STUDY OF MIXED SOLVENT COMPLEXES

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DEDICATION

I dedicate this dissertation to Kimberly Rider whose potential field helped bring me this far.

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The affairs of men and women have potential for goodness as bright as the most beautiful wildflowers of spring and derision as dark as a tornado's dark turbulence. I give my warmest thanks for making Stillwater, Oklahoma a peaceful cove in a stormy sea to my super-loving and concerned parents, to my advisor, Dr. C. M. Cunningham for his patience, tolerance, and guidance throughout our investigation, to my committee and the Physical Chemistry Division for a scientific climate, to Dr. N. Purdie for his instrumental guidance, To Dr. K. D. Berlin and O. C. Dermer for editing my dissertation, to Stan Sigle for operation of the NMR instrument, to Sue Heil and Janet Sallee as typists of this dissertation and to my fellow students who have given me so much aid.

The subject of the following dissertation is an investigation into the interactions between liquids. I write of liquids that when mixed form a homogeneous mixture like water and ethyl alcohol. When any two miscible liquids are mixed, frequently the resultant solution is found to have characteristics either enhanced or diminished over those of the individual components due to their interaction. Sometimes, a totally unexpected property emerges from the interaction because of what is called complexation.

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CHAPTER I

INTRODUCTION

Mixed solvent complexes form from intermolecular collision and/or collisions. However whereas molecular collisions occur in the time frame of 10^{-10} - 10^{-11} s, a molecular complex exhibits a "contact time" exceeding 10^{-10} s.[1] Solvent complexes fulfill this criterion.[2] However, the lifetimes of such species are significantly short so as to prevent their isolation at room temperature. Nevertheless, studies of solvent complexes can and have been studied indirectly.[3]

General Interactions

When two molecules interact in solution, they do so physically and/or chemically. Interaction results in a change of energy u(R) as shown in Figure 1. For two spherical molecules, this energy varies as a function of the intermolecular separation R. The energy is repulsive at very short distances, attractive at intermediate ones and goes to zero at large values of R.[4]

Forces giving rise to u(R) are of electric origin and termed short and long range. In the case of two hydrogen atoms, formation of a hydrogen molecule arises from short-range forces. Whereas these forces are attractive in the hydrogen bond, short-range forces can also be repulsive, as shown in Figure 1, at very short R. Long-range

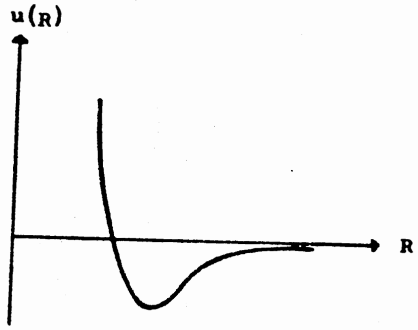


Figure 1. The Interaction Energy u(R) of Two Spherical Molecules as a Function of the Separation R of Their Centers.[4]

forces arise from modification of molecular charge distributions. They occur at moderate to large values of R and are classified as electrostatic, induction, dispersion, resonance, or magnetic.

The lattice structure of solids as well as the nature of liquids are recognized[5,6] to be determined by the short-range repulsive forces of the molecular cores. Long-range forces are seen only to be vital in vapor-liquid condensation. Nevertheless, the Gibbs-Duhem equation[7] specifies that both liquid and vapor have the same chemical potential at the condensation point. This makes possible the treatment of liquid behavior from highly accurate gas and minimum liquid phase measurements. This depends upon the validity of two assumptions:[8] one, that the gas phase is an ideal solution, and two, that the liquid volume is constant. All necessary information can be gathered from liquid-vapor equilibrium studies[9] and virial coefficient determinations.[10] Statistical mechanics provide the theoretical basis for the treatment of these systems.[11] Thermodynamic measurements dealing with a physical-chemical process such as that of condensation should include both nonspecific as well as specific molecular interactions[12] as considered herein.

Specific Interactions

If one of two interacting molecules donates an electron from its highest occupied molecular orbital to the other's lowest unoccupied molecular orbital resulting in an overall energy decrease, a donor-acceptor (DA) bond can be formed. This is a specific interaction between an electron-donating molecule, D, and an electron-accepting one, A. D takes on a partial positive charge and A, a partial negative one. Upon interaction D's ionization potential and A's electron affinity equalize in the formation of a charge-transfer (CT) bond.[13] Electron donation and acceptance takes place between molecules having lone pair (n), sigma (σ), and/or pi (π) electrons. The strength of the CT bond depends to a large degree on interaction between participating orbitals.[14]

Pyridine [N:] is an aromatic compound composed of a nitrogen atom possessing a lone pair of electrons. Methyl iodide [CH_3-I] possesses a highly polarized pair of sigma electrons owing to its electronegative iodine atom. Acetone [$(CH_3)_2C=O$] contains a carbonyl group wherein the carbon and oxygen atoms are polarized positive and negative, respectively. Two systems, pyridine--acetone and methyl iodide--acetone have been investigated in the present study for the formation of CT complexes, via analyses involving infrared (IR), ultraviolet-visible (UV-Vis) and nuclear magnetic resonance (NMR) spectroscopy.

Physico-chemical studies of non-ionizing solutions can supply information for implementation of analytical techniques in extraction and chromatography such as in terms of column efficiency, i.e. HETP values.[15] Such studies provide a foundation on which to extend investigations in mixtures with ionizing solvents such as water.[16]

Charge transfer (CT) is of importance in many reactions such as electrophilic aromatic substitution,[17] excited state quenching of alkyl p-acylbenzoates[18] and DDT complexation[19] with benzene and naphthalene as well as for configurational and conformational effects in polymerization.[20] The effect of pressure on some CT solids reveals in them neutral-to-ionic phase transitions.[21] This could well be of synthetic value in as much as the cycloaddition of tetracyanoethylene and styrene has been found to occur only at high pressures.[22]

Electrophilic aromatic substitution, polymerization and reactions such as [1,4]cycloaddition of tetracyanoethylene-styrene exhibit covalent bond formation which characteristically arise from short-range forces. Long-range electrostatic forces, however, aid in bringing donor and acceptor molecules together to permit charge transfer. In weak complexes such as benzene--DDT electrostatic forces are considered dominant in complexation.[19] In CT complexation, a unified theory of short- and long-range forces for the understanding of physical phenomena is needed such as in physics for the electrodynamic, weak interaction and strong interaction forces.[23] This is because the overlap of short- and long-range forces is great in weak complexes; these complexes can be influential in configurational and conformational aspects in chemical reactions.

System Interactions

Pyridine, methyl iodide and acetone are all liquids at the temperatures studied.[24] Some physical constants of compounds used in this study are given in Table I. From vapor-liquid studies of the methyl iodide--acetone[25] and pyridine--acetone[26] systems it can be seen that the liquids of each pair are completely miscible in all proportions. The mixing of pyridine and methyl iodide,[27] however, yields an isolatable product, i.e. methylpyridinium iodide. Product formation was later shown by Kosower[28] to come about via a charge-transfer process.

Acetone, methyl iodide and pyridine can all act as electron

TABLE I

PHYSICAL PROPERTIES OF SOLVENTS STUDIED[24]

Compound	Mol. wt.	m.p. (°C)	b.p. (°C)	n_D^{25}
Acetone	58.08	-95.35	56.2	1.357
Methyl iodide	141.94	-66.45	42.4	1.530
Pyridine	79.10	-42	115.5	1.507
Cyclohexane	84.16	6.55	80.74	1.424

donors.[29] Charge distribution in CT complexes stems from the ionization potential (IP) and electron affinity (EA) of their constituent parts. The roles of donor and acceptor in CT complexation depend upon the IP and EA of the complexing molecules. Pyridine, for instance, while normally a species acting as a donor, acts as an acceptor in its maleic anhydride CT complex.[30] Similarly, acetone in the benzene--acetone complex acts as an acceptor.[31]

Freezing point depression[32] and proton NMR complexation studies[33] of pyridine in dilute chloroform have revealed only the formation of 1:1, pyridine-chloroform complexes.[34] Similarly, methyl iodide associates with benzene only via 1:1 complexation.[34] Halogen atoms in halogenated organic compounds have been found to create CT interactions.[35] Acetone has a reported K_D value of 0.013 for dimerization in cyclohexane at 25 ^oC.[36] This self-complexation is very weak since ± 0.01 is the normal error in such a determination. Still, the dimerization of acetone creates the possibility for both 1:1 and 1:2 complexes in both the methyl iodide--acetone and pyridine--acetone systems. Approximate equilibrium constants for methyl iodide--acetone 1:1 and 1:2 complexes,[37] in fact, have been determined. However, these K_c values of 0.1 and 0.04, respectively, have an error of ± 50%.

The present investigation entails the spectral determination of K_c values for the methyl iodide--acetone system. Likewise, the pyridine--acetone system has been investigated for 1:1 complexation, as suggested by the large induced NMR shifts of pyridine--ketone systems.[38] Evaluation of calculated equilibrium constants determined from experimental thermodynamic methods will be the subject of discussion.

Thermodynamics

The free energy of mixing G^M for a real system minus that of a hypothetical ideal mixture of identical composition G^M (ideal) yields what is termed the "excess free energy of mixing".[39] This excess free energy of mixing G^E is an extensive property of a system expressed as:

$$G^E = RT \Sigma n_i \ln \gamma_i \tag{1.1}$$

where n and γ are number of moles and activity coefficient for each component i, respectively. Put in another way, G, the total free energy of a mixture, is related to the chemical potential μ of its components:

$$G = \Sigma n_i \mu_i \tag{1.2}$$

For an ideal mixture, the chemical potential of each component is given as

$$\mu_i = \mu_i^* + RT \ln X_i \tag{1.3}$$

where μ_i^* is dependent only upon temperature and pressure. X_i is the mole fraction of the i^{th} component. With a real solution, the chemical potential is related to the activity coefficient, γ:

$$\mu_i = \mu_i^* + RT \ln \gamma_i X_i \tag{1.4}$$

The difference between equations (1.3) and (1.4) yields G^E as in equation (1.1) but in terms of mole fractions X_i instead of number of moles n_i.

Differentiation of equation 1.1 at constant temperature yields:

$$dG^E = RT \Sigma n_i d\ln \gamma_i + RT \Sigma \ln \gamma_i dn_i \tag{1.5}$$

which follows from the Gibbs-Duhem equation,

$$-SdT + VdP - \Sigma\, n_i\, dn_i = 0 \qquad (1.6)$$

At constant temperature, pressure and composition n_j where $j \neq i$, equation (1.5) is changed to equation (1.7).

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j} = RT \ln \gamma_i \qquad (1.7)$$

For a binary system,[40] the excess entropy S^E is

$$S^E = -R\, X_1 \ln \gamma_1 X_1 - R\, X_2 \ln \gamma_2 X_2 - X_1\, RT \frac{\partial \ln \gamma_1}{\partial T} - X_2\, RT \frac{\partial \ln \gamma_2}{\partial T} \qquad (1.8)$$

For mixing of two liquids forming an ideal mixture at constant temperature, the excess enthalpy H^E and excess volume V^E are zero. The ideal entropy of mixing S^M (ideal) is:

$$S^M \text{ (ideal)} = -RT\, X_1 \ln X_1 - RT\, X_2 \ln X_2 > 0 \qquad (1.9)$$

Consequently, G^E is:

$$G^E = RT\, X_1 \ln X_1 + RT\, X_2 \ln X_2 \qquad (1.10)$$

Mixing of liquids gives rise to free energy terms in addition to those of equation 1.10. These terms arise from γ_i, the activity coefficient of each system component. G^E_i is the sum of all specific and nonspecific interactions of each component in solution and is computed from

$$G^E = \Sigma\, X_i\, \mu_i^E \qquad (1.11)$$

where

$$\mu_i^E = \Sigma\, x_i\, \mu_i^E \qquad (1.12)$$

Activity coefficients, γ_i, are commonly determined from vapor-liquid equilibrium studies.[25,26] In many cases, such as in the mixing of n-hexane--cyclohexane,[41] G^E arises entirely fron nonspecific intermolecular forces. These include London dispersion (attractive potential due to perturbation of electronic orbitals), induction effects (electrostatic deformation by surrounding neighbor molecules) and orientation energy (mutual alignment of molecules due to electrostatic effects). In other systems, however, the observed free energy of mixing exhibits a value not explainable in terms of nonspecific forces. As has been shown in the mixing of ethanol and carbon tetrachloride,[12] this behavior can be explained quantitatively in terms of complex formation.

Charge-transfer complexation has been implicated in the systems tetrachloroethylene--carbon tetrachloride,[42] monoaklylbenzenes--nitrobenzene[43] and tetrachloroethylene--aromatic hydrocarbons.[44] These studies have sought, in a quantitative way, to relate CT complexation and thermodynamic mixing without significant success. An author of one publication[43] expressed the view that the separation of specific and nonspecific forces is impossible.

Nonspecific forces, however, have been quantitatively understood in simple systems for some time.[40] Recently, new approaches of a semi-empirical nature have been developed for estimating the influence of nonspecific solvation on complex formation,[45] intermolecular potential on nonpolar molecules and dispersion in polar forms.[46]

Semi-empirical approaches evaluate contributions of nonspecific forces. Experimental techniques such as UV[47] and IR[48] spectroscopy can be used to measure the amount of charge transfer in complexation.

In addition, these techniques permit calculation of equilibrium constants and solution specie concentrations.

The excess free energy of mixing for a system is the sum of both nonspecific and CT forces. Many vapor-liquid G^E studies[50-53] of binary mixtures presumably undergoing charge transfer have assumed 1:1 and 1:2 complexing to occur and using the study's determined free energy data have calculated equilibrium constants. Binary mixtures were treated thermodynamically as ideal associated solutions[40] with the free energy of mixing arising from only mixed solvent complexation. This makes equilibrium constants from vapor-liquid G^E studies a conglomerate of specific and nonspecific forces.

If spectroscopic studies are performed on these same above systems, equilibrium constants can probably be calculated. Any difference between equilibrium constants from spectral measurements and those derived from vapor-liquid measurements should be associated due to nonspecific forces. Likewise, spectrally determined equilibrium constants can be converted to G^E energies to assess nonspecific forces in the investigated methyl iodide--acetone and pyridine--acetone systems.[12]

Spectroscopy

The donor-acceptor (DA) complex formed from donor and acceptor molecules was first noted[54] and given a resonance description by Mulliken:[55]

$$\Psi_G = a\,\phi_0\,(D,A) + b\,\phi_1\,(D^+,A^-) \tag{1.13}$$

where ϕ_0 represents a "no bond" and ϕ_1 a "dative" structure. In the pyridine--iodine complex ($Pyr\bullet I_2$) such DA complexation occurs:

$$Pyr + I_2 \rightleftharpoons Pyr\ I_2 \tag{1.14}$$

$$K = \frac{[Pry\bullet I_2]}{[Pyr][I_2]}\ \text{liter/mole} \tag{1.15}$$

The equilibrium constant, K = 290 liter/mole at 16.7 °C, was determined spectroscopically from the ultraviolet adsorption. The squares for each of the coefficients: $a^2 \approx 0.75$ and $b^2 \approx 0.25$ in equation 1.13 are approximately the fractions of "no bond" and "dative" character, respectively, in the $Pyr\bullet I_2$ bond. Ψ_G of equation 1.13 has a lower energy than ϕ_0 due to resonance stabilization of ϕ_0 by ϕ_1.

Charge transfer theory of DA complexes has advanced since Mulliken's proposal of it to include the use of nonorthogonal orbitals for weighing "no bond" and "dative" structures.[57] The concept of "interaction frontier orbitals" where only a few paired hybrid orbitals interact predominately is very similar to Mulliken's theory.[58]

Numerous studies of electronic absorption spectra[59-62] indicate charge transfer occurs between molecules with the formation of 1:1, 1:2, and higher complexes. The simplest association between a donor and an acceptor is one to one:

$$D + A \rightleftharpoons DA \tag{1.16}$$

The Benesi-Hildebrand (B-H) equation[63] has been commonly used for calculation of donor-acceptor equilibrium. The B-H equation is:

$$\frac{[A]_0\bullet L}{Ab} = \frac{1}{K_c\bullet [D]_0\bullet \varepsilon} + \frac{1}{\varepsilon} \tag{1.17}$$

where $[A]_0$ and $[D]_0$ are initial concentrations; Ab is the experimentally determined absorption; ε is complex DA's molar absorptivity; K_c is the concentration equilibrium constant of equation (1.16); and L is the cell path length. K_c and ε are determined experimentally from a plot of $[A]_0 \bullet L/Ab$ versus $[D]_0^{-1}$. The $[A]_0$ L/Ab and $[D]_0^{-1}$ values arise from a series of equations wherein A's concentration is held constant and $[D]_0 >> [A]_0$. Reversal of D and A concentrations, where $[A]_0 >> [D]_0$ and A's concentration is varied while D's concentration is held constant, is an equally valid experimental technique. In the present study, acetone's concentration as A was varied while methyl iodide or pyridine concentration as D was held constant. The plot in the presence of only 1:1 complexation is a straight line of slope $(K_c \bullet \varepsilon)^{-1}$ with an intercept of $(\varepsilon)^{-1}$.

The B-H equation has been criticized[64,65] for its use of the intercept $(\varepsilon)^{-1}$ in the calculation of K_c. For complexes where $(\varepsilon)^{-1}$ is small, significant errors result. These errors are magnified upon calculation of K_c. The Scott form of the B-H equation[66] is:

$$\frac{[D]_0 \bullet [A]_0 \bullet L}{Ab} = \frac{1}{K_c \bullet \varepsilon} + \frac{[D]_0}{\varepsilon} \qquad (1.18)$$

and enlarges the size of the intercept by a factor of $[D]_0$.

Spectroscopic studies of DA equilibria usually are studied in an inert solvent, S. For weak solvent complexes, the appearance of the solvent complexes such as DS_m, AS_n and DAS_p may be significant. Complexation of D, A and DA with a reactive solvent yields the equilibrium:

$$AS_n + DS_m \rightleftharpoons DAS_p + S_q \qquad (1.19)$$

where $q = n + m - p$. The B-H equation for this equilibrium is:[67]

$$\frac{[A]_0 \bullet L}{Ab} = \frac{1}{[D]_0} \bullet \frac{1}{K_c \bullet \varepsilon} + \frac{1}{\varepsilon} \bullet [1-q \bullet \frac{(m+1)}{K_c \bullet [S]_0}] \qquad (1.20)$$

This equation has been successfully applied to the equilibrium in the toluene--iodine and methyl biphenyls--1,3,5-trinitrobenzene systems[68] where the classical B-H equation fails yielding negative K_c values.

Activity coefficients determined by spectrometry are normally neglected in equilibrium studies. The equilibrium constant of equation (1.16) expressed in both mole fraction and molarity including activity coefficients (${}^X\gamma$ or ${}^C\gamma$, respectively) is:

$$K_X = \frac{X_{DA}}{X_D \bullet X_A} \bullet \frac{{}^X\gamma_{DA}}{{}^X\gamma_D \bullet {}^X\gamma_A}$$

$$K_c = \frac{[DA]}{[D][A]} \bullet \frac{{}^c\gamma_{DA}}{{}^c\gamma_D \bullet {}^c\gamma_A} \qquad (1.21)$$

where X and [DA], [D], [A] represent the mole fraction and concentration of the species, respectively. The studies are assumed to be carried out in dilute enough concentration of the reacting species that

$$\lim_{x_I \to 1} {}^x\gamma_K = \lim_{x_I \to 1} {}^c\gamma_K = 1 \qquad (1.22)$$

where I represents the inert solvent S and γ_K the reacting species, K ≠ I. The mole fraction and molar activities are related by the average solution volume, $\bar{V}$, and the inert solvent's molar volume, V_I, so that

$${}^c\gamma_K = \frac{\bar{V}}{V_I} \bullet {}^X\gamma_K \qquad (1.23)$$

and equilibrium constants,[69]

$$K_c = K_X \cdot V_I \tag{1.24}$$

The previous equilibrium expressions are derived assuming only 1:1 complexation between D and A. Higher-order complexes may, however, form in significant amounts even at experimental conditions where $[D]_0 \sim [S] >> [A]_0$. In the case of 1:1 and 2:1 complexation, the equilibrium is:

$$D + A \rightleftharpoons DA, \qquad K_1 = \frac{[DA]}{[D][A]}$$

$$D + DA \rightleftharpoons D_2A, \qquad K_2 = \frac{[D_2A]}{[D][DA]} \tag{1.25}$$

K_1 and K_2 are calculated:[67]

$$\frac{[A]_0 \cdot L}{Ab} = \frac{1 + K_1[D]_0}{K_1[D_0] \cdot \varepsilon_1 (1 + \frac{\varepsilon_2 \cdot K_2 \cdot [D]_0}{\varepsilon_1})} \tag{1.26}$$

by assuming $[D]_0 \sim [S]_0 >> [A]_0$ and, in addition, requiring $Ab = [DA]\varepsilon_1 + [D_2A]\varepsilon_2$.

Spectral characteristics of the studied liquids in certain systems are known.[70] Pyridine examined in 95% ethanol has two wavelength maxima (λ_M), one at 257 nm with a molar absorptivity (ε_M) of 2750 and the other at 270 nm with $\varepsilon_M = 450$. Both acetone and methyl iodide have been examined in hexane. Acetone has two λ_M, one at 188 nm with $\varepsilon_M =$ 1860 and the other at 279 nm with $\varepsilon_M = 15$. Methyl iodide has a reported λ_M at 259 nm with $\varepsilon_M = 400$.

Proper assessment of solvent complex stoichiometry is a useful first step in defining a system's equilibria.[71] Charge-transfer frequency bands are primary data cited for the existence of CT complexes. Absorptivity, however, is only secondary data because of its indirect treatment of CT formation using absorption intensity. Experimental information besides absorptivity would be useful in determining stoichiometry, since charge transfer bands are often obscured by spectral background.[72] Isosbestic points[59-62] can be used in this regard. Such analysis has been attempted in the examining of CT in methyl iodide--acetone and pyridine--acetone mixtures.

Nuclear Magnetic Resonance

Ultraviolet spectroscopy can provide direct evidence for the presence of DA complexes from their CT frequency bands. Rapid UV detection of electronic excitation, 10^{-14} - 10^{-12} s, is in contrast to radio-frequency measurements by nuclear magnetic resonance. NMR can detect active nuclei over a time frame of about 0.01 s.[73]

Chemical shifts, both ^{13}C and ^{1}H, for many pure solvents are available in the literature.[76,77] Chemical shifts of proton nuclei strongly solvated by mixed solvents, such as those in a solution of aluminum chloride in aqueous N-methylacetamide (NMA),[78] are directly observable by NMR. These shifts arise from ionic interactions between aluminum chloride and the mixed solvent (H_2O-NMA). Weak DA complexes, however, held together by charge transfer and nonspecific interactions with short lifetimes do not have directly observable chemical shifts. For such ^{1}H systems as chloroform--nitrogen bases,[79] chloroform--benzene[80] and aromatic compounds with ketones,[31,81] DA lifetimes are too short for detection. ^{13}C studies on similar systems[82,83] experience the same difficulty as with ^{1}H NMR analysis, namely a detection time of about 0.01 seconds. The location of the

DA chemical shift must be derived from DA's constituent parent (D and A) chemical shifts.[84]

In NMR spectral analysis of DA formation, two kinds of mixtures must be examined. One contains a constant concentration of the acceptor A and varying amounts of S and D at $[D]_0 >> [A]_0$. The other contains only acceptor A and inert solvent S, the concentration of A in both mixtures being the same in both. The chemical shift difference between A and S in the binary solution is δ_{free} shown in Figure 2A.[85] For each ternary solution, a δ_{obs} is obtained which is the shift difference between the A and S parent peaks shown in Figure 2B. The difference between δ_{free} and δ'_{obs} is Δ_{obs}, the shift difference caused by replacement of S by D.

The term Δ_{obs} is equivalent to the UV quantity, $(Ab/[A]_o \cdot L)$. When $(\Delta_{obs})^{-1}$ is substituted for $([A]_o \cdot L/Ab)$ in equation (1.17), the UV absorptivity ε transforms to Δ_c. The Benesi-Hildebrand equation for UV becomes for NMR:

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_c \cdot [D]_0 \cdot \Delta_c} + \frac{1}{\Delta_c} \qquad (1.27)$$

The Δ_c is the chemical shift difference between that of DA and the parent A peak. The dashed peaks of A and DA in Figure 2B are their true chemical shifts. Owing to the long NMR time scale, the true signals are not seen but instead an average signal for nuclei in the free and in the complexed forms yields, such as for A, the observed solid-line chemical shift where the δ_{obs} and Δ_{obs} arrowheads meet in Figure 2B. The signal of D in Figure 2B is an average of free and complexed nuclei forms (just as in A above) but since $[D]_0 >> [A]_0$, the shift due to complexation is insignificant.

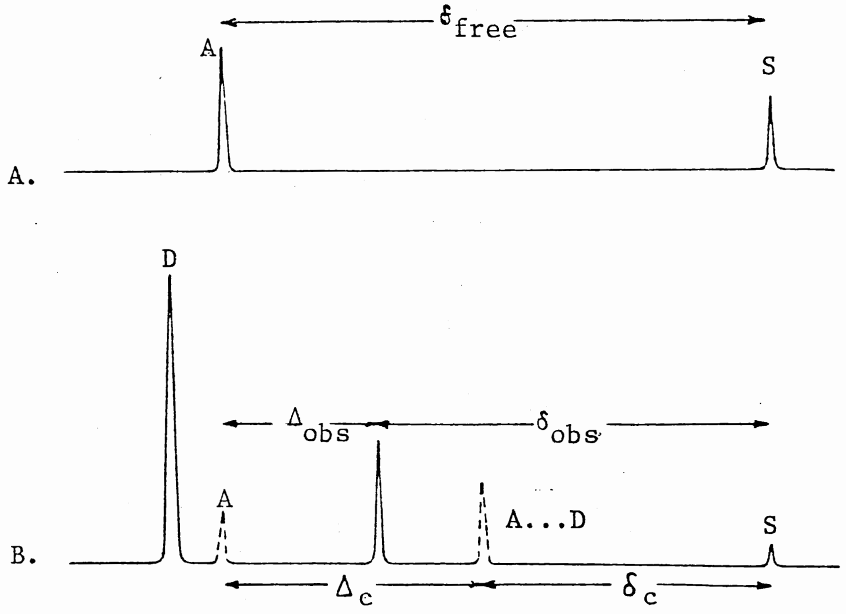


Figure 2. Schematic Spectra Illustrating the Effect on the Chemical Shift of a Species A Due to the Reaction with D According to A + D = A ... D. An inert material S is employed as a diluent and internal reference.[85]

Although NMR analysis is suitable for determining equilibrium constants of 1:1, 2:1, and solvent complexation,[67] the method can involve large anisotropic shielding effects.[86,87] These can obscure and complicate study of a system's equilibria. NMR also fails to indicate the stoichiometry of association between D and A except by brute force calculation. This second liability of NMR spectroscopy need not exclude its use. The character of DA association can be discerned by spectroscopy. Such an approach is being actively pursued by Skulski and coworkers[59-62,88,89] in their study of charge transfer complexation as being indicated by isosbestic points.

Ultraviolet spectroscopy investigations using isosbestic points permit evaluation of solution equilibria. Both UV and NMR methods use equivalent mathematical formulations in calculation of equilibrium constants. Since the techniques do not measure all of the same forces, they should be expected to differ.

D. E. Martire[90] has reviewed UV and NMR results in equilibrium determinations. UV spectroscopy is seen only to measure complexation arising from charge transfer forces whereas NMR measures CT forces in combination with electrostatic forces. Thus, NMR spectroscopy is seen to be of significant use in complexation studies.

The charge-transfer process, however, is not unaffected by the electrostatic environment. A recent UV study indicates[91] that charge-transfer equilibrium constants are, to a measurable degree, influenced by electrostatic forces.

