obtained by assuming ΔH to be constant

$$\ln K = \frac{-\Delta H}{RT} + C \quad (22)$$

where K is the association reaction equilibrium constant. Thus, ΔH may be determined if K's are known at several temperatures as in the case of the dilute TFA-carbon tetrachloride system.

The enthalpy change may also be evaluated without directly determining equilibrium constants if a quantity proportional to the equilibrium constant may be obtained. This may be readily done through spectroscopic measurements if it is possible to ascribe separate absorption bands to each of the species in equilibrium. The carboxylic acids, in general, have both hydroxyl and carbonyl absorption bands that may be assigned to monomeric and associated (dimer) species. Both vibrational modes have been used in the evaluation of association enthalpies.^{25,15} The carbonyl bands have a greater utility in this type of determination because the molar absorptivity values are larger than those of the hydroxyl bands and because they fall in a frequency region usually having fewer interfering absorption bands.

Evaluation of ΔH is accomplished in the following way. Assuming the validity of Beer's law for both absorption bands ($A_M = \epsilon_M bc_M$ and $A_D = \epsilon_D bc_D$, where A is absorbance, ϵ the molar absorptivity, b the path length, c the concentration, and the subscripts M and D refer to monomer and dimer) and the equilibrium expression $K_2 = c_D/c_M^2$, it is possible to obtain the equation

$$K = \frac{A_D}{A_M^2} \cdot \frac{\epsilon_M^2}{\epsilon_D} \quad (23)$$

This equation combined with equation 22 gives

$$\ln \frac{A_D}{A_M^2} + \ln \frac{\epsilon_M^2}{\epsilon_D} = - \frac{\Delta H}{RT} + C' \quad (24)$$

or

$$\ln \frac{A_D}{A_M^2} = - \frac{\Delta H}{RT} + C \quad (25)$$

if the ratio of absorptivities may be assumed constant with temperature. This appears to be a reasonable assumption within experimental error according to the work of Allen, et al.,²⁵ with benzoic acid carbonyl spectra over a thirty degree temperature range. It should be emphasized that it is not necessary to know the concentration of the associating compound or the individual species in order to determine ΔH by this method.

Table 10 lists the TFA carbonyl peak positions and half-peak-height band widths in cyclohexane, carbon tetrachloride and 1,2-dichloroethane. Spectra were not obtainable in benzene solution because of the presence of a strong benzene peak at approximately 1800 cm^{-1} . With a cell path length of 0.2 mm this band had an absorbance of 0.8. While a shorter path length cell could have been used to reduce the absorbance of this peak to a workable level the increase in formal TFA concentration needed to produce a useable TFA spectrum would be unacceptably high.

Table 10

TFA Carbonyl Frequencies

Solvent	$\nu_{\text{C=O}}^{\text{M}}$	$\nu_{\text{C=O}}^{\text{D}}$	$\nu_{\text{M}}^{\text{M}} - \nu_{\text{M}}^{\text{D}}$	$\Delta \nu_{\frac{1}{2}}^{\text{M}}$	$\Delta \nu_{\frac{1}{2}}^{\text{D}}$
Vapor	1830	1792	38		
C_6H_{12}	1816	1781	35	12	14
CCl_4	1813	1780	31	11	16
$\text{C}_2\text{H}_4\text{Cl}_2$	1805	1789	16	14	19

Carbonyl absorbance data as a function of temperature for the three TFA-solvent systems are given in Tables 11, 12, and 13; the absorbances are peak values. The data are plotted in Figures 11, 12, and 13 in the form $\log A_D/A_M^2$ vs. $1/T$. These plots are linear within experimental error. The enthalpies obtained were as follows: $-11.7 \pm .6$ kcal per mole in cyclohexane; $-9.2 \pm .4$ in carbon tetrachloride; $-7.0 \pm .8$ in 1,2-dichloroethane.

Since the monomer and dimer bands overlap--slightly in the cyclohexane and carbon tetrachloride systems and severely in the 1,2-dichloroethane system--wing corrections had to be made. These corrections were accomplished by the graphical procedure described below.

Figure 14 depicts the TFA carbonyl spectra in 1,2-dichloroethane at $32.^\circ\text{C}$. The dimer peak, having a larger half-band width than the monomer peak, infringes more on the monomer peak than the monomer does on it. Each peak appears to be nearly symmetrical with respect to the frequency of maximum absorption. It is assumed that band shape does not change significantly with temperature. The graphical wing correction process is carried out in the following way. The low frequency side of the dimer peak is reflected about the peak maximum, resulting in curve a in the figure. Curve a is subtracted point by point from the high frequency side of the monomer band envelope giving curve b which is then reflected about its maximum and subtracted from the low frequency side of the dimer envelope, giving curve c. Curve c, upon reflection about its maximum, gives curve d which is then subtracted from the high frequency side of the envelope, giving curve e. This process of reflection and subtraction is repeated

Table 11

TFA Carbonyl Absorbance in C_6H_{12} as a f(T).

b = 0.2 mm

$t^{\circ}C$	$1/T \times 10^3$	A_M	A_D	A_D/A_M^2	$\log A_D/A_M^2$
20.0	3.411	.040	.476	298.0	2.474
24.0	3.365	.044	.448	231.5	2.364
28.5	3.314	.055	.470	155.3	2.191
30.7	3.291	.056	.458	146.0	2.164
35.9	3.235	.060	.441	122.5	2.088
40.8	3.185	.078	.434	71.3	1.853
49.8	3.096	.092	.398	47.0	1.672

$$\Delta H = - 11.7 \pm .6 \text{ kcal/mole}$$

$$\text{RMSD } (\log A_D/A_M^2) = 0.0346$$

Table 12

TFA Carbonyl Absorbances in CCl_4 as a f(T)

b = 1.0 mm

$t^{\circ}\text{C}$	$1/T \times 10^3$	A_M	A_D	A_D/A_M^2	$\log A_D/A_M^2$
10.5	3.525	.184	.452	13.36	1.126
16.5	3.452	.217	.406	8.63	.936
22.0	3.388	.224	.346	6.90	.839
22.8	3.378	.214	.295	6.44	.809
25.3	3.350	.218	.306	6.44	.809
33.0	3.298	.247	.253	4.15	.618
40.5	3.188	.254	.177	2.74	.438
49.0	3.104	.253	.117	1.84	.264

$$\Delta H = - 9.2 \pm .4 \text{ kcal/mole}$$

$$\text{RMSD} (\log A_D/A_M^2) = 0.0262$$

Table 13

TFA Carbonyl Absorbances in $C_2H_4Cl_2$ as a f(T)

b = 0.2 mm

t°C	1/T x 10 ³	A _M	A _D	A _D /A _M ²	log A _D /A _M ²
9.8	3.524	.131	.286	16.68	1.222
14.9	3.471	.144	.287	13.83	1.141
18.0	3.434	.157	.285	11.57	1.062
25.7	3.346	.175	.280	9.15	0.962
29.8	3.300	.191	.246	6.75	0.829
32.8	3.268	.196	.256	6.66	0.824
41.4	3.179	.221	.232	4.75	0.677
51.2	3.083	.233	.205	3.78	0.578

$$\Delta H = - 7.0 \pm .8 \text{ kcal/mole}$$

$$\text{RMSD} (\log A_D/A_M^2) = 0.024$$

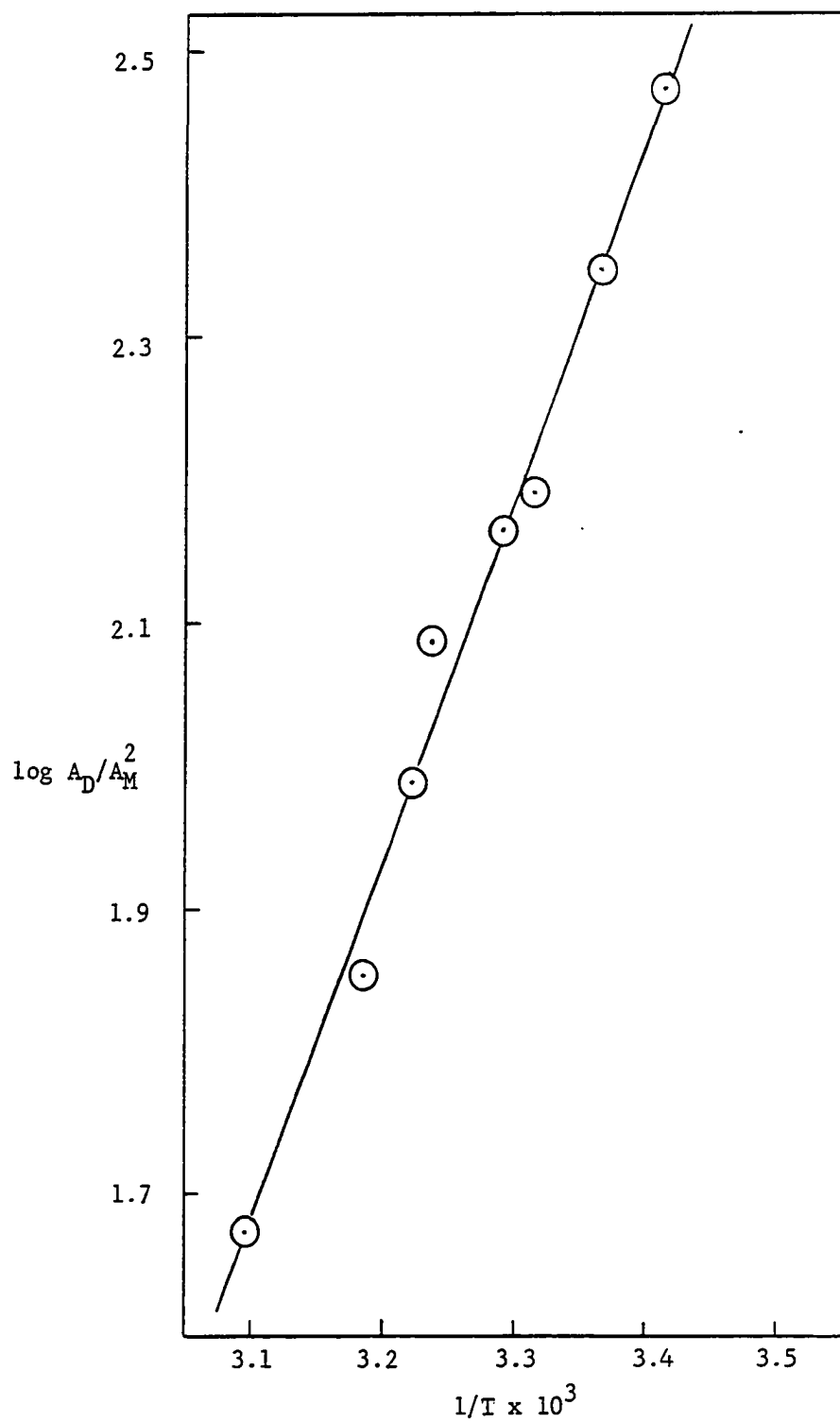


Figure 11. $\log A_D/A_M^2$ vs. $1/T$ Plot for TFA-C₆H₁₂ System.

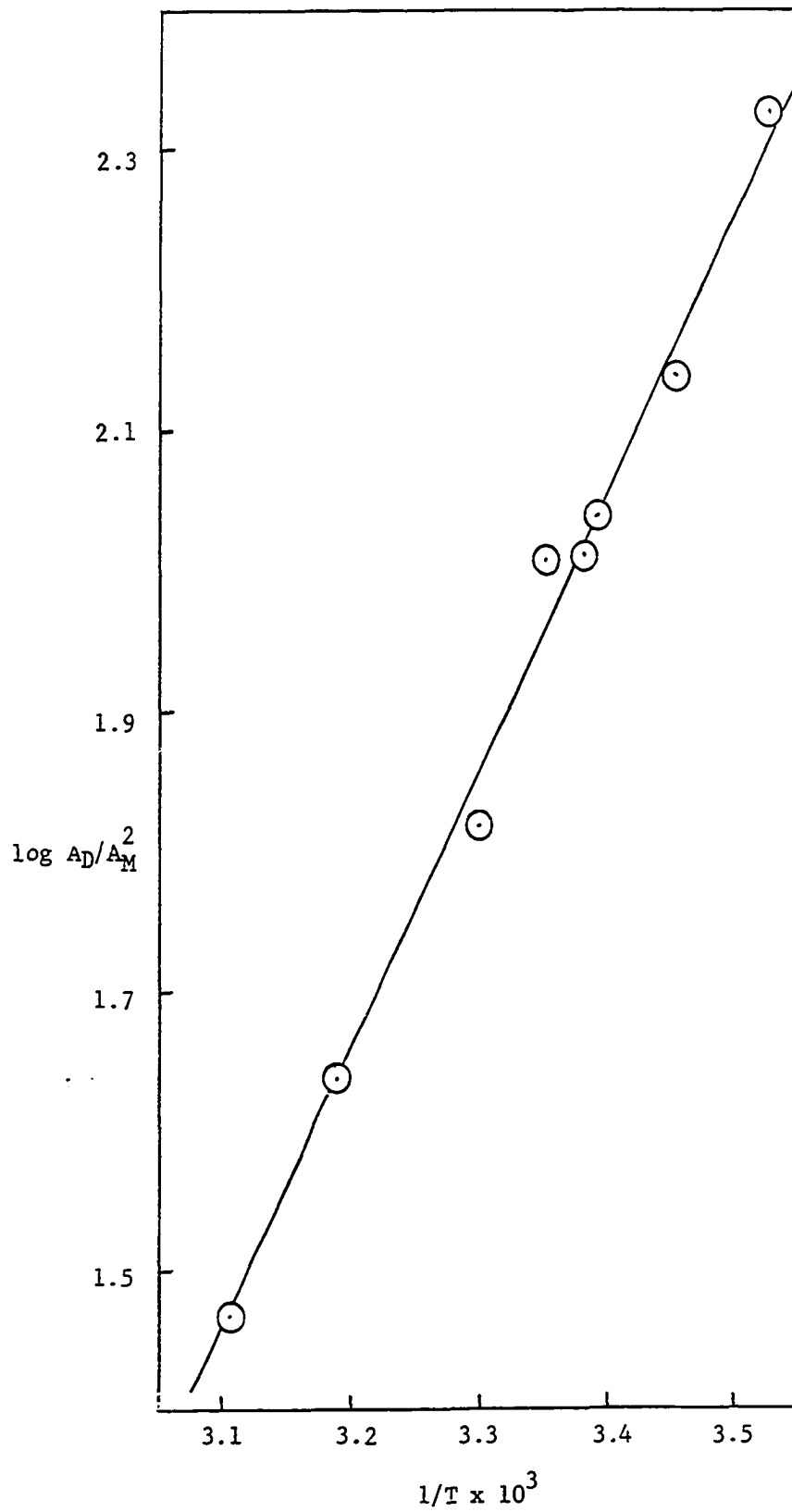


Figure 12. $\log A_D/A_M^2$ vs. $1/T$ Plot for TEA-CCl₄ System.

