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HYDRATION OF SEVERAL ALIPHATIC AMINES IN SOME NON-POLAR SOLVENTS.

A DIELECTRIC STUDY OF ALIPHATIC AMINE HYDRATES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

MERCER DUANE GREGORY

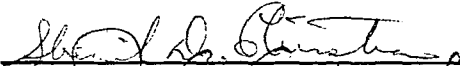

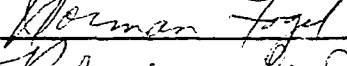
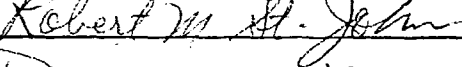
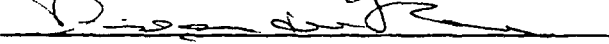
Norman, Oklahoma

April, 1968

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APPROVED BY

  
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DISSERTATION COMMITTEE

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# HYDRATION OF SEVERAL ALIPHATIC AMINES IN SOME NON-POLAR SOLVENTS.

## A DIELECTRIC STUDY OF ALIPHATIC AMINE HYDRATES

### CHAPTER I

#### INTRODUCTION

A study of the hydrogen bonding of amines is an interesting and worthwhile project from the standpoint that many reactions involving proteins depend on the reactivity of the N-H linkage. By investigating amines, which are much simpler molecules than proteins, it is possible to elucidate the properties of the N-H bond in a more direct manner. The problems of purification and low solubility, which are unavoidable in studies of proteins, are eliminated. It should be emphasized that the hydrogen bonding properties of amines will not be the same as the hydrogen bonding properties of the N-H site in a protein; however, the information which the studies of amines can yield should be very valuable and allow a direct comparison with results for the larger molecules. In view of the general importance of the solvation of molecules in aqueous systems, a study of the properties of amine-water complexes should yield new and valuable information.

This introduction to the literature concerning amine complexes begins with one of the earliest reports on amine hydrates and continues through three areas of general interest: 1. Amine hydrates and other

amine complexes. 2. Self-association of amines. 3. Dielectric properties of amine solutions.

Amine Hydrates and Other Amine Complexes

One of the earliest reports on amine hydrates is a lengthy article by Pickering<sup>1</sup> in which he determined the freezing points of amine-water solutions. Sixteen different amines were investigated, including triethylamine. An increase in the viscosity of the solution is observed when the two pure liquids are mixed. Pickering concluded from his data that amine hydrates do exist. Kartzmark<sup>2</sup> has confirmed Pickering's findings in a recent publication. He has studied the triethylamine-water system and has reported a dihydrate which melts at 22°. Moore<sup>3</sup> has determined the ionization constants and "hydration" constants of piperidine, ammonia, and triethylamine at a series of temperatures. The ionization constants were determined by a conductimetric method and the "hydration" constants were calculated from partition experiments in conjunction with the conductance data. The reported "hydration" constants are not actually the constants which relate the extent of interaction between amines and water, but are ratios of the amount of the quaternary ammonium base to the amount of free amine present.

$$K = \frac{R_3\text{NHOH}}{R_3\text{N}}$$

Since the equilibrium concentration of water is not taken into account, these "hydration" constants are in a sense poorly named. In another early study Moore and Winmill<sup>4</sup> have employed a technique similar to that described above in attempting to study the hydration of a series of aliphatic amines. Again it should be emphasized that the constants

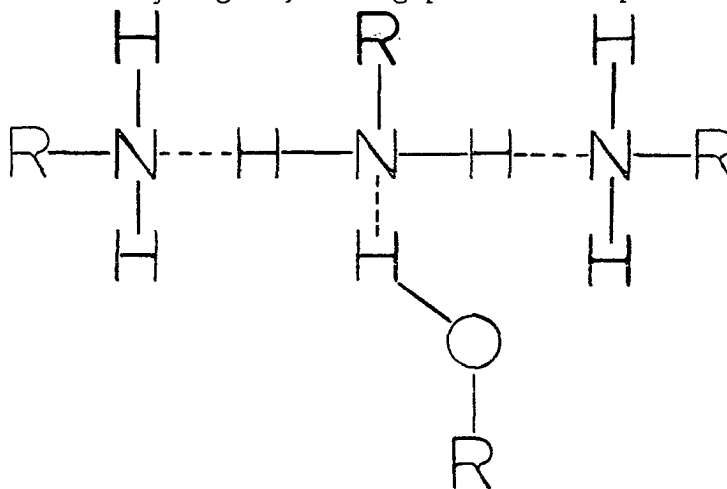
reported by these authors are not the mass action equilibrium constants for the interaction between amine molecules and water molecules. They report only a ratio of amine hydrate concentration to the free amine concentration.

H. W. Smith<sup>5</sup> has partitioned amines between water and several organic solvents. He reports that amines seem to be hydrated to a much greater extent than acids or other compounds. This fact is not sufficiently supported by the reported data and seems doubtful since no water concentrations were determined. Smith has apparently attempted to derive more information from the partition data than can be successfully done without determining water concentrations in the organic phase.

Bidet<sup>6</sup> has investigated the crystalline hydrates of n-amylamine, isoamylamine, and isobutylamine. The amines gradually combine with atmospheric water at room temperature and form comparatively stable solid hydrates. The only well-defined solid hydrate isolated was the isoamylamine dihydrate.

Somerville<sup>7</sup> has repeated the earlier work of Pickering<sup>1</sup> on the degree of hydration of the alkylamines in aqueous solution. The extent of hydration in the series of methyl and ethyl amines appears to be mono < di < tri. A method of calculating the degree of hydration of a solute directly from the conductivity of its solution is presented. The method is based on the Arrhenius principle which relates the degree of dissociation to equivalent conductance. Somerville finds that the order of hydration of amines is not the same as the order of basic strength, but appears to correspond exactly with the order of internal pressure. The greater the difference between the internal pressure of an amine and water, the greater the degree of hydration.

Freyman,<sup>8</sup> in a study of the infrared absorption of alcohol-amine mixtures, has found that the free OH band almost completely disappears in mixtures of aniline and  $(\text{CH}_3)_3\text{COH}$ , n-butylalcohol, phenol, resorcinol, and propylene glycol. In this early spectral study the disappearance of the hydroxyl band is attributed to the formation of a molecular compound with a one-electron link between the hydrogen of the hydroxyl group and the nitrogen of the amine group. Gordy<sup>9</sup> has concluded by IR spectroscopy that the acceptor properties of the amine hydrogen are much weaker than those of the hydroxyl hydrogen. For this reason one expects the hydrogen bonds between water or alcohol and an amine to be formed largely through the hydroxyl hydrogen. He finds that the primary and secondary amines reacting with  $\text{D}_2\text{O}$  cause the bonded OD peak to appear exceptionally broad. For this reason a more complicated complex species than the simple 1:1 aggregate is suggested. Such a linkage would decrease the effective negative charge on the nitrogen and thus increase the acceptor power of the amine hydrogens, making possible complexes of the type



In 1936, Huggins<sup>10</sup> wrote, "The hydrogen atoms of ammonia, primary amines and secondary amines can all form bridges to oxygen atoms of adjacent water molecules. The hydrogen atoms of one primary amine

molecule undoubtedly attract the electronegative side of a nitrogen in another molecule, but this attraction is weaker than for corresponding hydroxyl compounds." This statement represents the first indication that amines might hydrate or self-associate by a hydrogen bonding mechanism.

The thermodynamic constants of a series of amine "hydrates" have been determined by Briegleb.<sup>11</sup> Once again it must be emphasized that the constants determined are not for simple hydration reactions; the reactions studied involved the transfer of a proton between the amine molecules and water. The results of this work are shown below.

BRIEGLEB'S DATA<sup>a</sup>

AMINE	$\Delta G(\text{cal})$	$-T\Delta S(\text{cal})$	$\Delta H(\text{Kcal})$
Piperidine	15,060	1,760	11.5
Dimethylamine	14,687	2,828	11.0
Methylamine	14,484	1,396	10.4
Ethylamine	14,349	1,349	11.1
Trimethylamine	13,358	4,543	11.3
Ammonia	12,564	164	8.0
Hydroxylamine	8,126	-874	--
Pyridine	7,235	3,175	12.0

<sup>a</sup>for the reaction  $\text{BH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}_3\text{O}^+$  in aqueous solution

Mohr, Wilk, and Barrow<sup>12</sup> have reported an infrared spectral investigation of the hydration of various organic bases in carbon tetrachloride; they suggest that the water spectra are consistent with the existence of 1:1 hydrates at low base concentration and also bridged hydrates, involving two base molecules and one water molecule, at higher base

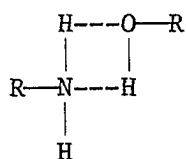
concentrations. Thompson<sup>13</sup> has found that pyridine and water form a 1:1 complex in carbon tetrachloride by IR absorption spectroscopy; Siderov<sup>14</sup> reports both the 1:1 and 2:1 hydrates for this system in another IR study.

The distribution of trimethylamine, diethylamine, and n-butylamine between water and several organic solvents is the subject of an article by Sandell.<sup>15</sup> Only the distribution constants for the systems have been reported and no mention is made of hydrate formation. The mean lives of three amine-water complexes have been determined using an isotopic exchange technique.<sup>16</sup> The mean lives extrapolated to dilute aqueous solution are  $2.0 \times 10^{-12}$  sec.,  $1.2 \times 10^{-11}$  sec., and  $1.0 \times 10^{-10}$  sec. for the above amines, respectively.

Findlay and Kidman<sup>17</sup> have studied the complexes of pyridine with various alcohols. Thermodynamic constants for the complexes are reported; the authors reach the doubtful conclusion that small quantities of dissolved water in the system have no effect on the pyridine-alcohol equilibria. The table below summarizes the infrared results of Zeegers-Huyskens<sup>18</sup> on amines and alcohols. The equilibrium constants are for the 1:1 complexes formed in carbon tetrachloride at 22°.

ZEEGERS-HUYSKEN'S DATA

ALCOHOL	AMINE	$K_{11} (M^{-1})$
$C_4H_9OH$	$C_4H_9NH_2$	1.58
$C_4H_9OH$	$(C_2H_5)_2NH$	3.40
$C_4H_9OH$	$(C_2H_5)_3N$	3.17
sec- $C_4H_9OH$	$C_4H_9NH_2$	0.68
sec- $C_4H_9OH$	$(C_2H_5)_2NH$	1.89



is the double hydrogen bonded structure proposed for this

complex. In a similar article the thermodynamic constants for a series of amine-alcohol complexes is reported.<sup>19</sup> The results of this study are presented in the following table.

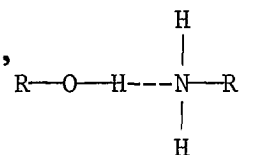
ALCOHOL	AMINE	$K_{11} (\text{M}^{-1})$	$-\Delta H (\text{Kcal/mole})$	$-\Delta S (\text{e.u.})$
Ethanol	n-butylamine	3.53	7.21	22.62
"	diethylamine	4.85	4.96	14.44
"	triethylamine	4.49	4.83	14.11
n-Butanol	n-butylamine	4.29	7.48	22.65
"	diethylamine	3.40	5.48	16.28
"	triethylamine	3.17	4.86	14.30
sec-Butanol	n-butylamine	2.96	7.76	24.34
"	diethylamine	1.89	5.41	17.21
"	triethylamine	1.70	4.98	15.95

The primary amines tend to form the strongest bonds, whereas the secondary and tertiary amines form weaker bonds of nearly equal strength. The n-butylamine complexes were studied in cyclohexane and the other complexes in carbon tetrachloride; therefore only general comparisons should be made with respect to the equilibrium constants found in the two solvents since they solvate the amine and alcohol molecules to a different extent.

Zeegers-Huyskens,<sup>20</sup> in another infrared investigation, has also studied n-propylamine complexed with proton donors having aqueous pKa values ranging from 16 to 0.8. She has concluded that for donors having pKa values of 9 or less, charge separation significantly alters the appearance



of the O—H---N and N-H stretch bands. The O—H---N band disappears in compounds with  $pK_a < 9$  and a large band appears in the region 2750 to  $2500\text{ cm}^{-1}$ . This new band is attributed to the N—H<sup>+</sup>---O stretching vibration. The proposed structure of the complex,



differs from that suggested previously.<sup>18</sup> This structure is the simplest and most plausible of those proposed by Zeegers-Huyskens. The ionic form mentioned above was proposed to explain the change in color of solution upon complex formation and a decrease of solubility of the complex in carbon tetrachloride, as well as the infrared spectra.

Nuclear magnetic resonance spectroscopy was employed by Creswell and Allred<sup>21</sup> to study the triethylamine-chloroform complex in cyclohexane. A 1:1 equilibrium constant of  $0.51\text{ M}^{-1}$  at  $25^\circ$  and a  $\Delta H^\circ$  of  $-4.2\text{ kcal/mole}$  are reported. This same value has been reported for the heat of formation of the diethylamine-chloroform complex in the gas phase.<sup>22</sup>

Condon<sup>23</sup> has written a lengthy theoretical discussion of the influence of hydration on base strength. Possible effects on the base strength resulting from hydration of the amine as well as the ammonium ion are considered. A general equation is proposed relating hydration effects to the number and nature of the substituents attached to nitrogen. In the development of the equation the author lets  $n$  be the number of hydrogens attached to nitrogen by primary bonds in the ammonium ion conjugate to the amine. Then  $n$  is also the number of water molecules hydrogen bonded to the amine; for  $n-1$  water molecules, the amine is a hydrogen donor. This theory is for general solvation in aqueous solution and will not apply to amines as solutes in organic solvents; however, it

is interesting to note how well the theory applies to aqueous systems since these systems are more like those encountered in nature.

The expression for the variation of the standard free energy of hydration,  $\delta G'_h$ , is given in pK units and is based on the general theory of substituent effects developed by Hammett,<sup>24</sup> Taft,<sup>25</sup> and others.<sup>26</sup>

$$\frac{\delta G'_h}{2.303RT} = pK'_h = pK'_\alpha + \rho'_\alpha \sum_{i=1}^3 \sigma_i + (n-1)pK'_\beta + (n-1)\rho'_\beta \sum_{i=1}^3 \sigma_i,$$

where  $\sigma_i$  is a polar substituent constant for the substituent  $R_i$ , on a scale relative to hydrated hydrogen as zero; that is  $\sigma_{H---OH_2} = 0$ .  $pK'_\alpha$  is the free energy of hydration (in pK units) for one water molecule acting as a hydrogen donor.  $\rho'_\alpha$  is a reaction constant relating this free energy to the structure of the amine through a sum of substituent constants,  $\sum \sigma_i$ .  $pK'_\beta$  is the free energy of hydration for one water molecule for which the amine acts as a hydrogen donor.  $\rho'_\beta$  is a reaction constant relating this free energy to the structure of the amine. In a subsequent paper<sup>27</sup> this theory is applied to aliphatic amines and N-substituted anilines. Plots of pKa(calcd) vs. pKa(obsd) are presented and it is clearly seen that data for the aliphatic amines more nearly follow the relation than do data for the anilines.

Finally, Barrow and Yerger<sup>28</sup> have determined the extent of association of triethylamine with chloroform and ethanol in carbon tetrachloride. 1:1 association constants of  $0.36 \text{ M}^{-1}$  and  $2.9 \text{ M}^{-1}$  are reported for the chloroform and ethanol complexes, respectively. A few years later Barrow<sup>29</sup> distinguished the acetic acid-pyridine complex from the acetic acid-triethylamine complex by calling the former a hydrogen bonded complex and the latter a hydrogen bonded ion pair.

### Self-association of Amines

Molecular association is the subject of an early paper by Peddle and Turner.<sup>30</sup> The freezing points and boiling points of a series of solutions in which carboxylic acids, phenol, and amines were dissolved as solutes in water, ethanol, and benzene were determined. No apparent association is found in any of the aliphatic amines. Turner and Merry<sup>31</sup> found, in general, that primary amines are slightly associated, while secondary and tertiary amines are non-associated in the liquid state. The extent of association is diminished with increasing molecular weight. Apparent molecular weights of several amines in benzene solution have been calculated.

Copley, Zellhoefer, and Marvel<sup>32</sup> have concluded from solubility measurements of amines dissolved in halogenated hydrocarbons that aliphatic amines are undissociated in solution and an aliphatic amine hydrogen is not sufficiently active to form hydrogen bonds. In the opinion of Copley, et al., the failure to form hydrogen bonds certainly cannot be due to any lack of donor properties on the part of the nitrogen atom. The lack of association in liquid amines indicated by the solubility data is in accord with cryoscopic behavior in non-polar solvents.

Cyclohexylamine and N-methylcyclohexylamine are reported to be partially self-associated in cyclohexane at 28°. <sup>33</sup> The criteria for self-association are the decrease in the individual absorptivities of each amine at higher concentrations. N-methylcyclohexylamine was found to be associated to a lesser extent than the primary amine. Unfortunately no dimerization constants are reported.

In three well-written articles, Whetsel and Lady<sup>34,35,36</sup> have determined many association constants of complexes involving amines. The first paper concerns the formation of N—H---N electron and H—N---H hydrogen bonds in cyclohexane solutions. Aniline and N-methylaniline are used as proton donors with benzene, N,N-dimethylaniline, pyridine, and N,N-dimethylcyclohexylamine as proton acceptors. The effects of complex formation upon the first overtone N-H stretching bands of the proton donors have been determined as a function of temperature and the thermodynamic properties of the complexes have been computed. The second paper presents a study of the self-association of aniline in cyclohexane solution. From the first overtone N-H stretching band the data have been interpreted in terms of self-association through hydrogen bonding. A model based on monomer, dimer, and tetramer equilibrium is consistent with experimental data up to 4 M.  $\Delta H^{\circ}$  values of  $-1.64 \pm 0.25$  and  $-7.7 \pm 0.5$  kcal/mole are reported for the formation of the dimer and tetramer, respectively. The third publication deals with amine-chloroform complexes. Again the N-H stretch band is used to determine the extent of complexation. The thermodynamic constants for the aniline and cyclohexylamine complexes are determined at temperatures between 10 and 50°. Self-association between cyclohexylamine monomers is found to be negligible.

ANILINE-CHLOROFORM

T°C	10	21.6	30.5	41.6	49.5
$K_{11} (M^{-1})$	0.590	0.522	0.500	0.438	0.404

$$\Delta H^{\circ} = -1.7 \pm 0.2 \text{ kcal/mole}$$

$$\Delta S_{25}^{\circ} = -7.1 \pm 0.7 \text{ e.u.}$$

CYCLOHEXYLAMINE-CHLOROFORM<sup>a</sup>

T <sup>o</sup> C	12	17.5	28	30	38	42.5	51.5
K <sub>11</sub> (M <sup>-1</sup> )	1.41	1.31	1.04	1.03	0.84	0.84	0.64

$$\Delta H^{\circ} = -3.6 \pm 0.3 \text{ kcal/mole}$$

$$\Delta S_{25}^{\circ} = -11.9 \pm 1.0 \text{ e.u.}$$

<sup>a</sup>These constants were determined from data taken at 2030  $\mu$ .

The  $\Delta H^{\circ}$  value for the aniline complex is comparable to the value of -1.93 kcal/mole reported by Davies<sup>37</sup> for the aniline-water complex in carbon tetrachloride.

Wolff and Eints<sup>38</sup> have conducted an infrared spectral study of primary amines interacting with tertiary amines. Methylamine complexed with trimethylamine and triethylamine has been studied over a large temperature range. The ethylamine-triethylamine complex was also studied at various temperatures. At sufficient dilution the spectra are interpreted as 1:1 association with only one hydrogen of the primary amine involved in a hydrogen bond. The same solutions at lower temperature show a band attributed to a 1:2 complex (one primary and two tertiary amines). Methylamine complexed with tripropylamine or tributylamine does not show the lower temperature absorption, thus indicating only 1:1 complexes; steric hindrance apparently prohibits formation of the 1:2 complex.

Vapor pressure measurements have been used to determine the extent of self-association of methyl-, ethyl-, and n-propylamine in saturated aliphatic hydrocarbons.<sup>39</sup> Vapor pressure isotherms have been determined over a wide temperature range. The heat of association is found to be approximately -2.2 to -2.0 kcal/mole for each amine aggregate.

Dielectric Properties of Amine Solutions

Bond and Smith<sup>40</sup> have complexed triethylamine with t-butyl- and n-butylalcohol. Values of the association constants are given as 86 and 330 (mole fraction units), respectively. This dielectric study employs a method by which both association constants and dipole moments of complexes were determined. The determined dipole moments of the complexes are 2.25 D. and 2.34 D., respectively. Cleverdon, Collins, and Smith,<sup>41</sup> in a similar study, have reported information for pyridine using the same technique. Association constants of 1200 and 2000 (mole fraction units) are reported for the t-butyl- and n-butylalcohol complexes, respectively. Dipole moments for the complexes are 3.16 D. and 3.37 D. The difference between the results for triethylamine and pyridine complexes corresponds to an additional moment along the OH axis of 0.18 D. and 0.25 D. in the n-butyl- and t-butylalcohol complexes. Smith<sup>42</sup> has found evidence that hydrogen bonding between weak acids and weak bases contributes a relatively small increment to the dipole moment of the complex formed. He has suggested that in the association of acids of medium strength with tri-n-butylamine or triethylamine the energies of the hydrogen bonded and ion pair forms become nearly equal, with the result that the two exist in tautomeric equilibrium in solution. Dipole moments are reported for a series of alcohol-amine and phenol-amine complexes.

One of the first reports stating that amines might form charge separated complexes in solution was presented by Hulett, Pegg, and Sutton.<sup>43</sup> The observed dipole moments of three trimethylamine complexes in cyclohexane solution were found to be much greater than the dipole

moments calculated from reasonable models of the complexes. Enhancements in the dipole moments (i.e., differences between observed and calculated dipole moments) equal to 1.00 D., 1.26 D., and 0.91 D. were reported for the phenol, p-chlorophenol, and p-cresol complexes, respectively.

Pyrrrole has been used as a proton donor by Bertin and Lumbroso,<sup>44</sup> who have determined the association constants and dipole moments of the complex formed by this donor with triethylamine. In cyclohexane the 1:1 association constant is  $3.2 \text{ M}^{-1}$  and the dipole moment is 3.12 D. In benzene the association constant drops to  $1.7 \text{ M}^{-1}$ , indicating the more powerful solvating power of this solvent; the dipole moment remains approximately the same as in cyclohexane.

The dipole moments of only a few amine-water complexes have been reported. Kazakova and Fel'dshtein<sup>45</sup> have found that the triethylamine-water and the pyridine-water complexes have dipole moments of 2.24 D. and 3.13 D., respectively. These constants were determined in benzene at  $20^\circ$ .

Affsprung, Derkosch, and Kohler<sup>46</sup> have found that water forms 1:1 complexes with weak bases at low base concentrations and 1:2 (water: 2 base) complexes at high base concentrations in complete agreement with Mohr, Wilk, and Barrow.<sup>12</sup> However, this conclusion is apparently true only for weak bases such as dioxane, tetrahydrofuran, and methylethylketone. The strong base triethylamine seems to form only the 1:1 complex over the concentration range studied. These authors have concluded that the hydrogen bond between water and strong bases is highly polar, indicating that there is an appreciable partial negative charge on the

hydroxyl group. It has been discovered that the water-triethylamine solutions in carbon tetrachloride have much higher dielectric constants than are predicted from the dielectric constants of binary solutions of triethylamine and water in carbon tetrachloride. The same experiment with water and dioxane yields only a small increment of the dielectric constant.

It is apparent that there is no widespread agreement in the literature concerning amine properties in solution. Christian and co-workers<sup>47-52</sup> have developed techniques for studying hydrogen bonding properties of a polar solute dissolved in an organic solvent. These techniques have been employed in the present investigation to study the hydration and self-association equilibria of several aliphatic amines. Cyclohexylamine (CHA), N-methylcyclohexylamine (NMCHA), and N,N-dimethylcyclohexylamine (DMCHA) have been employed as proton acceptors in this investigation along with triethylamine. The cyclohexylamines have been studied in benzene at 25 and 35°. Triethylamine has been studied in benzene, toluene, and cyclohexane at 25°.



## CHAPTER II

### OBJECTIVES

The objectives of this research were:

1. To determine thermodynamic parameters related to the self-association and hydration of amines in organic solvents.
2. To determine the effect of N-alkyl substitution on hydration equilibria.
3. To determine the dipole moment of some amine-water complexes and consequently the extent of charge separation in the complexes.
4. To relate the strength of some amine-water hydrogen bonds to the molecular structure and bonding properties of the amines.