Assessment

Early studies using the B-H equation and similar formulations of equilibrium were on moderate to strong CT complexes. Studies of systems such as benzene--1,3,5 trinitrobenzene[92] viewed the DA complex in a faucet-sink fashion, a 1:1 union. Criteria for use of the B-H equation were given by Person[93] and Deranleau.[94,95] For the equation to be valid one of the complexing species, D or A, must be in much greater amount. Only 1:1 complexation must take place.

Deranleau has discussed the theoretical minimum errors in K_c. He has shown that the most accurate K_c values are determined when the DA complex concentration is approximately equal to the concentration of the most dilute component. Taking the case where $[D]_0 >> [A]_0$, he defined a saturation fraction S where

$$S \equiv \frac{Ab}{Ab_{max}} = \frac{Ab}{\varepsilon \cdot [A]_0} = \frac{[DA]}{[A]_0} \qquad (1.28)$$

in UV and

$$S \equiv \frac{[DA]}{[A]_0} = \frac{\Delta_{obs}}{\delta_{free}} \qquad (1.29)$$

in NMR spectroscopy. Between S values of 0.2 and 0.8 the most accurate values are determined. Values obtained outside this range are highly uncertain.

The present investigation is an attempt to relate the thermodynamics from vapor-liquid data in the literature for the pyridine--acetone and methyl iodide-acetone systems to the experimentally calculated equilibrium constants determined herein. Calculated equilibrium constants are evaluated in terms of Person and Deranleau's criteria. The contributions of specific (CT) and nonspecific forces should then be analyzable from the contribution of each to the excess free energy (G^E) of the studied systems.

CHAPTER II

EXCESS FREE ENERGY

Equation (1.1) represents the excess free energy G^E of mixing real liquids at constant temperature and pressure. G^E is directly related to the activities (γ's) of the solution components:[12]

$$\frac{\partial G^E}{\partial n_i} = RT \ln \gamma_i \qquad (2.1)$$

Prigogine and others[96-98] have shown that in the mixing of two solvents most of G^E many times can be found to arise from specific interactions which are measurable spectroscopically. The contribution of specific interactions to G^E shall be defined G^E_{assc} because of its arising from association. The remainder of G^E not arising from G^E_{assc} may be termed G^E_{res}. In ethanol-heptane mixtures[99] electrostatic interactions completely account for G^E. G^E_{res} are nonspecific and include electrostatic interactions. G^E can be taken as the sum,

$$G^E = G^E_{assc} + G^E_{res} \qquad (2.2)$$

Intermolecular Interactions

In the studied systems all constituent molecules have dipole moments shown in Table II.[100-102] Dipoles (electrostatic in nature) preferentially orient molecules. They can thereby reinforce specific interactions. In hydrogen bonding[103] electrostatic forces are the major interaction contributor. Charge transfer is secondary.

TABLE II

FURTHER PROPERTIES OF SOLVENTS STUDIED

Parameter \ Compound	Acetone*	Methyl iodide**	Pyridine*
Critical pressure, P_c/atm	47.50	65.	56.40
Critical temperature, T_c/K	509.10	528.	620.00
Dipole moment, μ/Debye	2.86	1.6	2.20
Radius of gyration, R_D/Å	2.740	1.0458	3.050
N = association parameter	0.0	0.0	0.2***

*Reference 101.

**Reference 102.

***Reference 103.

Hydrogen bonding is seen to be minimal in the systems investigated. However, four types of electrostatic interaction do likely occur. They are the interactions arising from dipole-dipole, dipole-induced dipole, dispersion (induced-dipole-induced dipole), and repulsive overlap.[104]

Dipole-dipole interactions arising from all orientations of two molecular dipoles yield an average potential energy v(r):

$$v(r) = \frac{-2}{3kT} \frac{\mu_1^2 \mu_2^2}{r^6} \tag{2.3}$$

where μ_1 and μ_2 are the molecular dipole moments, r, the intermolecular distance, k, the Boltzmann constant and T, the absolute temperature (K).

Dipole-induced dipole interactions yield negative potential energies as do dipole-dipole interactions. Averaging over all orientations gives

$$v(r) = \frac{-2 \bullet \mu^2 \alpha}{r^6} \tag{2.4}$$

where α is the polarizability of a self-associating molecule.

Dispersion interactions arise from instantaneous fluctuations of electron density in molecules. Approximately,

$$v(r) = \frac{-3}{2} \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1 \alpha_2}{r^6} \tag{2.5}$$

I and α are the ionization potential and polarizability, respectively of molecules 1 and 2.

The three above described interactions are attractive. The fourth, a counter to the attractive aspects of charge transfer and electrostatic interaction, is the van der Waals repulsive overlap.

Mathematically the potential energy for this repulsive interaction is approximately

$$v(r) = c_i \, e^{-c_2 r} \qquad (2.6)$$

where c_1 and c_2 are characteristic constants for a given type of molecule. It arises when the intermolecular distance r is so reduced that it causes coulombic repulsion between the interacting nuclei. It takes on the identity of the short-range force depicted in Figure 1 at small R.

Besides electrostatic interactions, which as described include repulsive overlap, there is charge-transfer overlap. The energy, $h\gamma$, of spectroscopic charge transfer between a donor m orbital and an acceptor n orbital is the energy, V_{CT}:[105]

$$V_{CT} = \sum_{m,n}\sum \frac{-|KS_{mn}|^2}{h\gamma_{mn}} \qquad (2.6)$$

S is the overlap of orbitals m and n. K is estimated from the charge transfer molar absorptivity (ε).

Lastly, intermolecular interaction can arise purely on quantum mechanical grounds. This comes about from overlapping molecular charge distributions causing repulsion between electrons of identical spin. The exchange repulsion energy (V_{ER}) arising from pairwise summation over atomic orbitals i and j is:

$$V_{ER} = \sum_{i}\sum_{j} \frac{c_{ij} \, S^2_{ij}}{r_{ij}} \qquad (2.7)$$

where c_{ij} is a coefficient equalling c or 2c depending on whether the atomic orbitals are singly or doubly occupied. S is again the orbital overlap and r the orbital separation.

The excess free energy (Equation 2.1) is the summation of intermolecular interaction resultant from mixing two liquids. It is the sum of G^E_{assc} (specific) and G^E_{res} (nonspecific). Equations 2.3-2.6 represent G^E_{res}; and equations 2.7 and 2.8 represent G^E_{assc} for the most part.

Spectroscopic Dissociation Constant K_s

Spectroscopic equilibrium constants K_c[36] are normally derived for formation of the complex, DA. The spectroscopic dissociation constant K_s[12,106] is the reciprocal for that of complex formation. Both constants embody charge transfer and perhaps also electrostatic forces. If it is assumed that G^E_{assc} of Equation 2.2 represents only intermolecular interactions, G^E equals G^E_{assc} as G^E_{res} goes to zero. Knowledge of equilibrium constants then permit explicit evaluation of activity coefficients, G^E and other excess thermodynamic functions.

For a system consisting of only 1:1 complexation (Equation 1.16) by the law of mass action, the spectroscopic dissociation constant K_s can be defined as:

$$K_s = \frac{n_{D_1} n_{A_1}}{n_{DA}(n_{D_1} + n_{A_1} + n_{DA})} \qquad (2.9)$$

where n_{D_1}, n_{A_1} and n_{DA} are the number of moles in a solution of donor, acceptor and DA complex, respectively.

As n_{DA} goes to zero and K_s goes to infinity, n_{D_1}, n_{A_1} and n_{DA} are calculated:

$$n_{AD} = \frac{1}{2}\left[n_D + n_A - \left(n_D^2 + n_A^2 - 2n_D n_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right] \qquad (2.9a)$$

$$n_{D_1} = \frac{1}{2}\left[n_D - n_A + \left(n_D^2 - n_A^2 - 2n_A n_D \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right] \qquad (2.9b)$$

$$n_{A_1} = \frac{1}{2}\left[n_A - n_D + \left(n_D^2 + n_A^2 - 2n_D n_A \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right] \qquad (2.9c)$$

where n_D and n_A are the measured number of moles, D and A, before mixing. The values n_{DA}, n_{D_1} and n_{A_1} are used to calculate the mole fractions, χ_{DA}, χ_{D_1} and χ_{A_1}. Likewise, n_D and n_A are used to calculate χ_D and χ_A.

The excess free energy as well as other excess functions are calculatable using reactant activities. These are for the given system

$$\gamma_D = \frac{1}{\chi_{D_1}^{0}} \cdot \frac{\chi_{D_1}}{\chi_D} \qquad (2.10a)$$

and

$$\gamma_D = \frac{1}{\chi_{A_1}^{0}} \cdot \frac{\chi_{A_1}}{\chi_A} \qquad (2.10b)$$

where $\chi_{D_1}^{0}$ and $\chi_{A_1}^{0}$ are effective mole fractions of the monomeric component as its mole fraction goes to 1.

If $\chi_{D_1}^{0}$ and $\chi_{A_1}^{0}$ are set equal to unity, then γ_D and γ_A are solved for by substitution of equations 2.9 into equations 2.10. So,

$$\gamma_D = \frac{\chi_D - \chi_A + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}}{\chi_D\left[1 + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right]} \qquad (2.11a)$$

$$\gamma_A = \frac{\chi_D - \chi_A + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}}{\chi_A\left[1 + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right]} \qquad (2.11b)$$

The terms γ_D and γ_A are used to calculate ~~G~~^{E}, S^E and H^E:

$$G^E = \chi_D\, RT \ln \gamma_D + \chi_A\, RT \ln \gamma_A \qquad (2.12)$$

$$S^E = -\chi_D\, R \ln \gamma_D - \chi_A\, R \ln \gamma_A - \frac{2\chi_D\chi_A\, h_{T,P}}{T(1+K_s)\left[1 + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right]} \qquad (2.13)$$

$$H^E = \frac{2\chi_D\chi_A\, h_{T,P}}{(1+K_s)\left[1 + \left(\chi_D^2 + \chi_A^2 - 2\chi_D\chi_A \cdot \frac{1-K_s}{1+K_s}\right)^{\frac{1}{2}}\right]} \qquad (2.14)$$

where $h_{T,P}$ is the heat of reaction corresponding to the dissociation constant governed by K_s.

Use of Virial Coefficients

An equation of state attempts to give a mathematical description of matter at equilibrium according to its moles, volume, temperature and pressure. The virial equation is such an equation of state. Deviations from the ideal gas law, PV = nRT, are described by it. Expressed in terms of density ρ as an infinite power series, the virial equation[10] is:

$$\frac{PV_m}{RT} = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \qquad (2.15)$$

with B, C and D being the second, third, fourth and so on virial coefficient, respectively, $\rho = 1/V_m$ and V_m, the molar volumes.

The virial equation of state by what is called the quasi-chemical approach considers associating mixtures perfect gases. Clusters (complexes) in associating gas mixtures are considered the effective number of molecules. For equation (1.16)'s 1:1 complexation equilibrium between D and A,[10]

$$B_{DA} = -K_2 RT \qquad (2.16)$$

where B_{DA} is the experimentally determined second virial coefficient and K_2, the association constant between molecules D and A to form DA.

Imperfect Gas Mixtures

The second virial coefficient represents deviations to 1:1 associations. It is valid only in the gas phase. For a system studied spectroscopically in solution, all forces, nonspecific and specific, may contribute. In the gas phase, unless composed of highly polarizable molecules such as carboxylic acids,[107] only attractive van der Waals (dispersion) forces should contribute. By the use of virial and partition coefficients[11], equilibrium constants can be calculated for the gas phase.

The van der Waals pairs for a mixture of D and A consist of D_2, A_2 and DA. Using a Lennard-Jones potential for molecular interaction, association constants of D_2, A_2 and DA can be calculated. For D_2 or A_2 pairs, the association constant K^A is

$$K^A = \frac{2}{3} \pi r_0^3 - B_{AA} \qquad (2.17)$$

B_{AA} is A's second's virial coefficient; and r_0 is the approximate diameter from kinetic theory obtained using Chapman's equation built on the Sutherland model for a hard-sphere diameter r_0 in viscosity measurements.[108] For the formation of DA pairs, the association constant K^{DA} is:

$$K^{DA} = \frac{4}{3} \pi r_{0_{DA}}^{3} - 2B_{DA} \tag{2.18}$$

where $r_{0_{DA}}$ is taken as the mean of r_{0_D} and r_{0_A}. B_{DA} is the mixed virial coefficient for the mixed components D and A which are determined experimentally,[10] evaluated by use of partition coefficients,[11] or computed from vapor-liquid equilibrium data.[100]

Second Virial Coefficients

The second virial coefficient accounts for deviations in ideal gas behavior due to bimolecular interactions. Though the number of experimental virial studies are numerous, the number of systems are more so. Various predictive methods have been advanced in recent years[109,102] for second virial coefficients. The latest method[100] using only the five physical parameters given in Table II is able to do this.

Virial coefficients embody both specific and nonspecific bimolecular forces. For a second virial coefficient B_{ij} at a specified temperature,

$$B_{ij} = B_{ij}^{F} + B_{ij}^{D} \tag{2.19}$$

where

$$B_{ij}^{F} = (B^{F}_{nonpolar})_{ij} + (B^{F}_{polar})_{ij} \tag{2.19a}$$

and

$$B^D_{ij} = (B^D_{metastable})_{ij} + (B^D_{bound})_{ij} + (B^D_{chemical})_{ij} \qquad (2.19a)$$

Second virial coefficients for pure and mixed components are designated $i=j$ and $i \neq j$, respectively. B_{ij} is the sum of superscript F and D terms arising from "free" (weak physical) and associated (chemical) molecular forces, respectively.

Temperature-dependent correlations as well as the manner of calculation using the five physical constants listed in Table II are given in Appendix A of "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria" by J. Prausnitz.[100] All terms, $B^F_{nonpolar}$, B^F_{polar}, $B^D_{metastable} + B^D_{bound}$, and $B^D_{chemical}$[k] depend on the critical pressure (P_c), critical temperature (T_c), and the radius of gyration (R_D). B^F_{polar} and $B^D_{metastable} + B^D_{bound}$ depend, in addition on the molecular dipole moment (μ). $B^D_{chemical}$ is the only term dependent on the association coefficient, N.

Nonpolar (noninteracting) compounds have virial coefficients that are represented well by only the term, $B^F_{nonpolar}$. This is analogous to the good representation of G^E in the mixing of nonpolar compounds.[41] Polar compounds whose virial coefficients include also B^F_{polar} and $B^D_{metastable} + B^D_{bound}$ terms might well be expected to exhibit deviations in their excess free energies. Compounds, such as the mentioned carboxylic acids[107] that dimerize significantly, must have a large contribution from $B^D_{chemical}$ and should be expected to show large deviations in G^E.

Vapor-Liquid Equilibrium

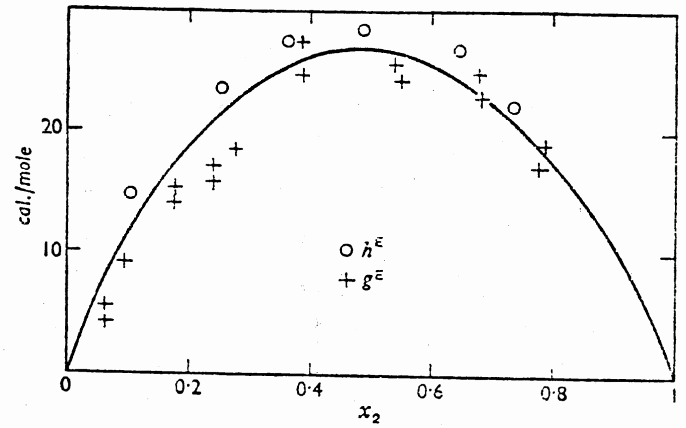
Vapor-liquid equilibrium studies provide vapor and liquid compositions for mixtures of compounds at constant temperature. From these vapor and liquid activities (γ), chemical potentials (μ) and excess free energies (G^E) can be calculated.[9] The Gibbs-Duhem equation (1.6) holds. If the excess volume of mixing V^E can be considered negligible,[12] then

$$G^E = H^E - TS^E \tag{2.20}$$

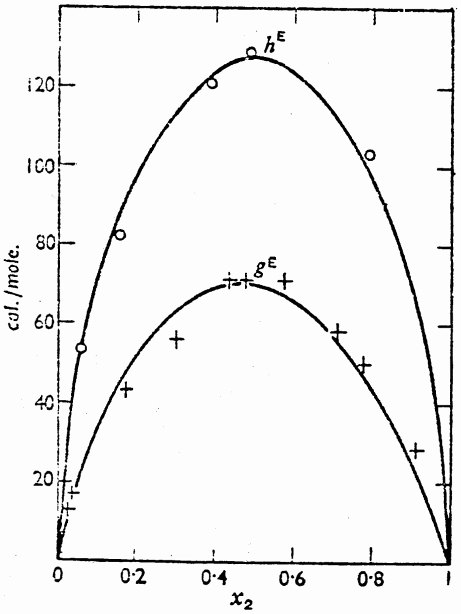
G^E is the difference or sum depending on the sign of H^E and S^E. The excess enthalpy H^E is determined calorimetrically[110] in practice and the excess entropy S^E from the sum or difference of G^E and S^E.

Figure 3[12] shows the excess enthalpy and free energy functions for the benzene--carbon tetrachloride and carbon disulfide--benzene systems. The benzene--carbon tetrachloride system's excess enthalpy and free energy functions (Figure 3A) nearly coincide indicating an S^E of near zero. This characterizes a regular solution of nonspecific interactions. The carbon disulfide--benzene system (Figure 3B), on the other hand, has H^E and G^E functions that are quite different. This difference is attributed to S^E arising from specific intermolecular forces.

The benzene--dimethyl sulfoxide (DMSO) system is shown in Figure 4.[111] The G^E and H^E functions are reversed to those of Figure 3B. DMSO self-complexation and "π-electron interaction" of benzene are seen to account for the reversal. Whereas interaction in the carbon disulfide--benzene system is between different chemical species, in the benzene--DMSO system interaction of the chemical species are of an



(A)



(B)

Figure 3. Thermodynamic Excess Functions for the Systems
A. Benzene(1)--Carbon Tetrachloride(2) and
B. Carbon Disulfide(1)--Benzene(2)[12]

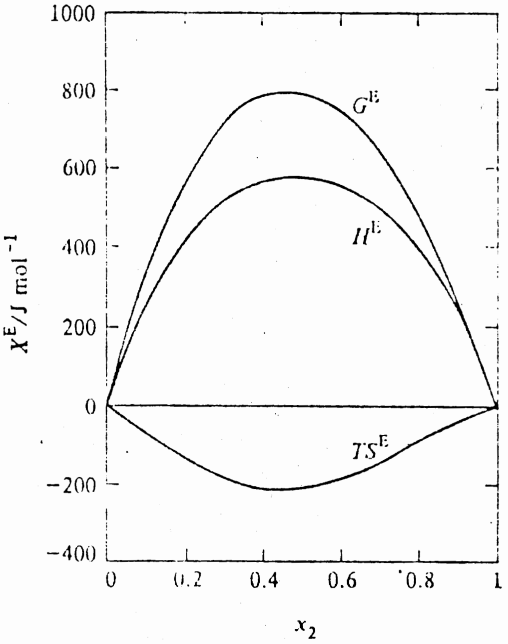


Figure 4. The Molar Excess Thermodynamic Properties at 25°C for Benzene(1)--DMSO(2).[113]

self-associative nature.

Exothermic interactions between benzene and carbon disulfide (Figure 3B) are weak as also between benzene and DMSO (Figure 4) where H^E and G^E are positive. Strong interactions such as occur in the pyridine--bromoform system,[112,113] in contrast, have highly negative H^E and G^E values. The strength of interaction is exhibited by solid formation when the components are mixed.

G^E is the sum-difference of the H^E and S^E functions. G^E versus mole fraction of a binary mixture is almost always smooth. Plots of H^E and S^E may, however, vary sinusoidally as does H^E in the water--ethanol system (Figure 5).[12] The sinusoidal curve arises from a changeover in specific molecular forces. In Figure 5 at high water, low ethanol, interactions between ethanol and water dominate. However, with increasing mole fraction ethanol, self-complexation of water and ethanol becomes more dominant. The influence of temperature on excess functions is also shown in Figure 5. Increased temperatures cause the excess functions to become more positive, indicating a lessening in interaction between the mixed components.

Investigated Systems

The excess free energies have been calculated in the literature from vapor-liquid equilibrium studies on the methyl iodide--acetone (Figure 6)[25] and pyridine--acetone (Figure 7)[114] systems. Comparison of the methyl iodide--acetone and benzene--carbon tetrachloride (Figure 3A) systems shows that the methyl iodide--acetone system deviates from the behavior of a regular solution. The S^E function indicates that methyl iodide and acetate interact to a significant degree only when

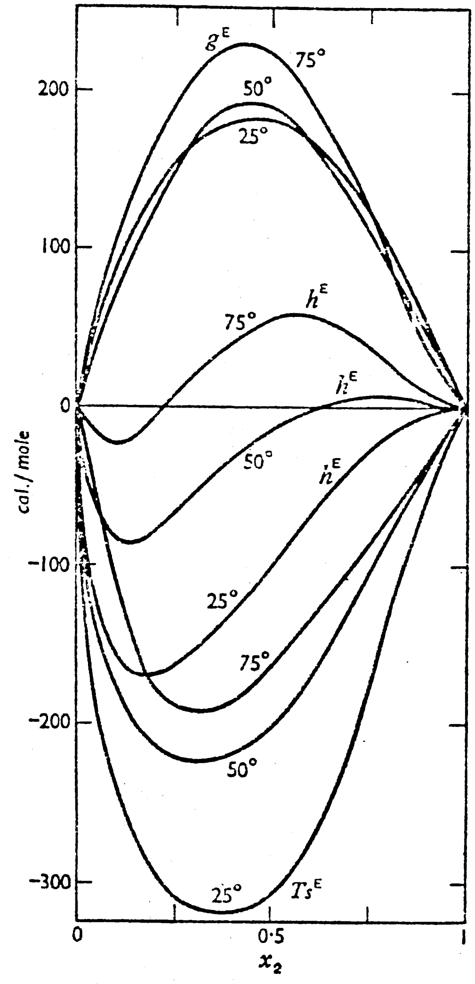


Figure 5. Thermodynamic Excess Functions for the System Water(1)--Ethanol(2) at 25°C, 50°C and 75°C.[12]

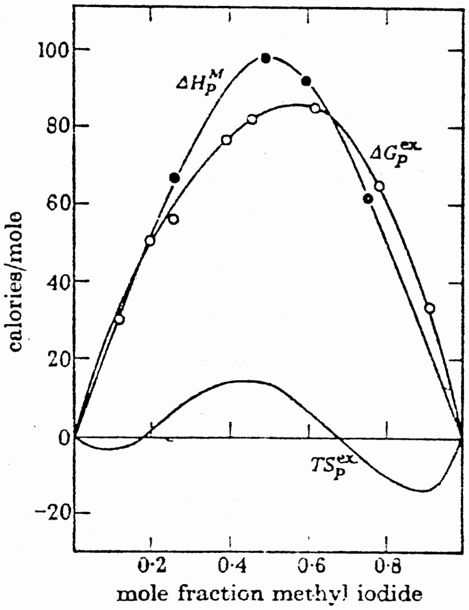


Figure 6. Excess Thermodynamic Functions at 25 °C for the Acetone--Methyl Iodide System.[25]

both are in high mole fraction.

The pyridine--acetone system (Figure 7) is not as easily examined as the methyl iodide--acetone system. This is because the H^E and S^E functions are not known. Still, the excess enthalpy H^E has been determined for the carbon tetrachloride--pyridine system (Figure 8).[115,116] H^E values are all negative except at high mole fraction carbon tetrachloride. This and the system's sinusoidal behavior similar to the behavior of the water-ethanol system (Figure 5) indicate that carbon tetrachloride and pyridine interact significantly. The pyridine--dimethyl sulfoxide system[117] additionally exhibits strong interaction between component molecules and most assuredly the pyridine-acetone system has interactions though not as large.

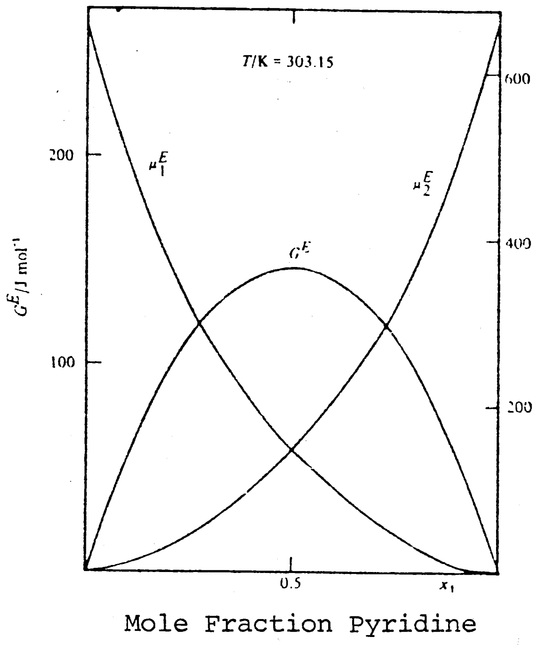


Figure 7. Excess Free Energy and
Activities at 30 °C
for the Acetone--
Pyridine System.[116]

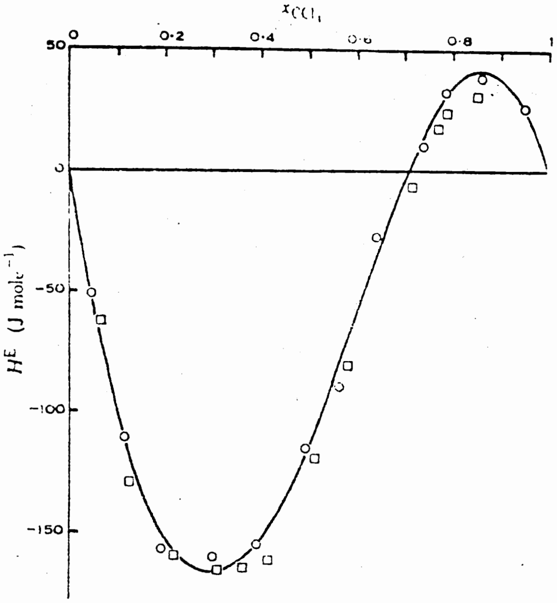


Figure 8. Heats of Mixing of CCl_4--C_5H_5N.117

CHAPTER III

EXPERIMENTAL

The preparation of all mixtures examined was done under nitrogen and in a dry box.[118] The box was kept under a small constant nitrogen pressure and flushed periodically and always before use with pure solvents. Dryness in the box was achieved by the constant presence of certified reagent phosphorus pentoxide (P_2O_5). Blue Drierite (anhydrous $CaSO_4$), which undergoes a color change to pink in the presence of water, remained blue in the dry box two weeks without developing the least tinge of pink.

Cyclohexane, acetone, pyridine, and methyl iodide were the solvents studied. Spectral grade (99.9%) pure Burdick and Jackson cyclohexane, acetone and pyridine contained (by Karl Fischer titration) from 0.001-0.003%, 0.13-0.22%, and 0.011-0.019% water, respectively. These were used as received in making up solutions except for certain batches of acetone which were further purified.[119,120] "Baker Analyzed" methyl iodide (99.8% pure) was purified in the same manner as the further purified acetone.

Methyl iodide, for instance, was added to Linde 5A molecular sieve roughly in the proportion of 5:1 in a round-bottom flask. The flask was capped, swirled and allowed to set 24 hours. The methyl iodide following that time was then distilled through a fractionation column under a dry nitrogen atmosphere. The first 10-20% of liquid distilled was collected but not used. Only the next 50-60% of the original volume distilled at constant temperature (42.4 ± 0.5 °C) was used in the present studies.

