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THE HYDROGEN BONDING OF PHENOL IN ORGANIC SOLVENTS: THE USE OF ACTIVITY DATA TO EVALUATE ASSOCIATION MODELS.

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE HYDROGEN BONDING OF PHENOL IN ORGANIC SOLVENTS: THE USE OF ACTIVITY DATA TO EVALUATE ASSOCIATION MODELS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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degree of

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LUNG-NAN LIN

Norman, Oklahoma

1975

THE HYDROGEN BONDING OF PHENOL IN ORGANIC SOLVENTS: THE USE OF ACTIVITY DATA TO EVALUATE ASSOCIATION MODELS

APPROVED BY

DISSERTATION COMMITTEE

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THE HYDROGEN BONDING OF PHENOL IN ORGANIC SOLVENTS: THE USE OF ACTIVITY DATA TO EVALUATE ASSOCIATION MODELS

CHAPTER I

INTRODUCTION

Hydrogen bonding has been great of interest for several decades. Thousands of papers on various aspects of hydrogen bonding have been published[1,2] since the beginning of this century. Several books[1-5] devoted solely to hydrogen bonding have appeared. Numerous review articles [6-14] also have been published to discuss both the experimental and theoretical aspects of hydrogen bonding. The important role of hydrogen bonding in living systems has been recognized in recent years. The fundamental role of tne hydrogen bond in the structure and function of DNA and proteins is also well known.[15,16]

Hydrogen bonding is an intermediate range intermolecular interaction. Pimentel and McClellan[1] in their famous book gave hydrogen bonding the following "operational definition":

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

(a) there is evidence of bond formation (association or chelation),

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

Various techniques, including spectroscopic and non-spectroscopic methods, have been developed to detect and study hydrogen bonding. Comprehensive treatments of these techniques are given in references 1 to 3.

The self-association of phenol in organic solvents has been a major subject for many authors in elucidating the properties of hydrogen bonding. In spite of numerous studies which have been made of the self-association of phenol, there is still considerable disagreement regarding the nature of molecular aggregates of phenol which exist in organic solvents. Many investigators have interpreted their experimental results in terms of a monomer-dimer equilibrium, while others have shown that the monomer-trimer model provides a better fit for experimental data. Recently, models involving more than one associated species have been proposed by several authors. A historical review of the work on self-association of phenol is given here:

The colligative technique was one of the earliest methods used for detecting hydrogen bonding. The abnormally high molecular weights which were found with polar solutes were often attributed to self-association. In 1893, Auwer,[17] using the freezing-point method, found a molecular weight of 145 grams/mole for phenol in a benzene solution containing 3 grams of phenol per 1000 grams of benzene. A summary of early cryoscopic data for phenol was given by Lassettre.[6] It has been noted[6,18] that the interpretation of cryoscopic data is subject to doubt because the high molecular weight deduced may not be due to the association of phenol but to the separation of a solid solution instead of the pure solid solvent. Also, the cryoscopic technique does not permit a study to be made over a temperature range, and the molecular weight is not determined

under isothermal conditions.[19] This technique is therefore not a very popular tool in studying hydrogen bonding. A recent cryoscopic study of association of phenolic compounds in benzene was published by Vanderborgh, et al.[20] The experimental results were interpreted in terms of monomer-dimer-trimer equilibrium.

The partition method has been used extensively in studies of hydrogen bonding of phenol since the beginning of this century. Ruthmund and Wilsmore[21] found in 1902 that the distribution ratio of phenol between benzene and water increases with increased concentration of phenol, indicating that self-association of phenol occurs in the benzene phase. In 1908 Hirobe[22] studied the partition of phenol between chlorobenzene and water and reached the conclusion that in chlorobenzene there exists a monomer-trimer equilibrium, while in the water phase only the phenol monomer is present. Philip and Clark[23] also reported from their partition studies that at phenol concentrations less than about 2.8 grams per liter of benzene solution, the association of phenol is negligible. In the more concentrated solutions, they concluded, a monomer-dimer equilibrium exists. They also noted that the addition of phenol greatly increases the amount of water in the benzene phase. In 1926 Endo[24] examined the partition of phenol between benzene and water and interpreted the experimental data in terms of a monomer-trimer equilibrium (only monomer phenol in the water phase was assumed when the concentration of phenol in the water phase was less than 0.24 M.). A trimerization constant of 1.07 M^{-2} was calculated for phenol in benzene at 25°C. Endo also carried out a cryoscopic study of phenol in water at concentrations larger than 0.24 M and reported the association constant

of phenol in water (also assuming monomer-trimer equilibrium) to be 0.5 M^{-2} at 0°C. In 1934 Philbrick[25] undertook an extensive distribution study of phenol between water and several organic solvents at 25°C. The concentrations of phenol in the water phase were confined to less than 0.1 M. Results of these investigations indicate that in these organic solvents the phenol appears to be present exclusively in single and double molecules. The dimerization constants of phenol in toluene, chlorobenzene, benzene and nitrobenzene were estimated to be 0.843 M^{-1}, 0.648 M^{-1}, 0.576 M^{-1}, and 0.196 M^{-1}, respectively. However, Philbrick was unable to obtain an association constant for phenol in carbon tetrachloride from experimental data. The differences in the association constants in various solvents was attribured to be different degree of solvation of phenol monomer. Badger and Greenough[26] measured the partition of phenol between water and carbon tetrachloride and reported that the self-association of phenol in carbon tetrachloride is greatly promoted by the presence of water. The dimerization constants were estimated to be 7.7 M^{-1} and 1.29 M^{-1} at 28°C for water-saturated carbon tetrachloride solution and anhydrous carbon tetrachloride solution, respectively. They concluded from partition and infrared spectroscopic studies[27] that the predominant species in wet carbon tetrachloride is a "hemihydrate dimer". More recently, Johnson, Christian, and Affsprung[28] carried out extensive studies on the self-association and hydration of phenol in organic solvents. By combining the partition data with water solubility data they concluded that the trimer is almost certainly one of the major species in dilute carbon tetrachloride solution and that the dimer does not appear to be an important species. They reported a trimerization constant of 4.1 M^{-2} for phenol in carbon

tetrachloride at 25°C. They also performed a similar study[29] of the hydration and self-association of phenol in benzene, 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, using partition, water solubility, and infrared techniques. Results of these experimental data are consistent with the assumption that the predominant associated solute species present in the three solvents are the cyclic aggregates, P_3, P_2W, PW_2, and W_3, where P and W represent monomeric units of phenol and water, respectively. The self-association constants of phenol (trimerization) were calculated to be 0.002 M^{-2}, 0.477 M^{-2}, and 0.263 M^{-2} for 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and benzene, respectively. Woolley, et al.,[30] also examined the distribution of phenol between water and carbon tetrachloride. Results have shown that the trimer is the major associated species in carbon tetrachloride saturated with water. A trimerization constant of 14.9 M^{-2} was determined for wet carbon tetrachloride. Although the partition method is a convenient technique in studying hydrogen bonding, the interpretation of experimental data is always complicated by the presence of water in the organic phase.

Using a unique apparatus, Lassettre and Dickinson[19] determined the concentration of phenol in benzene and the concentration of naphthalene in benzene for solutions having the same benzene vapor pressure. The higher formal concentration of the phenol solution, compared to the naphthalene solution at equilibrium, was attributed to the polymerization of phenol. They proposed that a monomer-dimer equilibrium exists in benzene solution and they reported dimerization constants of 0.57 M^{-1} and 0.416 M^{-1} at 25°C and 50°C, respectively. The heat of formation derived from these K values is -2,400±300 cal/mole. Bono,[31,32] Delvalle,[33]

and Chevalley[34] determined the vapor pressure lowering of phenol-carbon tetrachloride solutions and interpreted their data in terms of the self-association of phenol. However, no association constants were derived. A differential vapor pressure technique has been used by Coetzee and Mei-Shun Lok[35] to study the self-association of certain acids and bases in several nonhydrogen bonding solvents. A dimerization constant of 40 M^{-1} for phenol in 1,2-dichloroethane at 37°C was estimated from experimental data (concentration range from 0.02 to 0.1 M).