## CHAPTER III

### EXPERIMENTAL

#### Purification of Amines and Solvents

The cyclohexylamines were products of Eastman Organic Chemicals and Abbott Laboratories. Triethylamine was obtained from Matheson Coleman and Bell. The amines in the hydration experiments were distilled from KOH through a 25-plate column. No special effort was made to remove water from these amines since they were to be hydrated. The amines were stored in dark, air-tight containers and were used within one week after distillation. No apparent decomposition was observed in any of the amines on standing. The amines used in the dielectric experiments were also distilled, but were stored in a desiccator filled with Drierite. This procedure seemed to produce "dry" amines as evidenced by the dielectric measurements. Approximately 25% of the amine was collected as forerun; only the middle fraction, which boiled in most cases over a 1<sup>o</sup> temperature range, was retained for study. The amines were not difficult to purify, and they proved to be ideal solutes for a study of this type.

Reagent grade benzene, toluene, and cyclohexane were "scrubbed" with concentrated sulfuric acid until no brown coloration of the acid layer could be seen. The solvents were then washed with approximately 20% NaOH solution and finally with distilled water. A 30-plate Oldershaw

column was employed to distill the water saturated solvents. The solvents were distilled from  $\text{CaH}_2$ . The column head was equipped with a solenoid valve and Flexopulse timer from Eagle Signal Corp. All solvents were distilled at a reflux ratio of 10:1. The middle two thirds of the distillate were retained for use and stored over calcium hydride. This precautionary measure to insure dryness was not necessary for the hydration experiments; however, it was mandatory for the dielectric experiments. In addition, the benzene used in this case was stored in a column of approximately 2.5 l. containing 400 g. of molecular sieve type 4A (1/16 in. pellets) from Fisher Scientific Company. Molecular sieve was found to dry benzene more efficiently than any of the more common drying agents ( $\text{CaSO}_4$ ,  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{SO}_4$ ).

The benzene used for calibration of the dipole cell was reagent grade. It was "scrubbed" as described previously and distilled over  $\text{CaH}_2$ . The distillate was also stored over  $\text{CaH}_2$ . Approximately twenty-four hours before use, the benzene was transferred to a 300 ml. chromatographic column containing 40 g. of molecular sieve (4A).

The butylether was a product of Aldrich Chemical Co., Inc. It was distilled over  $\text{CaH}_2$  and only the middle fraction was retained for use. It was stored over  $\text{CaH}_2$  until transferral to the chromatographic column.

Fisher Certified Reagent "Spectroanalyzed" grade cyclohexane was used without further purification. It was stored over  $\text{CaH}_2$  before being transferred to the chromatographic column.

The solute isopiestic cells used for the water solubility studies were similar to those described previously.<sup>51</sup> The wide-mouth Mason

fruit jars, used as the equilibration cells, had a volume of one liter. A six-inch piece of glass tubing was taped vertically on the side of the jar. This tube was placed over a small brass rod in the constant temperature bath. This arrangement allowed the cell to move freely about the rod causing the solution inside to be constantly agitated. This constant agitation was probably responsible in part for the rapidity with which equilibrium was attained. Most isopiestic experiments are very slow in reaching equilibrium; however, hydration seemed to be complete in less than twenty-four hours. Nonetheless, no solutions were analyzed earlier than 48 hours after their preparation. The rapid attainment of equilibrium is due, no doubt, to the relatively small quantities of water which must be transferred through the vapor phase. The constant water activity solutions were placed in the cells in 100 ml. beakers. Sulfuric acid solutions could not be used because the amines were volatile enough to form salts with the acid. No change in the water activity of the calcium chloride solutions was detected after equilibrium was reached.

Before use, the fruit jar lids were cleaned (acetone was the best cleanser) and the rubber sealing strips were completely removed. A hole the size of a No. 9 glass stopper was drilled in each lid. Squares of polyethylene, large enough to cover a lid, were cut; three squares (each 1/16 in. thick) were cut for each lid. The lids were placed on a hot plate (underside up) sufficiently warm to melt the polyethylene. The lids were fitted to a fruit jar while the polyethylene was still warm so that a groove could be made in the lid the exact size of the jar mouth. This type of lid was found to be excellent for sealing purposes and also allowed more convenient preparation of samples than

those seals described previously.<sup>51</sup> After the lid cooled, the hole was redrilled and fitted with a ground glass stopper. Sampling was accomplished by removing the stopper and inserting a pipette equipped with a Propipette from Instrumentation Associates. Upon replacement of the stopper the seal was as good as the original.

The distribution experiments were carried out in 500 ml. ground glass stoppered Erlenmeyer flasks. The flasks were suspended by clamps in the constant temperature bath. Equilibrium was reached in less than forty-eight hours with the flasks being shaken two or three times during that period.

Two constant temperature water baths were used throughout the course of this work. The 25° bath held approximately 75 gallons of water and had a surface area of about 10 square feet. The temperature was controlled with a Princo Magna Set mercury regulator connected to a Model E-2 electronic relay from the Emil Greiner Co. This proved to be an excellent method for controlling the temperature of a large open water bath. The temperature gradient throughout the bath was found to be less than 0.03°. The bath was well stirred by two evaporative cooler pumps from Little Giant Corp. The bath was heated with two 200 watt lightbulbs activated by the mercury regulator. Coolant was supplied by a refrigeration bath equipped with a pump for circulating water through a copper coil in the 25° bath.

The 35° bath was somewhat smaller, holding approximately 50 gallons of water with a surface area of 6 square feet. Only one pump was necessary for adequate circulation in this smaller bath. The temperature was controlled to  $\pm 0.03^\circ$  with a Matheson Lab-Stat and a 200 watt

light bulb. The Lab-Stat was used in conjunction with a one degree thermometer (34.5-35.5°) whose temperature scale was 10 cm. long.

#### Calcium Chloride Water Activity Solutions

Reagent grade calcium chloride dihydrate (Baker Analyzed) was used to prepare the water activity solutions. At first a combination of data obtained from Robinson and Stokes<sup>53</sup> for molality vs. water activity and the International Critical Tables<sup>54</sup> for density vs. molality were used to determine the water activity of the solutions as a function of density. It soon became evident that a slight discrepancy existed between the analytical determinations of the solubility of water in benzene and that calculated from the presumed water activity. An experiment to determine the water activities of several calcium chloride solutions was conducted.

The most direct method for determining the water activity of an aqueous solution is to measure the partial pressure of water vapor above the solution. The water activity is defined as the ratio of the water vapor pressure above the solution to the vapor pressure of pure water ( $A_W = P_{sol.} / P_O$ ). This method was used in the present study. The vapor pressure measuring device was similar to the one described by Taha, et al.<sup>55</sup> Calcium chloride solutions were prepared to yield a series of solutions with water activity ranging from 0.4 to 1.00. Approximately 150 to 200 ml. portions of each of these solutions were introduced into the flask along with a teflon coated magnetic stirring bar. The dissolved air was removed by freezing the sample in a dry ice-acetone bath. After freezing, the system was evacuated and the solution was allowed to melt. This process was repeated until no gas bubbles appeared in the solution

upon remelting and the measured vapor pressure remained constant. Usually 8 to 10 freezing-thawing cycles were required to remove the dissolved air satisfactorily. Two constant temperature baths were maintained at  $25.00 \pm 0.01^\circ$  and  $35.00 \pm 0.04^\circ$ . The temperature control and stirring in these baths were similar to those described earlier in this section. Each solution was allowed to reach temperature equilibrium in each of the water baths, and the pressures were measured from the manometer with a Gaertner Scientific Corporation (2168A) cathetometer which could be read to  $\pm 0.05$  mm. The calcium chloride solutions were analyzed by titration with standard silver nitrate solution. The densities at  $25^\circ$  were determined with a Westphal balance. The data are presented in Table I. The agreement between the present work and the values of water activity and molality reported by Robinson and Stokes<sup>53</sup> is illustrated in Figure I. The difference in the activities of water at  $25^\circ$  and  $35^\circ$  are consistent with the variation expected from the relation  $\frac{d \ln a_w}{dT} = \frac{\Delta H}{RT^2}$ , where  $\Delta H$  is the partial molar heat of water in  $\text{CaCl}_2$  solution.

#### Quantitative Determinations and Procedure

Water concentrations were determined with a Beckman KF-3 aquameter using the Karl Fischer method. The Karl Fischer stock solution was prepared by dissolving 300 g. of iodine in 2 pints (946 ml.) of pyridine and 2300 ml. of methanol in a 4 l. container.<sup>56</sup> Approximately 500 ml. of stock solution was diluted with an equal amount of methanol and 60 ml. of liquid sulfur dioxide twenty-four hours before an analysis was to be made. The Karl Fischer reagent (KFR) was standardized in two ways. Originally weighed amounts of sodium tartrate dihydrate were titrated

Table I

## Water Activities and Vapor Pressures of Calcium Chloride Solutions

Molality CaCl <sub>2</sub>	Density 25°C	A <sub>w</sub>		P <sub>H<sub>2</sub>O</sub> <sup>mm</sup>	
		(25°)	(35°)	(25°)	(35°)
0.0		1.00	1.00	23.75	42.11
1.052	1.0880	0.945	0.945	22.45	39.80
1.673	1.1375	0.903	0.904	21.45	38.09
2.190	1.1750	0.852	0.855	20.25	36.01
2.785	1.2150	0.810	0.801	19.25	33.75
2.962	1.2447	0.762	0.753	18.10	31.73
3.536	1.2700	0.687	0.685	16.32	28.85
4.280	1.3095	0.597	0.602	14.17	25.35
5.158	1.3566	0.486	0.494	11.55	20.82
6.133	1.4044	0.384	0.392	9.12	16.52



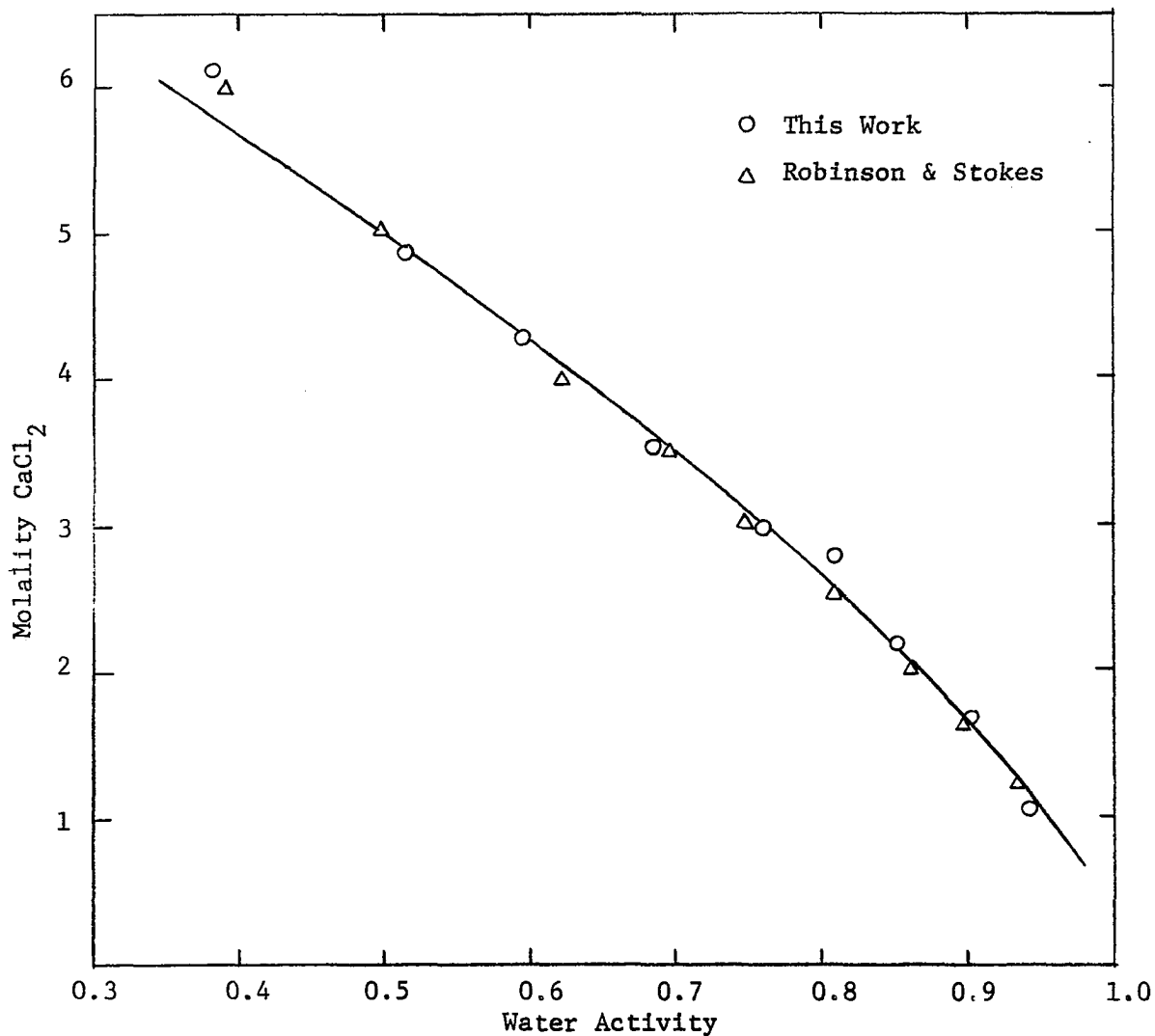


Figure I. Water Activity of Calcium Chloride Solutions at 25°.

to find the titer of KFR in mg.  $H_2O/ml.$  KFR. However, a more convenient method was developed once the solubility of water in benzene had been determined accurately. Ten or twenty-five ml. aliquots of water saturated benzene (at  $25^{\circ}$ ) were titrated and from the known solubility of water in benzene (0.0350 M)<sup>57</sup> the titer was easily and accurately determined. The solubility of water in benzene at  $35^{\circ}$  was found to be 0.0465 M. Taylor<sup>58</sup> found the concentration of water in benzene at  $35^{\circ}$  to be 0.0478 M using a similar method. The solubility of water in toluene and cyclohexane at  $25^{\circ}$  was found, by the isopiestic method, to be 0.0268 and 0.00297 M, respectively. These solubilities are similar in magnitude to those determined by Johnson.<sup>59</sup> This method exploited the convenience of incorporating an internal standard into the experiments in which benzene was used as the solvent. Also the titer determinations were done in exactly the same manner as the solution determinations, which is very important in timed dead-stop titrations. All endpoints were held for 30 seconds. It was found that excellent reproducibility was obtained only if each titration was done exactly as the previous one. Each reported water concentration is an average of 2 or 3 independent titrations. The aquameter was equipped with a 10 ml. buret which was read to 0.01 ml.

All amine concentrations were determined by titration with 0.1 N. HCl, which was standardized with  $Na_2CO_3$ .<sup>60</sup> The endpoints were determined with a Beckman Zeromatic II pH meter. Ten or twenty-five ml. aliquots were transferred to 300 ml. beakers and 50 ml. of distilled water was added before titrating. The solutions were stirred very rapidly during the titrations to facilitate the extraction of the amine into the water phase. The amines with large partition coefficients titrated much more slowly than those with low coefficients. Each amine titration was

duplicated and the two values were averaged to calculate the final concentration. An Exax 50 ml. buret was employed for all the titrations.

Solutions for the hydration study were prepared by measuring 150 ml. of solvent into each isopiestic cell. The volume of amine required to prepare the desired concentration was then pipetted into the cell with a 10 ml. graduated pipette. Fifty ml. of calcium chloride solution was then introduced into each cell in a 100 ml. beaker. The cell was sealed and placed in the constant temperature bath. Distribution samples were prepared by measuring 150 ml. of solvent into each 500 ml. flask. The amine was added, followed by 50 ml. of distilled water. The flasks were stoppered and shaken for 1 minute before placing them in the constant temperature bath.

The solutions for the dielectric experiment were prepared in a slightly different manner. The cells contained only amine and benzene and the 100 ml. beakers contained 20 g. of indicating Drierite to insure dryness in the cells. Benzene, stored over molecular sieve (4A) was allowed to flow directly into the cells from the column. This procedure prevented the solvent from being exposed to atmospheric moisture. The required volume of amine was introduced and the cells sealed and placed in the bath. The ternary systems (amine-water-benzene) were prepared in 500 ml. Erlenmeyer flasks described previously in this chapter. All hydrations were carried out at unit water activity.

Both sulfuric acid and calcium chloride solutions were employed as constant water activity sources in order to prepare solutions of water in benzene for the determination of the dipole moment of the water monomer. The calcium chloride solutions were distributed directly with

benzene and the acid solutions were employed in the isopiestic cells (vapor phase equilibration).

The dielectric constants were determined with the DM01 Dipolmeter distributed by Kahl Scientific Instrument Corp. A measuring sensitivity of  $\Delta\epsilon/\epsilon = 4 \times 10^{-5}$  can be attained with this instrument. The corresponding accuracy, is on the other hand, dependent on how exactly the dielectric constants of the calibration liquids are known. The instrument operates on the superposition (beat) method at approximately 2.0 megacycles. A Sola constant voltage transformer was used to maintain a stable current source. A DFL-1 cell (range 1.8 to 3.4 dielectric constant), also from Kahl Scientific Instrument Corp., was used for all measurements. The measuring volume of the cell was 20 ml. and it was plated with 5 g. of gold. The cell had a threaded cover equipped with a 10/30 ground glass joint. All measurements were made with the threaded cover in place and the inserted lid removed. The cell was provided with a thermostatic jacket for maintaining the solution temperature at a constant value. The cell was kept at  $25.00 \pm 0.02^{\circ}$  with a Haake Constant Temperature Circulator Model "F."

A 50 ml. Multifit syringe with a 12 inch tip was used for introducing the amine solutions into the cell. The tip of the syringe was inserted to the bottom of the cell so that during the time required to introduce a sample very little air entered the cell. A small bubble of trapped air in the cell can lead to erroneous results; consequently great care was taken to force all the air out of the cell by displacing it from the cell with solution. The transferral of the solutions to the dipole cell required approximately 1 minute, so that very little temperature change occurred in the solution.

The DFL-1 cell was calibrated with cyclohexane, benzene, and butylether at 25<sup>0</sup>. The values for the dielectric constants of these three liquids were the best that could be found in the literature. The following table shows the dielectric constant at 20<sup>0</sup> and the temperature coefficient of the three compounds.

DIELECTRIC PROPERTIES OF CALIBRATING LIQUIDS

Calibrating liquid	$\epsilon(20^0)^a$	$\Delta\epsilon/\Delta T$	Research worker
Cyclohexane	2.0230	$-1.6 \times 10^{-3}$	K. Rosswog <sup>61</sup>
Benzene	2.2832	$-1.96 \times 10^{-3}$	Mecke and Rosswog <sup>62</sup>
Butylether	3.0921	$-7.09 \times 10^{-3}$	Mecke and Specht <sup>63</sup>

<sup>a</sup>These values are from R. Mecke and H. Sprecht, Zeitschr. Elektrochemie, 66, 255 (1962).

The values at 20<sup>0</sup> were used in conjunction with the reported temperature coefficients to calculate the dielectric constants at 25<sup>0</sup>. The calculated dielectric constants used for the calibration of the DFL-1 cell were:

Cyclohexane . . .	2.0150
Benzene . . . . .	2.2734
Butylether. . . . .	3.0566

The procedure for calibration was similar to the method described by Oehme and Wirth.<sup>64</sup> The cell was cleaned and installed on the DM01. It was rinsed with anhydrous ether obtained from Mallinckrodt Chemical Works. After draining the ether, the cell was flushed with "dry" nitrogen until a constant "dry cell" reading was obtained. This procedure was carried out after each addition to the cell. Table II shows the results for the calibration of the DFL-1 cell at 25<sup>0</sup>. The dielectric constants

Table II

Calibration of the DFL-1 Dipole Cell at 25°

---

Calibrating liquid	$\epsilon$	$\Delta\epsilon$	S (scale reading)	$\Delta S$	$\Delta\epsilon/\Delta S \times 10^4$
Cyclohexane	2.0150		4.67.6		4.239
		0.2584		609.5	
Benzene	2.2734		1077.1		4.279
		0.7832		1830.1	
n-Butylether	3.0566		2907.2		4.269
		1.0416		2439.6	

AVERAGE  $\Delta\epsilon/\Delta S = 4.262 \times 10^{-4}$

---

of the solutions were determined by multiplying the average slope ( $\Delta\epsilon/\Delta S$ ) times the difference in scale readings between pure benzene and the benzene solutions. This value was added to the dielectric constant of pure benzene (2.2734) to determine the dielectric constant of the solutions.

## CHAPTER IV

### RESULTS AND INTERPRETATION OF DATA

#### Hydration of Amines

Water solubility and partition data have been used previously to determine hydration and self-association constants of phenol<sup>48</sup> and several ketones.<sup>49,65</sup> The individual solute species present in solutions studied by these methods are assumed to obey Henry's law. This assumption appears to be valid for the amines used in this investigation at concentrations of 0.5 M or less. Any deviation from ideality exhibited by the amine solutions has been attributed to hydrate formation. The hydrate was also assumed to obey Henry's law. The experimentally determined quantities in this study were the formal concentrations of amine ( $f_A$ ) and water ( $f_W$ ), along with the water activity of calcium chloride solutions ( $a_W$ ).

Assuming the simplest hydrate species (1:1) as the only complex formed in solution, the formal concentrations of amine and water may be expressed as

$$f_A = C_A + C_{AW} \quad (1)$$

and

$$f_W = C_W + C_{AW} \quad (2)$$

where  $C_A$  and  $C_W$  are the monomer concentrations of amine and water,



respectively.  $C_{AW}$  is the amine monomer monohydrate concentration. The hydrate is formed from the monomers according to the reaction  $A + W = AW$ , which is governed by the equilibrium constant

$$K_{AW} = \frac{C_{AW}}{C_A C_W} \quad (3)$$

Subtraction of  $C_W$  from both sides of equation (2) yields a quantity ( $\Delta f_W$ ) which corresponds to the additional amount of water dissolved in the solvent due to the presence of the amine solute. In the case of simple 1:1 hydrate formation  $\Delta f_W$  is equal to  $C_{AW}$ .

$$\Delta f_W = f_W - C_W = C_{AW} \quad (4)$$

From equation (1),  $C_A = f_A - C_{AW}$  and substitution for  $C_{AW}$  from equation (3) gives

$$C_A = f_A - K_{AW} C_A C_W \quad (5)$$

Combining equations (3) and (4) it can be seen that

$$\Delta f_W = K_{AW} C_A C_W \quad (6)$$

If the water present obeys Henry's law, the monomer concentration may be expressed as

$$C_W = C_W^0 a_W \quad (7)$$

where  $C_W^0$  is a reciprocal Henry's law constant corresponding to the solubility of water at unit water activity.

In order to interpret these data correctly, the molecular complexity of water in each solvent must be known. It has been shown that water dissolves primarily as monomeric units in each of the three solvents used in this study.<sup>59</sup>  $C_W^0$  is, therefore, the solubility of the water monomer in each organic solvent at saturation.

Combining equations (6) and (7),

$$\Delta f_W = K_{AW} C_A C_W^0 a_W$$

or

$$\Delta f_W = K'_{AW} C_A a_W, \text{ where } K'_{AW} = K_{AW} C_W^0 \quad (9)$$

From equations (5) and (6),

$$C_A = f_A - \Delta f_W.$$

Substitution for  $C_A$  in equation (8) yields

$$\Delta f_W = K_{AW}' (f_A - \Delta f_W) a_W \quad (10)$$

from which the hydration constant may be determined by plotting  $\Delta f_W$  vs.  $a_W(f_A - \Delta f_W)$ . The slope is equal to  $K'_{AW}$  and the true hydration constant,  $K_{AW}$ , is calculated from equation (9).

Plots of this type are extremely sensitive and provide an excellent method for the determination of the equilibrium constant and testing the functional relation predicted by the above analysis. For example, if species are present which are composed of more than one amine molecule a non-linear curve results, while species composed of more than one water molecule cause the lines representing the various water activities to separate.