Acetone (56.2 ± 0.5 °C) was distilled in the same manner. All liquids when not in use were stored in the dry box or a desiccator in the dark. All operations with methyl iodide, which is UV light sensitive,[121] were performed in yellow light.

The cyclohexane, acetone and pyridine used without further purification had refractive indices of 1.4259 ± 0.0005, 1.3586 ± 0.0003 and 1.5093 ± 0.0008, respectively at 20 °C. These values compare well with those of the literature,[23] 1.42662, 1.3588 and 1.5095, respectively. Methyl iodide, dried and purified by fractionation, had a measured refractive index of 1.526 at 25 °C. This value agrees fairly well with Table I's value of 1.530.

Investigated binary solutions of pyridine--cyclohexane, acetone--cyclohexane, methyl iodide--iodide--cyclohexane, methyl iodide--acetone--cyclohexane and pyridine--acetone--cyclohexane were made up volumetrically to a specified molar concentration. The volumetric tolerances for the 5-, 10-, 25- and 50-ml volumetric flasks were ± 0.02, 0.02, 0.03 and 0.05 ml, respectively. The pipet tolerances for the 1-, 2-, 3-, 5-, 10- and 25-ml pipets were ± 0.012, 0.012, 0.02, 0.02, 0.04 and 0.06 ml, respectively. Pipets were calibrated by density[122] measurement using acetone in the dry box. The tolerances of the 2- and 25-ml pipets were determined to increase to ± 0.02 and 0.08 ml, respectively.

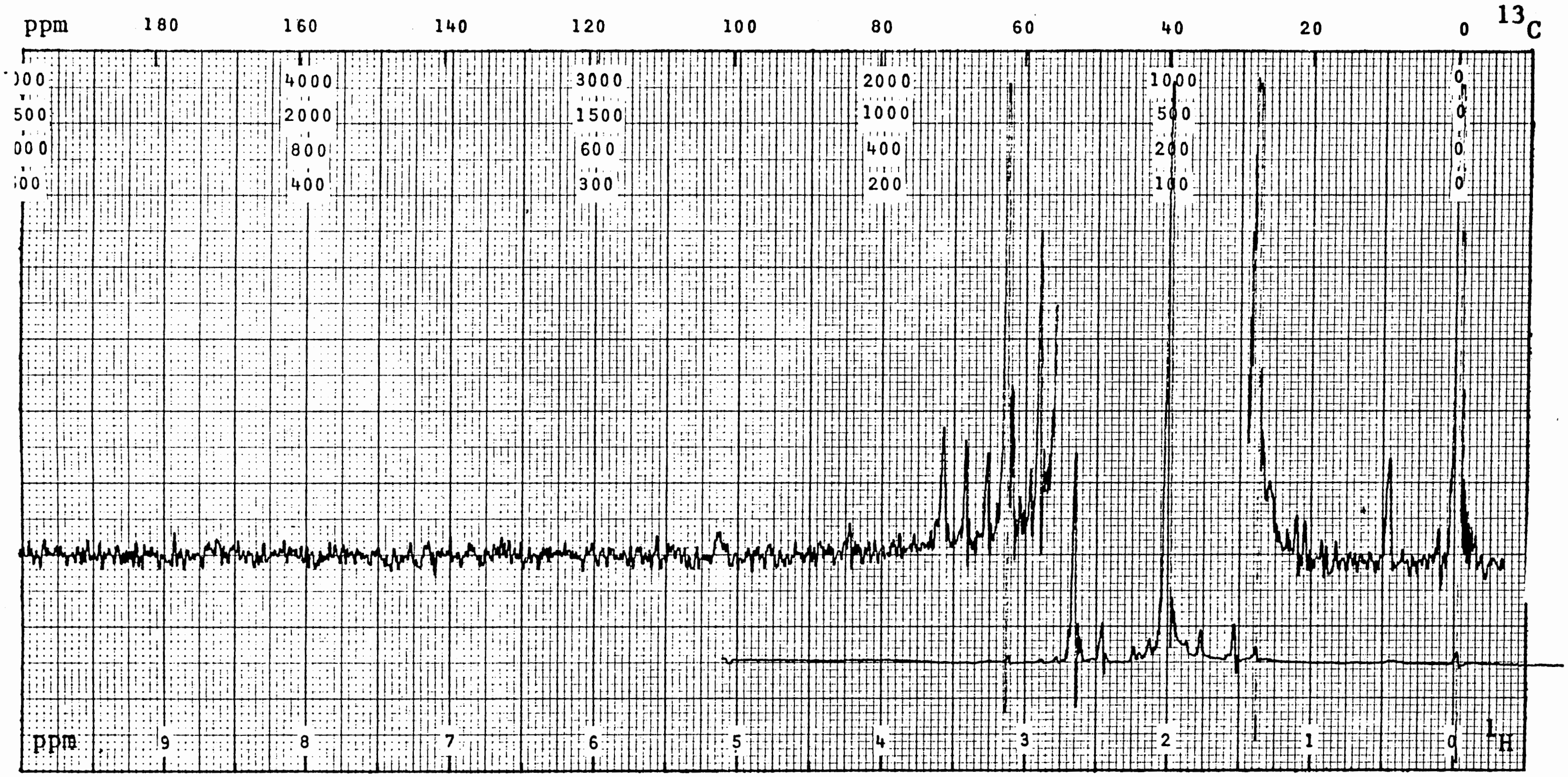
Davison molecular sieves (3A and 4A) activated in a 400 °C furnace overnight, when not fresh, were also used in drying methyl iodide and acetone. Upon removal of the sieves from the furnace, they were placed in a vacuum desiccator containing Drierite and phosphorus pentoxide and then connected to a vacuum pump. The pump was allowed to run overnight. The sieves were then quickly removed from the desiccator to the dry box where they were dispensed.

Initially stopcock grease was used to lubricate joints in the distillation apparatus. Traces of the grease appeared in the fractionated solvents and created an impurity which was observed in the NMR spectra. Therefore, Fisher brand Teflon sleeves were used in place of stopcock grease to seal ground glass joints. All solvents in storage were kept in bottles and sealed with American Can Company Parafilm "M".

NMR Spectra

A Varian XL-100(15) nuclear magnetic resonance spectrometer with probes for ^{1}H and ^{13}C nuclei with temperature control was used to study the three binary systems, namely methyl iodide, pyridine or acetone in cyclohexane, and two ternary systems, namely the methyl iodide--acetone--cyclohexane, pyridine--acetone--cyclohexane mixtures. These solutions were evaluated at 10 ± 1 ^{o}C, 20 ± 0.5 ^{o}C, and 30 ± 0.5 ^{o}C. Sample spectra for both single-sweep ^{1}H resonance and multi-sweep ^{13}C Fourier transform resonance are given in Figures 9, 10 and 11, 12, respectively.

In the preparation and running of an ^{1}H experiment, the sample was first made up volumetrically in the dry box. A sealed melting point capillary tube containing deuterobenzene and tetramethylsilane (Me_4Si) was placed in a 5-mm Wilmax NMR tube. With a disposable pipet, about

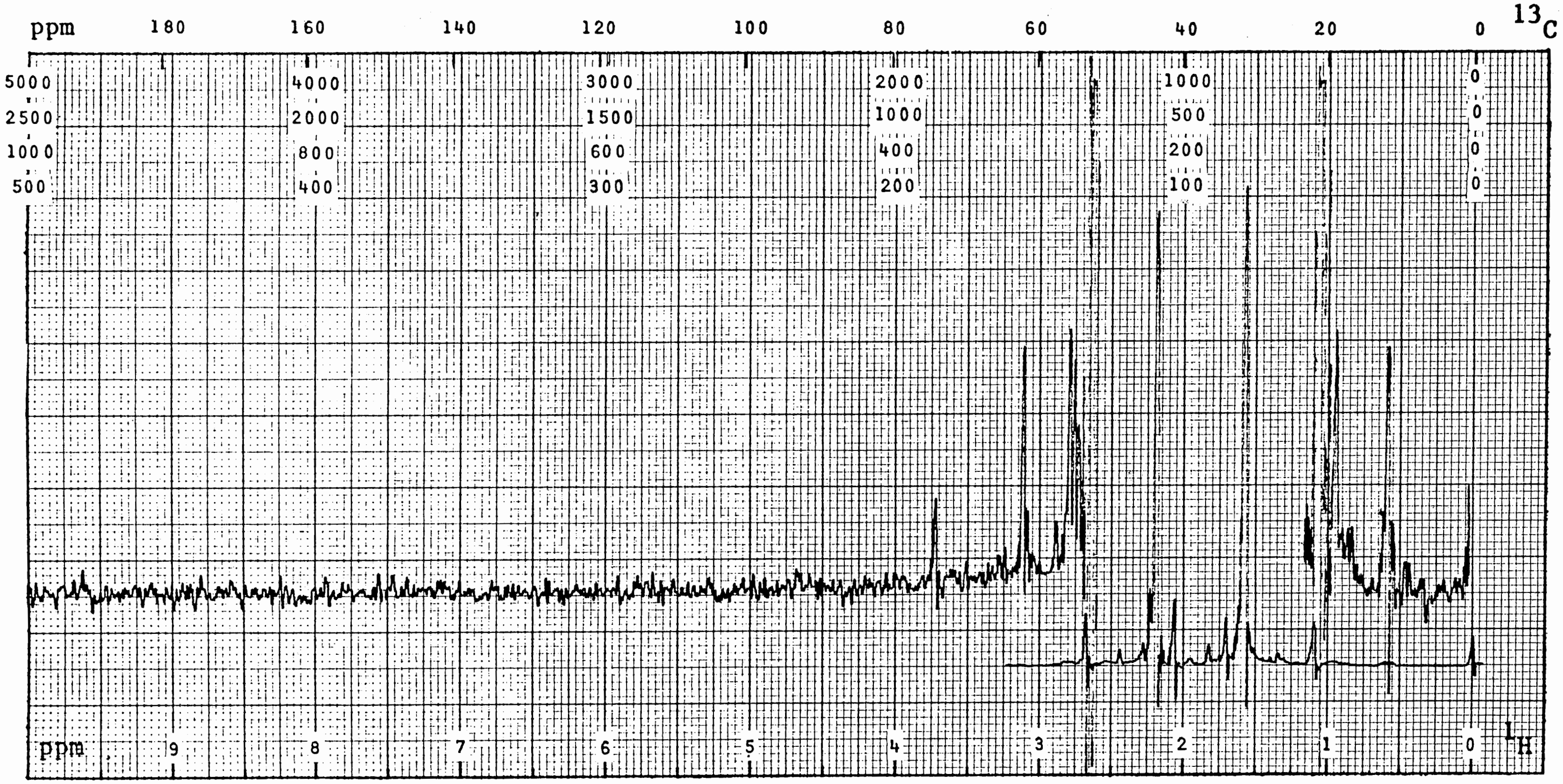


PFT _ CW X; Solvent. Cyclohexane; SO. 85771 Hz; PW. 1000 Hz; T. 30 °C; Acq/SA. 1.0

Size. N/A K; P2/RF. 70 μs/dB; SF. 100 Hz; FB. 2 Hz; Lock. C_6D_6; D5/ST. .250 s

DC. .N/A; Gated Off. .N/A; Offset. .N/A Hz; RF. .N/A W/dB; NBW. .N/A Hz

Figure 9. ^{1}H NMR Spectrum of a Solution of 4.8 M CH_3I in Cyclohexane at 30 °C.

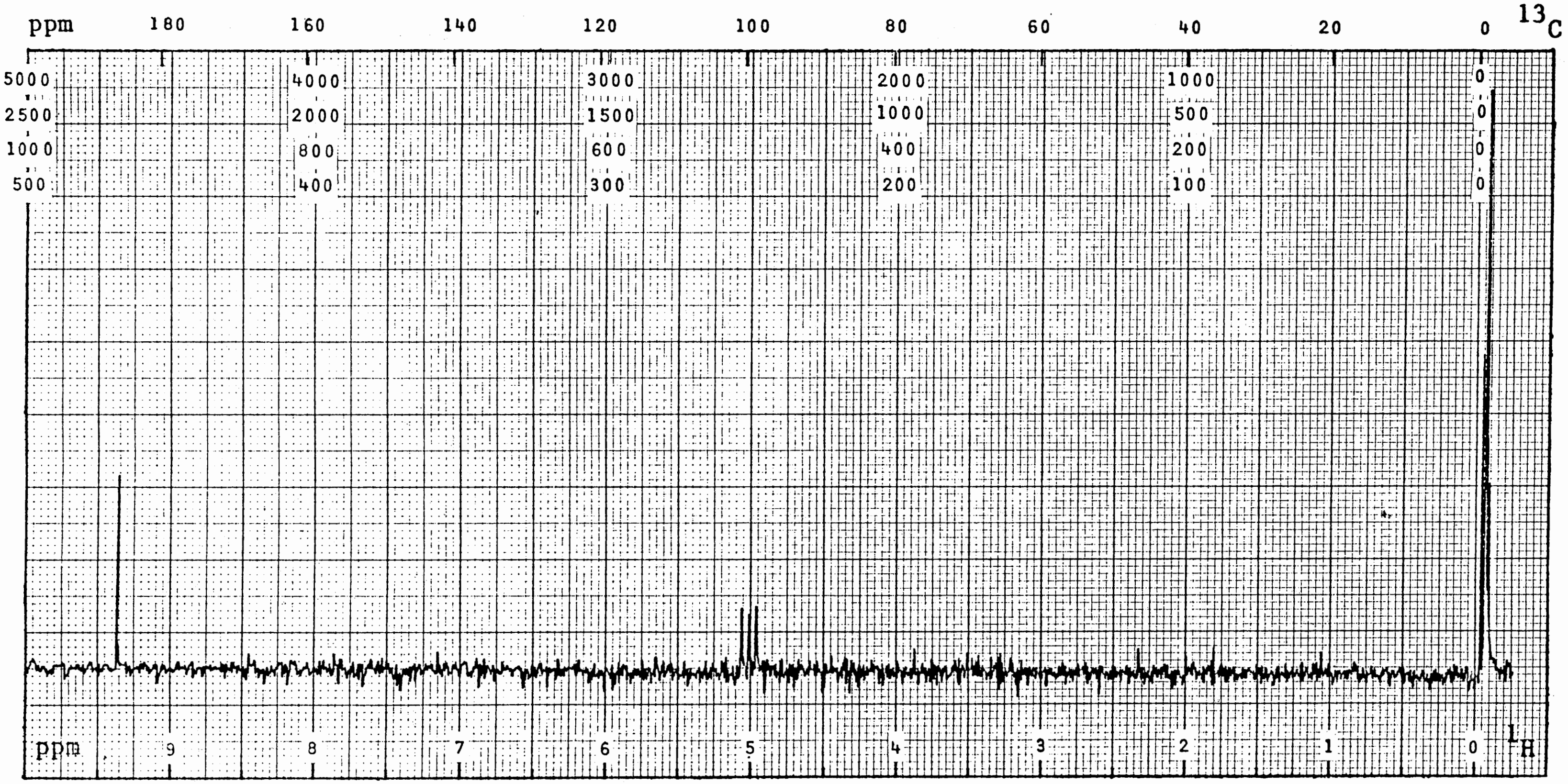


PFT _ CW X; Solvent. Cyclohexane; SO. 8577 Hz; PW. 1000 Hz; T. 30 °C; Acq/ SA. 1.0

Size. N/A K; P2/RF. 70 µs/dB; SF. 100 Hz; FB. 2 Hz; Lock. C_6D_6; D5/ST. 250 s

DC. . N/A; Gated Off. . N/A; Offset. . N/A; RF. . N/A W/dB; NBW. . N/A Hz

Figure 10. ^{1}H NMR Spectrum of a Solution of 0.32 M CH_3I and 6.8 M Acetone in Cyclohexane at 30 °C.

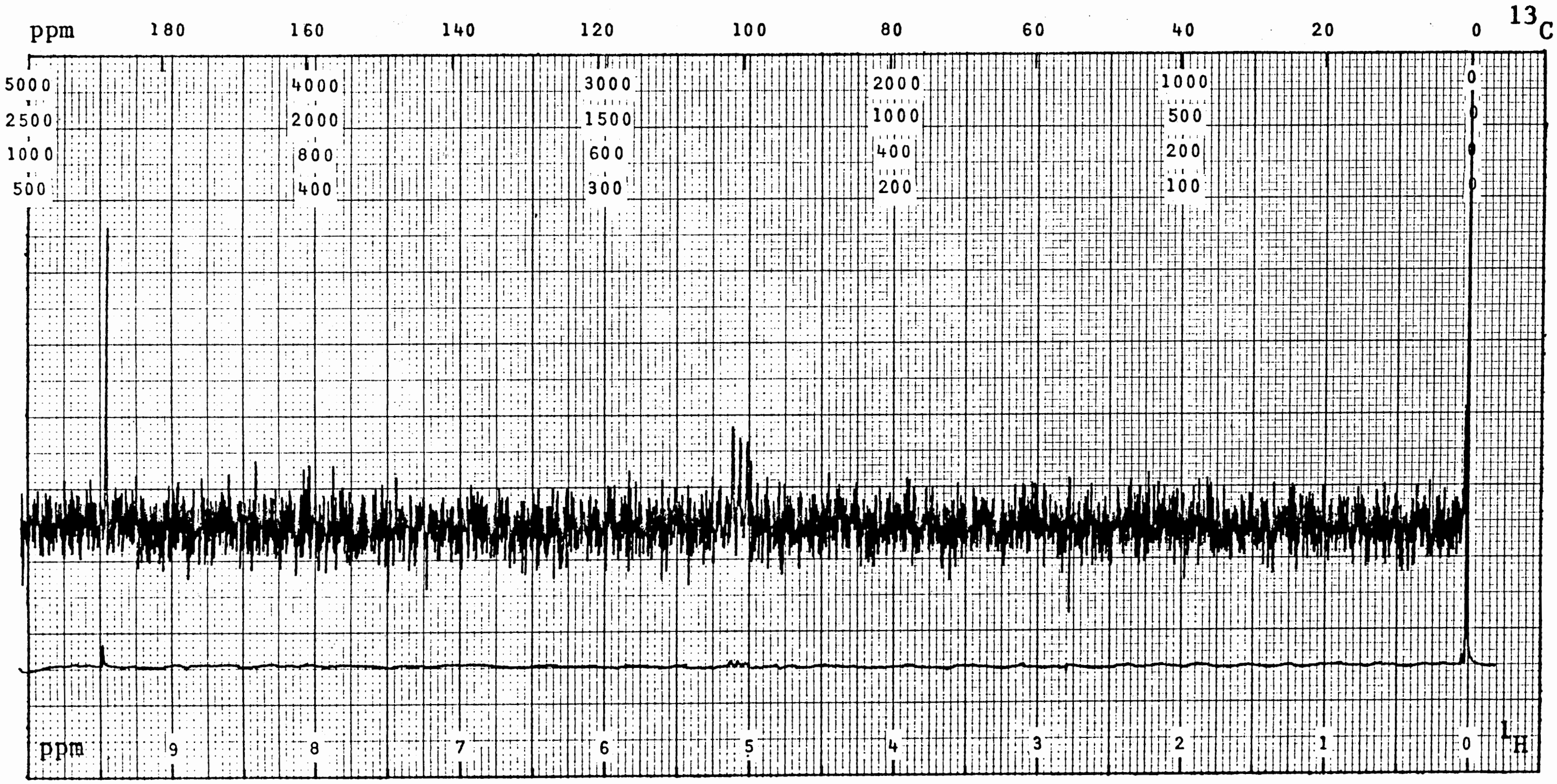


PFT X CW _; Solvent. Cyclohexane; SO. 35101 Hz; PW. 5000 Hz; T. 30 °C; Acq/SA. . 1200

Size. 8 K; P2/RF. 10 µs/dB; SF. 25.2 Hz; FB. 6000 Hz; Lock. C_6D_6; D5/ST. 6 s

DC. . ^{1}H; Gated Off. . N/A; Offset. 45315 Hz; RF. 9 W/dB; NBW. 100 Hz

Figure 11. ^{13}C NMR Spectrum of a Solution of 0.32 M CH_3I in Cyclohexane at 30 °C.



PFT X CW _; Solvent. Cyclohexane; SO. 35101 Hz; PW. 5000 Hz; T. 30 °C; Acq/SA. 44

Size. 8 K; P2/RF. . 10 μs/dB; SF. 25.2 Hz; FB. 6000 Hz; Lock. C_6D_6; D5/ST. 5s

DC. . ^{1}H; Gated Off. . N/A; Offset. . N/A Hz; RF. 9 W/dB; NBW. 100 Hz

Figure 12. ^{13}C NMR Spectrum of a Solution of 4.8 M CH_3I in Cyclohexane at 30 °C.

0.5 ml of the prepared solution was transferred to the NMR tube. The tube was then capped and sealed with parafilm. The NMR instrument operated at 100 MHz and was tuned to cover the ^1H frequency range. The sample was either cooled down to 10 °C with chilled air or heated to 30 °C by the instrument's temperature regulator.

The nmr tube containing the proton sample and sealed capillary tube was placed in the probe where it was spun by air jets and allowed to come to the probe's temperature. The instrumental settings were locked on the deuterium signal from the deuterobenzene in the sealed capillary within the spun NMR tube. The sample placed in the probe was subjected to a permanent magnetic field and then swept by an electromagnet in a measurement over a 5000 cm^{-1} frequency range. When the electromagnetic field frequency equalled that of a proton in the sample, a resonance signal peak was generated on a chart recorder as shown in Figures 9 and 10. Many of the peaks in these figures are spinning sidebands arising from the difference in magnetic field between the inner sealed capillary solution and the external proton sample. Sidebands have been used to determine absolute chemical shifts[123] and for temperature calibration of NMR instruments.[124]

Differentiation between true peaks in methyl iodide and cyclohexane and those of side bands (Figure 9) was done by adjustment of spin rate. An increase in the spin of the sample tube causes the side bands to move away from the sample peak and to diminish in intensity. The methyl iodide and cyclohexane proton peaks at δ 2.65 and 2.00, respectively, remain unchanged through the procedure of spin rate variation. The Me_4Si signal at δ 0.0, in the sealed capillary tube with the deuterobenzene, also remains unchanged.

Figure 10 is a proton spectrum of a ternary methyl iodide--acetone--cyclohexane solution at 30 °C. The cyclohexane, methyl iodide and acetone peaks relative to Me_4Si are δ 1.56, δ 2.28 and δ 2.45. The spectrum of the sample is locked onto the deuterium signal of deuterobenzene located in the inner capillary tube along with Me_4SI. Cyclohexane was used as internal reference in this study, and makes its chemical shift independent of Me_4Si and deuterobenzene used as external standards.

All solvents used in this study had no detectable impurities by NMR. Proton analysis of cyclohexane gave one peak at δ 1.79 as did methyl iodide at δ 2.38 and acetone δ 2.02, but pyridine gave three multiplet peaks at δ 6.7, 7.2 and 7.6. Water was seen only when deliberately added appeared at δ 5.2.

Two NMR runs were made at low temperatures using only pure acetone or mixtures of methyl iodide--acetone and pyridine--acetone. This was done in an attempt to resolve the individual monomer, dimer and complex chemical shifts if possible. Spectra were run at -30, -40 and -50 °C using deuterated methanol in the inner capillary tube as sample lock. No new peaks emerged except in the case of pure acetone. A peak, not a spinning sideband but possibly a ^{13}C-H satellite,[125] was detected at δ 3.2 downfield to the acetone peak at δ 1.9 at -50 °C. This peak which was only seen on an expended scale could well be the water as azeotropically incorporated in acetone.[120]

Carbon-13 samples were made up in the same manner as were the proton samples. The solution was transferred, however, to a Wilmax 12-mm coaxial NMR tube. An inner tube containing deuterated benzene and teflon-stoppered was placed in the 12-mm tube. The combined assembly is capped and sealed with parafilm.

The NMR instrument operated at 25.2 MHz with a ^{13}C probe was prepared for the measurement as before. The Fourier transform technique was used in the measurement of the ^{13}C resonance signal because its low natural abundance of 1.11% requires signal intensification. Signal enhancement was accomplished by making multiple scans (50-1000). As the number of scans increases, noise is averaged out. The signal-to-noise ratio is enhanced by a factor of $\sqrt{N}$ where N is the number of signal acquisitions (scans).[126]

Figures 11 and 12 are ^{13}C spectra of methyl iodide ran in cyclohexane at 30 ^{o}C. A ^{13}C chemical shift, as also for ^{1}H NMR, is the difference between the internal reference cyclohexane and methyl iodide signals. In carbon-13 NMR proton impurities in the deuterated benzene emit signals appearing about 100 ppm. The cyclohexane signal here has been arbitrarily set at 0 ppm. The methyl iodide signal is far downfield, at about 184 ppm. For pyridine with three different carbons, three carbon signals appear at about 95, 106 and 123 ppm for the β, γ and α carbons, respectively. Acetone containing two different carbons has two signals. Its methyl carbon is located at about 2,4 ppm and the carbonyl at about 173 ppm. All data tabulation and calculations were carried out in frequency units of Hertz since it was the most fundamental of data.

The frequency range for carbon-13 is from 0 to 5000 Hz. Intensities in the spectra represent combinations of concentration with number of acquisitions. Because of the mode of operation, the experimentally accumulated signal intensities have no significance. The proton NMR signal intensities, in this study, had significance but were not needed in equilibrium calculations. No carbon-containing impurities were detected.

IR Spectra

Samples were examined by IR using a Perkin-Elmer 621 grating spectrophotometer. Liquid cells with KBr windows and a 0.002-mm Teflon spacer held the studied samples. The instrument was operated in the double-beam mode. Sample solutions were made up volumetrically as previously indicated and run in the instrument versus air. The spectroscopic-grade acetone used in this study had a concentration of up to 0.22% water. A water band was reported by Lucchesi[127] in acetone as shown in Figure 13 (concentration of water given in parts per thousand, ppt). This band was reported for the most part eliminated by Jones[120] as shown in Figure 14. The band lies between 3300 and 3400 cm^{-1}. Figure 15 shows the IR spectrum of this region for cyclohexane (Figure 15a), acetone before purification (Figure 15b), acetone after purification (Figure 15c), and methyl iodide after purification (Figure 15d). Since the solvent of largest constant concentration was cyclohexane and its spectrum was much like that of acetone before and after purification, acetone was not purified further.

UV Spectra

The UV region of the spectrum was investigated using a Cary Model 14 double beam spectrophotometer with deuterium lamp. Two Starna Scientific quartz cells of 1 cm pathlength were used. The Cary-14 sample holder could be temperature regulated to permit study of solvents from 15 to 35 ^{o}C.

