

72-3418

MORROW, John Karl, 1941-
HYDROGEN BOND COMPLEXES OF 2-NAPHTHOL
AND WATER IN ORGANIC SOLVENTS.

The University of Oklahoma, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

THE UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

HYDROGEN BOND COMPLEXES OF 2-NAPHTHOL
AND WATER IN ORGANIC SOLVENTS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
JOHN KARL MORROW
Norman, Oklahoma

1971

HYDROGEN BOND COMPLEXES OF 2-NAPHTHOL
AND WATER IN ORGANIC SOLVENTS

APPROVED BY

Sheril D. Christian

Stanley E. Babh t.

Alfred J. Jellison

Stanley C. Reed

Arnold P. Hagen

DISSERTATION COMMITTEE

PLEASE NOTE:

**Some Pages have indistinct
print. Filmed as received.**

UNIVERSITY MICROFILMS

ACKNOWLEDGEMENT

The author wishes to express his appreciation and thanks to the following people:

Dr. Sherril D. Christian for his helpful suggestions and guidance throughout the course of this research.

Dr. Friedrich Kohler and the late Dr. Harold E. Affsprung for their help during the initial stages of his graduate studies.

Miss Alice Rosen for her assistance in obtaining the water solubility data, Mr. Ron Stermer for construction and installation of the vapor pressure lowering apparatus, Mr. Ronald L. Lynch for the use of the improved equilibration cells and Dr. Sutton Burns Farnham and Dr. Eric Enwall for helpful suggestions concerning computer programming.

The National Aeronautics and Space Administration for a one year Traineeship, and the Department of the Interior, Office of Saline Water and the National Science Foundation for funds to support this research.

Finally to the faculty and fellow graduate students for their helpful discussions, encouragement, and sincere friendship.

TABLE OF CONTENTS

LIST OF TABLES.	v
LIST OF ILLUSTRATIONS	vii
Chapter	
I. INTRODUCTION	1
II. EXPERIMENTAL	20
III. DATA TREATMENT AND CALCULATIONS.	29
IV. RESULTS AND DATA INTERPRETATION.	45
V. DISCUSSION AND CONCLUSIONS	101
BIBLIOGRAPHY.	143

LIST OF TABLES

Table	Page
1. Vapor Pressure Lowering Trial Species.	47
2. Comparison of fit for Various Hydration Equilibrium Constants.	51
3. Vapor Pressure Lowering Data for the 2-Naphthol-Carbon Tetrachloride System at 25°C	59-60
4. Vapor Pressure Lowering Data for the 2-Naphthol-Benzene System at 25°C.	61-62
5. Vapor Pressure Lowering Data for the 2-Naphthol- 1,2 Dichloroethane System at 25°C	63-65
6. Water Solubility Data for the 2-Naphthol- Carbon Tetrachloride System.	75
7. 2-Naphthol and Water Solubility Data for the Carbon Tetrachloride System.	76
8. Distribution Data for the 2-Naphthol-Water- Carbon Tetrachloride System.	77
9. Water Solubility Data for the 2-Naphthol- Benzene System	78
10. 2-Naphthol and Water Solubility Data for the Benzene System	79
11. Distribution Data for the 2-Naphthol- Benzene System	80
12. Water Solubility Data for the 2-Naphthol- 1,2 Dichloroethane System.	81

Table	Page
13. 2-Naphthol and Water Solubility Data for the 1,2 Dichloroethane System.	83
14. Distribution Data for the 2-Naphthol-1,2 Dichloroethane System.	84
15. Self-Association Constants and Hydration Constants for 2-Naphthol in CCl ₄	87
16. Self-Association and Hydration Constants for 2-Naphthol in Benzene.	87
17. Self-Association and Hydration Constants for 2-Naphthol in 1,2 Dichloroethane	87
18. Absorbance of Self-Association Peak in CCl ₄	94
19. Absorbance of Self-Association Peak in Benzene.	95
20. Absorbance of Self-Association Peak in 1,2 Dichloroethane	96
21. Absorbance at 3455 cm ⁻¹ due to Hydrated 2-Naphthol in Carbon Tetrachloride	97
22. Absorbance at 3388 cm ⁻¹ due to Hydrated 2-Naphthol in Benzene.	98
23. Absorbance at 3374 cm ⁻¹ due to Hydrated 2-Naphthol in 1,2 Dichloroethane	99
24. Summary of Results for 2-Naphthol and 2-Naphthol-Water Complexes at 25°C.	113
25. Spectral Results for 2-Naphthol Systems.	116
26. Comparison of Integrated Intensities	125
27. Spectral Properties for Bellamy Plots.	133

LIST OF ILLUSTRATIONS

Figure	Page
1. Vapor Pressure Lowering Apparatus.	22
2. Self-Association Peak Maximum in Dichloro- ethane and Benzene	26
3. Vapor Pressure Lowering Results for the 2-Naphthol CCl ₄ System	56
4. Vapor Pressure Lowering Results for the 2-Naphthol Benzene System.	57
5. Vapor Pressure Lowering Results for the 2-Naphthol Dichloroethane System	58
6. Hydration of 2-Naphthol in Carbon Tetra- chloride	66
7. Difference in Water Solubility at Satur- ated 2-Naphthol Concentration in CCl ₄	67
8. Difference in 2-Naphthol Solubility with Increasing Water Activity in CCl ₄	68
9. Hydration of 2-Naphthol in Benzene	69
10. Difference in Water Solubility at Satur- ated 2-Naphthol Concentration in Benzene	70
11. Difference in 2-Naphthol Solubility with Increasing Water Activity in Benzene	71
12. Hydration of 2-Naphthol in 1,2 Dichloro- ethane	72
13. Difference in Water Solubility at Saturated 2-Naphthol Concentration in 1,2 Dichloroethane	73

Figure	Page
14. Difference in 2-Naphthol Solubility with Increasing Water Activity in 1,2 Dichloroethane.	74
15. Distribution of 2-Naphthol between H ₂ O and CCl ₄	84
16. Distribution of 2-Naphthol between H ₂ O and Benzene	85
17. Distribution of 2-Naphthol between H ₂ O and 1,2 Dichloroethane.	86
18. Infrared Study of Self-Association of 2-Naphthol in CCl ₄	88
19. Infrared Study of Self-Association of 2-Naphthol in Benzene	89
20. Infrared Study of Self-Association of 2-Naphthol in 1,2 Dichloroethane.	90
21. Absorbance at 3455 cm ⁻¹ due to Hydrated 2-Naphthol in Carbon Tetrachloride.	91
22. Absorbance at 3388 cm ⁻¹ due to Hydrated 2-Naphthol in Benzene	92
23. Absorbance at 3374 cm ⁻¹ due to Hydrated 2-Naphthol in 1,2 Dichloroethane.	93
24. Difference Spectrum of Hydrated 2-Naphthol in CCl ₄	100
25. log K vs. Frequency shift Plot for Distribution and Trimerization Constants.	123
26. Peak Half-Width vs. Frequency Shift	126
27. 2-Naphthol vs. Phenol Monomer Peak Half-Width	127
28. Solvent G vs. Frequency Shift Plot for All Solvents.	130
29. Bellamy Plot of Monomer Frequency Shift	134
30. Bellamy Plot of Monomer vs. Trimer for 2-Naphthol in All Three Solvents.	135

HYDROGEN BOND COMPLEXES OF 2-NAPHTHOL
AND WATER IN ORGANIC SOLVENTS

CHAPTER I

INTRODUCTION

"The forces of attraction and repulsion which determine the solubility of one species of molecule in the liquid or solid phase of another control every kind of phase equilibrium between two or more components." This statement, made in 1948 by Hildebrand and Scott (1) serves as an introduction to this study. The forces of attraction and repulsion, which are the factors influencing not only solubility, but every physical property of liquids as well as solutions, are still the subject of interest and controversy today. It is felt that explanations and predictions of liquid and solution properties can be advanced by the experimental studies of solute properties and solvent effects described in this work.

Current interest in this topic is revealed not only by current literature, but also by the recent publication of books concerning solution properties including Spectrometry

of Fuels (2) and Regular and Related Solutions (3) in which Hildebrand states "New experimental results and new ideas have impelled us to write a considerably altered and in places greatly amplified book."

Molecular models, lattice theories of dilute solutions, dielectric theories, interaction theories, and regular solution theory require information that will further insight into the complex behavior of liquids in solutions. With increased understanding of solute and liquid behavior, the time approaches when a comprehensive theory of liquids will allow us to predict behavior of solutions used in complex biological systems, including the effects of pollutants on large macroscopic systems. For a shorter range view, however, a complete explanation of how and what forces interact to produce the observed properties of solutions is being sought.

Hydrogen bonding is one such interaction that is of interest. Hydrogen bonded complexes of alcohols and phenols have been under study for several years; Pimentel and McClellan (4) have presented a good review of work prior to 1959. Since then several review articles on the subject have been written (5, 30, 37). Most recently several pertinent papers have appeared on the subject. Much of the material in those to be discussed has a bearing on this study, in that many attempts have been made to study water and solute interactions by a variety of methods.

This research was undertaken to attempt to describe in detail a simpler system than that of phenol, which has

been widely studied with limited results due to its greater polymerization.

While debate over complexation of phenol in dilute solutions still continues (vide infra) it was decided that other phenolic molecules could be studied to gain evidence of associated species that may or may not support models of phenol itself. Johnson (6) has shown that phenol exists as trimers in organic solvents. Additional evidence of this type of association was sought through the study of a larger molecule having limited solubility in several solvents.

If the same type of association did not occur, its absence could not be construed as evidence against the phenol results. Results for the phenol systems have proven to be difficult to explain and models of several types have been presented in analysis of the data. These differing models made it difficult to use the data in tests of solvation theories. The present work, then, was undertaken in the hope that an investigation of the 2-naphthol system would lead to a more clear-cut model, and would provide the basis for a general model applicable to the association of aromatic alcohols in non-polar solvents.

The experiments under consideration here were performed on dilute solutions; they provided the basis for characterizing the properties of the systems 2-naphthol and 2-naphthol-water according to current dilute solution theories. In addition, studies of the naphthol systems,

which have limited solubilities in nonpolar solvents, provide additional data aiding the study of hydration in solution.

This type of study is dependent on the observation that the solubility of naphthol in certain solvents increases significantly with increasing water activity. This observation has been used in studying salicylic acid systems by Van Duyne (8). The advantage to be gained by using the solubility property of naphthol is that it provides additional information for use in elucidating the stoichiometry of the hydration processes. Finally, by studying the thermodynamics of hydrogen bonding reactions in solvents of differing dielectric constant (as in this study) information about solvent effects on these complexes can be obtained. There follows a discussion of some of the work done previously on phenols, naphthols, water and solvent effects. Also, a description of the objectives of this dissertation is included.

Phenols

Phenol has been studied by Johnson (6) who has found that different sets of association species are needed to explain the properties of dilute solutions in different solvents. In carbon tetrachloride (CCl_4) he calculated equilibria involving PW , P_3 , P_3W , P_3W_2 , P_6 , and P_6W_3 where PW symbolizes a 1:1 phenol-water complex etc. In benzene and 1,1,2,2, tetrachloroethane he found it necessary to postulate only one hydrated species, PW_2 and two anhydrous species, the dimer and trimer. The same species were postulated for

1,2 dichloroethane (DCE) except that of the phenol trimer, because even when included in the fit, the trimer had an insignificant concentration and consequently a very low K_{eq} .

Studies of phenol continue; one of the more recent is that of Whetsel and Lady (2) on the self-association of phenol in CCl_4 and cyclohexane. They consider several possible models, each of which gives an adequate representation of the data. However, they conclude that their results do not support one and two parameter models. They feel that the one-and two-parameter models actually correspond to self-association in a stepwise manner with one or more stepwise constants being very much larger than the others. Their attempts to fit the data to this type of model (using one or two large K 's plus smaller K 's) always gave negative values for at least one constant. Therefore, they did not seriously consider the one and two parameter fits and tested only the dimer stepwise n -mer and the dimer-trimer-stepwise n -mer over ranges of temperature.

It should be pointed out that there is no physical explanation for negative equilibrium constants; their occurrence implies an imbalance in mathematical treatment due to an incorrect set of postulated species or to systematic errors in one or more measurements. Whetsel and Lady's experimental procedure was to make absorbance measurements at a single frequency, that of the monomer peak, and to correct them for end-group absorbance. If they had further tested

their models by fitting the absorbance of the dimer and higher polymer peaks, in a manner similar to that suggested by Wojtkowiak (8) they could possibly have eliminated various models from consideration. It may have been difficult, however, to do such a study on this system due to overlap of the polymeric peaks.

Wojtkowiak proposed studies of self-association at both the free hydrogen stretching frequency and the bonded hydrogen stretching frequency. From the absorbances at both of these frequencies and from equations based on validity of the law of chemical equilibrium (see discussion in Chapter III, below) the equilibrium constant for self-association can be more accurately determined. This approach would be more valuable when attempting to fit different polymers using only the spectral data. While the number of studies where the two peaks are easily separated may not be large, there are several where this approach could be more valuable than studying only the concentration dependence of the monomer peak. For the infrared study to be presented here, the concentration dependence of the association peak only was studied, since the equilibrium constants had been previously determined by vapor pressure lowering and hydration studies.

Another investigation into the self-association of phenol in CCl_4 has just been completed by E. M. Wooley, et al. (9). These authors used distribution and calorimetric measurements and arrived at a different conclusion than that of

the infrared study by Whetsel and Lady. They propose that the principal association reaction of phenol in CCl_4 is trimerization, whether the CCl_4 is anhydrous or saturated with H_2O . They do not consider any hydrated species in interpreting their distribution results, but they do mention evidence by Johnson, Christian, and Affsprung (10) that such interactions play an important role in ternary solutions.

The result of not considering hydrated species is that in the same solvent at the same temperature they report two different values of K_3 : one for the anhydrous solution, $K_3=4.9 \text{ M}^{-1}$ and for the water saturated solution, $K_3=14.9 \text{ M}^{-1}$. Their evidence supports their conclusions concerning associated species, but they do not explain that the thermodynamic data for the association reaction are essentially combined K 's and ΔH 's. This equilibrium constant is a function of the anhydrous trimerization constant and the hydration constants for all hydrates that are dependent on the third order of monomer phenol concentration. This is the cause of the differing values for K_3 . They do explain that their value of K_D does not represent the monomer distribution constant, however, and use the value of Johnson et al. (10) (which had been corrected for hydration of phenol) for further calculations.

Other methods of studying self-association of phenol include the cryoscopic method used by Vanderbough, Armstrong, and Spall (11). They postulated that both a dimer and trimer species exist in benzene. They interpreted their data by

assuming that deviations of observed concentration from analytical concentration are due predominately to dimeric species in dilute solutions. Then at greater concentrations (up to about 0.8 Molar) they found it necessary to add the trimer species. They report that in no cases were association constants higher than trimerization necessary. However, they do not mention any attempts to fit the data with only a trimer constant even though one criterion of best fit they listed was that the least number of equilibrium constants necessary to describe the data be used. Also, there are no error parameters given for their constants since the fitting technique was entirely graphical.

Gramstad and Becker (12) have recently studied self-association and hydrogen bonding of phenol with carboxyl and phosphoryl compounds by NMR in CCl_4 and cyclohexane and have discussed the possibility of a 2:1 phenol: acceptor complex in addition to 1:1 phenol:acceptor complex. They also discuss the observation that there is a linear relation between the NMR chemical shift and shifts of stretching frequency for O-H bonds in IR spectra.

Naphthols

Specific studies of interactions of 2-naphthol have been presented by Wolf and Metzger (13). They used boiling point elevation in benzene to determine K 's and ΔH 's of mono- and dicarboxylic acids and 2-naphthol. They reported K 's based on assumptions of monomer-dimer equilibrium only.

The crystal structure of 2-naphthol was determined by Watson and Margreaves (14) who found that the molecules in the crystals formed a non-centrosymmetric structure, with every molecule attached by hydrogen bonds to two neighbors. These were linked into chains with adjacent molecules in chains being crystallographically non-equivalent. Although structure in crystals is frequently different than structure in solutions, this crystal structure indicated that 2-naphthol can be effective as both a proton donor and an acceptor.

Van Gemert (15) presented a comparison of phenol with naphthols from an infrared study of the solid and solutions of 2-naphthol over the frequency range of $1600-900\text{ cm}^{-1}$. He found that in 2-naphthol, as in phenol, the in-plane deformation that occurs near 1180 cm^{-1} is shifted to about 1200 cm^{-1} . The shift was assumed to be due to self-association through hydrogen bonding, but no model was specifically suggested.

Other studies on 2-naphthol alone have been done with NMR and dielectric relaxation techniques. An NMR study of 2-naphthol in dimethyl sulfoxide (DMSO) and CCl_4 was reported by Socrates (16). He observed that the chemical shifts for 2-naphthol are slightly greater than for phenol in both solvents. Socrates proposes a linear correlation between this shift and the pK_a for fifty-five aromatic compounds. There is a good correlation using DMSO as a solvent, but the correlation is poor when CCl_4 is the solvent. The chemical shifts that he reports are the values extrapolated to infinite

dilution, since chemical shift has a concentration effect caused by self-association. Comparison of the shifts of the O-H proton of 2-naphthol in DMSO with that in CCl_4 shows that the chemical shift is larger in DMSO. This can be interpreted as evidence that more complexation occurs in DMSO than in CCl_4 . Socrates states that the complexation that is occurring in infinitely dilute solution is in the form of a 1 to 1 complex with the solvent. He also explains that the better correlation of chemical shifts with pK_a for the DMSO solvent is due to the polar solvent's similarity to "that in which the dissociation constants were determined," or water.

Relaxation studies on complex dielectric constants by the waveguide method were done on 2-naphthol by Lutskii and Tromza (17). They believe that the basic relaxation phenomena arise not from the breaking of hydrogen bonds, but because of deformational rotations of inner chain molecules together with a distortion of two hydrogen bonds. This could be interpreted as evidence that strong hydrogen bonds exist in 2-naphthol.

The investigations that can give evidence concerning self-association of 2-naphthol are limited; much more evidence concerning hetero-association complexes of 2-naphthol exists.

Using calorimetric techniques, Neerinck, et al. (18) studied complexation of 2-naphthol with triethylamine in toluene. They discussed a new method of data treatment to arrive at equilibrium constants, and compared their calculations with those done using the simpler equations proposed by

Bolles and Drago (19). For complexes having small equilibrium constants, their calculated values agreed well with those obtained by the earlier method, but divergence became apparent at higher values for K_{eq} . By basing their equation on the Van't Hoff relation they have a more sound theoretical basis; however, their results are not compared with spectrophotometrically determined K's. The Bolles-Drago method agrees fairly well with spectrophotometric methods. There was divergence between the K's calculated by the Bolles-Drago method and those calculated by the method proposed by Neerinck, et al. This divergence is claimed to be due to a greater lack of precision of both methods in the concentration range used. It would have been, perhaps, more fruitful to compare these K values with K's determined by an independent method since the Bolles-Drago method is weak within the same concentration range as this method.

Ghosh and Basu (20) have also studied 1:1 complexes, reporting on the interaction of 2-naphthol with benzene, toluene, and p-xylene in n-heptane by IR (infrared spectroscopy). They later report the results of a study of the same systems by fluorescence spectroscopy (21). In this latter case, all equilibrium constants came out higher. They attributed this to the stronger proton donor character of 2-naphthol in the excited state. A similar study done by Szczepaniak et al. (22) reports data for phenols and 1-naphthol only, but their K's from an IR study are higher than

those of Ghosh and Basu for 1-naphthol and phenols. This could be due to the difference in calculations, since Szczepaniak et al. corrected for end group absorption while Ghosh and Basu did not.

Another fluorimetric study was done on proton photo-transfer in non-aqueous solutions by Kuzmin, et al. (23). Spectral and fluorimetric studies of 2-naphthol and diethylamine show that in the excited state a hydrogen bond complex between two molecules exists in cyclohexane, while ion pairs are formed in benzene, and dissociated ions are formed in ethanol. Fluorescence studies have also been done by Mataga, et al. (24) for complexes of 2-naphthol with various acetates in n-hexane.

Reports of 1:1 complexes of 1-naphthol with aldehydes have been made by Kuksina, et al. (25) and Ushkalova, et al. (26). The information available indicates that the equilibrium constants reported by Kuksina, et al. for complex formation between an aldehyde and phenol are about equal to those of 1-naphthol, but that all complexes with 1-naphthol had lower K's. Also only one complex (benzaldehyde-1-naphthol) gave evidence of additional complexes of 1:2 stoichiometry.

Other 1:1 complexes have been shown to exist by Kubota (27). He studied 2-naphthol and trimethylamine N-oxide and found a $K=6560 \text{ M}^{-1}$ at 20.5°C in dichloromethane. He reports a $K=54.4 \text{ M}^{-1}$ for the complex with triethylamine (TEA) in the same solvent. He also discusses the ultraviolet (UV)

spectra of the systems and compares his value for the TEA complex constant with the higher ones reported earlier for n-heptane as a solvent. The solvent effect and spectral shifts of 1- and 2-naphthols complexing with TEA, ether and nitromethane were reported by Nagakura and Gouterman (28). Their study utilized UV spectra with n-heptane as a solvent. For the 2-naphthol-TEA complex they report a $K=103 \text{ M}^{-1}$. Kubota, however, points out that his K's are of the same magnitude as those for phenol-TEA complexes studies in benzene by Mataga, et al. (24).

A study of 1:1 complexes of 2-naphthol and alcohols was reported by Kirshunov and Pakhovnov (29). They gave equilibrium constants for 2-naphthol with butyl alcohol, amyl alcohol, and hexanol. The data were gathered from a distribution study in which 2-naphthol was distributed between solid naphthalene and octane solutions of alcohol.

In addition to studies of various complexes of 2-naphthol, there have been several studies of interest concerning the behavior of water in organic solvents. Although there have been no published reports of water-naphthol complexes, some studies of H_2O behavior have been done.

Water

A method frequently used to study the self-association of a solute is partition between water and organic solvents. To accurately study the partition of monomer species, it is important to have knowledge of the behavior of water and

hydration of the solute in the organic phase. A review of the behavior of water as a solute has been given by Christian, Taka, and Gash (30). Information concerning the behavior of water in solvents used in this study was obtained from the results of Johnson (6).

Earlier studies have been done by Greinacher, Luttke, and Mecke (31) who conducted an IR investigation of water in organic solvents. They presented the spectra of H_2O in CCl_4 and benzene, among other solvents. They discussed the frequency shift as a function of dielectric constant of the solvent. A study of the relationship between activity and concentration of water in benzene, $CHCl_3$, and 1,2 dichloroethane (DCE) was conducted by Masterton and Gendrano (32). They found no evidence for association in benzene, but found it necessary to postulate a dimer in DCE and $CHCl_3$. They report a dimerization constant for H_2O in DCE of $0.54 M^{-1}$. They feel that there is no significant difference between the RMSD (root-mean-square deviation) of the dimer fit and the trimer or tetramer fit.

More recently, Joliceur and Cabana (33) discuss an IR study of water dissolved in DCE. Based on a linear relation of intensity of the shoulder with the third parameter of water concentration, they infer that trimers are the main polymeric species in these solutions.

Currently, Magnusson (34) has discovered apparent association of water in CCl_4 by IR techniques. His experimental

technique involved taking a differential spectrum through two cells of differing pathlength. Magnusson did not do a quantitative study, however, and was only able to give an estimate of a dimerization constant. Calculations show that the associated species comprise only about 3.6% of the water at saturation. Since he only gives an approximate value of $K_2=2.2 \text{ M}^{-1}$, further studies would be necessary on this system to determine the true extent of association.

Saugmagne (35) has reported on a comparison of the water dimer with 1:1 complexes of water and solutes or solvents. He shows that a linear relationship exists between frequency of the association and of the free O-H group in a complex water molecule. He points out that the frequency shifts reported in solid matrix isolation studies (36) agree with his earlier results of complexed water.

Infrared studies of water-solute complexes are discussed in the review article by Murthy and Rao (37). In addition other properties have been studied to obtain information about water-solute interactions. Recently, Reeves and Yue (38) have presented a paper on molecular association of water and acetone. They used nuclear spin-lattice relaxation techniques and required two interaction parameters to explain their data.

After correction for non-ideal behavior of water in a solvent has been made, the hydration of a solute can be taken into account. The techniques used to study complexes of water

mentioned in the paper above can be used to study hydration in organic solvents. With hydration and, as in this study, self-association information available, distribution constants for solute monomers can be determined for several solvents. It is these distribution constants which can provide additional information concerning solvent effects on hydrogen bonding.

Solvent Effects

Solvent effects generally come into consideration when comparisons are made of thermodynamic data obtained in various media. These data generally differ from one solvent to another and also differ from results obtained in the vapor phase. Investigations of solvent effects on molecular complex formation will aid in characterizing dilute solution properties, insofar as an understanding of these effects will promote a better idea of interactions in the liquid phase. A discussion of several studies on solvent effects follows.

A specific study of solvent effects in infrared spectroscopic studies of hydrogen bonding was done in 1962 by Allerhand and Schleyer (39). They studied the frequency shift of hydrogen bonded complexes in eleven organic solvents of varying dielectric constants. In interpreting their data they found that the solvent shifts of the O-H...O bands were proportional to the solvent shifts of a C=O bond. This indicated to them that there was a similarity in the mode of interaction of solvent with these groups. Tests of various dielectric

equations did not adequately explain the observed results of concentration dependence in some systems. They proposed an empirical relationship that was dependent on a "solvent shift parameter." A number of complexes gave poor correlations and reasons for this were discussed.

In a later paper Bellamy, Morgan, and Pace (40) presented an alternate explanation of the concentration dependence noted by Allerhand and Schleyer (39). They also discussed differences in solvent shifts for the methanol and phenol complexes with ether. Their explanation involves assumption of a "complex" of a solvent molecule with the existing complex of alcohol-ether. Their view is that the frequency shift is due to changes in the character of both terminal atoms. They do not consider solvent effects of acceptor solvents however, since these effects would not be explained by their theory unless there existed a free O-H group.

Changes in IR frequency shift for a series of adducts with substituted phenols were discussed recently by Drago and Epley (41). They claim that for an inert solvent the ΔH values should approach that of the gas phase reaction. They note that a solvent effect is seen in the K_{eq} value in CCl_4 and cyclohexane solvents.

Other solvent effects are discussed in the IR review article by Murthy and Rao (37). NMR studies of molecular complexes of trinitrobenzene with sulfoxides by Carper, Buess,

and Hipp (42) suggest that CCl_4 is the least interfering solvent of those studied (CS_2 , DCE, and CCl_4). They noted interaction of some sulfoxides with DCE and examined complexes of these two molecules in CCl_4 . Unfortunately, a weakness in their report is that the authors assumed that the constants obtained in CCl_4 would be valid in pure DCE (1,2 dichloroethane) (where multiple interactions certainly occur) and "corrected" those equilibrium constants obtained in DCE with their K for complexes of sulfoxides with DCE obtained in CCl_4 .

A study of mixed solvent interactions on carboxylic acids was done by Lahini and Aditaja (43). They tabulate a function of ΔG of interaction, but neglect the ΔG of transfer from one solvent to another. Davies (44) has discussed the influence of hydrogen bonding between polar molecules on dielectric constants of nonpolar solvent solutions. Also, Ryzhov (45) has discussed the role of the solvent during complexing. He studied the effect of solvents on stability of aldehyde-ketone complexes. He reports that the stability of several complexes in acetic acid is 10-15 times less than in CCl_4 . The stability of the same complexes in CCl_4 is 10-15 times less than in cyclohexane. The net result of his studies is that stabilities in HOAc are 200 times less than in benzene.

In general, solvent effects perform an important role in determining the extent of complex formation in solution.

The contributions discussed in this chapter have all pertained to the dilute solution. Studies of solutions of phenol, 2-naphthol, and water and studies of solvent effect have been done using various techniques. The work presented here was undertaken to accomplish the objectives presented below.

Objectives

To understand the interaction of solutes to produce the observed properties of solutions, information concerning different types of solutes is sought.

Specifically, the objectives of this research were: first, to determine the self-association of 2-naphthol in solvents of varied reactivities (DCE, benzene and CCl_4); second, to study the hydration and distribution of 2-naphthol with the same solvents and water; third, to calculate equilibrium constants for the molecular complexes formed in solution; fourth, to study the self-association using infrared spectroscopy, and fifth, to study the hydration by infrared spectroscopy to determine if the results inferred from the above experiments could be supported by these independent measurements.

CHAPTER II

EXPERIMENTAL

General

The 2-naphthol used in the experiments was a product supplied by Eastman Organic Chemicals and was cream colored when received. A product of similar specifications was obtained from Fischer Scientific Co. but was light brown and consisted of very dense particles and therefore was not used. The 2-naphthol from Eastman was recrystallized twice from distilled benzene and placed in a vacuum desiccator. The desiccator was evacuated and continuously pumped out for about thirty minutes or until all traces of benzene were removed. It was then stored in a dark brown bottle; no evidence of subsequent decomposition or hydration was discovered.

Reagent grade benzene, dichloroethane (DCE) and carbon tetrachloride (CCl_4) were purified by distillation through a 30 plate Oldershaw column. The CCl_4 and benzene were distilled from drierite and the DCE was distilled from CaH_2 . A reflux ratio of 10:1 was used for all distillations. The middle fraction of each distillation was taken in each case and had a boiling point range of less than 0.1°C . The solvents

that were to be used in anhydrous studies were stored in a large chromatographic column containing approximately 400 g. of type 4A molecular sieve from Fisher Scientific Company.

Vapor Pressure Lowering

These experiments were conducted in the apparatus illustrated in Figure 1. The apparatus was connected to a Texas Instruments precision pressure gage through a spiral glass bellows. All junctions were sealed glass with the exception of the evacuation ports which were closed with Delmar-Urry valves (DM-850).

Each solution flask was constructed from a 500 ml graduated cylinder. The flasks were calibrated for volume contained by admitting measured aliquots of water at 25°C. The meniscus within each flask was read with the aid of a Gaertner cathetometer. The procedure for the experiment itself closely paralleled that employed by Van Duyne (7, p. 34) with the following exceptions.

A different capsule was used which allowed the pressure of the pure solvent to be compared directly with the pressure of the solution in such a way that the pressure gage readout was in units of pressure difference (ΔP). The capsule was obtained from Texas Instruments, Inc. and was a Type 5 Bourdon tube capsule (Serial No. 3894).