Several water activities were employed in the hydration studies of the cyclohexylamines at 25°. Unit water activity data are not sufficient to determine whether or not species whose concentrations depend on the water activity to some power higher than unity are present. Once it had been determined that the 1:1 hydrate was the only complex species in solution, the need for employing several water activities vanished and, consequently, only one water activity (other than unity) was used

for the 35° work. Similarly, only two different water activities were employed in the triethylamine studies.

The partition data indicated that little or no amine self-association occurred. The solubility of benzene and the amines in water was low enough so that it could be assumed that the water was at unit activity. The distribution ratios ( $K_D$ ), as well as the amine concentration ranges for most of the systems studied are presented in Table III.  $K_D$  is defined as the ratio of the amine concentration in the organic phase to the concentration in the water phase.  $K_D$  was found to be virtually independent of concentration at constant temperature for each system. Since no polymerization of the amines was found, the distribution data were interpreted in the same manner as the water solubility data. The distribution constants reported in Table III are "bulk" distribution constants in that they represent the total amine concentration present in each phase. The constants reported in Chapter V differ from these constants in that they are corrected for hydrate formation in the organic phase and ionization in the water phase. Based on the constancy of the  $K_D$  values, within experimental error, it has been concluded that the amine monomer and amine monohydrate are the principal amine species present in the organic phase.

Tables IV and V show the data for the  $\text{CHA-H}_2\text{O-C}_6\text{H}_6$  system at 25 and 35°. Tables VI and VII present the water solubility data for the  $\text{NMCHA-H}_2\text{O-C}_6\text{H}_6$  system at 25 and 35°. Data for the  $\text{DMCHA-H}_2\text{O-C}_6\text{H}_6$  system are given in Tables VIII and IX. The partition and water solubility data for the triethylamine- $\text{H}_2\text{O}$  system in benzene, toluene, and cyclohexane are presented in Tables X, XI, and XII, respectively.

Table III

Distribution Constants for Amines at 25°

---

Amine	Solvent	Temp. °C	Concn. range M	K <sub>D</sub>
CHA	Benzene	25	0.067-0.149	4.18±0.15
CHA	Benzene	35	0.039-0.187	5.50±0.16
NMCHA	Benzene	25	0.040-0.131	11.35±0.82
DMCHA	Benzene	25	0.040-0.138	42.48±0.76
Triethylamine	Benzene	25	0.044-0.467	14.20±0.38
Triethylamine	Toluene	25	0.048-0.484	11.64±0.25

---

Table IV

Change in Water Solubility with Changes in Water Activity  
and Concentration of CHA at 25<sup>o</sup>

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0847	0.327	0.0038	0.0062
	0.440	0.0066	0.0081
	0.559	0.0087	0.0100
	0.712	0.0117	0.0122
	0.851	0.0133	0.0143
0.1102	0.327	0.0062	0.0080
	0.440	0.0094	0.0103
	0.559	0.0136	0.0127
	0.712	0.0163	0.0157
0.1491	0.327	0.0082	0.0094
	0.440	0.0114	0.0142
	0.559	0.0152	0.0175
	0.712	0.0187	0.0218
	0.851	0.0233	0.0252
0.0670	0.327	0.0059	0.0047
	0.440	0.0046	0.0058
	0.712	0.0086	0.0079
	0.851	0.0114	0.0087

Table IV (Continued)

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0469	1.000	0.0085	0.0090
0.0668		0.0133	0.0140
0.0872		0.0169	0.0165
0.1351		0.0265	0.0256
0.1752		0.0349	0.0331
0.0535		0.0102	0.0102
0.0792		0.0154	0.0150
0.1077		0.0210	0.0204
0.1590		0.0314	0.0300
0.1961		0.0402	0.0367

---

Table V

Change in Water Solubility with Changes in Water Activity  
and Concentration of CHA at 35<sup>o</sup>

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0390	1.00	0.0072	0.0076
0.0501		0.0086	0.0099
0.0565		0.0117	0.0107
0.0640		0.0126	0.0123
0.0729		0.0146	0.0139
0.0837		0.0167	0.0160
0.0944		0.0179	0.0183
0.1076		0.0194	0.0211
0.1086		0.0230	0.0204
0.0540	0.680	0.0071	0.0076
0.0843		0.0122	0.0117
0.1087		0.0146	0.0153
0.1351		0.0183	0.0190
0.1867		0.0258	0.0261

---

Table VI

Change in Water Solubility with Changes in Water Activity  
and NMCHA Concentration at 25<sup>o</sup>

$f_A$ , (M)	$a_W$	$\Delta f_W$ , (M)	$\Delta f_W$ (calcd), (M)
0.0405	1.00	0.0056	0.0064
0.0581		0.0086	0.0091
0.0820		0.0125	0.0128
0.1009		0.0160	0.0157
0.1147		0.0181	0.0178
0.1315		0.0209	0.0204
0.0383	0.580	0.0035	0.0037
0.0694		0.0064	0.0067
0.0946		0.0087	0.0092
0.1406		0.0127	0.0137
0.1554		0.0143	0.0151
0.0383	0.755	0.0043	0.0047
0.0694		0.0078	0.0086
0.0946		0.0111	0.0116
0.1406		0.0172	0.0172
0.1554		0.0189	0.0190
0.0383	0.909	0.0055	0.0055
0.0694		0.0100	0.0100



Table VI (Continued)

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0946		0.0142	0.0142
0.1406		0.0213	0.0200
0.1554		0.0233	0.0222
0.0405	1.00	0.0056	0.0064
0.0581		0.0086	0.0091
0.0820		0.0125	0.0128
0.1009		0.0160	0.0157
0.1147		0.0181	0.0178
0.1315		0.0209	0.0204

---

Table VII

Change in Water Solubility with Changes in Water Activity  
and NMCHA Concentration at 35<sup>o</sup>

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0418	0.680	0.0046	0.0050
0.0597		0.0066	0.0072
0.0809		0.0089	0.0097
0.0988		0.0111	0.0119
0.1150		0.0131	0.0138
0.1405		0.0167	0.0168
0.0420	1.00	0.0067	0.0070
0.0612		0.0097	0.0102
0.0782		0.0128	0.0130
0.1016		0.0175	0.0167
0.1237		0.0208	0.0205
0.1334		0.0232	0.0200

---

Table VIII

Change in Water Solubility with Changes in Water Activity  
and DMCHA Concentration at 25<sup>o</sup>

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W (\text{calcd}), (M)$
0.0421	0.580	0.0026	0.0031
0.0711		0.0042	0.0052
0.1012		0.0064	0.0074
0.1327		0.0086	0.0097
0.1580		0.0101	0.0115
0.0416	0.680	0.0032	0.0035
0.0711		0.0055	0.0060
0.1040		0.0074	0.0088
0.1373		0.0108	0.0116
0.1646		0.0194	0.0196
0.0421	0.702	0.0028	0.0037
0.0711		0.0054	0.0062
0.1012		0.0076	0.0088
0.1327		0.0106	0.0115
0.1580		0.0126	0.0137
0.0416	0.830	0.0040	0.0042
0.0711		0.0077	0.0071
0.1040		0.0095	0.0106

Table VIII (Continued)

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W (calcd), (M)$
0.1373		0.0137	0.0138
0.0421	0.929	0.0043	0.0047
0.0711		0.0073	0.0081
0.1012		0.0106	0.0113
0.1327		0.0147	0.0148
0.1580		0.0180	0.0176
0.0416	0.935	0.0051	0.0046
0.0711		0.0082	0.0079
0.1040		0.0115	0.0117
0.1373		0.0155	0.0153
0.0379	1.00	0.0051	0.0048
0.0400		0.0055	0.0046
0.0405		0.0055	0.0044
0.0594		0.0074	0.0071
0.0600		0.0082	0.0069
0.0790		0.0102	0.0093
0.0967		0.0126	0.0117
0.0996		0.0133	0.0112
0.1098		0.0151	0.0128
0.1176		0.0153	0.0138
0.1381		0.0175	0.0162

---

Table IX

Change in Water Solubility with Changes in Water Activity  
and DMCHA Concentration at 35°

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0396	0.680	0.0030	0.0033
0.0682		0.0048	0.0057
0.0814		0.0067	0.0076
0.1028		0.0088	0.0084
0.1216		0.0102	0.0102
0.1413		0.0112	0.0117
0.0451	1.00	0.0049	0.0053
0.0688		0.0082	0.0080
0.0836		0.0099	0.0097
0.1068		0.0126	0.0124
0.1283		0.0156	0.0149

---

Table X

Change in Water Solubility with Changes in Water Activity  
and Triethylamine Concentration in Benzene at 25<sup>o</sup>

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0442	1.00	0.0046	0.0048
0.0966		0.0100	0.0105
0.1343		0.0147	0.0145
0.1736		0.0198	0.0198
0.2256		0.0250	0.0240
0.2656		0.0290	0.0287
0.3064		0.0339	0.0330
0.3545		0.0386	0.0383
0.3898		0.0426	0.0433
0.4655		0.0528	0.0501
0.0922	0.680	0.0051	0.0072
0.1838		0.0132	0.0141
0.2563		0.0179	0.0193
0.3493		0.0261	0.0267
0.4670		0.0330	0.0358

---

Table XI

Change in Water Solubility with Changes in Water Activity  
and Triethylamine Concentration in Toluene at 25°

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0479	1.00	0.0044	0.0043
0.0922		0.0077	0.0084
0.1854		0.0168	0.0167
0.1835		0.0164	0.0166
0.2202		0.0200	0.0199
0.2808		0.0257	0.0254
0.3193		0.0290	0.0288
0.3547		0.0323	0.0321
0.3980		0.0365	0.0359
0.4429		0.0417	0.0399
0.0908	0.680	0.0056	0.0057
0.1748		0.0104	0.0111
0.2762		0.0168	0.0175
0.3606		0.0210	0.0229
0.4841		0.0295	0.0307

---

Table XII

Change in Water Solubility with Changes in Water Activity and  
Triethylamine Concentration in Cyclohexane at 25<sup>o</sup>

---

$f_A, (M)$	$a_W$	$\Delta f_W, (M)$	$\Delta f_W(\text{calcd}), (M)$
0.0426	1.00	0.00087	0.00087
0.0937		0.00188	0.00191
0.1335		0.00263	0.00272
0.1738		0.00321	0.00355
0.2207		0.00398	0.00451
0.2616		0.00492	0.00536
0.3069		0.00587	0.00626
0.3507		0.00685	0.00715
0.3801		0.00791	0.00774
0.4152		0.00850	0.00846
0.1880	0.830	0.00304	0.00319
0.2828		0.00503	0.00480
0.3637		0.00657	0.00621
0.5385		0.00987	0.00913

---



Figures II and III show the data for the two cyclohexylamine systems at 25 and 35°. The slopes of these plots were determined to be 0.2359 and 0.2391, respectively. In order to determine the hydration constants ( $K_{AW}$ ), the values of the slopes were divided by  $C_W^0$  (0.0350 M for systems at 25°; 0.0465 M for systems at 35°). The 1:1 equilibrium constants were found to be 6.74 M<sup>-1</sup> at 25° and 5.14 M<sup>-1</sup> at 35°. Figures IV and V exhibit the data taken for the NMCHA systems. From slopes of 0.1849 and 0.1995, the  $K_{AW}$  values were determined to be 5.28 M<sup>-1</sup> and 4.29 M<sup>-1</sup> at 25 and 35°, respectively. These constants are lower than those found for the primary amine, possibly indicating that the N-methyl group sterically hinders the formation of the hydrate to a slight extent. The corresponding plots for the DMCHA systems are displayed in Figures VI and VII. The slopes were found to be 0.1348 and 0.1320 yielding  $K_{AW}$  values of 3.85 M<sup>-1</sup> at 25° and 2.82 M<sup>-1</sup> at 35°. The equilibrium constants for the tertiary amine are somewhat decreased due partly, perhaps, to its slightly lower basicity. However, from the  $\Delta S$  value for the DMCHA-H<sub>2</sub>O complex reported in Table XIV, it is apparent that the N-methyl substituents offer considerable steric hindrance to the formation of the hydrate. Whetsel and Lady<sup>34</sup> have reported that the  $\Delta H$  of formation of amine-substituted aniline complexes is larger for tertiary amines than for primary and secondary amines. They also note that  $\Delta S$  becomes considerably more negative for complexes involving tertiary amines than for complexes of primary and secondary amines. The following table lists thermodynamic data compiled by Whetsel and Lady for amine complexes involving two of the amines involved in the present study.

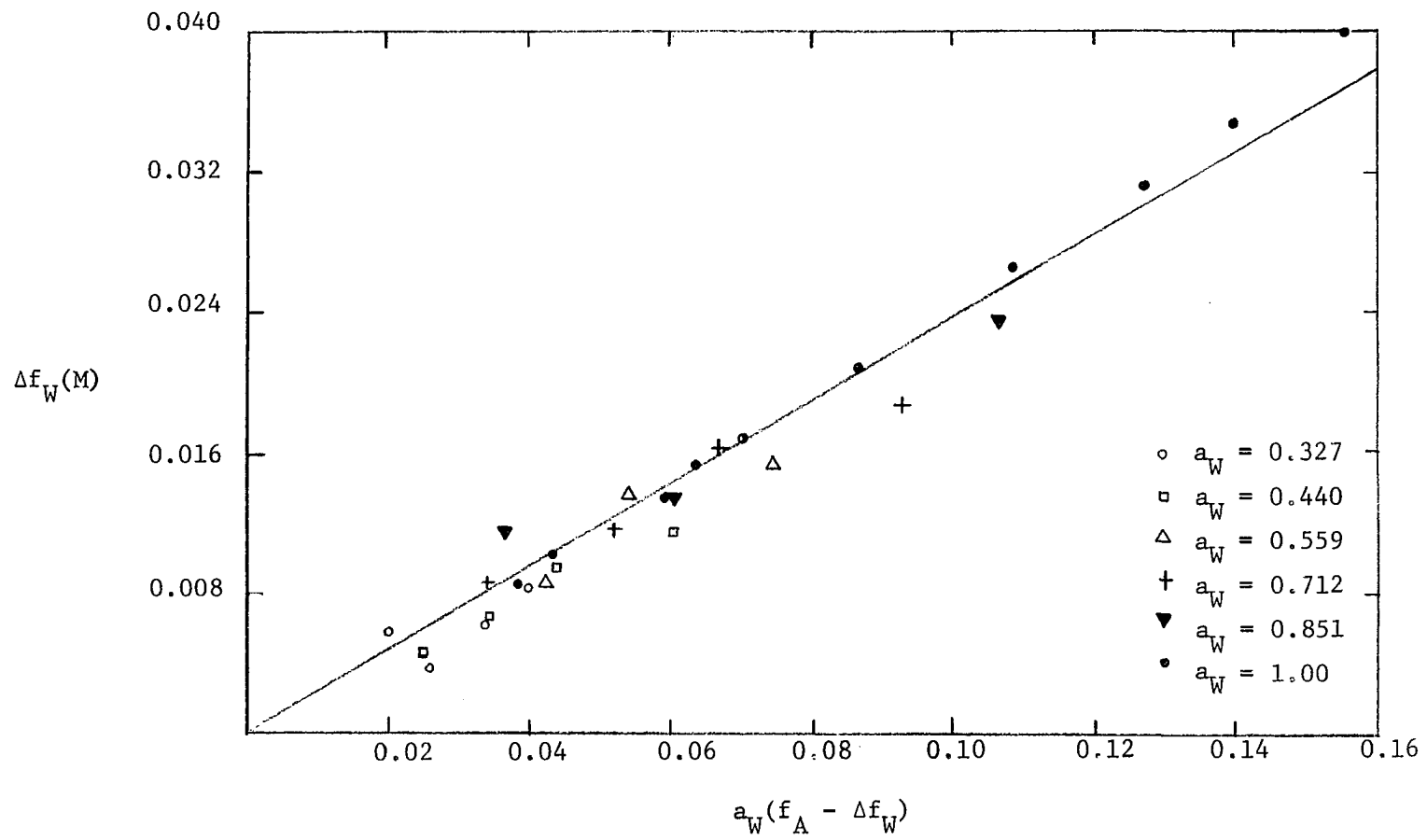


Figure II. Water Solubility Data for CHA-Benzene Solutions at 25°.

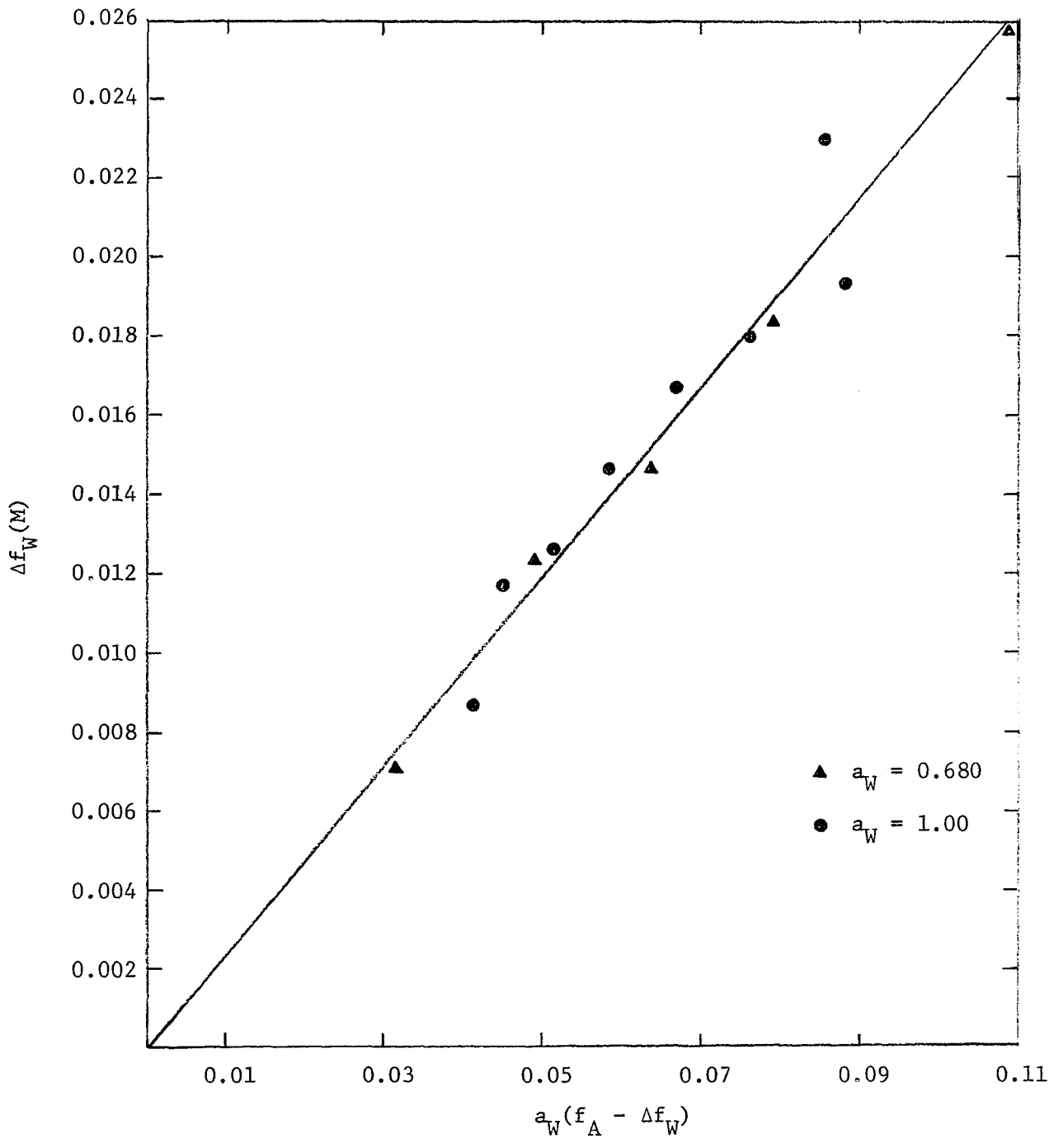


Figure III. Water Solubility Data for CHA-Benzene Solutions at 35°.

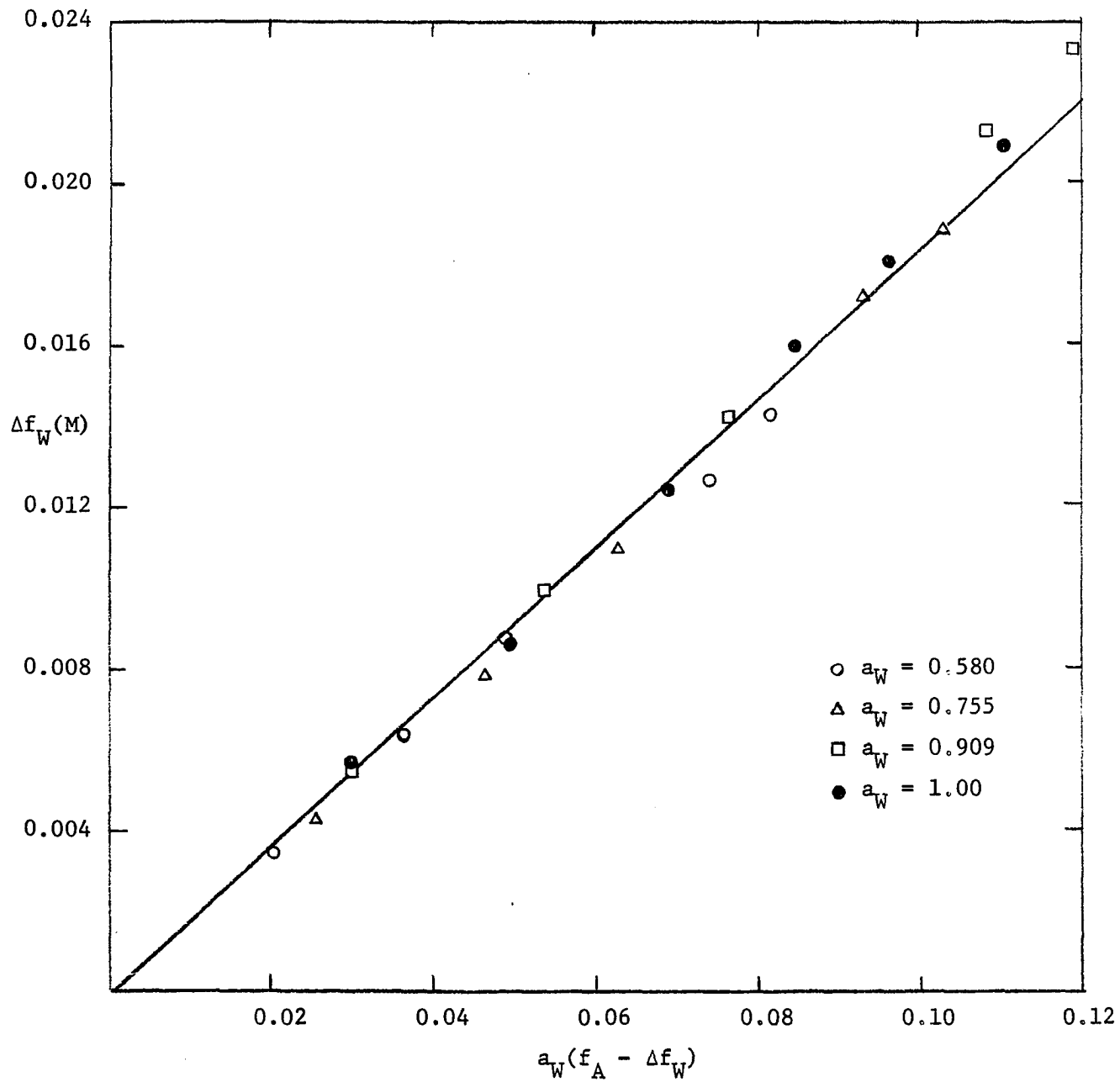


Figure IV. Water Solubility Data for NMCHA-Benzene Solutions at 25°.