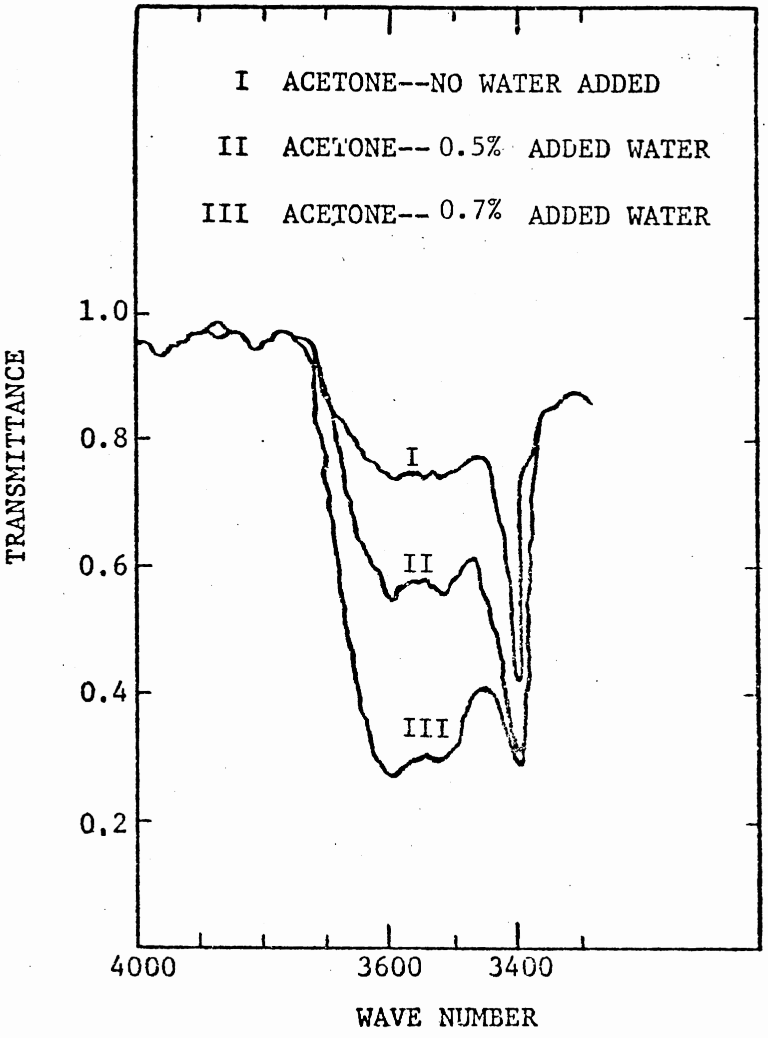


Figure 13. Lucchesi's Spectra of Acetone--Water Mixtures in the 3600 cm^{-1} Region.[127]

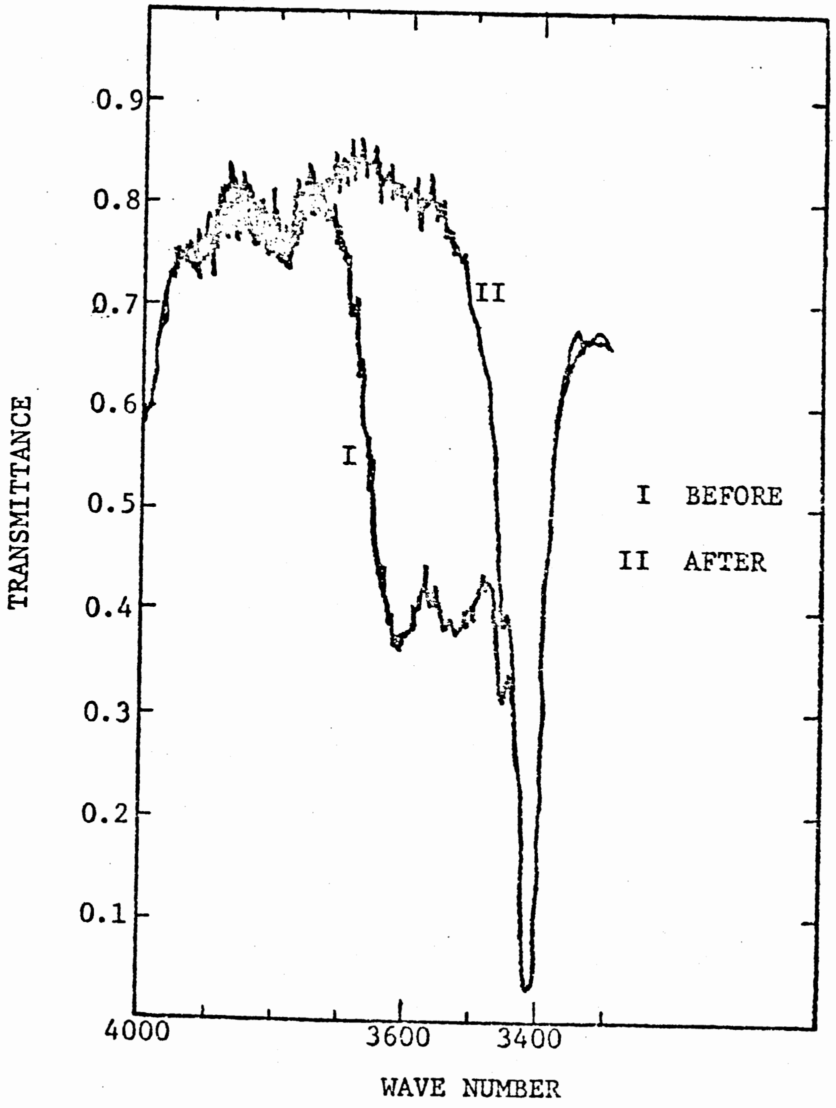
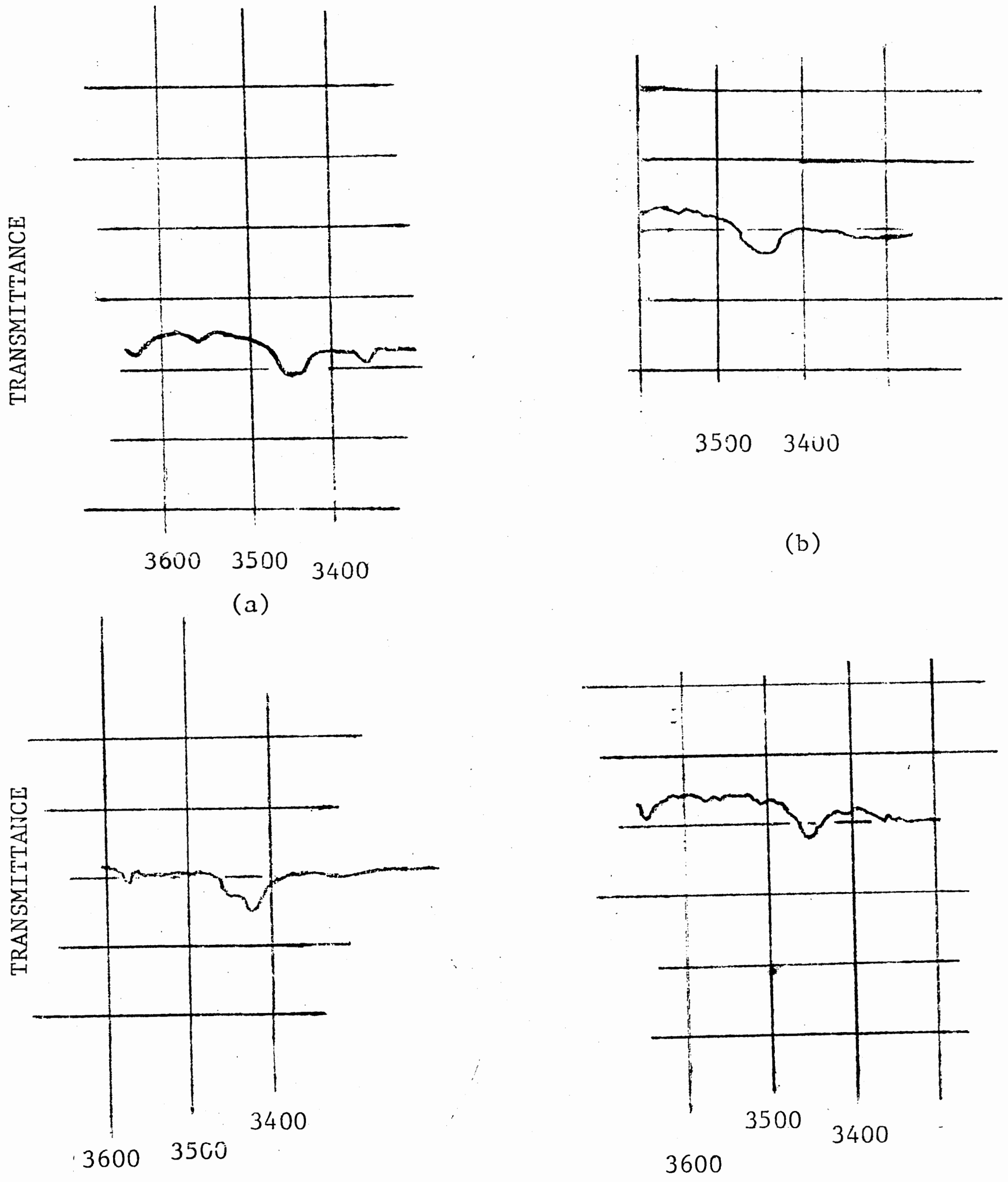


Figure 14. Spectrum of Acetone in the 3600 cm^{-1} Region Before and After Distillation.[120]



(a) (b) (c) (d)

Figure 15. Infrared Absorption from 3600-3400 cm^{-1} of a) Cyclohexane; b) 2.7 M Acetone in Cyclohexane before Purification; c) 2.7 M Acetone in Cyclohexane after Purification; and d) 3.2 M Methyl Iodide in Cyclohexane.

UV spectra of methyl iodide, pyridine, and acetone in cyclohexane were taken at room temperature. Beer's Law plots for the equation $A = \varepsilon bc$ were linear in each solvent's absorbance in the near UV. Methyl iodide in cyclohexane had a peak absorbance at 255 nm, $\varepsilon = 400$ (Table III, Figure 16). Pyridine in cyclohexane had a peak absorbance at 250 nm, $\varepsilon = 539$ (Table IV, Figure 17). Acetone in cyclohexane had a peak absorbance at 276 nm, $\varepsilon = 14.5$ (Table V, Figure 18). All three solvents had high absorption peaks in the far UV where the cyclohexane window character at 190 nm ended.

It was noted in the course of running UV spectra that the 276-nm peak had a slight shoulder towards the far UV. This is perhaps an indication of the water suggested by the I.R. peaks noted earlier. Still, the effect was believed minimal. In the carbon-13 spectra at 10 ^{o}C, the binary 6.8 M acetone in cyclohexane, there appeared carbonyl (C=O) absorption frequencies at 4417.35, 4416.64, 4412.14 and 4419.58 cm^{-1}. The value for the further purified acetone was the highest frequency observed, that of 4419.58. However, the scatter of the remaining data statistically fails to lead to 4419.58 cm^{-1} exclusion from the experimental body of information.[128]

TABLE III

ABSORPTION (Ab) AND ABSORPTIVITY (ε) OF METHYL IODIDE (CH_3I) IN CYCLOHEXANE AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT ROOM TEMPERATURE AND WAVELENGTH OF MAXIMUM ABSORBANCE (λ_M)

$[CH_3I] \times 10^4$	A	ε	λ_{M},nm
2.09	0.090	431	255
6.27	0.254	405	255
10.4	0.420	404	255
14.6	0.580	397	255
18.8	0.738	392	255
22.9	0.888	388	255
27.1	1.01	373	255

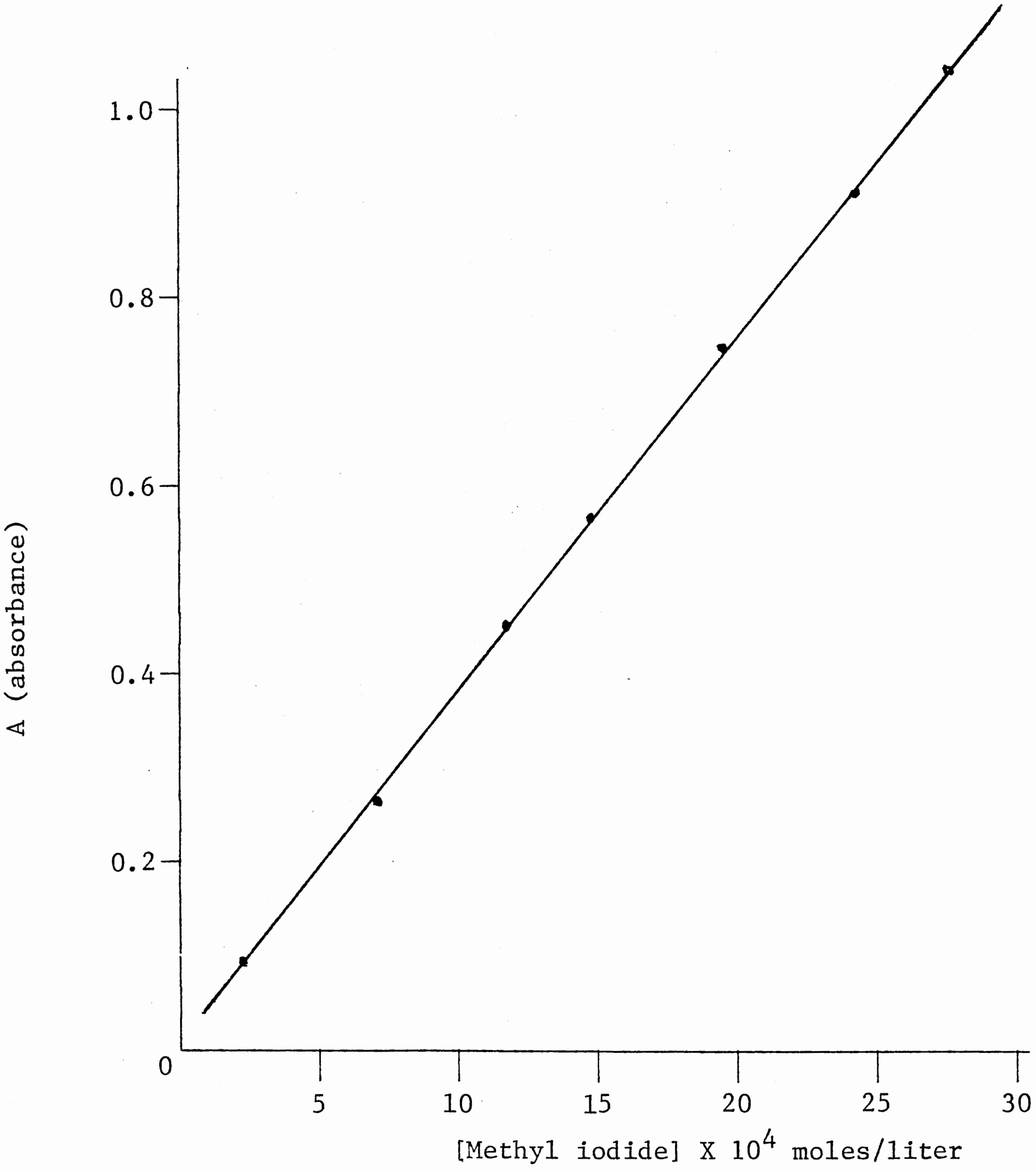


Figure 16. Plot of Absorbance Versus Methyl Iodide Concentration in Cyclohexane at 2.55 nm.

TABLE IV

ABSORPTION (Ab) AND ABSORPTIVITY (ε) OF PYRIDINE (Pyr) IN CYCLOHEXANE AS A FUNCTION OF PYRIDINE CONCENTRATION AT ROOM TEMPERATURE AND WAVELENGTH OF MAXIMUM ABSORBANCE (λ_M)

[Pyr] X 10^5	A	ε	λ_{M},nm
8.26	0.170	2058	249
16.5	0.350	2121	249
24.8	0.520	2097	249.5
33.0	0.690	2091	249.3
41.3	0.894	2165	250
49.5	1.066	2154	249.3
57.7	1.232	2135	249.5
66.0	1.405	2129	249.5
74.2	1.593	2149	249.5
82.4	1.770	2148	249.5

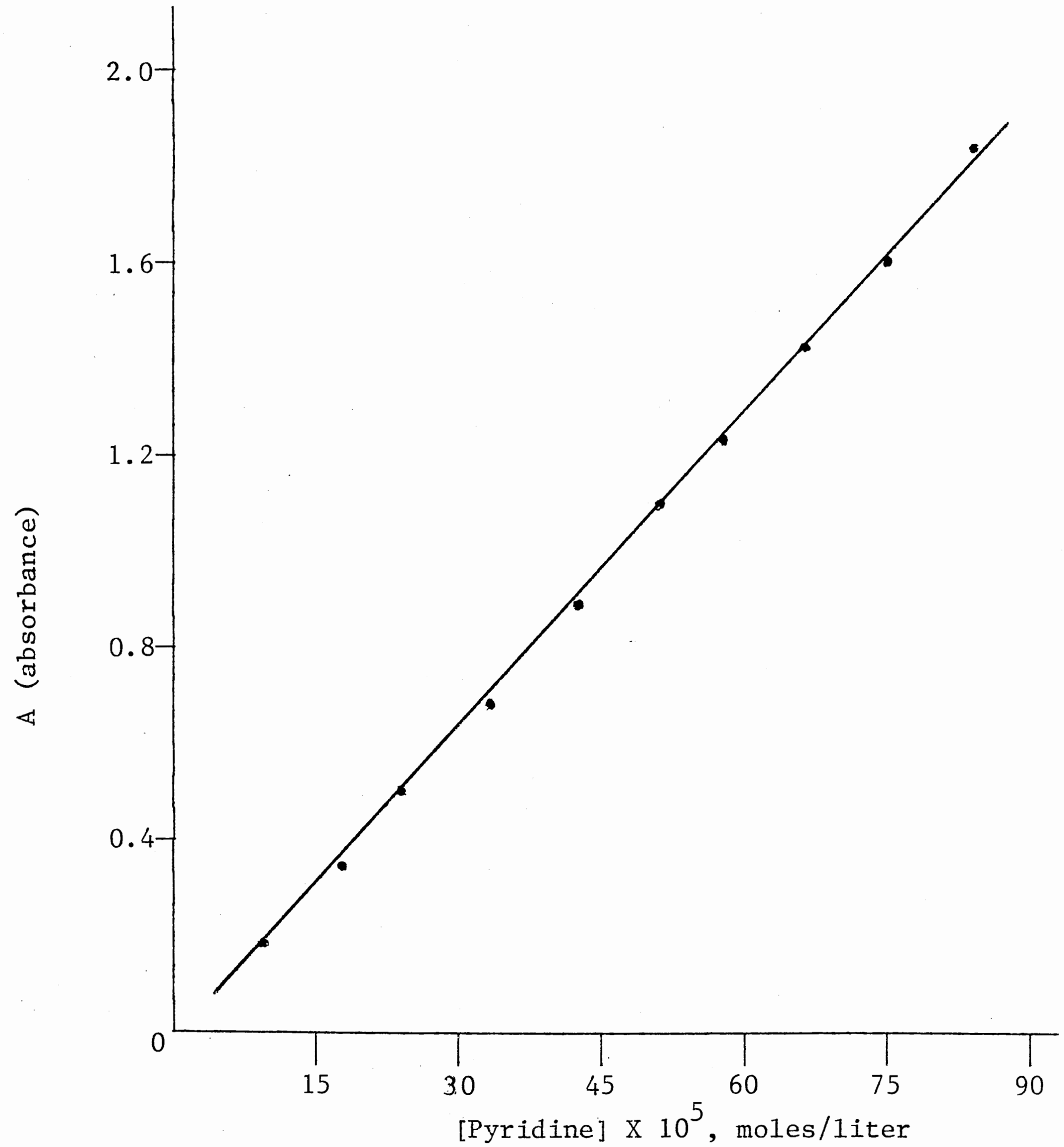


Figure 17. Plot of Absorbance Versus Pyridine Concentration in Cyclohexane at 250 nm.

TABLE V

ABSORPTION (Ab) AND ABSORPTIVITY (ε) OF ACETONE (Acet) IN CYCLOHEXANE AS A FUNCTION OF ACETONE CONCENTRATION AT ROOM TEMPERATURE AND WAVELENGTH OF MAXIMUM ABSORBANCE (λ_M)

[Acet] X 10^2	Ab	ε	λ_{M}, nm
1.13	0.162	14.3	275
2.26	0.337	14.9	276
3.38	0.501	14.8	277
4.50	0.655	14.6	276.5
5.62	0.807	14.4	277
6.73	0.960	14.3	276.5
7.84	1.115	14.2	277
8.95	1.262	14.1	276
10.05	1.415	14.1	276

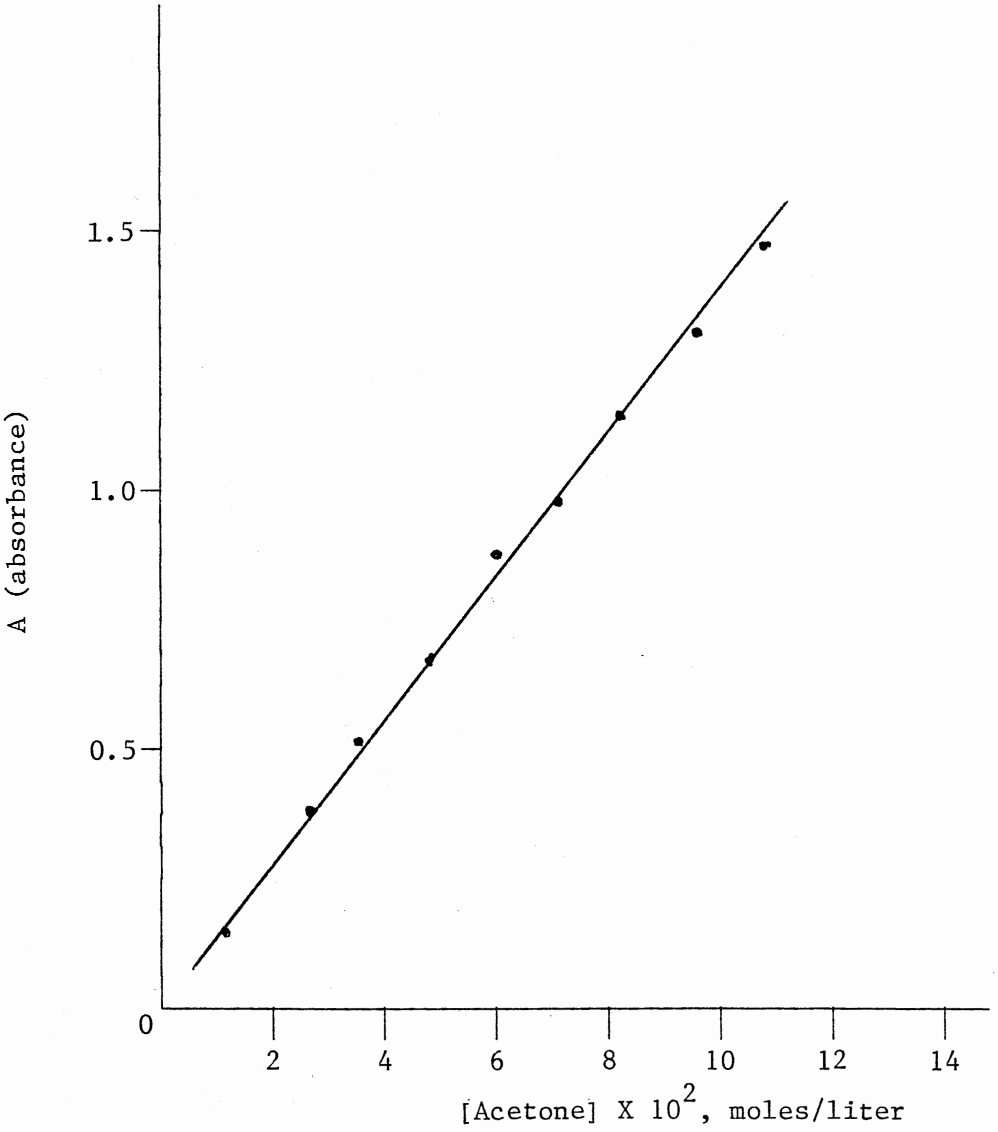


Figure 18. Plot of Absorbance Versus Acetone Concentration in Cyclohexane at 276 nm.

CHAPTER IV

RESULTS

The method of Prausnitz[100] was used to determine the pure and mixed component second virial coefficients of methyl iodide, pyridine, acetone, methyl iodide--acetone and byridine--acetone at 25 °C. These values were calculated to be -1472, -1935, -1674, -2062 and -2290 cm^3/mole, respectively.

NMR chemical shifts were corrected for magnetic susceptibility.[129] Corrected measurements of ^1H nuclei at 10 °C, 20 °C and 30 °C and ^{13}C nuclei at 10 °C and 30 °C are given in Appendices A and B. The binary solution data were used to calculate equilibrium constants of dimerization for the liquids, methyl iodide, pyridine and acetone in cyclohexane as given and shown in Appendix A.[36] These constants from ^1H and ^{13}C NMR data are listed for methyl iodide, pyridine and acetone in Table VI. Ternary solution data were used to calculate the equilibrium constants for formation of the methyl iodide-acetone and pyridine--acetone complexes in cyclohexane as given and shwon in Appendix B,[81] by the use of a modified Benesi-Hildebrand equation.

The equilibrium constants for the methyl iodide--acetone and pyridine--acetone systems solved using the modified Benesi-Hildebrand equation were also determined by iteratively solving equation B.9 in Appendix B.[130] These calculated equilibrium constants are listed for formation of the methyl iodide-acetone and pyridine--acetone complexes

TABLE VI

K_D, EQUILIBRIUM CONSTANT FOR DIMERIZATION OF METHYL IODIDE (CH_3I), PYRIDINE (PYR-β AND PYR-γ), AND ACETONE (CH_3 AND C=O) IN CYCLOHEXANE BY ^1H AND ^{13}C NMR AT 10 °C AND 30 °C

Nuclei	K_D	
	10 °C	30 °C
^1H, CH_3I	0.020	0.018
^{13}C, CH_3I	0.010	0.011
^1H, Pyr-β	-	-
^1H, Pyr-γ	-	-
^{13}C, Pyr-β	0.035	0.030
^{13}C, Pyr-γ	0.040	0.022
^1H, CH_3	0.040	0.018
^{13}C, CH_3	0.031	0.094
^{13}C, C=0	0.064	0.067

in cyclohexane in Tables VII and VIII, respectively. Computer input and output for Tables VII and VIII are given in Tables IX-XXIII.

IR spectra did not yield data sufficient for the calculation of equilibrium constants for either the methyl iodide--acetone--cyclohexane or pyridine--acetone--cyclohexane system. Although slight absorbance peak shifts in frequency were exhibited, they were too small to warrant equilibrium constant calculation.

Methyl iodide, pyridine and acetone in cyclohexane at room temperature exhibited absorbance maxima (λ_M) at 255, 250 and 276 nm, respectively in the ultraviolet spectrum. Molar absorptivities were calculated to be 378, 2124 and 14.4, respectively. These solvents' absorption spectrums overlap quite completely, so much so that attempts to calculate equilibrium constants in the manner of Chapter I yielded unreasonably large constants, such as for instance K_c = 1.52 for the pyridine--acetone in cyclohexane system. Therefore, interference of the reactants' absorptions with that of the complex masked and prevented equilibrium constant determination for the methyl iodide--acetone and pyridine--acetone pairs in cyclohexane.

A definite isosbestic point was determined for the pyridine--acetone in cyclohexane system at room temperature at 280 nm. However, no such point was found for the methyl iodide--acetone in cyclohexane system over the low-frequency UV spectrum. Still, all studied solvents, methyl iodide, pyridine and acetone exhibit large absorptions in the high-frequency UV, near the cyclohexane's cutoff at 190 nm, which made detection of isosbestic points difficult; and the methyl iodide--acetone in cyclohexane isosbestic point might well lie in this region.