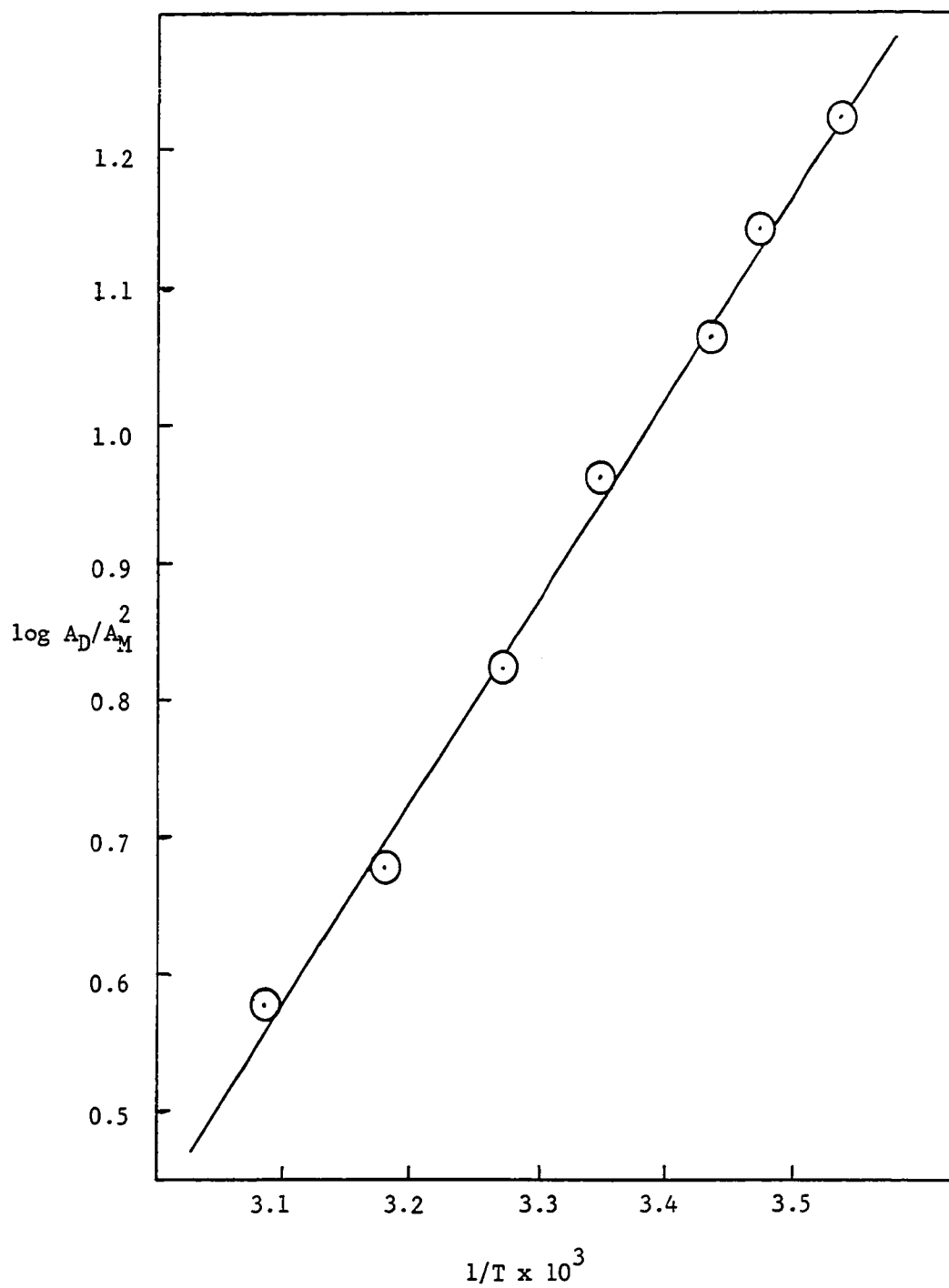


Figure 13. $\log A_D/A_M^2$ vs. $1/T$ Plot for TFA-C₂H₄Cl₂ System.

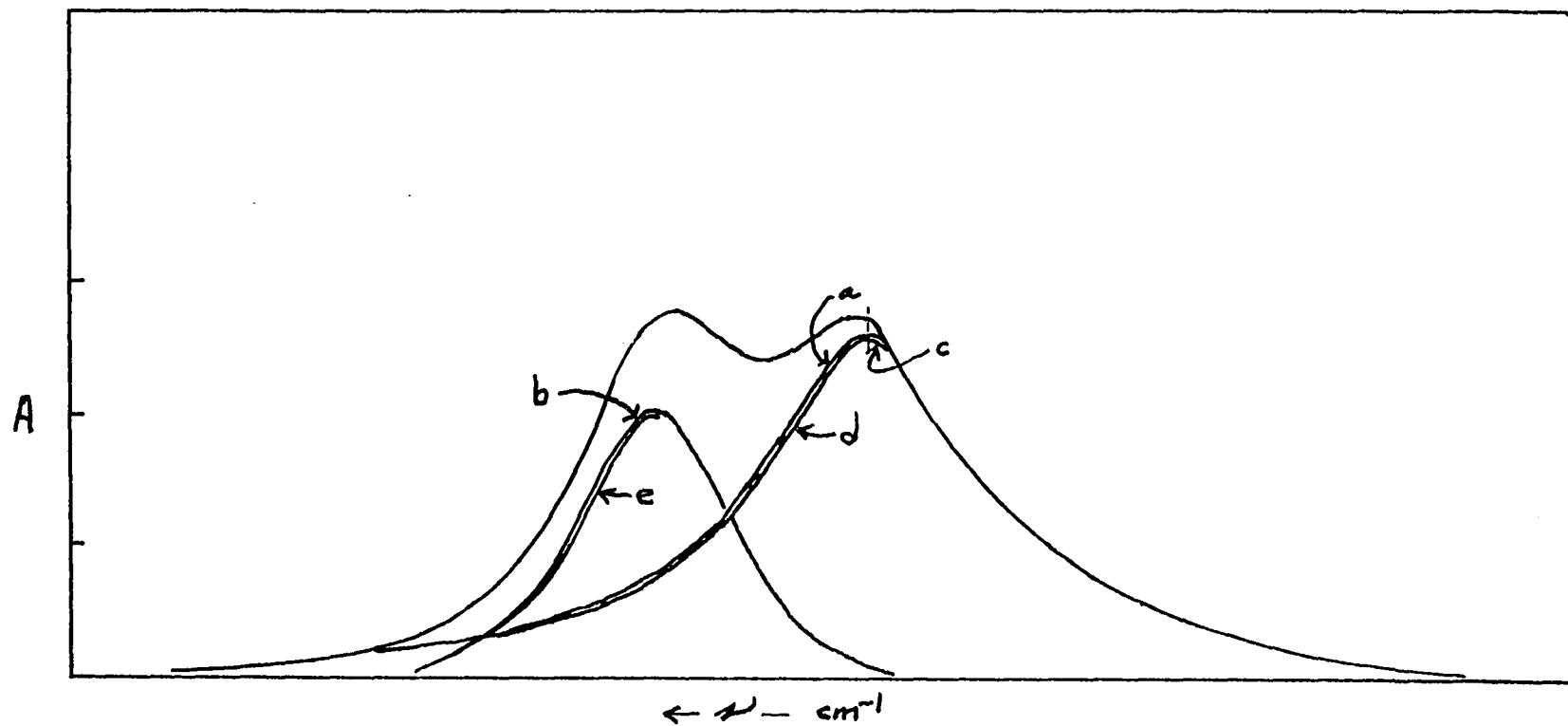
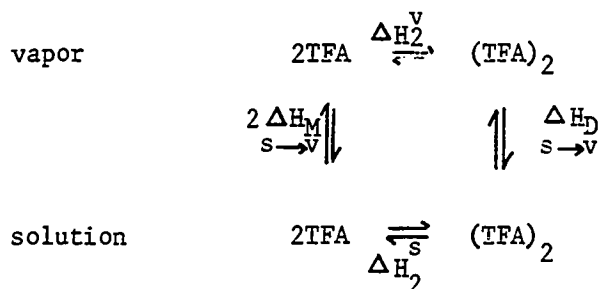


Figure 14. TFA Carbonyl Spectrum in $C_2H_4Cl_2$ at $32.8^{\circ}C$.

until the individual bands are consistent with the overall band envelopes; in most cases no more than two reflections of the dimer peak were required. Some disagreement between calculated and observed curves exceeding the experimental error of about ± 0.005 Å was noted in the valley region between the apparent peak maxima; however, quite good agreement was obtained over the peak maxima.

The energies involved in partitioning TFA between vapor and solution, as in the vapor-solution method, may be represented by the thermodynamic cycle



For the cycle, $\Delta H_2^v + \Delta H_D^v - \Delta H_2^s + 2\Delta H_M^v = 0$. The association enthalpies in the vapor, ΔH_2^v , and in solution, ΔH_2^s , are known. The enthalpies associated with the transfer of monomer and dimer molecules from solution to vapor can be obtained from the temperature dependence of the respective Henry's law constants. The vapor-solution method was used to obtain these quantities.

Tables 14 through 17 contain the data obtained for the four solvent systems. Formal TFA concentrations were calculated as before and were corrected for solvent density changes. Equilibrium constants at the lower temperatures were calculated from the known association enthalpies and equilibrium constants at 25°C. It was assumed that the vapor phase absorptivity of the TFA monomer hydroxyl peak does not

$t^{\circ}\text{C}$	A_M^v	$f_A, \text{ M}$	$p_M \text{ mm}$	$K_2^v \text{ mm}^{-1}$	$p_D \text{ mm}$	$K_2^s \text{ M}^{-1}$	$C_M \text{ M}$	$C_D \text{ M}$	$K_H^M \text{ mm M}^{-1}$	$K_H^D \text{ mm M}^{-1}$
25	.400	.0382	5.18	.30	8.19	192	.0088	.0147	590	556
18	.290	.0386	3.76	.52	7.29	305	.0072	.0157	522	464
10	.202	.0389	2.62	1.02	7.00	550	.0055	.0167	476	419

Data for Calculation of ΔH_M and ΔH_D in the TFA- C_6H_{12} System

$s \rightarrow v$ $s \rightarrow v$

Table 14

t_C^o	A_M^v	f_A, M	$p_M \text{ mm}$	$K_2^v \text{ mm}^{-1}$	$p_D \text{ mm}$	$K_2^s M^{-1}$	$C_M M$	$C_D M$	$K_H^M \text{ mm M}^{-1}$	$K_H^D \text{ mm M}^{-1}$
25	.218	.0385	2.82	.30	2.42	149	.0098	.0144	275	168
25	.296	.0668	3.83	.30	4.48	149	.0134	.0267	275	168
25	.256	.0513	3.31	.30	3.34	149	.0115	.0199	275	168
10	.137	.0681	1.77	1.02	3.20	340	.0093	.0294	190	109
10	.120	.0523	1.55	1.02	2.45	340	.0080	.0222	194	110
10	.107	.0392	1.38	1.02	1.94	340	.0069	.0162	200	120

Data for Calculation of ΔH_M and ΔH_D in the TFA-CCl₄ System
 $s \rightarrow v$ $s \rightarrow v$

Table 15

t °C	A_M^V	f_A , M	p_M mm	K_2^V mm ⁻¹	p_D mm	K_2^S M ⁻¹	C_M M	C_D M	K_H^M mm M ⁻¹	K_H^D mm M ⁻¹
25	.224	.130	2.90	.30	2.56	2.6	.089	.021	32.5	122
18	.131	.166	2.15	.52	2.38	3.5	.083	.024	25.9	99
10	.133	.114	1.48	1.02	2.24	5.1	.075	.029	19.8	77

Data for Calculation of ΔH_M and ΔH_D in the TFA-C₆H₆ System
 $s \rightarrow v$ $s \rightarrow v$

Table 16

$t^{\circ}\text{C}$	A_M^v	f_A, M	$p_M \text{ mm}$	$K_2^v \text{ mm}^{-1}$	$p_D \text{ mm}$	$K_2^s M^{-1}$	$C_M M$	$C_D M$	$K_H^M \text{ mm, } M^{-1}$	$K_H^D \text{ mm } M^{-1}$
25	.346	.294	4.48	.30	6.12	1.5	.188	.053	23.8	115
18	.254	.297	3.29	.52	5.58	2.0	.174	.062	18.9	90
10	.174	.300	2.25	1.02	5.16	2.8	.158	.071	14.2	73