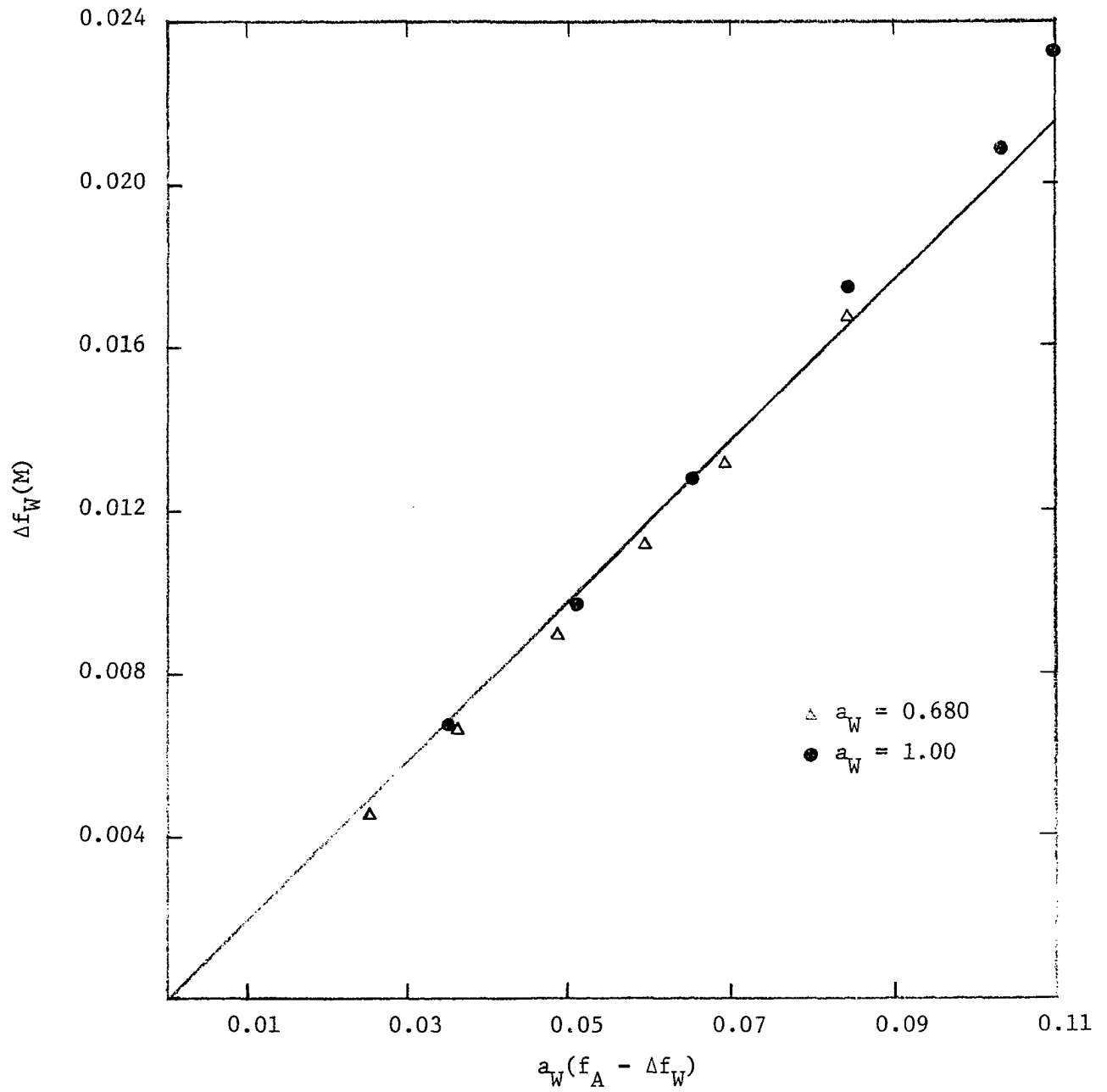


Figure V. Water Solubility Data for NMCHA-Benzene Solutions at 35°.

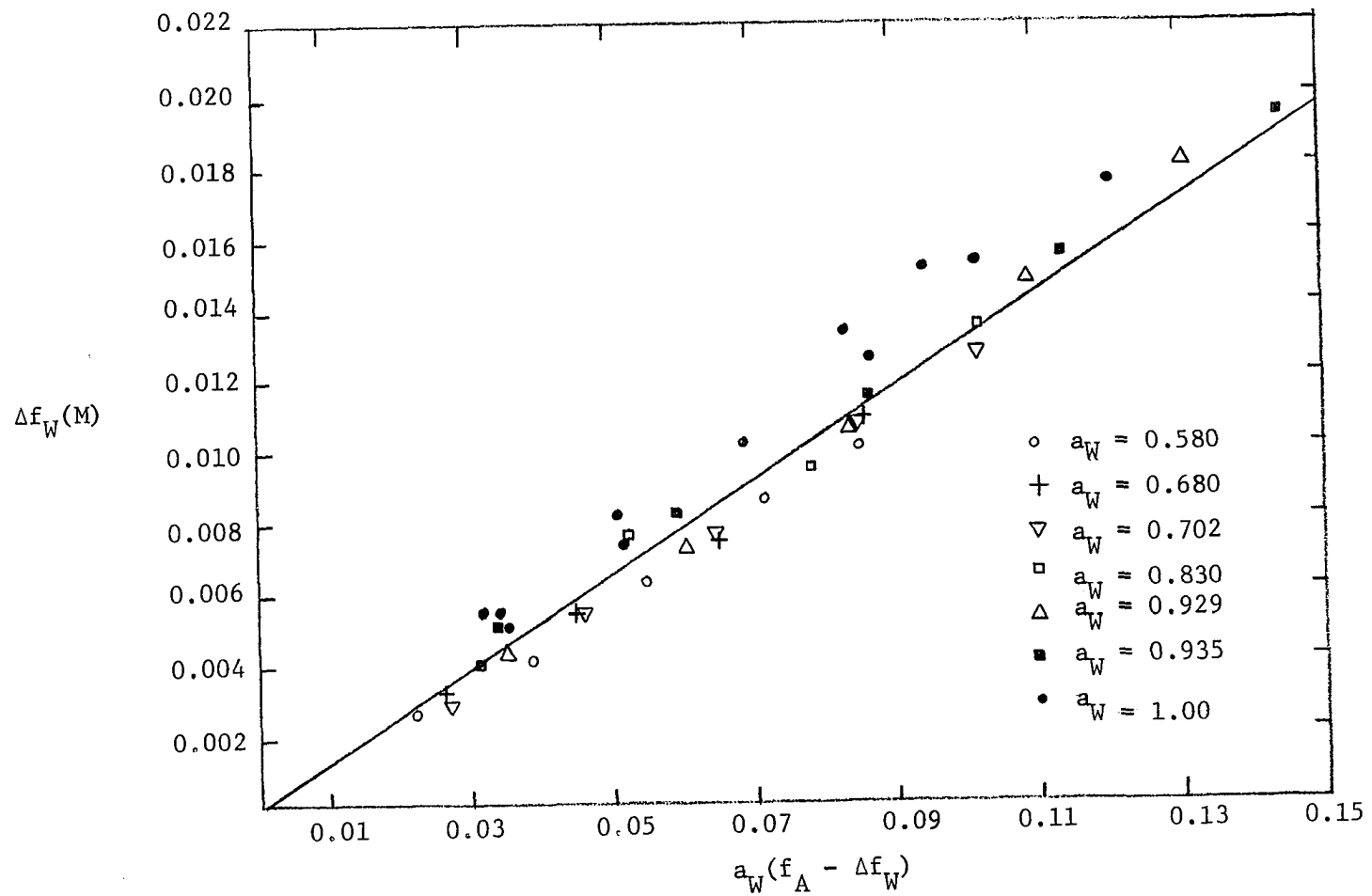


Figure VI. Water Solubility Data for DMCHA-Benzene Solutions at 25°.

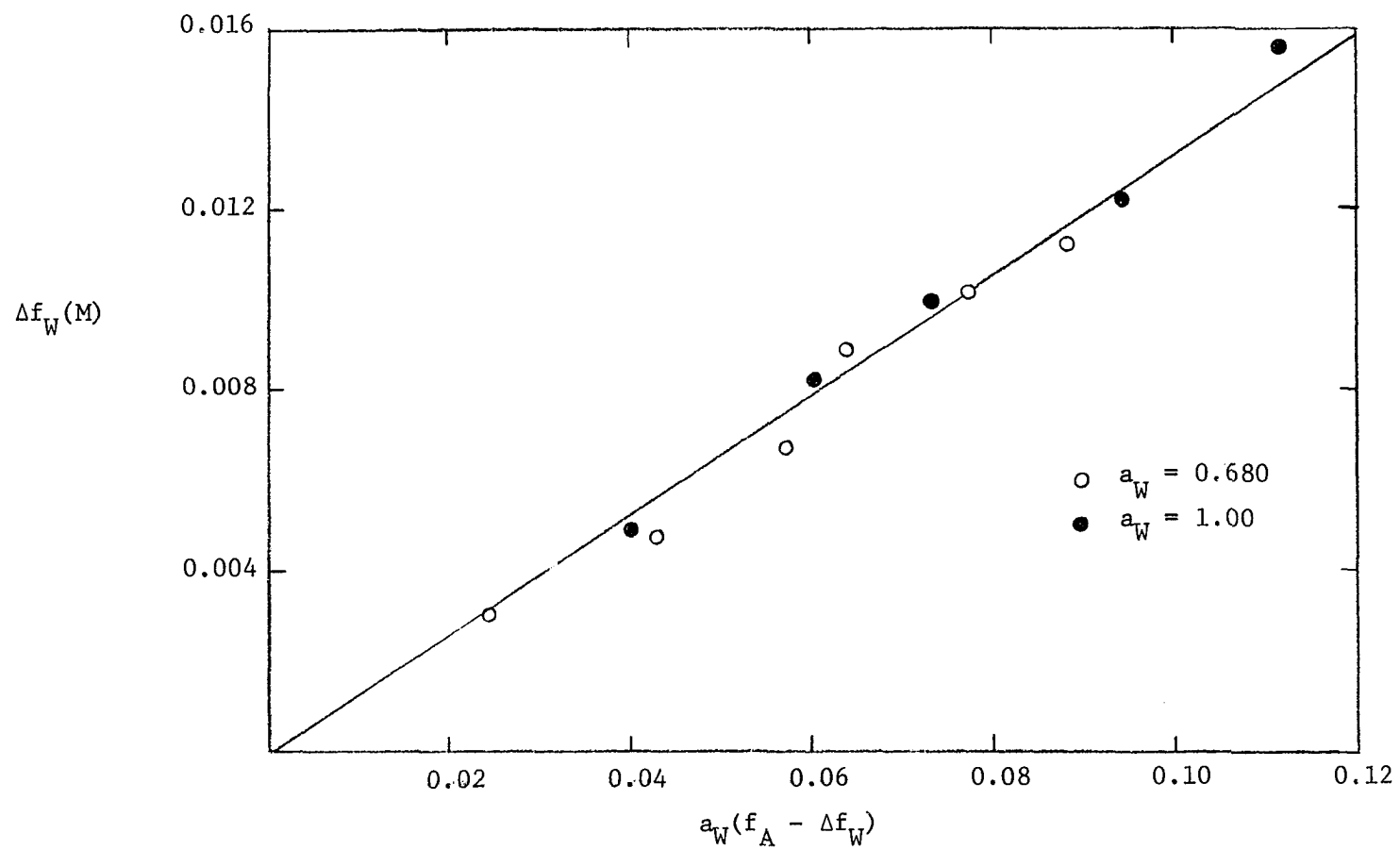


Figure VII. Water Solubility Data for DMCHA-Benzene Solutions at 35°.

## THERMODYNAMIC CONSTANTS FOR DMCHA AND CHA COMPLEXES

Complex	$K_{11} (M^{-1})$ at 25°	$\Delta H^{\circ}$ (kcal/mole)	$\Delta S^{\circ}$ (e.u.) at 25°	Ref.
N-methylaniline-DMCHA	0.57	-3.76	-13.7	34
Aniline-DMCHA	0.69	-3.35	-12.0	34
Chloroform-CHA	1.10	-3.6	-11.9	36

Figures VIII, IX, and X show the hydration data for triethylamine in benzene, toluene, and cyclohexane, respectively at 25°. These systems were studied at higher amine concentrations in order to determine if a 2:1 complex involving two amine molecules and one water molecule could be detected. As the figures indicate, only one parameter,  $K_{AW}$ , was required to fit the data sufficiently well over the entire concentration range. This is in agreement with the work of Affsprung, Derkosch, and Kohler,<sup>46</sup> who found that triethylamine forms only the 1:1 hydrate over a large concentration range.

The slopes of the graphs are 0.1214 for the benzene system, 0.09946 for the toluene system, and 0.02082 for the cyclohexane system. An equilibrium constant of  $3.47 M^{-1}$  was determined for the triethylamine-water complex in benzene. The resulting  $K_{AW}$  values for the toluene and cyclohexane systems are  $3.72 M^{-1}$  and  $7.01 M^{-1}$ , respectively. The  $K_{AW}$ 's for the benzene and toluene systems are approximately equal with the constant being only slightly larger in toluene. This is indicative of the slightly lower solvating power of toluene. The  $K_{AW}$  reported for the cyclohexane system, however, is twice as large as for the other solvents. Cyclohexane solvates the solute molecules (amine and water) to a lesser extent, leaving the reactive sites in each of these molecules more available for complex formation. Cyclohexane is similar in solvent properties to carbon tetrachloride, although somewhat less reactive.<sup>66</sup> Solvation effects are



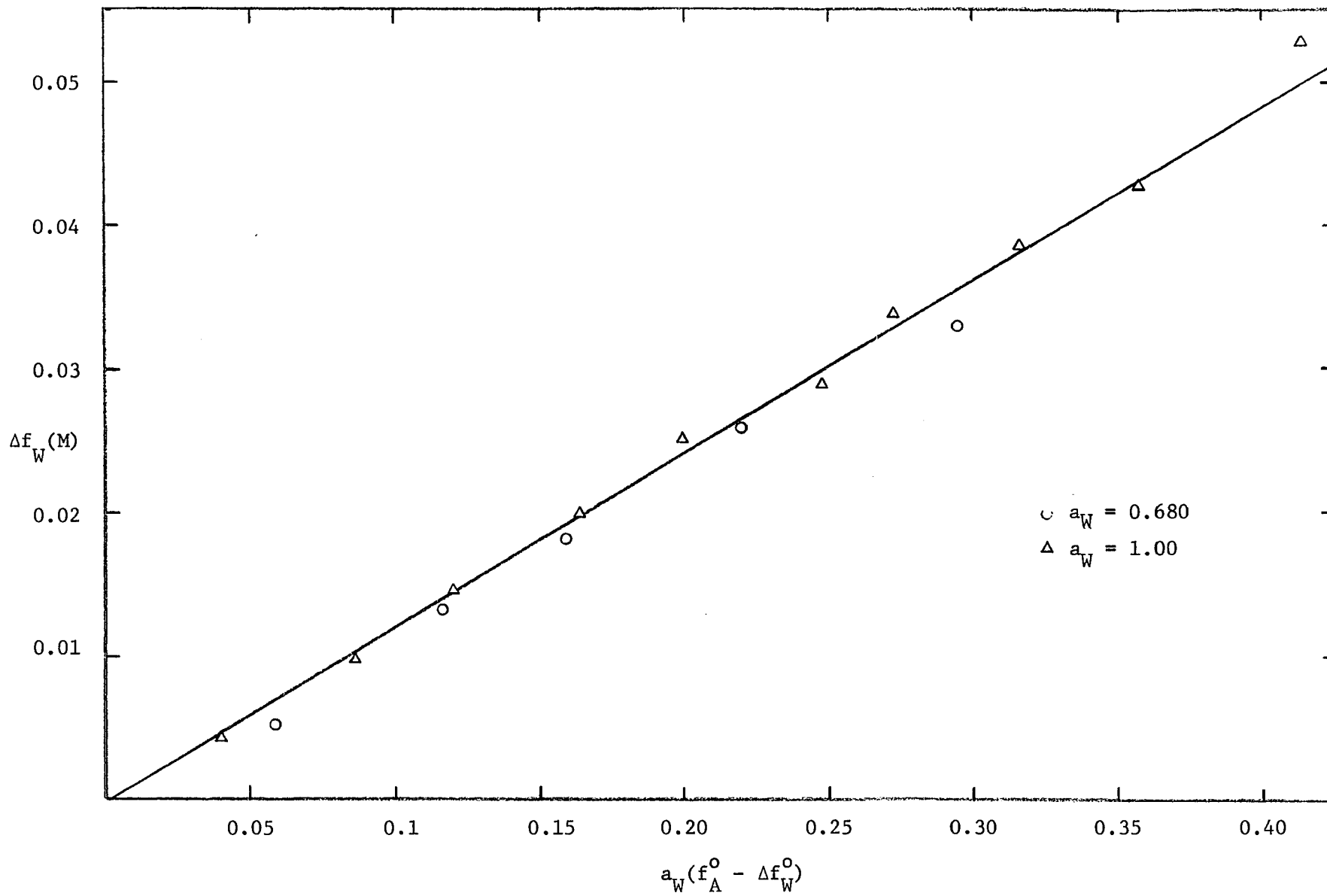


Figure VIII. Water Solubility Data for Triethylamine-Benzene Solutions at 25°.

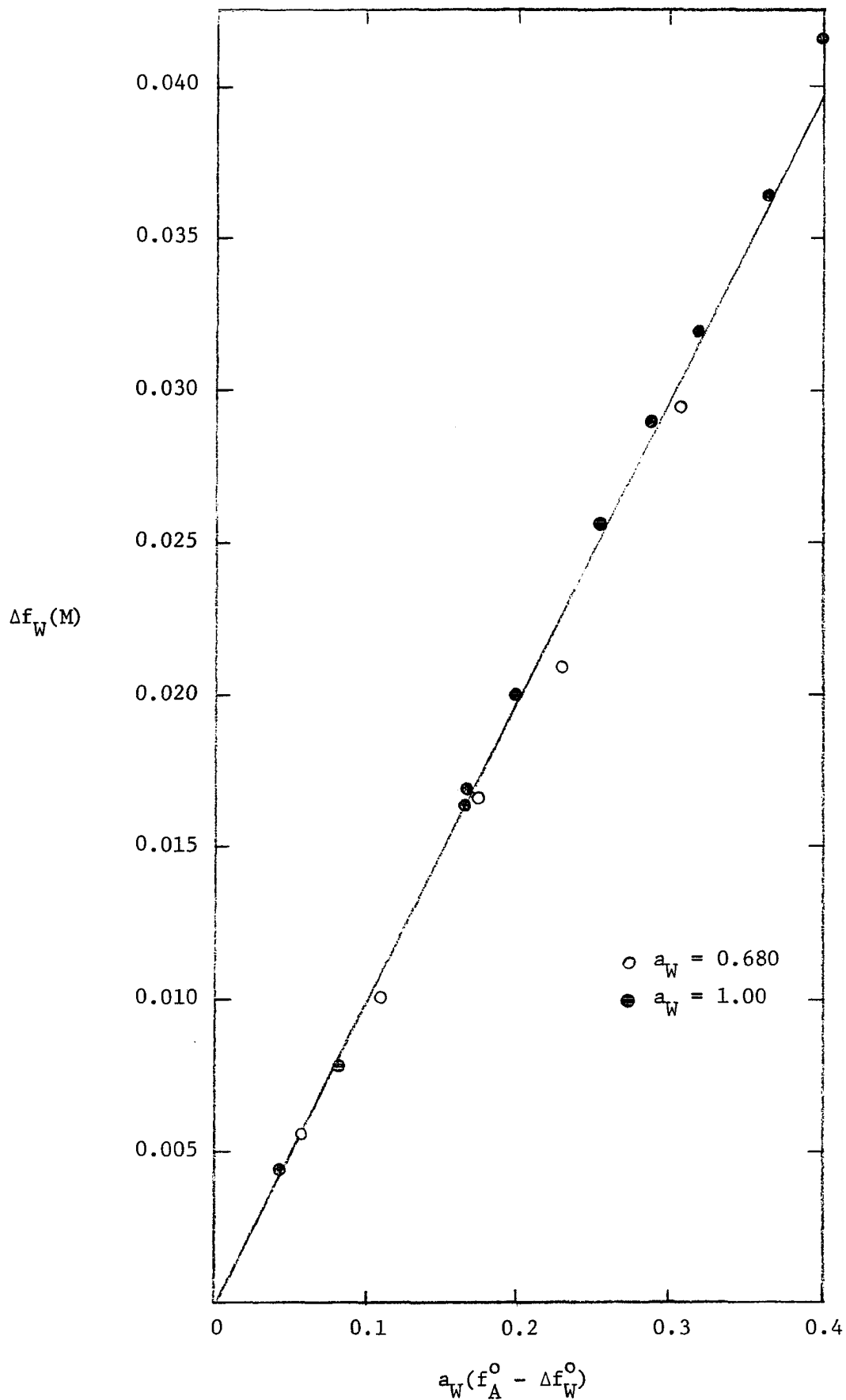


Figure IX. Water Solubility Data for Triethylamine-Toluene Solutions at 25°.

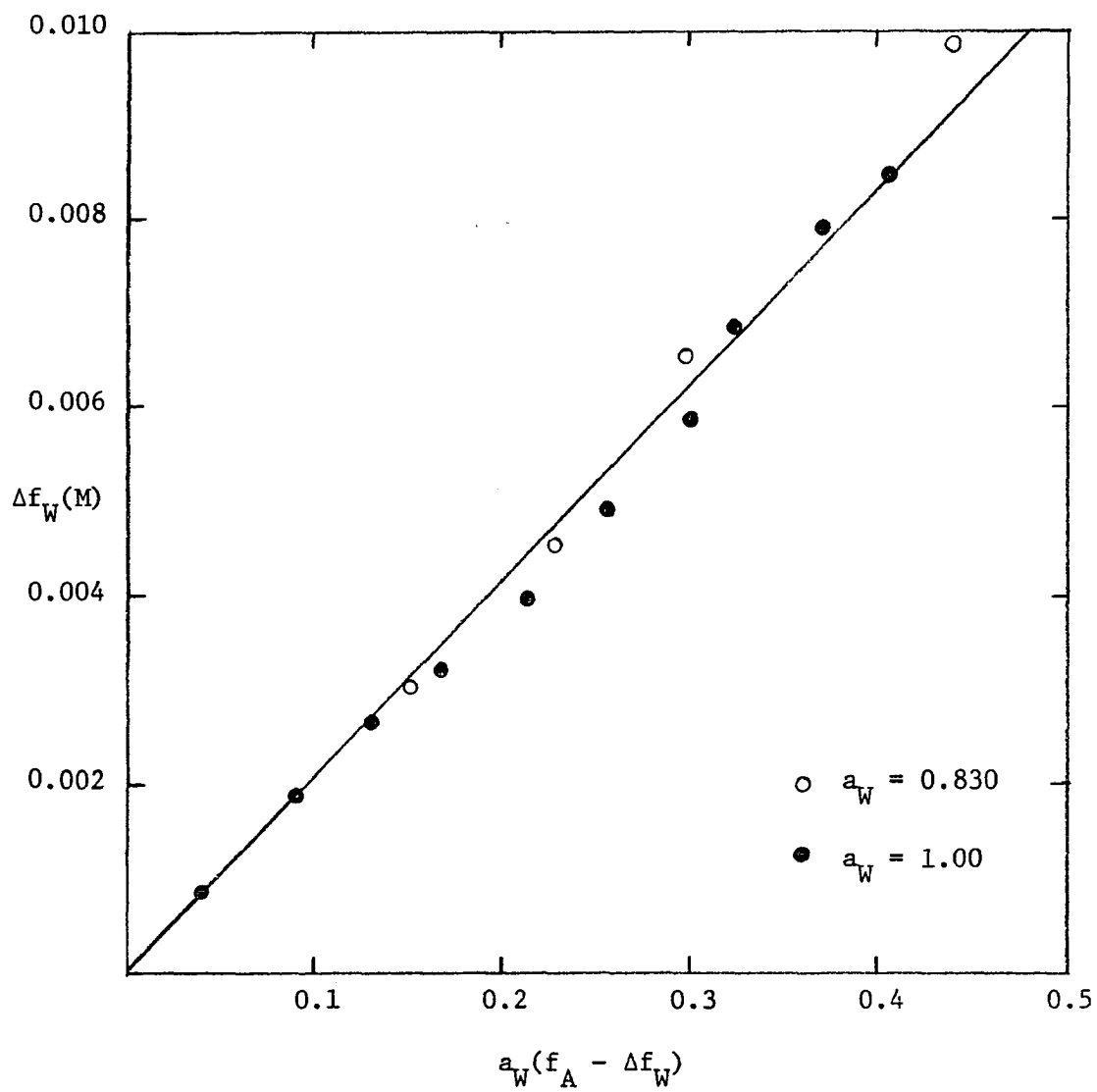


Figure X. Water Solubility Data for Triethylamine-Cyclohexane Solutions at 25°.

discussed in more detail in Chapter V. Carbon tetrachloride was not employed as a solvent in these studies because of a reaction between the amines and this solvent as previously observed.<sup>67,68,69</sup>

A non-linear least squares method was used to obtain the best values of  $K_{AW}$  consistent with equations (1), (6), and (7). It was assumed that all the experimental error resides in the  $\Delta f_W$  values since the water titrations are less accurate than the acid-base titrations. The calculated values of the increase in water solubility,  $\Delta f_W(\text{calcd})$ , appearing in the tables were obtained from the least squares treatment as were the solid lines appearing in all the figures. The points are experimental while the lines are calculated consistent with the assumption of 1:1 hydrate formation. The errors for the  $K_{AW}$  values were determined using the method for a one parameter system described by Christian.<sup>70</sup> It is observed that the single parameter  $K_{AW}$  provides an adequate fit of the data for each system. However, in view of the conclusions of Mohr, Wilk, and Barrow<sup>12</sup> and of previous investigations in this laboratory<sup>71</sup> that organic bases tend to form the dimer monohydrate at higher base concentrations, the data were also fitted assuming the presence of both the monomer monohydrate and the dimer monohydrate. This necessitated the incorporation of the additional terms  $K_{A_2W} C_A^2 C_W$  in equation (6) and  $2K_{A_2W} C_A^2 C_W$  in equation (5). Table XIII lists the values determined for the equilibrium constants along with their standard errors obtained using both the one-parameter and two-parameter non-linear least squares fitting methods. In most of the systems, the uncertainty in  $K_{A_2W}$  is at least as large as the best value of the constant and  $K_{AW}$  is not much affected by the inclusion of the second hydrate constant. It should be

Table XIII

## Hydration Constants of Amines

Amine	Temp. °C	$K_{AW}$ (assuming only 1:1 species)	$K_{AW}$ (assuming 1:1 and 2:1 species)	$K_{A_2W}$
CHA-C <sub>6</sub> H <sub>6</sub>	25	6.74±0.15	6.58±0.84	0.99±9.33
CHA-C <sub>6</sub> H <sub>6</sub>	35	5.14±0.13	5.38±0.30	negative
NMCHA-C <sub>6</sub> H <sub>6</sub>	25	5.28±0.08	5.12±0.185	1.88±1.98
NMCHA-C <sub>6</sub> H <sub>6</sub>	35	4.29±0.08	3.95±0.25	3.97±3.18
DMCHA-C <sub>6</sub> H <sub>6</sub>	25	3.85±0.09	3.81±0.48	1.31±4.89
DMCHA-C <sub>6</sub> H <sub>6</sub>	35	2.82±0.07	2.74±0.22	1.21±2.52
Triethylamine-C <sub>6</sub> H <sub>6</sub>	25	3.47±0.05	3.41±0.07	0.21±0.27
Triethylamine-C <sub>6</sub> H <sub>12</sub>	25	7.01±0.16	5.90±0.22	3.15±0.61
Triethylamine-C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	25	3.72±0.05	3.16±0.52	2.43±1.76

noted, however, that  $K_{A_2W}$  is positive for all of the systems but one. The magnitude of the root-mean-square deviation in  $\Delta f_W$  changes only slightly for each of the systems as the second constant is added. Although all but one of the values of  $K_{A_2W}$  are positive, it was not felt that the inclusion of this species was needed for a proper fit of the data.