TABLE VII

K_{AD}, EQUILIBRIUM CONSTANT FOR FORMATION OF METHYL IODIDE (CH_3I)--ACETONE IN CYCLOHEXANE BY ^1H NMR AT 10 °C, 20 °C, AND 30 °C AND BY ^{13}C NMR AT 10 °C AND 30 °C

Nuclei	K_{AD}		
	10 °C	20 °C	30 °C
^1H, CH_3I	0.34	0.23	0.18
^{13}C, CH_3I	0.22	-	0.21

TABLE VIII

K_{AD}, EQUILIBRIUM CONSTANT FOR FORMATION OF PYRIDINE (Py-β, Py-γ)--ACETONE IN CYCLOHEXANE BY ^{1}H NMR AT 10 °C, 20 °C and 30 °C AND BY ^{13}C NMR AT 10 °C AND 30 °C

Nuclei	K_{AD}		
	10 °C	20 °C	30 °C
^{1}H, Py-β	0.22	0.14	0.11
^{1}H, Py-γ	0.22	0.15	0.16
^{13}C, Py-β	0.18	-	0.20
^{13}C, Py-γ	0.19	-	0.24

TABLE IX

ASSOCIATION CONSTANT FOR METHYL IODIDE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF METHYL IODIDE $\delta(^1H)$, $\Delta\nu_R$ = 56.7 Hz, ν_R = 10 MHz AT 10°C

[MeI] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.325	0.275	58.8	58.8	0.588	0.021	0.015	-0.006
0.325	0.275	59.0	59.0	0.590	0.023	0.015	-0.008
0.325	0.275	58.6	58.6	0.586	0.019	0.015	-0.004
0.325	0.551	59.6	59.6	0.596	0.029	0.028	-0.001
0.325	0.551	60.2	60.2	0.602	0.035	0.028	-0.007
0.325	0.826	61.4	61.4	0.614	0.047	0.039	-0.007
0.325	0.826	61.6	61.6	0.616	0.049	0.039	-0.009
0.325	1.378	61.4	61.3	0.613	0.046	0.058	0.011
0.325	1.377	62.2	62.1	0.621	0.054	0.058	0.004
0.325	1.377	62.2	62.1	0.621	0.054	0.058	0.004
0.325	2.203	64.6	64.5	0.645	0.078	0.079	0.001
0.325	2.754	66.0	65.8	0.658	0.091	0.090	-0.002
0.325	2.756	65.6	65.4	0.654	0.087	0.089	0.002
0.325	4.132	67.8	67.5	0.709	0.108	0.109	0.001
0.325	4.134	66.8	66.5	0.675	0.098	0.109	0.011
0.325	6.892	72.2	71.7	0.665	0.150	0.132	-0.018
0.326	6.888	69.0	68.5	0.717	0.118	0.132	0.014
0.325	6.893	71.0	70.5	0.685	0.138	0.132	-0.006

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	1.89E-01	3.45E-01	1.15E-03	8.47E-03	2.12E 00 X AVE DEV
STD DEV =	0.15E-01	0.62E-01	0.72E-04		

TABLE X

ASSOCIATION CONSTANT FOR METHYL IODIDE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF METHYL IODIDE
$\delta(^1H)$, $\Delta\nu_R$ = 56.7 Hz, ν_R = 100 MHz AT 20°C

[MeI] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.321	1.360	61.4	61.3	0.613	0.046	0.052	0.006
0.321	1.360	62.4	62.3	0.623	0.056	0.052	-0.004
0.321	1.360	61.4	61.3	0.613	0.046	0.052	0.006
0.321	2.720	65.0	64.8	0.648	0.081	0.086	0.005
0.321	2.720	64.9	64.7	0.647	0.080	0.086	0.006
0.321	3.535	67.8	67.6	0.676	0.109	0.101	-0.008
0.321	4.080	70.8	70.5	0.705	0.138	0.110	-0.028
0.321	4.081	67.0	66.7	0.667	0.100	0.109	0.009
0.321	4.079	67.4	67.1	0.671	0.104	0.109	0.005
0.321	5.441	69.6	69.2	0.692	0.125	0.126	0.001
0.321	6.255	70.4	69.9	0.699	0.132	0.134	0.002
0.321	6.800	69.0	68.5	0.685	0.118	0.139	0.021
0.321	6.801	71.6	71.1	0.711	0.144	0.139	-0.005
0.321	6.800	72.2	71.7	0.717	0.150	0.139	-0.011

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	2.32E-01	2.26E-01	1.71E-03	1.19E-02	2.40E 00 X AVE DEV
STD DEV =	0.36E-01	0.72E-01	0.14E-03		

TABLE XI

ASSOCIATION CONSTANT FOR METHYL IODIDE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF METHYL IODIDE $\delta(^1H)$, $\Delta\nu_R = 56.7$ Hz, $\nu_R = 100$ MHz AT 30°C

[MeI] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.317	0.269	57.4	57.4	0.574	0.007	0.010	0.003
0.317	0.538	58.8	58.8	0.588	0.021	0.020	-0.001
0.317	0.807	59.2	59.2	0.592	0.025	0.029	0.004
0.317	0.807	60.2	60.2	0.602	0.035	0.029	-0.006
0.317	1.344	62.2	62.1	0.621	0.054	0.045	-0.010
0.317	1.344	61.6	61.5	0.615	0.048	0.045	-0.004
0.317	1.344	61.4	61.3	0.613	0.046	0.045	-0.002
0.317	1.343	61.4	61.3	0.613	0.046	0.045	-0.002
0.317	1.345	61.0	60.9	0.609	0.042	0.045	0.002
0.317	2.686	64.0	63.8	0.601	0.071	0.075	0.004
0.317	2.689	63.8	63.6	0.638	0.069	0.075	0.006
0.317	2.687	64.4	64.2	0.636	0.075	0.075	0.000
0.317	4.029	66.6	66.3	0.642	0.096	0.098	0.002
0.317	4.028	67.2	66.9	0.663	0.102	0.098	-0.004
0.317	4.031	66.0	65.7	0.669	0.090	0.098	0.008
0.317	5.370	68.6	68.2	0.657	0.115	0.115	-0.000
0.317	5.371	68.6	68.2	0.682	0.115	0.115	-0.000
0.317	6.714	70.0	69.5	0.682	0.128	0.128	0.000
0.317	6.712	70.2	69.7	0.695	0.130	0.128	-0.002
0.317	6.715	70.4	69.9	0.697	0.132	0.128	-0.004

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	2.38E-01	1.80E-01	3.35E-04	4.31E-03	2.25E 00 X AVE DEV
STD DEV =	0.15E-01	0.20E-01	0.19E-04		

TABLE XII

ASSOCIATION CONSTANT FOR METHYL IODIDE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF METHYL IODIDE

$\delta(^{13}C)$, $\Delta\nu_R$ = 4652.2 Hz, ν_R = 25.2 MHz AT 10°C

[MeI] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	Δ_{obs}-Δ_{cal} ppm
0.325	0.551	4663.7	4663.7	185.066	0.456	0.448	-0.008
0.325	0.826	4668.8	4668.8	185.269	0.659	0.641	-0.018
0.325	1.377	4676.4	4676.3	185.568	0.959	0.978	0.019
0.325	1.377	4678.3	4678.2	185.643	1.034	0.979	-0.055
0.325	2.203	4687.9	4687.8	186.022	1.413	1.387	-0.026
0.325	2.752	4692.3	4692.2	186.197	1.587	1.609	0.022
0.325	2.754	4693.0	4692.9	186.224	1.615	1.610	-0.004
0.325	4.133	4702.7	4702.4	186.603	1.993	2.049	0.056
0.325	4.129	4703.9	4703.7	186.653	2.044	2.049	0.005
0.325	5.508	4710.9	4710.5	186.926	2.316	2.370	0.054
0.325	6.891	4718.0	4717.5	187.201	2.592	2.616	0.024
0.325	6.892	4719.6	4719.1	187.265	2.655	2.617	-0.038
0.326	6.887	4720.1	4719.6	187.287	2.678	2.617	-0.061

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	4.40E 00	2.19E-01	1.73E-02	3.97E-02	1.57E 00 X AVE DEV
STD DEV =	0.12E 00	0.12E-01	0.16E-02		

TABLE XIII

ASSOCIATION CONSTANT FOR METHYL IODIDE AND ACETONE IN CYCLOHEXANE
FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF METHYL IODIDE
$\delta(^{13}C)$, $\Delta\nu_R$ = 4645.9 Hz, ν_R = 25.2 MHz AT 30°C