Data for Calculation of $\Delta H_{M_{s \rightarrow v}}$ and $\Delta H_{D_{s \rightarrow v}}$ in the TFA- $\text{C}_2\text{H}_4\text{Cl}_2$ System

Table 17

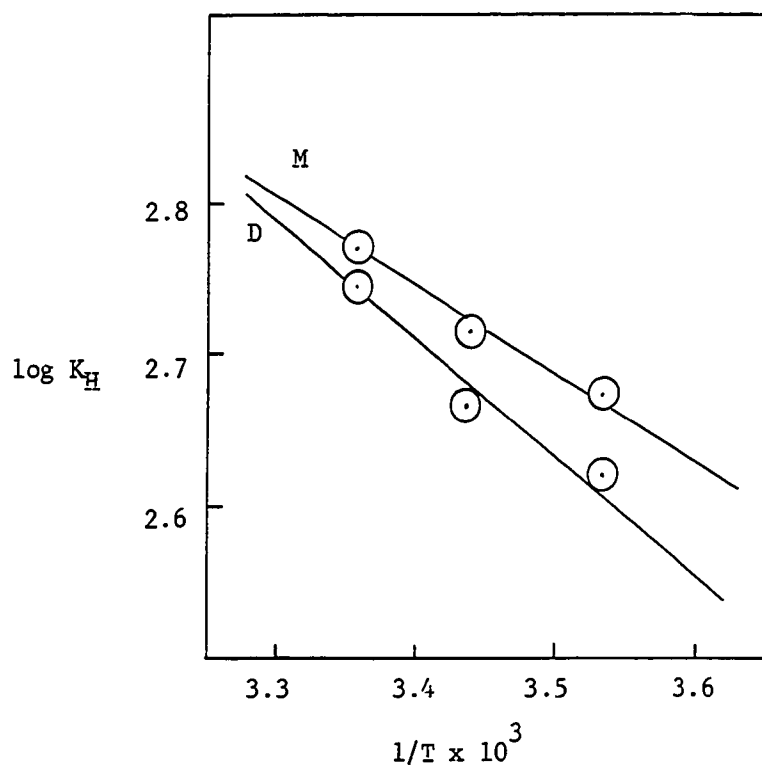


Figure 15. $\log K_H$ vs. $1/T$ Plot for TEA-C₆H₁₂ System.

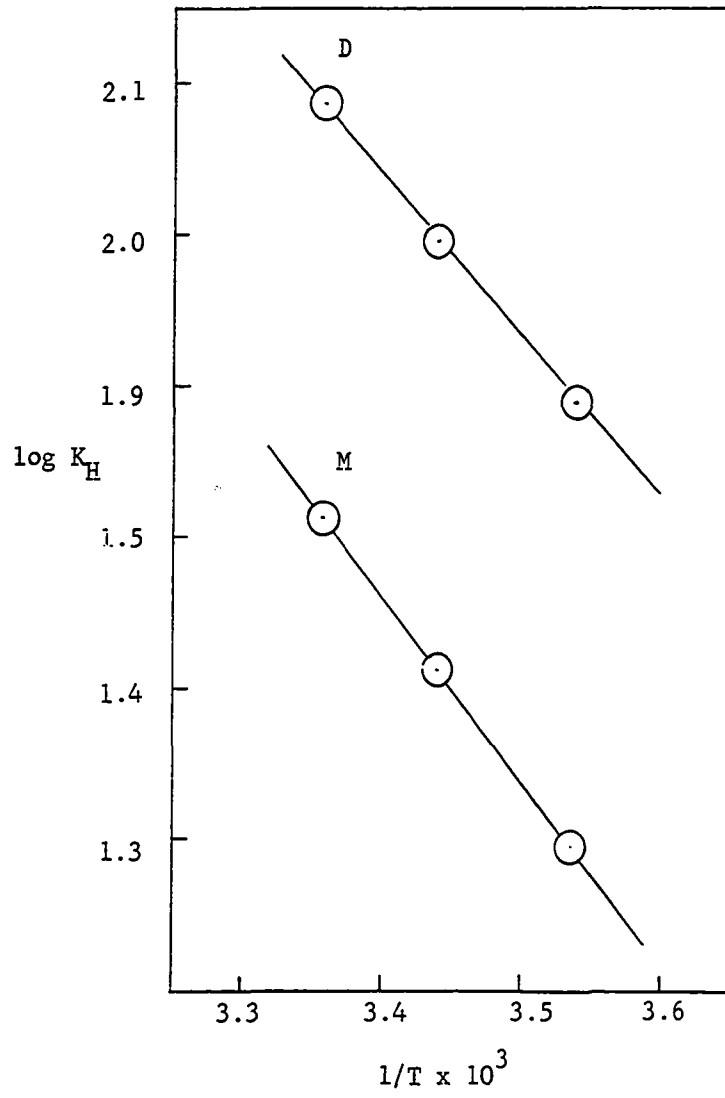


Figure 16. $\log K_H$ vs. $1/T$ Plot for C_6H_6 System.

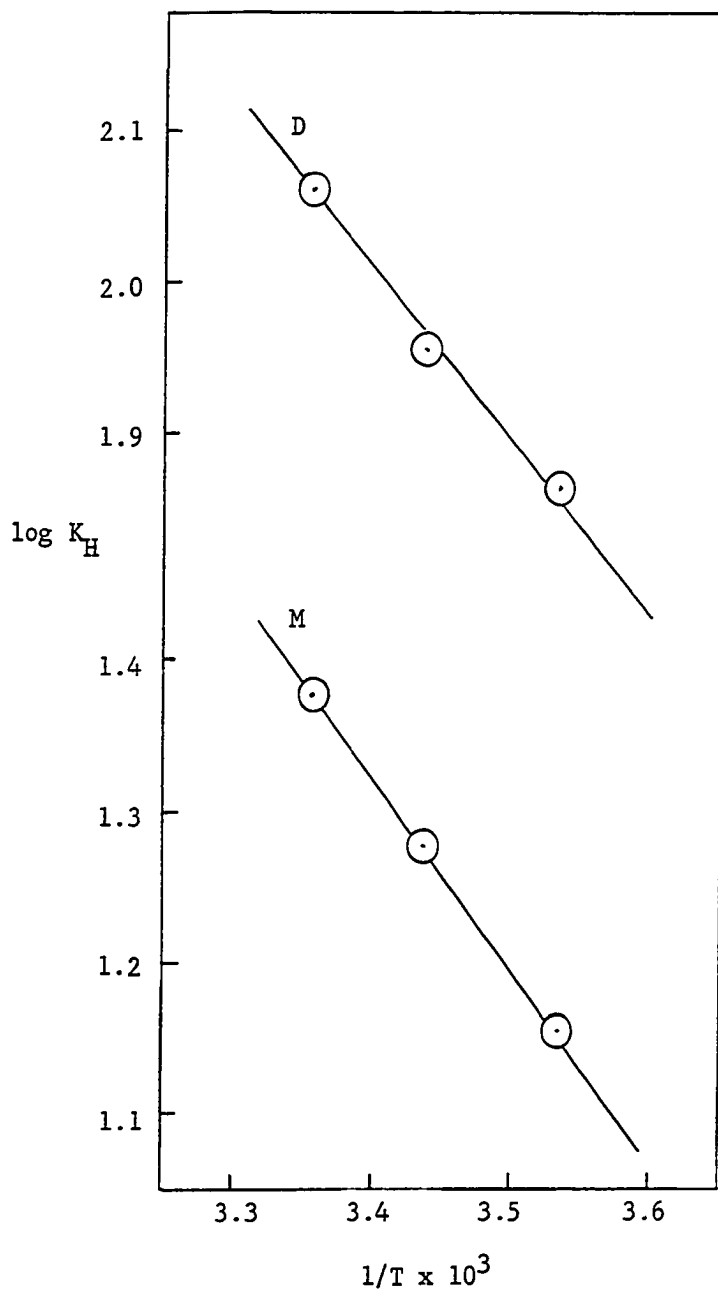


Figure 17. $\log K_H$ vs. $1/T$ Plot for TFA- $C_2H_4Cl_2$ System.

change with temperature. Monomer and dimer concentrations and pressures were calculated from these quantities. In the benzene system the solution ΔH_2 was assumed to be - 7.5 kcal/mole. This value was obtained by comparison with the enthalpy changes in the carbon tetrachloride and 1,2-dichloroethane systems and the similarity in solvation properties of benzene and 1,2-dichloroethane. While assumption of this value casts more uncertainty on the results for the benzene system it seems to be a reasonable estimate in light of the determined equilibrium constants and hydroxyl frequency shifts and the results reported by Allen, et al.²⁵ Figures 15, 16, and 17 are the $\log K_H$ vs. $1/T$ plots from which the ΔH 's were determined. The temperature range of these measurements was limited because of fogging of the cell windows. Results of this study are summarized below.

Table 18

Enthalpies of Vaporization of TFA Monomer and Dimer from Solution

Solvent	$\Delta H_{s \rightarrow v}^M$ <u>kcal</u> mole	$\Delta H_{s \rightarrow v}^D$ <u>kcal</u> mole
C_6H_{12}	2.7	3.6
CCl_4	3.8	4.4
C_6H_6	5.6	4.9
$C_2H_4Cl_2$	5.7	5.5

CHAPTER V

DISCUSSION AND CONCLUSIONS

In order to facilitate the discussion of the results obtained in this research on the hydrogen bonding behaviour of TFA, this chapter is divided into three major sections. Thermodynamic data for the association of TFA will be considered in the first section along with thermodynamic data describing the solution to vapor distribution of TFA. In the second section the effect of solvation on the association parameters of TFA will be examined in terms of the method of predicting solvation effects proposed by Christian and co-workers.²⁶ The use of group interaction energies (as developed in the Appendix) in calculating the parameter α will also be considered in this section. The last section of the discussion is devoted to empirical correlations of solvent induced frequency shifts of the TFA free and associated hydroxyl and carbonyl stretching bands and with various thermodynamic properties of the association reaction.

Thermodynamic Data

Thermodynamic data for the self-association of TFA in the vapor phase and the four solvents used in this study are summarized in Table 19. Entropy changes are based on standard states of one mole/liter.

Each system is adequately described by the monomer-dimer association scheme. In the few instances where literature results on the association of TFA in solution are available for comparison, good agreement is obtained. The association enthalpy in carbon tetrachloride solution ($-9.2 \pm .4$ kcal/mole from dilute solution equilibrium constants) agree quite well with each other and with the -8.85 kcal per mole value reported by Kagarise.¹⁵ The dimerization constant at 25°C in cyclohexane, 192 l/m, obtained by the vapor-solution method, is in fair agreement with the value 320 l/m reported by Thyriou and Decroocq from a dielectric study.²³ Thermodynamic parameters obtained for the TFA-carbon tetrachloride system by the vapor-solution and dilute solution methods are also in fair agreement. Taking the dilute solution work as a reference, the close agreement with the vapor-solution method implies that systematic errors have largely been eliminated from it.

In order to compare the thermodynamics of association of TFA with other substituted acetic acids, some of the available data from the literature are compiled in Table 20. Fairly complete data are available for the acids in carbon tetrachloride solution, but for the most part only equilibrium constants are available in benzene solution. It is seen that there is a marked decrease in the dimerization constant in both solvents as the electronegativity of the acid substituent increases. Enthalpy and entropy changes, in carbon tetrachloride solution, show some variation but exhibit no trend with type of substituent. There is a pronounced decrease in the equilibrium constant upon going from carbon tetrachloride to benzene as solvent for

Table 19

Thermodynamic Functions for the Dimerization of TFA

T = 298°K

Solvent	K ₂ , l/m	-ΔH, kcal/mole	-ΔS°, e.u./mole
vapor	5660 ± 370	14.0 ^b	29.8
C ₆ H ₁₂	192 ± 36	11.7 ± .6	28.7 ± 2.8
CCl ₄	149 ± 19	9.2 ± .4	21.0 ± 2.0
	128 ± 7 ^a	9.0 ± .4	20.6 ± 1.4
C ₆ H ₆	2.6 ± .9	(7.5) ^c	(23.3) ^c
C ₂ H ₄ Cl ₂	1.5 ± .4	7.0 ± .8	22.7 ± 3.2

^a dilute solution method values
^b C. Ling, reference¹⁶
^c estimated

all of the acids; the decrease is particularly large in the case of TFA. This decrease in the dimerization constant of TFA might be expected in view of the much greater acidity of TFA and the possibility of more extensive monomer-solvent interaction.

As shown in Table 19 there is a marked decrease in the TFA dimerization constant upon going from the vapor phase to solution. In solution K_2 decreases as the interacting ability of the solvent increases, i.e., in the order cyclohexane > carbon tetrachloride > benzene > 1,2-dichloroethane. A like trend is observed for the association enthalpy. The entropy function, interestingly, does not exhibit such a trend. ΔS values fall into two groups: vapor phase and cyclohexane values are of similar magnitude as are the carbon tetrachloride, benzene and 1,2-dichloroethane values. In comparison, the association entropy values for benzoic acid reported by Allen, et al.,²⁵ show a pronounced decrease in the solvents cyclohexane, carbon tetrachloride, and benzene, in that order.