Since the development of solution infrared techniques in early 1930's, infrared spectroscopy has been one of the most popular methods used in studying hydrogen bonding. The evidence of hydrogen bonding can be directly observed from infrared spectra. Gordy and Nielson,[36] and Errera and Mollet,[37] in investigating the infrared spectra of some compounds containing the hydroxyl group, observed a sharp absorption band and a much broader band at longer wavelengths in the fundamental O-H stretching region. They assigned the latter as an "associated" band, which diminished on dilution of the solution or increase in the temperature. Fox and Martin[38] reported in 1937 some studies on phenol in organic solvents using the infrared method and came to the conclusion that at moderate concentrations an equilibrium is set up between single and double (associated) phenol molecules. They were able to obtain an extinction coefficient for monomer phenol in carbon tetrachloride at the free OH stretching band frequency, but failed to estimate an association constant. Kempter and Mecke[39,40] examined the self-association of phenol using the free OH stretching frequency in the second overtone region and suggested that complexes of all orders were possible and that all the

equilibrium constants for the sucessive association of complexes were the same ($(Ph)_n + Ph = (Ph)_{n+1}$; n = 1,2,3,$\cdots$). Their experimental data appeared be consistent with this proposal. A dissociation constant of 0.443 M was determined for phenol in carbon tetrachloride at 25°C. Wulf and Jones[41] also examined phenol in the second overtone region and reported a phenol demerization constant of 1.8 M^{-1} in carbon tetrachloride solution at 25°C, which is in good agreement with the result of Kempter and Mecke. In 1951 Coggeshall and Saier[42] investigated phenol solution in the fundamental hydroxyl stretching region and found that a better agreement between theory and experiment was obtained if two equilibrium constants were used, one for the formation of dimer and one for the formation of higher polymer by successive addition of monomer to dimer. The formation constants of 1.4 M^{-1} and 2.95 M^{-1} were derived from their experimental data for dimerization and higher polymerization at 25°C in carbon tetrachloride solution. Moccia and Califano[43] determined the dimerization constant for phenol in carbon tetrachloride solution by measuring the integrated intensities of the hydroxyl vibration absorption. A value of 1.25 M^{-1} was obtained for phenol in carbon tetrachloride. However, unpublished infrared results by Rea[44] indicated that trimers are the most important associated species of phenol in carbon tetrachloride solution. In 1961, Maguire and West[45] measured the first overtone of the free hydroxyl stretching vibration and reported that the dimer is the predominant associated species for phenol in carbon tetrachloride at room temperature. Polymeric forms arise only at phenol concentrations above about 0.2 M at 30°C. A cyclic dimer-monomer equilibrium was proposed for phenol in carbon tetrachloride. Dimerization constants for several

temperatures in the range -17.5°C to 45°C were calculated by assuming that dimers do not contribute to the free OH peak. The values of ΔH, ΔG, and ΔS for phenol dimerization in carbon tetrachloride were estimated to be -5.12±0.1 Kcal/mole, -1.19 Kcal/mole (at 303° K) and -13.0 eu/mole (at 303° K), respectively. More recently, Whetsel and Lady[46] made a comprehensive study of the self-association of phenol by measuring the intensities of the first overtone O-H stretching band of phenol as a function of concentration and temperature. They found that a model requiring an equilibrium constant for dimerization and another for the stepwise formation of higher multimers provided the best fit for the first overtone data. They also made corrections for the end OH group absorptivity of polymers by computer iteration and concluded that end OH group interference is negligible in cyclohexane solution and relatively weak in carbon tetrachloride solution. They suggested that phenol forms both linear and cyclic dimers and that higher polymers probably exist as three dimensional aggtegates. A summary of their spectral and thermodynamic results are listed in Tables 27 and 28.

Ultraviolet spectroscopy, though not as powerful and popular as infrared spectroscopy, has also been used to study hydrogen bonding. A blue shifted band for phenol in organic solvents, upon formation of hydrogen bonds, has been observed by several investigators. Ito[47,48] measured the UV spectra of phenol in various organic solvents at several concentration and suggested a cyclic dimer-monomer equilibrium for phenol (concentration range from 5×10^{-4} M to 5.7 M). The values of dimerization constants of phenol in n-hexane at 27°C and in carbon tetrachloride at room temperature were roughly estimated to be 4.5 M^{-1} and 3.6 M^{-1}

respectively. Dearden,[49] after studying the UV spectrum of phenol in cyclohexane, found that the experimental data could be interpreted in terms of monomer-dimer, monomer-trimer or monomer-polymer equilibria. He reported the values of 1.28 M^{-1}, 5.4 M^{-2}, and 1.45 M for dimerization, trimerization and polymerization at 25°C.

Nuclear magnetic resonance also has been employed to investigate hydrogen bonding since the 1950's. The chemical shift of the OH proton to a higher field was observed with either an increase in temperature or a dilution of the solution. This chemical shift to a higher field was attributed to the breaking of hydrogen bonds either by dilution or by heating. In 1956, Huggins, et al.,[50] examined the self-association of phenol in carbon tetrachloride solution by measuring the chemical shift of the OH proton as a function of concentration and temperature. They found that at low concentrations only monomers and dimers are important. A dimerization constant of 0.65±0.3 M^{-1} was obtained for phenol at 25°C from the limiting slope of a plot of apparent chemical shift vs. mole fraction of phenol (the lowest concentration was about 0.01 mole fraction). The heat of formation was reported to be -4.35 Kcal/mole at 25°C. Later, Saunders and Hyne[51] reexamined the PMR spectra of phenol in carbon tetrachloride solution at much lower concentration (0.01 M) and concluded that the monomer-trimer model provides the best fit of their chemical shift data. However, Becker,[52] criticizing the Saunders and Hyne paper, pointed out that the model containing only one associated species is inadequate to explain the infrared evidence. He also found that Saunders and Hyne's data could be fitted well by assuming the presence of dimers in addition to higher polymers. Martin and Quiloeut[53] also made an PMR study on the self-association of

phenol in carbon tetrachloride and chloroform and suggested that the association constants for the formation of successive phenol polymers are all the same. Rao, et al.,[54] interpreted their PMR data in terms of a monomer-dimer-polymer equilbrium in carbon tetrachloride solution, but no thermodynamic parameters were derived. Ahlf and Platthaus[55] have measured the hydroxyl proton chemical shifts for phenol and some amides. They concluded, in agreement with Saunders and Hyne, that phenol exhibits predominantly a monomer-trimer equilibrium in the concentration range 0.015 M to 4.5 M. The trimerization values of 49.3 M^{-2}, 12.55 M^{-2}, 3.67 M^{-2} and 1.32 M^{-2} were obtained for phenol in carbon tetrachloride solution at -11.5° C, 10.0° C, 31.0° C and 52.0° C, respectively. The ΔH_3 and ΔS_3 values obtained from a van't Hoff plot were -9.7±0.8 Kcal/mole and -29±2 eu/mole, respectively. Recently, Dale and Gramstad[56,57] have studied the self-association of phenol in carbon tetrachloride and cyclohexane by PMR in the concentration range 0.004-0.4.M and found that the results obtained can be accounted for in terms of a monomer-trimer model for phenol self-association. The formation constants they obtained are:

Temperature (°C)	K_3 (M^{-2}) in CCl_4	K_3 (M^{-2}) in Cyclohexane
20	4.4	17.0
35	2.4	4.4
50	1.3	1.6

More recently, Bogachev, et al.,[58] measured the hydroxyl proton chemical shifts for phenol in cyclohexane, methylcyclohexane and carbon tetrachloride solutions and concluded that a monomer-trimer equilibrium model provided the best fit for their experimental data within the entire

temperature range (20^{o}-80^{o}) and throughout a wide concentration range. However, at low phenol concentrations, from 1 to 3 mole%, the monomer-dimer equilibrium was observed in cyclohexane, methylcyclohexane, and carbon tetrachloride solutions. They suggested that the associated species in these solvents can be assumed to be mainly cyclic trimers. They also concluded that the values of K, ΔH and ΔS for linear trimers are the same as for cyclic trimers, while the chemical shift of the linear trimer is 1.5 times larger than that of the cyclic trimer. Most recently, Nakashima, et al.,[59] measured ^{13}C chemical shifts of phenol (C1) in carbon tetrachloride solution and asserted that the monomer-dimer model accounts satisfactorily for the phenol association data. The calculated values of the dimerization constants are:

Temperature (^{o}K)	K_2 (Molality^{-1})
321	0.694
311	0.699
300	0.901
290	1.52
279	2.50
269	4.44
258	9.09

A high value of the enthalpy of dimerization (-8.3 Kcal/mole) was derived from the van't Hoff plot of K_2.

The calorimetric method has also been used to investigate the self-association of phenol. In 1970, Woolley, et al.,[24] studied the self-association of phenol in carbon tetrachloride solution at $25^{o}C$ using the partition method as well as calorimetric techniques.

By determining heats of dilution of phenol in anhydrous carbon tetrachloride, they concluded that trimerization is the principal association reaction. The best values of K_3 and ΔH_3 were calculated to be 5.6 M^{-1} and -8.54 Kcal/mole at 25° C. Later, Woolley and Hepler extended their calorimetric measurements to phenol in cyclohexane and benzene. After fitting their experimental data with various association models, they found that the monomer-trimer model provides a good fit of their experimental data for solutions of phenol in cyclohexane, whereas for solutions of phenol in benzene the monomer-dimer model gives good fits. They also showed that their experimental data can be interpreted in terms of monomer-dimer-trimer for both solutions as well. However, they found that the apparent molar enthalpies for phenol calculated using the K and ΔH values reported by Whetsel and Lady are inconsistent with those of calorimetric measurements. They attributed the discrepancies to possible large errors in ΔH values derived from near-IR data. Most recently, Kohler, et al.,[61] have studied the self-association of phenol with thermodynamic, dielectric and NMR methods. The results are interpreted in terms of competitive association to non-polar cyclic associate (trimer or tetramer) and to polar chain associates.