[MeI] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.317	0.269	4651.8	4651.8	184.596	0.237	0.215	-0.021
0.317	0.807	4661.5	4661.5	184.980	0.621	0.589	-0.032
0.317	1.344	4668.9	4668.8	185.270	0.911	0.900	-0.010
0.317	1.343	4668.9	4668.8	185.269	0.910	0.900	-0.010
0.317	2.686	4682.8	4682.6	185.819	1.460	1.490	0.030
0.317	2.686	4684.1	4683.9	185.869	1.510	1.491	-0.019
0.317	4.029	4693.2	4692.9	186.225	1.866	1.904	0.039
0.317	5.370	4701.2	4700.8	186.539	2.180	2.210	0.031
0.317	6.712	4709.2	4708.7	186.853	2.493	2.446	-0.047

```
              DELTA CMPLX   ASSOC CONST   SUM OF SQR   DEV EXT    DEV MAX
                4.20E 00      2.14E-01     7.81E-03   3.34E-02   1.44E 00 X AVE DEV
STD DEV =       0.15E 00      0.14E-01     0.11E-02
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TABLE XIV

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^1H\text{-}3)$, $\Delta\nu_R$ = 567.5 Hz, ν_R = 100 MHz AT 10°C

[Py] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.251	0.165	569.2	569.2	5.692	0.017	0.011	-0.005
0.252	0.165	569.6	569.6	5.696	0.021	0.011	-0.009
0.252	0.165	569.0	569.0	5.690	0.015	0.011	-0.004
0.252	0.275	567.6	567.6	5.676	0.001	0.018	0.018
0.252	0.275	570.0	570.0	5.700	0.025	0.019	-0.006
0.251	0.330	570.6	570.6	5.706	0.031	0.022	-0.009
0.252	0.330	570.8	570.8	5.708	0.033	0.022	-0.011
0.252	0.330	570.2	570.2	5.702	0.027	0.022	-0.005
0.251	0.496	572.2	572.2	5.722	0.047	0.032	-0.015
0.252	0.496	572.0	572.0	5.720	0.045	0.032	-0.013
0.252	0.496	572.0	572.0	5.720	0.045	0.032	-0.013
0.251	0.551	571.4	571.4	5.714	0.039	0.035	-0.003
0.252	0.661	573.6	573.5	5.689	0.060	0.041	-0.019
0.252	0.661	572.0	571.9	5.735	0.044	0.041	-0.003
0.252	0.825	572.8	572.7	5.719	0.052	0.050	-0.002
0.252	0.826	571.4	571.3	5.727	0.038	0.050	0.012
0.252	0.826	573.8	573.7	5.713	0.062	0.050	-0.012
0.252	0.826	572.0	571.9	5.737	0.044	0.050	0.006
0.252	1.375	575.8	575.7	5.719	0.082	0.076	-0.006
0.252	1.375	574.8	574.7	5.757	0.072	0.076	0.004
0.252	1.375	575.8	575.7	5.747	0.082	0.076	-0.006
0.252	1.375	574.4	574.3	5.757	0.068	0.076	0.008
0.252	1.376	574.2	574.1	5.743	0.066	0.076	0.010
0.252	1.376	574.6	574.5	5.741	0.070	0.076	0.006
0.252	2.751	580.0	579.8	5.745	0.123	0.124	0.002
0.252	2.751	579.8	579.6	5.798	0.121	0.124	0.004
0.252	2.752	579.8	579.6	5.796	0.121	0.124	0.004
0.252	2.752	579.4	579.2	5.826	0.117	0.124	0.008
0.252	2.753	580.0	579.8	5.796	0.123	0.124	0.002
0.252	4.129	583.6	583.3	5.792	0.158	0.158	-0.000
0.252	4.128	582.0	581.7	5.798	0.142	0.157	0.016
0.252	4.128	583.2	582.9	5.833	0.154	0.158	0.004
0.252	4.130	583.4	583.1	5.793	0.156	0.158	0.002
0.252	5.506	585.4	585.0	5.817	0.175	0.182	0.007
0.252	5.506	587.2	586.8	5.829	0.193	0.182	-0.011
0.252	5.506	587.2	586.8	5.831	0.193	0.182	-0.011
0.252	5.508	586.2	585.8	5.850	0.183	0.182	-0.001
0.252	5.508	585.4	585.0	5.868	0.175	0.182	0.007
0.252	6.887	589.2	588.7	5.868	0.212	0.200	-0.011
0.252	6.885	588.0	587.5	5.858	0.200	0.200	0.000
0.252	6.885	587.6	587.1	5.850	0.196	0.200	0.004
0.252	6.892	588.8	588.3	5.887	0.208	0.200	-0.007

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	3.31E-01	2.26E-01	3.14E-03	8.86E-03	2.16E 00 X AVE DEV
STD DEV =	0.17E-01	0.23E-01	0.79E-04		

TABLE XV

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^1H\text{-}3)$, $\Delta\nu_R = 566.6$ Hz, $\nu_R = 100$ MHz AT 20°C

[Py] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.249	1.359	573.0	572.9	5.729	0.063	0.064	0.001
0.249	1.359	573.6	573.5	5.735	0.069	0.064	-0.005
0.249	1.903	576.0	575.8	5.758	0.092	0.085	-0.008
0.249	2.718	577.6	577.4	5.774	0.108	0.111	0.003
0.249	2.718	577.6	577.4	5.774	0.108	0.111	0.003
0.249	3.263	579.6	579.3	5.793	0.127	0.126	-0.001
0.249	4.078	581.8	581.5	5.815	0.149	0.147	-0.002
0.249	4.078	580.4	580.1	5.801	0.135	0.147	0.012
0.249	4.623	583.0	582.6	5.826	0.160	0.159	-0.002
0.249	5.438	584.0	583.6	5.836	0.170	0.174	0.005
0.249	5.439	585.0	584.6	5.846	0.180	0.175	-0.005
0.249	5.983	586.0	585.5	5.855	0.189	0.184	-0.005
0.249	6.798	586.4	585.9	5.859	0.193	0.197	0.004
0.249	6.798	587.2	586.7	5.867	0.201	0.197	-0.004

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	4.00E-01	1.45E-01	3.62E-04	5.49E-03	2.16E 00 X AVE DEV
STD DEV =	0.30E-01	0.18E-01	0.30E-04		

TABLE XVI

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^1H\text{-}3)$, $\Delta\nu_R$ = 567.2 Hz, ν_R = 100 MHz AT 30°C

[Py] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.246	0.161	568.2	568.2	5.682	0.010	0.008	-0.002
0.246	0.268	567.2	567.2	5.672	-0.000	0.013	0.013
0.246	0.269	567.4	567.4	5.674	0.002	0.013	0.011
0.246	0.323	569.4	569.4	5.694	0.022	0.015	-0.007
0.246	0.484	568.8	568.8	5.688	0.016	0.022	0.006
0.246	0.538	570.0	570.0	5.700	0.028	0.024	-0.003
0.246	0.645	571.6	571.5	5.715	0.043	0.029	-0.015
0.246	0.806	570.2	570.1	5.701	0.029	0.036	0.006
0.246	0.806	570.6	570.5	5.705	0.033	0.036	0.002
0.246	0.806	571.8	571.7	5.717	0.045	0.036	-0.010
0.246	1.342	572.8	572.7	5.727	0.055	0.056	0.001
0.246	1.342	572.0	571.9	5.719	0.047	0.056	0.009
0.246	1.342	573.2	573.1	5.731	0.059	0.056	-0.003
0.246	1.343	574.4	574.3	5.743	0.071	0.056	-0.015
0.246	1.342	574.2	574.1	5.741	0.069	0.056	-0.013
0.246	1.343	572.2	572.1	5.721	0.049	0.056	0.007
0.246	1.343	572.4	572.3	5.723	0.051	0.056	0.005
0.246	2.684	577.6	577.4	5.774	0.102	0.099	-0.002
0.246	2.684	576.2	576.0	5.760	0.088	0.099	0.011
0.246	2.685	578.2	578.0	5.806	0.108	0.099	-0.008
0.246	2.684	577.0	576.8	5.780	0.096	0.099	0.003
0.246	2.684	577.2	577.0	5.768	0.098	0.099	0.001
0.246	2.686	577.0	576.8	5.770	0.096	0.099	0.004
0.245	2.688	577.8	577.6	5.768	0.104	0.099	-0.004
0.246	4.026	580.6	580.3	5.776	0.131	0.134	0.003
0.246	4.025	580.0	579.7	5.803	0.125	0.134	0.009
0.246	4.027	581.4	581.1	5.797	0.139	0.134	-0.005
0.246	4.025	581.0	580.7	5.767	0.135	0.134	-0.001
0.246	4.028	580.4	580.1	5.811	0.129	0.134	0.005
0.246	5.367	583.6	583.2	5.807	0.160	0.161	0.002
0.246	5.366	583.4	583.0	5.801	0.158	0.161	0.004
0.246	5.368	584.6	584.2	5.832	0.170	0.161	-0.008
0.246	5.370	584.0	583.6	5.830	0.164	0.161	-0.002
0.246	6.707	586.0	585.5	5.842	0.183	0.184	0.002
0.246	6.707	585.4	584.9	5.804	0.177	0.184	0.008
0.246	6.709	586.8	586.3	5.836	0.191	0.184	-0.006
0.246	6.707	586.8	586.3	5.855	0.191	0.184	-0.006
0.246	6.708	585.6	585.1	5.849	0.179	0.184	0.006
0.245	6.714	586.6	586.1	5.863	0.189	0.184	-0.004

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	4.24E-01	1.16E-01	1.96E-03	7.28E-03	2.03E 00 X AVE DEV
STD DEV =	0.32E-01	0.14E-01	0.53E-04		

TABLE XVII

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^1H\text{-}4)$, $\Delta\nu_R$ = 601.0 Hz, ν_R = 100 MHz AT 10°C

[Py] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.251	0.165	602.0	602.0	6.020	0.010	0.012	0.002
0.252	0.165	603.2	603.2	6.032	0.022	0.012	-0.010
0.252	0.165	601.2	601.2	6.012	0.002	0.012	0.010
0.252	0.275	600.4	600.4	6.004	-0.006	0.019	0.026
0.252	0.275	603.6	603.6	6.036	0.026	0.019	-0.006
0.251	0.330	603.0	603.0	6.030	0.020	0.023	0.003
0.252	0.330	604.6	604.6	6.046	0.036	0.023	-0.013
0.252	0.330	603.4	603.4	6.034	0.024	0.023	-0.001
0.251	0.496	606.6	606.6	6.066	0.056	0.034	-0.022
0.252	0.496	606.2	606.2	6.062	0.052	0.034	-0.018
0.252	0.496	605.8	605.8	6.058	0.048	0.034	-0.014
0.251	0.551	605.0	605.0	6.050	0.040	0.037	-0.003
0.251	0.661	603.0	602.9	6.029	0.019	0.043	0.024
0.252	0.661	607.4	607.3	6.073	0.063	0.044	-0.020
0.252	0.661	605.6	605.5	6.055	0.045	0.044	-0.002
0.252	0.825	606.0	605.9	6.059	0.049	0.053	0.003
0.252	0.826	605.0	604.9	6.049	0.039	0.053	0.013
0.252	0.826	607.8	607.7	6.077	0.067	0.053	-0.014
0.252	0.826	606.2	606.1	6.061	0.051	0.053	0.002
0.252	1.375	609.6	609.5	6.095	0.085	0.081	-0.004
0.252	1.375	608.8	608.7	6.087	0.077	0.080	0.004
0.252	1.375	609.6	609.5	6.095	0.085	0.081	-0.004
0.252	1.375	608.4	608.3	6.083	0.073	0.080	0.008
0.252	1.376	608.6	608.5	6.085	0.075	0.080	0.006
0.252	1.376	609.0	608.9	6.089	0.079	0.081	0.002
0.252	2.751	614.2	614.0	6.140	0.130	0.132	0.003
0.252	2.751	614.2	614.0	6.140	0.130	0.132	0.003
0.252	2.752	616.8	616.6	6.178	0.156	0.133	-0.023
0.252	2.752	613.4	613.2	6.166	0.122	0.132	0.010
0.252	2.753	614.2	614.0	6.132	0.130	0.132	0.003
0.252	4.129	618.2	617.9	6.140	0.169	0.169	-0.000
0.252	4.128	617.0	616.7	6.179	0.157	0.168	0.012
0.252	4.128	618.0	617.7	6.139	0.167	0.168	0.002
0.252	4.130	618.2	617.9	6.167	0.169	0.169	-0.000
0.252	5.506	620.4	620.0	6.177	0.190	0.195	0.005
0.252	5.506	620.0	619.6	6.179	0.186	0.195	0.009
0.252	5.506	619.4	619.0	6.200	0.180	0.195	0.015
0.252	5.508	621.0	620.6	6.196	0.196	0.195	-0.001
0.252	5.508	620.8	620.4	6.190	0.194	0.195	0.001
0.252	6.887	624.4	623.9	6.206	0.229	0.215	-0.013
0.252	6.885	623.6	623.1	6.204	0.221	0.215	-0.005
0.252	6.885	623.0	622.5	6.239	0.215	0.215	0.001
0.252	6.892	624.4	623.9	6.231	0.229	0.215	-0.013

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	3.63E-01	2.16E-01	5.16E-03	1.12E-02	2.28E 00 X AVE DEV
STD DEV =	0.23E-01	0.26E-01	0.13E-03		

TABLE XVIII

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^{1}H\text{-}4)$, $\Delta\nu_R$ = 600.1 Hz, ν_R = 100 MHz AT 20°C

[Py] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.249	1.359	607.4	607.3	6.073	0.072	0.071	-0.001
0.249	1.359	607.6	607.5	6.075	0.074	0.071	-0.003
0.249	1.903	610.2	610.0	6.100	0.099	0.094	-0.006
0.249	2.718	612.6	612.4	6.124	0.123	0.123	-0.000
0.249	2.718	612.6	612.4	6.124	0.123	0.123	-0.000
0.249	3.263	614.2	613.9	6.139	0.138	0.140	0.001
0.249	4.078	616.6	616.3	6.163	0.162	0.162	-0.000
0.249	4.078	615.4	615.1	6.151	0.150	0.162	0.012
0.249	4.623	618.0	617.6	6.176	0.175	0.175	-0.001
0.249	5.438	618.8	618.4	6.184	0.183	0.192	0.009
0.249	5.439	620.2	619.8	6.198	0.197	0.192	-0.005
0.249	5.983	621.8	621.3	6.213	0.212	0.203	-0.010
0.249	6.798	622.0	621.5	6.215	0.214	0.216	0.003
0.249	6.798	622.6	622.1	6.221	0.220	0.216	-0.003

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	4.35E-01	1.48E-01	4.06E-04	5.81E-03	2.04E 00 X AVE DEV
STD DEV =	0.31E-01	0.18E-01	0.34E-04		

TABLE XIX

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^{1}H\text{-}4)$, $\Delta\nu_R$ = 599.6 Hz, ν_R = 100 MHz AT 30°C

[Py] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	Δ_{obs}-Δ_{cal} ppm
0.246	0.161	601.6	601.6	6.016	0.020	0.010	-0.010
0.246	0.268	600.2	600.2	6.002	0.006	0.017	0.011
0.246	0.269	601.0	601.0	6.010	0.014	0.017	0.003
0.246	0.323	602.4	602.4	6.024	0.028	0.020	-0.008
0.246	0.484	604.8	604.8	6.048	0.052	0.030	-0.022
0.246	0.538	603.2	603.2	6.032	0.036	0.033	-0.003
0.246	0.645	605.2	605.1	6.051	0.055	0.038	-0.017
0.246	0.806	603.8	603.7	6.037	0.041	0.047	0.006
0.246	0.806	604.2	604.1	6.041	0.045	0.047	0.002
0.246	0.806	605.8	605.7	6.057	0.061	0.047	-0.014
0.246	1.342	607.2	607.1	6.071	0.075	0.073	-0.002
0.246	1.342	605.6	605.5	6.055	0.059	0.072	0.014
0.246	1.342	607.0	606.9	6.069	0.073	0.073	-0.000
0.246	1.343	608.4	608.3	6.083	0.087	0.073	-0.014
0.246	1.342	608.4	608.3	6.083	0.087	0.073	-0.014
0.246	1.343	606.0	605.9	6.059	0.063	0.073	0.010
0.246	1.343	606.6	606.5	6.065	0.069	0.073	0.004
0.246	2.684	611.4	611.2	6.112	0.116	0.123	0.007
0.246	2.684	610.8	610.6	6.106	0.110	0.123	0.013
0.246	2.685	612.8	612.6	6.156	0.130	0.123	-0.007
0.246	2.684	611.6	611.4	6.126	0.118	0.123	0.005
0.246	2.684	612.4	612.2	6.114	0.126	0.123	-0.003
0.246	2.686	611.6	611.4	6.122	0.118	0.123	0.005
0.245	2.688	612.6	612.4	6.114	0.128	0.123	-0.005
0.246	4.026	615.4	615.1	6.124	0.155	0.160	0.005
0.246	4.025	614.6	614.3	6.151	0.147	0.160	0.013
0.246	4.027	616.4	616.1	6.143	0.165	0.160	-0.004
0.246	4.025	615.2	614.9	6.113	0.153	0.160	0.007
0.246	4.028	615.8	615.5	6.161	0.159	0.160	0.002
0.246	5.367	618.6	618.2	6.149	0.186	0.189	0.003
0.246	5.366	618.0	617.6	6.155	0.180	0.189	0.009
0.246	5.368	620.0	619.6	6.182	0.200	0.189	-0.011
0.246	5.370	619.6	619.2	6.176	0.196	0.189	-0.007
0.246	6.707	621.0	620.5	6.196	0.209	0.211	0.002
0.246	6.707	620.8	620.3	6.156	0.207	0.211	0.004
0.246	6.709	621.8	621.3	6.192	0.217	0.211	-0.005
0.246	6.707	621.8	621.3	6.205	0.217	0.211	-0.005
0.246	6.708	621.2	620.7	6.203	0.211	0.211	0.000
0.245	6.714	622.2	621.7	6.213	0.221	0.211	-0.009

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	3.98E-01	1.72E-01	3.10E-03	9.16E-03	2.41E 00 X AVE DEV
STD DEV =	0.24E-01	0.18E-01	0.84E-04		

TABLE XX

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^{13}C\text{-}3)$, $\Delta\nu_R$ = 2407.8 Hz, ν_R = 25.2 MHz AT 10°C

[Py] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	Δ_{obs}-Δ_{cal} ppm
0.251	0.165	2409.0	2409.0	95.595	0.047	0.046	-0.001
0.252	0.275	2409.7	2409.7	95.622	0.074	0.076	0.001
0.251	0.330	2410.5	2410.5	95.654	0.106	0.090	-0.016
0.252	0.496	2410.5	2410.5	95.653	0.106	0.131	0.026
0.251	0.551	2412.5	2412.5	95.732	0.185	0.145	-0.040
0.251	0.661	2412.2	2412.1	95.720	0.172	0.171	-0.002
0.252	0.661	2411.5	2411.4	95.692	0.145	0.171	0.026
0.252	0.826	2413.3	2413.2	95.763	0.216	0.208	-0.007
0.252	0.826	2412.6	2412.5	95.735	0.188	0.208	0.020
0.252	0.826	2413.2	2413.1	95.759	0.212	0.208	-0.003
0.251	0.826	2413.5	2413.4	95.771	0.224	0.209	-0.015
0.252	1.375	2415.7	2415.6	95.857	0.309	0.321	0.012
0.252	1.375	2416.4	2416.3	95.885	0.337	0.321	-0.016
0.252	1.925	2418.7	2418.5	95.974	0.426	0.418	-0.008
0.252	2.752	2421.7	2421.5	95.876	0.543	0.540	-0.003
0.252	2.752	2421.5	2421.3	96.091	0.535	0.540	0.005
0.252	2.752	2421.0	2420.8	96.083	0.515	0.540	0.025
0.252	2.755	2422.3	2422.1	96.063	0.567	0.541	-0.026
0.252	3.301	2423.2	2422.9	96.114	0.601	0.609	0.008
0.252	4.129	2425.2	2424.9	96.148	0.678	0.698	0.021
0.252	4.128	2426.0	2425.7	96.225	0.709	0.699	-0.011
0.252	5.508	2428.8	2428.4	96.257	0.816	0.818	0.002
0.252	5.506	2429.0	2428.6	96.364	0.824	0.818	-0.006
0.252	6.885	2431.3	2430.8	96.372	0.911	0.912	0.001
0.252	6.887	2431.1	2430.6	96.459	0.903	0.912	0.008
0.252	6.887	2431.2	2430.7	96.451	0.907	0.912	0.005
0.252	6.892	2431.8	2431.3	96.455	0.931	0.912	-0.019

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	1.66E 00	1.81E-01	6.84E-03	1.65E-02	2.41E 00 X AVE DEV
STD DEV =	0.48E-01	0.95E-02	0.27E-03		

TABLE XXI

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^{13}C\text{-}3)$, $\Delta\nu_R$ = 2406.6 Hz, ν_R = 25.2 MHz AT 30°C

[Py] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.246	0.161	2407.8	2407.8	95.547	0.047	0.048	0.001
0.246	0.268	2408.8	2408.8	95.586	0.086	0.078	-0.008
0.246	0.269	2408.9	2408.9	95.590	0.090	0.078	-0.012
0.246	0.269	2408.5	2408.5	95.574	0.074	0.078	0.004
0.246	0.323	2409.1	2409.1	95.598	0.098	0.093	-0.005
0.246	0.484	2410.5	2410.5	95.653	0.153	0.136	-0.017
0.246	0.538	2411.1	2411.1	95.677	0.177	0.150	-0.027
0.246	0.645	2411.2	2411.1	95.680	0.180	0.176	-0.004
0.246	0.806	2412.0	2411.9	95.771	0.212	0.214	0.003
0.246	1.343	2415.0	2414.9	95.712	0.329	0.328	-0.001
0.246	2.684	2420.2	2420.0	95.992	0.531	0.543	0.012
0.245	2.688	2420.6	2420.4	95.829	0.547	0.544	-0.003
0.246	4.027	2423.8	2423.5	96.031	0.670	0.694	0.025
0.246	5.367	2426.9	2426.5	96.047	0.788	0.806	0.018
0.246	5.368	2427.4	2427.0	96.170	0.808	0.807	-0.001
0.246	6.709	2429.7	2429.2	96.288	0.895	0.893	-0.002
0.246	6.708	2429.7	2429.2	96.308	0.895	0.893	-0.002
0.245	6.714	2430.3	2429.8	96.395	0.919	0.894	-0.025

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	1.54E 00	2.09E-01	3.09E-03	1.39E-02	1.95E 00 X AVE DEV
STD DEV =	0.46E-01	0.12E-01	0.19E-03		

TABLE XXII

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE
$\delta(^{13}C\text{-}4)$, $\Delta\nu_R$ = 2700.3 Hz, ν_R = 25.2 MHz AT 10°C

[Py] mole/L	[Me_2CO] mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.251	0.165	2701.8	2701.8	107.214	0.059	0.064	0.005
0.252	0.275	2702.5	2702.5	107.241	0.086	0.105	0.018
0.251	0.330	2703.2	2703.2	107.269	0.114	0.125	0.011
0.251	0.551	2705.6	2705.6	107.240	0.209	0.201	-0.008
0.251	0.661	2706.2	2706.1	107.363	0.232	0.236	0.004
0.252	0.826	2707.6	2707.5	107.387	0.287	0.288	0.001
0.252	0.826	2707.4	2707.3	107.284	0.279	0.288	0.009
0.251	0.826	2707.8	2707.7	107.442	0.295	0.288	-0.007
0.252	1.375	2712.0	2711.9	107.386	0.460	0.442	-0.018
0.252	1.375	2711.9	2711.8	107.434	0.456	0.442	-0.014
0.252	1.925	2715.0	2714.8	107.450	0.577	0.574	-0.003
0.252	2.752	2718.8	2718.6	107.615	0.726	0.739	0.014
0.252	2.755	2720.0	2719.8	107.611	0.773	0.740	-0.033
0.252	3.301	2721.1	2720.8	107.732	0.815	0.832	0.017
0.252	4.129	2723.8	2723.5	107.694	0.920	0.951	0.031
0.252	4.128	2724.6	2724.3	107.880	0.951	0.951	-0.000
0.252	5.508	2728.3	2727.9	107.928	1.094	1.110	0.016
0.252	5.506	2728.9	2728.5	107.970	1.118	1.110	-0.008
0.252	6.885	2732.5	2732.0	108.074	1.256	1.233	-0.023
0.252	6.887	2731.2	2730.7	108.106	1.205	1.233	0.028
0.252	6.887	2731.9	2731.4	108.249	1.233	1.233	0.001
0.252	6.892	2732.6	2732.1	108.273	1.260	1.234	-0.027

	DELTA CMPLX	ASSOC CONST	SUM OF SQR	DEV EXT	DEV MAX
	2.19E 00	1.91E-01	6.16E-03	1.76E-02	1.90E 00 X AVE DEV
STD DEV =	0.52E-01	0.85E-02	0.31E-03		

TABLE XXIII

ASSOCIATION CONSTANT FOR PYRIDINE AND ACETONE IN CYCLOHEXANE FROM THE CHEMICAL SHIFT IN THE NMR SPECTRUM OF PYRIDINE $\delta(^{13}C\text{-}4)$, $\Delta\nu_R$ = 2698.6 Hz, ν_R = 25.2 MHz AT 30°C

[Py] mole/L	$[Me_2CO]$ mole/L	$\Delta\nu_{obs}$ Hz	$\Delta\nu_{cor}$ Hz	δ_{obs} ppm	Δ_{obs} ppm	Δ_{cal} ppm	$\Delta_{obs}-\Delta_{cal}$ ppm
0.246	0.161	2700.0	2700.0	107.142	0.055	0.067	0.012
0.246	0.268	2702.1	2702.1	107.225	0.138	0.110	-0.028
0.246	0.269	2701.6	2701.6	107.205	0.118	0.110	-0.008
0.246	0.269	2701.8	2701.8	107.213	0.126	0.110	-0.016
0.246	0.323	2701.7	2701.7	107.209	0.122	0.131	0.009
0.246	0.484	2703.7	2703.7	107.288	0.201	0.190	-0.011
0.246	0.538	2704.5	2704.5	107.320	0.232	0.209	-0.023
0.246	0.645	2704.7	2704.6	107.327	0.240	0.246	0.006
0.246	0.806	2706.1	2706.0	107.470	0.295	0.299	0.004
0.246	1.343	2711.0	2710.9	107.382	0.488	0.455	-0.033
0.246	2.684	2717.1	2716.9	107.754	0.726	0.744	0.019
0.245	2.688	2717.7	2717.5	107.575	0.749	0.745	-0.004
0.246	4.027	2721.7	2721.4	107.813	0.904	0.945	0.041
0.246	5.367	2726.1	2725.7	107.837	1.074	1.091	0.017
0.246	5.368	2726.1	2725.7	107.991	1.074	1.091	0.017
0.246	6.709	2729.7	2729.2	108.161	1.213	1.203	-0.010
0.246	6.708	2729.6	2729.1	108.161	1.209	1.203	-0.006
0.245	6.714	2730.4	2729.9	108.300	1.240	1.203	-0.037

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            DELTA CMPLX  ASSOC CONST   SUM OF SQR  DEV EXT   DEV MAX
              2.01E 00     2.27E-01     7.35E-03  2.14E-02  1.92E 00 X AVE DEV
STD DEV =     0.64E-01     0.15E-01     0.46E-03
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CHAPTER V

DISCUSSION

The manner of calculation of equilibrium constants using second virial coefficients shown in Chapter II is strictly for the gaseous phase at low and moderate pressures. This arises from the fact that terms in the virial expansion (Equation 2.15) do not converge at high pressures.[131] Still, by the use of second virial coefficients along with vapor-liquid G^E studies, equilibrium constants have been computed for several systems in the liquid phase in the literature.[50-53] This method has not been found suitable for the calculation of equilibrium constants for methyl iodide--acetone and pyridine--acetone in cyclohexane. Its unsuitability is attributed to dominance of nonspecific over specific forces, which is discussed in a later section.

Understand and predicting of liquid phase behavior is immensely complex. Although the gas phase is well understood and at condensation[132,133] the liquid-phase and gas-phase activities are equal, any quantitative understanding of the liquid phase is limited. In a liquid, potentials act on a molecule from nearest neighbors whereas such forces are not operative in a gas except at high pressure. The Wilson[134] and UNIQUAC equations[135,136] have been developed to predict gas-liquid behavior. Further study is needed.

Second Virial Coefficients

The second virial coefficients of methyl iodide, pyridine and acetone have been calculated by use of the five parameters listed in Table II. While P_c, T_c and M_D are experimentally determined values, R_D and N are mere estimates in the literature. Experimental second virial coefficients reported in the literature marked with a dot, •, are plotted versus temperature for the pure solvents studied, methyl iodide (Figure 19),[137] pyridine (Figure 20)[138] and acetone (Figure 21).[139-143] A curve is drawn through the experimentally determined literature second virial coefficients. The point marked with an X in each figure shows this study's calculated second virial coefficient. The difference between this calculated value and the literature curve ones varies from 400 cm^3/mole for methyl iodide and 600 cm^3/mole for pyridine to 200 cm^3/mole for acetone.

Van Ness[114] lists the second virial coefficients of pyridine and acetone as -2300 and -1850 cm^3/mole, respectively. These values, labeled ⊙ , are better for acetone and worse for pyridine (in comparison to the literature curve). The values calculated by the Prausnitz method are seen to be comparable. The magnitude of difference between the results of Van Ness and those of this study for the pure components is compounded in the mixed-component second virial coefficient of the pyridine--acetone system. Van Ness lists a value of -1650 cm^3/mole for the mixed-component second virial coefficient of the pyridine--acetone system, which is 600 cm^3/mole less negative than the value obtained in this study's. How Van Ness obtained the second virial coefficients cited in his paper is not specified. His values were

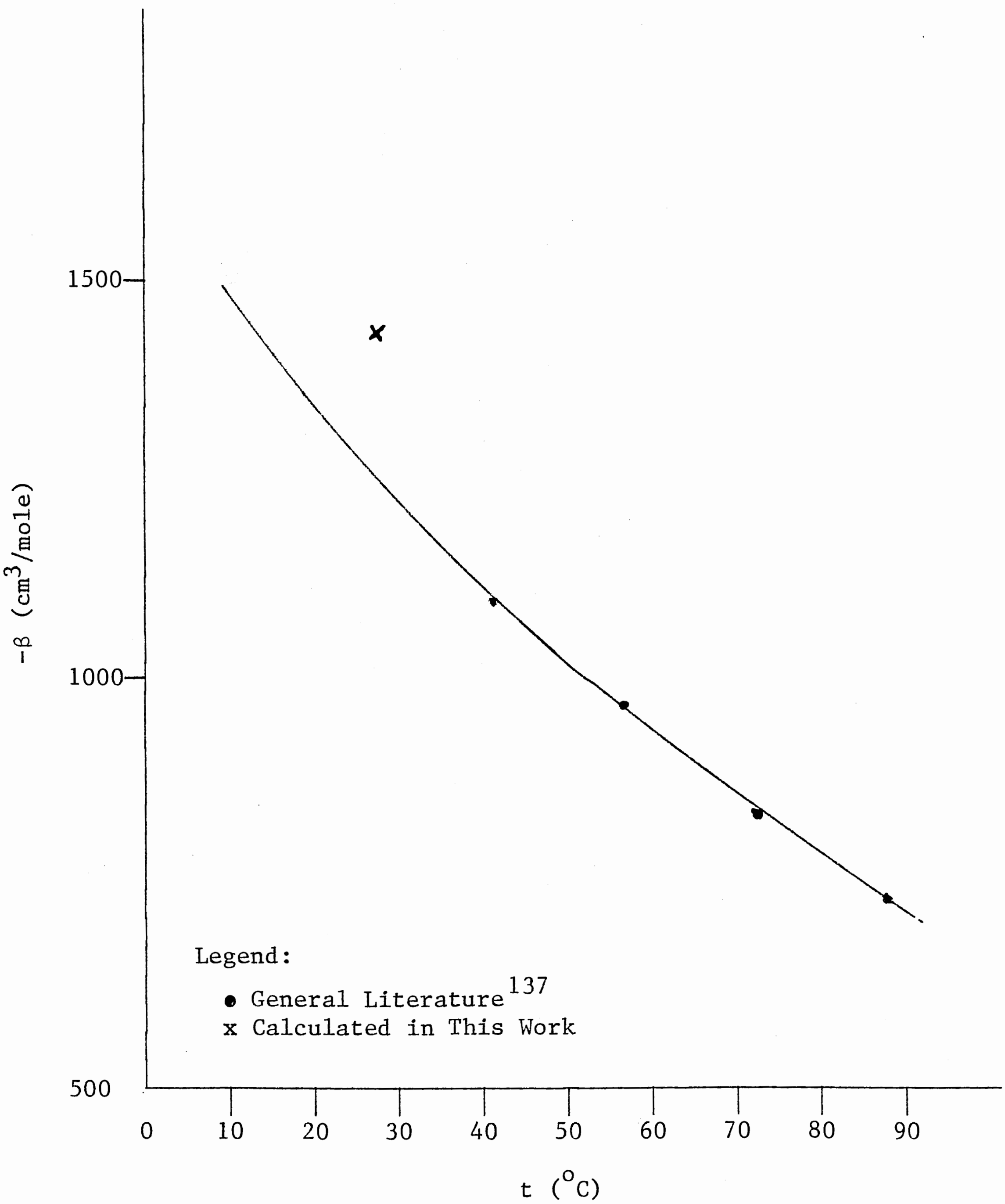

Figure 19. Plot of -β Values in the Literature Versus Temperature for Methyl Iodide.

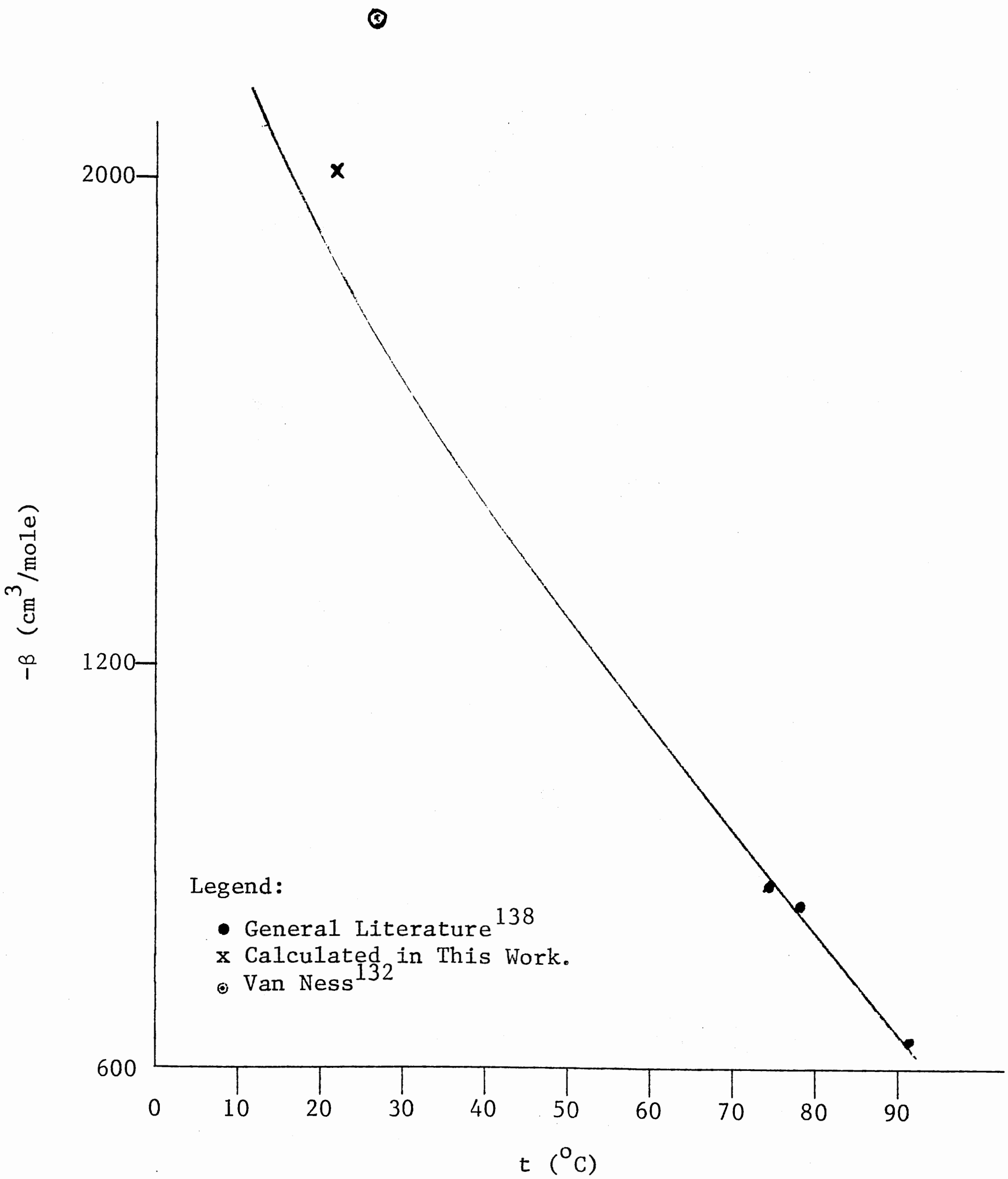

Figure 20. Plot of -β Values in the Literature Versus Temperature for Pyridine.

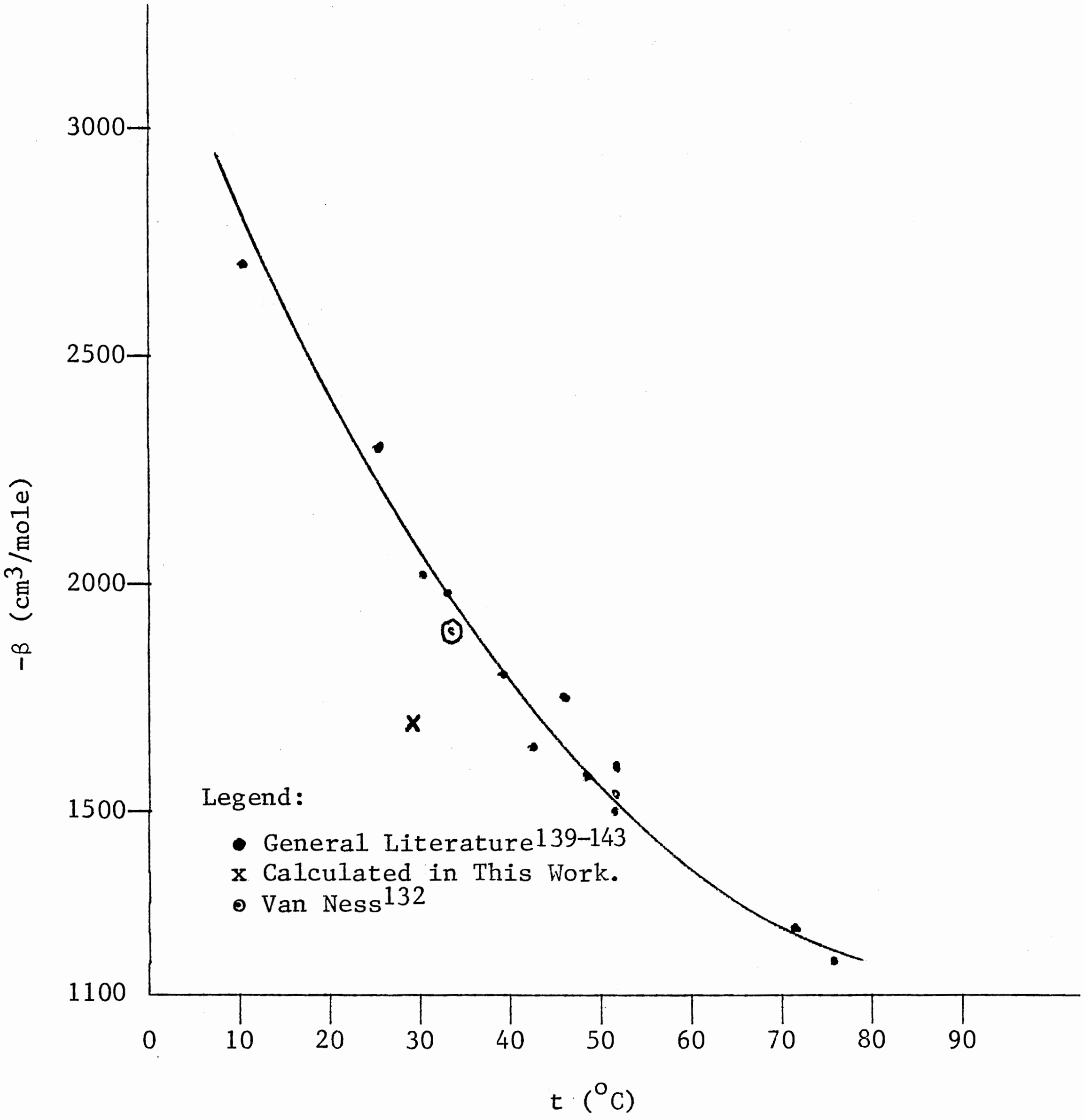

Figure 21. Plot of -β Values in the Literature Versus Temperature for Acetone.

probably estimates from the known experimental literature which according to Prausnitz is a tool still heavily relied upon.

Systems for Gaseous Equilibrium Constants

Equilibrium constants for gaseous systems cannot be quantitatively compared with those determined in solution in an inert solvent as done in this study. They may, however, provide a qualitative estimate of the potential for molecular association. The equilibrium constants obtained by using equation 2.16 for methyl iodide, pyridine and acetone self-association (dimerization), and methyl iodide--acetone and pyridine--acetone association in terms of K_c are 0.007, 0.009, 0.008, 0.009 and 0.010, respectively.

Charge-Transfer Complexes

In the concept of charge transfer, the "dative" structure, $b\phi_1$ (D^+, A^-), formed from electron donation by a molecule D to another molecule A is the basis for the emergence of new UV absorption maxima and changes in the vibrational-rotational modes (IR frequencies) in solutions containing donor and acceptor. Mulliken[54,55] first proposed the concept to explain the emergence of new UV peaks when iodine is dissolved in benzene.

In the studied systems no reasonable equilibrium constants could be calculated by IR spectroscopy. Frequency shifts in IR spectroscopy were not significant enough for determination of equilibrium constants. This is taken as evidence for the weakness of the CT complex. Equilibrium constants for formation of strong complexes such as trimethylamine--iodine (calculated K_c of 1.95 liter/mole) were readily determined by Drago[144] using IR spectroscopy.

Study of the UV absorption of all studied systems failed to detect a charge-transfer band, a fundamental need in the Mulliken theory. Failure, however, to detect the needed CT absorption does not mean it was not present. Each of the studied liquids had significant absorption in the UV spectrum which is thought to have masked any CT absorption and prevented valid calculation of equilibrium constants. This is similar to the case of charge-transfer absorption known to occur in the systems, methyl iodide--O_2, pyridine--O_2 and acetone--O_2[145] for which equilibrium constants are not calculatable for the same reason.