In Table 21 are given the Henry's law constants and enthalpy changes for the solution to vapor distribution of TFA monomer and dimer species. The K_H 's indicate increasing solvation of the monomer in the order cyclohexane < carbon tetrachloride < benzene < 1,2-dichloroethane with a considerable increase shown between carbon tetrachloride and benzene solution. The enthalpy change for transferring a mole of monomer from solution to the vapor phase increases in the same order; here, however, the biggest difference in solvation occurs between cyclohexane and the three other solvents. The enthalpy changes for transfer of monomer or dimer from solution to the vapor phase show several

Table 20

Thermodynamic Functions for the Dimerization of

Various Substituted Acetic Acids

T = 298°K

Carbon Tetrachloride Solution

Acid	K ₂ , l/m	-ΔH, kcal/mole	-ΔS°, e.u./mole
Trimethylacetic ⁶	2750 ± 150	9.6 ± .5	16.1
Acetic ³²	2020 ± 250	10.7 ± 1.2 10.7 (15)	20.8
Trichloroacetic ³²	271 ± 30	7.9 ± 1.2 10.3 (15)	15.4
Trifluoroacetic	149 ± 19	9.2 ± .4 8.85 (15)	21.0 ± 2.0

Benzene Solution

Acid	K ₂ , l/m
Trimethylacetic ³⁴	420
Acetic ³⁵	360
Trichloroacetic ³⁶	24
Trifluoroacetic	2.6 ± .9

Table 21

Henry's Law Constants and Solution $\rightarrow$ Vapor

Distribution Enthalpies for TFA

	C_6H_{12}	CCl_4	C_6H_6	$C_2H_4Cl_2$
$K_H^M, \text{ mm M}^{-1}$	592 ± 110	275 ± 35	32.5 ± 3.5	23.8 ± 4.2
$K_H^D, \text{ mm M}^{-1}$	556	168	122	115
$\Delta H_{M, s \rightarrow v}, \text{ kcal/mole}$	2.7	3.8	(5.6) ^a	5.7
$\Delta H_{D, s \rightarrow v}, \text{ kcal/mole}$	3.6	4.4	(4.9) ^a	5.5

^a using estimated ΔH_2

significant features. First, in progressing from the least active (in the sense of solvating ability) solvent, cyclohexane, to the most active, 1,2-dichloroethane, the TFA monomer is increasingly extensively solvated. In cyclohexane and carbon tetrachloride the monomer solvation energy is slightly less than the dimer solvation energy; in both benzene and 1,2-dichloroethane the monomer is solvated to a slightly greater extent than the dimer. Secondly, it is seen that the dimer solvation energy also increases regularly from cyclohexane to 1,2-dichloroethane solution.

The TFA free hydroxyl-stretching spectra qualitatively show the same trend in solvation effects in the frequency shifts from the vapor phase to solution. The vapor to solution frequency shifts, $\nu_M^V - \nu_M^S$, (Table 9) fall into the same two groups to do the monomer Henry's law constants; cyclohexane and carbon tetrachloride in one and benzene and 1,2-dichloroethane in the other. The associated hydroxyl-stretching band, found at approximately $3115 \pm 5 \text{ cm}^{-1}$ in the four solvents, does not reflect the trend shown by the dimer Henry's law constants. Rather, this indicates that the hydrogen bonded hydroxyl group is in roughly the same environment in each of the solvents. This is in accord with the view that solvent frequency shifts are primarily due to specific interactions.

Correlation of Solvent Effects by the
Method of Christian, et al.²⁶

One of the major problems encountered in studies of association reactions is predicting variations of the association reaction thermodynamic parameters as the solvent is changed. Qualitatively, the

solubility of water in various organic solvents is a good index to solvation ability. Attempts have been made to correlate thermodynamic properties of association reactions with solvent dielectric constant but this has generally been an unsuccessful approach.^{1,3} The method of predicting solvent effects on association reaction thermodynamics recently proposed by Christian and co-workers²⁶ has been successfully applied to several hydrogen bonding reactions in a variety of solvents.^{27,28}

The data describing the self-association of TFA and its distribution between solution and vapor may be treated by and used to examine the validity of the solvation theory of Christian, et al.,²⁶ in several ways. The parameter α may be obtained from the equilibrium constants and Henry's law constants by a log-log plot of equation 26. The slope of this plot is $\alpha - 1$.

$$K_2^s/K_2^v = (K_D^2)^{\alpha-1} \quad (26)$$

K_D is the reduced (or relative) solution-vapor distribution constant of the monomer. It may be calculated from the monomer Henry's law constant. K_H in mm/molar units is converted to the vapor standard state of one mole per liter by multiplying by the factor $5.38(10^{-5})$ mole/liter/mm (at 25°C). K_D is then taken as K_H^{-1} . The relevant data are given in Table 22. Figure 18 is the $\log K_2$ vs. $2 \log K_D$ or α -plot.

It was expected from the solvation theory that the parameter α would be nearly constant for a given association reaction in various non-polar solvents. The α -plot of the TFA data appears to define two lines. The carbon tetrachloride, cyclohexane and vapor phase data define a line giving an $\alpha = 0.55$. Considering the vapor phase, benzene

Solvent	$\log K_2$	$K_H^M, \text{ mm M}^{-1}$	$K_H^M, \frac{M^V}{M^S}$	$K_D = \frac{1M}{K_H^M}$	$2 \log K_D$
Vapor					
C_6H_{12}	2.283	592	0.0319	31.4	2.994
CCl_4	2.179	275	0.0148	68.5	3.672
C_6H_6	0.415	32.5	0.00175	571	5.512
$\text{C}_2\text{H}_4\text{Cl}_2$	0.176	23.8	0.00128	780	5.784

Data for the Graphical Determination of the Parameter α

Table 22

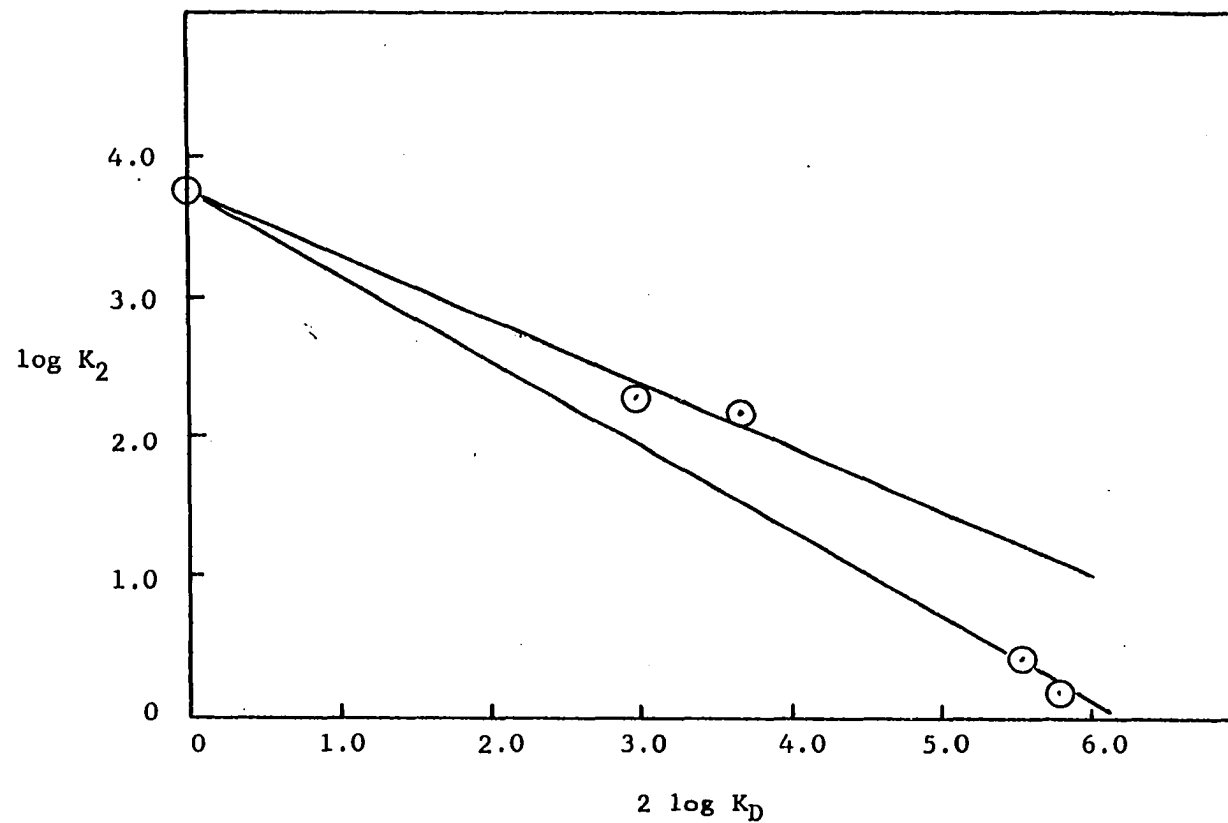


Figure 18. $\log K_2$ vs. $2 \log K_D$ Plot for Determination of the Parameter α .

and 1,2-dichloroethane data together gives an α of 0.39. This is not surprising considering that the spectral and thermodynamic parameters are similarly grouped.

Values of α may be obtained directly for each solvent from the monomer solution-vapor distribution enthalpies by using equation 27.

$$\alpha = \frac{\frac{\Delta U_{A,s \rightarrow v}^2}{2 \Delta U_{s \rightarrow v}^A}}{\quad} \quad (27)$$

It is necessary to subtract 0.6 kcal from the $\Delta H_{s \rightarrow v}$ values to obtain $\Delta U_{s \rightarrow v}$. Internal energies are used here because of the irrelevance of the $P\Delta V$ term to solvation energies. α values calculated in this manner are given below.

Solvent	C ₆ H ₁₂	CCl ₄	C ₆ H ₆	C ₂ H ₄ Cl ₂
α	0.72	0.59	0.43	0.48

Considerable variation in the value of the parameter α is seen. Part of the difference undoubtedly arises from the uncertainty of the $\Delta U_{s \rightarrow v}$ values, especially in the case of the cyclohexane data.

Specific monomer-solvent interaction effects could account for the lower value of α in the solvents benzene and 1,2-dichloroethane. This is supported by the hydroxyl frequency shifts discussed above. It is known that the hydroxyl group in acids and alcohols can interact with pi-electron systems.^{37,38} While only a single monomer hydroxyl peak was observed in these two solvents, the half-peak-height band width showed a two- to three-fold increase over that in cyclohexane or carbon tetrachloride.

The parameter α may be estimated from group interaction energies given in the Appendix by calculating the energy of vaporization of TFA monomer and dimer from infinitely dilute solution and using equation 27. In terms of the individual group interaction energies, the $\Delta U_{s \rightarrow v}$'s are given by the equations (from equation 3 of the Appendix) below.

$$\Delta U_{A_2} = 6\epsilon_{FH_1} + 2\epsilon_{O'H_1} + 4\epsilon_{OH_1} - 6\epsilon_{H_1H_1}$$

$$\Delta U_A = 3\epsilon_{FH_1} + 2\epsilon_{O'H_1} + 2\epsilon_{OH_1} + \epsilon_{OHH_1} - 4\epsilon_{H_1H_1}$$

Cyclohexane is the solvent chosen for this sample calculation. The terms ϵ_{FH_1} , $\epsilon_{O'H_1}$, ϵ_{OH_1} , ϵ_{OHH_1} , and $\epsilon_{H_1H_1}$ refer to the fluoro-, keto-oxygen lone-pair electrons-, etheric oxygen lone-pair electrons-, hydroxyl group-, and solvent-solvent group interactions. Substitution of the appropriate interaction energies for the specific groups, from Table 29. in the Appendix, gives the following results: $\Delta U_{A_2} = 5.4$ kcal and $\Delta U_A = 6.2$ kcal. From equation 27 α is found to be 0.44. This is slightly lower than the value 0.55 obtained from the α -plot and considerably lower than the 0.72 obtained from experimentally determined ΔU_{A_2} and ΔU_A . Values of α from group interaction energies in carbon tetrachloride and benzene are 0.59 and 0.56. It was necessary to estimate the interaction energies ϵ_{FC1} , $\epsilon_{FH'}$, and $\epsilon_{O'H_1}$ in these calculations, since the required heat of mixing data were not available for their calculation. The estimation was accomplished by comparing series of similar interaction energies and recognizing trends within the appropriate group-solvent interactions. The values used were 1.0, 1.2, and 2.0 kcal, respectively. These values are in slightly better agreement, although still lower than,

the α 's from the α -plot and experimental ΔU_s 's: $\alpha = 0.55$, and 0.59 , respectively for the carbon tetrachloride system; $\alpha = 0.39$, and 0.43 , respectively, for the benzene system.

Calculation of α from group interaction energies for association reactions in solvents with two or more different sites, such as 1,2-dichloroethane, presents a problem since the ϵ_{ij} 's were derived by considering only solvents with a single site. This problem was treated by taking the arithmetic mean of the individual interaction energies. For example, ϵ_{FE} (fluoro-1,2-dichloroethane interaction) was taken as $\frac{2}{5}\epsilon_{FH} + \frac{3}{5}\epsilon_{FCl}$. This gave ϵ_{FE} a value of 0.91 kcal. The remaining TFA-1,2-dichloroethane group interactions were obtained similarly. The value of α for TFA in 1,2-dichloroethane was found to be 0.42 from this type treatment. Comparatively, the α -plot gave $\alpha = 0.39$; experimental $\Delta U_{s \rightarrow v}$ yielded 0.48 . Table 23 summarizes the values obtained by the three independent methods.