The properties of phenol in aprotic solvents have also been studied with other techniques[1-3] such as dielectric relaxation,[62] ultrasonic absorption[63,64] and chromatography.[65] However, few formation constants have been derived from these methods. Recently, advances in instrumentation and experimental technique[66] have made it possible to observe hydrogen bond stretching frequencies in far infrared region (10-300 cm^{-1}). A strong broad absorption band centered at 177 cm^{-1} has been assigned to

the stretching mode of the hydrogen bond of phenol solutions.

From the above literature review, it is clear that little agreement has been reached regarding the nature of the molecular aggregate of phenol in solutions. For example, the recent results of calorimetric data are incompatible with the monomer-dimer-stepwise-n-mer model, which provides a satisfactory explanation for infrared data. And recent NMR studies tend to interpret experimental data in terms of only one associated species in contrast to IR evidence, which shows that at least two associated species of different orders are present in solutions. Furthermore, the assumption that the dimer is the first major associated species has been objected to by some workers.[28,29,44,68] They have argued that the first important associated species appears to be the trimer. The stability of trimer has been attributed to the cooperative effect in hydrogen bonding of linear trimers[68] or to the formation of cyclic trimers,[28,29] which are assumed to be energetically favored. Most studies of phenol hydrogen bonding have used only one experimental technique. It should be very instructive to combine data of several types for the same phenol-solvent systems over the same concentration and temperature range. In the case of the volatile aliphatic alcohols methanol and tert-butanol,[67,68] a combination of infrared and NMR spectral data and vapor pressure results provides evidence that trimers and larger polymers are present in solutions in carbon tetrachloride and hydrocarbon solvents, even at concentrations well below unit molarity.

It should be worth exploring whether vapor pressure methods can be used to evaluate alternative models for the association of phenol. Although phenol is not volatile enough to permit use of conventional

vapor pressure techniques, the strong absorptivity of phenol vapor in the ultraviolet region makes it possible to measure phenol vapor absorbances above solid phenol and solutions of phenol in various organic solvents. The absorbance should serve as an indicator of the partial pressure or activity of phenol in solutions. The fact that such widely different results have been obtained with different techniques makes it desirable to develop an activity method for assessing the validity of other individual methods for studying the self-association of phenol. From the viewpoint of solution thermodynamics, any association model for phenol solutions derived from various experimental techniques should be consistent with reliable activity results; i.e., the values of the concentration of phenol monomer obtained from various techniques should vary linearly with the thermodynamic activity.

CHAPTER II

OBJECTIVES AND APPROACH

The objectives of this research were to develop and apply a new technique to investigate the self-association of phenol in organic solvents. The technique involves determining the activity and concentrations of phenol at various temperatures from absorbance measurements on phenol vapor in equilibrium with phenol solutions. In the concentration range below 1 M, it was considered reasonable to attribute deviations of activity data from Henry's law to the formation of specific hydrogen-bonded complexes. Models of association and the thermodynamic parameters were to be inferred from the activity data. It was planned to compare results from this new technique with those obtained by other techniques, especially the near-IR method.

CHAPTER III

EXPERIMENTAL

Chemicals

Phenol (from Mallinckrodt, Analytical Reagent) was purified by subliming it in vacuo at room temperature. Phenol vapor was condensed on the wall of the flask by immersing the flask in a dry ice-acetone mixture. The pure phenol obtained was stored in a desiccator over Drierite (anhydrous $CaSO_4$) and kept in the dark to protect it from possible decomposition.

Cyclohexane was purchased from Eastman Co. as technical grade and purified by distillation through a 30-plate Oldershaw Column. A constant reflux ratio of 10:1 was maintained during the distillation process by a Flexopulse cycle timer which controlled a solenoid-operated valve contained in the column head. Only the middle fraction of the distillate was collected and this had a boiling point range of less than $0.1^{\circ}C$. The purified solvent was stored in the desiccator over Drierite. Carbon tetrachloride (Fisher Co. certified ACS) was distilled from P_2O_5 in the same way as cyclohexane and stored over a drying agent (Linde 4Å molecular sieve) in a three-foot glass column.

Instrument, Spectral Cells and Temperature Control

A single-beam Beckman Model DU-2 spectrophotometer equipped with a temperature-regulated cell holder was used in the spectral measurements. Silica cylindrical cells (Beckman, 22 mm diameter) with pathlengths of 10 cm, 5 cm, and 2 cm were used in absorbance measurements of the vapor of solid phenol at various temperatures in order to obtain an empirical relation between vapor absorbance and vapor concentration. In order to measure the absorbances of phenol vapor over solutions, indentations were made in the bottom of a 10 cm cell (see Figure 1) so that about 1 ml of solution could be placed in the cell without contaminanting the cell windows. Special care was taken in making the indentations to ensure that the cell windows were still parallel to each other and that the cell pathlength was not changed. The heights of the indentations were also carefully controlled so that they would not interfere with passage of the light beam.

The precise control of cell temperature was important for the experiment since even slight temperature fluctuations in the phenol solution (or solid) in the cell would significantly change the vapor pressure of the sample. In this work a temperature-regulated cell holder was used to control the cell temperature during the spectral measurements. The temperature of the cell holder was controlled by circulating water from an auxiliary thermostatted circulator (Lauda/Brinkman circulator, model K-2/R), with which the temperature can be adjusted from -10°C to $+150^{\circ}$ C. The temperature of circulating water was controlled to within 0.03° C in the experimental temperature range. The temperature of the solution in the cell was calibrated by use of a small thermocouple probe (Bailey Instrument Co. #8506-75) which could be immersed in the solution.

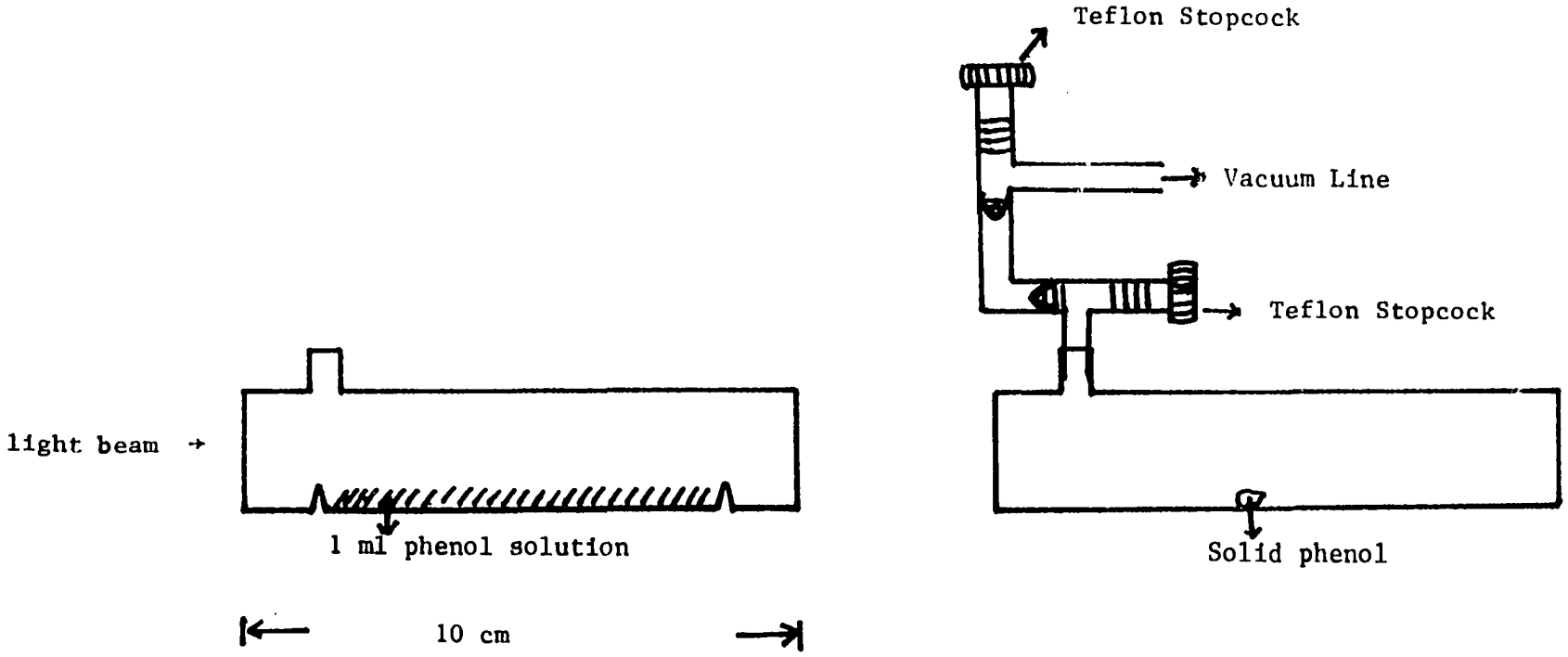


Figure 1. (a) The Special 10 cm Cell for Measuring the Phenol Vapor Absorbance above Phenol Solutions.