Based on the one-parameter fitting method, approximate values of  $\Delta H$  and  $\Delta S$  were calculated for the formation of the 1:1 hydrates for the three cyclohexylamines in benzene. Although the temperature range over which the equilibrium constants were determined is rather small, there are many data points at each temperature, thus increasing the credibility of the thermodynamic constants. The constants and their estimated uncertainties are given in Table XIV. The standard state used in calculating  $\Delta S$  was 1 M for each solute species. The  $\Delta H$  values show no important trend, although  $\Delta H$  is somewhat larger for the tertiary amine than for the secondary and primary amines. Since  $K_{AW}$  decreases from primary to secondary to tertiary amine, the entropy effect seems to predominate over that of the enthalpy in limiting the formation of the hydrate.

The values of the hydration constants reported in Table XIII lie in the same range as the equilibrium constants reported by Zeegers-Huyskens<sup>18</sup> and Lamberts and Zeegers-Huyskens<sup>19</sup> for the formation of 1:1 complexes between aliphatic alcohols and amines in carbon tetrachloride. The  $K_{AW}$  for the triethylamine-H<sub>2</sub>O complex in cyclohexane is more than twice that reported by Zeegers-Huyskens for the 1-butanol-triethylamine complex in CCl<sub>4</sub> ( $3.17 \text{ M}^{-1}$  at 22°).

Table XIV

Thermodynamic Constants for the Cyclohexylamine Hydrates

---

Amine	$-\Delta H, (\text{kcal/mole})$	$-\Delta S, (\text{e.u.})$
CHA	$4.94 \pm 0.86$	$12.8 \pm 2.8$
NMCHA	$3.82 \pm 0.63$	$9.5 \pm 2.1$
DMCHA	$5.6 \pm 0.65$	$16.1 \pm 2.1$

---

The Dielectric Constant of Benzene Solutions of Amines and Water

The results of this study were interpreted by using a form of the Clausius-Mosotti equation suitable for treating dielectric data for dilute solutions of polar solute molecules in a non-polar solvent:

$$\epsilon = n_m^2 + 4\pi f_A ((n_m^2 + 2)\mu/3)^2 / 3kT, \quad (11)$$

where  $n_m$  is the refractive index of the pure solvent (1.5 for benzene at 25°),  $\mu$  is the dipole moment of the solute and  $f_A$  is the molar concentration of the solute. This equation was derived by Onsager<sup>72</sup> for the sake of comparison with certain approximations derived from his equation. The assumptions involved in the derivation of the equation are:

1. The inner field of Lorentz is a valid approximation of the reaction field as well as the directing field.
2. There is no volume change on mixing.
3. There is no association.
4. The difference between the dielectric constants of the solution and the pure solvent is small, i.e.,  $\epsilon_m \gg \epsilon - \epsilon_m$ .  $\epsilon$  is the dielectric constant of the solution and  $\epsilon_m$  is the dielectric constant of the pure solvent.
5. According to the derivation, the refractive indices involved correspond to the far infrared values.

All of these assumptions are reasonably valid for the dilute solution with the exception of 3. Association does occur in the dilute solution; however, if the extent of association is known, it can be accounted for, and the original equation should remain valid. A



procedure of this description was employed during the course of this study and the results indicate that this method of compensation allows one to interpret the dielectric data in a simple, straightforward manner.

The dielectric constant ( $\epsilon$ ) and solute concentration ( $f_A$ ) were found to be linearly related in all of the systems studied. According to equation (11) a plot of  $\epsilon$  vs.  $f_A$  should yield a straight line whose slope is:

$$\text{slope} = 4\pi((n_m^2 + 2)\mu/3)^2/3kT$$

or rearranging and substituting for known constants, the dipole moment of the solute is

$$\mu = \sqrt{\frac{\text{slope} (3) (1.38 \times 10^{-16} \text{ erg/deg}) (298^\circ)}{8(3.14) (6.02 \times 10^{23} / \text{mole})}} \quad (12)$$

Table XV gives the data obtained for CHA-benzene solutions. These data are shown graphically in Figure XI. The dipole moment of the CHA monomer calculated from the slope of  $0.216 \text{ M}^{-1}$  was found to be 1.33 D. This moment compares very favorably with that found by Lewis and Smyth<sup>73</sup> of 1.33 D. and 1.34 D. determined by Aroney and LeFèvre.<sup>74</sup>

Tables XVI and XVII present the dielectric data for the NMCHA and DMCHA systems. Both of these systems were found to produce the straight lines in Figures XII and XIII. From the least squares slopes of  $0.1254 \text{ M}^{-1}$  and  $0.0567 \text{ M}^{-1}$ , dipole moments of 1.01 D. and 0.68 D. were calculated for the NMCHA and DMCHA monomers, respectively. No values for the dipole moments of these two amines were found in the literature; however, the dipole moments determined in the present investigation do compare favorably with the dipole moments obtained for other secondary and tertiary amines. Data for the determination of the dipole moment of triethylamine

Table XV

The Dielectric Constant of CHA-Benzene Solutions at 25<sup>o</sup>

---

$f_A, (M)$	Dielectric Constant, $\epsilon$
0.0512	2.2908
0.1170	2.3041
0.1736	2.3153
0.1938	2.3209
0.2886	2.3399
0.3152	2.3464
0.3808	2.3602
0.4038	2.3655
0.4155	2.3713
0.5223	2.3920

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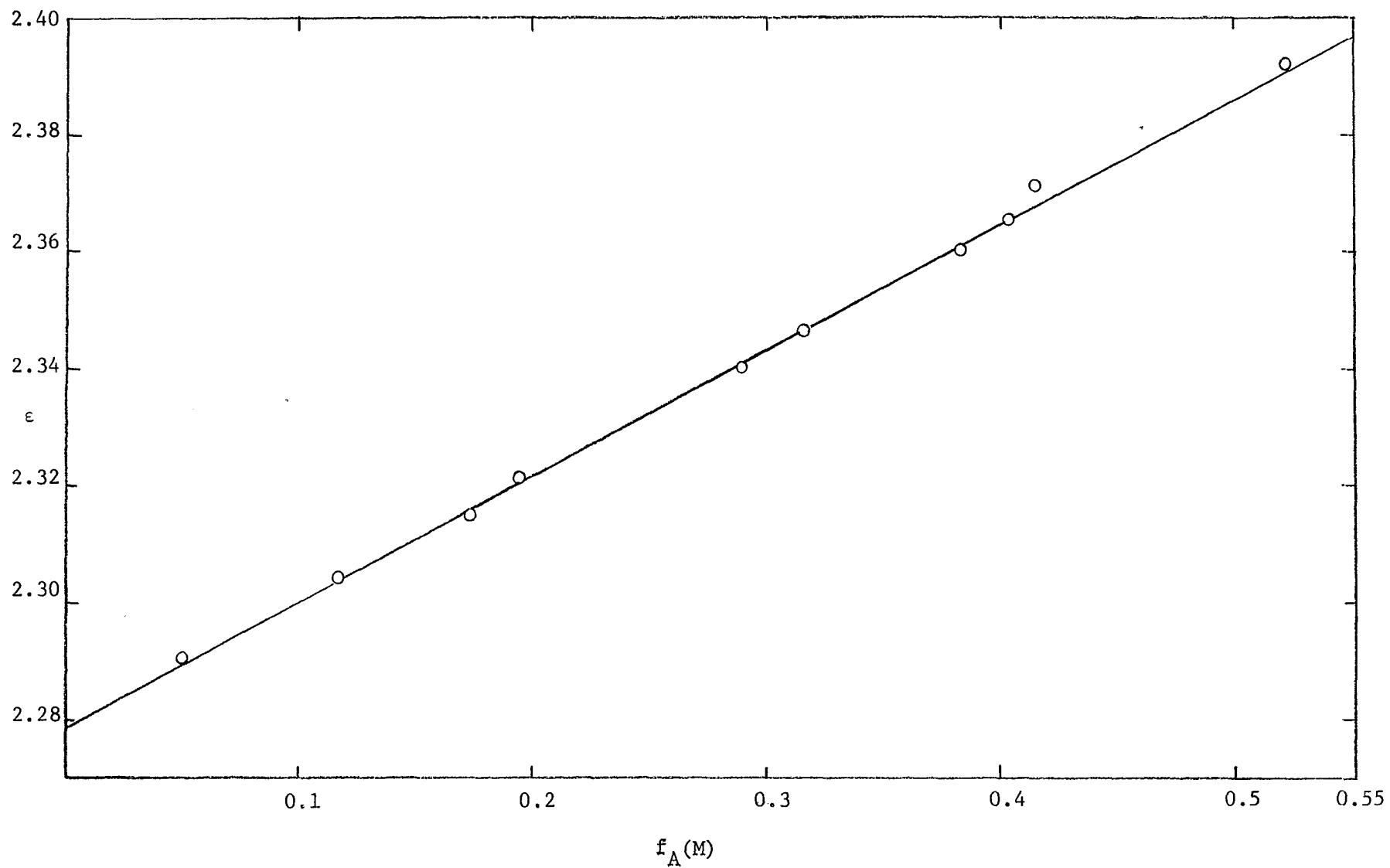


Figure XI. The Dielectric Constant of CHA-Benzene Solutions at 25°.

Table XVI

The Dielectric Constant of NMCHA-Benzene Solutions at 25°

---

$f_A, (M)$	Dielectric Constant, $\epsilon$
0.04918	2.2799
0.09753	2.2855
0.1485	2.2919
0.1950	2.2974
0.2430	2.3048
0.2865	2.3091
0.3302	2.3146
0.3768	2.3203
0.4186	2.3260
0.4615	2.3316

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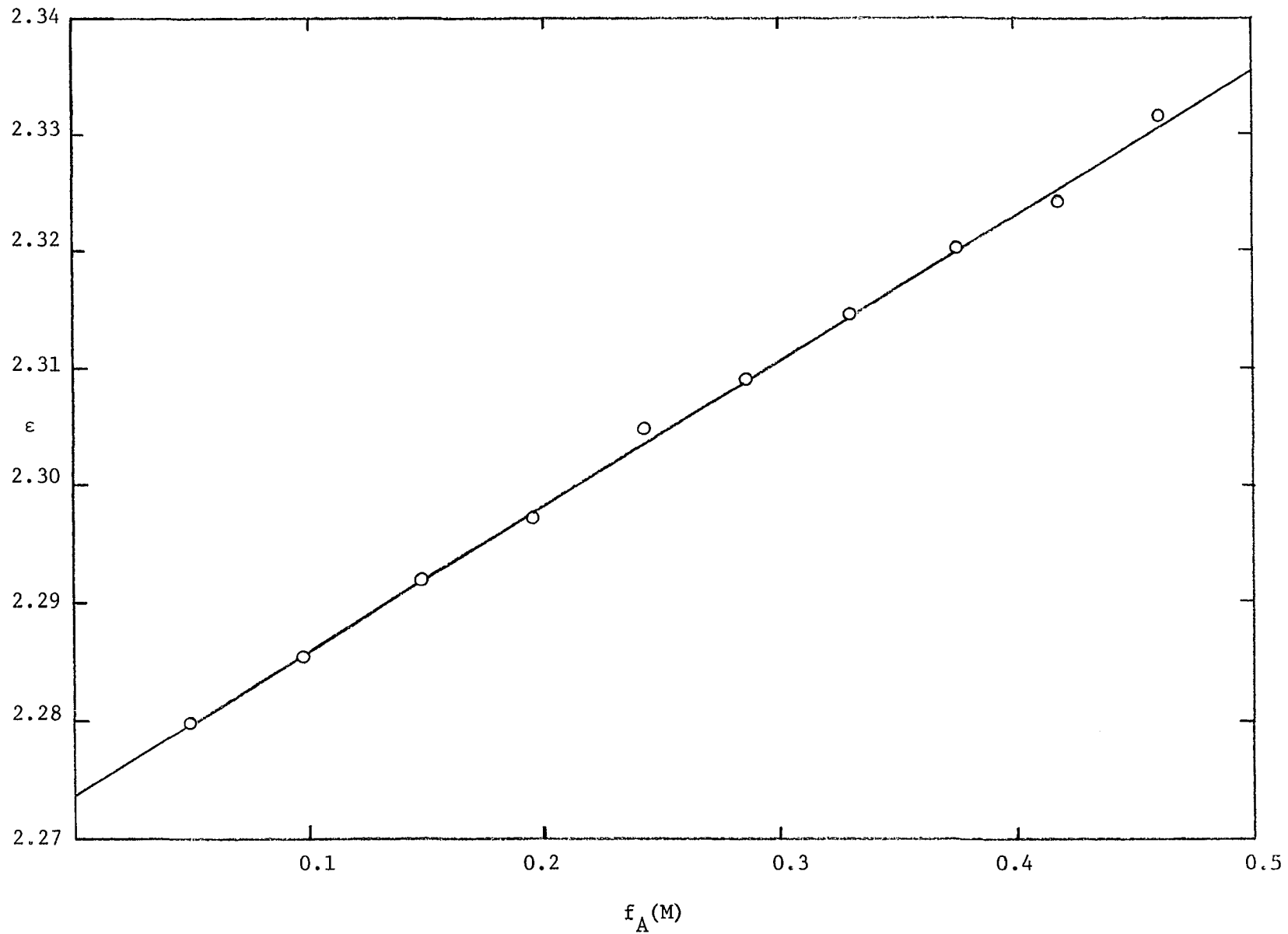


Figure XII. The Dielectric Constant of NMCHA-Benzene Solutions at 25<sup>o</sup>.

Table XVII

The Dielectric Constant of DMCHA-Benzene Solutions at 25°

---

$f_A, (M)$	Dielectric Constant, $\epsilon$
0.04816	2.2761
0.1012	2.2792
0.1454	2.2816
0.1918	2.2842
0.2391	2.2870
0.2855	2.2897
0.3261	2.2917
0.3695	2.2943
0.4263	2.2974
0.4566	2.2992

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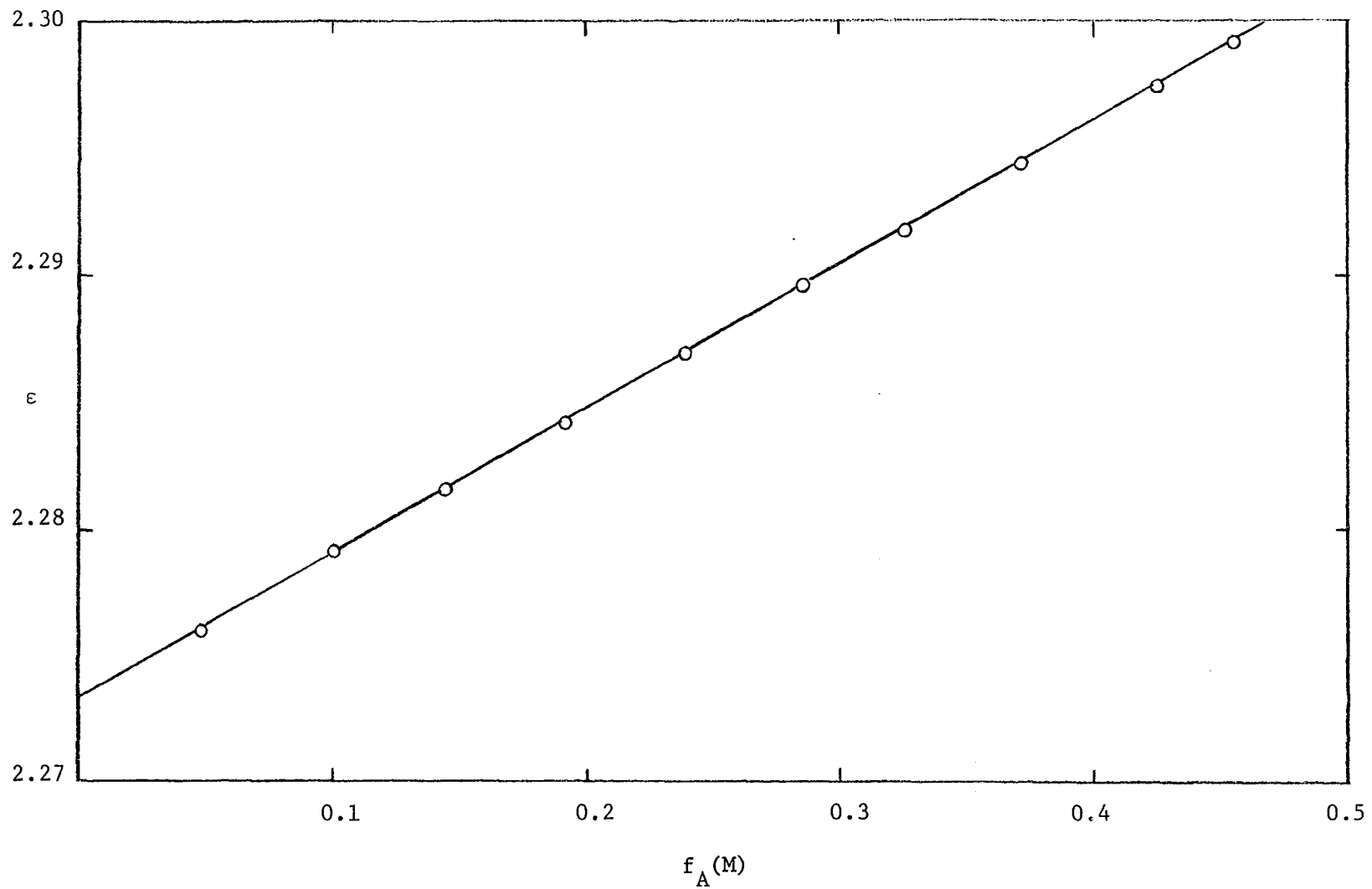


Figure XIII. The Dielectric Constant of DMCHA-Benzene Solutions at 25°.

is given in Table XVIII. Figure XIV indicates a linear relationship between  $\epsilon$  and  $f_A$ ; the slope of  $0.0316 \text{ M}^{-1}$  yields a dipole moment (from equation (12)) of 0.51 D. This value is slightly lower than those values reported previously for triethylamine in benzene at  $25^\circ$ . LeFèvre<sup>75</sup> reports a value of 0.64 D., Higashi,<sup>76</sup> 0.79 D., and Boud and Smith,<sup>40</sup> 0.80 D.

Table XIX presents the data taken for solutions of water in benzene at  $25^\circ$ . The dipole moment calculated from the slope of  $0.375 \text{ M}^{-1}$  (Figure XV) was determined to be 1.76 D. This value compares favorably with those reported previously (1.71 D.,<sup>77</sup> 1.72 D.,<sup>78</sup> 1.835 D.<sup>79</sup>).