The solutions were prepared gravimetrically and were run to saturation. Since the solute vapor pressure in these experiments was lower than in the studies by Van Duyne it was

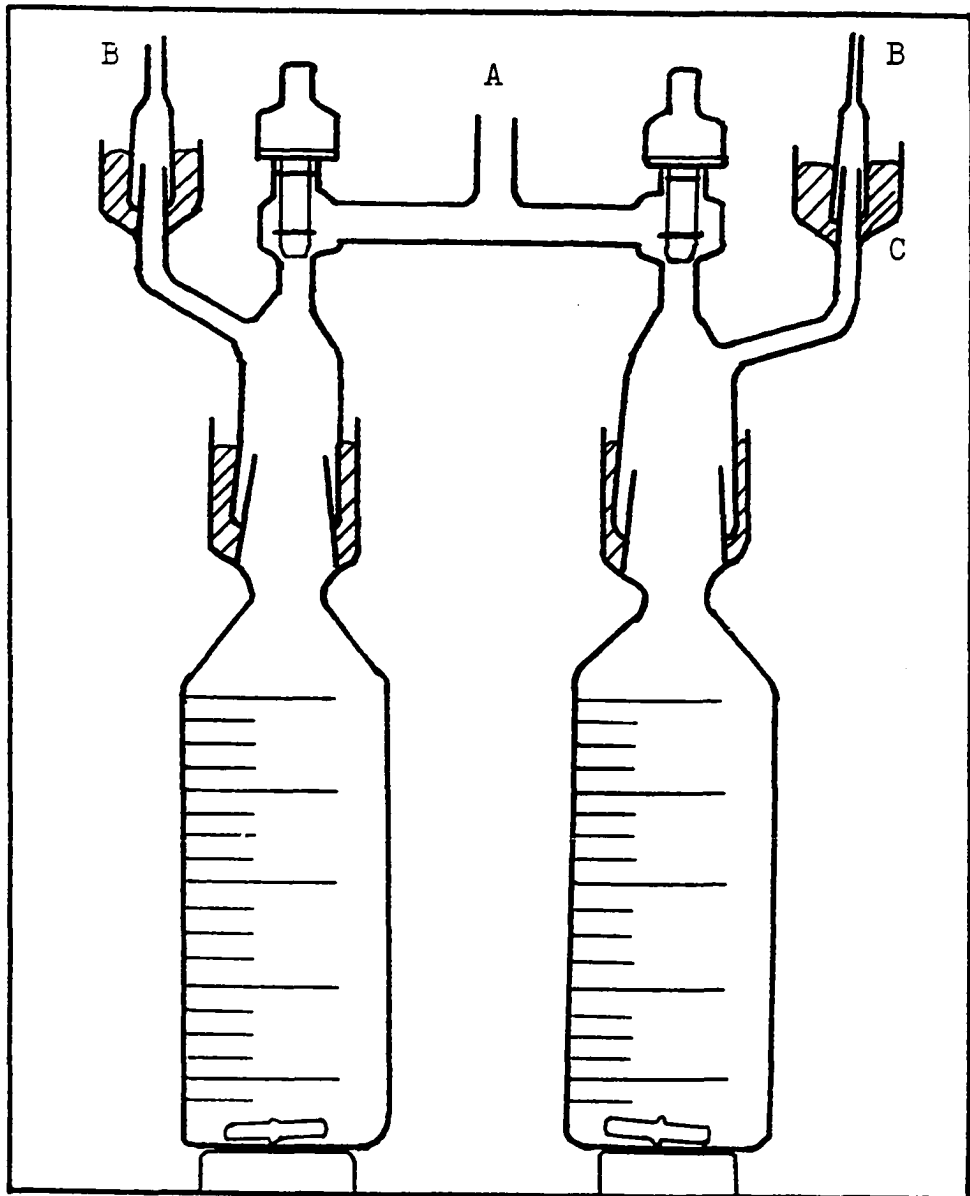


Fig. 1.--Vapor pressure lowering apparatus. Outlet to vacuum pump is at A; outlets to pressure gage are at B; mercury seals are at C.

assumed that the total amount of non-volatile 2-naphthol did not vary as solvent was removed.

Since there was a continuous readout, the solution ΔP was monitored until it reached an equilibrium value, which usually occurred within 10 minutes. During this time, the inside walls of the flask were scrubbed with a Teflon covered magnetic stirring bar using an externally manipulated magnet. This was done to remove solid 2-naphthol from the walls, where it had been deposited by splashing of solution during degassing and subsequent evaporation of solvent.

Hydration and Distribution Experiments

The experimental procedure used in the hydration and distribution experiments was essentially the same as that described by Gregory (46, p. 18). In addition to the wide mouth Mason jars later experiments used an improved design by R. Lynch (66).

The improved type of isopiestic equilibrator cell consisted of a cylindrical jar approximately 3 inches wide which had a concentric cylinder one inch in diameter constructed in its center. The cylinder was sealed to the base of the jar but ended about one inch from the top, thus allowing vapor phase equilibration of the two solutions. There were two narrow mouth screw tops in the upper end of the jar. One top was positioned directly above the center cylinder and the other was close to the outer wall, thereby allowing samples to be taken from either part of the cell. These tops had

Teflon liners and could be securely tightened and easily opened for withdrawing samples.

The solubility experiments were done at the same time and in the same manner as the hydration experiments. The sampling of the solutions did pose a problem at first, since the 2-naphthol crystals were small and light and did not adhere to the flask. A tube was therefore constructed, which had at its base a sintered glass disk of medium porosity. This tube was placed in the solution and a pipette was inserted to withdraw the solution, with no solid particles coming through the disk. The solutions were analyzed spectrophotometrically for total naphthol using a Beckman DU Spectrophotometer. Absorbances were measured at a peak wavelength of 274.4 μ , with a slit width of 0.1 mm and a path length of 0.1 cm for DCE and benzene and a pathlength of 1.0 cm for CCl_4 . Beer's Law plots were made for solutions prepared gravimetrically and diluted with anhydrous methanol to the correct concentration range. To avoid error due to absorbance by benzene at this wavelength a standard solution was prepared by diluting pure benzene to the same concentration range. The solutions were analysed for water using a Beckman KF-3 Aquameter and Karl Fischer reagent. The procedure has been described by Van Duyne (7, p. 23). The reagent was standardized twice daily, once at the beginning and once at the end of each day's run. A stock solution of methanol and water was run after each titration to ensure that the reagent

was stable. In the case of CCl_4 titrations, the weak reagent did change its titer over the course of a day, and the methanol water mixture was used in this case as a secondary standard.

Infrared Spectral Study

The experimental procedure for this study used essentially a modified baseline method to determine the absorbance of each solution at the wavelength under study. A Beckman IR-18A spectrophotometer was used with the slit width set at program #5. This gave a resolution of plus or minus 1 cm^{-1} , at frequencies close to 3600 cm^{-1} . The spectrophotometer was calibrated with polystyrene film. The solution under study was first scanned with the reference beam blanked by a cell containing solvent only. For the self association studies the maximum of the self association peak could be approximately determined by this method. Then the spectrophotometer was set at a specific wavelength and the absorbance was measured. For a series of wavelengths around the maximum, the one giving the highest absorbance was easily determined. For benzene and DCE the peak appeared as a shoulder, in this case the maximum was taken to be at the highest wavelength (lowest wavenumber) on the flat part of the shoulder, since this was most likely the peak maximum. (See Figure 2.) A procedure similar to the above was used to determine the actual wavenumber.

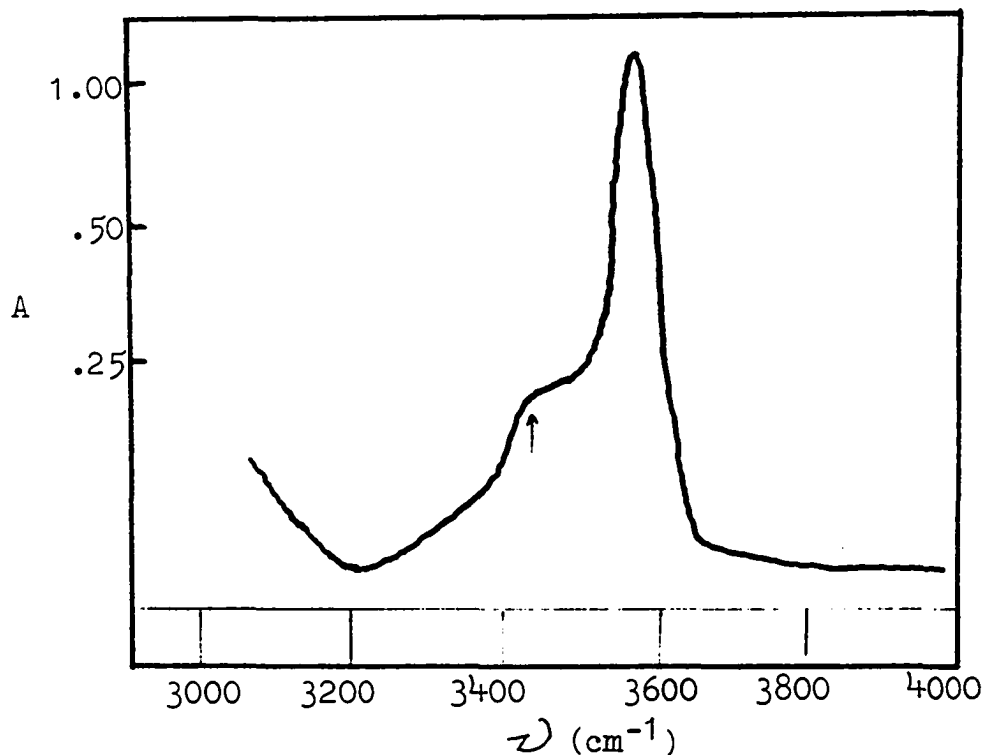


Fig. 2.--Self-association peak maximum in DCE and benzene.

In the case of the hydration experiments, a spectrum was run with an anhydrous solution of equal monomer concentration in the reference beam, thus subtracting the absorbance due to monomer and anhydrous polymers. By the procedure described above the maximum of the hydration peak was determined. Once the frequency was known, the spectrum was scanned vs. pure solvent and at least five separate readings were made of the absorbance at the peak frequency. This was done to insure that variables such as machine drift; wavelength setting and temperature were compensated for. The baseline was checked after each solution and was found to remain

constant over three to four hours. The time period for each solution, the scan plus the five readings of absorbance, was less than half an hour in all cases.

By subtracting the absorbance of an anhydrous solution at the frequency of the hydrated peak, the data for the ΔA plots was obtained. There are two reasons for using this method instead of direct differential readings. First, the solvents DCE and benzene both absorb in this region and second, and most important, is that better temperature control could be obtained for a single cell than for two cells requiring thermostatted jackets. The temperature of a non-thermostatted solution in the sample compartment of the IR-18A approaches 39°C . The temperature of the solution and the sample cells was measured with a Yellow Springs Instrument Co. Model 42SC Tele-Thermometer.

The cell was thermostatted with a WJ-1 water jacket obtained from Beckman Instruments. The cooling water was circulated with a Haacke Type F constant temperature apparatus. It was found that the circulating water had to be approximately 23°C to maintain 25°C in the sample cell, due to the heating by the Nernst glower as an IR source.

The solutions at equilibrium were transferred to the cell with a 1 ml syringe. The cell was rinsed three times before final filling. It was then immediately placed into the thermostatted cell holder, and the total time elapsed in all cases was less than three minutes. The cells were allowed

to equilibrate to constant temperature for about 10 minutes before recording the absorbances.

The sample cell used was a VT-01 (variable temperature, from Beckman) with KBr windows for the anhydrous work and AgCl windows for the hydrate work. Both cells had a path length of 1.0 mm and were used for DCE and benzene spectra. In CCl_4 the lower solubility required a 20 mm path length cell of IR Silica to be used with the cell holder which was described by Stevens (47, p. 12). For the hydration study a cell of path length of 20 mm was also satisfactory, and was used with the same cell holder. A VT-01 cell of path length 0.19 mm with AgCl windows was used for the hydration study in DCE.

CHAPTER III

DATA TREATMENT AND CALCULATIONS

General

In solution studies it is customary to assume that the equation for Henry's law, which is valid in dilute solutions such as those employed here, holds independently for each solute species in solution (4, 6). In addition, the Gibbs-Duhem equation can be applied to show that if the solute obey's Henry's law in dilute solution the solvent obeys Raoult's law (1).

We assume that the solutions under study obey the ideal solution relations discussed above since they are studied in the region of dilute concentration (all mole fractions are less than 0.05). Deviations from a linear relationship can then be expressed in terms of new molecular species, each of which obeys Henry's law.

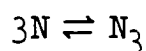
By application of the law of chemical equilibrium, association and hydration equilibrium constants can be derived which represent the experimental data. It is necessary to assume that the activity coefficient approaches the

value of one in the dilute solution so that the activity is approximately equal to the concentration of each species.

In this way, these equilibrium constants determined in the dilute region will closely approximate the thermodynamic K_a and may therefore be treated as such (i.e. it will be assumed that $K_\gamma = 1.0$). The law of chemical equilibrium, or the mass action law, may then be applied to determine constants in the following manner. For an equation of total (formal, f_N) concentration, a representative equation might be:

$$f_N = [N] + 3[N_3]$$

To obtain the concentration of trimer in a form explicit in monomer concentration we consider the following reaction:



For which the equilibrium constant may be written:

$$K_3 = \frac{[N_3]}{[N]^3}$$

and then solving for trimer concentration and putting the result back into the total concentration equation gives:

$$f_N = [N] + 3K_3[N]^3$$

Constants calculated from expressions similar to those above will then represent equilibrium constants. For polar molecules in dilute solution in non-polar solvents, this

approach is especially useful to characterize hydrogen-bonding equilibria, since these equations indicate the functional dependence of the data.

Vapor Pressure Lowering Experiments

In these experiments the observed variables included the difference in pressure, ΔP , between the reference flask containing pure solvent and the flask containing the solution, which had a lower pressure. The other observable was the volume of solution, V_s , from which the true concentration of 2-naphthol was calculated, since the total number of grams of 2-naphthol was known. If Raoult's law holds for the solvent we can derive an expression that correlates the observables. Raoult's law states:

$$P_1 = P_1^{\circ} X_1$$

where P_1° is the vapor pressure of the pure solvent and P_1 is the observed vapor pressure of the solvent in the solution. X_1 is the mole fraction of solvent, as given by:

$$X_1 = \frac{n_1}{n_1 + n_N + n_{N_2} + n_{N_3} + \dots}$$

where the denominator expresses the total number of moles of all possible species present in solution. These will affect the ΔP as single entities, since vapor pressure lowering is a colligative property. Dividing the number of moles in numerator and denominator by V_s gives us concentrations:

$$X_1 = \frac{n_1/V_s}{n_1/V_s + (n_N + n_{N_2} + \dots)/V_s} = \frac{M_1}{M_1 + M_{app}}$$

where M_{app} will be the apparent molality of 2-naphthol calculated from this colligative property. This will differ from M_{total} , the formal concentration of 2-naphthol only if association of the solute occurs. The quantities can be represented as:

$$M_{total} = [N] + 2[N_2] + 3[N_3]$$

$$M_{app} = [N] + [N_2] + [N_3]$$

where N represents a naphthol molecule, N_2 represents a dimer, etc. In the absence of association into higher order species, both molarities equal the monomer concentration. The equation we now have is:

$$P_1^{\circ} X_1 = P_1^{\circ} \frac{M_1}{M_1 + M_{app}} = P_1$$

which can be rearranged to give:

$$M_{app} = \frac{M_1 P_1^{\circ}}{P_1} - M_1 = M_1 \left[\frac{P_1^{\circ}}{P_1} - 1 \right] = M_1 \left[\frac{P_1^{\circ} - P_1}{P_1} \right]$$

To calculate the concentration of solvent in moles/liter the following procedure was used. First the total volume of solution, which was observed, was described as:

$$V_s = V_1 + V_2$$

To calculate the volume of solute, V_2 , the density of liquid 2-naphthol was extrapolated to 25°C. When this was determined, one could calculate the volume of 2-naphthol by the following equation, assuming only a negligible volume change on mixing with the solvent:

$$V_2 = g.(\text{naphthol}) \times [g./cc.(\text{density})]^{-1}$$

Then by subtraction $V_1 = V_s - V_2$, and the number of moles of solvent becomes:

$$n_1 = V_1 (\text{cc.}) \times d_1 (g./cc.) \times [M_1 (g./mole)]^{-1}$$

Now we may substitute the value of M_1 in the equation for M_{app} derived above giving the result:

$$M_{\text{app}} = \frac{n_1}{V_s} \left[\frac{P_1^{\circ} - P_1}{P_1} \right] = \frac{n_1}{V_s} \left[\frac{\Delta P}{P_1^{\circ} - \Delta P} \right]$$

From this equation we can calculate the value to be used in comparison with M_{total} to describe the self-association of 2-naphthol in any solvent.

The equations to be considered are:

$$M_{\text{app}} = C_N + C_{N_n} + C_{N_m} + \dots$$

$$M_{\text{total}} = C_N + nC_{N_n} + mC_{N_m} + \dots$$

where C_N is defined as the molar concentration of the monomer, C_{N_n} is the concentration of the polymer of order n (dimer,

trimer, etc.) and other polymers as may be required.

Using the Law of Chemical Equilibrium we may express these concentrations in a linear form in powers of monomer concentration. This gives us the following equations:

$$M_{\text{app}} = [N] + K_3[N]^3 + \dots \quad (1)$$

$$M_{\text{tot}} = [N] + 3K_3[N]^3 + \dots \quad (2)$$

For each solvent studied it was necessary to postulate only one polymer to adequately fit the experimental data. The data were fit with a linear and non-linear least squares program to be described below; the equations used were (1) and (2) above. The monomer concentration was first calculated with a Newton's method using equation (2) and the graphical estimate of the constant K_3 . Then values of M_{app} were calculated and compared to the observed values. The error function was calculated and then minimized. The RMSD (root-mean-square deviation) was not changed by the addition of more polymer species. The RMSD was a minimum for the trimer in the solvents benzene and DCE and it was approximately equal for the dimer and the trimer in CCl_4 .

Hydration and Distribution Experiments

In these experiments the observed variables included the formal, or total, concentration of water and naphthol and the activity of the water.

If Henry's Law is obeyed for solutions of H₂O in which no self-association occurs, we have the following expressions:

$$P_W = k C_W \quad \text{where } C_W = \text{concentration of water monomer,}$$

and

$$\frac{P_W}{P_W^0} = a_W = k' C_W$$

At activity = 1 the concentration of water will be at its saturation value, which in the absence of self-association will be all monomers:

$$a_W = 1 = k' C_W^0$$

This relation implies that the reciprocal of the Henry's Law constant is the saturation concentration of water, so that:

$$C_W = 1/k' (a_W) = C_W^0 a_W$$

A plot of a_W vs. f_W (total of formal concentration of H₂O) will be linear if there are only monomers present. On the other hand, if there are polymers of water, say trimers as in DCE, the formal concentration will be:

$$f_W = C_W + 3C_{W_3}$$

Here again we can apply the law of mass action to the trimer concentration to give the resulting equation:

$$f_W = C_W + 3K_3 C_W^3 = C_W^0 a_W + 3K_3 C_W^0{}^3 a_W^3 \quad (3)$$

and in this case, a plot of f_W vs. a_W will not be linear. The representation in equation (3) above can be used to explain the curvature seen in such a plot. The trimer, however, may still be said to obey Henry's Law since its partial pressure will be directly proportional to its concentration, or:

$$P_{W_3} = k' C_{W_3}$$

To study the hydration of a solute in a solution of organic solvent in which water does not self-associate, we can express the total formal water concentration as:

$$\begin{aligned} f_W &= [W] + [N_2W] + 2[NW_2] = [W] + K_{21}[N]^2[W] + 2K_{12}[N][W]^2 \\ &= C_W^0 a_W + K_{21} C_N^2 C_W^0 a_W + 2K_{12} C_N C_W^0 a_W^2 \end{aligned}$$

where $[N_2W]$ is the concentration of dimer monohydrate, etc. To obtain the amount of water concentration due to the presence of hydrates one subtracts the amount of water due to monomer alone:

$$f_W - C_W a_W = \Delta f_W = K_{21} C_N^2 C_W^0 a_W + 2K_{12} C_N (C_W^0 a_W)^2 \quad (4)$$

The resulting equation may then be fit for trial species if one has a procedure for obtaining the monomer concentration of naphthol (or other solute).

A preliminary indication of the types of species to be expected can often be determined from inspection of the

data, with only a small amount of manipulation required. In addition, it is frequently possible to obtain graphical estimates of constants.

For example, linearity in f_W vs. f_N plots is evidence for formation of monohydrates since it shows an increase proportional to the first power of naphthol concentration. The slope of this linear portion can be considered proportional to the magnitude of the constant. Positive curvature at higher f_W is evidence for more highly hydrated species. Negative curvature would imply a monohydrate of a naphthol polymer with a large value for the constant.

The hydrate data were fit using equations like (4) and various combinations of hydrate species. Two species were required to adequately fit the data. The concentration of naphthol monomer was calculated by a Newton's method procedure using the derived constants and an equation of the form for f_W . The hydration data were first fit along with the distribution data to be discussed below. The species that gave the lowest RMSD fit to both sets of data were chosen as the best representation of the hydrated system.

The distribution study uses the Nernst Distribution Law to derive applicable equations. This law states that a solute will distribute itself between two phases in contact until its chemical potential is equal in both phases. The distribution law can be expressed as:

$$\frac{X_2^a}{X_2^b} = \frac{k^a}{k^b} = K_D$$

where K_D , the distribution constant, is the ratio of the Henry's Law constants. Alternatively,

$$K_D' = C_N^O / C_N^W$$

It is in this last form that we will apply the distribution law. Classically, solutes have been distributed between water and an organic phase, and occasionally erroneous distribution constants were reported due to failure to account for the hydration occurring in the organic phase. In addition, the rearranged equation:

$$C_N = K_D C_N^W$$

predicts a linear relation between concentrations in each phase; deviations from this line are to be attributed to hydration and self-association of the solute.

The observable data in the experiment were the naphthol concentration in each phase and the water concentration in the organic phase. Since water is a solvent of high dielectric constant and also since the concentrations of 2-naphthol in the water phase did not go above a mole fraction of 0.001, it was assumed that naphthol was monomeric in this phase.

The following types of equations were used to determine the distribution constant from this type of data and to determine hydration constants in concert with the hydration data:

$$\begin{aligned}
 f_N^o &= C_N^o + 3K_3C_N^3 + 2K_{21}C_N^{o2}C_W + K_{12}C_N^oC_W^2 \\
 &= K_D C_N^w + 3K_3K_D^3 C_N^{w3} + 2K_{21}(K_D C_N^w)^2 C_W + K_{12}K_D C_N^w C_W^2 \quad (5)
 \end{aligned}$$

where f_N^o is the concentration of naphthol in the organic phase. The data may be inspected for evidence of hydrate and anhydrous polymer formation by plotting C_N^w vs. f_N^o . Curvature in this plot indicates deviation from the ideal distribution law. The error function obtained by calculation of K_D was combined with that from the hydration experiments and this function was then minimized. Later fits incorporated the solubility data discussed below, as a third addition to the error function.

Solubility Experiments

The observed variables in this experiment were the concentration of 2-naphthol at the saturation limit for various activities of water, the total concentration of water at each activity, and the known activities themselves. The advantages to be gained from a study of solubility is that at saturation the activity of the solute is constant and we can treat increases in solubility (as H_2O is increased) as a function of the hydration of the solute.

The equations to be used are:

$$f_N = C_N + 3C_{N_3} + 2C_{N_2W} + C_{NW}$$

$$\Delta f_N = f_N - (C_N + 3C_{N_3}) = 2C_{N_2W} + C_{NW}$$

Also the increase in water solubility due to the hydration of the acid can be written:

$$\Delta f_W = C_{N_2W} + 2C_{NW_2}$$

Plots of these values against water monomer concentration (or $C_W^0 a_W$) will be nearly linear if monohydrates are the prevailing hydrate species. If there are significant concentrations of higher order hydrates, the dependence of a_W^2 or a_W^3 would cause curvature in these graphs.

In calculating the error parameter, the equation for Δf_N was used to compare calculated with observed values. These data were fit along with the hydration data and the distribution data in a function that added the weighted RMSD's for each experiment and minimized the total.

Data Fitting

The calculation of constants and error parameters was done on an IBM-360 digital computer. The equations used in each case have been described in this chapter. In this section, the general scheme will be described.

To calculate the constants for various plausible sets of association or hydration models, equations similar to (4) and (5) above were used. Values of the constants would be used to calculate a value for f_N and this value would be compared to the observed experimental value. From this comparison an error function, S , would be calculated. Systematic

variations in each constant were made in order to obtain a minimum value for S, where

$$S = \sqrt{\frac{\sum_i (y_{\text{obs}} - y_{\text{calc}})^2}{N - P}}$$

The programs used to perform this procedure were similar to those described by L. G. Sillen and co-workers (48) and were based on the graphical least squares analysis of S. D. Christian (49) and T. F. Lin (50).

Two types of programs were used in fitting the data. One, a matrix linear least squares program, calculated the constants and their errors and calculated a minimum value for S when linear equations were used. This program was also used to get first approximations to the hydration constants but it did not minimize S since the equations were non-linear. The non-linear least squares program, called an optimizer, calculated constants, errors and the function S, and then computed an optimum value for S which resulted in a minimum for this error function.

The error function S is defined as the RMSD, root-mean-square deviation, since it is related in form to that function. As used here it actually calculated the deviation of a non-linear function F(y), where

$$F(y) = f(C_N, a_w, K_1, K_2, K_3, \dots K_n)$$

While in certain cases the equations used were linear, with the use of the optimizer it was not necessary to have the

equations in linear form. This resulted in a considerable amount of time saved in manipulation of data. For good initial approximations of values of constants, convergence to a minimum in S was fairly rapid and facilitated testing of several models.

The equations whose form provided the best fit to the data, as evidenced by the lowest value of the error function (hereafter called RMSD) were chosen as the most representative of the major species in solution. Other tests, such as the rule of maximum simplicity for adequate explanation of observed data (Ockham's Razor [5, 51], as quantified by Hamilton [52]), were occasionally invoked.

For the combined hydration, distribution and solubility data a three part error function was used. This function took the form:

$$S^2 = \frac{1}{W_h} \frac{\sum (h - h_{calc})^2}{N - P} + \frac{1}{W_d} \frac{\sum (d - d_{calc})^2}{N - P} + \frac{1}{W_s} \frac{\sum (s - s_{calc})^2}{N - P}$$

where W_h is the weight factor for the hydration data, W_d is the weight factor for the distribution data, and W_s is the weight factor for the saturation data. The weight factor allowed the errors to be normalized so that the absolute minimum in S would be 1.0. This error function allowed the three observed variables of water concentration, distribution ratio and naphthol concentration to be fit to a minimum RMSD simultaneously.

Infrared Spectroscopic Studies

For these experiments, the observable variables were the total concentration of naphthol, the activity of water, and the absorbance of the solution. Along with other ideal solution assumptions discussed previously, Beer's Law was assumed to hold for each of the species in solution. It was then possible to fit the absorbance data at the associated or hydrated peak by testing the various models for which equilibrium constants had previously been obtained. The best fit for equations of the type discussed below was the fit that gave the lowest RMSD consistent with the previously derived constants.

In the case of self-association in anhydrous solvents, the activity of water was zero. The monomer concentrations of naphthol were calculated from a Newton's method formula using the self-association constants (derived previously) and the value of f_N for every solution in the equation:

$$f_N = C_N + 3K_3C_N^3$$

The absorbance peak was then fit with a two-dimensional optimizer since there was some overlap of the monomer peak with each of the peaks corresponding to self-associated species. The equation for the anhydrous solutions was:

$$A^{3485} = \epsilon_1 1(N) + \epsilon_3 1(N_3) = \epsilon_1 1(N) + \epsilon_3 1K_3(N)^3$$

Trial values of the product ϵ_{n1} were entered and the absorbance was calculated for each point.

Treatment of data from the hydration experiments required the same program. The monomer concentrations for naphthol were calculated using the same method but the equation also included the hydrated species. The water monomer concentration was calculated from the total monomer concentration multiplied by the activity for each point. Once again the previously derived hydration constants were used. By subtracting the absorbance at the hydrate peak frequency that was due to an anhydrous solution of equal monomer concentration of naphthol, a ΔA was obtained that represented the absorbance due only to the hydrate. This was fit using the equation:

$$\begin{aligned}\Delta A^{3442} &= \epsilon_{211}(N_2W) + \epsilon_{121}(NW_2) \\ &= \epsilon_{211}K_{21}(N)^2(C_W^{\circ}a_W) + \epsilon_{121}K_{12}(N)(C_W^{\circ}a_W)^2\end{aligned}$$

The results of these calculations and the others discussed previously are presented in the next chapter.

CHAPTER IV

RESULTS AND DATA INTERPRETATION

General

The results of this study indicate that self association can be ascribed primarily to trimeric forms of 2-naphthol. Infrared evidence supports this result. The hydration results indicate that there exists a mixture of 1:1, 1:2 and 2:1 hydrates in solution with different forms predominating in various solvents. The results for each solvent are capable of being fit with only two of the three hydration parameters mentioned. Infrared evidence supports the two parameter results.

The results to be presented will be discussed in the following order: first, self-association; second, hydration and saturation; third, distribution results and fourth, infrared results.

Self-association

The results of the vapor pressure lowering data were analyzed as described in the preceding chapter. Both one- and two-parameter fits of the data were tried. The results

were fit satisfactorily using only one parameter. That is, for the successful two species fits, the RMSD of the fit was not significantly better than that of the fit with one species. Fits that gave a negative equilibrium constant were considered as unsuccessful fits.

For benzene and DCE (1,2 dichloroethane), the trimer species gave the lowest RMSD of the three most plausible trial species. The dimer and tetramer were the other one-parameter fits tried. The tetramer was the worst fit in all cases. The two parameter fit, incorporating both the dimer and trimer as trial species was not significantly better than the one parameter fit.

In the CCl_4 case, the vapor pressure lowering data were taken in a much lower concentration range than in the other two solvents, due to the lower solubility of 2-naphthol in CCl_4 . This lower concentration range resulted in lower differences in vapor pressure during this experiment. One reason for the greater apparent scatter in these data would be lack of precision at these low pressure differences and the greater fluctuations caused by temperature gradients during the experiment. As a result, it was difficult to determine the predominant species in CCl_4 from vapor pressure lowering data alone. These results did in fact give a lower RMSD for the 1-2 fit than for the 1-3 fit. Due to the scatter of these data, however, the difference in RMSD might not have as much significance as in the other two solvents. The

self-association data in CCl_4 taken in the infrared study however, showed a definite preference for the trimer fit over that of the dimer. There is much less scatter in the spectral data, and the significant superiority of the 1-3 fit was taken as evidence that the trimer is predominant in CCl_4 as well as in the DCE and benzene solvents. For DCE and benzene the trimer fit was generally as good as the dimer fit for IR self-association data. Further discussions of IR data will be presented below.