Spectral methods not available in this study but which with their high resolution and sensitivity perhaps would have yielded equilibrium constants involve the use of contact charge-transfer lasers,[146] Raman[147] and modulation[148] spectroscopy. High-resolution NMR, based as it is on the time-averaged radio-frequency absorption of nuclei in free and associated states,[84] was successfully used in calculation of equilibrium constants for the studied systems. As mentioned in the Introduction[90] equilibrium constants determined by NMR arise from charge-transfer interactions and also, in addition, electrostatic interactions. This matter is discussed in succeeding sections.

K_c and K_D Determination by NMR Spectrometry

The NMR-derived equilibrium constants are given in Chapter IV for dimerization of methyl iodide, pyridine and acetone, and methyl iodide--acetone and pyridine--acetone association. When these results are compared with equilibrium constants in the gas phase of 0.007, 0.009, 0.008, 0.009 and 0.010 in the respective systems by using equation 2.16, on going from gas to liquid phase in cyclohexane, the self-association constants of methyl iodide, pyridine, and acetone are seen to increase in magnitude from about two to four. The association constants of methyl iodide--acetone and pyridine--acetone are enhanced from 10 to 30 times. Upon comparing kinetic rates on going from the gas to an inert liquid phase, Benson[149] has shown that unimolecular reaction rates are in general neither enhanced nor diminished while in second-order reactions the rate is increased nearly 20-fold. An equilibrium constant, K, is the ratio of the forward over the reverse rate constant at constant temperature and pressure for a gas phase system and constant activities for a liquid system.[150] If it is assumed that both forward and reverse reaction constants are influenced proportionately in going from the gas to the liquid phase, the NMR-determined equilibrium constants should exhibit the 20-fold increase in magnitude shown by Benson,[149] since all systems studied experimentally by NMR in the liquid phase and theoretically from virial coefficients in the gas phase were presumably second-order reactions.

The 10 to 30-fold enhancement of the methyl iodide--acetone and pyridine--acetone association constant in the liquid phase over that in the gas phase is what is to be expected if the above made assumption is correct. However, the 2 to 4-fold enhancement for the self-association of methyl iodide, pyridine, and acetone is low compared to that expected. The comparison of gas-phase and liquid-phase equilibrium constants indicates that the methyl iodide--acetone and pyridine--acetone systems do associate while the separate liquids, methyl iodide, pyridine and acetone, self-associate little.

Excess Free Energies Derived from K_c Values Determined by NMR for the Methyl Iodide--Acetone and Pyridine--Acetone Systems

Figure 22 shows a plot of calculated free energies versus mole fraction for an A--B system at 25 °C. The G^E values were calculated and plotted versus mole fraction component A by computer using equations 2.9, 2.10, 2.11 and 2.12. The association constant, K_c, for the plotted system is 0.84. The most negative excess free energy is -14.68 calories/mole at 0.5 mole fraction.

For an A--B system of $K_c = 0.24$, a curve very much as that shown in Figure 22 is plotted. The most negative excess free energy falls to -9.3 calories/mole. The equilibrium constant of 0.24 is a reasonable one for the methyl iodide--acetone in cyclohexane determined by ^1H NMR at 10 °C and 30 °C interpolated to 25 °C. Comparing the excess free energy of -9.3 calories/mole at 0.5 mole fraction with the methyl iodide--acetone free energy plot of Figure 6, no agreement is found. The excess free energy at mole fraction 0.5 in Figure 6 is +85 calories/mole. Similarly, for the pyridine--acetone system of Figure 7 all excess free energies for the experimental system are positive while excess free energies generated assuming 1:1 association by equations 2.9, 2.10, 2.11 and 2.12 are negative. It is concluded that for both the methyl iodide--acetone and pyridine--acetone systems nonspecific electrostatic, etc. interactions of endothermic nature overshadow exothermic 1:1 A--B Type interactions in the studied systems.

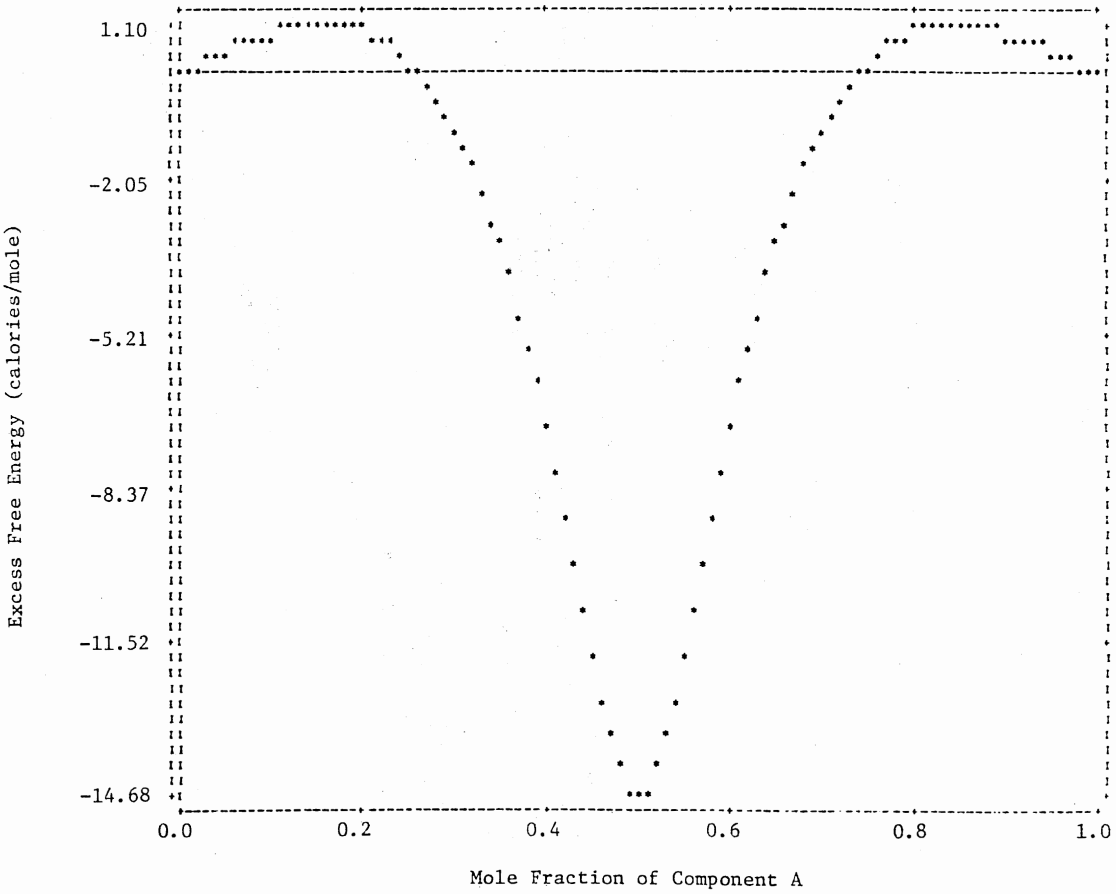

Figure 22. Excess Free Energies at 25 °C for an A--B System for which $K_c = 0.84$.

Analysis of NMR Results

The goodness of the calculated equilibrium constants in Tables VI (Appendix A), VII and VIII (Tables IX-XXIII), and those in Appendix B using a modified Benesi-Hildebrand equation is, of course, subject to legitimate skepticism until examined statistically. The K_D values of Table VI were determined by the method described in Appendix A[35] which sets the term $4K_D[\mathrm{Acet}_2]$ in equation A.3 to zero. The monomer concentration of the self-associated compound used in the K_D calculation was arrived at by extrapolation of Δ_{obs} to infinite dilution.[151] The K_c values for the studied ternary systems in Appendix B were determined by the method described in Appendix B[81] which sets the term

$$\frac{\Delta_{obs}}{\Delta_0^2} \cdot \frac{[A]_0}{([A]_0+[D]_0)}$$

in Equation B.9 equal to zero. Both the K_D and K_c values of the above calculations according to Appendices A and B, respectively, were carried out using only concentrations of 2.7 M or greater of the varied component. Neglected terms in Appendices A and B necessitate this. K_c values of Tables VII and VIII and those in Appendix B were determined for the same systems; however, K_c values of Table VII and VIII were determined by a generalized least squares method[130] permitting the use of low concentrations of the varied component in all cases that of acetone.

Using the approximations of Appendices A and B, the number of measurements for each system determined by ^1H and ^{13}C NMR at 10 °C, 20 °C, and 30 °C varied from 5 for methyl iodide ^{13}C to as many as

20 for ^1H. Correlation coefficients, r, for the linear plots were calculated and are given in the Appendices. The calculated r values indicate linear correlation[152] to better than 1000:1. ^{13}C correlations always had better r values than ^1H correlations. Still, more ^1H measurements were always run, compared to those for ^{13}C, and this led to the likelihood of greater scatter.

The equilibrium constants of Tables IX-XXIII are listed along with the error from a complete error analysis. The standard deviation for each of these equilibrium constants is given along with the value of the constant. Normal Gaussian data distributed cannot always be expected with less than 20 measurements.[153] Nearly all the K_c values for pyridine--acetone in cyclohexane K_c values in Appendix B determined at 10 °C and 30 °C were calculated from nearly 20 or more measurements. For the K_c values of the methyl iodide--acetone in cyclohexane system calculated according to Appendix B determined at 10 °C and 30 °C, nearly 20 or more measurements by ^1H NMR were made, but for ^{13}C NMR at these temperatures and for ^1H NMR at 20 °C for both studied systems, only about ten were made.

The equilibrium constants calculated according to Appendix B nearly always fell within or just outside the error limits of the K_c values in Tables VII and VIII when determined by ^{13}C NMR. Equilibrium constants obtained from ^1H NMR spectra, in contrast, were significantly lower. Because of the use of more data by the generalized least-squares method, the ternary system equilibrium constants of Tables VII and VIII were concluded to be more reliable than those of Appendix B calculated by a Benesi-Hildebrand method.

The validity of the K_D values was evaluated by calculation of

Deranleau's solubility parameter, S (Equation 1.25). The concentrations of dimer for methyl iodide, pyridine, and acetone in cyclohexane were calculated using Equation A.4. These values divided by their lowest and highest initial reactant concentrations yielded the minimum and maximum S values for these systems. Deranleau[94] concluded that only systems with S values between 0.2-0.8 were investigated correctly and that for determination of a good K value, 75% of the specified S value range should be investigated. The S values for the binary systems studied (Table IV) range from 0.015 to 0.08. Extending the investigated concentration range by use of a generalized least-squares method for K_D calculation would only lower S minimum to 0.005. S values above 0.8 and below 0.2 are subject to a high degree of error. Therefore, not a great deal of confidence can be placed in the K_D values calculated herein.

The S values were calculated by Equation 1.25 for the ternary systems studied. The complex concentration was calculated by solving equation B.7 in Appendix B. S values ranging from 0.3 to 0.6 were calculated using the 2.7-6.8 $\underline{M}$ data. The S value range was extended from 0.2 to 0.6 by the generalized least-squares method using concentrations of acetone from 0.27-6.8 $\underline{M}$. These ranges are within the 0.2-0.8 S value range required but cover only 50 and 67%, respectively, of the 75% range required by Deranleau's S value. Nevertheless, confidence in the calculated K_c values is much greater than the K_D values.

Chemistry of the Studied Systems

The equilibrium constants for self-association (dimerization) of methyl iodide, pyridine, and acetone cannot be given much confidence for the following reasons. First, equilibrium constants for the liquid phases determined by NMR were only at most nine times the magnitude of equilibrium constants calculated through use of virial coefficients in the gas phase, whereas what is to be expected is a 20-fold increase. Second, calculations of Deranleau's proposed solubility parameter, S, for the above systems showed the calculated K_D's to be of high uncertainty. Third, the magnitude of the equilibrium constants for self-association are equal or else fall within the error of equilibrium constant calculation. General analyses of data used in the generalized least-squares method had error limits of $\pm$ 0.01 to $\pm$ 0.07. These limits for methyl iodide--acetone and pyridine--acetone in cyclohexane should be roughly applicable to the solutions of methyl iodide, pyridine, and acetone in cyclohexane. The studied liquids, methyl iodide, pyridine, and acetone, are thus not seen to self-associate to any significant extent.

Calculations of excess free energies of mixing for the methyl iodide--acetone (Figure 6) and pyridine--acetate (Figure 7) systems are shown (Figure 22) to be dominated by the non-specific and endothermic mixing of their components. The negative free energies arising from 1:1 association of system components, specific interactions such as from charge transfer, are not observable.

<u>The Pyridine--Acetone--Cyclohexane System</u>. Pyridine is an aromatic compound containing five carbons and one nitrogen atom. The two carbon atoms adjacent to the nitrogen atom are designated the alpha (α) carbons. The two carbon atoms two sites away from the nitrogen atom are called the beta (β) carbons. The carbon atom three

sites away from the nitrogen atom is the gamma (γ) carbon. The nitrogen and carbon atoms form a six-membered ring which is planar because of the three double bonds within it. The double bonds are equidistantly spaced about the ring. The π electrons of pyridine's double bonds generate a ring current above and below the ring. The nitrogen atom possesses two lone pair (n) electrons also generate an electronic current but in this case it extends into space to the point where it envelopes the pyridine α position.[79] Also to each α, β, and γ carbon is bonded one hydrogen atom similarly labelled α, β, and γ.

In NMR experiments with pyridine in cyclohexane the α, β, and γ signals for both the proton and carbon nuclei of pyridine are shifted far downfield relative to Me_4Si in the order $\alpha > \gamma > \beta$.[148] This arises from the ring current. If pyridine is treated as a substituted benzene[154] where nitrogen is substituted for a benzene carbon, the order $\alpha > \gamma > \beta$ is proper according to mesomeric and inductive effects.[155] For unassociated pyridine the $\alpha > \gamma > \beta$ order also is followed in the magnitude of chemical shift downfield with increasing polarity of the solvent such as in carbon tetrachloride/diethyl ether mixtures.[156]

A clear departure from the above unassociated pyridine behavior is seen in the pyridine--acetone--cyclohexane system. The magnitudes of the pyridine chemicals shift downfield are $\gamma > \beta > \alpha$. While the ring current establishes the initial nuclear resonances, the participation of the nitrogen lone pair electrons in complexation such as in formation of the pyridinium ion, $PyrH^+$,[157,158] produces the same order $\gamma > \beta > \alpha$. This is because the α nuclei while deshielded in unassociated pyridine are not so upon complexation with H^+. The lone pair electronic current[79] which has been deshielding the alpha position is shifted to form the N-H bond.

The inductive effect causes the downfield shift of the alpha position. Complexation of nitrogen causes an α upfield shift. In the pyridine--acetone system, the inductive and complexation α position effects apparently cancel leaving the alpha positions unsuitable as a basis for calculation of equilibrium constants. The β and γ shifts for the positions, being unaffected by this anisotropy behavior of nitrogen,[159] could be used for calculations of equilibrium constants.

The calculated equilibrium constants for the pyridine--acetone system as determined by ^1H and ^{13}C NMR were invariant with temperature (Table VIII). The K_c value of 0.11 for the β pyridine protons at 30 ^oC is low compared to the other calculated equilibrium values, but can be rationalized perhaps by regarding the β position as least sensitive to complexation. The higher thermal energy at 30 ^oC might with such insensitivity decrease the role of the β protons in pyridine--acetone complexation. The mean of all pyridine--acetone equilibrium constants in cyclohexane, both by ^1H and ^{13}C NMR, is 0.18 liter/mole. A complete error analysis of the NMR method found the largest possible error to be 0.07, and all equilibrium constants are within this range.

Methyl Iodide--Acetone--Cyclohexane. Methyl iodide is composed of a methyl (CH_3) group bonded to a highly polarizable iodine atom. The protons of methyl iodide, in contrast, to those of pyridine are not constrained to vibration in a set molecular plane; the methyl group can freely rotate through space. The motion of methyl carbon is constrained, as the carbons in pyridine are, fixed in spatial orientation to its bonded group which for the methyl group is the iodine atom.

In methyl iodide there are no anisotropic[87] effects due to electronic currents. Chemical shifts of the ^{1}H and ^{13}C measurements arise from purely inductive forces. The finding that the equilibrium constants calculated by ^{1}H NMR increase significantly with decreased temperature while those by ^{13}C NMR remain essentially constant indicates that rotation of the methyl group affects its equilibrium constant. The equilibrium constants of methyl iodide--acetone at 10 °C and 30 °C by ^{13}C NMR were 0.22 and 0.21 liter/mole, respectively. The equilibrium constants at 10 °C, 20 °C and 30 °C by ^{1}H NMR were 0.34, 0.23, and 0.18 liter/mole, respectively. The strength of proton complexation appears to be a function of the ability of the methyl group to rotate.

Summary. In the studied systems the ratio of acetone to cyclohexane was varied while keeping the concentration of either methyl iodide or pyridine constant. With increasing acetone concentration, the "reaction field" as described by Buckingham[160] causes all nuclei to be increasingly deshielded. The insignificant self-association of acetone in cyclohexane compared to the cross-association in the two studied ternary systems all in the presence of Buckingham's "reaction field" indicates, as does the $\gamma > \beta > \alpha$ behavior of pyridine, that a kind of complexing is occurring. In the pyridine-acetone system association between the pyridine nitrogen and the acetone carbonyl group is indicated. For the methyl iodide--acetone complexation the association of iodide with the carbonyl group of acetone is readily postulated. Perhaps the calculated equilibrium constants determined by ^{1}H NMR vary with temperature by the thermal constraints on rotation.

In conclusion, the equilibrium constants for the methyl iodide--acetone and pyridine--acetone in cyclohexane systems as determined by ^{13}C NMR at 10 °C and 30 °C were temperature invariant. The pyridine--acetone equilibrium constants system as determined by ^{1}H NMR at 10 °C, 20 °C and 30 °C were temperature invariant while those for the methyl iodide--acetone system determined by the same method and at the same temperatures were temperature dependent. These results indicate that the methyl group rotation of the nuclei examined by NMR analysis perhaps is superimposed onto the measured equilibrium constant with change in temperature.

Pyridine and methyl iodide are known to react with one another with large equilibrium constant and mixtures of them have been studied for variation in reaction rate by change in solvent composition of benzene and acetone.[27,161] A reaction is the sum of the equilibria composing it. The methyl iodide--acetone and pyridine--acetone equilibria are two such parts. Future investigation in terms of methyl iodide--benzene and pyridine--benzene equilibria together with the present study should elucidate how solvent complex equilibria influence kinetic reactions.

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APPENDIX A[36]

DERIVATION OF K_D FOR NMR MEASUREMENTS

The dimerization of acetone may be represented as

$$\text{Acet} + \text{Acet} \rightleftharpoons \text{Acet}_2 \tag{A.1a}$$

$$K_D = \frac{[\text{Acet}_2]}{[\text{Acet}]^2} \tag{A.1b}$$

where

$$[\text{Acet}] = [\text{Acet}]_0 - 2[\text{Acet}_2] \tag{A.1c}$$

Substituting (A.1c) into (A.1b) yields

$$K_D = \frac{[\text{Acet}_2]}{[[\text{Acet}]_0 - 2[\text{Acet}_2]]^2} \tag{A.2}$$

Multiplying out (A.3),

$$K_D[\text{Acet}]_0^2 - 4K_D[\text{Acet}]_0[\text{Acet}_2] + 4K_D[\text{Acet}_2]^2 = [\text{Acet}_2] \tag{A.3}$$

This is the equation needed to be solved for exact calculation of K_D. If $4[\text{Acet}_2]^2$ can be considered to go to zero, (A.3) can be rearranged to

$$[\text{Acet}_2] = \frac{K_D[\text{Acet}]_0^2}{1 + 4K_D[\text{Acet}]_0} \qquad (A.4)$$

If acetone is assumed to undergo rapid exchange between its Acet and Acet_2 forms, the observed solution shift is δ_{obs}.

$$\delta_{obs} = \rho_{\text{Acet}_2}\,\delta_{\text{Acet}_2} + \rho_{\text{Acet}}\,\delta_{\text{Acet}} \qquad (A.5)$$

where the ρ's are probabilities. Now,

$$\rho_{\text{Acet}_2} = \frac{[\text{Acet}_2]}{[\text{Acet}]_0}$$

and

$$\rho_{\text{Acet}} = \frac{[\text{Acet}]}{[\text{Acet}]_0} = \frac{[\text{Acet}]_0 - 2[\text{Acet}_2]}{[\text{Acet}]_0} \qquad (A.6)$$

Substituting (A.6) into (A.5) yields after rearrangement

$$(\delta_{obs} - \delta_{\text{Acet}})\cdot[\text{Acet}]_0 = (\delta_{\text{Acet}_2} - 2\delta_{\text{Acet}})[\text{Acet}_2] \qquad (A.7)$$

Set Δ_{obs} equal to $\delta_{obs} - \delta_{\text{Acet}}$, the chemical shift of the dimerized solution and Δ_0 equal to $\delta_{\text{Acet}_2} - 2\delta_{\text{Acet}}$, chemical shift for the complexed dimer relative to uncomplexed Acet. (A.7) becomes

$$\Delta_{obs}\cdot[\text{Acet}]_0 = \Delta_0[\text{Acet}_2] \qquad (A.8)$$

Substituting (A.4) into (A.8) yields on rearrangement,

$$\frac{\Delta_{obs}}{[\text{Acet}]_0} = -4K_D \cdot \Delta_{obs} + \Delta_0 K_D \qquad (A.9)$$

A plot of $\Delta_{obs}/[\text{Acet}]_0$ versus Δ_{obs} yields a slope of $-4K_D$ and an intercept of $\Delta_0 K_D$.

Substituting K_D and the initial acetone concentration, $[\text{Acet}]_0$, into (A.4), the acetone dimer concentration, $[\text{Acet}_2]$, can be calculated.

TABLE XXIV

K_D, DIMERIZATION CONSTANT FOR METHYL IODIDE IN CYCLOHEXANE BY ^1H AND ^{13}C NMR AT 10 °C AND 30 °C

	CH_3I*
^1H, 10 °C	0.0204 [154.7]** [[55.6]]*** (12)# ((0.908))&
^{13}C, 10 °C	0.0104 [1647.00] [[4649.12]] (9) ((0.992))
^1H, 30 °C	0.0178 [159.1] [[5.55]] (12) ((0.934))
^{13}C, 30 °C	0.0113 [1518.00] [[4638.96]] (5) ((0.996))

*CH_3I = methyl iodide.

**Intercept in [ ].

***Chemical shift at infinite dulution in cm^{-1} [[ ]].

#Number of points taken between 3.2 and 8.0 <u>M</u> CH_3I.

&Correlation coefficient, r, in (( )).

TABLE XXV

K_D, DIMERIZATION CONSTANT FOR PYRIDINE IN CYCLOHEXANE BY ^1H AND ^{13}C NMR AT 10 °C AND 30 °C

	Pyr-β*	Pyr-γ
^1H, 10 °C	- -** [[567.6]]*** (14)# -&	- - [[602.1]] (14) -
^{13}C, 10 °C	0.0348 [38.5] [[2405.76]] (9) ((0.992))	0.0400 [245.5] [[2697.24]] (10) ((0.992))
^1H, 30 °C	- - [[567.8]] (18) -	- - [[600.3]] (13) -
^{13}C, 30 °C	0.0301 [200.7] [[2405.50]] (7) ((0.995))	0.0216 [292.8] [[2699.79]] (6) ((0.945))

*Pyr = pyridine.

**Intercept in [ ].

***Chemical shift at infinite dilution in cm^{-1} [[ ]].

#Number of points taken between 2.5 and 6.2 <u>M</u> pyridine.

&Correlation coefficient, r, in (( )).

TABLE XXVI

K_D, DIMERIZATION CONSTANT FOR ACETONE IN CYCLOHEXANE BY ^{1}H AND ^{13}C NMR AT 10 °C AND 30 °C

	Acet-CH$_3$*	C=O
^{1}H, 10 °C	0.0401	-
	[62.15]**	-
	[[53.6]]***	-
	(17)#	-
	((0.887))&	-
^{13}C, 10 °C	0.0309	0.0636
	[94.96]	[623.4]
	[[60.58]]	[[4354.49]]
	(11)	(11)
	((0.891))	((0.986))
^{1}H, 30 °C	0.0184	-
	[103.6]	-
	[[52.4]]	-
	(13)	-
	((0.934))	-
^{13}C, 30 °C	0.0943	0.0667
	[87.30]	[621.1]
	[[53.37]]	[[4346.50]]
	(8)	(8)
	((0.992))	((0.996))

*Acet = acetone.

**Intercept in [ ].

***Chemical shift at infinite dilution in cm^{-1} [[ ]].

#Number of points taken between 2.7 and 6.8 M acetone.

&Correlation coefficient, r, in (( )).

TABLE XXVII

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF METHYL IODIDE (CH_3I) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 10 °C

$[CH_3I]$, Moles/Liter	$^{\nu}$Values, cm^{-1}
0.064	55.6
0.128	56.2
0.129	56.6
0.160	56.2
0.193	56.6
0.193	57.0
0.321	56.8
0.321	56.2
0.321	56.6
0.645	58.0
0.643	57.8
0.640	58.0
0.640	58.0
0.643	58.0
0.967	59.6
0.965	59.0
0.965	59.2
1.611	61.1
1.609	60.5
1.609	61.5
1.930	61.7
2.252	62.5
2.252	61.9
2.574	62.3
2.574	62.9
3.198	63.5
3.217	64.1
3.213	63.7
3.217	63.9
3.209	63.7
3.225	63.5
4.826	66.4
4.837	66.2
6.404	68.2
6.434	68.6
6.434	69.0
8.024	71.7

TABLE XXVIII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF METHYL IODIDE (CH_3I) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 20 °C

$[CH_3I]$, Moles/Liter	ν values, cm^{-1}
0.160	57.8
0.161	57.4
0.192	55.6
0.320	57.6
0.321	56.8
0.321	56.8
0.321	56.6
0.321	56.4
3.209	62.5
3.206	63.5
3.202	62.5
3.209	63.5
4.808	65.4
6.404	67.8
8.024	70.3

TABLE XXIX

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF METHYL IODIDE (CH_3I) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 30 °C

$[CH_3I]$, Moles/Liter	ν Values, cm^{-1}
0.064	56.0
0.129	55.8