(b) The Vacuum Unit Used for Measuring the Absorbance of Phenol Vapor Equilibrated with Solid Phenol

The temperature was monitored using a digital thermometer (Bailey Instrument Inc. Model BAT-8), which indicates temperatures to 0.1°C. Throughout the entire experiment, it was observed that the difference in temperature between the circulating water and the cell was 0.1°C or less. From the experimental data, it appears that the temperature of a solution (or solid) in the cell was controlled to within 0.1°C. In case of experimental temperatures higher than room temperature an additional device was used to prevent the condensation of vapor on the cell windows, which would cause erratic absorbance readings. A nichrome heating wire, controlled by a powerstat, was attached to the cell windows to warm them a few degrees above the experimental temperature. The effect of warming up cell windows on the temperature of solutions (or solids) in the cell was almost negligible except for the 2 cm cell.

Experimental Procedures

Phenol solutions up to about 1 M were made up gravimetrically in both carbon tetrachloride and cyclohexane. A stock solution was first prepared by dissolving the weighed phenol in the solvent in a volumetric flask held in a water bath at 20°C and diluting the solution to the mark on the flask. Then aliquots of the stock solution were added to weighed volumes of solvents in volumetric flasks. The exact concentration of each solution was calculated from the known concentration of the stock solution and the weights and densities of the solvent and stock solution. All solutions were stored in the dark and sealed with parafilm to prevent possible decomposition and evaporation. In order to reduce the probability of dissolution of traces of water from the air into solution, particular

care was taken in the preparation of the solutions. All solution concentrations are reported as molarity (M).

Because the Beer-Lambert law is not followed by phenol vapor except at very small spectral slit-widths, the relation between concentration (or vapor pressure) and vapor absorbance has to be determined by an empirical method. Generally, there are two reasons for deviations from the Beer-Lambert law; one is related to molecular properties of the substances investigated, the other arises because of instrumental limitations. In this work, the phenol vapor undergoing UV measurements has a pressure less than 1 torr over the experimental temperature range. It is unlikely[70] that significant quantities of associated phenol are present in the vapor phase under such circumstances. Thus, deviations from the Beer-Lambert law due to chemical changes of phenol vapor can probably be ruled out. The reason for such deviation can be attributed to the limitations of the spectral instrument used. Strictly speaking, the Beer-Lambert law should hold rigorously only for truly monochromatic radiation. Such conditions are not realizable because of the finite slit width of the monochromators, which is necessary for instrumental reasons. However, it is possible to determine empirically the actual relationship between the absorbance and the concentration for any particular set of instrument conditions. Such a calibration curve should be suitable for use in quantitative spectral analysis, provided the conditions of analysis once selected are kept constant. In this work, the vapor of pure solid phenol was used to obtain a standard curve. An optimum slit width of 0.2 mm, which is equal to spectral slit widths of 0.54 nm at 275 nm, 0.48 nm at 268 nm, and 0.46 nm at 262 nm, was maintained

throughout the whole work so that a reliable absorbance could be read even at low vapor pressure, with instrument noise at a low level. Although a smaller slit width increases the absorptivity of phenol vapor, it also increases the instrument noise. A good standard curve may be obtained provided that concentrations (or vapor pressures) and absorbances can be measured with high precision throughout the whole concentration (or vapor pressure) range. Because the vapor pressure of solid phenol is small, it is difficult to determine it with high accuracy at ambient temperatures. Furthermore, the precise relation between vapor pressure and temperature and the exact cell temperature have to be known. However, what we are interested in in this work is the activity data, i.e., the ratio of vapor pressure of phenol solution to that of solid phenol at the same temperature. Therefore, if a variable pathlength cell (1 cm - 20 cm) or a set of cells with pathlength from 1 cm to 20 cm (the more, the better) were available, the dependence of the vapor absorbance of solid phenol on the cell pathlength could be determined accurately at each temperature, and knowledge of the relation between the vapor pressure of solid phenol and temperature would be unnecessary. Thus activity could be expressed in terms of the ratio of cell pathlengths with high accuracy. Unfortunately, only a set of cells with pathlengths of 2 cm, 5 cm, and 10 cm were available in the present study. There is no way to fit a curve (vapor absorbance vs. cell pathlength) precisely with only three points. Therefore, it has been necessary to measure the vapor absorbance of solid phenol with these three cells at several temperatures in order to obtain enough points for fitting. This calibration requires knowledge of the variation of vapor pressure with temperature. The detailed data treatment will

be discussed in the next chapter.

The three intense peaks of phenol vapor at about 275.1 nm, 268.2 nm, and 262.6 nm were chosen for absorbance measurements. In order to check on the possible condensation of phenol vapor or solvent vapor on the cell windows, the absorbance data at 360 nm, 320 nm, 300 nm, and 290 nm were also taken along with data at the three peaks. Any fogging of the cell windows could be detected by observation of abnormally high absorbances at these wavelengths. Because the phenol vapor absorbance peaks are so sharp, it was necessary to move the wavelength control knob slightly in the vicinity of the peaks during absorbance measurements until a maximum absorbance was obtained. A small wavelength change (about 0.5 to 1 nm) was observed for the maximum absorbance peaks when the instrument was in operation for a long period of time. This is probably due to a slight temperature change in the monochromator. All absorbances were determined point by point at the three peaks for both the solutions and solid phenol.

In practical operation, the absorbance of a clean empty cell vs. air was determined at wavelengths of 275.1 nm, 268.2 nm, and 262.6 nm as well as at wavelengths of 360 nm, 320 nm, 300 nm, and 290 nm. Then a small crystal of purified solid phenol was placed in the bottom of the cell. The cell was stoppered with a special unit (Figure 1b) and evacuated to accelerate the equilibrium between solid and vapor and to prevent fogging. Then the cell was positioned in the temperature-regulated cell holder and a period of 30 - 40 minutes was allowed for equilibrium to be attained. The vapor absorbance of solid phenol was obtained by subtracting the absorbance of the empty cell from the absorbance of the cell with phenol. It was observed that the vapor absorbance of solid phenol at

360 nm was only on the order of 0.001 and was less than 0.01 at 290 nm when the cell windows were not contaminated by condensation of the phenol vapor. The exact temperature of phenol in the cell was monitored by a thermocouple probe as previously described.

The procedures for measuring the absorbance of phenol vapor above the solutions were similar to those for solid phenol, except for evacuation of the cell. The special 10 cm cell shown in Figure 1a was used. After the absorbance of the empty cell had been measured, exactly 1 ml of phenol solution was delivered with a 1 ml pipette into the cell positioned in the temperature-regulated cell holder. Then the cell was stoppered in the usual way. A period of 20 minutes was allowed for equilibrium to be established before absorbance data was taken. In order to correct for the vapor absorbance of solvent above the solution, the vapor absorbance of pure solvent at each experimental temperature was also measured in the same way as for the solutions. The absorbance of phenol vapor was obtained by subtracting the vapor absorbance of pure solvent at the same temperature and the absorbance of the empty cell from the vapor absorbance above the solution. Here the reasonable assumption was made that the absorbance due to the solvent vapor above phenol solution is equal to that of pure solvent. The vapor absorbance of pure cyclohexane at the three peaks was estimated to be about 0.004 at 37.7°C, whereas the vapor absorbances of pure carbon tetrachloride at 37.8°C were about 0.003, 0.005, and 0.007 at 275.1 nm, 268.2 nm, and 262.6 nm, respectively. At lower temperatures these absorbances decrease substantially.

In order to compare directly these results of the near-IR data of Whetsel and Lady, this work was performed over temperature and concen-

tration ranges similar to those of the near-IR study. The absorbance measurements were made at 11.85, 20.7, 29.1, and 37.8°C for carbon tetrachloride solutions and at 13.3, 22.2, 32.2, and 37.7°C for cyclohexane solutions. The vapor absorbance data for solid phenol at various temperatures and at three wavelengths are reported in Tables 1 to 3, while the absorbances of phenol vapor above the solutions are given in Tables 4 to 11, along with the derived activity data.