The vapor pressure lowering results for the dimer only and trimer only fits are presented in Table 1 below.

Table 1
Vapor Pressure Lowering Trial Species

Solvent	Equilibrium Constant	RMSD
1,2 Dichloroethane	$K_2 = 0.380 \pm 0.018$	8.02×10^{-3}
	$K_3 = 0.457 \pm 0.019$	7.09×10^{-3}
Benzene	$K_2 = 0.747 \pm 0.032$	3.44×10^{-3}
	$K_3 = 1.797 \pm 0.063$	2.69×10^{-3}
CCl_4	$K_2 = 12.14 \pm 0.66$	0.93×10^{-3}
	$K_3 = 169.9 \pm 15.4$	1.44×10^{-3}

The results for these experiments are presented in Figures 3 to 5 and Tables 3 to 5. The tables list values of total or analytical (M_{tot}) naphthol concentration, the apparent naphthol concentration calculated from the observed

ΔP , and the value of the apparent concentration calculated from the equation:

$$M_{\text{app}} = C_N + K_3 C_N^3$$

using the values given above for the trimerization equilibrium constant. Figures 3 to 5 (pages 56 to 58) show the data plotted as the apparent concentration, M_{app} , versus the total concentration, M_{tot} . The negative curvature of these plots is evidence that as the concentration increases there is a smaller increase in the value of apparent concentration due to solute molecules forming larger numbers of associated aggregates.

In calculating the value of M_{app} , equation (1) of Chapter III was used. The values which were used for the vapor pressures of the pure solvents were 95.05 mm Hg for benzene, 113.89 mm Hg for carbon tetrachloride and 78.74 mm Hg for dichloroethane (7). Molar volumes of the solvents were calculated from molecular weights and solvent densities. The values for the densities at 25°C are: 0.8734 g/cc. and 1.5843 g/cc. for benzene and CCl_4 respectively (53), and 1.2455 g/cc for dichloroethane (54).

Hydration and Saturation

The results of the hydration data, and the results of the hydration at the saturation limit of 2-naphthol, were also analyzed as described in the preceding chapter. Both one- and two-parameter hydrated species were tried. In

addition, three hydrated species were also used to fit the data.

The total RMSD of the two-parameter fit was superior to that of the one-parameter fit, and it was therefore considered necessary to use at least two parameters, or two different hydrated species, to adequately fit the hydration data.

In Figure 6 the hydration data for CCl_4 are presented. The slight downward curvature is evidence for a naphthol polymer monohydrate coexistent with a monomer monohydrate. In Figure 9 and 12 are shown the data for the benzene and dichloroethane systems, respectively. Both these plots show slight upward curvature indicating that a higher hydrate exists, but the absence of a very marked curvature in both cases suggests competition from a polymer monohydrate. The curves in these figures were calculated using the two hydration parameter fit.

The results of these two parameter fits were felt to be limited however, when those species giving the best fit in each solvent were compared. While the 1:2 and 2:1 species gave the best fit for DCE and benzene, the 1:1 and 2:1 species gave a better fit for CCl_4 . Although there may be many reasons for this discrepancy, it was felt that this evidence suggested that in benzene and DCE, while the 1:2 and 2:1 may have been the predominant species, there may also be present in solution a small percentage of 1:1 complex. Similarly, CCl_4 may have a small percentage of 1:2 complex.

Since the hydration data in these solvents were fit adequately using only two parameters however, the results displayed in Figures 6-14 and Tables 6-14 were derived with the two hydration constants and the distribution constant that provided the best fit. On the other hand, the three hydration parameter fit was expected to yield an RMSD at least equal to or even lower than the two species fit had provided. This was to be expected since addition of extra adjustable parameters nearly always improves such fits, unless an actual minimum in RMSD has been found. This actual minimum will be the result of over all experimental error, and will be independent of mathematical models applied to the data.

The results for the two and three parameter hydration cases are presented in Table 2. For the discussion of these results in the following chapter, we will consider mainly the two-parameter fit since the use of the three-parameter fit did not significantly improve the RMSD and in fact was unsatisfactory in the case of the solvent DCE.

To arrive at the species that would provide the best fit of the data, several combinations of species were tried. All one-parameter fits for hydration species gave RMSD's about 50% higher than those reported for the two-parameter fits. For the two-parameter fits all combinations up to 1:4 and 2:4 were tried and several combinations using monomer and trimer naphthol species up to a 1:3 and a 3:3 pair were also

tried. In addition, some two parameter fits were tried using pairs of monomer species and using mixtures of dimer and trimer naphthol species. Of these combinations many fits resulted in a negative constant for one species. Of those that had both constants positive and species presented here provided the lowest RMSD and therefore the best fit to the observed data. As an example of this criterion, four of the fits for the dichloroethane system gave the following RMSD's:

<u>Species</u>	<u>RMSD</u>
1:2, 2:1	2.16
1:3, 2:1	2.45
1:1, 2:2	5.92
1:1, 3:3	6.18

Table 2
Comparison of fit for Various Hydration
Equilibrium Constants

Solvent	K_{11}	K_{12}	K_{21}	RMSD
CCl ₄	9.428±0.026	-	120±85	3.099
	7.01±2.18	115±5200	145±580	3.028
C ₆ H ₆	-	60.32±3.50	23.12±.35	2.149
	0.605±.116	53.9±16.3	22.04±.66	2.082
C ₂ H ₄ Cl ₂	-	15.96±.59	5.87±0.03	2.166
	-0.545±.067	18.11±1.87	6.308±0.051	2.132

The curves displayed in Figures 6-14 were calculated using the procedure described in Chapter III. For a typical two-parameter case the equations used were of the form:

$$\Delta f_W(\text{calc}) = 2K_{12}C_N C_W^2 + K_{21}C_N^2 C_W$$

and for the three-parameter case:

$$\Delta f_W(\text{calc}) = K_{11}C_N C_W + 2K_{12}C_N C_W^2 + K_{21}C_N^2 C_W$$

After arriving at the value of the K's that gave the lowest difference between the Δf_W (observed) and the Δf_W (calculated) for each point, the program added the value for the water concentration in pure solvent at the given activity of water to arrive at f_W (calc) which is presented in the tables.

The saturation experiments involved the study of increases in solubility of 2-naphthol at constant water activity in these solvents. These data were fit in the form:

$$\Delta f_N(\text{calc}) = K_{12}C_N C_W^2 + 2K_{21}C_N^2 C_W$$

or, for the three parameter case:

$$\Delta f_N(\text{calc}) = K_{11}C_N C_W + K_{12}C_N C_W^2 + 2K_{21}C_N^2 C_W$$

where Δf_N is the difference between the anhydrous solubility and the solubility in a water saturated solvent.

In Tables and Figures 7 and 8 are presented the CCl_4 data; in Tables and Figures 10 and 11 that for the benzene and in Tables and Figures 13 and 14 that for the DCE. Overall, these data were not fit as closely as the hydration data, as is evidenced by the variation of the calculated curve

from the observed data. This is probably because there were many more data available for the water solubility fits than for the naphthol fits, and since the weighted errors depended on the number and precision of data available, the hydration data were weighted more heavily. These results are displayed in the form of Δf_N and Δf_W since this type of plot provides the maximum information for graphical estimates of the type mentioned in Chapter III (pages 36 through 40).

Distribution Results

The distribution constant, K_D , was determined in each case by calculation of the monomer naphthol concentration in each solvent at unit water activity using the hydration and self-association constants described above. These constants plus the data concerning the amount of naphthol in each phase and the water concentration in the organic phase were used. Trial values of K_D were calculated and adjusted to provide a minimum in the distribution error function. The best value was then used to calculate the curves in Figures 15 to 17. The calculated and observed values are presented in Tables 8, 11 and 14 for CCl_4 , benzene and DCE, respectively.

Curvature in plots of this type is an indication of the association occurring in the organic phase. The amount of deviation from linearity is related to the amount of higher order association occurring in the non-aqueous phase. In this case, the distribution constant plus hydration species and

anhydrous trimer have adequately represented the distribution data.

A summary of thermodynamic data for each solvent will be found following the hydration data. Results for CCl_4 , benzene and DCE are in Tables 15, 16 and 17, respectively.

Infrared Study

The results of the infrared study were handled as described in Chapter III. As previously mentioned, the self-association data gave good fits in all cases using the trimer self-association constants derived from the vapor pressure lowering data.

These results are presented in Tables and Figures 18 to 20. The RMSD's of these fits were all about 0.008 absorbance units. The overlap of the monomer peak required that a monomer extinction coefficient be determined at the self-association frequency. For CCl_4 , there was much better peak separation than in the other two solvents and the monomer extinction coefficient came out reasonably small.

For the infrared hydration study the results are less precise. The best RMSD values were around 0.020 absorbance units and the extinction coefficient values therefore do not have the precision of fit found in the self-association study.

There exists only one hydrate band, which is rather broad, in all three solvents. By fitting the peak absorbance with the best values of the hydration constants it is possible to derive the value of the extinction coefficient for each

absorbing species. This was done using the results of the two-parameter hydration fit, since it appeared that these species were the predominant ones in each solution.

The major assumption in this case, aside from the postulated species, is that both hydrates have maximum absorption at the same frequency. Since the type of hydrogen bonding is the same for each complex and different than that of self-association, it is expected that these two water naphthol complexes will absorb at nearly the same frequency.

The results of the hydrate study are presented in Tables and Figures 21 to 23. The frequency shifts and extinction coefficients for the complexes in CCl_4 are presented along with those for benzene and 1,2 dichloroethane in Table 25.

In Figure 24 is presented a sketch of the difference spectra used to discover the hydrate peak maximum in CCl_4 . The hydration studies in the other two solvents presented similar difference spectra.

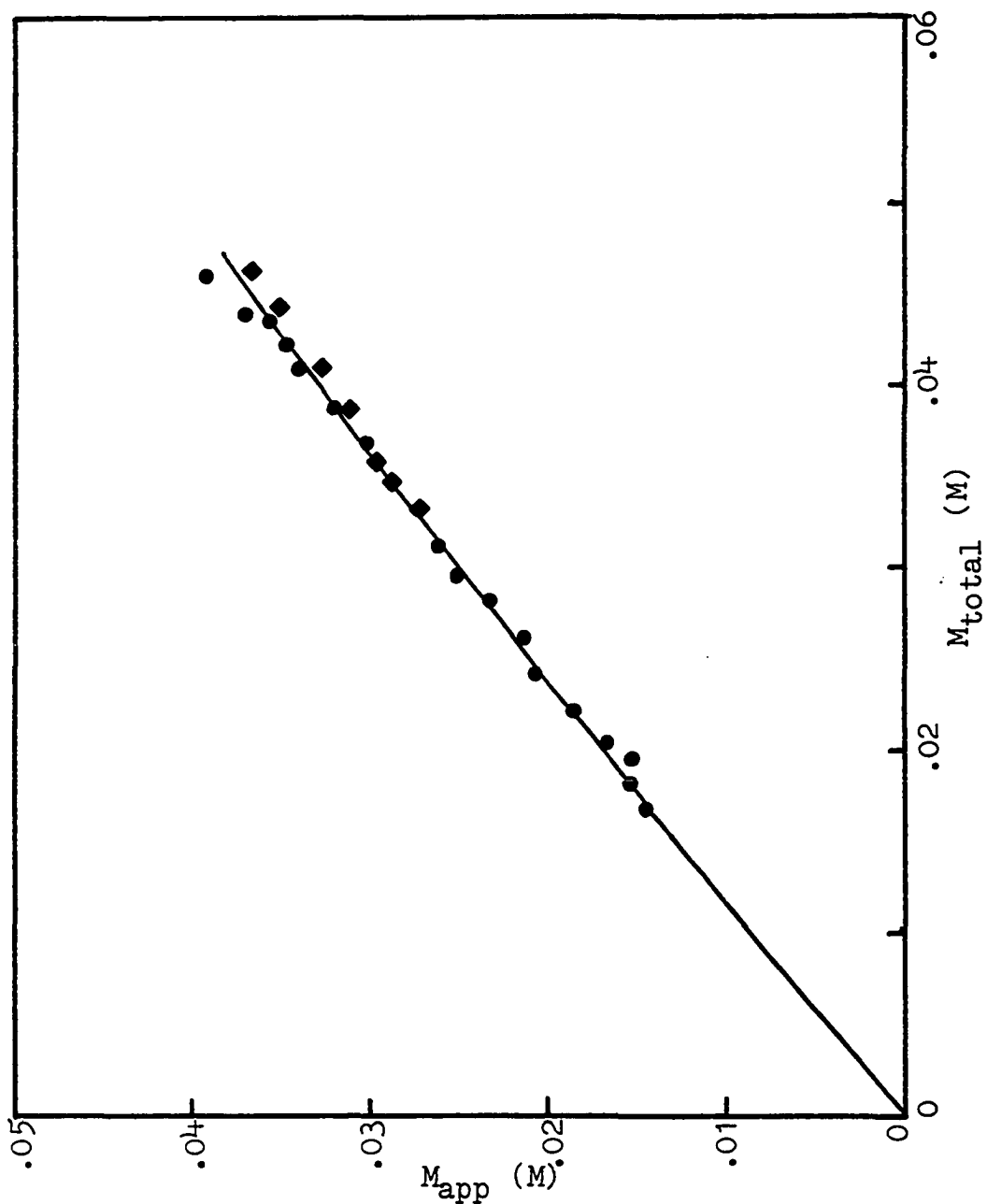


Fig. 3.--Vapor pressure lowering results for the 2-Naphthol CCl_4 System. ●, first experiment; ◆, second experiment. Several points have not been plotted but all were used to calculate the line.

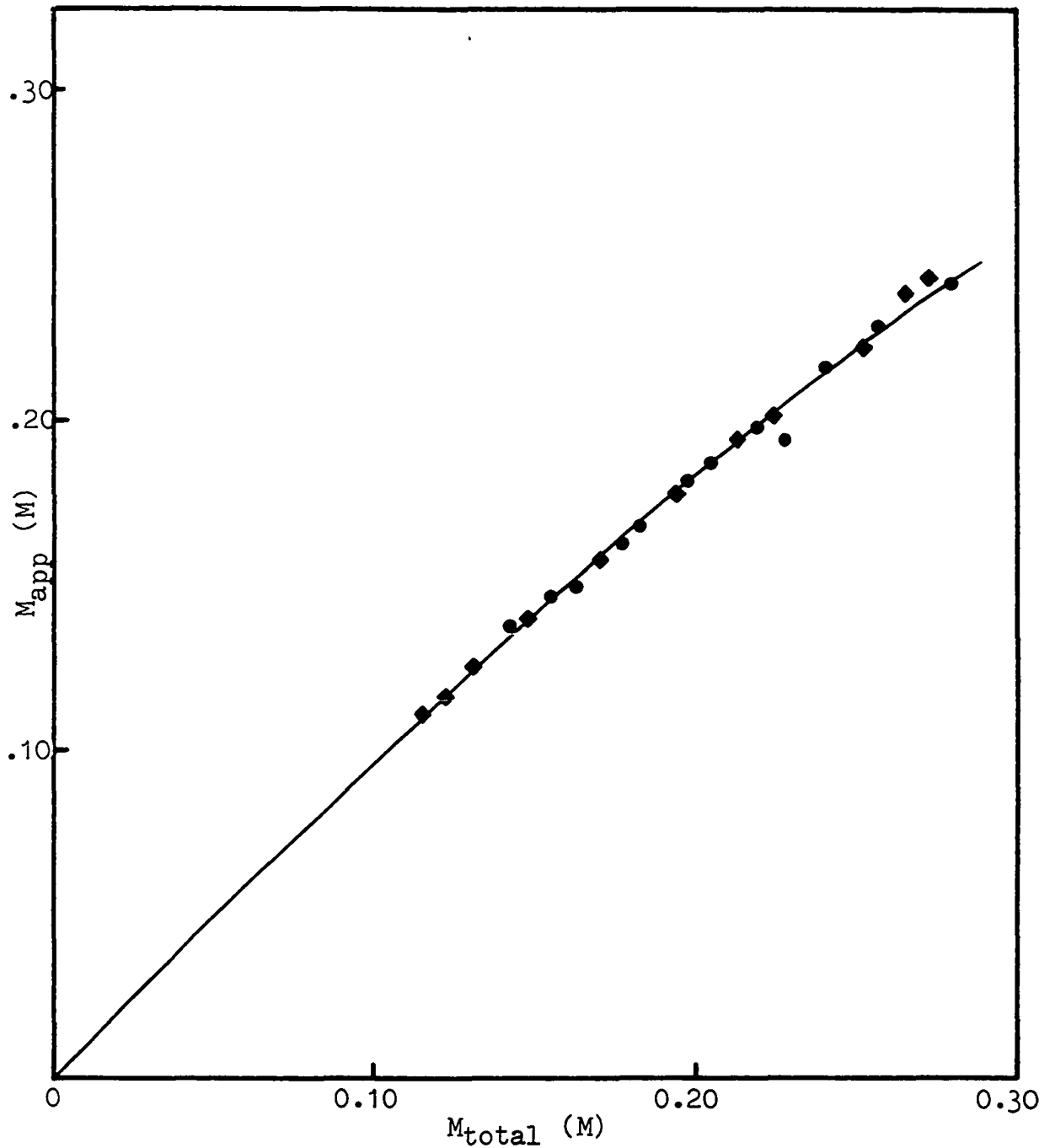


Fig. 4.--Vapor pressure lowering results for the 2-naphthol benzene system. ●, first experiment; ◆, second experiment. Several points have not been plotted but all were used to calculate the line.

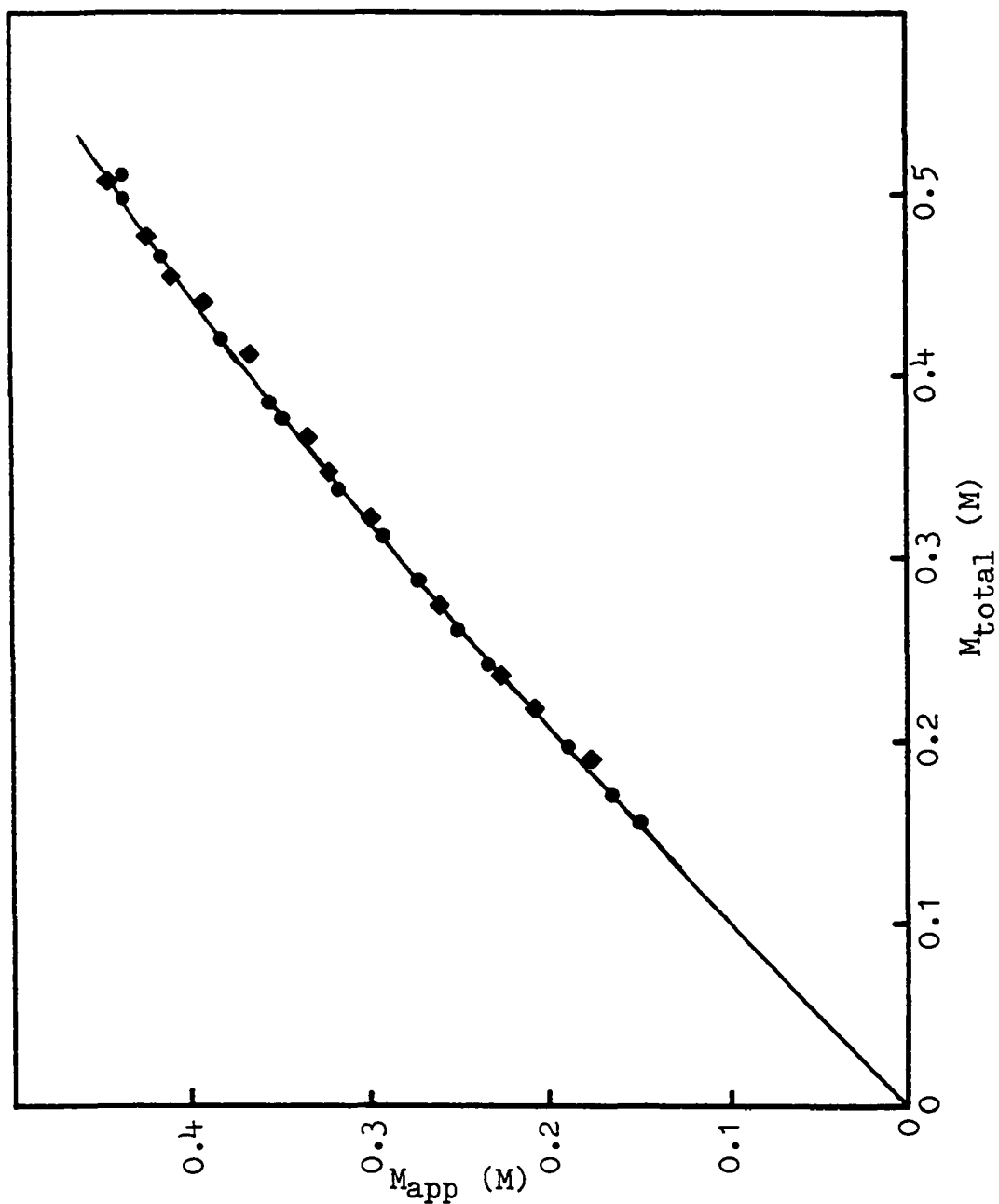


Fig. 5.--Vapor pressure lowering results for the 2-naphthol dichloroethane system. ●, first experiment; ◆, second experiment. Several points have not been plotted but all were used to calculate the line.

Table 3

Vapor Pressure Lowering Data for the 2-Naphthol-
Carbon Tetrachloride System at 25°C

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.0460	0.0394	0.0360
0.0439	0.0370	0.0346
0.0430	0.0357	0.0346
0.0424	0.0347	0.0337
0.0421	0.0352	0.0336
0.0409	0.0340	0.0328
0.0388	0.0321	0.0315
0.0369	0.0302	0.0303
0.0349	0.0284	0.0289
0.0330	0.0276	0.0277
0.0311	0.0263	0.0264
0.0297	0.0251	0.0254
0.0282	0.0233	0.0243
0.0271	0.0216	0.0235
0.0261	0.0214	0.0228
0.0253	0.0219	0.0223
0.0241	0.0207	0.0214
0.0231	0.0197	0.0206
0.0222	0.0185	0.0199
0.0214	0.0175	0.0192
0.0205	0.0169	0.0186
0.0201	0.0159	0.0183

Table 3--Continued

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.0197	0.0155	0.0180
0.0196	0.0153	0.0179
0.0194	0.0168	0.0178
0.0193	0.0158	0.0177
0.0189	0.0145	0.0174
0.0183	0.0154	0.0168
0.0180	0.0154	0.0166
0.0174	0.0149	0.0162
0.0171	0.0145	0.0159
0.0464	0.0366	0.0362
0.0444	0.0352	0.0350
0.0429	0.0342	0.0341
0.0410	0.0329	0.0329
0.0397	0.0314	0.0321
0.0387	0.0312	0.0314
0.0373	0.0304	0.0305
0.0360	0.0297	0.0297
0.0350	0.0288	0.0290
0.0331	0.0273	0.0277

Table 4

Vapor Pressure Lowering Data for the
2-Naphthol-Benzene System at 25°C

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.1017	0.0980	0.0984
0.1033	0.1005	0.0999
0.1055	0.1019	0.1019
0.1084	0.1045	0.1045
0.1106	0.1060	0.1065
0.1115	0.1074	0.1073
0.1160	0.1109	0.1113
0.1193	0.1135	0.1143
0.1230	0.1165	0.1176
0.1278	0.1207	0.1218
0.1322	0.1249	0.1256
0.1398	0.1311	0.1322
0.1486	0.1385	0.1396
0.1551	0.1438	0.1451
0.1717	0.1570	0.1589
0.1812	0.1650	0.1667
0.1946	0.1765	0.1773
0.2078	0.1872	0.1877
0.2144	0.1944	0.1928
0.2254	0.2006	0.2011
0.2537	0.2219	0.2221
0.2672	0.2380	0.2319

Table 4--Continued

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.2738	0.2429	0.2366
0.1322	0.1330	0.1256
0.1389	0.1362	0.1314
0.1441	0.1372	0.1359
0.1503	0.1400	0.1411
0.1562	0.1453	0.1461
0.1640	0.1488	0.1526
0.1671	0.1517	0.1552
0.1710	0.1563	0.1584
0.1776	0.1620	0.1637
0.1837	0.1672	0.1687
0.1918	0.1751	0.1751
0.1990	0.1805	0.1808
0.2057	0.1865	0.1860
0.2123	0.1914	0.1911
0.2201	0.1973	0.1971
0.2284	0.1947	0.2034
0.2423	0.2159	0.2138
0.2581	0.2278	0.2253
0.2821	0.2411	0.2425
0.2868	0.2438	0.2457

Table 5

Vapor Pressure Lowering Data for the 2-Naphthol-
1,2 Dichloroethane System at 25°C

M_{tot}	M_{app}	$M_{app}(calc)$
0.1558	0.1503	0.1526
0.1609	0.1528	0.1574
0.1643	0.1587	0.1606
0.1708	0.1661	0.1667
0.1759	0.1697	0.1715
0.1894	0.1439	0.1840
0.1979	0.1885	0.1918
0.2106	0.2017	0.2033
0.2190	0.2123	0.2109
0.2406	0.2286	0.2302
0.2428	0.2348	0.2321
0.2469	0.2538	0.2357
0.2620	0.2496	0.2489
0.2888	0.2716	0.2720
0.3123	0.2926	0.2919
0.3389	0.3174	0.3139
0.3583	0.3337	0.3296
0.3780	0.3491	0.3454
0.3865	0.3554	0.3521
0.4083	0.3713	0.3692
0.4154	0.3772	0.3747
0.4211	0.3814	0.3791

Table 5--Continued

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.4297	0.3895	0.3857
0.4362	0.3954	0.3906
0.4458	0.4022	0.3979
0.4626	0.4120	0.4106
0.4664	0.4148	0.4134
0.4759	0.4215	0.4205
0.4833	0.4328	0.4260
0.4871	0.4256	0.4287
0.4979	0.4380	0.4367
0.5105	0.4379	0.4458
0.5116	0.4390	0.4466
0.1911	0.1756	0.1855
0.2010	0.1896	0.1946
0.2186	0.2097	0.2105
0.2386	0.2277	0.2284
0.2543	0.2421	0.2422
0.2749	0.2597	0.2601
0.2983	0.2805	0.2801
0.3237	0.2992	0.3014
0.3484	0.3210	0.3216
0.3679	0.3342	0.3373
0.3865	0.3478	0.3521
0.4126	0.3672	0.3725

Table 5--Continued

M_{tot}	M_{app}	$M_{\text{app}}(\text{calc})$
0.4419	0.3907	0.3950
0.4601	0.4072	0.4087
0.4778	0.4215	0.4219
0.4947	0.4357	0.4343
0.5093	0.4462	0.4450
0.5336	0.4632	0.4625

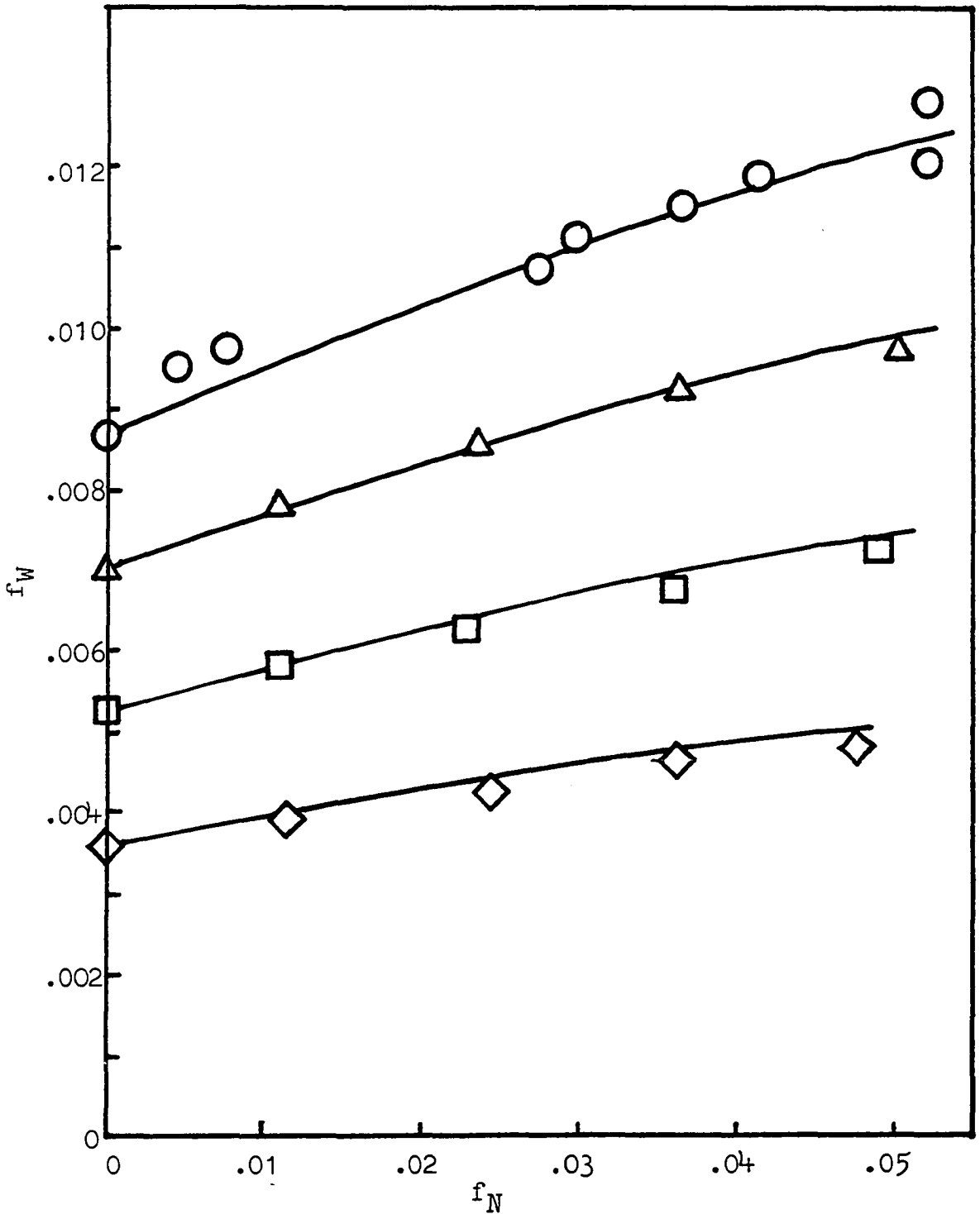


Fig. 6.--Hydration of 2-naphthol in carbon tetrachloride. $\circ, a_w=1.00$; $\Delta, a_w=0.805$; $\square, a_w=0.607$; $\diamond, a_w=0.415$. All lines in these figures are calculated.