The solvation theory of Christian, et al.,²⁶ is probably best tested in this case by comparison of predicted and observed enthalpy changes. From the available data there are two routes to this comparison. First, α values obtained from free energies (the α -plot) may be combined with the experimentally determined monomer enthalpy changes for the solution to vapor distribution by means of equation 28.

$$\Delta H_2^S = \Delta H_2^V - (\alpha - 1) (2 \Delta H_M)_{s \rightarrow v} \quad (28)$$

Alternately, the α values determined from the group interaction energies may be used. Both methods have been used and the results are presented in Table 24. The benzene system was not included in this

Table 23

Values of the Parameter α Calculated by Three Independent Methods

	<chem>C6H12</chem>	<chem>CCl4</chem>	<chem>C6H6</chem>	<chem>C2H4Cl2</chem>
α -plot	0.55	0.55	0.39	0.39
ΔU 's	0.72	0.59	0.43	0.48
s $\rightarrow$ v				
Group Inter- action Energies	0.44	0.59	0.56	0.42
Average Value α $\pm$ avg. dev.	$0.57 \pm .10$	$0.58 \pm .02$	$0.46 \pm .07$	$0.43 \pm .03$

Table 24

Experimental and Predicted Association Enthalpies

	<chem>C6H12</chem>	<chem>CCl4</chem>	<chem>C2H4Cl2</chem>
Experimental - ΔH	11.7	9.0	7.0
- ΔH , α from α -plot	11.5	10.5	7.2
- ΔH , α from group interaction energies	11.0	10.8	7.5

comparison because ΔH_M was determined from an assumed ΔH_2 . Good agreement between experimental and calculated values is observed except for the carbon tetrachloride system value. Here the calculated values are about 1.5 to 2 kilocalories higher than experimental. This may probably be accounted for by the uncertainty in the monomer distribution enthalpy. The agreement for the other two systems is within the estimated error of the experimental values.

From the standpoint of calculation of the parameter α from the group interaction energies, TFA does not appear to be a very good choice as a test compound because the strong inductive effect of the perfluoromethyl group makes the keto and etheric oxygen and hydroxyl group interactions atypical. While the assumption that group interaction energies are independent of other molecular structural factors is not strictly true, the variation in calculated solvation energies does not appear to severely effect the calculated values of the parameter α beyond use. Undoubtedly this is partly because the errors due to these variations tend to compensate in the calculation of α since a ratio of energies is taken.

Spectral Effects

The effect of solvent on IR absorption band frequencies is a subject closely related to the solvent effect on association thermodynamics. Considerable work has been done in attempting to correlate frequency shifts and solvent properties.³⁹ Frequency shifts in general have been treated from the standpoint of bulk dielectric effects--

such as the Kirkwood-Bauer-Magat relationship^{40,41}--and more recently, qualitative approaches have been made on the basis of specific solvent-solute interactions.^{42,43} The effect of solvent properties on the stretching vibrations of hydrogen bonded groups has been studied by a number of workers.^{3,44,45,46,47,77}

Bellamy and co-workers have studied the effect of solvent on the frequencies of a number of common bond vibrations and have suggested that frequency shifts may be correlated by plotting the relative frequency shift, $(\nu^v - \nu^s)/\nu^v$, against the relative shift of a reference compound.⁴² They propose the reference compound pyrrole for X-H type bonds and acetophenone for carbonyl bonds.⁴⁹ The $\Delta\nu/\nu$ vs. $(\Delta\nu/\nu)_R$ type plot should eliminate those solvent properties which operate to similar extents on both reference and test compound X-H bonds. Thus, if the frequency shifts were solely dependent upon some bulk property of the solvent, such as dielectric constant, a simple linear relationship with a slope of one should result, but if properties of the test molecule were also involved, a line of different slope would be obtained. In cases where the interaction between the test and reference solutes and any one solvent are entirely different in character a marked departure from the linear relationship should occur. Local association effects of a dipolar or hydrogen bonding nature are claimed to be the dominant factors in producing frequency shifts.

The effect of solvent of the monomer TFA hydroxyl-stretching vibration is quite pronounced compared with other hydroxyl compounds.

Frequency shifts, relative to the vapor phase, are given for TFA, trichloroacetic acid, acetic acid, phenol and methanol in the solvents used in this work in Table 25. The relative frequency shifts are plotted against the corresponding shifts for methanol in Figure 19. Methanol may be taken as the reference compound since it gives a slope of almost unity on a $\Delta\nu/\nu$ methanol against $\Delta\nu/\nu$ pyrrole plot.⁴⁸ In this plot linear relationships are observed, although the lines do not pass through the origin. In Figure 20, $\Delta\nu_{\frac{1}{2}}$ of TFA is plotted against $\Delta\nu_{\frac{1}{2}}$ of phenol. Again a nearly linear relationship is obtained. These plots indicate that the TFA hydroxyl group interacts in a similar manner, although to a greater extent, with a given solvent than do other less acidic hydroxyl compounds.

The monomeric carbonyl-stretching vibration of TFA reveals the same sort of linear relationship when the relative frequency shift is plotted against the relative frequency shift of acetophenone (Figure 21). The relevant data for TFA, and acetic acid are given in Table 26. The acetic acid data lie above those for TFA and both lines pass through the origin. The fact that the TFA data fall below those for acetic acid is not surprising considering again the nature of the perfluoromethyl group's inductive effect in reducing the electron density of the carbonyl oxygen, thereby reducing its potential for interacting with the solvent.

Allerhand and Schleyer⁴⁴ proposed the empirical free energy relationship $(\nu^0 - \nu^s)/\nu^s = aG$ for correlating hydrogen bonded IR vibrations; ν^0 is the vapor phase frequency of the X-H vibration in

	TFA			Methanol			Phenol		
	ν_{OH}^M	$\Delta \nu/\nu \times 10^3$	$\Delta \nu_{\frac{1}{2}}$	ν_{OH}^M	$\Delta \nu/\nu \times 10^3$	ν_{OH}^M	$\Delta \nu/\nu \times 10^3$	$\Delta \nu_{\frac{1}{2}}$	
Vapor	3589			3685		3652			
C ₆ H ₁₂	3519	19.5	46	3646	10.6	3616	9.6	13.0	
CCl ₄	3508	22.6	65	3646	11.1	3611	11.0	17.03	
C ₆ H ₆	3390	55.5	105	3615	19.0	3563	24.4	57.0	
C ₂ H ₄ Cl ₂	3381	58.0	183	3618	18.2	3558	25.7	41.0	

Acetic Acid⁵⁸

ν_{OH}^M $\Delta \nu/\nu \times 10^3$

3584

--

3536

12.5

3466

32.1

--

Trichloroacetic Acid⁵⁸

ν_{OH}^M $\Delta \nu/\nu \times 10^3$

3583

--

3508

20.5

3389

54.0

--

Relative Frequency Shifts for Several Hydroxyl Compounds

Table 25

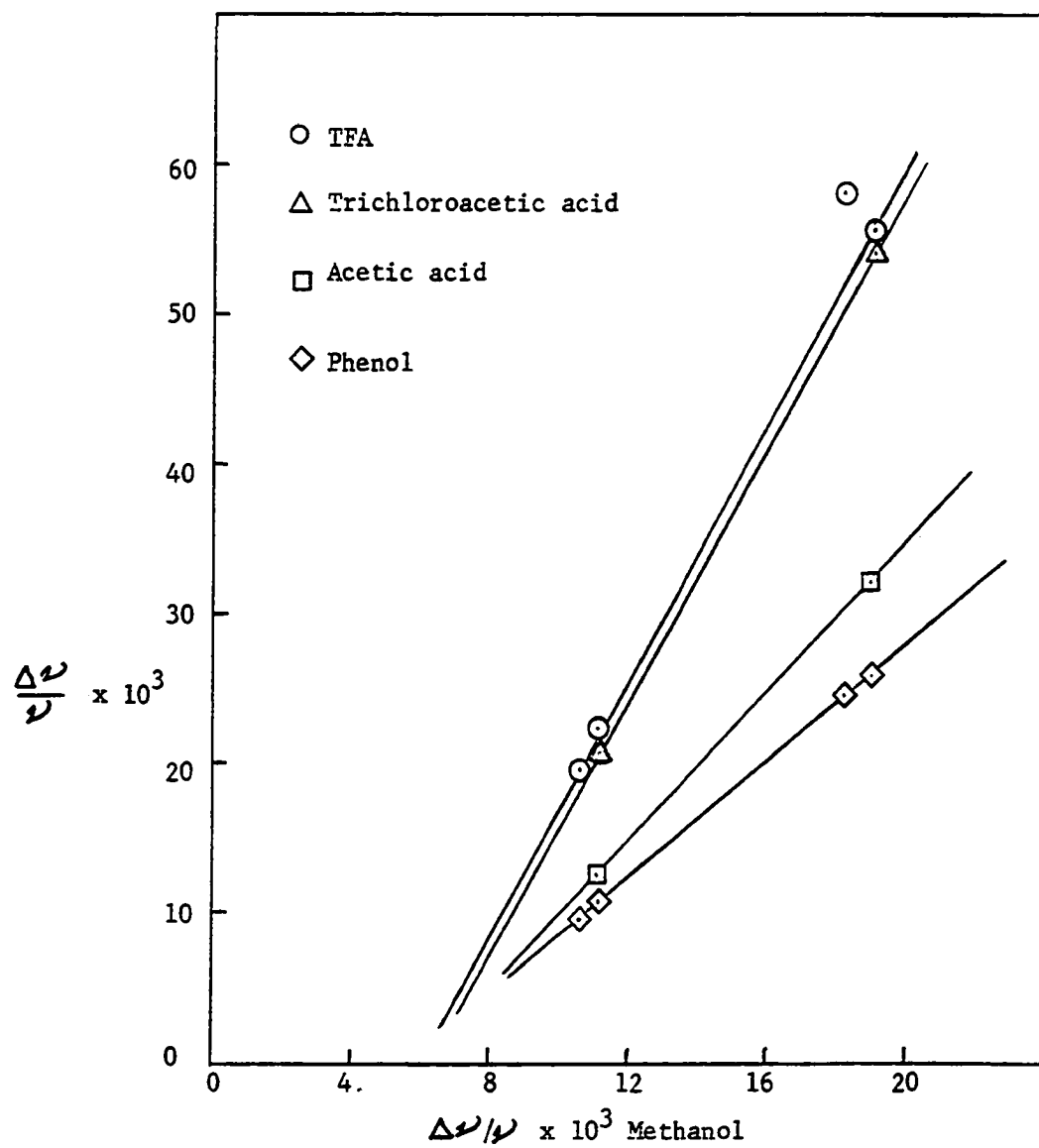


Figure 19. $\frac{\Delta n}{n}$ vs. $\frac{\Delta n}{n}$ Methanol Plot for Several Hydroxyl Compounds.

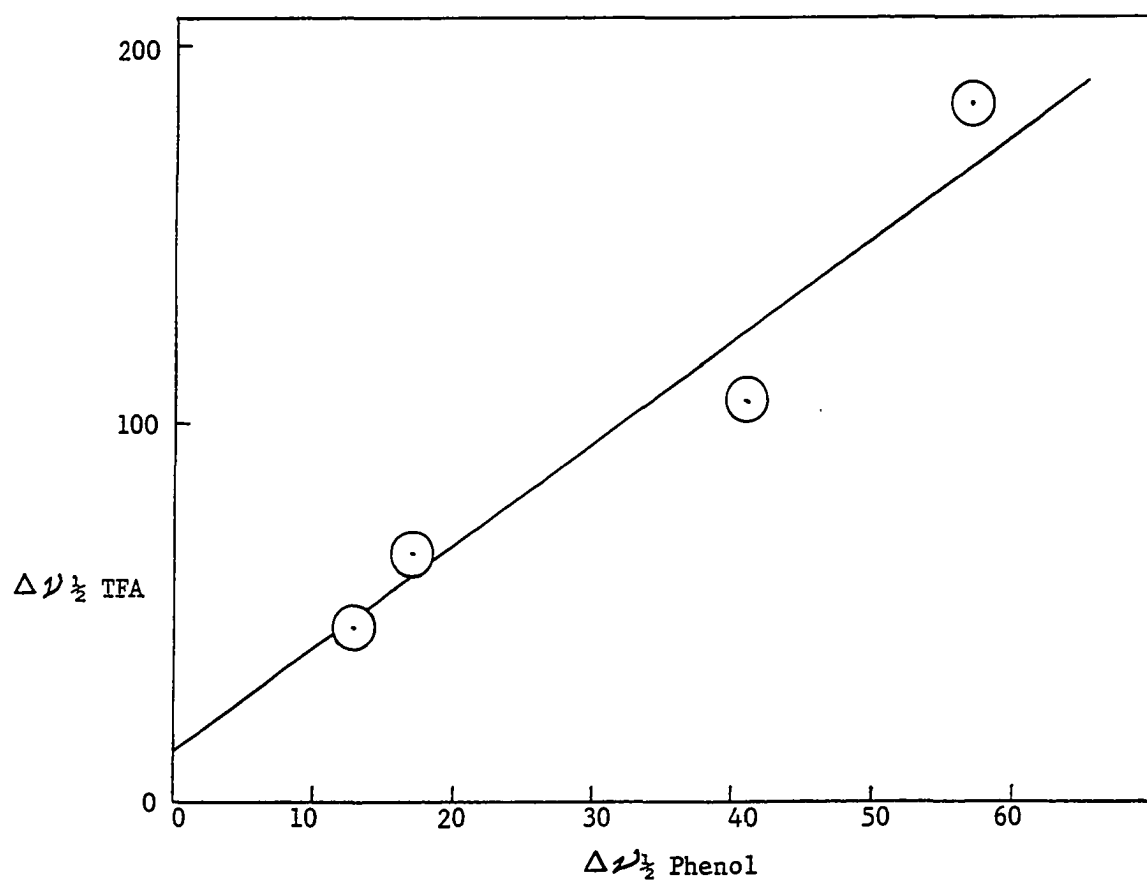


Figure 20. $\Delta\nu_{\frac{1}{2}}$ TFA vs. $\Delta\nu_{\frac{1}{2}}$ Phenol Plot.