The data of Risbourg and Liebaert<sup>79</sup> are also indicated in Figure XV. These authors' data begin to deviate from linearity at water concentrations greater than about 0.02 M. They note that the dielectric constant increases less rapidly for a given increment in water concentration at higher water activity, and from the curving over of their plot of  $\Delta\epsilon/\epsilon$  vs.  $f_W$ , they attempt to calculate polymerization constants for water in benzene. The negative curvature reported by Risbourg and Liebaert was not detected in the present study even though the dielectric data recorded in Figure XV cover a wide range of concentrations extending all the way to saturation of benzene by water (0.0350 M). Possibly the observed curvature resulted from the method used by these workers to prepare their samples; water was apparently added directly to benzene and the heterogeneous mixture warmed several degrees above room temperature, with shaking, to promote dissolution of the water. We have been unsuccessful in preparing homogeneous solutions of water in benzene using this method. For example, if approximately half as much water as



Table XVIII

The Dielectric Constant of Triethylamine-Benzene Solutions at 25°

---

$f_A, (M)$	Dielectric Constant, $\epsilon$
0.0366	2.2750
0.0758	2.2771
0.1145	2.2775
0.1505	2.2787
0.2041	2.2810
0.2494	2.2824
0.2819	2.2829
0.3340	2.2843
0.3585	2.2860
0.4495	2.2882

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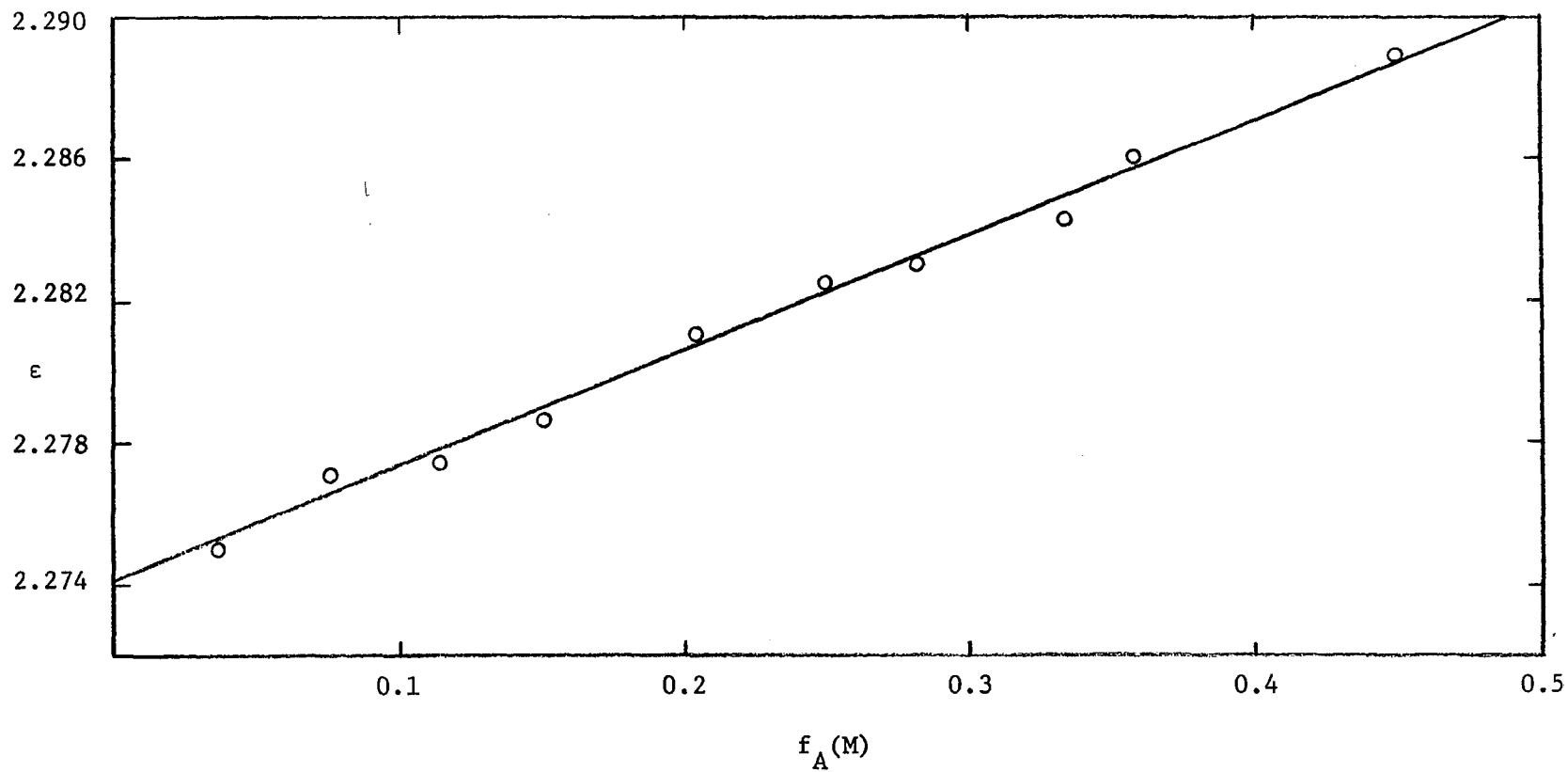


Figure XIV. The Dielectric Constant of Triethylamine-Benzene Solutions at 25<sup>o</sup>.

Table XIX

The Dielectric Constant of Water-Benzene Solutions at 25°

---

$f_w, (M)$	Dielectric Constant, $\epsilon$
0.00519	2.2754
0.00794	2.2762
0.01132	2.2775
0.01258	2.2779
0.01472	2.2789
0.01613	2.2791
0.01794	2.2801
0.01998	2.2806
0.02127	2.2814
0.02283	2.2818
0.02462	2.2827
0.02469	2.2826
0.02703	2.2832
0.02730	2.2837
0.02928	2.2841
0.03097	2.2849
0.03120	2.2851
0.03301	2.2856
0.03500	2.2867

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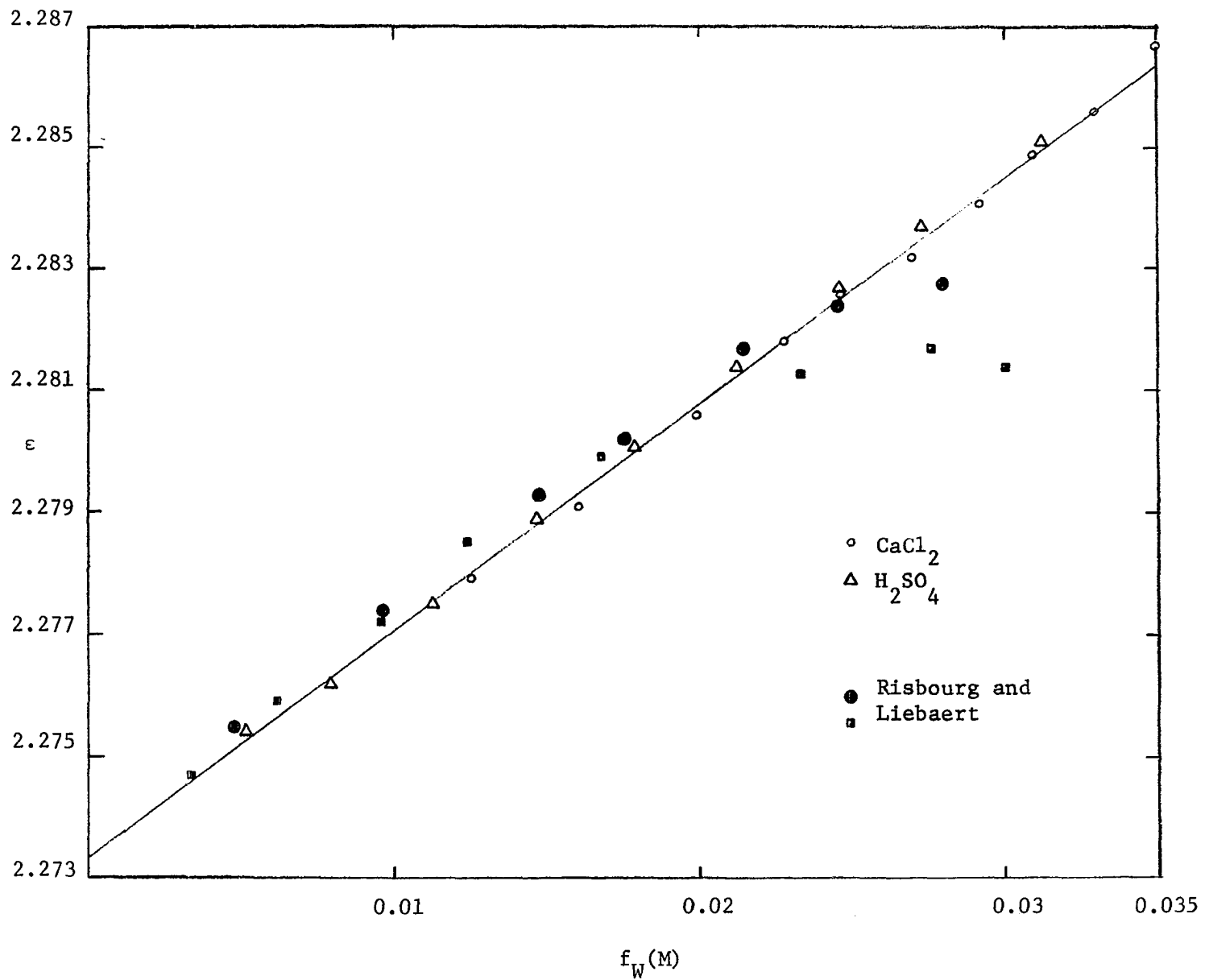


Figure XV. The Dielectric Constant of Water-Benzene Solutions at  $25^\circ$ .

is required for saturation is added to pure, anhydrous benzene, vigorous shaking for over 24 hours does not cause all the water to dissolve. On the other hand, it has been demonstrated that isothermal equilibration of pure benzene with water solutions of known activity (either directly by distribution of the two phases or by vapor phase equilibration) does lead to the attainment of equilibrium within 8 to 10 hours.<sup>51</sup> It is believed the slowness of attainment of equilibrium in experiments in which water is added directly to pure benzene is due to the very small surface area of the water droplets in comparison with the interfacial areas of the organic and aqueous solutions employed in the equilibration methods utilized in the present study.

The conclusion from this study that water is essentially monomeric in benzene is in agreement with the results of recent isopiestic and vapor pressure studies of water-benzene mixtures.<sup>57,80</sup>

Ternary mixtures of the amines, water, and benzene were prepared by partitioning the amines between water and benzene. This technique for preparing the solutions simplified the interpretation of the data, inasmuch as the concentration of one of the reactive species (the water monomer) is held constant in the ternary system. Due to the low solubility of the amines and benzene in the water phase, the water activity was assumed to be unity, maintaining the concentration of the water monomer at 0.0350 M in each organic phase. The dielectric constant of water saturated benzene at 25<sup>o</sup> was found to be 2.2867 as indicated in Table XIX. If the dielectric constant of pure benzene is subtracted from this constant, the resulting value is the constant increment to the dielectric constant of the solutions contributed by the water

monomer (0.0133). This step makes it possible to infer the contribution of the associated species to the dielectric constant of the solution with a minimum of calculation. With the constant contribution to the dielectric constant by the water monomer, the increase in the dielectric constant of the ternary mixtures with increase in amine concentration at constant water activity may be attributed to only two species, the amine monomer and the amine monohydrate.

The concentration of the complex was determined by calculating  $\Delta f_W$  for each solution. According to equation (4),  $\Delta f_W = C_{AW}$ , so that the concentration of the hydrate may be determined by water titration alone. An alternative method in which the hydration constants in Table XIII, along with the amine monomer and water monomer concentrations, may be used to calculate  $C_{AW}$ . The amine monomer concentration,  $C_A$ , is determined from equation (1). From the calculated  $C_A$  concentration and the data in Figures XI through XIV ( $f_A = C_A$ , where no association occurs), the contribution of free amine monomers to the increase in the dielectric constant may be calculated and subtracted from the observed increase in dielectric constant attributable to both amine species. The difference,  $\Delta \epsilon$ , is assumed to be due solely to the amine monohydrate present.  $\Delta \epsilon$  is plotted against  $C_{AW}$  (or  $\Delta f_W$ ) to construct plots similar to those used to determine the dipole moments of the amine monomers. This method for determining the dipole moment of the complex is similar to the one used by Lin.<sup>81</sup>

Tables XX through XXIII show the dielectric data for the CHA, NMCHA, DMCHA, and triethylamine hydrates, respectively. Figure XVI yields a least squares slope of  $0.971 \text{ M}^{-1}$  for the CHA system from which a dipole moment for the complex of 2.82 D. is calculated using

Table XX

Dielectric Data for the Determination of the  
Dipole Moment of the CHA-Water Complex

---

$C_{AW}$ (M)	$\Delta\epsilon$
0.00852	0.0084
0.01821	0.0179
0.02763	0.0288
0.03751	0.0370
0.04881	0.0480
0.05797	0.0574
0.07180	0.0705
0.0814	0.0803
0.0986	0.0969
0.1111	0.1077

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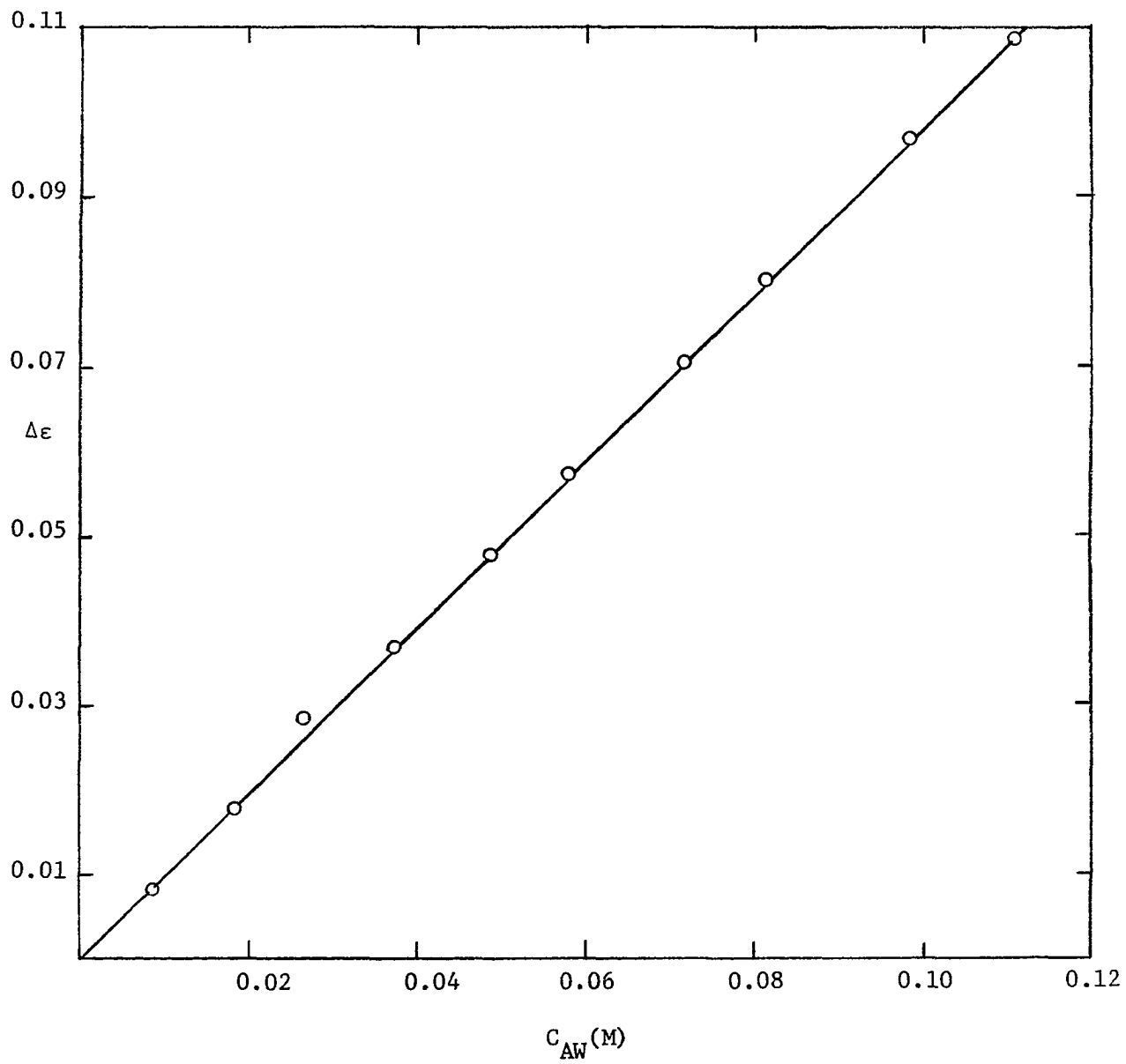


Figure XVI. The Increase in the Dielectric Constant of CHA-Water-Benzene Solutions Due to the CHA-Hydrate at 25°.



Table XXI

Dielectric Data for the Determination of the  
Dipole Moment of the NMCHA-Water Complex

---

$C_{AW}$ , (M)	$\Delta\epsilon$
0.00777	0.0073
0.01575	0.0151
0.02391	0.0231
0.03257	0.0314
0.04044	0.0389
0.05046	0.0488
0.05882	0.0568
0.06930	0.0670
0.07510	0.0780
0.08450	0.0878

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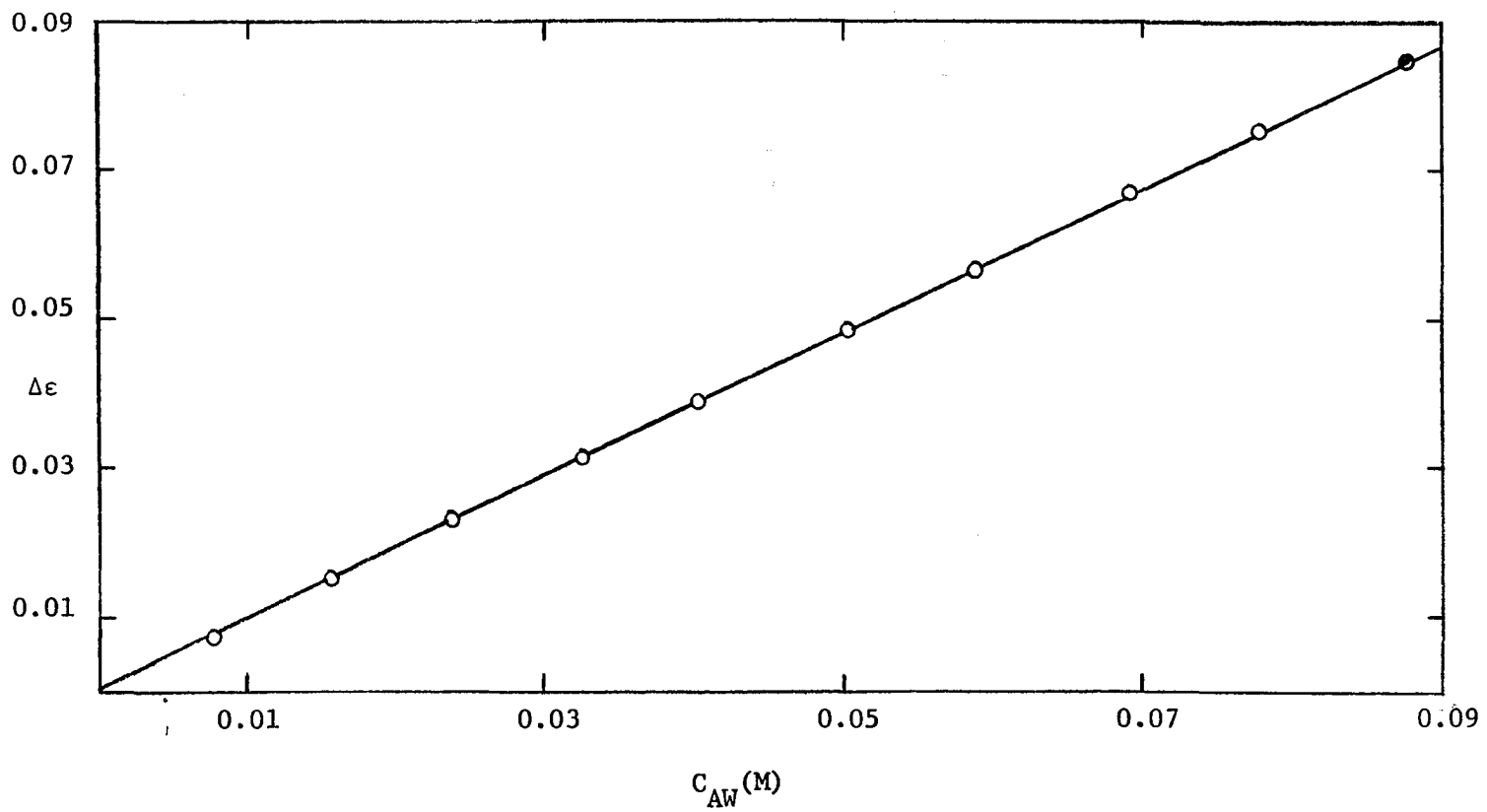


Figure XVII. The Increase in the Dielectric Constant of NMCHA-Water-Benzene Solutions Due to the NMCHA Hydrate at 25°.

Table XXII

Dielectric Data for the Determination of the  
Dipole Moment of the DMCHA-Water Complex

---

$C_{AW}$ , (M)	$\Delta\epsilon$
0.00618	0.0054
0.01230	0.0109
0.01819	0.0163
0.02484	0.0221
0.03082	0.0273
0.03747	0.0331
0.04412	0.0391
0.05010	0.0442
0.05732	0.0506
0.06264	0.0563

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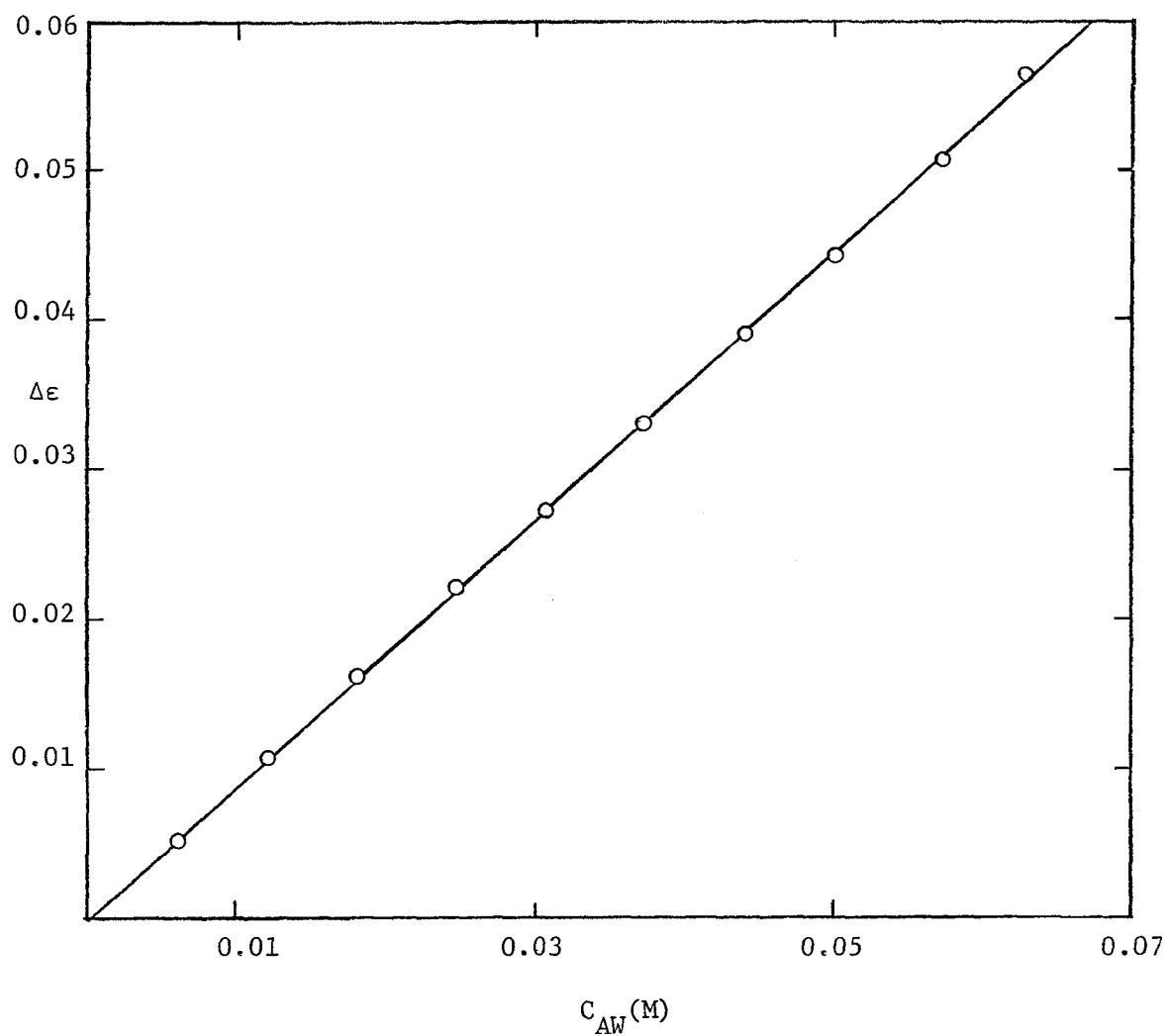


Figure XVIII. The Increase in the Dielectric Constant of DMCHA-Water-Benzene Solutions Due to the DMCHA Hydrate at 25°.