TABLE 1

VAPOR ABSORBANCE DATA FOR SOLID PHENOL AT 275.1 nm AT VARIOUS TEMPERATURES IN 10 cm, 5 cm, AND 2 cm CELLS

Temperature (°C)	Absorbance		
	10 cm	5 cm	2 cm
37.9	.9120	.5390	-
35.0	.7520	-	-
32.2	.6370	.3770	.1800
29.5	.5375	.3180	.1470
22.2	.3315	.1910	.0840
21.65	.3180	.1840	.0810
20.7	.2975	.1680	.0765
18.4	.2530	.1420	.0625
16.2	.2130	.1185	.0515
13.3	.1700	.0945	.0400
11.85	.1510	.0830	.0350

TABLE 2

VAPOR ABSORBANCE DATA FOR SOLID PHENOL AT 268.2 nm AT VARIOUS TEMPERATURES IN 10 cm, 5 cm and 2 cm CELLS

Temperature (°C)	Absorbance		
	10 cm	5 cm	2 cm
37.9	1.0100	.5520	-
35.0	.8165	-	-
32.2	.6710	.3680	.1575
29.5	.5545	.3020	.1270
22.2	.3140	.1665	.0680
21.65	.3025	.1600	.0670
20.7	.2770	.1450	.0615
18.4	.2310	.1190	.0505
16.2	.1880	.0975	.0400
13.3	.1460	.0765	.0310
11.85	.1270	.0660	.0270

TABLE 3

VAPOR ABSORBANCE DATA FOR SOLID PHENOL AT 262.6 nm AT VARIOUS TEMPERATURES IN 10 cm, 5 cm, AND 2 cm CELLS

Temperature (°C)	Absorbance		
	10 cm	5 cm	2 cm
37.9	.7240	.3775	-
35.0	.5720	-	-
32.2	.4610	.2455	.1015
29.5	.3760	.2000	.0875
22.2	.2050	.1040	.0410
21.65	.1965	.1035	.0405
20.7	.1820	.0925	.0360
18.4	.1485	.0745	.0315
16.2	.1195	.0610	.0250
13.3	.0930	.0475	.0200
11.85	.0810	.0410	.0170

TABLE 4

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CARBON TETRACHLORIDE SOLUTIONS AI 37.8°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a*	
	A	a	A	a	A	a	2λ	3λ
1.02413	.5650	.5312	.5680	.5139	.3870	.5143	.5141	.5198
.85347	.5390	.4983	.5390	.4834	.3660	.4839	.4839	.4886
.73151	.5195	.4741	.5165	.4600	.3525	.4644	.4622	.4662
.64008	.5030	.4539	.4960	.4388	.3360	.4406	.4397	.4444
.56892	.4890	.4369	.4830	.4255	.3255	.4256	.4256	.4294
.51206	.4785	.4243	.4700	.4122	.3160	.4121	.4121	.4161
.45521	.4580	.4001	.4500	.3921	.3025	.3929	.3925	.3950
.38405	.4400	.3792	.4360	.3780	.2860	.3696	.3738	.3756
.34141	.4155	.3514	.3985	.3410	.2665	.3423	.3417	.3449
.29262	.3930	.3264	.3745	.3176	.2510	.3207	.3192	.3216
.23661	.3610	.2918	.3395	.2842	.2260	.2863	.2853	.2874
.17082	.3075	.2369	.2820	.2307	.1860	.2323	.2315	.2333
.13389	.2645	.1954	.2390	.1920	.1575	.1945	.1933	.1940
.09319	.2100	.1465	.1835	.1439	.1195	.1453	.1446	.1452
.06695	.1640	.1085	.1405	.1080	.0920	.1105	.1093	.1090
.05951	.1500	.0975	.1270	.0970	.0820	.0981	.0975	.0975
.05021	.1290	.0817	.1075	.0813	.0700	.0832	.0823	.0821
.04463	.1175	.0733	.0970	.0730	.0630	.0747	.0738	.0737
.03825	.1030	.0630	.0845	.0632	.0550	.0649	.0641	.0637
.03090	.0860	.0514	.0690	.0512	.0440	.0517	.0514	.0514
.02232	.0640	.0371	.0510	.0375	-	-	.0375	.0373
.01217	.0355	.0197	.0280	.0203	.0175	.0202	.0203	.0201
.02736	.0750	.0441	.0600	.0443	.0390	.0457	.0450	.0447
.01785	.0510	.0290	.0400	.0292	.0250	.0291	.0291	.0291

* In Tables 4 to 11 activity data (a) have been averaged for the data at wavelengths (268.2 nm and 262.6 nm) and at all three wavelengths (see page 45)

TABLE 5

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CARBON TETRACHLORIDE SOLUTIONS AT 29.1°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
1.02819	.3510	.5877	.3330	.5808	.2200	.5811	.5810	.5833
.85686	.3390	.5616	.3190	.5538	.2100	.5527	.5533	.5560
.73441	.3250	.5316	.3050	.5262	.2010	.5273	.5268	.5284
.64262	.3195	.5200	.2970	.5107	.1960	.5132	.5120	.5147
.57117	.3140	.5085	.2910	.4992	.1910	.4992	.4992	.5023
.51410	.3025	.4846	.2790	.4763	.1825	.4755	.4759	.4788
.45702	.2895	.4580	.2660	.4516	.1740	.4519	.4517	.4538
.38557	.2750	.4290	.2510	.4235	.1640	.4242	.4239	.4256
.34276	.2660	.4112	.2420	.4067	.1575	.4064	.4065	.4081
.29378	.2530	.3860	.2290	.3827	.1490	.3831	.3829	.3839
.23731	.2325	.3472	.2070	.3427	.1350	.3465	.3446	.3455
.17150	.2000	.2882	.1740	.2838	.1125	.2849	.2843	.2856
.13443	.1745	.2441	.1495	.2410	.0965	.2427	.2418	.2426
.09356	.1395	.1870	.1180	.1874	.0755	.1881	.1877	.1875
.06721	.1085	.1397	.0900	.1409	.0570	.1407	.1408	.1404
.05975	.1000	.1273	.0830	.1295	.0530	.1306	.1301	.1291
.05041	.0870	.1088	.0710	.1101	.0450	.1105	.1103	.1098
.04480	.0785	.0970	.0640	.0989	.0410	.1005	.0997	.0988
.03840	.0690	.0841	.0560	.0862	.0350	.0855	.0859	.0853
.03102	.0565	.0676	.0450	.0689	.0285	.0694	.0691	.0686
.02241	.0440	.0517	.0350	.0533	.0215	.0522	.0527	.0524
.01222	.0245	.0279	.0190	.0287	.0120	.0290	.0288	.0285

TABLE 6

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CARBON TETRACHLORIDE SOLUTIONS AT 20.7°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
1.03327	.2145	.6673	.1895	.6612	.1220	.6590	.6601	.6625
.86109	.2065	.6368	.1810	.6291	.1165	.6279	.6285	.6312
.73804	.2000	.6123	.1755	.6085	.1125	.6053	.6069	.6087
.64580	.1955	.5954	.1695	.5861	.1085	.5827	.5844	.5881
.57399	.1905	.5769	.1660	.5730	.1060	.5689	.5708	.5728
.51664	.1850	.5585	.1600	.5508	.1030	.5518	.5513	.5537
.45928	.1790	.5349	.1550	.5323	.0995	.5323	.5323	.5331
.38748	.1725	.5115	.1485	.5084	.0945	.5044	.5064	.5081
.34446	.1675	.4938	.1430	.4883	.0920	.4905	.4894	.4909
.29524	.1590	.4639	.1355	.4610	.0865	.4600	.4605	.4616
.23849	.1490	.4295	.1260	.4268	.0800	.4242	.4255	.4268
.17218	.1270	.3560	.1055	.3538	.0675	.3559	.3548	.3552
.13496	.1115	.3063	.0920	.3064	.0585	.3071	.3068	.3066
.09393	.0915	.2446	.0745	.2459	.0470	.2454	.2456	.2453
.06754	.0715	.1858	.0575	.1881	.0370	.1922	.1902	.1887
.06004	.0660	.1702	.0530	.1730	.0330	.1711	.1721	.1714
.05066	.0570	.1451	.0455	.1479	.0285	.1474	.1477	.1468
.04503	.0520	.1313	.0415	.1347	.0260	.1343	.1345	.1334
.03859	.0455	.1138	.0360	.1165	.0225	.1160	.1163	.1155
.03117	.0380	.0940	.0295	.0950	.0190	.0978	.0964	.0956
.02252	.0285	.0694	.0220	.0706	.0130	.0667	.0686	.0689
.01228	.0155	.0370	.0115	.0367	.0070	.0358	.0363	.0365

TABLE 7

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CARBON TETRACHLORIDE SOLUTIONS AT 11.85°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
1.0414	.1195	.7707	.0990	.7687	.0630	.7700	.7694	.7698
.86787	.1165	.7484	.0955	.7403	.0600	.7323	.7363	.7403
.74384	.1135	.7263	.0935	.7240	.0585	.7135	.7187	.7213
.65088	.1095	.6970	.0900	.6957	.0565	.6884	.6921	.6937
.57851	.1070	.6788	.0880	.6795	.0550	.6697	.6746	.6760
.52070	.1050	.6643	.0855	.6594	.0540	.6572	.6583	.6603
.46287	.1020	.6427	.0830	.6393	.0530	.6447	.6420	.6422
.39053	.0975	.6106	.0795	.6113	.0495	.6011	.6062	.6077
.34717	.0950	.5929	.0770	.5913	.0480	.5825	.5869	.5889
.29756	.0910	.5648	.0730	.5594	.0460	.5577	.5585	.5606
.24036	.0855	.5266	.0690	.5277	.0430	.5205	.5241	.5249
.17353	.0735	.4451	.0585	.4449	.0360	.4343	.4396	.4414
.13602	.0650	.3888	.0510	.3864	.0320	.3853	.3858	.3868
.09467	.0535	.3146	.0420	.3167	.0265	.3182	.3174	.3165
.06801	.0430	.2489	.0335	.2514	.0210	.2514	.2514	.2506
.06045	.0395	.2274	.0305	.2286	.0195	.2333	.2310	.2298
.05100	.0350	.2001	.0270	.2020	.0170	.2031	.2026	.2017
.04534	.0320	.1821	.0245	.1830	.0155	.1851	.1841	.1834
.03886	.0290	.1643	.0220	.1641	.0140	.1670	.1656	.1651
.03139	.0235	.1320	.0185	.1377	.0120	.1430	.1404	.1376
.02267	.0165	.0916	.0125	.0928	.0080	.0940	.0940	.0932