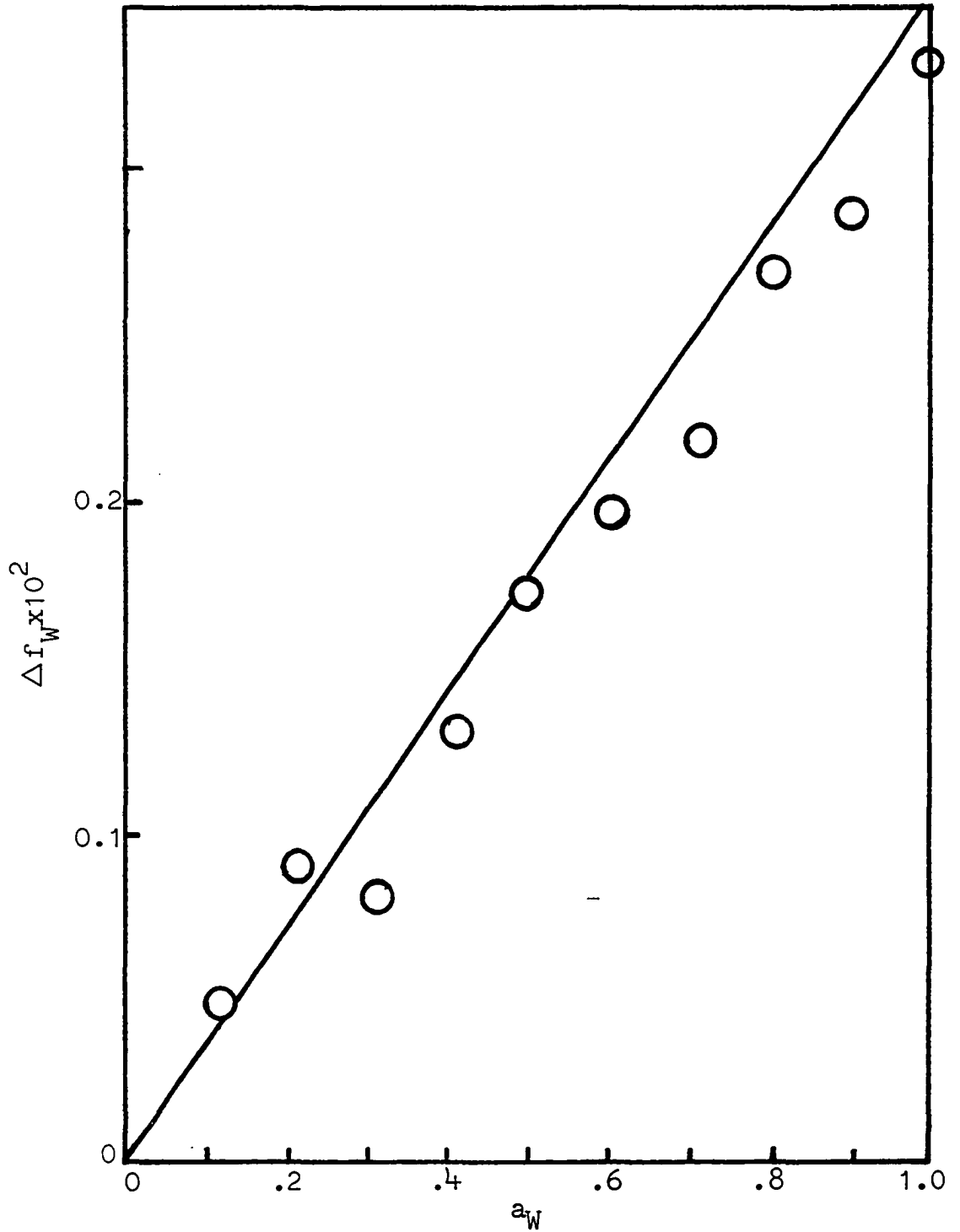


Fig. 7.--Difference in water solubility at saturated 2-naphthol concentration in CCl_4 .

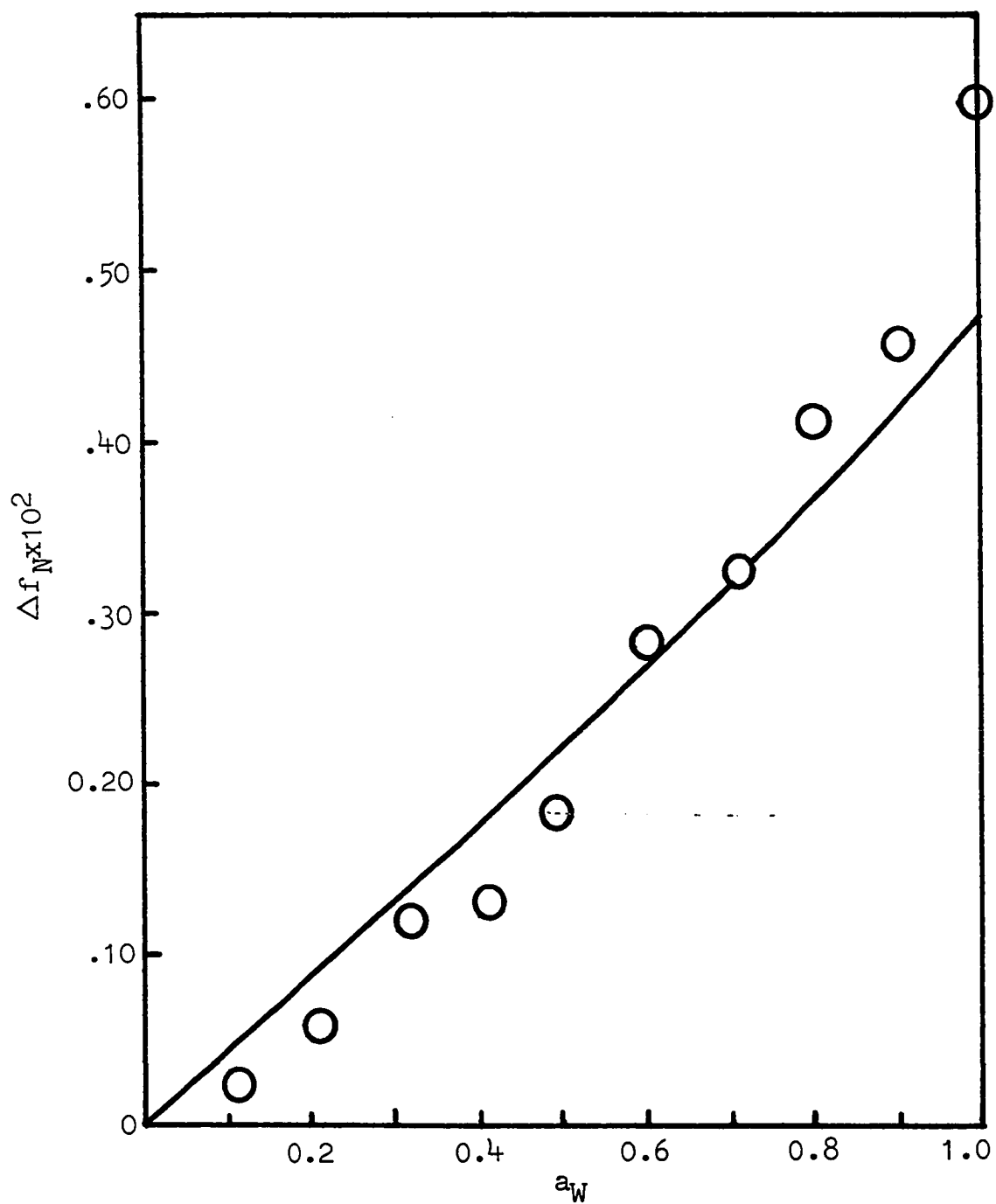


Fig. 8.--Difference in 2-naphthol solubility with increasing water activity in CCl_4 .

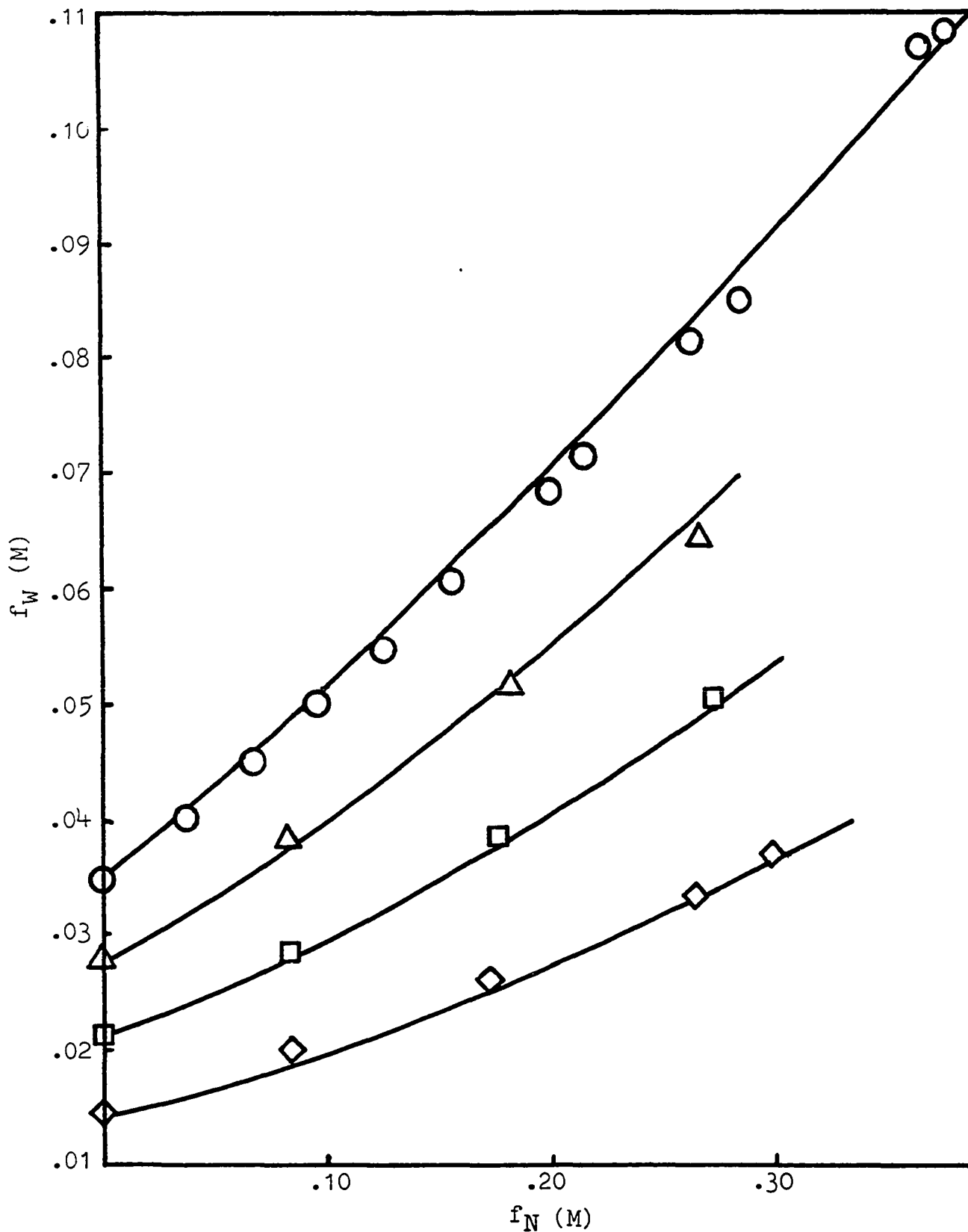


Fig. 9.--Hydration of 2-naphthol in benzene. $\circ, a_W = 1.00$; $\Delta, a_W = 0.805$; $\square, a_W = 0.607$; $\diamond, a_W = 0.415$. All lines in these figures are calculated.

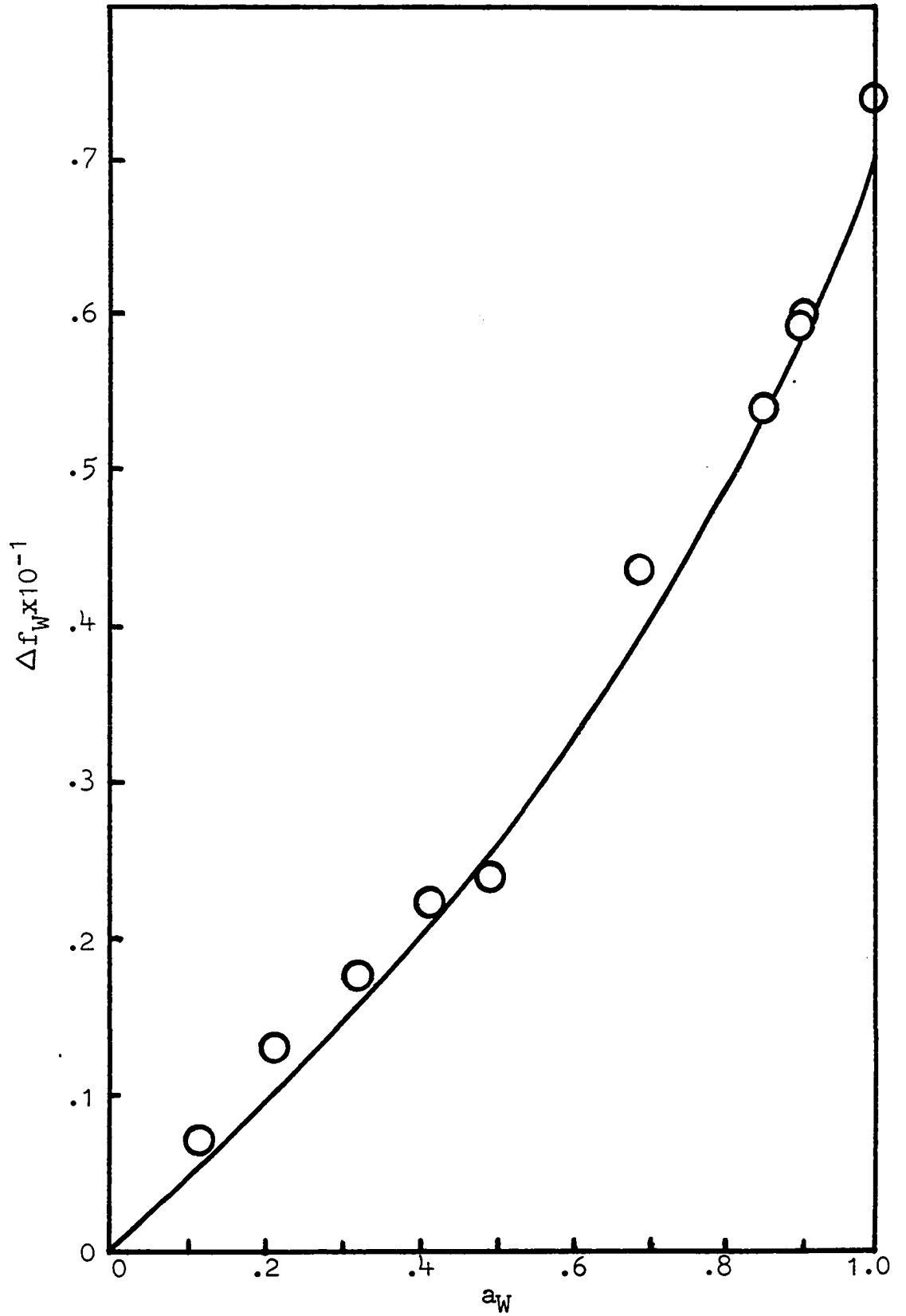


Fig. 10.--Difference in water solubility at saturated 2-naphthol concentration in benzene.

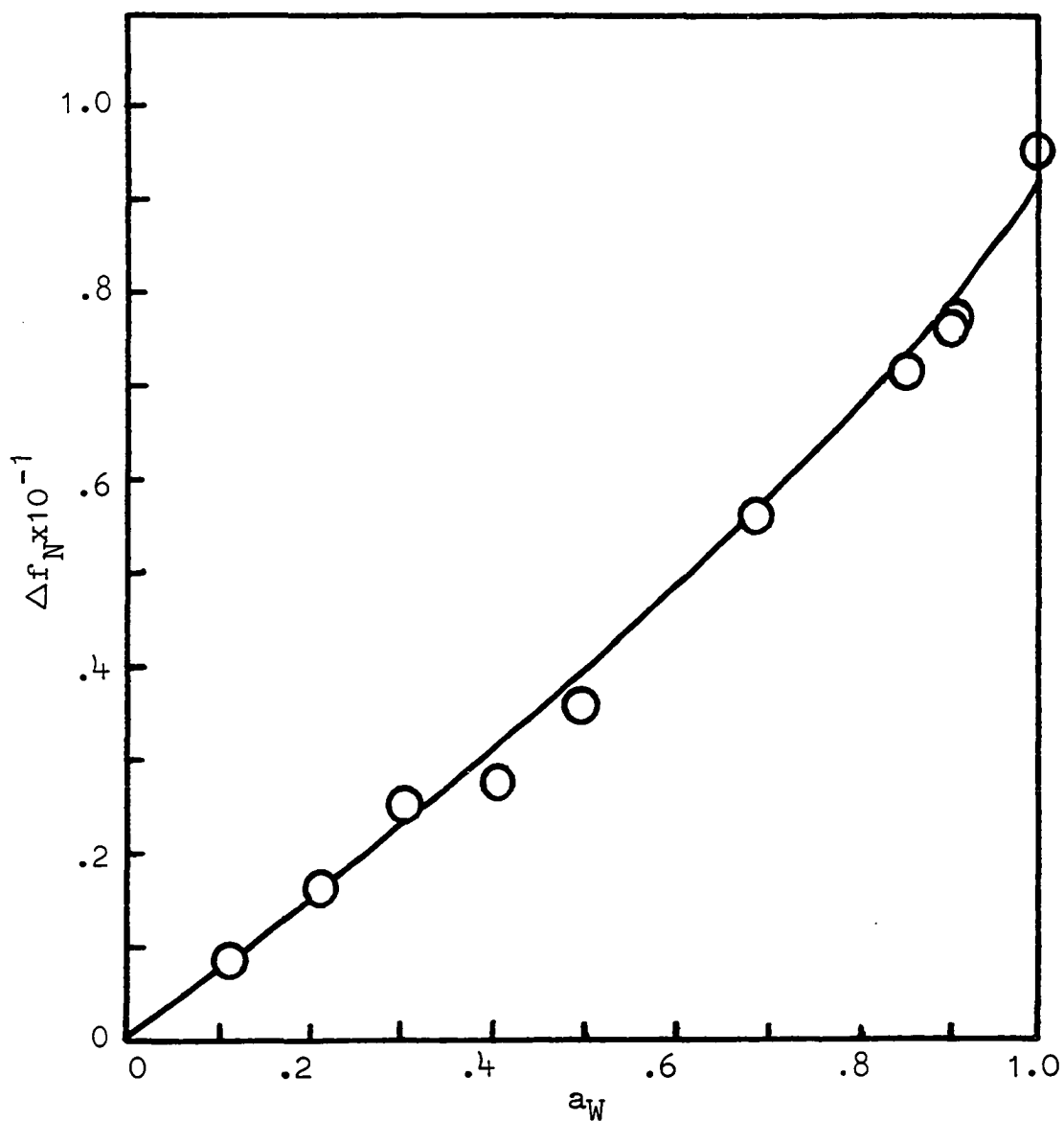


Fig. 11.--Difference in 2-naphthol solubility with increasing water activity in benzene.

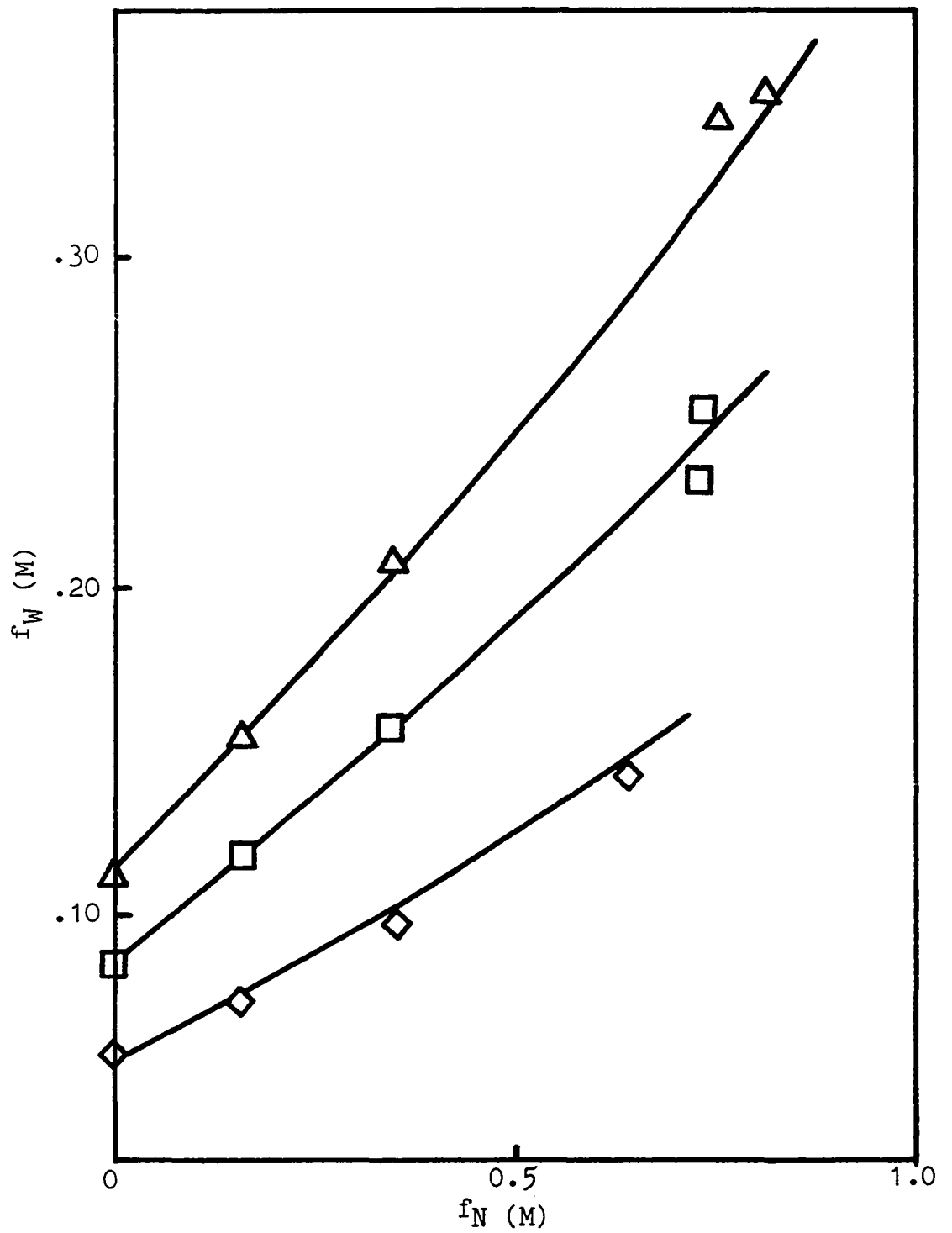


Fig. 12.--Hydration of 2-naphthol in 1,2 dichloroethane. Δ , $a_W=0.901$; \square , $a_W=0.714$; \diamond , $a_W=0.50$. All lines in these figures are calculated.

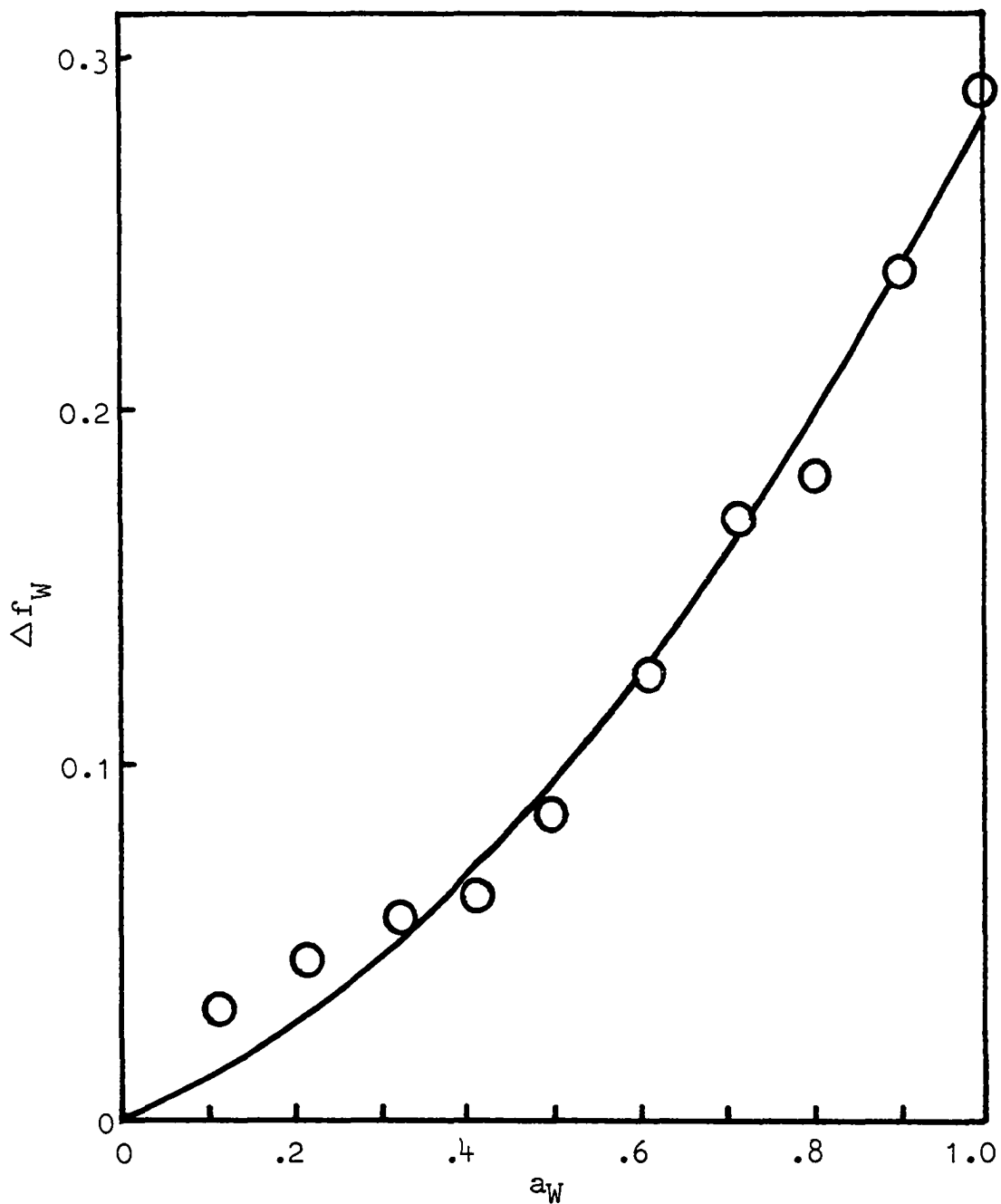


Fig. 13.--Difference in water solubility at saturated 2-naphthol concentration in 1,2 dichloroethane.

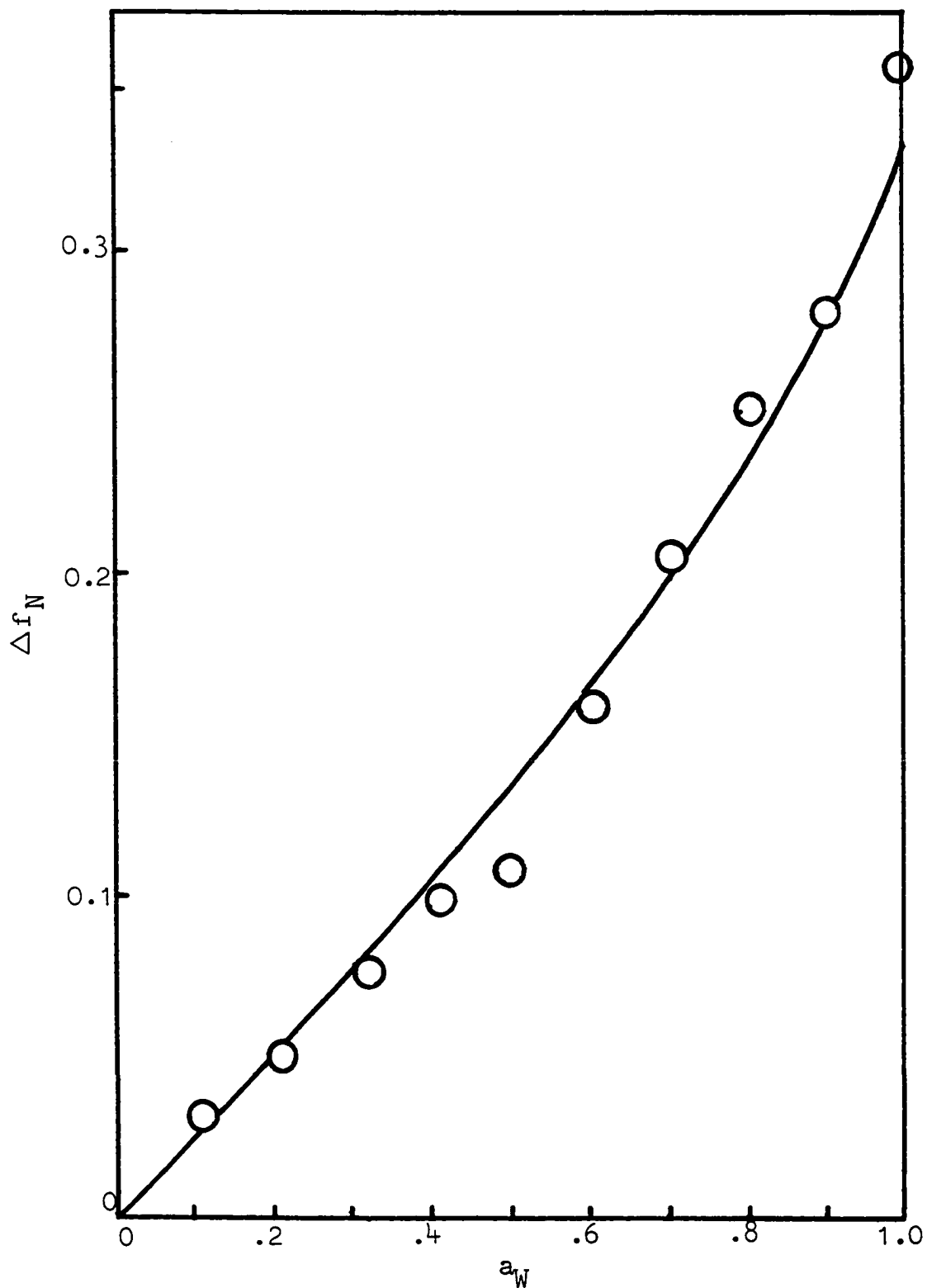


Fig. 14.--Difference in 2-naphthol solubility with increasing water activity in 1,2 dichloroethane.