	TFA		Acetic Acid ¹²²		Acetophenone ⁴⁹
	$\nu_{\text{C}=\text{O}}^{\text{M}}$	$\Delta \nu/\nu \times 10^3$	$\nu_{\text{C}=\text{O}}^{\text{M}}$	$\Delta \nu/\nu \times 10^3$	$\Delta \nu/\nu \times 10^3$
Vapor	1830		1791		
C ₆ H ₁₂	1816	7.6	1773	10.0	7.6
CCl ₄	1813	9.3	1762	10.0	9.9
C ₆ H ₆	--		1767	13.4	11.1
C ₂ H ₄ Cl ₂	1805	13.6	1762	16.2	13.5

Relative Carbonyl Frequency Shifts for TFA, Acetic Acid and Acetophenone

Table 26

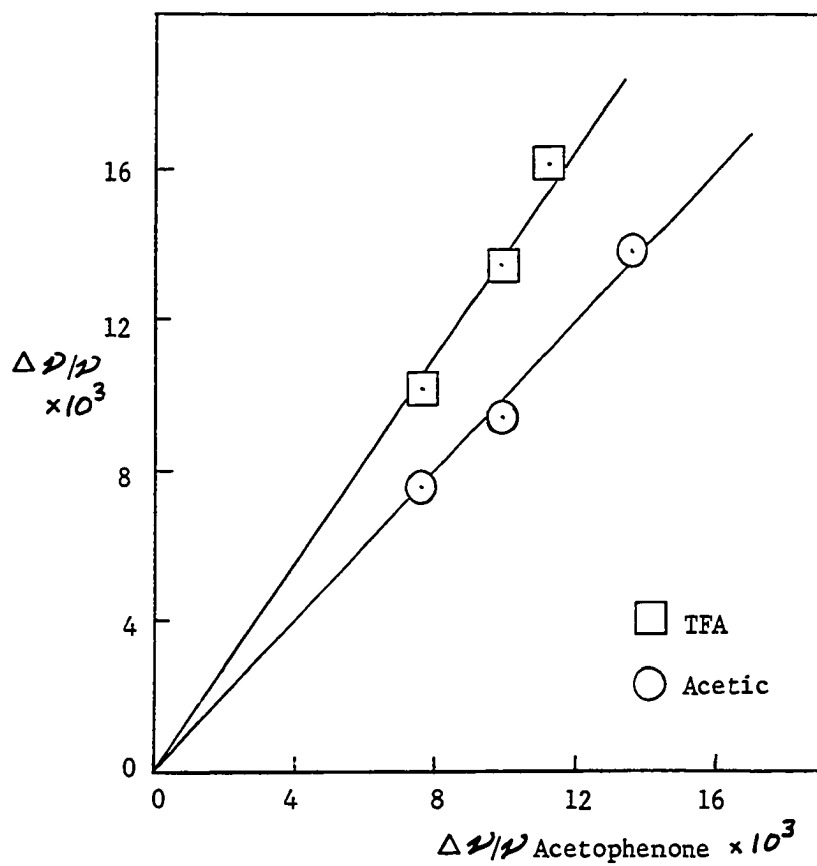


Figure 21. $\Delta D/D$ TFA Free Carbonyl and Acetic Acid Free Carbonyl vs. $\Delta D/D$ Acetophenone.

the complex, ν^s is the solution value of the same vibration. a is a function of the particular vibration and is a measure of its solvent sensitivity. G is a function of the solvent only, determined from the solvent shift of various carbonyl compounds. G has the value 0, 49, 69, 80 and 95 in the vapor phase, cyclohexane, carbon tetrachloride, benzene and 1,2-dichloroethane, respectively. The TFA associated hydroxyl frequency data are plotted, in Figure 22, according to the above equation. The plot does not appear to be linear. This is in accord with specific interaction approach to solvent shifts.^{42,49} Since the O—H group is already involved in hydrogen bonding it is not available to interact with the solvent. Therefore the O—H group is in a relatively constant environment. It should be observed, however, that it is rather difficult to determine accurate values of the frequencies in solution because the bands are broad and overlap significantly.^{51,52}

The associated carbonyl-stretching band exhibits virtually the same frequency in cyclohexane and carbon tetrachloride. In 1,2-dichloroethane, however, it is found some seven or eight cm^{-1} higher. This is interesting considering that the free carbonyl frequency in 1,2-dichloroethane correlated well with the corresponding frequencies in cyclohexane and carbon tetrachloride.

Many attempts have been made to correlate spectral changes with other properties of hydrogen bonding systems.³ Badger and Bauer⁵³ proposed a linear relationship between the difference in free and associated hydroxyl stretching bands and the association enthalpy. The TFA data, plotted in this form in Figure 23, indicate the relationship between $\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{D}}$ and ΔH_2 is not a simple one. Such a

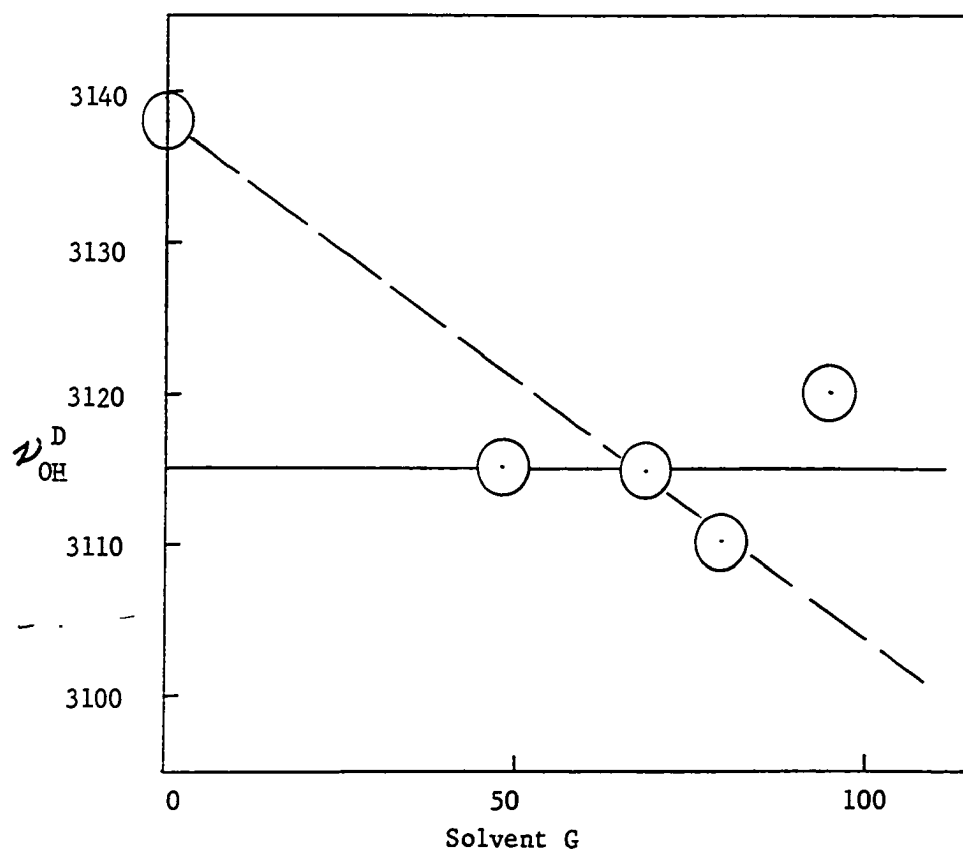


Figure 22. TFA Associated Hydroxyl Frequency vs. Solvent G.

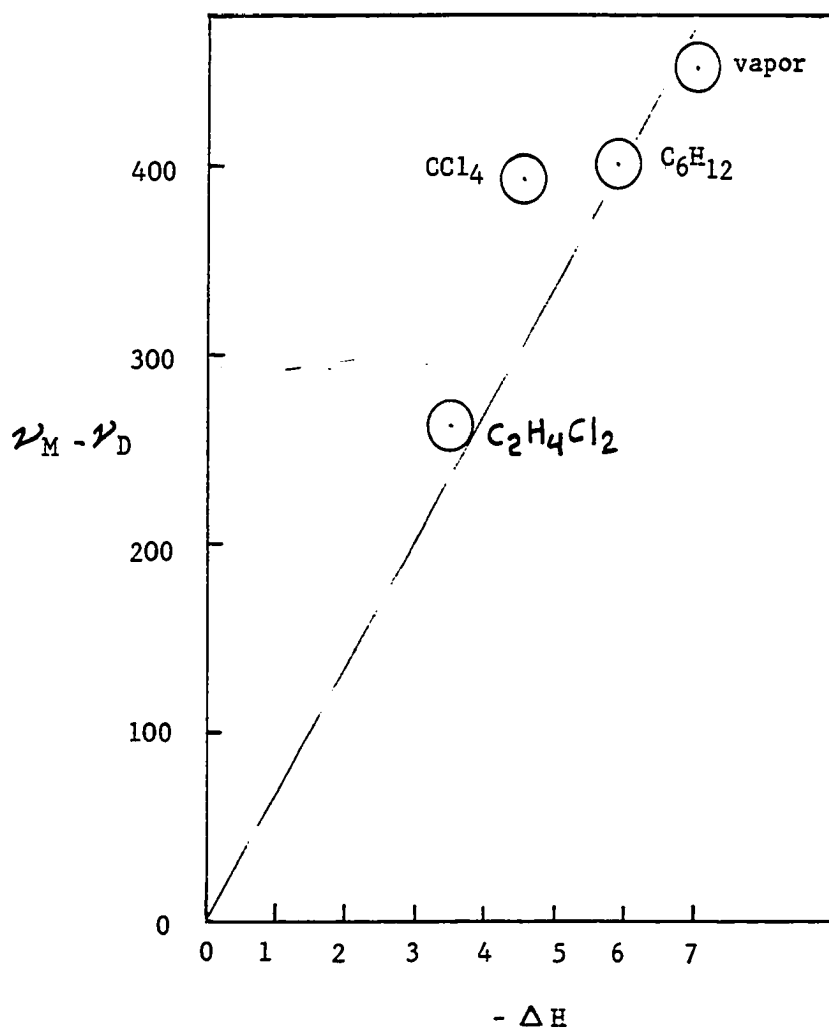


Figure 23. $\nu_M - \nu_D$ vs. $-\Delta H$ Plot for TFA.

relationship is, however, of qualitative value.

Josien⁵⁴ noted a systematic correlation between $\nu^v - \nu^s$ for either methanol or pyrrole and the Henry's law constant of HCl in a series of aromatic solvents. A nearly linear relationship obtains (Figure 24) between the frequency shift of the TFA monomer hydroxyl group upon going from vapor to solution and the logarithm of the monomer Henry's law constant. The data tend to cluster, as in the α -plot, into two groups; cyclohexane and carbon tetrachloride in one and benzene and 1,2-dichloroethane in the other. This again indicates the similarity of the solvation effect on spectra and thermodynamic parameters and points to the importance of specific solute-solvent interactions.

A relationship between $\nu_{OH}^v - \nu_{OH}^s$ and $\Delta H_{M, s \rightarrow v}$ might be expected on the basis of similarity of spectral and thermodynamic solvation effects. Figure 25 is such a plot. A roughly linear relationship is obtained and it is seen that the data again fall into two groups; the 'inert' solvents cyclohexane and carbon tetrachloride and the 'active' but non-polar solvents benzene and 1,2-dichloroethane.

It is clear that the TFA monomer hydroxyl group interacts strongly with benzene and 1,2-dichloroethane. An interesting extension would be the spectral study of the ternary systems TFA-benzene- and TFA-1,2-dichloroethane-carbon tetrachloride in order to observe spectral effects of the specific TFA interaction and also to obtain thermodynamic parameters for the interaction.

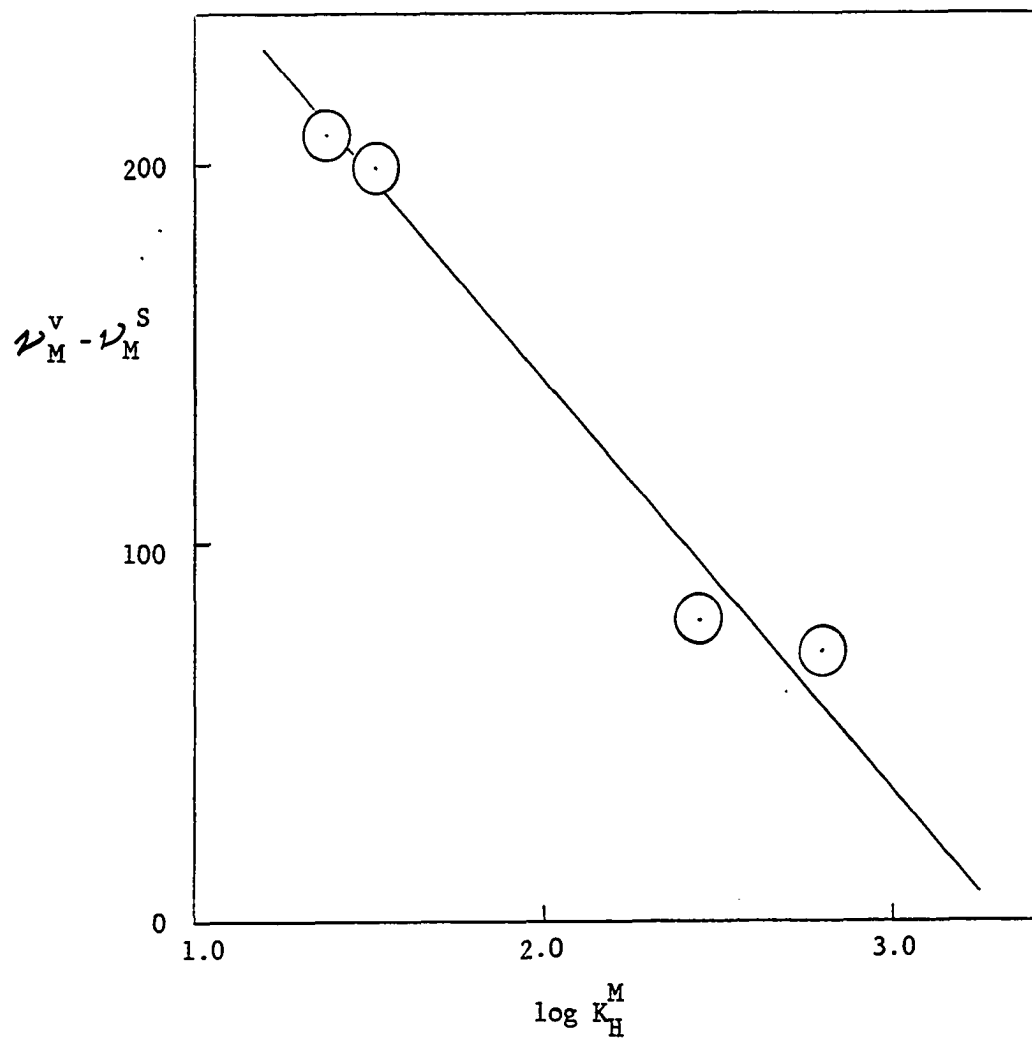


Figure 24. $\nu_M^V - \nu_M^S$ vs. $\log K_H^M$ for TFA.