TABLE 8

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CYCLOHEXANE SOLUTIONS AT 37.7°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2 λ	3 λ
.92258	.7740	.8221	.8180	.7964	.5680	.7884	.7924	.8023
.80690	.7525	.7911	.7960	.7711	.5550	.7689	.7700	.7770
.73313	.7435	.7776	.7820	.7551	.5445	.7532	.7541	.7620
.66187	.7335	.7641	.7670	.7380	.5345	.7382	.7381	.7468
.58882	.7225	.7485	.7570	.7267	.5280	.7284	.7275	.7345
.51569	.7045	.7232	.7350	.7018	.5090	.6999	.7008	.7083
.46175	.6920	.7058	.7190	.6838	.5005	.6872	.6855	.6923
.40346	.6765	.6843	.7015	.6642	.4845	.6632	.6637	.6706
.36694	.6640	.6672	.6870	.6480	.4735	.6468	.6474	.6540
.33127	.6500	.6481	.6720	.6313	.4630	.6311	.6312	.6368
.29501	.6330	.6251	.6510	.6082	.4480	.6088	.6085	.6140
.25810	.6115	.5964	.6230	.5775	.4275	.5784	.5779	.5841
.22100	.5900	.5680	.5995	.5520	.4090	.5510	.5515	.5570
.18430	.5575	.5259	.5625	.5123	.3835	.5135	.5129	.5172
.16657	.5375	.5005	.5400	.4885	.3685	.4915	.4900	.4935
.14752	.5170	.4749	.5160	.4632	.3495	.4639	.4635.	.4673
.12983	.4940	.4466	.4885	.4347	.3305	.4363	.4355	.4392
.11090	.4580	.4034	.4480	.3933	.3015	.3947	.3940	.3971
.09243	.4210	.3605	.4075	.3527	.2720	.3529	.3528	.3554
.07430	.3720	.3061	.3535	.2992	.2340	.2998	.2995	.3017
.05556	.3105	.2419	.2870	.2372	.1905	.2403	.2387	.2398
.03682	.2320	.1671	.2065	.1649	.1355	.1672	.1661	.1664
.01834	.1315	.0842	.1110	.0848	.0720	.0864	.0856	.0851
.04607	.2770	.2089	.2510	.2044	.1660	.2074	.2059	.2069
.02764	.1870	.1281	.1630	.1276	.1060	.1296	.1284	.1283
.01229	.0935	.0569	.0765	.0574	.0490	.0582	.0578	.0575
.00670	.0540	.0311	.0440	.0325	.0280	.0329	.0327	.0322
.00351	.0285	.0158	.0220	.0160	.0140	.0163	.0162	.0161

TABLE 9

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL

IN CYCLOHEXANE SOLUTIONS AT 32.2°C AT THREE PEAKS

Formal Concentration(M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
.92631	.5890	.8986	.6010	.8779	.4090	.8737	.8758	.8834
.80935	.5750	.8697	.5870	.8540	.3990	.8504	.8522	.8580
.66455	.5555	.8300	.5610	.8099	.3825	.8119	.8109	.8173
.59120	.5495	.8178	.5555	.8006	.3765	.7980	.7993	.8055
.51725	.5375	.7937	.5420	.7779	.3670	.7759	.7769	.7825
.46315	.5280	.7748	.5290	.7562	.3580	.7551	.7557	.7620
.73610	.5680	.8554	.5765	.8361	.3930	.8364	.8363	.8426
.40468	.5110	.7413	.5125	.7288	.3460	.7275	.7281	.7325
.36805	.5025	.7247	.5030	.7131	.3395	.7126	.7128	.7168
.33261	.4950	.7101	.4930	.6967	.3330	.6976	.6972	.7015
.29590	.4850	.6909	.4825	.6795	.3240	.6771	.6783	.6825
.25889	.4680	.6585	.4615	.6454	.3105	.6463	.6458	.6501
.22167	.4535	.6313	.4455	.6193	.2980	.6180	.6186	.6229
.18486	.4295	.5871	.4195	.5782	.2810	.5797	.5790	.5817
.16707	.4180	.5663	.4045	.5546	.2705	.5562	.5554	.5590
.14796	.4000	.5342	.3865	.5264	.2565	.5250	.5257	.5285
.13008	.3860	.5096	.3690	.4994	.2450	.4996	.4995	.5029
.11123	.3620	.4683	.3420	.4581	.2265	.4589	.4585	.4618
.09271	.3330	.4199	.3115	.4123	.2050	.4122	.4122	.4148
.07445	.2990	.3653	.2750	.3587	.1805	.3596	.3592	.3612
.05573	.2500	.2910	.2255	.2880	.1470	.2890	.2885	.2893
.03693	.1870	.2032	.1625	.2017	.1050	.2028	.2023	.2026
.01839	.1070	.1052	.089	.1066	.0575	.1087	.1076	.1068
.04621	.2205	.2487	.1965	.2478	.1265	.2466	.2472	.2474
.02773	.1510	.1572	.1285	.1570	.0820	.1568	.1569	.1570
.01232	.0745	.0701	.0605	.0714	.0385	.0721	.0718	.0712
.00672	.0425	.0381	.0340	.0396	.0215	.0399	.0398	.0392
.00352	.0230	.0200	.0185	.0213	.0115	.0212	.0213	.0209

TABLE 10

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CYCLOHEXANE SOLUTIONS AT 22.2°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
.81264	.3290	.9999	.3085	.9866	.2020	.9814	.9840	.9893
.73909	.3240	.9803	.3040	.9705	.1990	.9658	.9681	.9722
.66725	.3185	.9588	.2980	.9491	.1950	.9450	.9470	.9510
.59360	.3135	.9394	.2920	.9277	.1910	.9242	.9259	.9304
.51988	.3100	.9259	.2890	.9170	.1885	.9112	.9141	.9180
.46551	.3025	.8971	.2820	.8923	.1840	.8880	.8901	.8925
.40674	.2960	.8724	.2735	.8624	.1780	.8571	.8597	.8640
.36992	.2905	.8517	.2685	.8448	.1745	.8391	.8419	.8452
.33396	.2885	.8442	.2665	.8379	.1730	.8314	.8347	.8378
.29710	.2800	.8126	.2575	.8065	.1670	.8008	.8036	.8066
.25994	.2730	.7868	.2500	.7805	.1620	.7752	.7778	.7808
.22257	.2650	.7576	.2405	.7479	.1560	.7447	.7463	.7501
.18543	.2520	.7110	.2270	.7018	.1475	.7017	.7018	.7048
.16758	.2460	.6897	.2220	.6848	.1430	.6791	.6819	.6845
.14857	.2385	.6635	.2125	.6528	.1370	.6490	.6509	.6551
.13061	.2270	.6238	.2015	.6160	.1305	.6165	.6163	.6189
.11158	.2175	.5916	.1925	.5861	.1235	.5817	.5839	.5865
.09299	.1995	.5319	.1750	.5318	.1120	.5249	.5284	.5295
.07468	.1850	.4851	.1605	.4815	.1020	.4760	.4787	.4808
.05584	.1570	.3982	.1335	.3954	.0855	.3961	.3957	.3966
.03704	.1230	.2989	.1020	.2975	.0640	.2935	.2955	.2966
.01845	.0700	.1582	.0555	.1581	.0350	.1583	.1582	.1582
.04635	.1450	.3624	.1220	.3594	.0775	.3577	.3585	.3598
.02781	.1000	.2357	.0825	.2383	.0515	.2348	.2366	.2363
.01236	.0490	.1074	.0385	.1087	.0245	.1079	.1083	.1080
.00674	.0280	.0594	.0215	.0602	.0135	.0604	.0603	.0600