Table 6

Water Solubility Data for the 2-Naphthol-Carbon
Tetrachloride System

a_W	$f_N(M)$	$f_W(M)$	$f_W(M, \text{calc})$
0.415	0.0000	0.00361	0.00361
	0.0116	0.00393	0.00402
	0.0245	0.00423	0.00445
	0.0364	0.00462	0.00479
	0.0475	0.00490	0.00507
0.607	0.0000	0.00528	0.00528
	0.0112	0.00579	0.00585
	0.0229	0.00627	0.00641
	0.0360	0.00672	0.00696
	0.0491	0.00725	0.00744
0.805	0.0000	0.00700	0.00700
	0.0112	0.00780	0.00774
	0.0236	0.00860	0.00852
	0.0364	0.00923	0.00922
	0.050	0.00970	0.00988
1.000	0.0000	0.00870	0.00870
	0.0045	0.00960	0.00905
	0.0078	0.00980	0.00932
	0.0274	0.01074	0.01082
	0.0299	0.01120	0.01109
	0.0365	0.01150	0.01100
	0.0413	0.01190	0.01170
	0.0523	0.01280	0.01230

Table 7

2-Naphthol and Water Solubility Data for
the Carbon Tetrachloride System

a_W	$f_W \times 10^2$	$f_W(\text{cals})$	$f_N \times 10^2$	$f_N(\text{calc})$
0.116	0.048	0.041	0.021	0.052
0.216	0.090	0.076	0.057	0.098
0.322	0.081	0.113	0.118	0.146
0.415	0.130	0.146	0.130	0.187
0.499	0.171	0.176	0.183	0.225
0.607	0.197	0.216	0.282	0.277
0.714	0.218	0.253	0.322	0.325
0.805	0.270	0.288	0.413	0.370
0.901	0.287	0.322	0.456	0.414
1.00	0.333	0.362	0.596	0.467

Table 8

Distribution Data for the 2-Naphthol-
Water-Carbon Tetrachloride System

$C_N^W \times 10^2 (M)$	$f_N^O (M)$	$f_N^O (M, calc)$
0.0475	0.0037	0.0034
0.2181	0.0190	0.0179
0.2573	0.0239	0.0222
0.2722	0.0246	0.0236
0.3410	0.0328	0.0319
0.4131	0.0413	0.0414
0.4372	0.0446	0.0449
0.4811	0.0491	0.0508
0.4964	0.0521	0.0536
0.0609	0.0045	0.0044
0.1012	0.0078	0.0075
0.1666	0.0133	0.0139
0.2915	0.0274	0.0260
0.3189	0.0299	0.0290
0.3748	0.0365	0.0361
0.4175	0.0413	0.0417
0.4964	0.0523	0.0538

Table 9

Water Solubility Data for the
2-Naphthol-Benzene System

a_W	$f_N(M)$	$f_W(M)$	$f_W(\text{calc})$
0.322	0.2926	0.0271	0.0264
0.384	0.2982	0.0311	0.0323
0.415	0.0869	0.0201	0.0186
	0.1747	0.0260	0.0250
	0.2775	0.0333	0.0334
0.607	0.0843	0.0286	0.0279
	0.1767	0.0387	0.0382
	0.2713	0.0506	0.0496
0.805	0.0846	0.0386	0.0384
	0.1812	0.0517	0.0532
	0.2651	0.0646	0.0668
1.000	0.0384	0.0403	0.0408
	0.0673	0.0452	0.0459
	0.0963	0.0502	0.0513
	0.1255	0.0549	0.0570
	0.1567	0.0609	0.0632
	0.1979	0.0686	0.0715
	0.2141	0.0716	0.0748
	0.2615	0.0815	0.0844
	0.2828	0.0851	0.0887
	0.3649	0.1076	0.1050

Table 10

2-Naphthol and Water Solubility Data
for the Benzene System

a_W	f_W	$f_W(\text{calc})$	f_N	$f_N(\text{calc})$
0.116	0.0071	0.0048	0.0094	0.0089
0.216	0.0131	0.0095	0.0166	0.0168
0.322	0.0177	0.0152	0.0241	0.0255
0.415	0.0225	0.0204	0.0277	0.0328
0.491	0.0240	0.0255	0.0360	0.0397
0.687	0.0438	0.0402	0.0559	0.0581
0.852	0.0587	0.0541	0.0712	0.0740
0.901	0.0596	0.0586	0.0763	0.0790
0.903	0.0600	0.0586	0.0771	0.0794
1.000	0.0742	0.0700	0.0959	0.0921

Table 11

Distribution Data for the 2-Naphthol-
Benzene-Water System

$C_N^W \times 10^2$	f_N^0	$f_N^0(\text{calc})$
0.0665	0.0384	0.0324
0.1228	0.0673	0.0625
0.1831	0.0963	0.0976
0.2221	0.1255	0.1229
0.2645	0.1567	0.1524
0.3214	0.1979	0.1952
0.3378	0.2141	0.2090
0.3982	0.2615	0.2603
0.4367	0.2828	0.2929
0.5114	0.3649	0.3713

Table 12

Water Solubility Data for the 2-Naphthol-
1,2 Dichloroethane System

a_W	$f_N(M)$	$f_W(M)$	$f_W(M, calc)$
0.491	0.0000	0.0553	0.0553
	0.6401	0.1157	0.1466
0.500	0.0000	0.0563	0.0563
	0.1613	0.0736	0.0755
	0.3572	0.0967	0.1050
	0.6437	0.1416	0.1502
0.714	0.0000	0.0837	0.0837
	0.1651	0.1172	0.1172
	0.3440	0.1559	0.1579
	0.7328	0.2319	0.2464
	0.7393	0.2528	0.2478
0.901	0.0000	0.1104	0.1104
	0.1629	0.1532	0.1568
	0.3500	0.2070	0.2129
	0.7567	0.3416	0.3306
	0.8155	0.3498	0.3468

Table 13

Water and 2-Naphthol Solubility Data for
the 1,2 Dichloroethane System

a_W	f_W	$f_W(\text{calc})$	f_N	$f_N(\text{calc})$
0.116	0.0317	0.0158	0.0323	0.0283
0.216	0.0458	0.0323	0.0502	0.0534
0.322	0.0507	0.0532	0.0760	0.0818
0.415	0.0628	0.0743	0.0991	0.1077
0.500	0.0853	0.0939	0.1097	0.1294
0.607	0.1231	0.1270	0.1579	0.1667
0.714	0.1691	0.1641	0.2053	0.2061
0.805	0.1823	0.2002	0.2516	0.2433
0.901	0.2394	0.2364	0.2815	0.2769
1.000	0.2913	0.2899	0.3582	0.3315

Table 14

Distribution Data for the 2-Naphthol
Water-1,2 Dichloroethane System

c_N^w	f_N^o	$f_N^o(\text{calc})$
0.00035	0.0329	0.0342
0.00119	0.1296	0.1257
0.00222	0.2564	0.2581
0.00305	0.3927	0.3858
0.00372	0.4991	0.5011
0.00408	0.5731	0.5705
0.00541	0.8509	0.8592

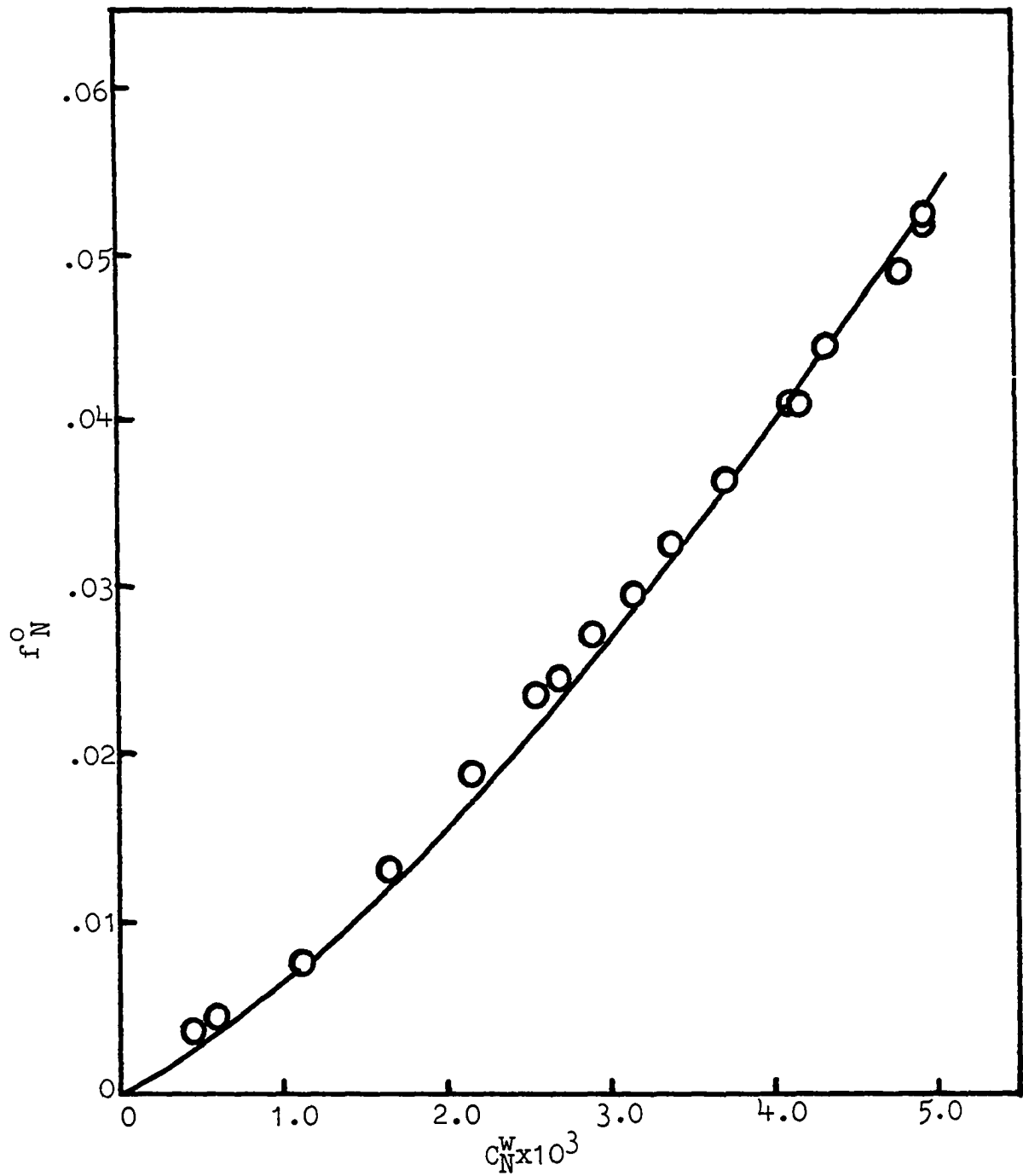


Fig. 15.--Distribution of 2-naphthol between H_2O and carbon tetrachloride. Line is calculated.

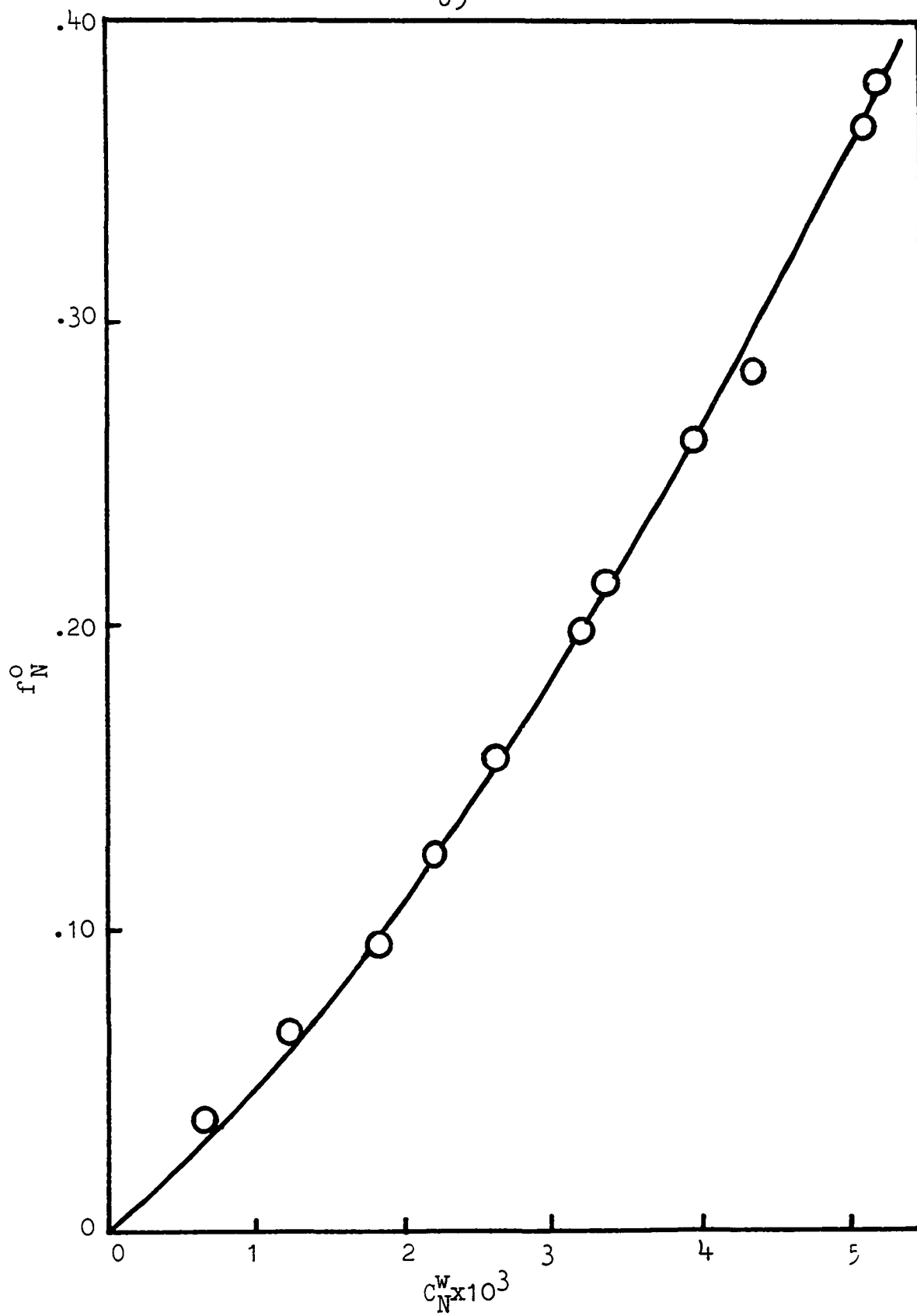


Fig. 16.--Distribution of 2-naphthol between H_2O and benzene. Line is calculated.

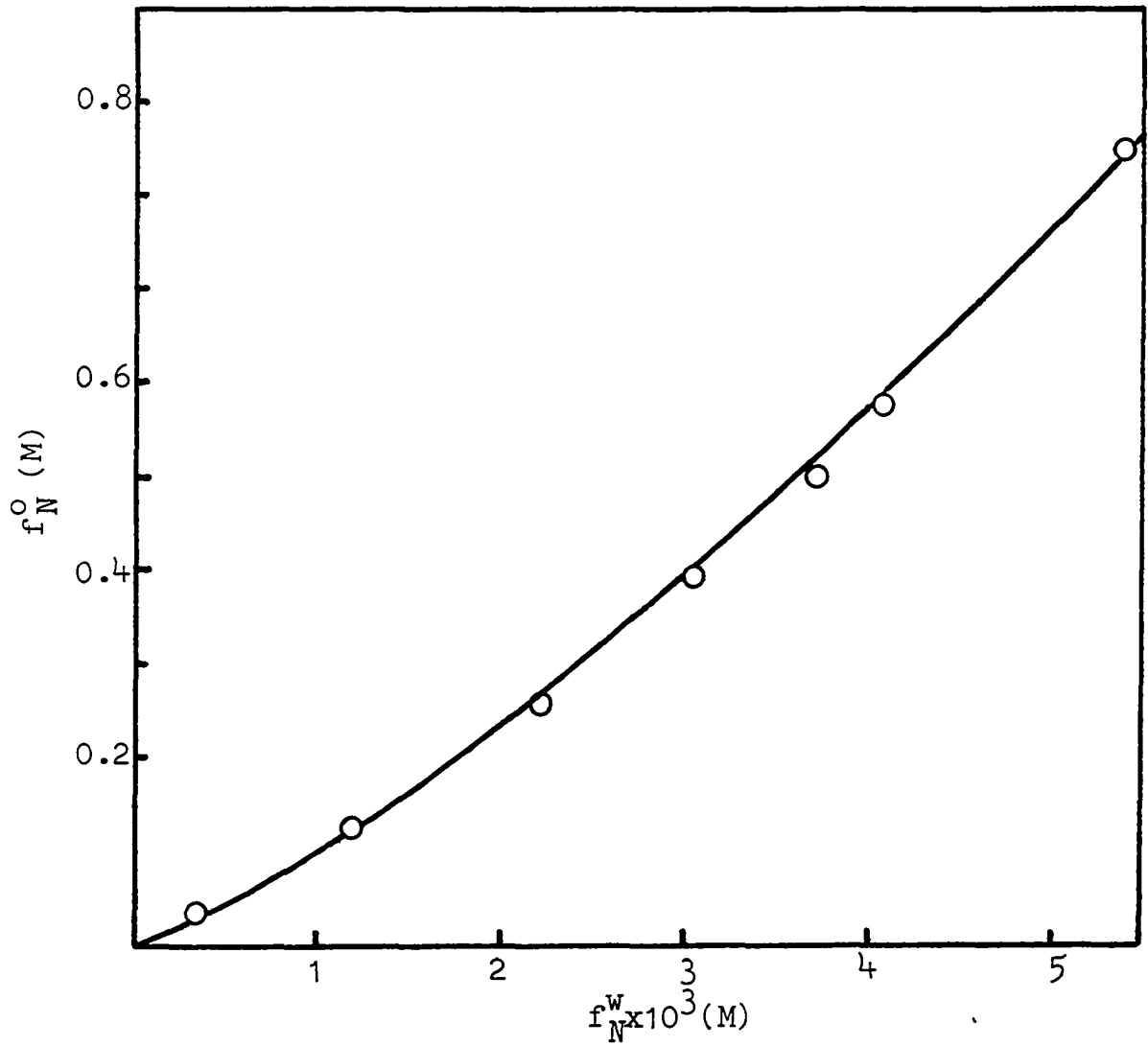


Fig. 17.--Distribution of 2-naphthol between H_2O and 1,2 dichloroethane. Line is calculated.

Table 15

Self-Association and Hydration Constants
for 2-Naphthol in CCl_4

Reaction	Equilibrium Constant
$\text{N (aqueous phase)} = \text{N (CCl}_4 \text{ Phase)}$	$\cdot K_D = 6.606 \pm 0.016$
$3\text{N} = \text{N}_3$	$\cdot K_3 = 169.9 \pm 15.4 \text{ M}^{-2}$
$\text{N} + \text{W} = \text{NW}$	$\cdot K_{11} = 9.43 \pm 0.03 \text{ M}^{-1}$
$2\text{N} + \text{W} = \text{N}_2\text{W}$	$\cdot K_{21} = 120 \pm 84 \text{ M}^{-2}$

Table 16

Self-Association and Hydration Constants
for 2-Naphthol in Benzene

Reaction	Equilibrium Constant
$\text{N (aqueous phase)} = \text{N (benzene phase)}$	$\cdot K_D = 43.21 \pm 0.10$
$3\text{N} = \text{N}_3$	$\cdot K_3 = 1.797 \pm 0.063 \text{ M}^{-2}$
$\text{N} + 2\text{W} = \text{NW}_2$	$\cdot K_{12} = 60.32 \pm 3.50 \text{ M}^{-2}$
$2\text{N} + \text{W} = \text{N}_2\text{W}$	$\cdot K_{21} = 23.12 \pm 0.35 \text{ M}^{-2}$

Table 17

Self-Association and Hydration Constants
for 2-Naphthol in 1,2 Dichloroethane

Reaction	Equilibrium Constant
$\text{N (aqueous phase)} = \text{N (DCE phase)}$	$\cdot K_D = 79.92 \pm 0.17$
$3\text{N} = \text{N}_3$	$\cdot K_3 = 0.457 \pm 0.019 \text{ M}^{-2}$
$\text{N} + 2\text{W} = \text{NW}_2$	$\cdot K_{12} = 15.96 \pm 0.59 \text{ M}^{-2}$
$2\text{N} + \text{W} = \text{N}_2\text{W}$	$\cdot K_{21} = 5.87 \pm 0.03 \text{ M}^{-2}$

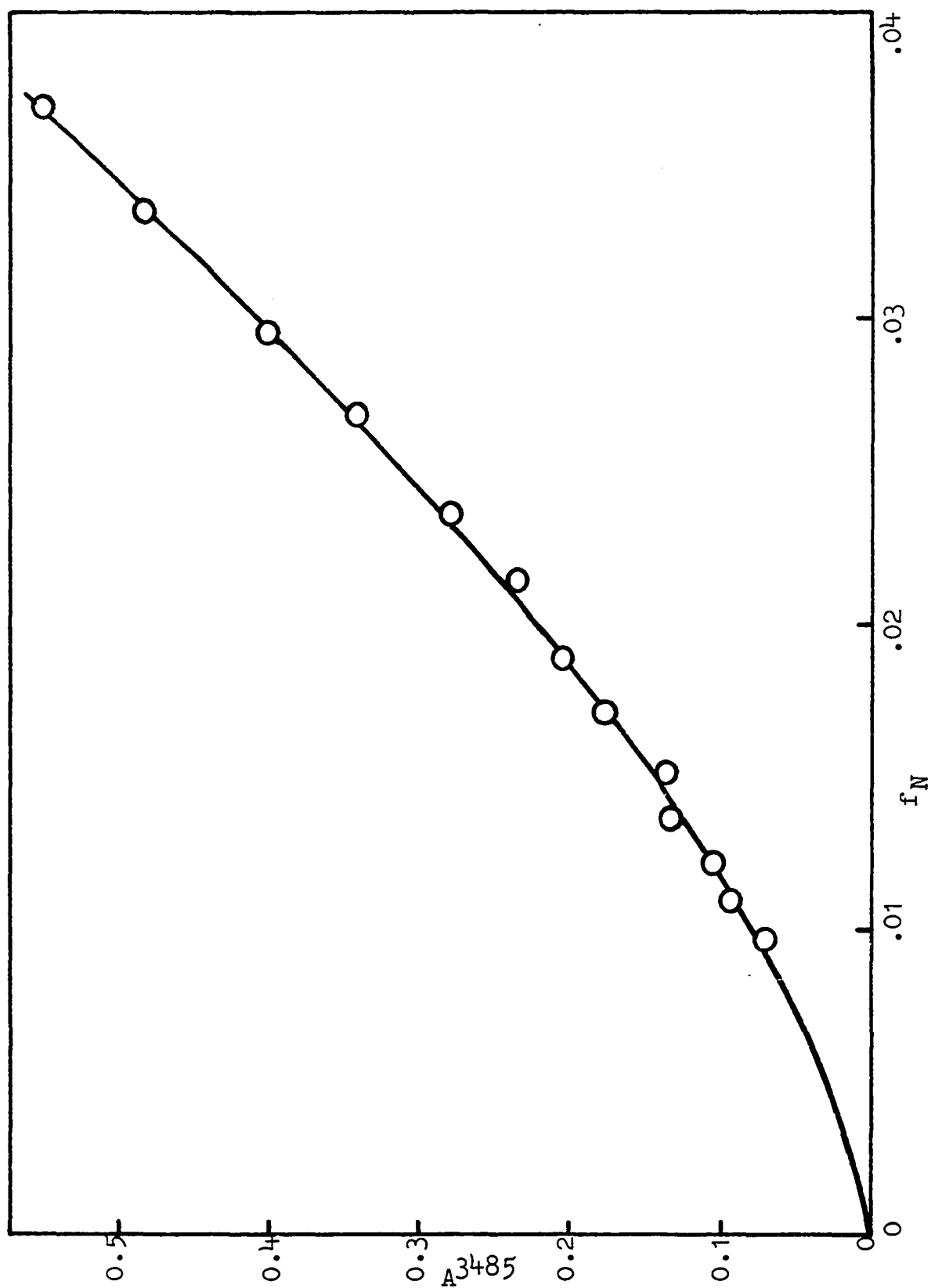


Fig. 18.--Infrared study of self-association of 2-naphthol in carbon tetrachloride. Line is calculated.

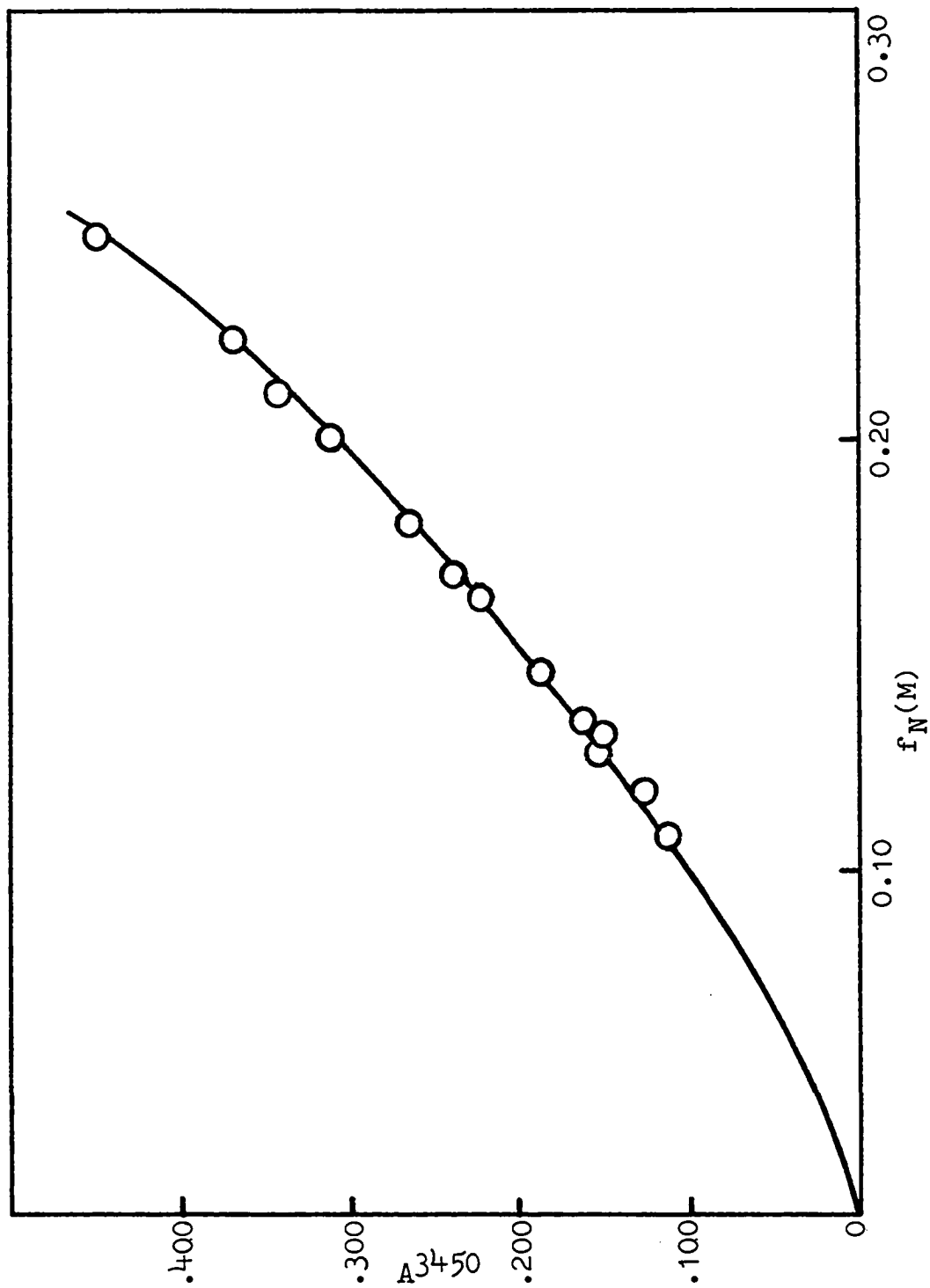


Fig. 19.--Infrared study of self-association of 2-naphthol in benzene. Line is calculated.