0.160	56.0
0.193	55.6
0.193	55.4
0.322	56.2
0.320	56.6
0.322	56.2
0.645	57.2
0.643	57.6
0.643	57.4
0.967	58.4
0.965	57.8
1.611	59.3
1.609	59.5
1.930	60.3
2.252	60.9
2.574	61.1
3.209	62.7
3.209	62.5
3.213	62.7
4.803	65.5
4.826	65.0
4.837	64.8
6.434	67.6
6.434	67.2
8.004	69.1
8.043	69.9

TABLE XXX

CHEMICAL SHIFT DIFFERENCE OF THE CARBON-13 SIGNAL (ν-FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF METHYL IODIDE (CH_3I) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 10 °C

[CH_3I], Moles/Liter	ν Values, cm^{-1}
0.128	4500.24
0.192	4645.98
0.193	4650.98
0.322	4651.88
0.320	4652.51
0.643	4657.89
0.640	4658.44
0.644	4657.08
0.959	4663.07
0.964	4662.99
0.967	4662.31
1.287	4668.12
1.607	4674.06
1.599	4673.98
1.611	4673.90
1.930	4677.85
1.919	4679.18
2.252	4691.74
2.239	4683.81
2.574	4695.46
2.558	4688.76
3.217	4697.52
3.198	4697.54
3.213	4697.50
3.213	4698.18
4.797	4716.91
6.396	4735.98
7.995	4751.34

TABLE XXXI

CHEMICAL SHIFT DIFFERENCE OF THE CARBON-13 SIGNAL (ν-FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF METHYL IODIDE (CH_3I) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 30 °C

$[CH_3I]$, Moles/Liter	ν Values, cm^{-1}
0.160	4642.35
0.193	4643.16
0.322	4645.86
0.643	4650.51
0.965	4655.00
0.965	4660.68
1.599	4665.24
1.609	4666.01
1.919	4670.16
3.209	4687.36
4.826	4706.53
6.412	4724.23
6.434	4724.85
8.043	4740.54

TABLE XXXII

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF PYRIDINE (Pyr) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 10 °C

[Pyr], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}
0.100	568.4	602.0	708.4
0.149	568.2	602.0	708.2
0.149	568.2	602.0	708.2
0.149	567.2	604.4	706.8
0.237	567.2	600.2	707.0
0.247	567.4	600.8	706.4
0.247	568.4	601.8	708.0
0.248	567.4	600.2	707.4
0.249	568.2	601.8	708.6
0.398	568.8	602.0	708.6
0.498	568.2	601.4	707.6
0.498	568.6	601.8	708.4
0.742	568.8	601.0	709.0
0.747	568.6	601.0	708.0
1.237	569.4	602.8	711.0
1.731	570.4	604.0	710.0
2.471	571.8	605.6	711.4
2.476	573.0	605.4	712.4
2.481	571.6	605.4	710.8
2.486	572.4	605.8	712.2
3.706	574.0	607.6	713.8
3.710	574.2	607.4	713.6
3.721	573.6	607.4	714.0
4.942	576.2	609.6	716.8
4.947	575.6	608.4	716.2
4.962	576.2	608.8	716.4
6.177	578.8	611.4	719.8
6.190	578.4	611.2	719.6
6.184	578.0	610.6	719.2
6.202	578.2	610.4	719.6

TABLE XXXIII

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF PYRIDINE (Pyr) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF PYRIDINE CONCENTRATION AT 20 °C

[Pyr], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}
0.099	566.0	599.4	705.8
0.124	566.0	598.8	705.6
0.247	566.4	600.0	706.2
0.247	566.8	600.4	707.0
0.247	566.6	600.0	706.6
2.471	570.8	604.6	710.4
2.473	571.6	604.6	710.4
3.710	573.4	606.4	712.6
6.184	577.2	610.0	718.4

TABLE XXXIV

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF PYRIDINE (Pyr) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 30 ^{o}C

[Pyr], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}
6.184	576.6	609.8	718.2
6.190	577.4	610.4	718.8
6.202	576.8	609.6	718.4
6.184	577.2	609.8	718.0
0.149	567.8	601.4	708.0
0.150	567.6	602.0	707.0
0.247	566.2	599.4	705.8
0.247	565.8	599.4	706.0
0.248	566.4	599.8	706.2
0.247	566.4	599.2	706.4
0.247	567.6	599.8	706.2
0.247	567.6	600.8	707.6
0.248	566.6	599.4	708.0
0.249	567.2	600.2	707.6
0.398	568.2	600.8	707.8
0.495	566.4		706.6
0.498	566.4	600.0	706.2
0.498	566.8	601.2	708.0
0.747	568.4	601.6	707.6
0.742	568.2	602.0	708.2
1.236	568.6	602.0	708.2
1.238	569.4	602.4	708.4
1.237	568.2	601.6	707.8
1.731	569.4	601.8	708.4
2.476	570.2	604.2	709.8
2.474	571.0	604.4	710.6
2.481	570.6	604.4	710.4
3.714	573.2	606.8	713.2
3.710	572.8	605.2	712.6
3.721	573.0	606.0	712.6
4.942	574.4	607.6	715.2
4.962	574.6	608.0	715.4
4.947	574.2	607.4	714.6

TABLE XXXV

CHEMICAL SHIFT DIFFERENCE OF THE CARBON-13 SIGNAL (ν-β, ν-γ, ν-α FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF PYRIDINE (Pyr) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 10 °C

[Pyr], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}
0.100	2406.77	2698.69	3091.49
0.149	2407.41	2699.50	3091.28
0.248	2408.92	2702.30	3090.58
0.247	2408.21	2700.76	3091.36
0.247	2408.84	2701.04	3091.59
0.248	2407.56	2699.60	3091.36
0.495	2409.09	2702.37	3091.41
0.498	2409.12	2702.30	3091.96
0.742	2410.69	2703.98	3091.53
0.747	2410.54	2703.93	3091.43
1.236	2413.38	2707.56	3091.53
1.238	2412.87	2707.56	3091.43
1.238	2413.38	2707.58	3091.99
1.237	2413.44	2707.61	3091.61
1.731	2415.61	2710.63	3091.56
2.476	2418.47	2714.22	3092.14
2.474	2418.59	2714.85	3092.22
2.481	2418.64	2714.95	3092.29
3.710	2422.83	2720.10	3093.06
3.721	2422.41	2720.08	3092.94
4.947	2425.87	2723.93	3093.74
4.962	2426.41	2724.43	3094.19
6.190	2428.76	2727.88	3095.02
6.184	2428.886	2728.06	3095.02

TABLE XXXVI

CHEMICAL SHIFT DIFFERENCE OF THE CARBON-13 SIGNAL (ν-β, ν-γ, ν-α FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF PYRIDINE (Pyr) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF METHYL IODIDE CONCENTRATION AT 30 °C

[Pyr], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}
0.050	2405.46	2699.40	3091.46
0.075	2406.38	2699.60	3090.96
0.297	2406.85	2695.74	3089.24
0.248	2407.73	2700.86	3090.58
0.247	2406.80	2698.79	3090.76
0.248	2406.85	2698.87	3091.49
0.498	2408.35	2700.98	3091.51
0.742	2409.70	2702.95	3091.36
0.747	2409.78	2703.08	3091.99
1.238	2411.94	2705.97	3091.43
1.237	2411.50	2705.54	3091.48
1.731	2414.18	2709.00	3092.06
2.476	2417.15	2713.35	3092.18
2.481	2417.00	2717.33	3092.26
3.721	2420.80	2717.33	3092.88
4.962	2424.35	2722.16	3093.69
6.190	2426.74	2724.75	3094.49
6.202	2427.22	2725.31	3094.49

TABLE XXXVII

CHEMICAL SHIFT DIFFERENCE OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 °C

[Acet], Moles/Liter	ν Values, cm^{-1}
0.054	54.0
0.055	53.4
0.109	54.0
0.109	53.8
0.164	54.0
0.270	54.2
0.270	53.8
0.272	53.8
0.272	54.2
0.273	54.6
0.436	55.0
0.540	54.4
0.544	54.6
0.545	55.8
0.546	55.2
0.813	55.2
0.818	55.6
1.353	56.0
1.354	56.4
1.364	57.0
1.632	57.6
1.891	56.8
1.896	57.6
2.701	58.9
2.709	58.5
2.709	58.1
2.728	58.5
3.241	58.5
4.052	59.5
4.063	59.5
4.592	60.3
5.418	60.7
5.457	60.5
5.943	61.4
6.764	61.8
6.772	61.8
6.782	61.8
6.821	61.8
6.772	61.6
6.802	61.6

TABLE XXXVIII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 20 °C

[Acet], Moles/Liter	ν_{Values}, cm^{-1}
0.054	52.8
0.055	52.4
0.109	53.4
0.109	52.8
0.164	52.8
0.270	53.6
0.270	54.0
0.270	53.2
0.273	53.4
0.272	53.8
0.273	53.6
0.540	53.6
0.544	53.8
0.545	54.0
0.546	54.4
0.816	54.6
0.817	54.8
1.353	55.2
1.360	55.6
1.894	55.1
2.706	56.9
2.706	56.5
2.731	56.7
2.724	56.7
3.247	57.5
4.058	58.3
4.599	59.1
5.441	59.9
5.449	59.9
5.952	60.0
6.763	61.0
6.802	60.8
6.782	61.2
6.811	61.0

TABLE XXXIX

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 ^{o}C

[Acet], Moles/Liter	ν Values, cm^{-1}
0.054	52.8
0.055	52.4
0.109	53.4
0.109	52.8
0.164	52.8
0.270	53.6
0.270	54.0
0.270	53.2
0.273	53.4
0.272	53.8
0.273	53.6
0.540	53.6
0.544	53.8
0.545	54.0
0.546	54.4
0.816	54.6
0.817	54.8
1.353	55.2
1.360	55.6
1.894	55.1
2.706	56.9
2.706	56.5
2.731	56.7
2.724	56.7
3.247	57.5
4.058	58.3
4.599	59.1
5.441	59.9
5.449	59.9
5.952	60.0
6.763	61.0
6.802	60.8
6.782	61.2
6.811	61.0

TABLE XXXX

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-CH_3, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 °C

[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-C=O, cm^{-1}
0.082	60.86	4356.80
0.271	61.17	4361.41
0.273	61.68	4326.90
0.272	61.71	4362.14
0.540	62.41	4372.94
0.544	62.46	4372.97
0.545	61.82	4373.17
0.816	63.13	4381.80
1.353	63.90	4394.49
1.353	63.95	4393.79
1.351	64.01	4395.80
1.360	63.99	4395.90
1.891	65.36	4406.88
1.904	64.84	4404.73
2.706	66.10	4417.26
2.706	65.55	4416.58
2.701	66.90	4419.50
3.241	67.45	4425.34
4.052	68.33	4433.48
4.058	68.81	4435.39
4.592	69.15	4438.59
5.457	70.45	4445.11
5.410	69.84	4445.27
5.943	70.58	4447.76
6.764	71.06	4451.78

TABLE XXXXI

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-CH_3, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 °C

[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-C=O, cm^{-1}
0.109	58.75	4351.03
0.164	58.88	4353.42
0.270	59.54	4357.70
0.270	59.47	4357.73
0.273	59.53	4358.46
0.272	59.01	4357.70
0.273	58.87	4357.73
0.544	60.28	4368.03
0.546	59.68	4368.10
0.816	60.50	4376.31
0.816	61.05	4376.08
1.360	62.44	4390.03
1.360	61.84	4389.38
1.351	61.78	4387.18
1.904	63.13	4398.11
2.076	64.14	4412.85
2.721	64.46	4411.36
2.721	64.62	4411.36
4.081	66.63	4426.79
5.441	68.18	4438.44
6.753	68.89	4446.51
6.802	69.12	4447.47
6.782	68.97	4445.83

APPENDIX B[81]

DERIVATION OF K_c FOR NMR MEASUREMENTS

For two species A and D of interest that complex,

$$A + D \rightleftharpoons AD \tag{B.1}$$

The NMR shift of a studied D nucleus where $[A]_o >> [D]_o$ is the sum of the shifts of the forms of that nucleus.

$$\delta_{obs} = \rho_D \delta_D + \rho_{AD} \delta_{AD} \tag{B.2}$$

where the ρ's are probabilities

$$\rho_{AD} = \frac{[AD]}{[A]_0} \tag{B.3}$$

$$\rho_A + \rho_{AD} = 1 \tag{B.4}$$

The equilibrium of (B.1) may be described as

$$K^{AD} = \frac{[AD]}{[A][D]} \tag{B.5}$$

with

$$[A] = [A_0] - [AD] \tag{B.5a}$$

and

$$[D] \;=\; [D_0] - [AD] \qquad \text{(B.5b)}$$

Combining (B.2) and (B.4) and rearranging gives

$$\rho_{AD} = \frac{\delta_{obs} - \delta_D}{\delta_{AD} - \delta_D} = \frac{\Delta_{obs}}{\Delta_c} \qquad \text{(B.6)}$$

$\delta_{obs} - \delta_D$, Δ_{obs}, is considered to be the observed chemical shift relative to the shift of the donor. $\delta_{AD} - \delta_D$, Δ_c, is the constant chemical shift of the complex relative to the shift of the donor.

Now, by substituting (B.5a) and (B.5b) into (B.5),

$$K^{AD} = \frac{[AD]}{[[A]_0 - [AD]][[D]_0 - [AD]]} \qquad \text{(B.7)}$$

Rearrangement of (B.7) gives

$$\frac{1}{K^{AD}} = \frac{[D]_0}{[AD]} - 1 \quad [A]_0 - [AD] \qquad \text{(B.8)}$$

Substituting (B.6) into (B.8) and rearranging gives

$$\frac{1}{\Delta_{obs}} \cdot \frac{[D]_0}{([A]_0 + [D]_0)} = \frac{\Delta_{obs}}{\Delta_c^{\,2}} \cdot \frac{[A]_0}{([A]_0 + [D]_0)}$$

$$\frac{1}{K^{AD}} \cdot \frac{1}{\Delta_c} \cdot \frac{1}{([A]_0 + [D]_0)} + \frac{1}{\Delta_c} \qquad \text{(B.9)}$$

(B.9) gives the parameters K_D and Δ_c in terms of the variables Δ_{obs} and $[A]_0$. $[D]_0$ is held constant. If the term

$$\frac{\Delta_{obs}}{\Delta_c^{\ 2}} \cdot \frac{[A]_0}{([A]_0+[D]_0)}$$

can be neglected,

$$\frac{1}{\Delta_{obs}} \cdot \frac{[D]_0}{([A]_0+[D]_0)} = \frac{1}{K^{AD}} \cdot \frac{1}{\Delta_c} \cdot \frac{1}{([A]_0+[D]_0)} + \frac{1}{\Delta_c} \qquad \text{(B.10)}$$

K_c and Δ_c can be found by plotting $[D]_0/(\Delta_{obs}([A]_0+[D]_0))$ versus $1/([A]_0 + [D]_0)$ to yield a slope, $1/K^{AD}\Delta_c$. K^{AD} is calculated by dividing the intercept by the slope. Δ_c is the simple reciprocal of the intercept.

TABLE XXXXII

K_{AD}, EQUILIBRIUM CONSTANT, FOR FORMATION OF METHYL IODIDE--ACETONE IN CYCLOHEXANE BY ^{1}H AND ^{13}C NMR AT 10 °C AND 30 °C

	CH$_3$I*
^{1}H, 10 °C	0.327 [20.43]** [[56.6]]*** (8)# ((0.960))&
^{13}C, 10 °C	0.222 [112.91] [[4652.20]] (8) ((0.996))
^{1}H, 30 °C	0.0917 [37.5] [[56.3]] (12) ((0.978))
^{13}C, 30 °C	0.190 [113.10] [[4645.86]] (5) ((0.994))

*CH$_3$I = methyl iodide.
**Intercept in cm^{-1} [ ].
***Chemical shift of 0.32 M methyl iodide in cyclohexane in cm^{-1} [[ ]].
#Number of points taken between 2.7 and 6.8 M acetone.
&Correlation coefficient, r, in (( )).

TABLE XXXXIII

K_{AD}, EQUILIBRIUM CONSTANT, FOR FORMATION OF METHYL IODIDE--ACETONE IN CYCLOHEXANE BY ^1H NMR AT 10 °C, 20 °C AND 30 °C

	CH_3I*
^1H, 10 °C	0.327 [20.43]** [[56.6]]*** (8)# ((0.960))&
^1H, 20 °C	0.141 [31.80] [[56.8]] (11) ((0.975))
^1H, 30 °C	0.0917 [37.51] [[56.3]] (12) ((0.978))

*CH_3I = methyl iodide.

**Intercept in cm^{-1} [ ].

***Chemical shift of 0.32 M methyl iodide in cyclohexane [[ ]].

#Number of points taken between 2.7 and 6.8 M acetone in ( ).

&Correlation coefficient, r, in (( )).

TABLE XXXXIV

K_{AD}, EQUILIBRIUM CONSTANT FOR FORMATION OF PYRIDINE--ACETONE IN CYCLOHEXANE BY ^{1}H AND ^{13}C NMR AT 10 °C AND 30 °C

	Pyr-β*	Pyr-γ
^{1}H, 10 °C	0.175	0.172
	[38.53]**	[41.74]
	[[567.5]]***	[[600.9]]
	(17)#	(17)
	((0.981))&	((0.986))
^{13}C, 10 °C	0.158	0.178
	[45.10]	[57.48]
	[[2408.38]]	[[2700.92]]
	(14)	(12)
	((0.994))	((0.993))
^{1}H, 30 °C	0.132	0.152
	[41.37]	[42.73]
	[[566.7]]	[[599.8]]
	(20)	(20)
	((0.985))	((0.979))
^{13}C, 30 °C	0.176	0.202
	[42.08]	[54.21]
	[[2407.06]]	[[2698.57]]
	(8)	(8)
	((0.996))	((0.995))

*Pyr = pyridine.
**Intercept in cm^{-1} [ ].
***Chemical shift of 0.27 M pyridine in cyclohexane in cm^{-1} [[ ]].
#Number of points taken between 2.7 and 6.8 M acetone.
&Correlation coefficient, r, in (( )).

TABLE XXXXV

K_{AD}, EQUILIBRIUM CONSTANT FOR FORMATION OF PYRIDINE--ACETONE IN CYCLOHEXANE BY ^1H NMR AT 10 °C, 20 °C AND 30 °C

	Pyr-β*	Pyr-γ
^1H, 10 °C	0.175	0.172
	[38.53]**	[41.74]
	[[567.5]]***	[[600.9]]
	(17)#	(17)
	((0.981))&	((0.986))
^1H, 20 °C	0.160	0.156
	[38.98]	[43.50]
	[[566.6]]	[[600.1]]
	(13)	(13)
	((0.993))	((0.997))
^1H, 30 °C	0.132	0.152
	[41.37]	[42.73]
	[[566.7]]	[[599.8]]
	(20)	(20)
	((0.985))	((0.979))

*Pyr = pyridine.

**Intercept in cm^{-1} [ ].

***Chemical shift of 0.24 <u>M</u> pyridine in cyclohexane [[]].

#Number of points taken between 2.7 and 6.8 <u>M</u> acetone in ( ).

&Correlation coefficient, r, in (( )),

TABLE XXXXVI

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-CH_3, ν-C=O FREQUENCY UNITS) IN THE ^{1}H NMR SPECTRUM OF METHYL IODIDE (CH_3I)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 °C

[CH_3I], Moles/Liter	[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-CH_3I, cm^{-1}
0.321	0.544	55.0	59.6
0.322	0.545	56.0	60.2
0.321	0.816	55.8	61.4
0.322	0.817	56.4	61.6
0.321	1.360	57.4	62.2
0.322	1.366	57.4	61.6
0.321	2.176	58.6	64.6
0.321	2.721	58.4	65.9
0.322	2.732	58.5	65.5
0.321	4.081	60.3	67.7
0.322	4.098	59.7	66.7
0.320	5.418	61.1	68.7
0.321	5.441	60.7	69.9
0.320	6.772	60.6	68.8
0.322	6.831	62.0	70.8

TABLE XXXXVII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-CH_3I, ν-CH_3 FREQUENCY UNITS) IN THE ^1H NMR SPECTRUM OF METHYL IODIDE (CH_3I)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 20 °C

$[CH_3I]$, Moles/Liter	[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-CH_3I, cm^{-1}
0.320	1.354	57.0	62.4
0.321	1.356	56.0	61.4
0.321	1.358	55.0	61.4
0.320	2.709	59.3	65.9
0.321	2.713	58.3	64.9
0.321	3.532	59.7	67.7
0.321	4.075	57.5	66.9
0.321	4.070	59.7	70.9
0.320	4.063	59.9	69.3
0.321	5.426	60.7	69.5
0.321	6.248	60.8	70.2
0.321	6.782	60.8	72.2
0.321	6.792	61.4	71.4

TABLE XXXXVIII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-CH_3I, ν-CH_3 FREQUENCY UNITS) IN THE ^1H NMR SPECTRUM OF METHYL IODIDE (CH_3I)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 °C

[CH_3I], Moles/Liter	[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-CH_3I, cm^{-1}
0.322	0.272	53.2	57.4
0.322	0.436	54.2	58.8
0.322	0.817	56.6	59.2
0.322	0.819	55.4	60.2
0.322	1.362	56.2	62.2
0.322	1.365	55.8	61.6
0.321	1.360	55.8	61.4
0.321	1.356	56.0	61.4
0.322	1.366	54.8	61.0
0.322	2.180	57.6	62.2
0.321	2.721	57.7	64.3
0.321	2.713	57.5	63.9
0.322	2.732	57.7	63.7
0.321	4.081	58.7	66.5
0.321	4.069	59.3	67.1
0.322	4.098	58.1	67.9
0.321	5.434	60.3	68.5
0.321	5.441	60.3	68.5
0.322	6.826	61.4	69.8
0.321	6.792	61.6	70.0
0.322	6.831	62.0	70.2

TABLE IL

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-CH_3I, ν-CH_3, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF METHYL IODIDE (CH_3I)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 °C

[CH_3I], Moles/Liter	[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-C=O, cm^{-1}	ν-CH_3I, cm^{-1}
0.321	0.544	63.91	4375.95	4663.66
0.321	0.816	64.06	4384.19	4668.80
0.321	1.360	65.56	4397.60	4676.37
0.321	1.360	66.06	4398.79	4678.26
0.321	2.176	67.48	4412.85	4687.86
0.321	2.721	68.27	4420.88	4692.96
0.320	2.705	67.64	4420.90	4692.28
0.322	4.087	69.72	4435.56	4702.58
0.320	4.058	69.77	4436.19	4703.85
0.320	5.410	70.65	4445.81	4710.79
0.322	6.826	78.46	4456.05	4719.54
0.322	6.811	72.68	4479.94	4717.95
0.320	6.763	72.57	4455.39	4719.98

TABLE L

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-CH_3I, ν-CH_3, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF METHYL IODIDE (CH_3I)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 °C

[CH_3I], Moles/Liter	[Acet], Moles/Liter	ν-CH_3, cm^{-1}	ν-C=O, cm^{-1}	ν-CH_3I, cm^{-1}
0.322	0.273	61.041	4362.10	4651.80
0.322	0.818	62.478	4379.10	4661.51
0.322	1.364	63.133	4391.47	4668.75
0.321	1.356	63.128	4392.15	4668.70
0.321	2.713	65.854	4414.20	4684.06
0.161	2.724	64.683	4412.83	4682.98
0.321	2.717	65.545	4413.72	4682.89
0.321	4.075	66.923	4428.17	4693.05
0.321	5.434	68.478	4438.64	4701.15
0.321	6.792	70.374	4448.74	4709.01
0.161	6.811	69.111	4446.68	4709.01

TABLE LI

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α, ν-CH_3 FREQUENCY UNITS) IN THE ^1H NMR SPECTRUM OF PYRIDINE (Pyr)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 °C

[Pyr], Moles/Liter	[Acet], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}	ν-CH_3, cm^{-1}
0.249	0.164	569.2	602.0	707.2	53.2
0.249	0.163	569.6	603.2	708.1	53.4
0.249	0.163	569.0	601.2	707.2	53.2
0.248	0.271	570.0	603.6	707.6	54.8
0.249	0.327	570.6	603.0	708.0	
0.249	0.326	570.8	604.6	708.6	54.6
0.249	0.326	570.2	603.4	707.6	54.0
0.249	0.490	572.2	606.6	709.0	54.4
0.249	0.490	572.0	606.2	709.0	55.2
0.249	0.490	572.0	605.8	708.6	
0.249	0.546	571.4	605.0	707.2	54.4
0.249	0.653	572.0	605.6		54.6
0.248	0.813	572.8	606.0	707.0	55.0
0.248	0.814	571.4	605.6	706.4	54.8
0.249	0.816	573.8	607.6	708.4	55.8
0.249	0.816	572.0	606.2	706.6	55.4
0.247	1.351	575.8	609.6	708.4	56.4
0.247	1.349	574.8	608.8	706.8	56.2
0.247	1.349	575.8	609.6	707.8	
0.248	1.353	574.4	608.4	707.0	56.0
0.248	1.356	574.6	609.0	707.4	
0.247	2.701	579.8	614.0	707.8	58.6
0.247	2.697	579.6	614.0	707.6	58.0
0.248	2.709	579.2	613.2	707.6	57.8
0.248	2.713	579.8	614.0	708.0	58.0
0.248	4.058	583.4	618.0	709.2	59.4
0.247	4.046	581.8	617.0	708.0	59.4
0.247	4.046	583.0	617.8	708.4	59.4
0.248	4.063	583.2	618.0	709.0	59.4
0.247	5.395	585.2	620.2	708.6	60.6
0.247	5.396	587.0	619.8	708.8	60.4
0.247	5.395	587.0	619.2	709.0	60.4
0.248	5.411	586.0	620.8	709.8	60.2
0.248	5.418	585.2	620.6	712.0	60.6
0.248	6.764	588.8	624.0	710.8	62.0
0.247	6.743	587.6	623.2	709.8	61.4
0.247	6.743	587.2	622.6	709.8	61.6
0.249	6.821	588.4	624.0	711.0	62.4

TABLE LII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α, ν-CH_3 FREQUENCY UNITS) IN THE ^1H NMR SPECTRUM OF PYRIDINE (Pyr)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 20 °C

[Pyr], Moles/Liter	[Acet], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}	ν-CH_3, cm^{-1}
0.247	1.351	573.6	607.6	706.0	55.6
0.247	0.349	573.0	607.2	706.2	55.2
0.248	1.896	575.9	610.1	706.5	56.3
0.247	2.701	577.5	612.5	706.5	57.5
0.247	2.697	577.5	612.5	706.7	57.3
0.248	3.251	579.5	614.1	707.3	58.1
0.247	4.052	581.5	616.5	708.1	58.7
0.247	4.046	580.3	615.3	707.1	58.7
0.248	4.605	582.9	617.9	708.1	59.3
0.247	5.395	583.9	618.7	708.1	60.2
0.248	5.418	584.9	620.1	709.1	59.9
0.248	5.960	585.9	621.7	709.7	61.3
0.247	6.743	586.2	621.8	709.0	61.2
0.247	6.753	587.0	622.4	709.8	61.0

TABLE LIII

CHEMICAL SHIFT OF THE PROTON SIGNAL (ν-β, ν-γ, ν-α, ν-CH_3 FREQUENCY UNITS) IN THE ^1H NMR SPECTRUM OF PYRIDINE (Pyr)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 °C

[Pyr], Moles/Liter	[Acet], Moles/Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}	ν-CH_3, cm^{-1}
0.249	0.163	568.2	601.6	707.6	52.0
0.247	0.270	567.2	600.2	707.0	53.4
0.248	0.271	567.4	601.0	705.4	52.2
0.249	0.326	569.4	602.4	707.4	53.4
0.249	0.490	568.8	604.8	708.6	54.4
0.249	0.546	570.0	603.2	707.0	53.8
0.248	0.814	570.2	603.8	706.4	54.0
0.248	0.814	570.6	604.2	706.2	54.0
0.249	0.816	517.8	605.8	707.0	54.2
0.247	1.351	572.8	607.2	706.4	55.8
0.247	1.349	573.2	607.0	706.8	55.4
0.248	1.353	574.4	608.4	708.0	56.0
0.248	1.351	572.2	606.0	706.2	54.6
0.248	1.351	572.4	606.6	706.4	55.6
0.247	2.701	577.5	611.3	707.3	57.3
0.248	2.706	578.1	612.7	707.1	57.5
0.247	2.701	577.1	612.3	707.3	57.1
0.248	2.713	576.9	611.5	707.1	56.7
0.249	2.728	577.7	612.5	707.3	57.0
0.247	4.052	580.5	615.3	707.3	58.1
0.247	4.046	579.9	614.5	707.1	
0.248	4.058	681.3	616.3	708.9	58.5
0.247	4.046	580.9	615.1	707.5	58.7
0.248	4.052	580.3	615.7	707.9	58.1
0.247	5.402	583.7	618.5	708.1	60.1
0.247	5.395	583.3	617.9	707.7	59.3
0.248	5.411	584.5	619.9	709.7	59.9
0.248	5.402	583.9	619.5	708.7	59.9
0.247	6.743	585.8	620.8	710.8	60.8
0.247	6.743	585.2	620.6	709.0	60.0
0.248	6.764	586.6	621.6	710.0	60.6
0.247	6.743	586.6	621.2	710.8	61.2
0.247	6.753	585.6	621.0	709.0	60.8
0.249	6.821	586.4	622.0	710.0	61.4

TABLE LIV

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-β, ν-γ, ν-α, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF PYRIDINE (Pyr)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 10 ^{o}C

[Pyr], Moles/ Liter	[Acet], Moles/ Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}	ν-CH$_3$, cm^{-1}	ν-C=O, cm^{-1}
0.249	0.120	2409.00	2701.76	3091.33	61.83	4364.46
0.248	0.271	2409.71	2702.49	3090.80	61.80	4368.66
0.249	0.327	2410.43	2703.20	3091.23	62.51	4371.69
0.249	0.490	2410.52	2703.80	3090.01	62.51	4373.98
0.249	0.546	2412.51	2705.58	3091.17	63.70	4379.77
0.249	0.654	2412.21	2706.19	3090.78	63.29	4382.09
0.249	0.653	2411.46		3090.71	62.68	4379.26
0.248	0.814	2413.32	2707.59	3090.18	63.87	4387.22
0.249	0.816	2413.20	2707.44	3091.39	63.85	4384.88
0.249	0.817	2413.46	2707.72	3090.68	63.97	4387.22
0.248	1.353	2415.64	2711.96	3091.30	64.70	4397.46
0.238	1.353	2416.37	2711.94	3090.74	6468	4399.53
0.247	1.891	2418.62	2714.92	3090.10	66.15	4385.53
0.248	2.706	2421.57		3091.16	66.91	4420.92
0.248	2.706	2421.45		3091.21	67.44	4419.25
0.248	2.706	2420.94	2718.68	3091.49	66.35	4420.21
0.247	2.701	2421.01	2719.01	3091.24	67.89	4420.84
0.249	2.728	2422.19	2719.94	3090.71	67.57	4422.38
0.247	3.237	2423.14	2721.00	3090.73	67.69	4427.83
0.248	4.058	2425.04	2723.58	3091.98	68.21	4433.30
0.247	4.046	2425.84	2724.44	3091.96	69.04	4436.45
0.248	5.411	2428.81	2728.24	3092.76	70.55	4446.45
0.247	5.395	2428.87	2728.87	2092.86	70.65	4447.43
0.247	6.743	2431.14	2732.38	3092.87	71.94	4455.51
0.248	6.764	2430.94	2731.02	3092.79	71.16	4453.21
0.248	6.764	2431.02	2731.68	3093.35	71.82	4454.63
0.249	6.821	2431.67	2732.38	3092.77	72.00	4455.38

TABLE LV

CHEMICAL SHIFT OF THE CARBON-13 SIGNAL (ν-β, ν-γ, ν-α, ν-CH$_3$, ν-C=O FREQUENCY UNITS) IN THE ^{13}C NMR SPECTRUM OF PYRIDINE (Pyr)--ACETONE (Acet) AS REFERENCED FROM CYCLOHEXANE AND AS A FUNCTION OF ACETONE CONCENTRATION AT 30 °C

[Pyr], Moles/ Liter	[Acet], Moles/ Liter	ν-Pyr-β, cm^{-1}	ν-Pyr-γ, cm^{-1}	ν-Pyr-α, cm^{-1}	ν-CH$_3$, cm^{-1}	ν-C=O, cm^{-1}
0.249	0.163	2407.76	2700.35	3091.38	59.67	4360.00
0.247	0.267	2408.79	2702.09	3091.25	60.30	4225.07
0.248	0.268	2408.93	2701.58	3091.38	60.80	4364.98
0.248	0.268	2408.47	2701.68	3090.90	59.62	4364.46
0.249	0.326	2409.06	2701.73	3090.80	60.33	4365.92
0.249	0.490	2410.47	2703.70	3091.42	61.00	4371.66
0.249	0.546	2411.06	2704.42	3091.32	60.98	4376.12
0.248	0.814	2413.94	2708.30	3090.68	64.00	4387.88
0.249	0.816	2412.02	2706.05	3090.93	61.20	4380.62
0.247	1.351	2419.11	2715.42	3091.90	66.02	4411.25
0.248	1.356	2414.94	2710.96	3091.32	63.08	4392.95
0.247	2.701	2420.13	2717.02	3090.81	64.74	4414.36
0.249	2.728	2420.56	2717.62	3090.71	65.34	4415.01
0.248	4.058	2423.68	2721.59	3091.38	66.19	4428.21
0.247	5.402	2426.79	2725.94	3093.68	67.77	4439.39
0.248	5.411	2427.20	2725.87	3092.05	68.20	4439.21
0.248	6.764	2429.50	2729.46	3092.77	69.60	4448.15
0.247	6.753	2429.50	2729.77	3092.77	69.60	4448.68
0.249	6.820	2430.16	2730.26	3092.64	70.39	4449.38

VITA

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