TABLE 11

VAPOR ABSORBANCE AND DERIVED ACTIVITY DATA FOR PHENOL IN CYCLOHEXANE SOLUTIONS AT 13.3°C AT THREE PEAKS

Formal Concentration (M)	275.1 nm		268.2 nm		262.6 nm		Averaged a	
	A	a	A	a	A	a	2λ	3λ
.29954	.1640	.9708	.1400	.9627	.0895	.9612	.9619	.9649
.26207	.1600	.9426	.1360	.9334	.0870	.9333	.9334	.9364
.22440	.1555	.9111	.1315	.9006	.0835	.8943	.8975	.9020
.18695	.1515	.8833	.1275	.8715	.0810	.8665	.8690	.8738
.16895	.1470	.8523	.1250	.8533	.0785	.8388	.8461	.8481
.14963	.1430	.8250	.1200	.8172	.0760	.8112	.8142	.8178
.13155	.1375	.7878	.1155	.7849	.0730	.7781	.7815	.7836
.11238	.1320	.7510	.1095	.7419	.0690	.7341	.7380	.7423
.09366	.1245	.7015	.1030	.6956	.0650	.6902	.6929	.6958
.07522	.1155	.6432	.0945	.6355	.0600	.6356	.6356	.6382
.05624	.1010	.5517	.0825	.5514	.0520	.5488	.5501	.5506
.03731	.0820	.4363	.0655	.4340	.0410	.4304	.4322	.4336
.01857	.0485	.2457	.0385	.2515	.0240	.2498	.2507	.2490
.04669	.0930	.5024	.0750	.4994	.0470	.4948	.4971	.4989
.02801	.0660	.3432	.0530	.3489	.0330	.3452	.3471	.3458
.01245	.0335	.1659	.0260	.1687	.0160	.1659	.1673	.1668
.00679	.0185	.0895	.0150	.0967	.0085	.0878	.0922	.0913

CHAPTER IV

DATA TREATMENT AND RESULTS

Two fundamental assumptions were made in data treatment: (1) Henry's law is obeyed by each of the individual phenol species in solution; (2) The ideal gas law is obeyed by phenol vapors. Here, the activity of phenol solutions was defined as:

$$a = \frac{p}{p^o} \tag{1}$$

where p^o is the vapor pressure of solid phenol at one temperature, p is the phenol vapor pressure above phenol solution at the same temperature. If the Beer-Lambert law is obeyed by phenol vapor, absorbance can be expressed as

$$A = \varepsilon \ell C \tag{2}$$

where ε is extinction coefficient, ℓ is cell pathlength in cm, and C is the concentration of phenol vapor in mole/liter (M). If phenol vapor behaves as an ideal gas, we can write

$$pV = nRT$$

or

$$p = CRT \tag{3}$$

From equation (1), (2), and (3), activity can be expressed in terms of

absorbance.

$$a = \frac{p}{p^o} = \frac{\frac{A}{\varepsilon \ell} \times RT}{\frac{A^o}{\varepsilon \ell} \times RT} = \frac{A}{A^o} \qquad (4)$$

where A^o is the vapor absorbance of solid phenol at one temperature, A is the vapor absorbance of phenol above solution at same temperature with same cell pathlength. So in the case where the Beer-Lambert law is obeyed by phenol vapor, the activity of phenol solutions can be directly determined from the ratio of vapor absorbances (A/A^o) with high accuracy. As mentioned in Chapter III, phenol vapor does not follow the Beer-Lambert law and the empirical relation between absorbance and concentration (or vapor pressure) had to be determined. Before the vapor absorbance data in Tables 1 to 3 can be treated, a correlation of vapor pressure of solid phenol with temperature has to be known. The first low-temperature vapor pressure measurements for phenols were reported by Balson.[69] Recently, Biddiscombe and Martin[70] have measured the vapor pressures of liquid m-cresol and solid phenol, o-and p- cresol in the temperature range 0-40°C with more advanced techniques. The purity of phenol used was reported to be 99.96±0.02 mole%. Both the gas saturation technique and diaphragm manometer methods were employed for vapor pressure measurements. In the gas saturation procedure, the prassure is calculated from the weight of phenol evaporated, assuming there is no association in the vapor phase. The second method directly measures the vapor pressure using a diaphragm manometer. The experimental data obtained have been fitted to the Antoine

equation:

$$\log p^{o} = A - \frac{B}{(t + 273)} \tag{5}$$

where p^{o} (in torr) is the vapor pressure of pure solid phenol at t ^{o}C. The two parameters, A and B, were obtained by Biddiscombe and Martin ; they reported the least squares values A=11.56 and B=3586, which can be used to obtain calculated values of p^{o} which should be accurate to within 1 %.(This assumes that only random errors of measurement are present in the reported pressure values.) The following equation is proposed to fit the present absorbance data as a function of pressure and temperature:

$$\frac{p^{o}\ell}{T} = \alpha A + \beta A^{2} + \gamma A^{3} \tag{6}$$

where A is the vapor absorbance of solid phenol at temperature T (Kelvin), ℓ is the cell pathlength (in cm), and p^{o} is the vapor pressure of solid phenol (in torr) at temperature T, calculated from Equation (5). α, β, and γ are the adjustable parameters to be found; we assume that these constants do not change with temperature. A modified weighted linear least squares method proposed by Christian, et al.,[71] has been used to obtain these parameters. The algorithm of this method is briefly described as follows:

In the linear least squares method, the sum of the weighted squared residuals (S)

$$S = \sum_{i=1}^{n} \left[W_i R_i^2 \right] \tag{7}$$

is minimized with respect to the fitting parameters (α,β,γ). Here, the residual for the ith point is

$$R_i = \frac{p_i^{o}\ell_i}{T_i} - \alpha A_i - \beta A_i^{2} - \gamma A_i^{3} \tag{8}$$

and the weight is

$$W_i = \frac{1}{\sigma^2_{\frac{p_i^o \ell_i}{T_i}} + \alpha^2 \sigma^2_{A_i} + \beta^2 \sigma^2_{A_i^2} + \gamma^2 \sigma^2_{A_i^3}} \tag{9}$$

Now equation (7) can be expressed as

$$S = \sum_{i=1}^{n} \left[\frac{\left(\frac{p_i^o \ell_i}{T_i} - \alpha A_i - \beta A_i^2 - \gamma A_i^3\right)^2}{\sigma^2_{\frac{p_i^o \ell_i}{T_i}} + \alpha^2 \sigma^2_{A_i} + \beta^2 \sigma^2_{A_i^2} + \gamma^2 \sigma^2_{A_i^3}} \right] \tag{10}$$

In ordinary least squares treatments, the vaiation of W_i with α,β,γ in differentiating S to obtain $\partial S/\partial\alpha$, $\partial S/\partial\beta$, and $\partial S/\partial\gamma$ has been ignored and the following normal equations are obtained:

$$\begin{bmatrix} \Sigma W_i A_i^2 & \Sigma W_i A_i^3 & \Sigma W_i A_i^4 \\ \Sigma W_i A_i^3 & \Sigma W_i A_i^4 & \Sigma W_i A_i^5 \\ \Sigma W_i A_i^4 & \Sigma W_i A_i^5 & \Sigma W_i A_i^6 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix} = \begin{bmatrix} \Sigma W_i A_i \frac{p_i^o \ell_i}{T_i} \\ \Sigma W_i A_i^2 \frac{p_i^o \ell_i}{T_i} \\ \Sigma W_i A_i^3 \frac{p_i^o \ell_i}{T_i} \end{bmatrix} \tag{11}$$

In order to calculate α,β,γ values, the matrix at the left hand side is inverted and an iterative procedure is used to obtain the best values of the parameters. However, Christian, et al.,[71] have argued that the parameters (α,β,γ) in the denominator of equation (10) should be taken into account in the differentiation of S. Using this method the normal equations obtained appear as:

$$\begin{pmatrix} \Sigma W_i A_i^2 - \Sigma W_i^2 \sigma_{A_i}^2 R_i^2 & \Sigma W_i A_i^3 & \Sigma W_i A_i^4 \\ \Sigma W_i A_i^3 & \Sigma W_i A_i^4 - \Sigma W_i^2 \sigma_{A_i}^2 R_i^2 & \Sigma W_i A_i^5 \\ \Sigma W_i A_i^4 & \Sigma W_i A_i^5 & \Sigma W_i A_i^6 - \Sigma W_i^2 \sigma_{A_i}^2 R_i^2 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} \Sigma W_i A_i \frac{p_i^o \ell_i}{T_i} \\ \Sigma W_i A_i^2 \frac{p_i^o \ell_i}{T_i} \\ \Sigma W_i A_i^3 \frac{p_i^o \ell_i}{T_i} \end{pmatrix} \quad (12)$$

The α, β, and γ values obtained from equation (11) are used to calculate the R_i values of equation (12). It may be noted that the only difference between equations (11) and (12) is in the principal diagonal terms of the 3×3 matrix on the left hand side.

In fitting equation (6), the errors in measured absorbances are assumed to be 0.002 for all points and errors in the left hand side of equation (6) are assumed to be one percent. The best least squares values of α, β, γ at three wavelengths obtained using the method of Christian, et al., (equation (12)) are given in Table 12. The results obtained using the regular linear least squares method (equation (11)) are also included in the Table 12 for comparison. Little difference in values of parameters and the goodness of fitting is observed between two methods. This indicates that contributions arising from the additional subtractive terms in the diagonal elements are nearly negligible in this case. The plots of absorbance vs. $p^o\ell/T$ are given in Figures 2 to 4. Curves are calculated from the parameters (using the method of Christian, et al.); points are experimental data. For clarity, some points at low absorbances are not plotted. The good fit as shown in Figures 2 to 4 can justify our assumption that the α, β, and γ values do not change with temperature.