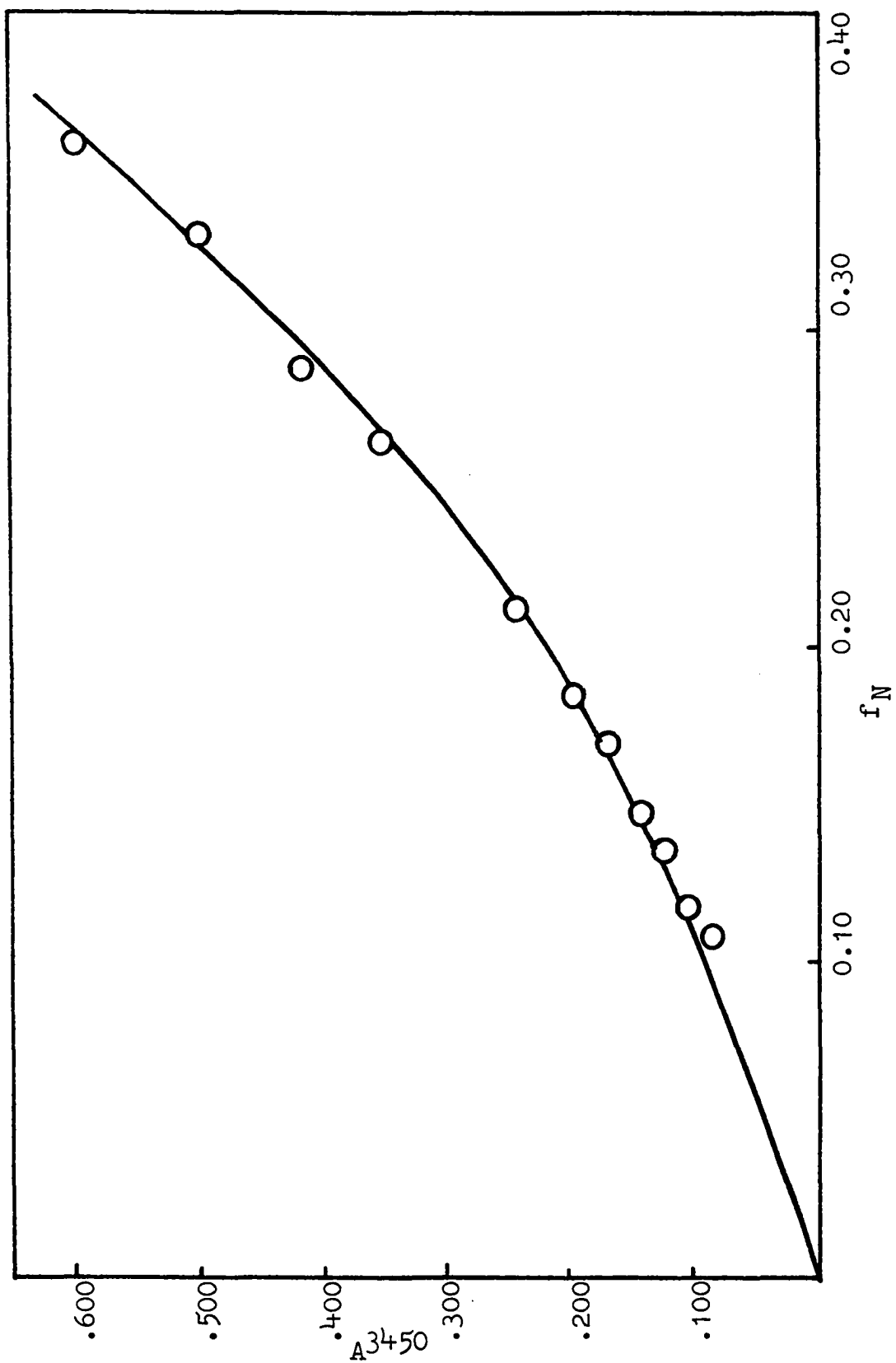


Fig. 20.--Infrared study of self-association of 2-naphthol in 1,2 dichloroethane. Line is calculated.

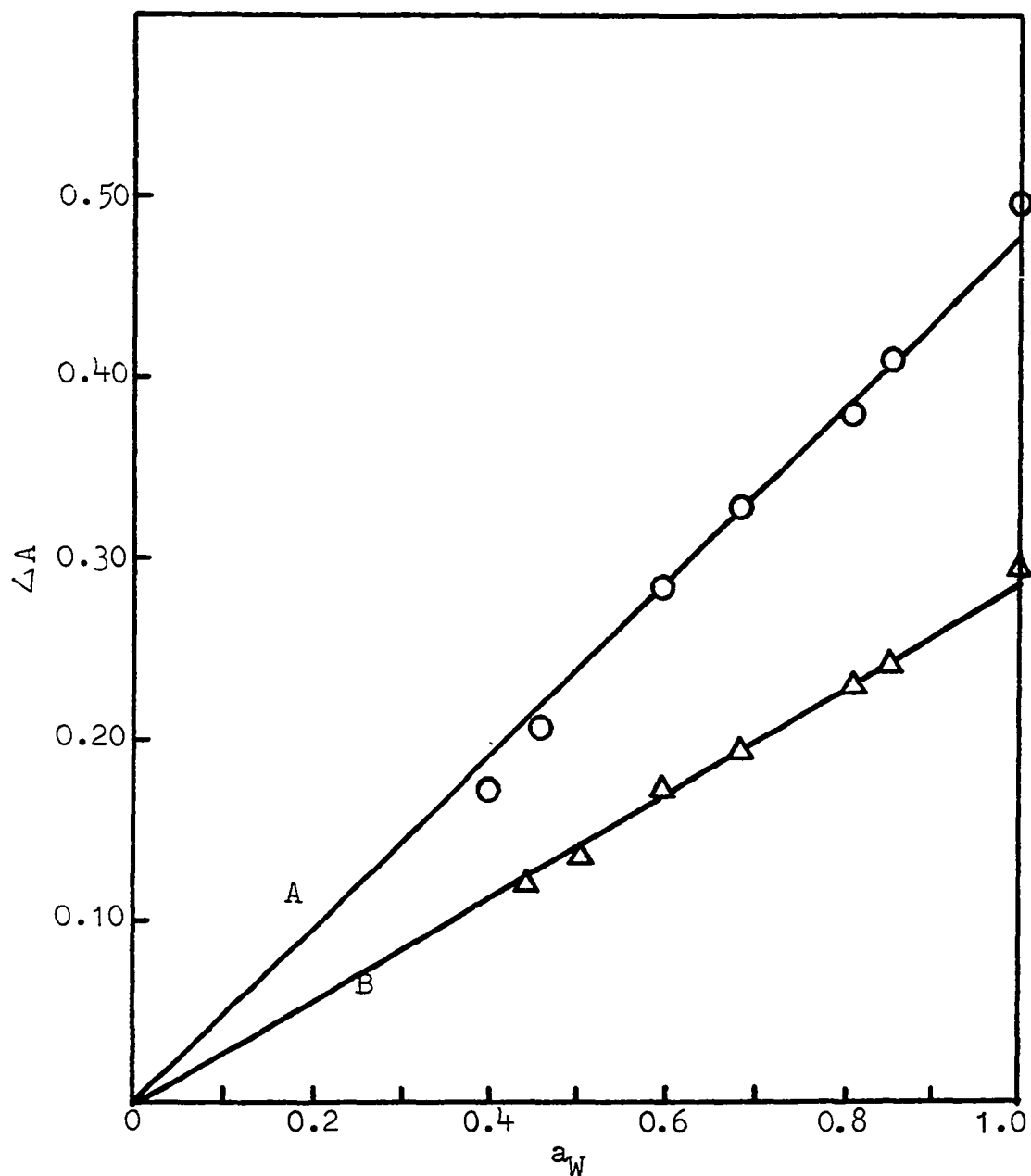


Fig. 21.--Absorbance at 3455 cm^{-1} due to hydrated 2-naphthol in carbon tetrachloride. \circ , $f_N=0.0270$ M; Δ , $f_N=0.0161$ M. All lines in these figures are calculated.

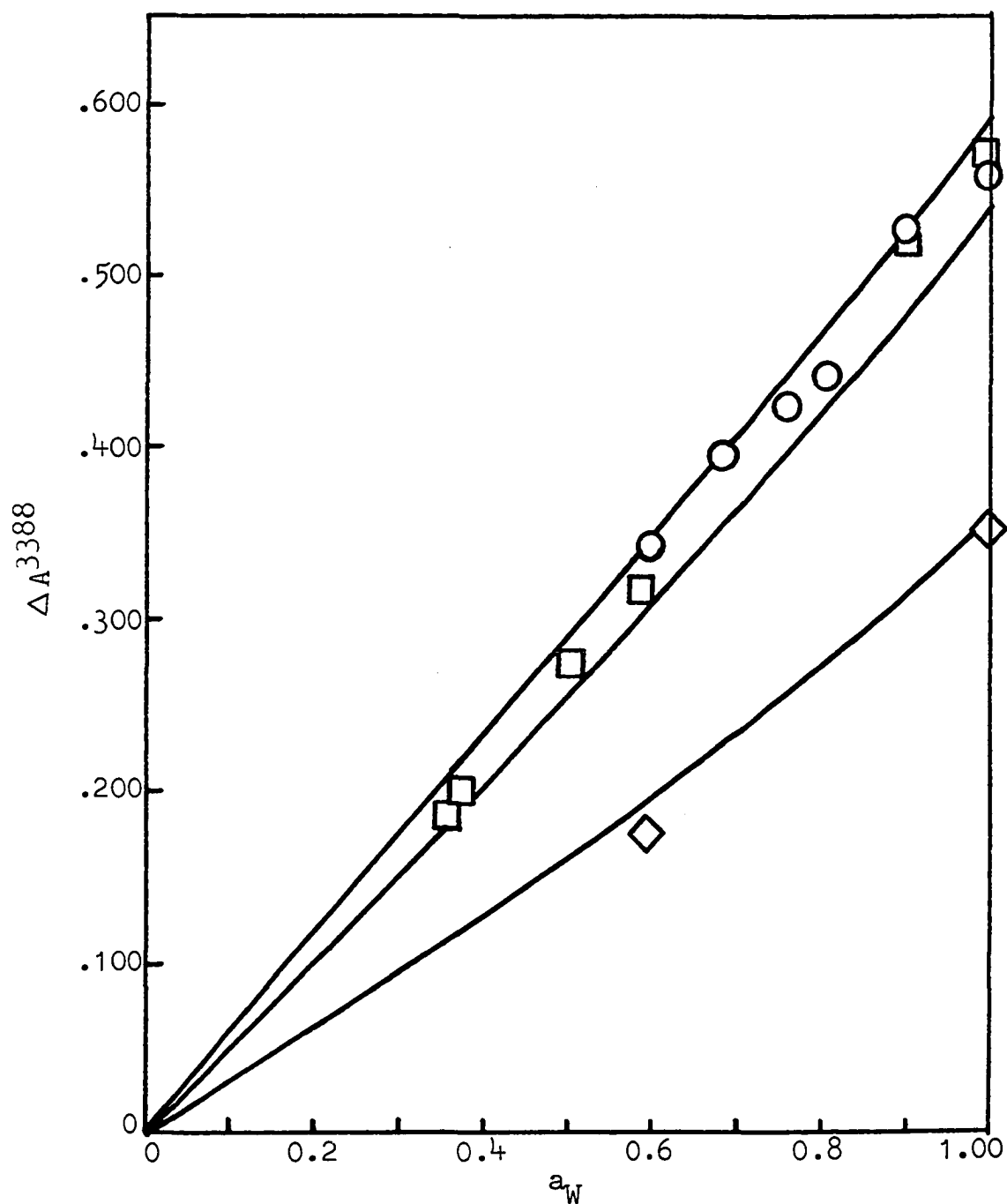


Fig. 22.--Absorbance at 3388 cm^{-1} due to hydrated 2-naphthol in benzene. \circ , $f_N=0.220$ M; \square , $f_N=0.202$ M; \diamond , $f_N=0.146$ M.

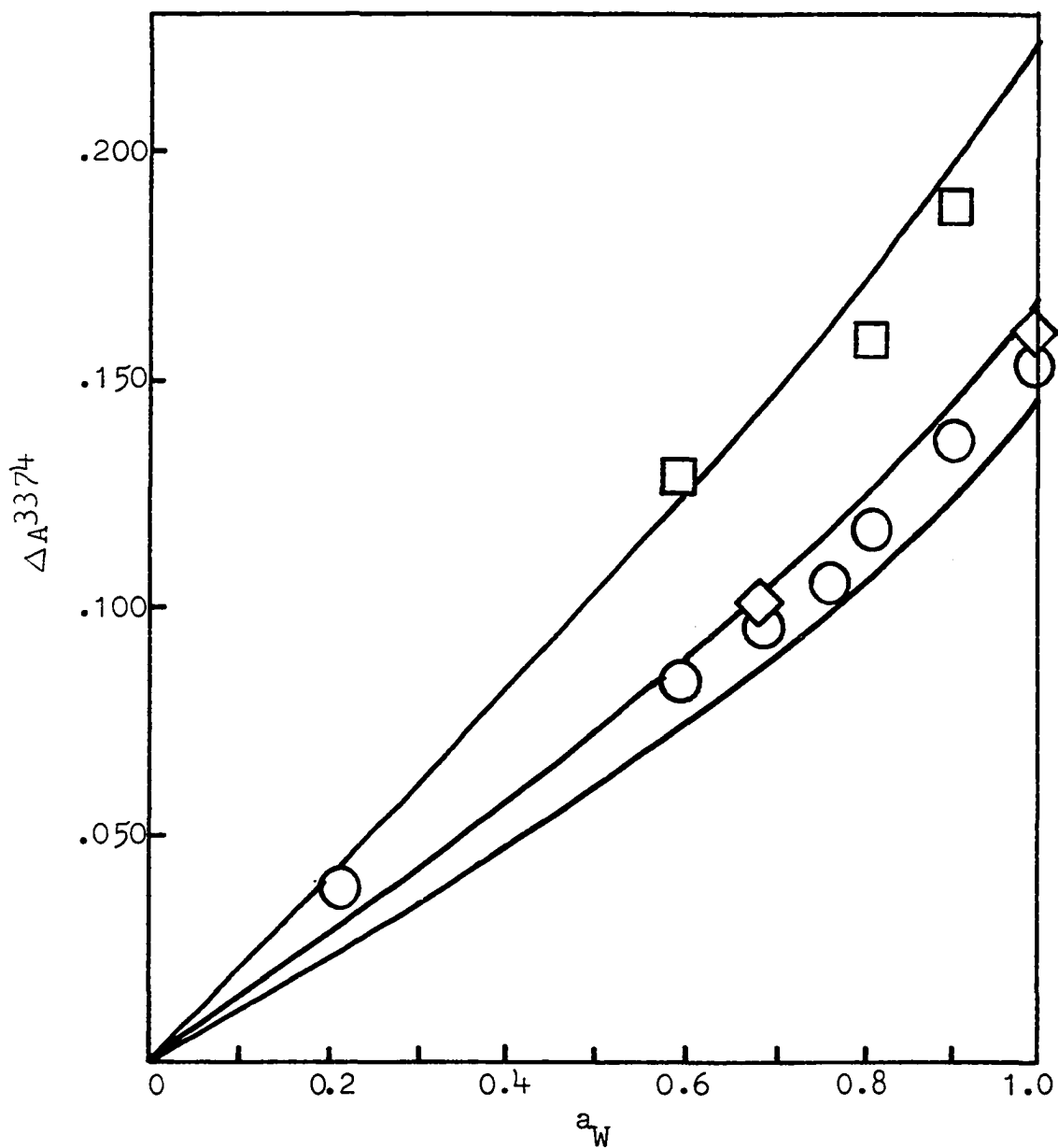


Fig. 23.--Absorbance at 3374 cm^{-1} due to hydrated 2-naphthol in 1,2 dichloroethane. \square , $f_N=0.400$ M; \diamond , $f_N=0.280$ M; \circ , $f_N=0.240$ M.

Table 18

Infrared Study: Self Association in CCl_4

$f_N(M)$	A	A(calc)
.00966	.073	.078
.01097	.094	.092
.01207	.104	.105
.01372	.134	.126
.01508	.135	.144
.01715	.177	.173
.01887	.205	.200
.02144	.234	.242
.02358	.278	.280
.02680	.342	.341
0.2948	.401	.395
.03350	.484	.481
.03684	.551	.556

Table 19

Infrared Study: Self Association in Benzene

$f_N(M)$	A	A(calc)
.1080	.113	.113
.1185	.127	.130
.1316	.151	.154
.1319	.150	.154
.1350	.162	.160
.1463	.181	.183
.1625	.221	.218
.1687	.238	.232
.1806	.264	.260
.2006	.311	.311
.2109	.342	.339
.2229	.367	.373
.2477	.446	.447

Table 20

Infrared Study: Self Association in 1,2 Dichloroethane

$f_N(M)$	A	A(calc)
.1081	.085	.095
.1176	.105	.106
.1351	.125	.127
.1470	.143	.142
.1689	.170	.173
.1836	.199	.196
.2111	.245	.243
.2638	.354	.350
.2871	.417	.404
.3298	.497	.513
.3589	.599	.596

Table 21

Infrared Study: Hydration in CCl_4

a_w	$f_N(M)$	A	A(calc)
1.00	.02696	.497	.472
	.01610	.295	.282
.852	.02696	.421	.407
	.01610	.243	.244
.810	.02696	.381	.389
	.01610	.231	.233
.687	.02696	.330	.333
	.01610	.195	.200
.597	.02696	.285	.292
	.01610	.175	.175
.504	.01610	.137	.149
.461	.02696	.209	.228
.443	.01610	.121	.132
.401	.02696	.174	.200

Table 22

Infrared Study: Hydration in Benzene

a_w	$f_N(M)$	A	A(calc)
1.000	.2201	.559	.591
	.2022	.571	.533
	.1462	.352	.357
.903	.2201	.528	.530
	.2022	.520	.478
.810	.2201	.440	.473
.762	.2201	.423	.443
.687	.2201	.395	.398
.597	.2201	.341	.344
	.1462	.175	.198
.590	.2022	.318	.304
.505	.2022	.276	.258
.374	.2022	.202	.188
.360	.2022	.187	.181

Table 23

Infrared Study: Hydration in 1,2 Dichloroethane

a_w	$f_N(M)$	A	A(calc)
1.000	.2786 .2399	.159 .154	.167 .144
.903	.3943 .2399	.187 .137	.205 .125
.810	.3983 .2399	.158 .118	.179 .107
.762	.2399	.106	.098
.687	.2828 .2399	.101 .096	.100 .084
.597	.4287 .2399	.128 .084	.129 .069
.418	.2250	.064	.038
.331	.2250	.057	.027
.216	.2399	.038	.017

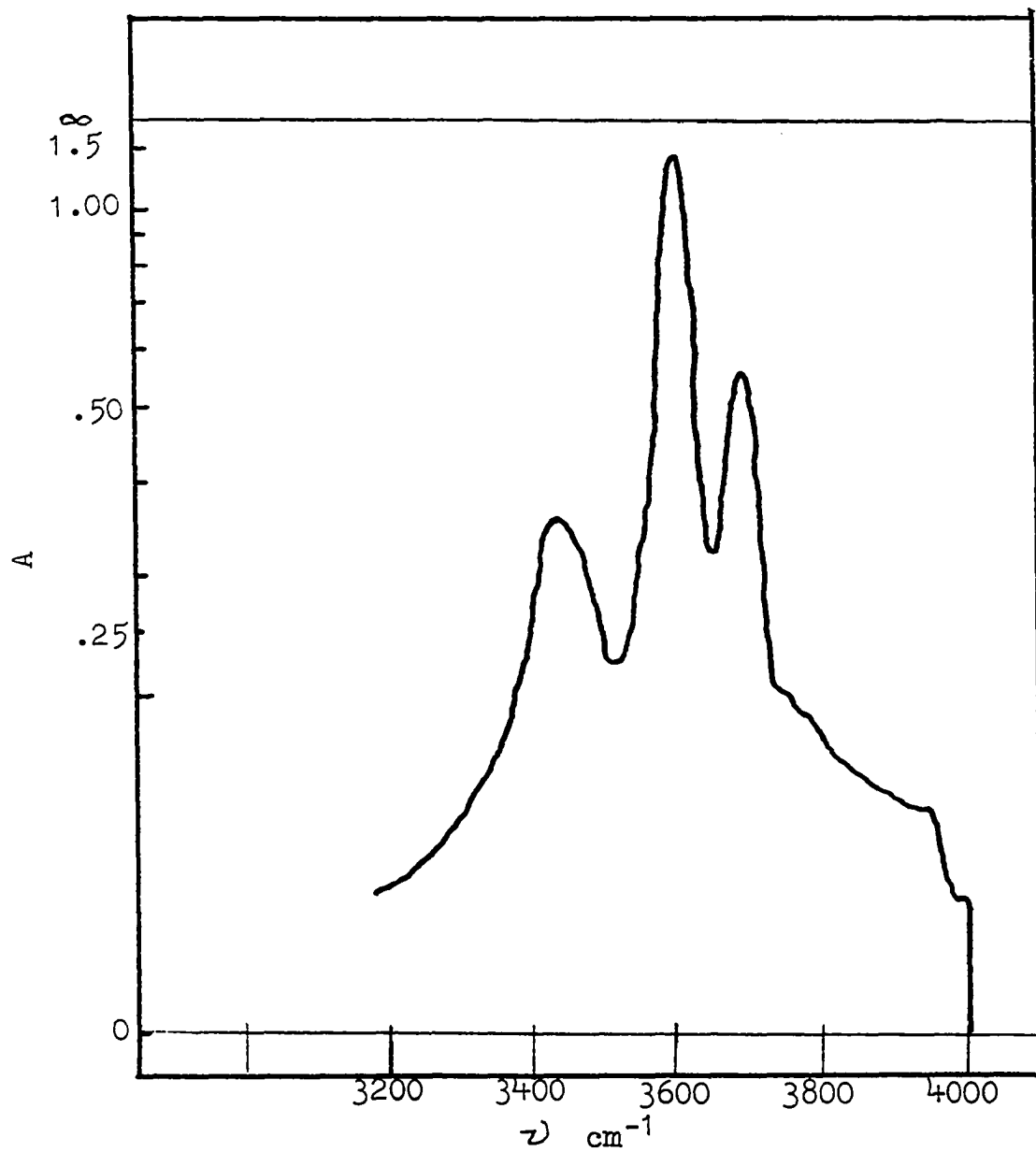


Fig. 24.--Difference spectrum of hydrated 2-naphthol in CCl_4 . Reference beam has been blocked with anhydrous 2-naphthol solution.

CHAPTER V

DISCUSSION AND CONCLUSIONS

In general, previous investigations of the association of alcohols and phenols have involved difficulties, in that ambiguous results are sometimes obtained when there is only one physical property studied. While the use of several different properties does not guarantee the elimination of ambiguities, it does provide a more critical test of the results derived from each property investigated.

The results of this study provide new and interesting information relevant to the development of theories of association and solvent effects and augment our knowledge of the nature of alcohol association. This discussion will be concerned first with a comparison of thermodynamic results and models, and second with a comparison of the spectral data and solvent effects of this study with other reports. A short summary will conclude this chapter.

Thermodynamic Data

Lately, studies of alcohols and other oxygen containing compounds have provided evidence for trimeric and other

complexes having different stoichiometry than that of a 1:1 complex. The results of this study also indicate a preference for an association model having three molecules per unit. These results lend support to those found by Johnson (6) and to the three molecule heterocomplexes discussed by Farnham (55) and by Tucker (56). In addition to these results, association studies of alcohols, phenols, and water by authors outside of this group have recently shown increased consideration of trimers and higher order species (33), (35), (60).

The self-association data for 2-naphthol from both the vapor pressure lowering experiments and the infrared spectral study have been interpreted successfully as representing an equilibrium between monomer and trimer species. The hydration studies indicate a preference for 1:2 and 2:1 complexes in the two solvents where a sufficient concentration of water monomer can be achieved to provide the basis for this stoichiometry. The apparent unimportance of the 1:2 hydrate in CCl_4 fits can be interpreted as an initial indication that there is not a sufficient concentration of water monomer present in this solvent to produce the 1:2 dependence through the mass action law. Alternatively, there should be a concentration of the 1:1 hydrate complex in all three solvents, but the fact that the two-parameter fits do not provide evidence for this species indicates that it exists in minor concentration compared to the other hydrates mentioned.

Although there have been few studies of the self-association of 2-naphthol itself, a comparison of our results with those for naphthol and phenol association complexes obtained by other authors will be of interest.

To examine the self association of 2-naphthol, Wolf and Metzger (57) determined the boiling point elevation of benzene solutions of 2-naphthol, from which they found a dimerization constant $K = 0.33 \text{ M}^{-1}$ at 80°C . They assumed that there were only dimeric species present and did not attempt to examine their data for higher order dependence. It is difficult to make a valid comparison of Wolf and Metzger's result with ours because of the large difference in temperatures between these two experiments. The general temperature dependence of hydrogen bonding K 's indicates that there would be only fair agreement with our results. Other self-association work concerning related compounds will be discussed below.

Up to now, most research on the association of 2-naphthol has been limited to studies of 1:1 interactions. These were found for systems where donor and acceptor structure were favorable for only 1:1 complexes, which commonly result from Lewis acid-base interactions.

For complexes of 2-naphthol with various amines, Murthy and Rao (37) give results from several IR studies. Bonnett and Julg (58) report equilibrium constants for 1:1 complexes of 2-naphthol with triethylamine (102 M^{-1}),

mono-butylamine (128 M^{-1}) and di-n-butyl amine (138 M^{-1}) in heptane at 25°C . Bhowmik and Basu (59) give K's for 2-naphthol and diethyl ether (10.58 M^{-1}) and dioxane (12.87 M^{-1}) in cyclohexane at 27°C . Other infrared studies yield similar values for related donor-acceptor reactions.

The results above also agree with those of an ultraviolet spectroscopic study done by Nagakura and Gouterman (28). They report K's for 2-naphthol with triethylamine (103 M^{-1}), with diethyl ether (14.5 M^{-1}) and nitromethane (103 M^{-1}) in n-heptane at 25°C .

Korshunov and Pakornov (29) report stability constants for complexes between 2-naphthol and alcohols in octane. For the naphthol complex with n-butyl alcohol they report a $K = 33 \text{ M}^{-1}$, with hexanol, $K = 37 \text{ M}^{-1}$ and with amyl alcohol, $K = 36 \text{ M}^{-1}$.

The values for these equilibrium constants all seem to fall in a range that is in reasonable agreement with those presented here (see Table 24).

The self-association results for 2-naphthol presented here can be compared with those for phenol, a slightly stronger acid. Johnson reports a $K_3 = 4.1 \text{ M}^{-2}$ for the trimerization reaction of phenol in CCl_4 , but this was assumed to co-exist with a phenol hexamer in this solution ($K_6 = 432 \text{ M}^{-5}$). Presumably, his trimer constant would have been higher had he been able to account for all association with only that species. In benzene, $K_3 = 0.263 \text{ M}^{-2}$ and in DCE

the trimerization constant dropped to 0.002 M^{-2} . In DCE however, it has been previously shown that there is little self-association even in anhydrous solutions at the concentrations used. It is interesting to compare the magnitudes of these trimerization constants with those of 2-naphthol. The largest change for the phenol systems was from benzene to dichloroethane as a solvent, where the reduction in K_3 amounted to two orders of magnitude. The increase in K when changing the solvent benzene to CCl_4 was only one order of magnitude. For the naphthol case however, the largest change was observed between the benzene solvent and CCl_4 , where the change was equal to two orders of magnitude. The decrease in K values between benzene and DCE however, only amounted to about one order of magnitude. The values of K in Table 2⁴ clearly show that 2-naphthol is much more highly associated even in the solvent DCE ($K_3 = 0.457 \text{ M}^{-2}$) than is phenol. The closest numerical value for K_3 in these two studies is observed for the solvent benzene, where (for 2-naphthol) $K_3 = 1.80 \text{ M}^{-2}$ is still one order of magnitude larger than the phenol constant. In CCl_4 , the naphthol $K_3 = 170 \text{ M}^{-2}$, which indicates considerably more association for the naphthol than for phenol. Although the amount of association differs considerably for these two similarly structured molecules, it is important to note that the best fit for these systems involved predominantly the trimer species, and that it was not necessary to include the dimer for an adequate representation.

Whetsel and Lady (2) discuss the self-association of phenol in CCl_4 and in cyclohexane. They report their results and fit their infrared data to various self association models. For the trimer-only fit of phenol in CCl_4 they report a $K_3 = 20.0$ at 20.7°C . This gives a relatively good figure with which to compare the more highly associated 2-naphthol trimerization constant of 170 M^{-2} in CCl_4 at 25°C . Of the multiparameter models that they tested (including fits up to an octamer species) they found only three models which gave positive values for all of the constants. Two of these fits in turn required the assumption of a stepwise "n-mer" constant for a series of higher order polymers. They chose to use the monomer-dimer-stepwise n-mer models, since their dimer constant for the other stepwise fit (monomer-dimer-trimer-stepwise n-mer) gave poor temperature dependence. The one good fit that they dismissed, as discussed in the introduction (Chapter I) was that having the monomer-trimer-hexamer model proposed by Johnson (6). The important point to observe in this study is that there were considerable improvements in the fit of their data when they considered the possibility of trimeric species. In fact, the multiparameter fit of the monomer-dimer-trimer-stepwise n-mer did give a lower standard error than the one they chose to use. On the basis of the evidence presented here, it is predicted that a superior fit would have been obtained if Whetsel and Lady had tried a monomer-trimer-stepwise n-mer model to fit their

data. It is even possible that there might have been good temperature dependence of all constants derived from the monomer-trimer hexamer model which they did not test in this manner.

Vanderbough, Armstrong, and Spall (11) employ the dimer and trimer species of phenol in benzene to explain their cryoscopic data. The work previously mentioned by Wooley et al. (9) indicated only the trimer as the main species in both anhydrous and water saturated CCl_4 . They tested their data for other species and found that all their results were fit best with only a monomer-trimer equilibrium. For p-cresol, the results of an NMR study by Baron and Lumbroso-Bader (60) can be accounted for by assuming that there is a competition between closed trimers (predominant species) and closed dimers. For the system 2,6 dimethylphenol in CCl_4 they assume open trimers and open dimers.

It can be seen that the trimer is an important species in phenol studies. Other self-association studies that show the importance of the trimer are those of water in organic solvents. Johnson, Christian and Affsprung (10) have presented evidence in favor of the trimeric form of water in nine solvents, including DCE. Jolicoeur and Cabana (33) have presented IR evidence favoring the cyclic trimer form of associated water in DCE. Masterton and Gendrano (32) concluded from an isopiestic study that either a monomer-trimer or a monomer-dimer equilibrium could be responsible

for their findings. Other results from vapor pressure experiments indicate that the most likely associated species are trimers or tetramers in DCE (61).

In addition to self-associated species consisting of three molecule complexes, evidence has been presented by several authors for different trimeric and higher order heteromolecular complexes. These consist mainly of H₂O and molecules containing alcohol groups or other oxygen containing molecules.

Farnham (55) has postulated the existence of 1:2 and 2:1 complexes of fluoroalcohols with methanol in hexadecane over a range of temperatures from 15° to 35° C. He has also found a mixture of 1:1, 4:1, and 3:1 complexes for systems studied in diphenylmethane.

Tucker (56) has found evidence for mono- and dihydrate complexes of water and diethylamine in benzyl ether. His one to one complexes have K's of 10.97 M⁻¹ in n-hexadecane and 8.52 M⁻¹ in diphenylmethane at 25° C. That compares with the naphthol-water 1:1 complex, K = 9.43 M⁻¹ in CCl₄ reported here. In the solvent benzyl ether, Tucker postulated both 1:1 and 1:2 amine-water complexes and reported equilibrium constants of 2.81 M⁻¹ and 9.7 M⁻¹, respectively, for the 1:1 and 2:1 species. These results can be compared with the values derived for 2-naphthol (0.605 M⁻¹ for the 1:1 and 22 M⁻¹ for the 2:1) in the three-parameter fit for the solvent benzene.