Table XXIII

Dielectric Data for the Determination of the Dipole  
Moment of the Triethylamine-Water Complex

---

$C_{AW}$ , (M)	$\Delta\epsilon$
0.00467	0.0043
0.00920	0.0085
0.01250	0.0148
0.01650	0.0194
0.0202	0.0243
0.0245	0.0296
0.0290	0.0335
0.0318	0.0369
0.0348	0.0405
0.0418	0.0489

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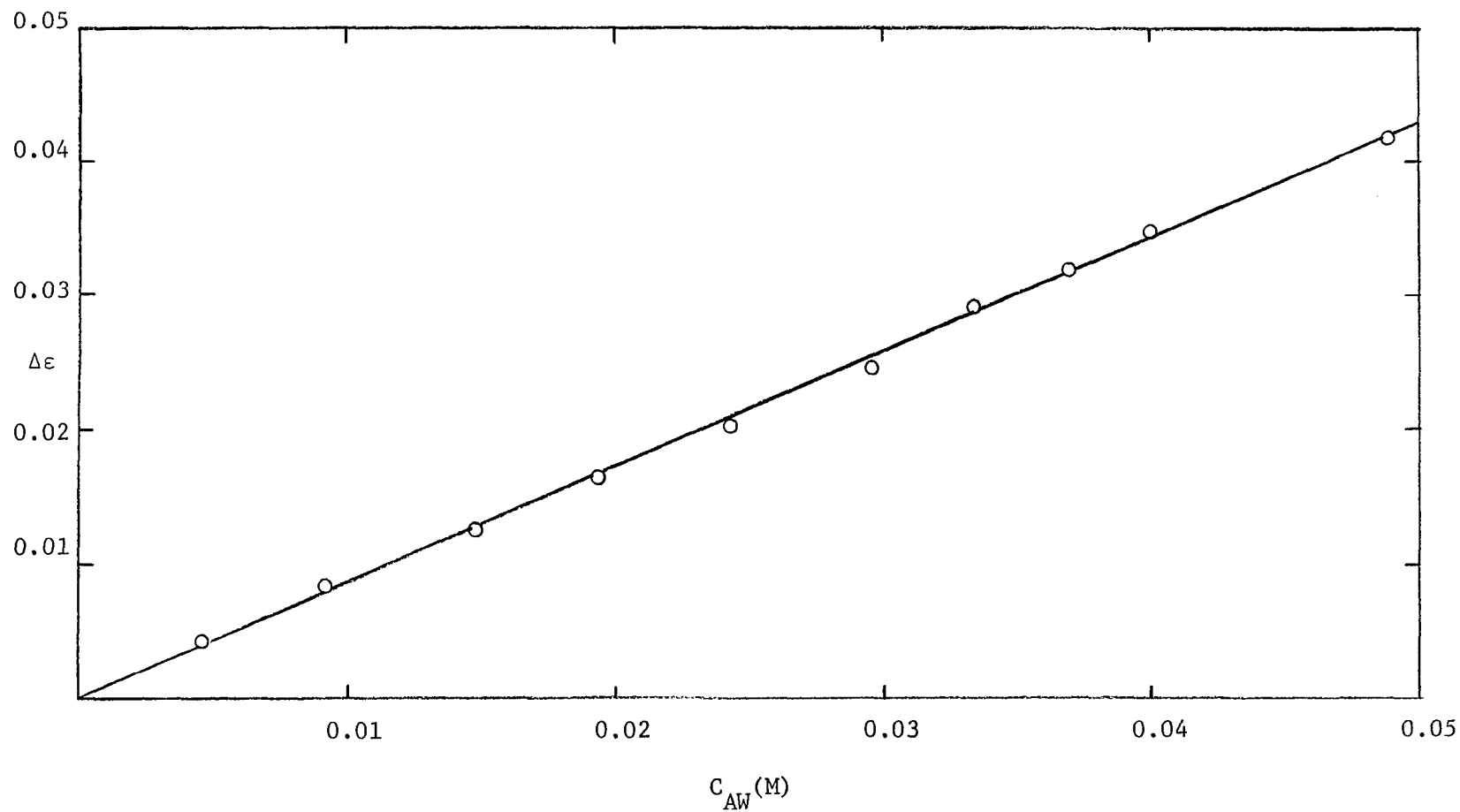
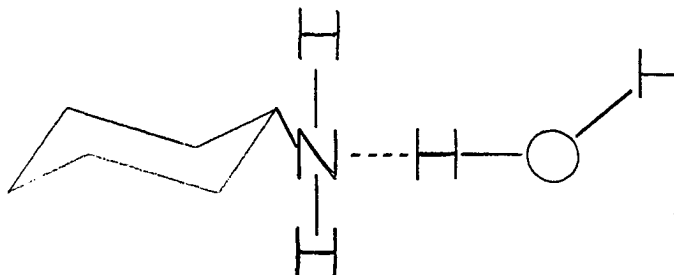


Figure XIX. The Increase in the Dielectric Constant of Triethylamine-Water-Benzene Solutions Due to the Triethylamine Hydrate at 25°.

equation (12). From slopes of  $0.965 \text{ M}^{-1}$  (Figure XVII) and  $0.885 \text{ M}^{-1}$  (Figure XVIII), the NMCHA and DMCHA hydrates were found to have dipole moments of 2.80 D. and 2.68 D., respectively. The dipole moment of the triethylamine hydrate was found to be 2.64 D. from the slope of  $0.855 \text{ M}^{-1}$  in Figure XIX.

A reasonable model for the CHA-water complex is shown below.



The dipole moment of the amine is assumed to be directed along the N---H---O axis and that the water molecule is free to rotate about this axis. If no charge separation were to occur on formation of the hydrogen bond, this model would lead to a predicted value of the dipole moment of the complex of 2.40 D. (as computed from vector addition of the values of the dipole moments of the amine and water monomers). The H---O---H angle is assumed to be  $105^\circ$ . A similar model was employed for each amine complex resulting in predicted dipole moments from 0.4 to 1.00 D. less than the observed dipole moments. Table XXIV presents the observed and predicted dipole moments of the amine hydrates along with the apparent enhancement of the dipole moment due to hydrogen bond formation.

Kazakova and Fel'dshtein<sup>45</sup> have conducted a similar study with triethylamine and pyridine hydrates. They used essentially the same model for calculating the dipole moment of the complex. However, rather than allowing the dipole vectors of the amine and water monomers to interact directly, they interacted the amine dipole with the partial dipole moment attributed to each OH bond. The calculated dipole moment

Table XXIV

Dipole Moments and Apparent Enhancements of the  
Dipole Moments of the Amine-Water Complexes

---

Complex	(Observed (D.) Dipole Moment	Calculated (D.) Dipole Moment	(D.) Enhancement
CHA-Water	2.82	2.40	0.42
NMCHA-Water	2.80	2.08	0.72
DMCHA-Water	2.68	1.75	0.93
Triethylamine-Water	2.64	1.57	1.07

---



of the triethylamine-water complex was found to be 1.81 D. using the previous model. This compares to the observed moment of 2.24 D. reported by the authors. An apparent enhancement of 0.43 D. is reported. This enhancement is considerably less than that found for the triethylamine-water complex in the present study (1.07 D.). Unfortunately no details of how the dipole moments of the amine-water complexes were calculated are given in the Kazakova and Fel'dshtein paper. They have also reported that the dipole moment of the pyridine-water complex is very nearly equal to the moment predicted from the model of the complex.

The observed dipole moments of the amine hydrates in the present investigation are similar in magnitude to moments reported for other hydrogen bonded complexes of amines with hydroxylic proton donors. Several dipole moments of complexes taken from the literature are given in the following table.

DIPOLE MOMENTS OF SEVERAL AMINE COMPLEXES

Complex	$\mu$ (D.)	Reference
Triethylamine-n-butylalcohol	2.34	40,42
Triethylamine-tert-butylalcohol	2.24	40,42
Triethylamine-chloroform	2.07	82
Triethylamine-water	2.24	45
Triethylamine-pyrrole	3.10	44
Pyridine-water	3.13	45
Pyridine-phenol	3.44	83
Pyridine-n-butylalcohol	3.37	41

It has been concluded that the difference between the observed and computed dipole moments of the amine-water complexes is due to charge

separation. This conclusion seems reasonable, although it should be recognized that the hydrogen bond can be very easily distorted and thereby might increase the atomic polarization of the complex to a value larger than the sum of the atomic polarizations of the constituents. This increase would appear as an apparent enhancement of the dipole moment. Mecke, Reuter, and Schupp<sup>84</sup> have reported that in associated species, where individual dipole moments are in line, the individual dipole moments are usually decreased in the complex, which would produce an effect opposite to that observed in this study. Several authors have proposed that a charge separation occurs when an amine bonds to a proton donor.<sup>20,42,85,86</sup> I. R. spectra and dielectric measurements have been the primary methods utilized in these studies. In many cases an apparent enhancement of the dipole moment of the complex over that which was calculated from an appropriate model is found. The data from the present investigation appear to be among the first to report quantitative information concerning the extent of charge separation in amine-water complexes.

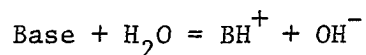
## CHAPTER V

### DISCUSSIONS AND CONCLUSIONS

Previous investigations of the hydration of amines have involved measurements on aqueous solutions.<sup>3,4,7,11</sup> In most of these studies, attempts have been made to infer hydration constants of amines by applying mass action relations involving the concentration of the solvent (water). This method for determining equilibrium constants requires that the solvent activity be varied over a considerable range before the stoichiometries and equilibrium constants for complexes involving the solvent may be determined with any confidence. In order to achieve a sufficient solvent activity range, high solute concentrations must be employed. At high concentrations it is most difficult (if not impossible) to determine the relative importance of specific and non-specific solute-solvent interactions which affect the activity coefficients of the solutes. That is, the apparent equilibrium constant determined in concentrated solution will reflect not only a specific interaction but many unknown non-specific effects. These "constants" are probably not constant, but vary over the large concentration range since the activity coefficients of the solute species cannot be accurately predicted. The "hydration" constants reported by Moore<sup>3</sup> represent the relative basicities of different amines in aqueous solution. The water concentration does not appear in the mass action expression

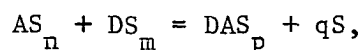
$k_2 = \frac{R_3NH\text{---}OH}{R_3N}$  . These are not, therefore, hydration constants in the same sense as the constants reported in the present study.

Briegleb<sup>11</sup> has also reported "hydration" parameters for a number of amines in aqueous solution. The equilibrium constants for the reaction,



are not reported; however, enough thermodynamic data are given to calculate the constants. It must be emphasized that this reaction is not a simple hydration reaction of the type considered in the present study, but a reaction involving the complete transfer of a proton from a solvent molecule to the amine.

In connection with the method for determining the effect of the solvent on complexation, Carter, Murrell, and Rosch<sup>87</sup> have attempted to account for solvation effects by assuming each species present (in an association reaction) is surrounded by a solvation shell composed of a specific number of solvent molecules. A mass action expression is derived for the reaction



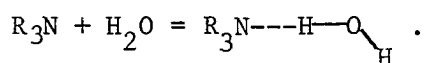
where A and D are acceptor and donor molecules and  $S_n$ ,  $S_m$ , and  $S_p$  represent the number of solvent molecules in the solvation shell of each molecule.  $qS$  is the number of solvent molecules "squeezed out" by the association of A and D. This study is typical of numerous attempts to determine the role of the solvent in a reaction by incorporating the solvent concentration in a mass action expression.

A somewhat simpler method for attempting to account for the role of the solvent in association reactions is to assume that the uncomplexed

solvent obeys Raoult's law. As in the present study any deviation from the assumed law is interpreted as some kind of specific solute-solvent interaction. However, this method is subject to the same objections as those mentioned above in that relatively high solute concentrations must be employed in order to produce significant deviations from Raoult's law.

It is probably fair to say that studies of the dilute solution region provide about the only reliable method for inferring values of complex formation constants. The hydration constants reported in this dissertation appear to be the only constants that have been determined for aliphatic amines in dilute non-aqueous solution. The individual solutes (amines and water) were found to obey Henry's law over the entire concentration range studied; deviations from Henry's law in solutions containing both amine and water were attributed to the formation of the 1:1 hydrate. By treating data for dilute solutions, the stoichiometry and association constants of a reaction can be determined in a straightforward, thermodynamically justifiable way. None of the prohibitive factors mentioned previously for the concentrated solution have to be dealt with when working in the Henry's law region.

The hydration reaction is



It must be emphasized that the individual species involved in the reaction (amine, water, and complex) are solvated, although the solvent does not appear explicitly in the equation.

Although no thorough studies of amine hydration have been conducted previously, many articles in the literature deal with various amine

complexes. Many amine complexes involving alcohols, chloroform, and other miscellaneous proton donors have been investigated. These complexes provide interesting comparisons with the amine-water complexes examined in this study. Lamberts and Zeegers-Huyskens<sup>19</sup> have found an association constant of  $4.49 \text{ M}^{-1}$  for the reaction between ethanol and triethylamine in carbon tetrachloride at  $20^\circ$ . This compares to  $7.01 \text{ M}^{-1}$  found in this study for the triethylamine-water complex in cyclohexane at  $25^\circ$ . Carbon tetrachloride is a slightly more reactive solvent than cyclohexane, generally causing association constants to be lower in  $\text{CCl}_4$ . n-Butylamine complexed with ethanol, n-butanol, and sec-butanol gives association constants of  $3.53 \text{ M}^{-1}$ ,  $4.29 \text{ M}^{-1}$ , and  $2.96 \text{ M}^{-1}$ , respectively. These constants are in the range of those found in the present investigation. However, the equilibrium constant determined here for the primary amine complex (CHA) is  $6.74 \text{ M}^{-1}$  in benzene, which is a much more reactive solvent than  $\text{CCl}_4$ . The term "reactive solvent" is used rather loosely to indicate the extent to which the monomers involved in the association reaction are solvated by the solvent, thereby diminishing the extent of complex formation. In previous hydration studies reported from this laboratory it has been noted that the solubility of water in various solvents is indicative of the solvating ability of the solvent.<sup>71,88</sup>

The association constants for DMCHA complexed with N-methylaniline and aniline in cyclohexane at  $25^\circ$  are reported to be  $0.57 \text{ M}^{-1}$  and  $0.69 \text{ M}^{-1}$ , respectively.<sup>34</sup> These constants are only 15 to 20% as large as that reported here for the DMCHA-water complex ( $3.85 \text{ M}^{-1}$ ). This effect is in line with the weak proton donating anilines as compared to the water molecule. CHA interacting with chloroform<sup>36</sup> yields an equilibrium

constant of  $1.10 \text{ M}^{-1}$ , which seems reasonable when compared to  $6.74 \text{ M}^{-1}$  reported here for the  $\text{CHA-H}_2\text{O}$  complex.

Bertin and Lumbroso<sup>44</sup> have complexed triethylamine with pyrrole in benzene and cyclohexane. They report a 1:1 association constant of  $3.2 \text{ M}^{-1}$  for the complex in cyclohexane as compared to  $1.7 \text{ M}^{-1}$  in benzene. A similar reduction in association constant due to the greater solvating power of benzene is reported in this study. (A more detailed explanation of solvation effects follows in this chapter.) The 1:1 constant for the triethylamine-water complex studied here was found to be  $7.01 \text{ M}^{-1}$  in cyclohexane as compared to  $3.47 \text{ M}^{-1}$  in benzene. The association constants appear to decrease in the same ratio going from cyclohexane to benzene. Chakrabarti and Basu<sup>89</sup> have investigated the interaction between aromatic hydrocarbons and aromatic amines. They have concluded that the spectral changes induced in naphthylamine in the presence of benzene, toluene, and xylene are due to  $\Pi$ -hydrogen bond formation between the amino hydrogen and the  $\Pi$ -electron system of each hydrocarbon. The systems were studied in cyclohexane. Association constants of  $0.26 \text{ M}^{-1}$ ,  $0.32 \text{ M}^{-1}$ , and  $0.34 \text{ M}^{-1}$  were reported for the benzene, toluene, and xylene systems, respectively. In a related study Oki and Mutai<sup>90</sup> have reported bond energies of approximately 2.0 kcal/mole for each  $\text{N-H} \cdots \Pi$  bond. It is evident that benzene is not the "inert" solvent which some investigators have proposed.

It should perhaps be re-emphasized at this point that the thermodynamic constants determined in the present study are for the solvated monomers interacting to form a solvated complex. The solvent molecules tend to reduce the ability of the solute monomers to interact with each

other; therefore, the equilibrium constants and enthalpies are lower than one would expect to find in the vapor phase where no solvation effects are present.

There seems to be no apparent agreement among investigators concerning the extent of self-association in aliphatic amines. Turner and Merry<sup>31</sup> have reported that primary amines are slightly associated, whereas the secondary and tertiary amines are non-associated in the liquid state. Other authors have concluded that all aliphatic amines are non-associated.<sup>32</sup> NMR is employed by Fenney and Sutcliffe<sup>91</sup> for the determination of self-association constants in liquid amines. The results appear to be best interpreted in terms of monomer-tetramer equilibrium. Association constants for the formation of tetramers of ethylamine and diethylamine are  $3 \times 10^{-3} \text{M}^{-3}$  and  $1 \times 10^{-3} \text{M}^{-3}$ , respectively. At fairly high amine monomer concentrations, the tetramer concentration remains very small so that even though the higher amine polymers are present, they represent only a very small percentage of the total concentration. An enthalpy of  $-1.7 \text{ kcal/mole}$  was reported for the formation of the tetramer. The enthalpy reported by these authors seems somewhat small; the enthalpy per hydrogen bond appears to be about  $0.4$  to  $0.5 \text{ kcal}$ . Most amine hydrogen bond energies are several times as large. Arbuzov and Kataeva<sup>92</sup> have determined the parachor for 16 amines; the differences from calculated values were interpreted in terms of molecular association. It was concluded that primary aliphatic amines do self-associate. The extent of association apparently decreased with increasing molecular weight. Among the secondary amines, only dimethylamine and diethylamine were found to associate. Tertiary amines



showed no tendency toward self-association. All of these studies were conducted with the pure, liquid amines.

Pannetier, et al.<sup>33</sup> have concluded that CHA and NMCHA are partially self-associated in cyclohexane solution, as indicated by infrared spectral data. The absorptivities of CHA and NMCHA decrease with increasing amine concentration. No association constants were reported, but the absorptivities are expressed as a cubic function of the amine concentration. In contrast, Whetsel and Lady have shown that the self-association of CHA in cyclohexane solution is negligible. They found that the concentration of the CHA dimer was nearly zero based on spectral data taken at 2060  $\mu$ . The results of the present study are in agreement with those of the latter authors. The distribution constants of the four aliphatic amines were found to be constant over the entire concentration range. Self-association would cause the distribution constants to increase with increasing amine concentration. The nitrogen of the amino group is an excellent electron donor so that the lack of self-association in aliphatic amines must be attributed to the relatively weak acidity of the amino protons.

The enthalpy and entropy values determined in this investigation are of the same order of magnitude as those reported for amine-alcohol complexes. The heats of hydration which Briegleb<sup>11</sup> and others<sup>3,4</sup> report for amines have been determined in aqueous solution so that they may not be compared directly with the energy and entropy of one specific interaction such as that found in the present investigation. The thermodynamic constants reported by Lamberts and Zeegers-Huyskens<sup>19</sup> are given in Chapter I. Both the enthalpy and entropy of complex formation with alcohol are seen to decrease from primary to secondary to tertiary amine.

The enthalpies of the n-butylamine complexes are all approximately -7.5 kcal/mole, while the triethylamine complexes have enthalpies of formation of about -5 kcal/mole. The reported entropies are also larger for the primary amine complexes and lowest for the tertiary amine complexes. The tertiary amine studied here (DMCHA) has been found to form a stronger hydrogen bond with water than either the primary or secondary amine. The ability of DMCHA to form strong hydrogen bonds was also observed by Whetsel and Lady.<sup>34</sup> Enthalpies of -3.76 and -3.35 kcal/mole for DMCHA complexed with N-methylaniline and aniline, respectively, were reported. The  $\Delta H$  values correspond to the formation of N—H---N bonds, while those bond energies determined in the present investigation are for N---H—O bonds. Corresponding entropy changes for the DMCHA complexes were reported to be -13.7 e.u. and -12.0 e.u. These constants may be compared to a  $\Delta S$  of -16.1 e.u. for the DMCHA-water complex. These constants are slightly larger than those previously mentioned; however, water is a much stronger proton donor than the aromatic amines. Whetsel and Lady also noted the large steric effect attributable to the methyl groups of DMCHA. Some thermodynamic data for the CHA-chloroform complex have also been determined.<sup>36</sup> An enthalpy of -3.6 kcal/mole and an entropy of -11.9 e.u. were reported. These thermodynamic constants are comparable to -4.94 kcal/mole and -12.8 e.u. determined for the CHA-water complex.

The  $K_{AW}$  values reported here decrease from primary to secondary to tertiary amine. This decrease may be attributed, for the most part, to steric hindrance caused by the N-methyl substituents, since the base strengths of the three cyclohexylamines are approximately equal.

pKa	Amine
10.9	NMCHA <sup>a</sup>
10.6	CHA <sup>b</sup>
10.3	DMCHA <sup>c</sup>

a) Technical Bulletin No. 11, Abbott Laboratories, North Chicago, Illinois.

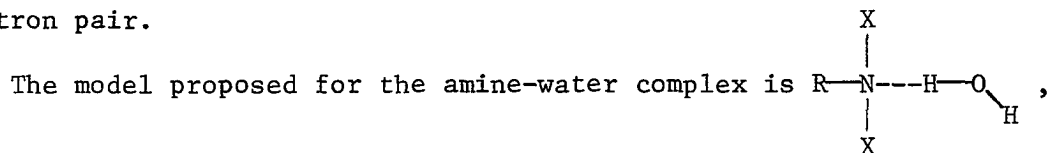
b) N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc., 54, 3469 (1932).

c) Technical Bulletin No. 8, Abbott Laboratories, North Chicago, Illinois.

Several authors have attempted to find a functional relationship between the pKa of an acid or base and some characteristic thermodynamic variable. Mateos, Cetina, and Chao<sup>93</sup> have found from NMR spectra that the chemical shifts of NH protons of ethylenediamine, dimethylamine, piperidine, pyrrolidine, and m-chloroaniline in diluted pyridine solutions correlate well with corresponding pKa values. No simple relationship exists between the equilibrium constants for the amine-pyridine interaction and the pKa of the amines. Values of the equilibrium constants for amine-chloroform systems (determined by NMR shift of the chloroform proton) gave a good correlation with amine basicity. Bhowmik and Basu<sup>94</sup> found that the equilibrium constants for the hydrogen bonded complexes of diethylnitrosamine with phenol, p-chlorophenol, m-cresol, and p-cresol increase linearly with the pKa values of the phenols. A method is suggested for estimating the pKa values of alcohols and amines from the equilibrium constant for hydrogen bond formation. It appears that good correlations are found only when there are no steric hindrances to complex formation.

Unfortunately the pKa values of the amines employed in the present study are so nearly equal that no correlation with reaction parameters has been attempted. It is interesting, however, that the weakest

base (DMCHA) forms the strongest hydrogen bond with water. Perhaps the two methyl groups in the DMCHA molecule are not only responsible for the low association constant, but also cause this complex to be the strongest. The two methyl substituents which surround the N---H---O section of the complex probably cause these three atoms to acquire a more nearly linear configuration than that assumed by either the primary or secondary amine complex. The large negative entropy determined for the DMCHA-H<sub>2</sub>O complex indicates that a considerable amount of ordering occurs. According to Luck,<sup>95</sup> hydrogen bonds should be strongest when the Y---H---X partners are on a straight line. The direction of the line should coincide with the axis of symmetry of the orbitals of the free electron pair.



where X is either H or R. The data reported here are consistent with this model, which is similar to models reported previously in the literature. This type of complex is the only one that appears reasonable for the tertiary amines; however, the primary and secondary amines have amino protons which might be capable of hydrogen bonding to the water oxygen. The probability of the amine hydrogens forming hydrogen bonds with water seems remote, however, in view of the relatively weak tendency for primary and secondary amines to self-associate. The amino protons are not acidic enough to compete for basic sites with the more acidic protons available from the water molecules. The proposed model is analogous to the one employed by Kazakova and Fel'dshtein<sup>45</sup> to interpret dielectric data on triethylamine-water and pyridine-water complexes. Also, Zeegers-Huyskens<sup>20</sup> has interpreted her infrared spectral data on amine-alcohol complexes with a similar model.

The 1:1 amine hydrate was found to be the major complex in all the systems investigated during the course of this study. One reason for the apparent unimportance of the 2:1 hydrate in the systems reported here may be that the strong hydrogen bond formed in the 1:1 complex significantly reduces the acidity of the water molecule hydrogen which is not bonded. Frank and Wen<sup>96</sup> have proposed that the water oxygen becomes more basic when one of the water hydrogens interacts with an electron donor, whereas the non-bonded hydrogen loses acidity. This effect would be less important in the case of solutions of weaker bases, such as ketones or pyridine, in which apparently both the 1:1 and 2:1 hydrates are present in significant concentrations.<sup>14,65</sup> These observations have all had partial confirmation from studies of the infrared spectrum of water with triethylamine and dioxane in carbon tetrachloride, and of water as a solute in triethylamine and dioxane.<sup>97</sup> Also, dielectric constant measurements by Kohler, et al.,<sup>46</sup> of water + triethylamine and water + dioxane in  $\text{CCl}_4$  and benzene have indicated that the water-amine hydrogen bond is much more polar than the bond between water and dioxane.