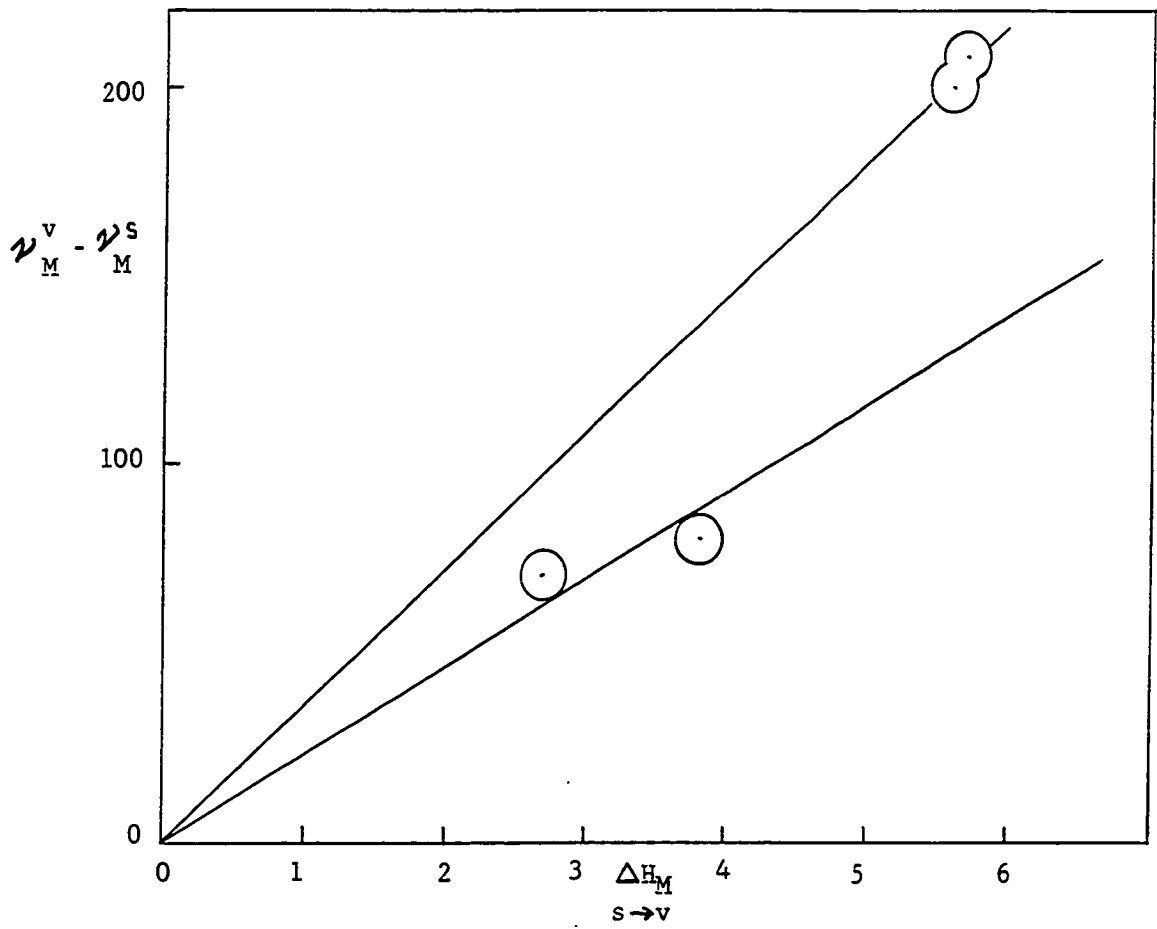


Figure 25. $\nu_M^v - \nu_M^s$ vs. ΔH_M Plot for TFA.
 $s \rightarrow v$

Brief Summary

The self-association of TFA has been studied in the vapor phase and in the solvents cyclohexane, carbon tetrachloride, benzene and 1,2-dichloroethane. A monomer-dimer association scheme is sufficient to describe the data in each system. Thermodynamic data have been obtained for the association reaction and for transfer of monomer and dimer species from solution to vapor. Equilibrium constants and association enthalpies decrease in the order of increasing monomer-solvent interaction, i.e., cyclohexane > carbon tetrachloride > benzene > 1,2-dichloroethane.

The vapor-solution method developed here has some potential as a method of general utility for studying association reactions of highly volatile compounds.

The TFA spectral frequency shifts have been examined and are consistent with the view that frequency shifts are due primarily to specific solute-solvent interactions. The TFA hydroxyl group interacts strongly with benzene and 1,2-dichloroethane.

The solvation theory of Christian and co-workers has been used to correlate the association thermodynamics of TFA with fair success. It is clear that the theory has great potential utility in correlating and predicting the effect of solvent on association reaction thermodynamics. Calculation of the parameter α from group interaction energies as developed here (Appendix) will be a valuable adjunct to the solvation theory.

APPENDIX

APPLICATION OF A SIMPLE LATTICE THEORY OF SOLUTIONS TO THE CALCULATION OF α

a priori calculation of the parameter α , in the solvation theory of Christian, et al.,²⁶ for an association reaction involving monomer and postulated complex structures, would be of great value in predicting thermodynamic parameters from a limited amount of data. For such predictions one would need to know, in addition to α , the equilibrium constant, preferably in the vapor phase or inert solvent such as cyclohexane, and the monomer distribution constants between the reference medium and the solvent of interest. This would permit estimation of the equilibrium constant in that solvent through equation 1.

$$\frac{K_{AB}^H}{K_{AB}^*} = (K_{D,A} K_{D,B}) \alpha^{-1} \quad (1)$$

Estimation of ΔH for the association reaction would require knowing the corresponding enthalpy changes.

Such a calculation of α could be carried out if it were possible to determine specific interaction energies between solute and solvent. The parameter α is then given by equation 2.

$$\alpha = \frac{\Delta U_{AB}^{S \rightarrow V}}{\Delta U_A^{S \rightarrow V} + \Delta U_B^{S \rightarrow V}} \quad (2)$$

where the ΔU 's refer to the energy change in transferring one mole of complex and of monomer from infinitely dilute solution to the vapor phase--solvation energies--calculated from specific interaction energies.

Examination of the literature revealed several approaches to the determination of group interaction energies. Langmuir,⁶⁰ in 1925, discussed the distribution and orientation of organic molecules in terms of group (e.g. - CH₃, - CH₂CH₃, - OH) surface energies. Interestingly, a promised second paper further explaining and utilizing this concept did not appear. Barker⁶¹ developed a lattice theory of solutions for treating the thermodynamic properties of mixing of binary solutions. This theory is based on a quasi-lattice model that has been generalized by considering different types of sites in a molecule, interacting with surrounding molecular sites in a pair-wise manner. Barker's theory has been applied with fair success to mixtures of polar and non-polar molecules where strong orientational forces are involved.⁶²⁻⁶⁹ A much simplified lattice model is used here to treat infinitely dilute solutions in order to develop a consistent set of molecular group interaction energies.

In the simplified lattice model it is assumed that the main structural atoms of a molecule occupy locational sites on the coordinated lattice. Following Goates, et al.,⁶⁴ a four-fold lattice is chosen. Each atom attached to, and lone-pair electrons of, the structural atoms are considered to interact on a one-to-one basis with adjoining solvent sites. Thus, methanol for example, has two locational sites, C—O, and a total of six interacting sites: three C—H, two lone

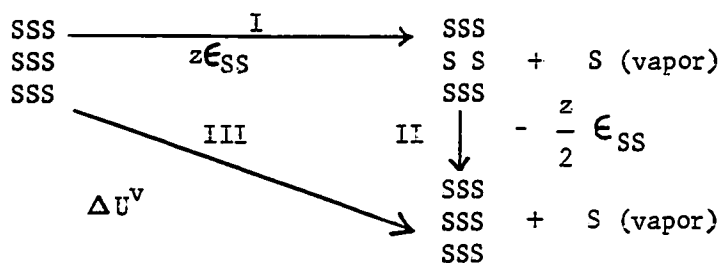
pairs from the oxygen, and the O—H group. Typical groups and the number of interacting sites ascribed to them are given below, again following Goates, et al.⁶⁴

Group	Number of Interacting Sites
—H (non-aromatic)	1
—H (aromatic)	2
—O—	2
=O:	2
>N: (aromatic)	2
—F	1
—Cl	3
—Br	3
—O—H (hydrogen)	1
—N—H (hydrogen)	1
>N:	1

The number of sites on a given molecule is obtained from its structural formula, using the above table.

This treatment is simplified by assuming the infinitely dilute solution. Any solute molecule in the infinitely dilute region (monomer or complex) interacts only with solvent molecules.

Values of group interaction energies are obtained from heats of vaporization and heats of infinite solution in the following manner. First consider a pure solvent and the process of vaporization illustrated in the following schematic diagram.



In the bulk liquid, by the model, each molecule is interacting through the sites s with sites on surrounding molecules. z represents the number of sites of a given type. In this example a molecule with only one type of site is being considered. If the energy per interaction is denoted by ϵ_{ss} , a total energy of $z\epsilon_{ss}$ must be supplied to transfer a single molecule to the vapor phase, leaving a 'hole' in the liquid. This process is illustrated by step I in the diagram. Upon collapse of the hole, step II, $z/2$ new interactions are formed with a lowering of energy $z/2\epsilon_{ss}$. This can be explained by noting that the molecules surrounding the hole lack a total of z interactions. When the liquid rearranges to eliminate the hole, $z/2$ new interactions (each of energy $-\epsilon_{ss}$) will result since each interaction involves two of the available z sites. The net result, vaporization (step III) takes place on a mole basis with the energy of vaporization ΔU^V . Thus, for the cycle, $\Delta U^V = z\epsilon_{ss} - \frac{z}{2}\epsilon_{ss} = \frac{z}{2}\epsilon_{ss}$, and the interaction energy ϵ_{ss} may be obtained. In this way the specific group interaction energies of the commonly used non-polar solvents have been evaluated.

Interaction energies for the functional groups mentioned above are evaluated in a similar manner by a step-wise process of expansion, using available heat of solution and heat of vaporization data. An important assumption made at this point is that a group interaction energy calculated from one type of molecule is unchanged in a different type of molecule; i.e., it is independent of the nature of the molecule. Langmuir termed this the principle of independent surface action. In the context of this discussion it might be called the principle of independent group interaction energy.

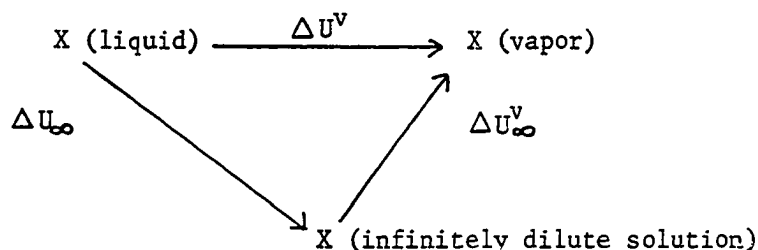
Consider the vaporization of a solute molecule with two different types of sites, a and b, from an infinitely dilute solution in a solvent having all sites of type s. The vaporization energy from the infinitely dilute solution, ΔU_{∞}^v , of the solute is then given by the equation

$$\Delta U_{\infty}^v = z_A \epsilon_{AS} + z_B \epsilon_{BS} - \frac{z_A + z_B}{2} \epsilon_{SS} \quad \text{where } z_A \text{ and } z_B \text{ represent the}$$

number of A and B type sites and ϵ_{AS} and ϵ_{BS} are the specific site-solvent interaction energies. In general this process may be formulated

$$\Delta U_{\infty}^v = \sum_i z_i \epsilon_{is} - \frac{\sum_i z_i}{2} \epsilon_{ss} \quad (3)$$

The energy of vaporization from the infinitely dilute solution, U_{∞}^v , is obtained from the energy cycle below.



ΔU_{∞} represents the energy of infinite dilution; this is practically the same as the heat or enthalpy of infinite dilution. By the cycle $\Delta U^v = \Delta U_{\infty} + \Delta U_{\infty}^v$ or

$$\Delta U_{\infty}^v = \Delta U^v - \Delta U_{\infty} \quad (4)$$

Heats of infinite dilution have been obtained from the literature--directly in a few cases, but usually indirectly from excess heat of mixing data. The data are given in Table 27. For functional groups other than the OH, CH, or CCl groups, data were rarely found for more than one compound. Good agreement was obtained for different CH- and CCl-solvent interactions. Rather poor agreement in the OH-solvent

interactions calculated from different alcohols--usually methanol, ethanol, and butanols--was obtained. This appears to be due to several factors. First, many published heat of dilution data are unreliable; where possible, data from recent systematic studies were chosen. Second, rather variant ΔU^V values for the pure alcohols were found. Last, and probably most important, these variation in the ϵ_{OHS} values are due to intrinsic differences in alcohol acidities, which depend on structural features. Stated differently, the assumption that group interaction energies are independent of the bonding and structure in the remainder of the molecule is only a loose approximation. The ϵ_{OHS} listed in the table are compromise values.