The results of the alcohol studies by Farnham and the amine studies by Tucker have been interpreted by these authors as support for the theory of hydrogen bond enhancement or inductive effect. This theory had been discussed for alcohols by Bellamy and Pace (62). For hydrogen bonding in water, Frank and Wen (63) discuss a similar "cooperative effect." Whether or not this is the cause still remains to be proven by additional work, but the observed effect is definitely one that is supported by the results presented here.

Other 2:1 and/or 1:2 complexes have been postulated for systems involving amines by Gregory (46), HCl-ether complexes by Keenan (64) and by McIntosh and Mass (65), for systems involving butanedione and water by Lin (50), for cyclopentanone and water by Lynch (66) and for systems involving pyrrolidone and water by Worley (67) and also by Mueller (68). Most of these reports also included 1:1 complexes as species as well. There is other evidence for the trimeric unit in charge-transfer systems and in inorganic complexing systems but we will limit our discussion here to H-bond systems.

Two types of water-pyridine aggregates have been postulated by Siderov (69), one in which a water molecule is bonded to two pyridine molecules (2:1) and the other one in which the water is bonded to one molecule of pyridine. A discussion of water complexes of 1:1 and 2:1 stoichiometry is

also referred to by Saugmagne in a discussion of the structure of a water dimer (35).

In hydration studies of salicylic acid, Van Duyne (7) found evidence for 1:1, 1:2, and 2:1 hydrate complexes in the same three solvents used in this study. His value for the 1:1 complex in CCl_4 was 11.0 M^{-1} which compares favorably with $.43 \text{ M}^{-1}$ obtained for the naphthol-water 1:1 complex in the same solvent at 25°C . Most of the other constants derived for salicylic acid are of the same magnitude as those found for 2-naphthol, but further comparisons would not be fruitful owing to the difference in structure.

In the case of phenol, however, structure and functional group are nearly identical. Johnson's previously mentioned phenol studies can be examined with reference to the results presented here. In his systems, Johnson postulated only the 1:2 and 2:1 hydrates in benzene, dichloroethane, and tetrachloroethane. These species are precisely the same ones found to predominate with 2-naphthol in benzene and in DCE. However, in CCl_4 , the hydration data required assumption of a 1:1 complex along with 3:1, 3:2, and a 6:3 complexes of phenol water. In the case of naphthol, a different set of species was also required, and a 1:1 and a 2:1 complex were found satisfactory for the naphthol-water case in CCl_4 . It is interesting to note that in studies of trifluoroacetic acid by Stevens (47), comparisons of solvent effects on frequency shifts indicate that data fall into two

groups: the "inert" solvents cyclohexane and CCl_4 and the other group of "active" solvents benzene and dichloroethane. In addition, this same dichotomy of properties is also evidenced in a thermodynamic parameter plots in which comparison of frequency shift with ΔH of monomer transfer from vapor to solvent was made. Other plots comparing frequency shift and distribution and dimerization constants also showed this evidence.

In consideration of the phenol data then, it would seem that indications of a different form of interaction between solute complexes and solvent could be discerned in the results reported by Johnson, as well as those presented here. Further discussion of this possibility will be deferred to the section below on solvent effects. The constants reported by Johnson for the 1:2 and the 2:1 in dichloroethane are 12.97 M^{-2} and 3.37 M^{-2} respectively. For naphthol in dichloroethane the 1:2 has a value of 15.96 and the 2:1 is 5.87 M^{-1} . Very good agreement is also found for the benzene case where Johnson reports 50.03 M^{-2} for the 1:2 species and 15.74 M^{-2} for the 2:1 species. The naphthol results give, for benzene as a solvent, 60.32 for the 1:2 and 23.12 for the 2:1 complex.

Comparisons of the phenol data and naphthol data in the solvent CCl_4 are limited by the different species used to explain the phenol data as compared to those used for the naphthol data. However, good agreement with the 1:1 value

is found, in that for phenol-water, $K = 5.75 \text{ M}^{-1}$ and for the naphthol-water, $K = 9.43 \text{ M}^{-1}$.

The complexes discussed above reproduce the data to a high degree of precision. It is not unlikely that they are present as predominant species in solution. In general, then, it can be seen that this work agrees with that presented by earlier authors, especially Farnham and Johnson, with respect to the fact that in a functional dependence test the best fit is for trimeric associated species. In fact, using those species which resulted in the best fit for the two-parameter case in an expanded fit involving a 1:1 constant (or a "dimeric" species) it is seen (in Table 2 in the previous chapter) that the fit is little improved, and in fact, in dichloroethane results in a physically meaningless negative equilibrium constant for the 1:1 species. Although positive K_{11} 's could be fit to these data it would be necessary to postulate different species for the three parameter fit than were used for the best two parameter fit, in order to avoid negative values for one or two of the constants.

While it seems likely that there are small concentrations of 1:1 complex present in all these solutions it seems apparent that this species does not influence the fit to any great extent. This fact may imply that, as in the cases of self-association reported by many authors, the association of hetero-molecular hydrogen bond complexes involves stabilization of a trimeric unit. This trimeric form has in some

Table 24
 Summary of Results for 2-Naphthol and 2-Naphthol-
 Water Complexes at 25°C

Sol-vent	K_D	$K_3 (M^{-2})$	$\Delta\nu_{N_3}$	Hydration Data		
				$\Delta\nu_{HYD}$	K_{11}	K_{21}
CCl ₄	6.606±0.016	169.9±15.4	123 cm ⁻¹	153 cm ⁻¹	9.43±0.03 M ⁻¹	120.1±84 M ⁻²
					K_{12}	K_{21}
C ₆ H ₆	43.21±0.10	1.797±0.063	108 cm ⁻¹	170 cm ⁻¹	60.32±3.50 M ⁻²	23.12±0.35 M ⁻²
					K_{12}	K_{21}
DCE	79.92±0.17	0.457±0.019	96 cm ⁻¹	170 cm ⁻¹	15.96±0.59 M ⁻²	5.87±0.03 M ⁻²

cases perhaps been overlooked due to the common assumption that dimeric species must predominate.

In light of this evidence, it would be interesting to speculate on the possible structures of such a trimeric unit. This is considered in the discussion of infrared evidence and solvent effects in the following section.

Infrared Evidence and Solvent Effects

The results of the infrared study supported the results derived from the previously discussed investigations. The anhydrous trimer postulated to explain the vapor pressure lowering data provided an excellent fit for the infrared data in each solvent.

The hydrated species proposed in the water and naphthol solubility studies allowed an adequate fit of the differential spectral data. The larger deviation evident in the hydration study is due primarily to the larger error introduced by measurements at low absorbance values. In addition, subtraction of absorbance due to anhydrous species introduced an additional factor to the experimental error.

In addition to this information however, the IR studies can provide comparisons of fundamentally molecular properties with thermodynamic properties. These data can be useful for obtaining a semi-quantitative estimate of other properties of the 2-naphthol systems.

In Table 25 are presented the derived results of the infrared study. The frequency shift ($\Delta\nu$) reported for the

monomer is the difference between the gas phase frequency and that observed in the solvent. In this case, the gas phase frequency of phenol is used since that for naphthol is not available. For the complexes, the frequency shift is relative to the monomer in the solvent under consideration, and is used for hydrogen bond correlations in this discussion. The frequency shift of the complex should have an approximate linear relationship to the enhancement of the band width for true hydrogen bonded species (4). Similarly, $\Delta\nu$ is also related to the change in integrated absorption, B, of the fundamental modes. These spectral properties can then in turn be related through other empirical formulas to ΔH , to Hammett σ and to interatomic distances between H-bonding sites.

We can combine this spectral information with the thermodynamics results to obtain information relating to the structure of these complexes. The frequency shift of these complexes is due to the change in stretching frequency upon hydrogen bonding with another molecule. The amount of the shift relative to the monomer peaks is generally taken to be indicative of the strength of the hydrogen bond. The trimer frequencies in benzene and dichloroethane are reported as the same, but the uncertainty in this assignment is large, due to the overlapping of this peak with the monomer peak. Certainly the wavelength of the trimer in CCl_4 is very much different from that in benzene or DCE. Also since the monomer peaks in benzene and DCE have easily determined frequencies,

Table 25

Spectral Data for 2-Naphthol Systems

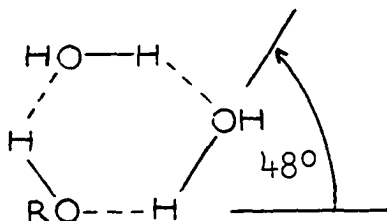
Sol-vent	Peak	ν	$\Delta\nu$	$\Delta\nu_{1/2}$	ϵ_{\max}	B
CCl ₄	monomer	3608	44	32	33.6	0.39
	trimer	3485	123	193	56.2	3.92
	hydrates	3455	153	172	94	5.83
	H ₂ O (ν_3)	3710	-	77	38	0.46
	H ₂ O (hyd)	3690	20	90	121	2.21
C ₆ H ₆	monomer	3558	94	67	174	4.21
	trimer	3450	108	140	199	10.05
	hydrates	3388	170	227	118	9.66
	H ₂ O (ν_3)	3685	-	32	74	0.85
	H ₂ O (hyd)	3657	28	39	107	1.51
DCE	monomer	3544	108	75	131	3.54
	trimer	3450	96	128	246	11.36
	hydrates	3374	170	233	107	8.99
	H ₂ O (ν_3)	3676	-	54	66.7	1.30
	H ₂ O (hyd)	3656	20	56	85.3	1.72

the frequency shifts of the trimer are more informative than the frequencies themselves.

For the H₂O peaks, the absorbance was fairly low due to the conditions imposed by solvent absorbance, path length, and low concentrations of H₂O. As a result, the figures for the intensity of those peaks must be considered at best only approximate. For the spectra of the hydrates however, the frequency shift of the asymmetric stretch (ν_3) of the water O-H bond is reliable. This shift indicates that one or both of the hydrates have a dangling O-H group that is affected upon hydrate formation (70). Since the symmetric stretch appears under the monomer peak, information about that peak is not available for this system. The naphthol peak is considerably shifted upon hydrate formation. But obtaining information about the structure of the hydrates from examination of this peak is difficult due to its complicated dependence on two hydrates.

Some discussion of the structure of the trimer will be fruitful. The work presented here suggests there is a stability factor in complexes consisting of three molecules that has generally been neglected by those assuming only monomer-dimer equilibrium. There may be a factor providing for extra stability via the formation of a cyclic species for the trimer. However, what would be the effect on the preferred (by most authors) linear hydrogen bonds if a trimer were to be cyclic? In order for all bonds to be linear there

would be a requirement that the structure be similar to that of a triangle with the H atoms off center on each side. However, studies of solids having H-bonds have shown deviations from linearity on the order of 15° (4) and deviations may be even greater in solution. In the figure below is a representation of a cyclic trimer. It is representative of the structure expected if the tetrahedral angle of H_2O and of ROH is constant at 109° . This causes a deviation from linearity of 48° for the hydrogen bond.



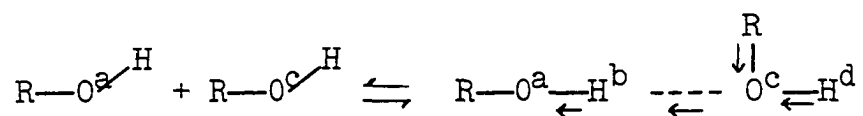
There should be allowance for a little rearrangement of the tetrahedral structure. The electronic structure of these compounds is changed due to hydrogen bonding (as shown by electronic spectra as well as IR evidence in the form of a different extinction coefficient signifying a change in transition dipole). There is, therefore, an effect on the oxygen lone pair of electrons which must alter the geometry of the hybrid orbitals on oxygen. This effect, in turn, may cause a change in the spatial position of the hydrogen bond forming lone pair, allowing a more linear H-bond. This is essentially the same as the effect seen in high pressure forms of ice; the increase in non-nearest-neighbor coordination is accomplished by a distortion from the angular

geometry of ideal tetrahedral coordination. Even if the H---O-H angle changed to 100° (which would require a considerable amount of energy) the linearity would only change to about 38° , or more than the change seen in crystal structures. Neutron diffraction studies on H-bonds in crystals (71, page 458) indicate that most of the O-H---O angles are between zero and 20° . For inorganic salt hydrates, angles larger than 20° occasionally appear, but the maximum so far observed is near 28° . In addition, it is unlikely that all of the H-bonds would have such a large distortion. It can easily be seen that the cyclic tetramer might be even more stable, since the H-bonds could be more nearly linear, however this structure would be considerably less statistically favored, from the viewpoint of the mass action law, than the trimer.

So even if there is a considerable rearrangement of the lone pair hybrids, there will still be a relatively large amount of ring strain in the systems if we require a cyclic structure with nearly linear hydrogen bonds. In the absence of stability due to a cyclic structure the predominance of the trimer must be due to some other factor.

The answer may lie in consideration of the cooperative effect proposed by Frank and Wen (63) and related to the structure of hydrogen bonded trimers by Tucker (56). This effect can be considered by the illustration below as explained by Tucker. "In the process of forming the hydrogen

bond in the dimer pictured below a shift of



electron density takes place in the direction indicated by the arrows. The net effect of this shift is to render hydrogen atom (d) more acidic and oxygen atom (a) more basic in the sense of the electron density now present at these positions compared to the free molecules. The dimer is now more susceptible to attack at either position. A third alcohol molecule can attach itself at either (a) or (d). In this fashion a polymer is formed."

This process therefore implies that there would be added stability for polymeric forms of associated species. A similar conclusion is drawn from the stability factors treatment by Farnham (55) in which the effect of an adjacent bond upon a central bond is represented by the product of the stability factors of both bonds. Dominance of the trimer species was also shown to be an effect attributable to contributions from each bond by Johnson, Christian and Affsprung (72). The terminal O-H group in a structure of this type is free to associate with either the solvent or another molecule to form higher species. The fact that the trimer happens to be predominant may then be attributed to the combination of stability versus statistical factors that prevent larger aggregates from forming. It is interesting to speculate on the possibility that the much higher trimerization constant

found for CCl_4 may be due to the lack of favorable acceptor sites for terminal hydrogen bonding with the solvent. In fact, there may have been quantities of higher order species such as the hexamer proposed by Johnson for phenol in CCl_4 . Hydrogen bonding with the solvent will be considered at greater length in the solvent effects discussion below. However, the evidence concerning structure seems to imply that a linear structure is to be favored for the trimer.

More concrete information concerning the structure of the trimers and hydrates could be obtained by studies of the overtone region in combination with a more complete investigation of the fundamental bands than attempted in this study. Also it is possible that information might be gained from studies of the R-O-H bending modes.

Assuming that the linear species would be the most stable for the anhydrous trimer, it would be reasonable to expect a similar structure for the hydrates, which would also explain the frequency shift of the asymmetric H_2O stretch. Such structures are depicted below.



The more acidic naphthol O-H would presumably be bonded to the oxygen of the water in this case, as opposed to the structures proposed by Mohr, Wilk and Barrow (70) for complexes of water with bases. However, they found the same decrease in frequency for the asymmetric stretch of water in

the case of 1:1 complexes. The H_2O molecule on the end of the chain would not be expected to have an asymmetric stretch much different from the "free" H_2O in these solvents, so the shift can be said to be due to the central water molecule in the 1:2 hydrate. In CCl_4 the shift must be due to the central water molecule in the 2:1 hydrate, assuming the terminal molecule is one of the naphthol molecules in the complex.

In addition to structures of species proposed on the basis of thermodynamic and spectral information, we can compare spectral properties with equilibrium constants of species for additional information concerning the nature of these solutions. Figure 25 shows the relationship between the free energy expressed as $\log K$ and the frequency shift (37). The figure illustrates this relation for both K_3 and K_D . An excellent correlation is shown for these constants. This relation implies that the same factors which operate to cause the frequency shift also have an effect on the thermodynamic constants.

The fact that this relation holds for the distribution constant almost as well as for the trimerization constant can be interpreted two ways. On the one hand, this could imply that the frequency shift is due to a bulk solvation property of the solvent since there is a similar relation whether we compare monomer properties by the K_D or associated species properties with the K_3 . On the other hand it could

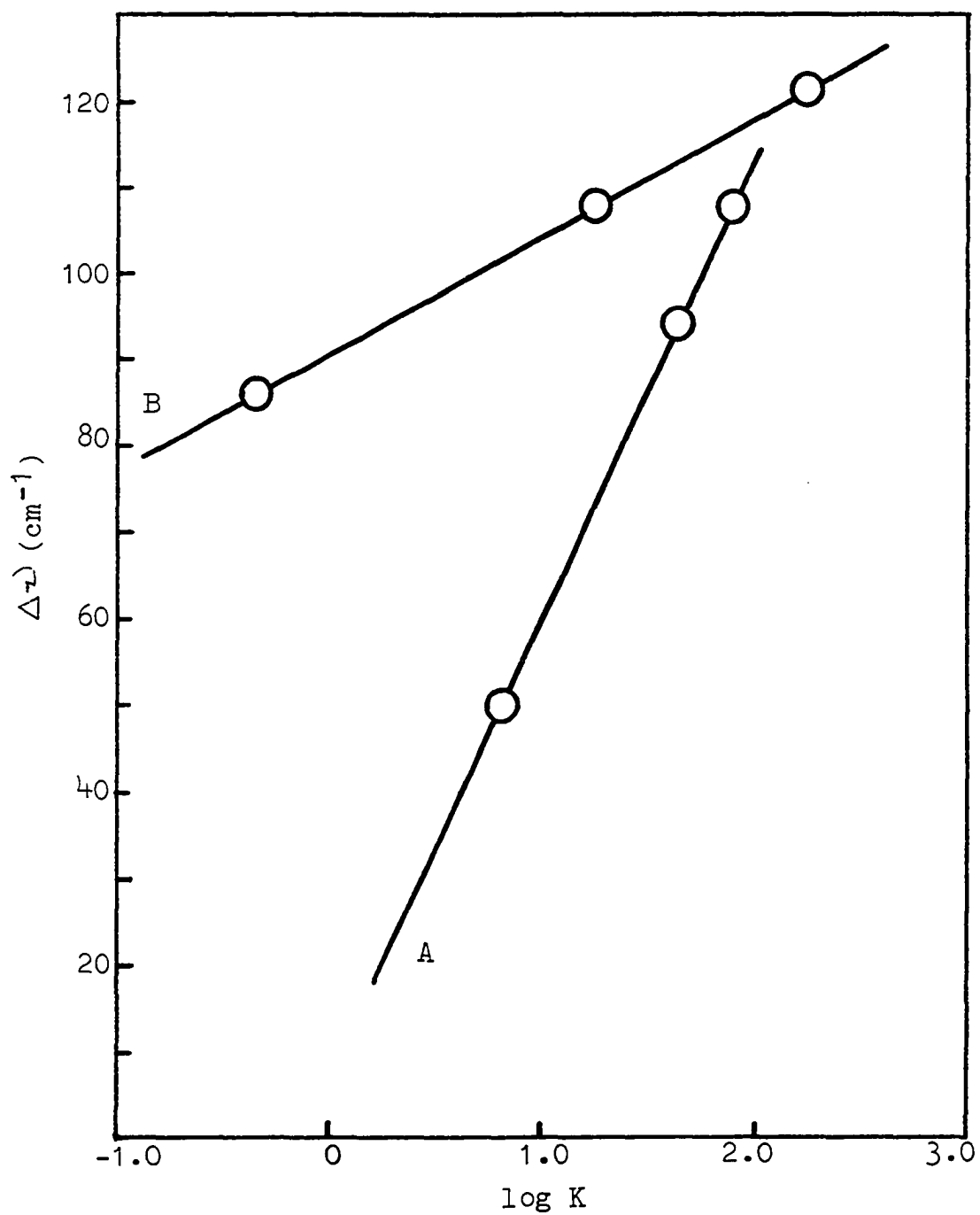


Fig. 25.--Log K vs. frequency shift. Line A represents K_D of the monomer; line B represents K_3 of the trimer.

be that for an open, or linear, trimer the specific interactions with the solvent will not vary extensively.

These results for the spectral properties of solutions coincide in general, with those that have been presented for phenol by Tsubomura (73). Table 26 compares the intensification factors of phenol complexes with the 2-naphthol complexes presented here. It is seen that for these naphthol complexes there is considerable intensification of the naphthol O-H stretching band. It must be stated that due to the nature of these bands and the uncertainties in band widths of the complex bands, the B values discussed could be considerably in error, although they do serve as a self-consistent method of comparison in this study.

Figure 26 indicates that frequency shifts and peak half-widths correlate well, as observed for alcohols by Huggins and Pimentel (74). This linear relation joins this quantity to the other properties which will be correlated with frequency shift. The half peak width also correlates well with that of phenol as shown in Figure 27. This would imply that the solvent interactions on naphthol which cause this effect are similar to those interactions on phenol, but occur to a different extent since the slope is not equal to one.

It may be noted that Table 24 provides evidence of a solvent effect, in that the data for the same complexes differ from one solution to another. Of course, evidence

Table 26

Comparison of Integrated Intensities

Donor	Acceptor	Solvent	B	Ref.
phenol	chlorobenzene	CCl ₄	2.25	a
	tetrachloroethane		1.99	
	ethyl ether		8.03	
	hexamethyl tetraamine		12.4	
2-naphthol	H ₂ O	CCl ₄	5.83	b
		C ₆ H ₆	9.66	
		DCE	8.99	
phenol	- (monomer)	CCl ₄	3.2	c
		C ₆ H ₆	16.0	
		CCl ₄	1.2	d
		Ether	8.5	
		CCl ₄	1.27	a
methanol	- (monomer)	CCl ₄	0.33	a
		C ₇ H ₁₆	1.16	
2-naphthol	- (monomer)	CCl ₄	0.39	b
		C ₆ H ₆	4.21	
		DCE	3.54	

References to Table 26: a) Tsubomura, H., J. Chem. Phys. 24, 927 (1956); (b) This work; (c) Huggins, C. M. and Pimentel, G. C., J. Phys. Chem. 60, 1675 (1956); (d) Barrow, G. M., J. Phys. Chem. 59, 1129 (1955).

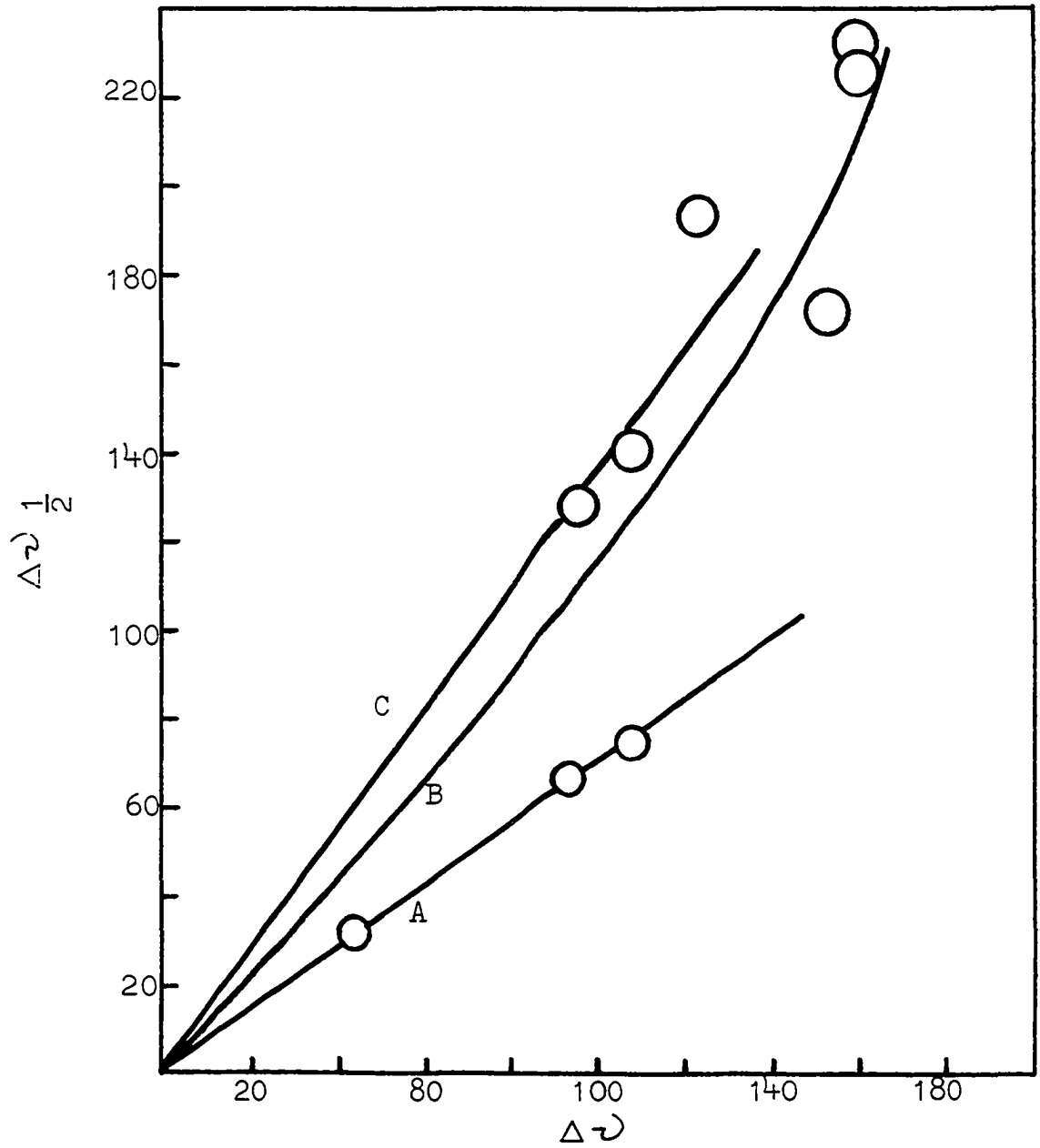


Fig. 26.--Peak half-width vs. frequency shift. Line A, monomer; line B, hydrates; line C, trimer; in each solvent.

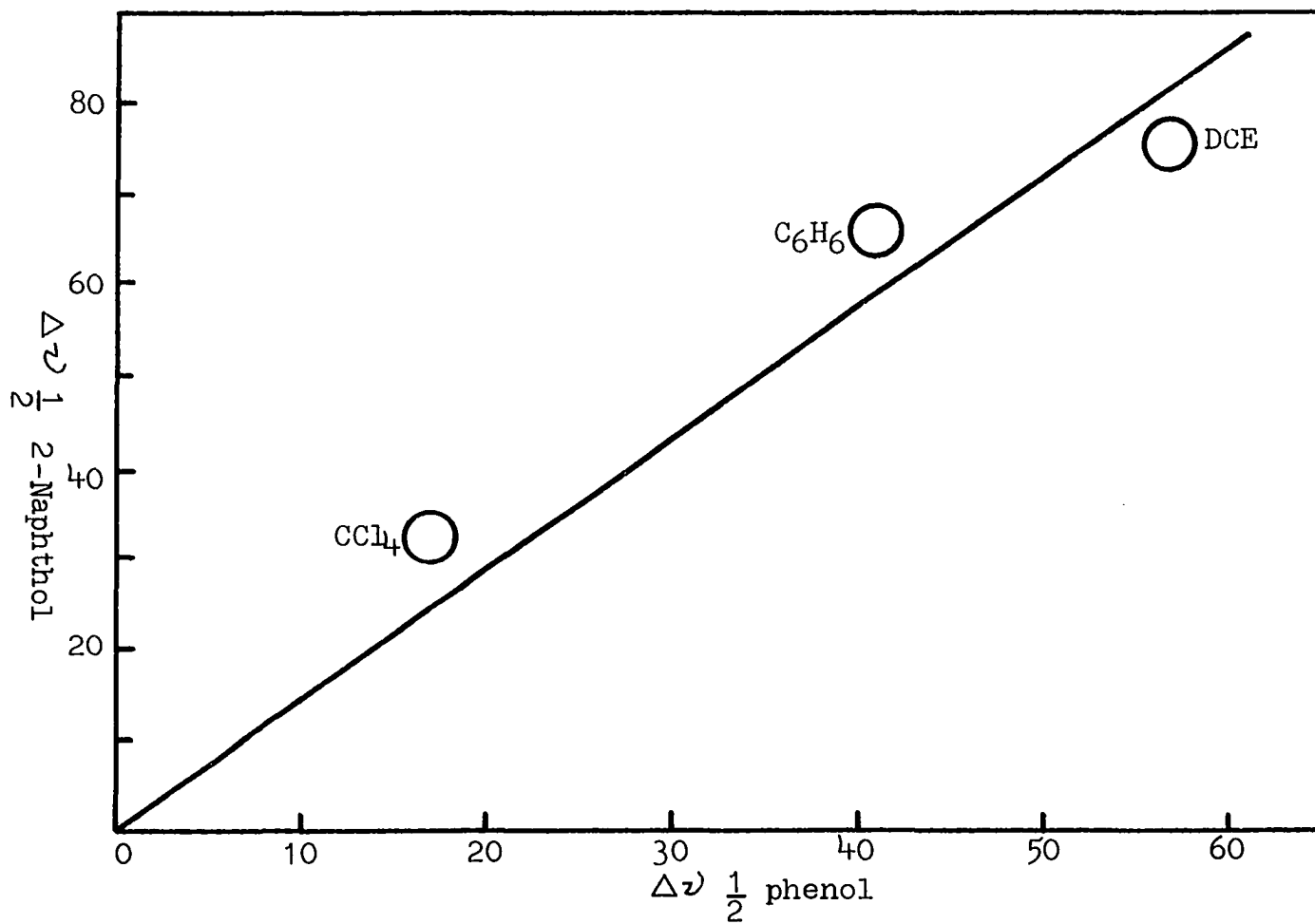


Fig. 27.--2-Naphthol vs. phenol monomer peak half-width.

for the effect of solvent was also seen in the thermodynamic results in that the equilibrium constants varied with the activity of the solvent. There has been a reluctance on the part of some authors to admit that thermodynamic constants for molecular complexes determined in solution in the so-called inert solvents should be different than constants determined in the vapor phase. A decade ago Allerhand and Schleyer (39) explained that most IR studies of H-bonding were done in "inert" solvents due to vapor phase experimental difficulties. They discussed the effect of solvents on infrared spectra and presented an interpretation different than that of Bellamy and colleagues (75). Since then solvent effects on complexing reactions have been considered to have a more manifest importance.

Understanding the effects of solvent on reactions will provide information on the types of interactions undergone by solutes. Information about the nature and magnitude of the forces responsible for properties of liquids can also be obtained. Consideration of solvent effects leads to the conclusion that equilibrium constants for the complexes presented here differ in these solvents because the medium in which the reaction takes place has both specific and non-specific effects which alter the thermodynamics.