#### The Effect of Solvation on the Triethylamine-Water Complex

A method for predicting the change in the equilibrium constant for a simple donor-acceptor interaction occurring in a series of solvents (including the vapor) has been proposed by Christian, et al..<sup>98,99</sup> These authors have derived equations from which the equilibrium constants of several pyridine-water complexes have been predicted for various solvents. The method requires that the equilibrium constant in one solvent be known along with the monomer distribution constants

for each solute species between the solvents of interest. In addition, the fraction of solvation energy ( $\alpha$ ) of the donor and acceptor that is retained by the complex must be calculated.  $\alpha$  has been defined by the relation

$$\alpha = \frac{\Delta E_{AW}^{I \rightarrow II}}{\Delta E_A^{I \rightarrow II} + \Delta E_W^{I \rightarrow II}} \quad (13)$$

where  $\Delta E_{AW}^{I \rightarrow II}$  represents the energy change in transferring 1 mole of the complex from solvent I to solvent II.  $\Delta E_A^{I \rightarrow II}$  and  $\Delta E_W^{I \rightarrow II}$  represent the energy change in transferring 1 mole of amine and 1 mole of water from solvent I to solvent II. The parameter  $\alpha$  is presumably less than unity since it is expected that the donor and acceptor monomers will be solvated to a greater extent than the complex (because the monomers tend to interact with one another at the most reactive site in each molecule, leaving these sites unavailable for solvation).  $\alpha$  is also considered to have only a slight temperature dependence and variation with the choice of solvent.

Two methods have been proposed for the calculation of  $\alpha$ ; one is a graphical method,<sup>98</sup> the other<sup>100</sup> employs a lattice model of the liquid state similar to that proposed by Barker<sup>101,102</sup> and others.<sup>103,104,105</sup> The graphical method requires measurement of association constants for at least two solvents and employs the equation

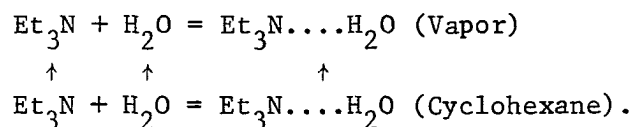
$$K_{AW}^{II}/K_{AW}^I = (K_{D,A} K_{D,W})^{\alpha-1} \quad (14)$$

where  $K_{AW}^{II}$  and  $K_{AW}^I$  are the association constants in solvents I and II and  $K_{D,A}$  and  $K_{D,W}$  are the distribution constants for the amine and water monomers (between solvents I and II) mentioned previously. This

relation predicts that a plot of  $\log K_{AW}$  vs.  $\log (K_{D,A} K_{D,W})$  for a series of solvents will be linear with a slope of  $\alpha-1$ .

Stevens<sup>100</sup> has attempted to predict values of  $\alpha$  from a lattice model of the liquid state. He has collected heat of mixing and heat of vaporization data from the literature and compiled a table of fairly consistent values of site interaction energies. The present investigation has employed the lattice model along with Stevens' interaction energies to predict  $\alpha$ .

In order to estimate  $\alpha$ , consider the removal of 1 mole of triethylamine, water, and the triethylamine-water complex from the ideal dilute solution in cyclohexane to the vapor phase. The cyclohexane molecule is considered to have 12 interaction sites. The energy of a cyclohexane site interacting with another cyclohexane site is designated by  $\epsilon_{H \sim H}$ . The triethylamine molecule is considered to have 16 sites (1 for each C-H and 1 for the tertiary nitrogen). Water is considered to have four reactive sites (2 O-H hydrogen sites and 2 sites for the electron pairs of the water oxygen). Consider the reaction



The energy required to vaporize a triethylamine molecule from cyclohexane to the vapor is

$$\begin{array}{l} \Delta E_{\text{Et}_3\text{N}} \\ \text{C}_6\text{H}_{12} \rightarrow \text{vapor} \end{array} = 15\epsilon_{\text{HH}'} + \epsilon_{\text{H} \sim \text{N}} - 8\epsilon_{\text{H} \sim \text{H}'}$$

where  $15\epsilon_{\text{HH}'}$  is the interaction energy between the aliphatic portion of the amine and cyclohexane.  $\epsilon_{\text{H} \sim \text{N}}$  represents the interaction energy

for a tertiary nitrogen interacting with cyclohexane.  $8\epsilon_{\text{H}\cdots\text{H}}$  represents the energy of the cyclohexane interactions which occur after the amine has left the cavity. Substitution for these interaction energies yields

$$\frac{\Delta E_{\text{Et}_3\text{N}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} = [15(1.10) + 1(2.5) - 8(1.23)] \text{ kcal/mole}$$

$$\frac{\Delta E_{\text{Et}_3\text{N}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} = 9.16 \text{ kcal/mole}$$

A similar calculation for the vaporization of a water molecule follows.

$$\frac{\Delta E_{\text{H}_2\text{O}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} = 2\epsilon_{\text{OHH}} + 2\epsilon_{\text{OH}} - 2\epsilon_{\text{H}\cdots\text{H}}$$

$2\epsilon_{\text{OHH}}$  represents the interaction energy between each water hydroxyl and cyclohexane and  $2\epsilon_{\text{OH}}$  represents the interaction energy of the water oxygen with cyclohexane.

$$\frac{\Delta E_{\text{H}_2\text{O}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} = [2(2.10) + 2(0.5) - 2(1.23)] \text{ kcal/mole}$$

The  $\epsilon_{\text{OH}}$  value is a rough estimate based on the interaction energies of various alcohols with cyclohexane.

$$\frac{\Delta E_{\text{H}_2\text{O}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} = 2.7 \text{ kcal/mole}$$

The energy required to vaporize a molecule of the complex from cyclohexane solution involves the following interactions

$$\begin{aligned} \frac{\Delta E_{\text{Et}_3\text{N}\cdot\text{H}_2\text{O}}}{\text{C}_6\text{H}_{12} \rightarrow \text{vapor}} &= 15\epsilon_{\text{HH}} + 2\epsilon_{\text{OH}} + 1\epsilon_{\text{OHH}} - 9\epsilon_{\text{H}\cdots\text{H}} \\ &= [15(1.10) + 2(0.5) + 1(2.1) - 9(1.23)] \text{ kcal/mole} \end{aligned}$$



$$\Delta E_{\text{Et}_3\text{N}\cdot\text{H}_2\text{O}} = 8.5 \text{ kcal/mole}$$

$$\text{C}_6\text{H}_{12} \rightarrow \text{vapor}$$

Incorporation of the derived energies into equation (13) yields

$$\alpha = \frac{8.5 \text{ kcal/mole}}{(9.16 + 2.7) \text{ kcal/mole}} = 0.72$$

This value of  $\alpha$  compares very favorably to 0.71 which was calculated for the 1:1 pyridine-water complex by the graphical method.<sup>99</sup>

The monomer distribution constants in equation (14) differ from those distribution constants reported in Table III. The constants in Table III represent the ratio of the formal (total) amine concentration in the organic phase to the formal concentration in the aqueous phase. Values for the monomer distribution coefficients were calculated by correcting the amine concentration in the organic phase for the amine contained in the complex and correcting the concentration in the water phase for ionization. The calculated values are given in the following table.

#### MONOMER DISTRIBUTION CONSTANTS

Solvent	(Triethylamine)	(Water)
	$K_D$	$K_D$
Benzene	16.1	0.0350
Toluene	13.1	0.0268
Cyclohexane	14.9	0.00297

$K_D(\text{water})$  values are simply the solubility of water in each solvent at unit water activity.

The calculated value of  $\alpha$  along with the experimentally determined  $K_{D,A}$  and  $K_{D,W}$  values have been incorporated into equation (14). For convenience, the distribution constants have been calculated with reference

to cyclohexane. In order to illustrate more clearly what  $K_{D,A}$  represents, consider a hypothetical ternary system composed of benzene, water, and cyclohexane in which triethylamine has been distributed among the three phases. The fact that such a system cannot be formed in no way discredits the information gleaned from such an assumption.

$C_6H_6$	$Et_3N$
-----	
$H_2O$	$Et_3N$
-----	
$C_6H_{12}$	$Et_3N$

There is a distribution constant for the triethylamine monomers between benzene and water,  $K_{D,B} = C_A^B/C_A^W$ , and also a distribution constant for the amine monomer between cyclohexane and water,  $K_{D,C} = C_A^C/C_A^W$ . At equilibrium, the amine concentration in the aqueous phase is constant so that  $K_{D,B}/K_{D,C} = C_A^B/C_A^C = K_{D,A}$ . Similar calculations provide values of  $K_{D,W}$ . These constants are calculated for each solvent (benzene and toluene in the present work) with reference to cyclohexane.

As an example of a typical calculation to predict the equilibrium constant for the triethylamine-water complex in going from cyclohexane to benzene, consider the following.

$$\frac{K_{AW}^{C_6H_6}}{K_{AW}^{C_6H_{12}}} = (K_{D,A} K_{D,W})^{\alpha-1} \quad (14)$$

The known value of  $K_{AW}^{C_6H_{12}}$  is  $7.01 M^{-1}$ . From the previous table of monomer distribution constants,

$$K_{D,A} = \frac{16.1}{14.9} = 1.08$$

$$K_{D,W} = \frac{0.0350}{0.00297} = 11.8.$$

$$\alpha = 0.72$$

Substituting into (14) and rearranging

$$K_{AW}^{C_6H_6} = 7.01 M^{-1} (1.08 (11.8))^{0.72-1}$$

or

$$\log K_{AW}^{C_6H_6} = \log 7.01 - 0.28 \log (12.73)$$

$$\log K_{AW}^{C_6H_6} = 0.533$$

$$K_{AW}^{C_6H_6} = 3.41 M^{-1}$$

This constant agrees amazingly well with the observed value of  $3.47 M^{-1}$ . Similar calculations on the toluene system yields a calculated  $K_{AW}$  of  $3.90 M^{-1}$  as compared to the observed value of  $3.72 M^{-1}$ .

#### COMPARISON OF OBSERVED $K_{AW}$ TO $K_{AW}$ CALCULATED BY $\alpha$ -THEORY

##### Triethylamine-Water Complex

Solvent	$K_{AW}$ (observed)	$K_{AW}$ (calculated)
Benzene	$3.47 \pm 0.05 M^{-1}$	$3.41 M^{-1}$
Toluene	$3.72 \pm 0.05 M^{-1}$	$3.90 M^{-1}$

The agreement between the observed and calculated equilibrium constants indicates that a single value of  $\alpha$  is sufficient to explain the effect of the three solvents, benzene, toluene, and cyclohexane on complex formation.

Recalling the rather large enhancement of the dipole moment in the triethylamine-water complex, it is interesting to make an approximate calculation of the interaction energy between this excess dipole moment and the surrounding medium. It is believed that in solvents of widely varying dielectric constant, this interaction energy would have to be

incorporated into lattice model energy calculations in order to correlate observed and predicted equilibrium constants.

According to Böttcher,<sup>106</sup> the work required to bring an unpolarizable dipole,  $\mu$ , from an infinite distance outside a dielectric to some point (not at the center of a cavity) is,

$$W = \frac{\epsilon-1}{2\epsilon+1} \frac{\mu^2}{a^3} \left[ 1 + \frac{6(2\epsilon+1)}{3\epsilon+2} \cdot \left(\frac{s}{a}\right)^2 + \frac{18(2\epsilon+1)}{4\epsilon+3} \cdot \left(\frac{s}{a}\right)^4 + \frac{40(2\epsilon+1)}{5\epsilon+4} \cdot \left(\frac{s}{a}\right)^6 + \dots \right] \quad (15)$$

where  $\mu$  is the enhancement of the dipole for this case,  $a$  is the radius of the cavity, and  $s$  is the distance of the dipole from the center of the cavity. Notice that the interaction energy is strongly dependent on the dielectric constant of the medium. Since the dielectric constants of the three solvents employed in the present work are approximately equal, this interaction energy is very nearly the same for all three solvents and, consequently, need not be considered here; however, this interaction will become important when comparing association constants determined in the vapor phase to those determined in solution.

As a rough approximation the molar volumes of triethylamine and water were calculated in order to determine a value of  $a$ . Values of 140 ml./mole for triethylamine and 18.1 ml./mole for water were added to give a total of 158.1 ml./mole for the molar volume of the complex. However, since contraction probably occurs when the triethylamine and water monomers interact, an approximate value of 150 ml./mole was used for the molar volume of the complex. This volume yields a radius of the cavity of 3.9 Å, which was used in equation (15).

An  $s$  value of 1.95 Å was introduced into equation (15), to account for the fact that a model of the complex shows the dipole to be located toward one side of the cavity rather than at the center. The dielectric

constants of all three solvents were averaged to determine an intermediate value which was close to the dielectric constant of each solvent ( $\epsilon = 2.20$  and  $s/a = 0.5$ ).

$$W = - \frac{1.2}{5.4} \cdot \frac{4.51 \times 10^{-36} \text{esu}^2 - \text{cm}^2}{59.5 \times 10^{-24} \text{cm}^3} (1 + 0.942 + 0.515 + 0.225 + \dots)$$

$$w = -1.68 \times 10^{-14} \text{erg} (2.682)$$

$$W = -4.52 \times 10^{-14} \text{erg/molecule} (6.02 \times 10^{23}/\text{mole})/4.184 \times 10^7 \text{erg/cal}$$

$$W = -650 \text{ cal/mole}$$

Although this interaction energy is not large, it probably is large enough so that it must be considered in the calculation of  $\alpha$  values in going from the vapor phase to dilute solution.

#### Dielectric Study of Amine Hydrates

The results of the dielectric study support the conclusion of the hydration study that the hydrates of the amine dimer or higher polymers are not present in significant concentrations. It is interesting to consider how the presence of species other than the 1:1 hydrate would influence the dependence of  $\Delta\epsilon$  on solute concentration. If only the 1:1 hydrate is present, the ratio  $\Delta\epsilon/\Delta fw$  (recalling from Chapter IV that  $\Delta fw = C_{AW}$ ) is given by

$$\frac{\alpha_{AW} K_{AW} C_A C_W}{K_{AW} C_A C_W}$$

where  $\alpha_{AW}$  is the proportionality constant between the concentration of the complex ( $C_{AW}$ ) and the increment in the dielectric constant contributed by this species.  $C_A$  and  $C_W$  are the concentrations of the amine and water monomers, and  $K_{AW}$  is the formation constant for the 1:1 hydrate. The slope of the  $\Delta\epsilon$  vs.  $\Delta fw$  plot is  $\alpha_{AW}$ , from which the

dipole moment is calculated. If several different hydrates of the monomer of a solute are present,  $\Delta\epsilon/\Delta fw$  will be given by

$$\frac{\alpha_{AW} K_{AW} C_A C_W + \alpha_{AW_2} K_{AW_2} C_A C_W^2 + \dots}{K_{AW} C_A C_W + 2 K_{AW_2} C_A C_W^2 + \dots}$$

where the symbols have the same meaning as above.  $K_{AW_2} \dots$  are the formation constants for the monomer dihydrate, . . . . Since  $C_A$  is present to the first power in each term in the numerator and denominator, the ratio  $\Delta\epsilon/\Delta fw$  is constant at fixed water activity. Therefore, in spite of the fact that any number of distinct hydrates of the monomer are present, a plot of  $\Delta\epsilon$  vs.  $\Delta fw$  will be linear.

On the other hand, if a hydrate of the dimer (or other polymeric species of the polar solute) exists in addition to the hydrates of the monomer, curvature is expected in a plot of  $\Delta\epsilon$  against  $\Delta fw$ . For example, if only the 1:1 and 2:1 hydrates exist (which seem to be the predominant species mentioned in the literature),

$$\Delta\epsilon/\Delta fw = \frac{\alpha_{AW} K_{AW} C_A C_W + \alpha_{A_2W} K_{A_2W} C_A^2 C_W}{K_{AW} C_A C_W + K_{A_2W} C_A^2 C_W}$$

or dividing out common terms

$$\Delta\epsilon/\Delta fw = \frac{\alpha_{AW} K_{AW} + \alpha_{A_2W} K_{A_2W} C_A}{K_{AW} + K_{A_2W} C_A}$$

Except in the unique case where each complex species contributes an equal increment to the dielectric constant ( $\alpha_{AW} = \alpha_{A_2W}$ ), the ratio will depend on  $C_A$  and hence upon  $\Delta fw$ . (When  $\alpha_{AW} = \alpha_{A_2W}$ ,  $\Delta\epsilon/\Delta fw$  reduces to  $\alpha_{AW}$  and no curvature would be observed.) Therefore, the linearity of the  $\Delta\epsilon$  vs.  $\Delta fw$  plots are consistent with the conclusion of the hydration

study that hydrates of the polymeric amine species are not present in significant concentrations. It must nonetheless be recognized that the dielectric results at unit water activity do not by themselves preclude the possibility that polyhydrates of the amine monomer exist.

The method for calculating the dipole moments of the amine hydrates is a simple, straightforward calculation using a form of the Clausius-Mosotti equation as derived by Onsager.<sup>72</sup> This method is subject to the constraints and assumptions involved in the derivation (see Chapter IV) and in dilute solution these conditions seem to be present. Strictly speaking only the polarizations caused by different constituents are additive; however, increments in the dielectric constant caused by each solute species seem to present a valid approximation for the polarization effects.

The common methods available for the determination of the dipole moment of a complex are basically similar. Generally, the dielectric polarization of the mixture is compared to the dielectric polarization of solutions of the individual components. From a study of the changes in the dielectric data, the existence of a complex along with its dipole moment can be determined. In a typical study of this type Cleverdon, Collins, and Smith<sup>41</sup> have determined both the equilibrium constant and dipole moment of three pyridine-alcohol complexes. The method employed by these authors is mathematically sound; however, the extent of association between pyridine and the alcohols must be within certain limits before reliable results may be obtained. The problems involved in this technique are similar in many respects to those encountered with the Benesi-Hildebrand<sup>107</sup> or Scott<sup>108</sup> methods for the determination of

equilibrium constants and absorptivities of complexes from spectral data alone. The method will give reasonable results for the equilibrium constants so long as the extent of association lies between 20 and 80%.<sup>109</sup> If the extent of complexation is not within these limits, the graphical or numerical techniques from which the equilibrium constant and dipole moment are calculated become very insensitive, and at approximately 0 or 100% complexation the methods will not yield any result at all. Basically, the problem is the determination of two parameters from only one type of data. In the present investigation this problem has been eliminated by determining the equilibrium constants by an independent method and using the dielectric data for determining only the dipole moment of the complex. In this way only one parameter is determined from each independent set of data. Most of the problems dealt with in this laboratory have been approached with this consideration in mind.

The dipole moments calculated for the amine-water complexes are in good agreement with those calculated previously for amine complexes. Kazakova and Fel'dshtein,<sup>45</sup> in the only paper found in the literature concerning the dipole moments of amine hydrates, have determined the dipole moment of the triethylamine-water complex to be 2.24 D. By employing a model of the complex similar to the one used in this investigation, an enhancement of the dipole moment of 0.43 D. was reported. This value is considerably lower than that found here (1.07 D.); however, the enhancement reported here is probably somewhat high due to the low value determined for the dipole moment of the triethylamine monomer. The dipole moment of the amine monomer was found to be approximately 0.25 D. lower than the value used by the above authors in the calculated value of the



dipole moment. This discrepancy is reflected only in the  $\Delta\mu$  value and not in the absolute dipole moment of the complex found in this study (2.64 D.). The previously mentioned authors have also determined the dipole moment of the pyridine-water complex. A moment of 3.13 D. was determined as compared to the calculated value of 3.25 D. Unfortunately not enough information is given to show how the dipole moments of the complexes were experimentally determined. The pyridine-water complex is described as dipole-dipole association, while the triethylamine-water bond, being more polar, is called a hydrogen bond.

The dipole moment of the pyrrole-triethylamine complex has been calculated to be 3.10 D., although no information is available about the enhancement of the dipole moment due to complex formation.<sup>44</sup> Hulett, Pegg, and Sutton<sup>43</sup> have determined  $\Delta\mu$  for trimethylamine complexed with phenol, p-chlorophenol, and p-cresol. The reported enhancements are 1.00 D., 1.26 D., and 0.91 D., respectively. A table of the dipole moments of several amine complexes is presented in Chapter IV. These moments are all in the range reported for the amine-water complexes in this study. Charge separation in amine complexes has been reported previously; however, virtually no data have been reported concerning the amine-water interaction.

It has been concluded from this study that the dielectric method should be used more widely than it presently is in inferring the geometry and charge distribution of complexes. However, it is believed that reasonable conclusions can be drawn only if equilibrium constants and stoichiometries of association reactions are known from spectral or classical studies before attempts are made to interpret dielectric results.

Suggested Studies

There are several areas which may be investigated that would elucidate more fully the nature of the amine-water interaction. A study of several amines with widely varying pKa values should yield valuable information concerning the relation between reaction parameters and the pKa of the amines. In order to test further the applicability of the  $\alpha$ -theory to the solvation of amine hydrates, it would be interesting to determine the extent of association between amines and water in several solvents of varying dielectric constant. A study of this nature would be complicated by the problem of employing chlorinated solvents, such as  $\text{CCl}_4$ , ethylenedichloride, or trichloropropane, which are known to interact with aliphatic amines.

A determination of the effect that various substituents in amine molecules have on the association equilibria should yield valuable information. One interesting area of study in which very little information is available is the determination of molar volumes of complexes. Certainly the aliphatic amine-water complexes present a simple system (1:1 hydrate), from which the molar volumes could be determined without the interference of other complex species. Probably a dilatometric method would be preferable to density determinations since the density change upon complexation would be very small. It is granted that the volume change would also be small; however, this change should be measurable with a capillary. By knowing the molar volumes of the complexes, the interaction energies between the enhanced dipoles and the solvent might be more accurately calculated.

It could be interesting to determine the amount of extra charge residing on the nitrogen and oxygen atoms (assuming that all the excess

charge resides on these atoms). In order to make a crude calculation, the length of the N---H---O bond would have to be measured or estimated from previous data. The extra charge on each atom could then be found by setting the enhancement of the dipole equal to the bond distance times the charge on each atom.

$$\begin{aligned}\mu_{\text{excess}} &= (\text{bond distance})(\text{excess charge}) \\ \text{excess charge} &= \frac{\mu_{\text{excess}}}{\text{bond distance}}\end{aligned}$$

Future workers would perhaps want to determine the additional charge on each atom experimentally. In this case an appropriate experimental procedure would have to be found.

#### Brief Summary

The extent of association of water with four aliphatic amines (cyclohexylamine, N-methylcyclohexylamine, N,N-dimethylcyclohexylamine, and triethylamine) in several organic solvents has been determined. In each system the water solubility and partition data have been interpreted in terms of the formation of 1:1 hydrates which exist in equilibrium with the water and amine monomers. The cyclohexylamines have been studied in benzene at 25 and 35°; triethylamine has been investigated in benzene, toluene, and cyclohexane at 25°. Thermodynamic constants have been reported for the cyclohexylamines. Equilibrium constants were found to decrease from primary to secondary to tertiary amine; since the pKa's of the amines are approximately equal, the decrease is attributed to steric hindrance rather than electronic effects.

The variation of the equilibrium constant for the formation of the triethylamine-water complex in going from cyclohexane to benzene to toluene has been interpreted by means of a solvation theory developed

by Christian, et al.<sup>98</sup> The theory appears to do an excellent job in predicting the effect which a change in solvent will have on the association constant.

The dipole moments of each of the amine-water complexes have been determined from dielectric measurements. A comparison of the observed dipole moment with the dipole moment calculated from a reasonable model of the complex reveals that a partial charge separation exists in each of the complexes. The extent of charge separation (in Debye units) has been reported. A rough approximation of the interaction energy between the increase in the dipole moment due to complexation and solvents has been calculated to be about -650 cal/mole.

The data reported in this dissertation appear to be the first concerning aliphatic amine-water interactions in dilute non-aqueous solution. Previous investigators have limited their attempts to infer hydration constants of amines to studies of aqueous solutions.

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