For the purpose of illustration the interaction energy of a keto oxygen with an alkyl hydrogen will be calculated. The heat of infinite dilution of acetone in n-hexane was reported to be 2.15 kcal/mole by Murikami, et al..⁸¹ The energy of vaporization of pure acetone is 7.2 kcal/mole.¹⁰⁹ From equation 4 the energy of vaporization of acetone from infinitely dilute n-hexane solution is $7.2 - 2.15 = 5.05$ kcal/mole. The total number of interactions of acetone with n-hexane, from the structural formula of acetone, is eight; six alkyl hydrogen-alkyl hydrogen (ϵ_{HH}) interactions and two keto oxygen-alkyl hydrogen ($\epsilon_{O'H}$) interactions. By equation 3 the energy of vaporization of acetone from the infinitely dilute solution is

$$\Delta U_{\infty} = 6\epsilon_{HH} + 2 \epsilon_{O'H} - 4 \epsilon_{HH}$$

The value of ϵ_{HH} (1.00 kcal) was previously found from the energies of vaporization and heats of infinite dilution of various alkanes by means

of equation 3. By substitution of $\Delta U_{\infty} = 5.05$ and $\epsilon_{HH}=1.00$ in the above equation, $\epsilon_{O'H}$ is found to be 1.6 kcal.

Using the values of group interaction energies in Table 29, it is possible to calculate the energy required to vaporize a molecule (complex or monomer) from infinitely dilute solution: that is, the solvation energy of the molecule considered. The parameter α is then calculated from equation 2.

Values of α obtained by this method have been used to correlate association data in several hydrogen bonded systems. Johnson, et al.,²⁷ studied the hydration of pyridine in several organic solvents by distribution, water solubility, and water activity measurements. Experimental values of α for the pyridine-monohydrate, dipyridine-hydrate, and pyridine-trihydrate complexes in carbon tetrachloride were reported to be 0.71, 0.75, and 0.33, respectively. Values of α calculated from the group interaction energies are 0.75, 0.71, and 0.51 for the same series of complexes. This is rather encouraging agreement, with the exception of the α value calculated for the trihydrate species. Gregory²⁸ studied the hydration of triethylamine in various solvents, again by distribution, water solubility, and water activity measurements. Using the experimental association and distribution constants for the hydration reaction in cyclohexane along with the parameter α calculated from the group interaction energies it was possible to calculate the equilibrium constant for the association reaction in benzene and toluene. By way of example the solvation energy $\Delta U_{A_{S \rightarrow V}}$ for the triethylamine-water complex in cyclohexane solution is calculated from group interaction energies below. From the assumed structure of the complex

(C₂H₅)₃N⁺ HOH there are fifteen alkyl hydrogen-solvent interactions, two etheric oxygen-solvent interactions, and one hydroxyl-solvent interaction. Thus,

$$\Delta U_{A, s \rightarrow v} = 15 \epsilon_{HH_1} + 2 \epsilon_{OH_1} + \epsilon_{OHH_1} - 9 \epsilon_{H_1H_1}$$

Substitution of interaction values from the table gives 8.5 kcal/mole.

Similar considerations for the triethylamine and water monomers gives

$$\Delta U_{A, s \rightarrow v} = 9.2 \frac{\text{kcal}}{\text{mole}} \text{ and } \Delta U_{W, s \rightarrow v} = 2.7 \frac{\text{kcal}}{\text{mole}} .$$

From equation 2 α is found to be 0.72, in comparison with 0.71 from the ' α -plot' for the pyridine-water complex. Monomer distribution constants were calculated between cyclohexane and benzene and cyclohexane and toluene. Application of equation 1 gave the predicted association constants 3.41 M⁻¹ in benzene and 3.90 M⁻¹ in toluene. These predicted values are in very good agreement with the experimentally determined values of 3.47 M⁻¹ in benzene and 3.72 M⁻¹ in toluene.

This method of calculating energies of vaporization and the parameter α has been applied to TFA and used in predicting enthalpies of association in several solvents (in Chapter 5) with fair success.

It is hoped that the group interaction energy values in Table 29 can be refined and expanded as additional heat of mixing data becomes available, particularly for evaluation of hydroxyl group-solvent interactions.

Table 27

Heats of Infinite Dilution

T = 25° unless otherwise noted

<u>System</u>	<u>ΔH_{∞} Dilution kcal/mole</u>	<u>Reference</u>
$C_2H_4Cl_2 - C_6H_{12}$	1.38	70
$C_2H_4Cl_2 - CCl_4$	0.57	
$C_2H_4Cl_2 - C_6H_6$	0.62	
$n-C_6H_{14} - CCl_4$	.18	71
$CCl_4 - n-C_6H_{14}$	.29	
$C_6H_6 - CCl_4$	.104	72
$C_6H_6 - C_5H_{10}$	.56	73
$C_6H_6 - C_6H_{12}$	.812	74
$CCl_4 - C_6H_{12}$	.14	75
$C_6H_6 - C_6H_5CH_3$	.07	76
$C_6H_6 - n-C_6H_{14}$	.694	
$n-C_6H_{14} - C_6H_6$	1.07	
$C_6H_{12} - C_6H_5CH_3$	.567	
$C_6H_5CH_3 - C_6H_{12}$	.472	
$C_6H_{12} - n-C_6H_{14}$	.078	
$n-C_6H_{14} - C_6H_{12}$	.222	
$n-C_7H_{16} - n-C_6H_{14}$	.015	
$C_6H_6 - C_6H_{12}$	.442	
$C_6H_{12} - C_6H_6$	.725	
$C_6H_6 - n-C_7H_{16}$	1.17	

Table 27 (Continued)

<u>System</u>	<u>ΔH_{∞} Dilution kcal/mole</u>	<u>Reference</u>
n-C ₇ H ₁₆ - n-C ₆ H ₁₄	.015	
C ₆ H ₆ - C ₆ H ₁₂	.442	
C ₆ H ₁₂ - C ₆ H ₆	.725	
C ₆ H ₆ - n-C ₇ H ₁₆	1.17	
n-C ₇ H ₁₆ - C ₆ H ₆	1.17	
C ₆ H ₁₂ - n-C ₇ H ₁₆	.123	
n-C ₇ H ₁₆ - C ₆ H ₁₂	.252	
C ₆ H ₁₂ - CCl ₄	.144	78
C ₆ H ₁₂ - C ₅ H ₁₀	.565	73
C ₆ H ₆ - C ₆ H ₁₂	.663	
C ₆ H ₁₂ - C ₇ H ₁₄	.635	
C(CH ₃) ₄ - CCl ₄ (0°)	.30	79
MeOH - CCl ₄	4.56	80
EtOH - CCl ₄	4.89	
PrOH - CCl ₄	4.73	
n-BuOH - CCl ₄	4.78	
i-BuOH - CCl ₄	5.22	
s-BuOH - CCl ₄	4.88	
t-B OH - CCl ₄	5.04	
n-BuOH - C ₆ H ₆	4.51	80
n-BuOH - C ₆ H ₁₂	4.40	
n-BuOH - C ₆ H ₁₄	5.31	

Table 27 (continued)

<u>System</u>	<u>ΔH_{∞} Dilution kcal/mole</u>	<u>Reference</u>
n-BuOH - C ₆ H ₁₄	5.5	81
EtOH - C ₆ H ₆	3.1	92
n-PrOH - C ₆ H ₆	2.65	
n-BuOH - C ₆ H ₆	3.0	
MeOH - CCl ₄ (20°)	1.14	75
MeOH - Bz (20°)	2.20	
MeOH - Bz	1.585	116
EtOH - CCl ₄ (45°)	2.73	84
t-BuOH - C ₆ H ₆ (30°)	3.26	85
EtOH - i-C ₈ H ₁₈	1.3	86
C ₄ H ₈ O ₂ - CCl ₄	-.226	87
(n-Bu) ₂ O - n-C ₆ H ₁₄	0.10	81
(Et) ₂ O - C ₆ H ₁₂	.48	88
C ₄ H ₈ O ₂ - C ₆ H ₁₂ (20°)	2.0	89
(Et) ₂ O - CCl	-.603	90
(Et) ₂ O - C ₆ H ₆	0.06	91
H ₂ O - C ₆ H ₆	6.53	92
H ₂ O - CCl ₄	5.16	93
C ₅ H ₁₀ O - C ₆ H ₁₂ (20°)	.62	124
C ₃ H ₆ O - C ₆ H ₁₄	2.15	81
C ₃ H ₆ O - C ₆ H ₆ (45°)	.31	95
C ₃ H ₆ O - CCl ₄ (45°)	.07	

Table 27 (continued)

<u>System</u>	<u>ΔH_{∞} Dilution kcal/mole</u>	<u>Reference</u>
$C_3H_6O - CCl_4$	.625	96
$C_3H_6O - C_6H_6$ (30°)	.24	97
$C_3H_6O - C_6H_{14}$ (20°)	2.24	98
$C_3H_6O - C_5H_{12}$ (20°)	2.22	
$C_3H_6O - n-C_7F_{16}$ (35°)	1.0	99
$C_5H_5N - CCl_4$	-.32	90
$C_5H_5N - C_6H_5CH_3$	.1	100
$(Et)_3N - C_6H_{12}$	.35	
$C_5H_5N - CCl_4$	-.01	101
$n-C_7F_{16} - i-C_8H_{18}$ (30°)	2.97	102
$n-C_6F_{14} - n-C_6H_{14}$	4.06	
$n-C_5F_{12} - n-C_5H_{12}$	2.15	103
$C_6F_6 - C_6H_6$	.16	104
$C_6H_6 - C_6F_6$	-.57	
$n-C_6F_{14} - n-C_6H_{14}$ (35°)	4.17	105
$C_6H_5F - C_6H_{12}$ (25°)	.87	106
$C_6H_5F - CCl_4$ (30°)	.23	107
$CCl_4 - C_6H_5F$ (30°)	.22	
$C_6H_5NH_2 - C_6H_6$	.96	108
$C_6H_5NH_2 - CCl_4$	1.82	
$C_5H_{10}NH - C_6H_{12}$ (20°)	1.24	124

Table 28

Energies of Vaporization

Compound	ΔU_{298}^V kcal/mole	Reference
CCl_4	7.35	109
C_6H_6	7.45	110
$\text{C}_6\text{H}_5\text{CH}_3$	8.48	94
C_6H_{12}	7.37	111
C_5H_{10}	6.38	94
n- C_6H_{14}	6.97	110
n- C_7H_{16}	8.15	
H_2O	9.90	109
n- C_5H_{12}	5.37	
$\text{C}_5\text{H}_5\text{N}$	9.06	94
$\text{C}_4\text{H}_8\text{O}_2$	8.36	112
n- C_5F_{12}	5.48	
n- C_6F_{14}	7.15	110
n- C_7F_{16}	8.09	
C_6F_6	7.99	113
MeOH	7.44	109
EtOH	9.52	
n- PrOH	10.45	
C_3H_6	7.20	
Et_2O	5.83	
Et_3N	7.1	57

Table 28
(continued)

Compound	ΔU_{298}^v kcal/mole	Reference
$C_5H_{10}NH$	8.79	114
$C_5H_{10}O$	7.75	115

Table 29

Calculated Group Interaction Energies

Interaction	Symbol	ϵ_{ij} kcal
alkyl-alkyl	ϵ_{HH}	1.00
c-alkyl-c-alkyl	ϵ_{H,H_1}	1.23
aromatic-aromatic	$\epsilon_{H'H'}$	1.24
chloro-chloro	ϵ_{ClCl}	1.22
fluoro-fluoro (alkyl)	ϵ_{FF}	0.98
fluoro-fluoro (aromatic)	$\epsilon_{F'F'}$	1.33
alkyl-c-alkyl	ϵ_{HH_1}	1.10
alkyl-aromatic	$\epsilon_{HH'}$	1.05
c-alkyl-aromatic	$\epsilon_{H,H'}$	1.18
alkyl-chloro	ϵ_{HCl}	1.10
c-alkyl-chloro	ϵ_{H_1Cl}	1.21
aromatic-chloro	$\epsilon_{H'Cl}$	1.22
alkyl-fluoro	ϵ_{HF}	0.77
c-alkyl-fluoro	ϵ_{H_1F}	0.73
aromatic-aromatic fluoro	$\epsilon_{H'F'}$	1.30
ether-alkyl	ϵ_{OH}	0.50
ether-c-alkyl	ϵ_{OH_1}	1.10
ether-aromatic	$\epsilon_{OH'}$	1.36
ether-chloro	ϵ_{OCl}	1.50
keto-alkyl	$\epsilon_{O'H}$	1.57
keto-c-alkyl	$\epsilon_{O'H_1}$	(2.0)

Table 29

(continued)

Interaction	Symbol	ϵ_{ij} kcal
keto-aromatic	$\epsilon_{O'H'}$	2.80
keto-chloro	$\epsilon_{O'Cl}$	2.43
keto-fluoro	$\epsilon_{O'F}$	2.56
hydroxyl-alkyl	ϵ_{OHH}	1.80
hydroxyl-c-alkyl	ϵ_{OHH_i}	2.70
hydroxyl-aromatic	$\epsilon_{OHH'}$	2.80
hydroxyl-chloro	ϵ_{OHCl}	2.00
pyridine N-chloro	$\epsilon_{N'Cl}$	3.0
pyridine N-aromatic	$\epsilon_{N'H'}$	3.0
ter-amine-c-alkyl	ϵ_{NH_i}	2.5
amine-c-alkyl	ϵ_{NHH_i}	1.1
amine-c-alkyl	ϵ_{NH_i}	1.53

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