One approach to characterizing the non-specific effects of solvents is that of Allerhand and Schleyer (39). They explained a theory of solvent effects based on empirical

G parameters which are related to dielectric properties of common solvents. The use of this relation is applied in Figure 28. The upper line shows a plot of solvent G against frequency for the monomer (this scale is on the right). For the trimer, a plot of $\Delta\nu/\nu$ versus solvent G also reveals a straight line. In this case however, we have modified the relation somewhat by plotting the relative difference in frequency of the complex from the monomer peak rather than from the gas phase value, which is not available. This has the effect of correcting for the solvation of the monomer, but otherwise the effect should be the same. The almost linear relation observed supports the evidence that a significant portion of the solvent effects are due to bulk dielectric properties of the solvents.

The fact that these plots do show some scatter could be related to the solvent properties discussed by Stevens (47). It will be remembered that the thermodynamic discussion referred to evidence by Stevens that there was a difference in behavior between the solvents benzene-DCE and the solvents CCl_4 -heptane. It may be that there is evidence in these plots of some specific interactions occurring along with these dielectric effects that cause deviations from this plot.

Such an interpretation is one that has been advanced by Bellamy and co-workers (75, 76). Bellamy's treatment is concerned with solvent effects that cause infrared frequency

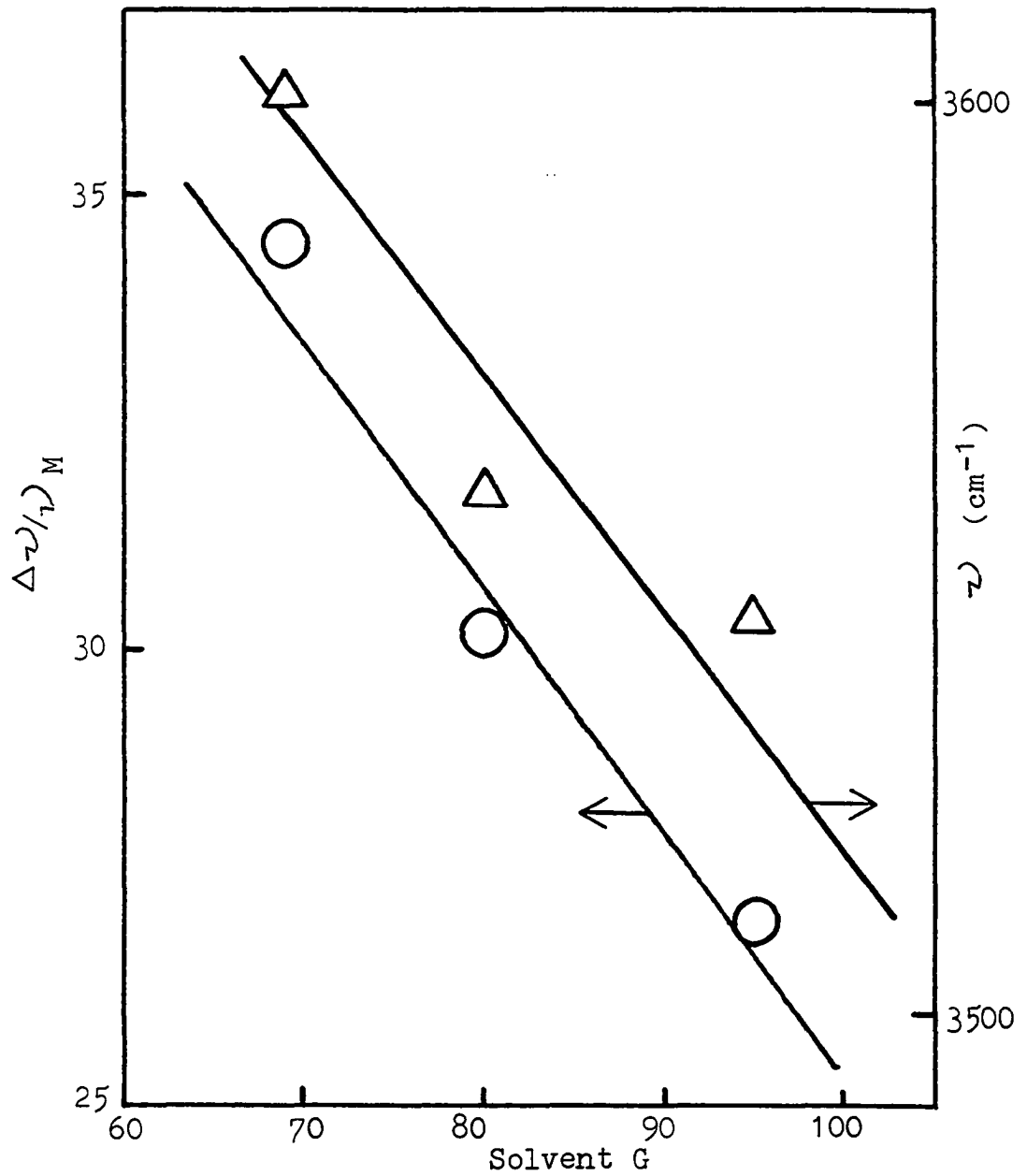


Fig. 28.--Solvent G vs. frequency shift for all solvents. Values of G are: CCl_4 , 69; benzene, 80; DCE, 95. \circ , trimer, scale at left; Δ , monomer, scale at right.

shifts. His evidence proves mainly that a similar mechanism is responsible for these shifts in all solvents. He maintains that this mechanism is one which includes specific H-bonding of solute to solvent molecules.

Evidence of correlation between frequency shift and dielectric properties (such as solvent G), and equilibrium constants, indicate however, that the mechanism is not entirely due to specific interactions. Frequency shift also involves some non-specific, generalized solvation effect on the complexes. This effect would account for the difference in equilibrium constant which is due to the solvent cage around the complex. With this in mind, it would be interesting to consider Bellamy's theory.

Bellamy and colleagues have compared the effect of solvent on the frequencies of bond vibrations. They have suggested comparing the relative frequency shift from vapor to solvent $(\nu^V - \nu^S)/\nu^V$, with a reference compound. If the graphical comparison results in a straight line with a slope = 1, it can be said that the frequency shifts are solely dependent on some bulk property of the solvent.

This is because the direct correlation implies that the effect of the solvent is the same on the different structures of the molecules involved. Also if specific interaction were occurring between a test molecule and the solvent to a greater extent than with the reference compound, a deviation from unit slope and perhaps departure from linearity would occur.

The effect of solvent on several of the frequencies observed here are summarized in Table 26. Since methanol gives a slope almost equal to one with the reference compound proposed by Bellamy, it is used as the reference compound for the comparison of phenol and 2-naphthol in Figure 29. It is seen that phenol and naphthol both give linear plots compared to methanol. There may be some involvement of molecular properties of these molecules with these solvents since the slope is not equal to one.

The solvent effect on the monomer peak could be due to a number of interactions with the solvent. The specific interaction explanation seems to be not entirely adequate, however, since there is a similar effect on the bonded peaks as one compares increasingly active solvents. The similarity of effect is seen by plotting monomer frequency shift and trimer frequency shift together as in Figure 30. The frequency shift on the monomer can be due only to solvent effects on the O-H bond. In the case of the trimer however, this shift is due to the interaction of one O-H with another of the same molecule. In fact, there should be no difference in this shift if the hydrogen bonds in the trimer were equal in each solvent. So, the inference from this evidence must be that the solvent, since it evidently affects the shift of hydrogen bonding frequency from the monomer frequency, must have an effect of the hydrogen bonds within the complex or else, that the specific interaction theory of the monomer

Table 27
Spectral Properties for Bellamy Plots

	Methanol		Phenol			2-Naphthol			
	ν_{OH}^M	$\Delta\nu_{OH} \times 10^3$	ν_{OH}^M	$\Delta\nu_{OH} \times 10^3$	$\Delta\nu_{OH} \frac{1}{2}$	ν_{OH}^M	$\Delta\nu_{OH} \times 10^3$	ν_{OH}^{trimer}	$\Delta\nu_{OH} \times 10^3$
Vapor	3685	-	3652	-		3652			
CCl ₄	3646	11.1	3611	11.0	17	3608	12.0	3485	34.4
C ₆ H ₆	3615	18.2	3563	24.4	57	3558	25.7	3450	30.3
DCE	3618	19.0	3558	25.7	41	3544	30.4	3450	27.0

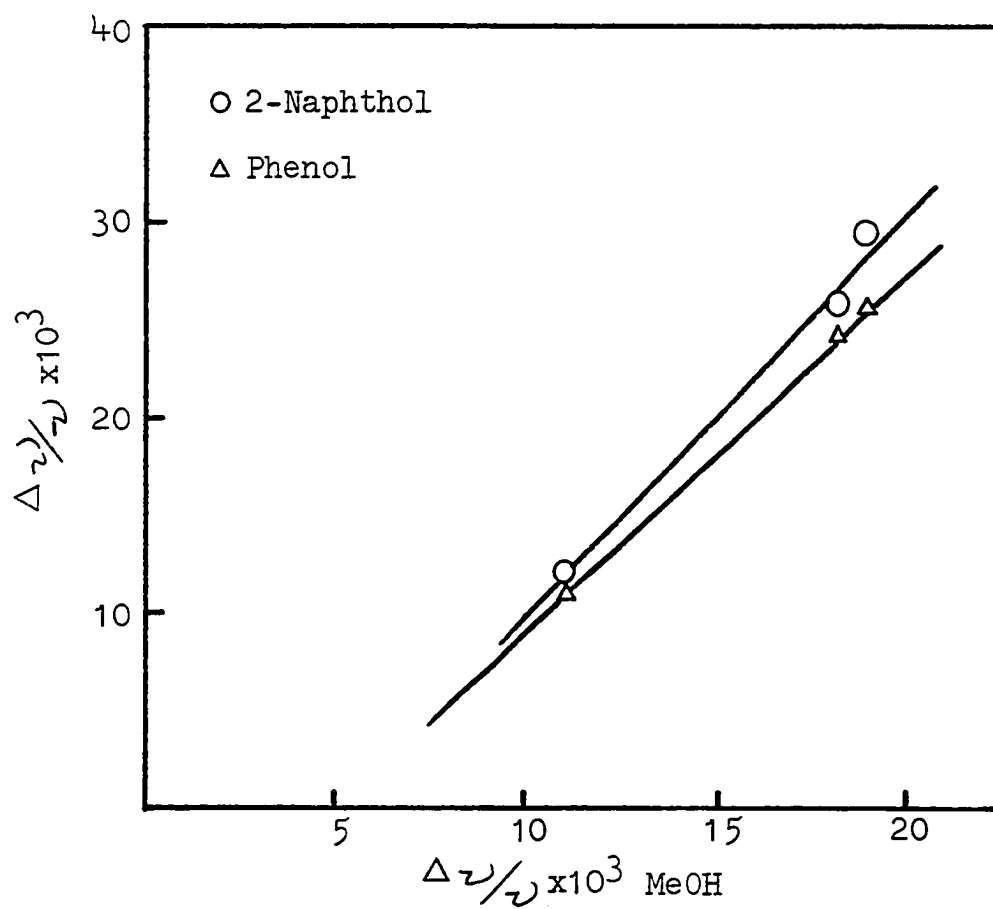


Fig. 29.--Bellamy plot of monomer frequency shift.

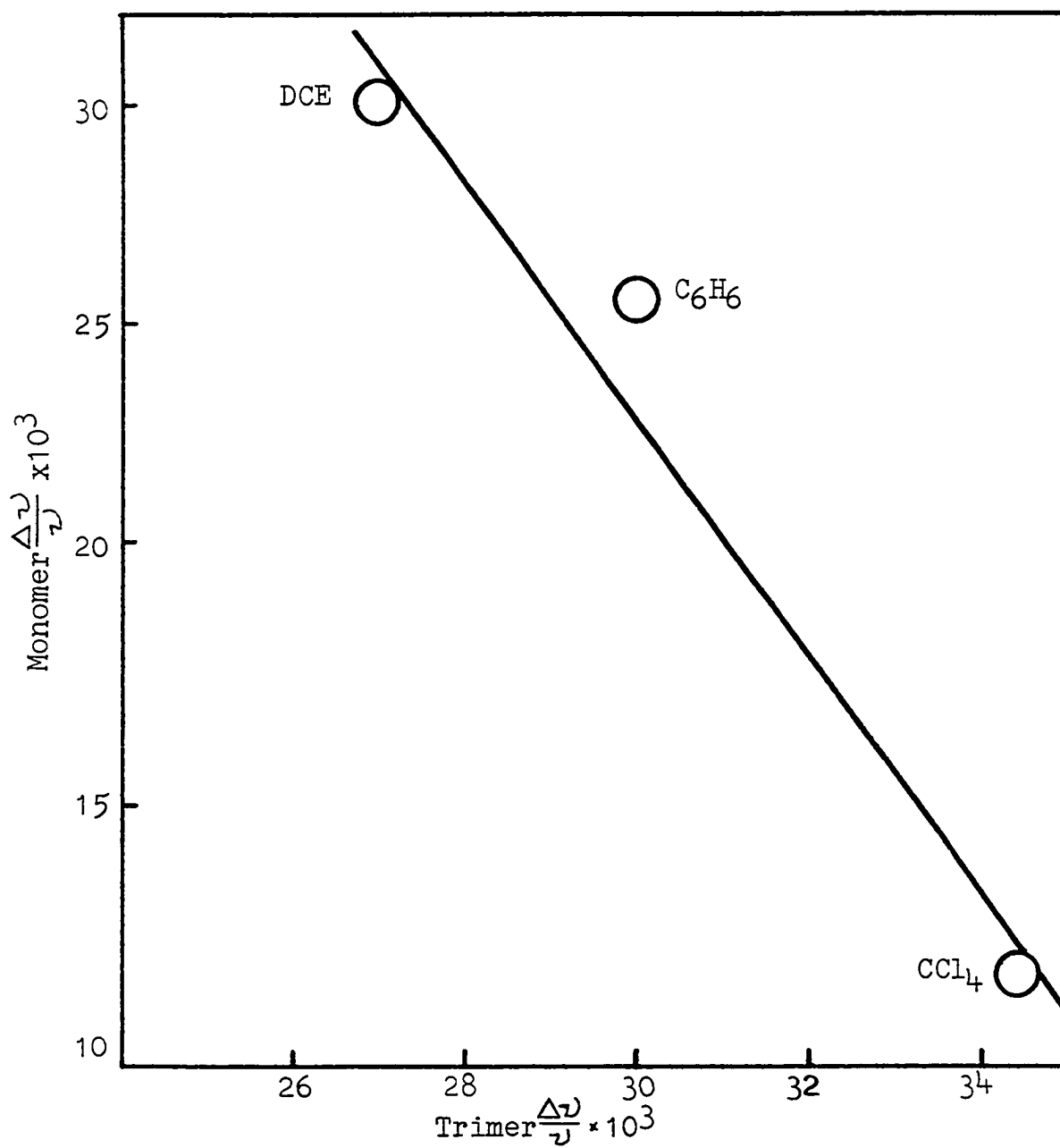


Fig. 30.--Bellamy plot of monomer vs. trimer in all three solvents.

frequency shift is not totally correct. If, in fact, the frequency shift of the monomer peak from one solvent to another is not dependent on specific interactions, but on some bulk solvent property, we would predict the same effect on the frequency shift of the associated species as well, since they are solvated by the same forces of bulk solvent effect.

Since specific interaction theory has been able to explain cases with these correlations when the dielectric theory breaks down (as in cases where there is a maximum in dielectric constant due to complex formation), it might well be that correlations which appear to be similar for each solvent do in fact involve a specific interaction with solvent molecules. Allowing that these interactions occur does not invalidate the evidence for a more general effect. This general effect has been effectively cancelled in the approach by Bellamy (76, 77) in that comparisons of O-H frequency shifts neglect the remainder of the molecule. These comparisons also tend to equalize any effect other than specific O-H bonding by comparisons with reference molecule's spectra in the same solvent. This is what Bellamy was attempting to do, and there is no criticism implied in this statement. But it is a possibility that there may have been effects that were ignored when making only comparisons of the O-H stretching frequency.

The correlations with both dielectric theory and specific interactions theory then point to one conclusion.

Solvents have both specific interactions with functional groups and also have solvation energies independent of these specific effects. These essentially inseparable effects both affect the thermodynamic results. But in many cases, the specific effects have a greater influence on the spectral properties.

This combination of effects is more in line with current solution theories based on thermodynamic evidence. The Regular solution theory of Hildebrand et al. (3) accounts for non-specific effects of solvents on properties of solutes, and, in general, applies where orientation effects are unimportant. However, there are numerous theories of interacting systems in which specific solute-solvent effects are considered.

An approach to solvent effects on thermodynamic parameters of molecular complexing reactions has been proposed by Christian et al. (78). One relation which has been proposed in this treatment is that the ratio of free energy involved in transfer of a complex from one solvent molecule to another or from the gas phase to solvated molecules and complexes, remains constant. This constant is defined by the equation:

$$\alpha = \frac{\Delta G_{AB}^{\circ}}{v \rightarrow s} \bigg/ \frac{\Delta G_A^{\circ}}{v \rightarrow s} + \frac{\Delta G_B^{\circ}}{v \rightarrow s}$$

in which ΔG° for each species refers to the changes in free energy for the transfer from the ideal vapor phase to

infinite dilution. While this treatment provides insight into solvent effects it requires calculation on ΔG 's for one specific complex which is present in all solvents. As was mentioned earlier, the 1:1 hydrate complex was not predominant in all solvents and thus this relation was not tested on these data. It does however support the evidence for non-specific reaction between solutes and solvents in that the relation can be physically described as a function of the number of solvent molecules that are "squeezed out" as the complex molecule is formed from the solvated monomers.

Another method of predicting solvent effects on reactions in solution appears to have promise for the dilute solution region. This is the non-polar analogue theory (NPA) also proposed by Christian, et al. (79). From the results of this theory it may be possible to estimate the effects of different solvents on the activity coefficients of polar molecules in non-polar solvents. This would facilitate calculations on systems similar to those in this report in a manner that is presently done only for solutions of non-polar molecules.

An interesting treatment of the effect of solvents on changing activities of solute species has recently been discussed by Childs (80). He has shown that there may be an effect in charge-transfer systems that alters the monomer or uncomplexed concentration when the concentration of one of the species is increased. In the systems considered here,

this would have the effect of lowering the equilibrium constants for the hydration and saturation studies. It would not however, alter the stoichiometry of the best fit since it is essentially a baseline correction.

From the evidence discussed here it seems more reasonable to attribute a significant portion of the observed solvent effect to non-specific solvation and to allow a smaller portion to be due to complexing of one part of the molecule with a solvent molecule. That is to say that the spectral properties in particular, although they are related to the functional group interactions with other molecules (i.e. association peaks are shifted) cannot be totally related to this behavior. There must be also some effect on peak half-width and on frequency shift that is due to bulk properties of the solvent or "dielectric" effects. Comparisons with vapor phase spectra seem to show this.

It is reasonable to assume that these interatomic interactions occur all along the solvent solute interface (described in atomic dimensions) so evidently these effects would be expected to vary with the solvent molecule's surface electron density. Since these interactions do occur, the solvent cage has different "electrical" as well as spatial dimensions and creates an overall non-specific effect on the solute molecules immersed in it. This effect can be treated as separate atom-atom interactions or by a modified lattice theory treatment as utilized by Stevens, but applications of these models have had only limited success.

Since complexation by hydrogen bonding is essentially an electronic interaction, the electron environment will therefore change the energy requirements for reaction as compared to the gas phase. This effect is seen by comparison of the gas phase frequency with the frequency in solution of a non-polar compound. The difference in frequency is due to an effect that results from damping an oscillation of a bond dipole by surrounding it with outer electron clouds of solvent molecules.

A theory of interactions which neglects this effect is only applicable when this effect is small in comparison to specific interactions. But it should be realized that both effects operate on molecules and should both be examined more closely for a truly general theory of solutions. A promising new method that may have applications for studies of intermolecular interactions appears to be photoelectron spectroscopy.

Once we define these forces of interaction we can then attempt to calculate them from the properties of the solvent and solute molecules. This will lead us to the objective of inferring and predicting liquid state structure or interactions, allowing us ultimately to acquire as complete an understanding of the liquid state as that which exists today concerning the solid state. This information could eventually help correlate solid state knowledge with gas phase knowledge for a more complete understanding of intermolecular forces.

Summary

The hydration and self-association of 2-naphthol has been studied in the solvents carbon tetrachloride, benzene and 1,2 dichloroethane. The experimental procedures used involved measurements of vapor pressure lowering, distribution, isopiestic hydration, solubility and infrared spectra. The data were interpreted as representative of specific associated species and the predominant species were found by non-linear least squares analysis and their association constants were evaluated.

A monomer-trimer equilibrium is sufficient to describe the self-association data in each system. In addition, the importance of the trimeric hetero-associated complexes is apparent. For dichloroethane and benzene, only the 1:2 and the 2:1 naphthol water species were required in fitting data. In carbon tetrachloride only the 1:1 and the 2:1 species were needed. A rationale for the preponderance of trimeric species is presented.

Infrared studies on these systems have been done and they generally support the thermodynamic results. Spectral data have been presented and analyzed to detect solvent effects on frequencies characteristic of the monomer and complexed species. It has been shown that the effect of solvent on these species is dependent on both specific and non-specific interactions and that these effects can be related to the observations presented. The results indicate the

importance of the inductive effect discussed by earlier workers and provide evidence of specific solvent-solute interactions.

BIBLIOGRAPHY

1. Hildebrand, J. H. and Scott, R. L., "The Solubility of Nonelectrolytes," Third Ed., Dover Publications, New York (1964).
2. Friedel, R. A., Ed., "Spectrometry of Fuels," Plenum Press, New York, (1970), Chapter 20.
3. Hildebrand, J. H., Prausnitz, J. M. and Scott, R. L., "Regular and Related Solutions," Van Nostrand Reinhold Company, New York, (1970).
4. Pimentel, G. C. and McClellan, A. L., "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, (1960).
5. Scott, R. L. and Fenby, D. V., Ann. Rev. Phys. Chem., 20, 111 (1969).
6. Johnson, J. R., Ph.D. Dissertation, University of Oklahoma, (1966).
7. Van Duyne, R. L., Ph.D. Dissertation, University of Oklahoma, (1969).
8. Wojtkowiak, B., C. R. Acad. Sci., Paris, Ser. C, 268, 24 (1969).
9. Woolley, E. M., Travers, J. G., Erno, B. P., and Hepler, L. G., private communication, to be pub. (1971).
10. Johnson, J. R., Christian, S. D. and Affsprung, H. E., J. Chem. Soc. (A), 764 (1967).
11. Vanderborgh, N. E., Armstrong, N. R., and Spall, W. D., J. Phys. Chem., 74, 1734 (1970).
12. Gramstad, T. and Becker, E. D., J. Mol. Struct., 5, 253 (1970).
13. Wolf, K. and Metzger, G., Ann. (Justus Liebig), 563, 157 (1949).

14. Watson, H. C. and Hargreaves, A., *Acta Cryst.*, 11, 556 (1958).
15. Van Gemert, J. T., *Aust. J. Chem.*, 21, 2203 (1968).
16. Socrates, G., *Trans. Faraday Soc.*, 66, 1052 (1970).
17. Lutskii, A. E. and Tromza, B. A., *Zh. Strukt. Khim.*, 11, 421 (1970).
18. Neerinck, D., Van Audenhage, A., Lambert, L., and Huyskens, P., *Nature*, 218, 461 (1968).
19. Bolles, T. F. and Drago, R. S., *J. Amer. Chem. Soc.*, 87, 5015 (1965).
20. Ghosh, B. and Basu, S., *Trans. Faraday Soc.*, 61, 2097 (1965).
21. Ghosh, B. and Basu, S., *J. Chim. Phys. Physicochim. Biol.*, 65, 1587 (1968).
22. Szczepaniak, K., Golinska, M., and Mikolajczyk, J., *Acta Phys. Pol.*, 34, 421 (1968).
23. Kuz'min, M. G., Uzhinov, B. M., and Chan, D. T., *Zh. Prikl. Spektrosk.*, 12, 476 (1970).
24. a) Mataga, N., Kawasaki, Y., and Torihashi, Y., *Theoret. Chim. Acta*, 2, 168 (1964).
b) Mataga, N., Kaibe, Y., and Koizumi, M., *Nature*, 175, 731 (1955).
25. Kuksina, V. N., Gol'tsev, V. D., and Tronov, B. V., *Sb. Dokl. Sib. Soveshch. Spektrosk.*, 3rd Krasnoyarsk, USSR 1964, 175 (pub. 1966) See CA69:6602.
26. Ushkalova, V. N., Gol'ttsev, V. D., and Tronov, B. V., *Spektrosk.*, Tr. Sib. Soveshch., 4th 1965, 47 (pub. 1969). CA74:17500.
27. Kubota, T., *J. Amer. Chem. Soc.*, 88, 211 (1966).
28. Nagakura, S. and Gouterman, M., *J. Chem. Phys.*, 26, 881 (1957).
29. Korshunov, I. A. and Pakhornov, L. G., *Tr. Khim. Khim. Tekhnol.*, 1967, 8 (1967).
30. Christian, S. D., Taha, A. A., and Gash, B. W., *Quart. Rev.*, 24, 20 (1970).

31. Greinacher, E., Luttko, W., and Mecke, R., Zeit. Elektrochem., 59, 23 (1955).
32. Masterton, W. L. and Gendrano, M. C., J. Phys. Chem., 70, 2895 (1966).
33. Jolicoeur, C. and Cabana, A., Can. J. Chem., 46, 567 (1968).
34. Magnusson, L. B., J. Phys. Chem., (1971) in press.
35. Saugmagne, P., J. Chem. Phys., 53, 3768 (1970).
36. Tursi, A. J. and Nixon, E. R., J. Chem. Phys., 52, 1521 (1970).
37. Murthy, A. S. N. and Rao, C. N. R., Appl. Spectrosc. Rev., 2, 69 (1968).
38. Reeves, C. W. and Yue, C. D., Can. J. Chem., 48, 3307 (1970).
39. Allerhand, A. and von R. Schleyer, P., J. Amer. Chem. Soc., 85, 371 (1963).
40. Bellamy, L. J., Morgan, K. J. and Pace, R. J., Spectrochim. Acta, 22, 535 (1966).
41. Drago, R. S. and Epley, T. D., J. Amer. Chem. Soc., 91, 2883 (1969).
42. Carper, W. R., Buess, C. M., and Hipp, G. R., J. Phys. Chem., 74, 4229 (1970).
43. Lahiri, S. C. and Aditya, S., Z. Phys. Chem. Leipzig, 244, 351 (1970).
44. Davies, M., J. Chem. Educ., 46, 17 (1969).
45. Ryzhov, V. D., Zh. Fiz. Khim., 44, 2554 (1970).
46. Gregory, M. D., Ph.D. Dissertation, University of Oklahoma, (1966).
47. Stevens, T., Ph.D. Dissertation, University of Oklahoma, (1968).
48. Sillen, L. G., Acta Chem. Scand., 18, 1085 (1964).
49. Christian, S. D., J. Chem. Educ., 45, 713 (1968).

50. Lin, T. F., Ph.D. Dissertation, University of Oklahoma, (1966).
51. Ockham, W., "Summa totius logicae" Part I, Chapter 12 (ca. 1320) Transl. by S. C. Torney in "Ockham Studies and Selections," Open Court Publ. (1938), p. 100.
52. Hamilton, W. C., "Statistics in Physical Science," Ronald Press Co., New York, (1964).
53. Lewis, G. L. and Smyth, C. P., J. Amer. Chem. Soc., 61, 3067 (1939).
54. Bair, E. J. and Kraus, C. A., J. Amer. Chem. Soc., 73, 2459 (1951).
55. Farnham, S. B., Ph.D. Dissertation, University of Oklahoma (1970).
56. Tucker, E. E., Ph.D. Dissertation, University of Oklahoma (1969).
57. Wolf, K. and Metzger, G., Ann. (Justus Liebig), 563, 157 (1949).
58. Bonnett, M., and Julg, A., J. Chim. Phys., 59, 723 (1962).
59. Bhowmik, B. B. and Basu, S., Trans. Faraday Soc., 59, 813 (1963).
60. Baron, D. and Lumbroso-Bader, N., J. Chim. Phys., 66, 1927 (1969).
61. Johnson, J. R., Christian, S. D. and Affsprung, H. E., J. Chem. Soc. (A), 77, (1966).
62. Bellamy, L. J. and Pace, R. J., Spectrochim. Acta (A), 25, 319 (1969).
63. Frank, H. S. and Wen, W. Y., Disc. Faraday Soc., 24, 133 (1957).
64. Keenan, B. M., M.S. Thesis, University of Oklahoma (1969).
65. Mass, O. and McIntosh, D., J. Amer. Chem. Soc., 35, 535 (1913).
66. a) Lynch, R. L., M.S. Thesis, University of Oklahoma (1967).
b) Lynch, R. L., Ph.D. Dissertation, University of Oklahoma, in prep.

67. Worley, J. D., Ph.D. Dissertation, University of Oklahoma (1964).
68. Mueller, D. D., Ph.D. Dissertation, University of Oklahoma (1966).
69. Siderov, A. N., Optics and Spect., 8, 24 (1960).
70. Mohr, S. C., Wilk, W. D., and Barrow, G. M., J. Amer. Chem. Soc., 87, 3048 (1965).
71. Donohue, J. in "Structural Chemistry and Molecular Biology," Ed. by A. Rich and N. Davidson, W. H. Freeman and Co., San Francisco (1968), p. 443.
72. Johnson, J. R., Christian, S. D., and Affsprung, H. E., J. Chem. Soc. (A), 1924 (1967).
73. Tsubomura, H., J. Chem. Phys., 24, 927 (1956).
74. Huggins, C. M. and Pimentel, G. C., J. Phys. Chem., 60, 1675 (1956).
75. a) Bellamy, L. J. and Hallam, H. E., Trans. Faraday Soc., 55, 220 (1959).
b) Bellamy, L. J., Hallam, H. E., and Williams, R. L., Trans. Faraday Soc., 54, 1120 (1958).
76. Bellamy, L. J. and Pace, R. J., Spectrochim. Acta, 25A, 319 (1969).
77. Osawa, E. and Yoshida, Z., Spectrochim. Acta, 23A, 2029 (1967).
78. Christian, S. D. and Grundnes, J., Acta Chem. Scand., 22, 1702 (1968).
79. Christian, S. D., Yeo, K. O., and Tucker, E. E., J. Phys. Chem., in press, (1971).
80. Childs, J. D., Ph.D. Dissertation, University of Oklahoma, (1971).