Now, the activity (a) of phenol solution may be expressed as:

TABLE 12

LEAST SQUARES PARAMETER FOR $\frac{p^{o}\ell}{T} = \alpha A + \beta A^2 + \gamma A^3$

AT 275.1 nm, 268.2nm, AND 262.6 nm

		χ^2
At 275.1nm:		
	α = 0.0178±0.0002 (0.0178±0.0002)	
	β = 0.0299±0.0012 (0.0299±0.0012)	25.87 (25.87)
	γ = -0.0086±0.0014 (-0.0085±0.0014)	
At 268.2 nm:		
	α = 0.0243±0.0002 (0.0243±0.0002)	
	β = 0.0136±0.0008 (0.0136±0.0008)	12.26 (12.27)
	γ = -0.0038±0.0008 (-0.0038±0.0008)	
At 262.6 nm:		
	α = 0.0391±0.0003 (0.0391±0.0003)	
	β = 0.0206±0.0020 (0.0208±0.0020)	12.59 (12.59)
	γ = -0.0122±0.0026 (-0.0124±0.0026)	

Note: Values in parenthese were obtained using the conventional least squares method.

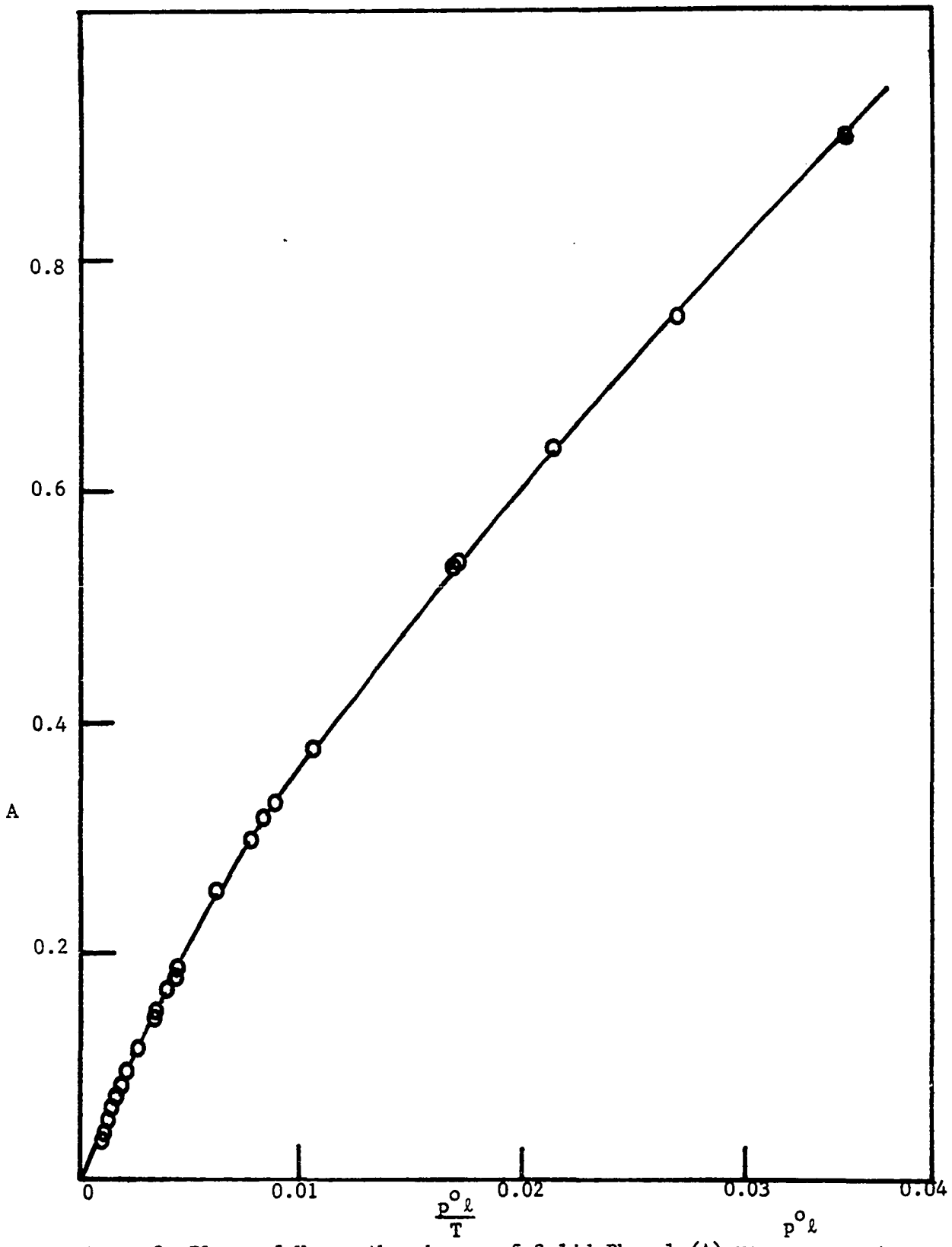


Figure 2. Plots of Vapor Absorbance of Solid Phenol (A) vs. $\frac{p^{o}_{\ell}}{T}$ at 275.1 nm (line is calculated from α, β, and γ values)

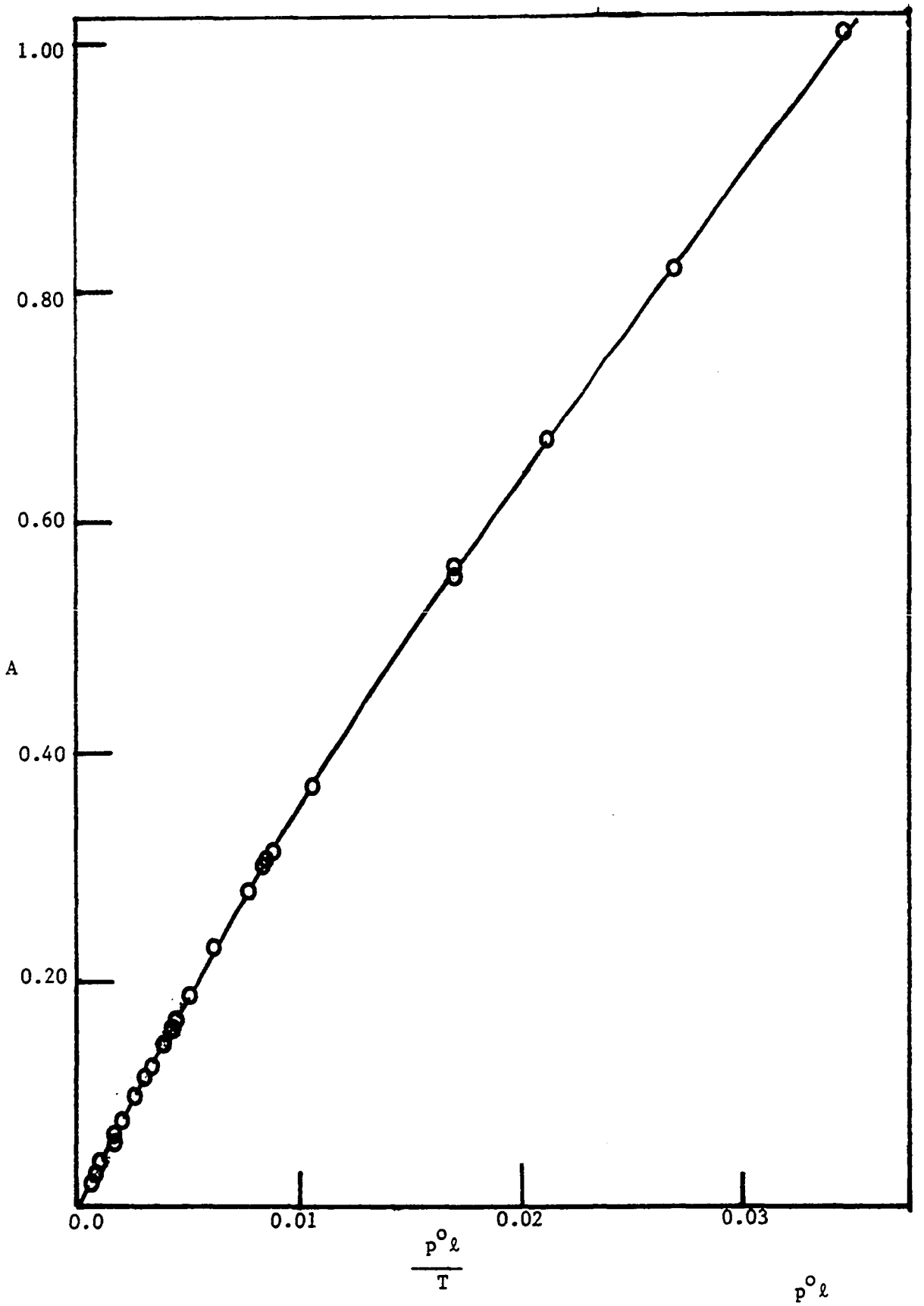


Figure 3. Plots of Vapor Absorbance of Solid Phenol (A) vs. $\frac{p^{o}\ell}{T}$ at 268.2 nm (line is calculated from α, β, and γ values)

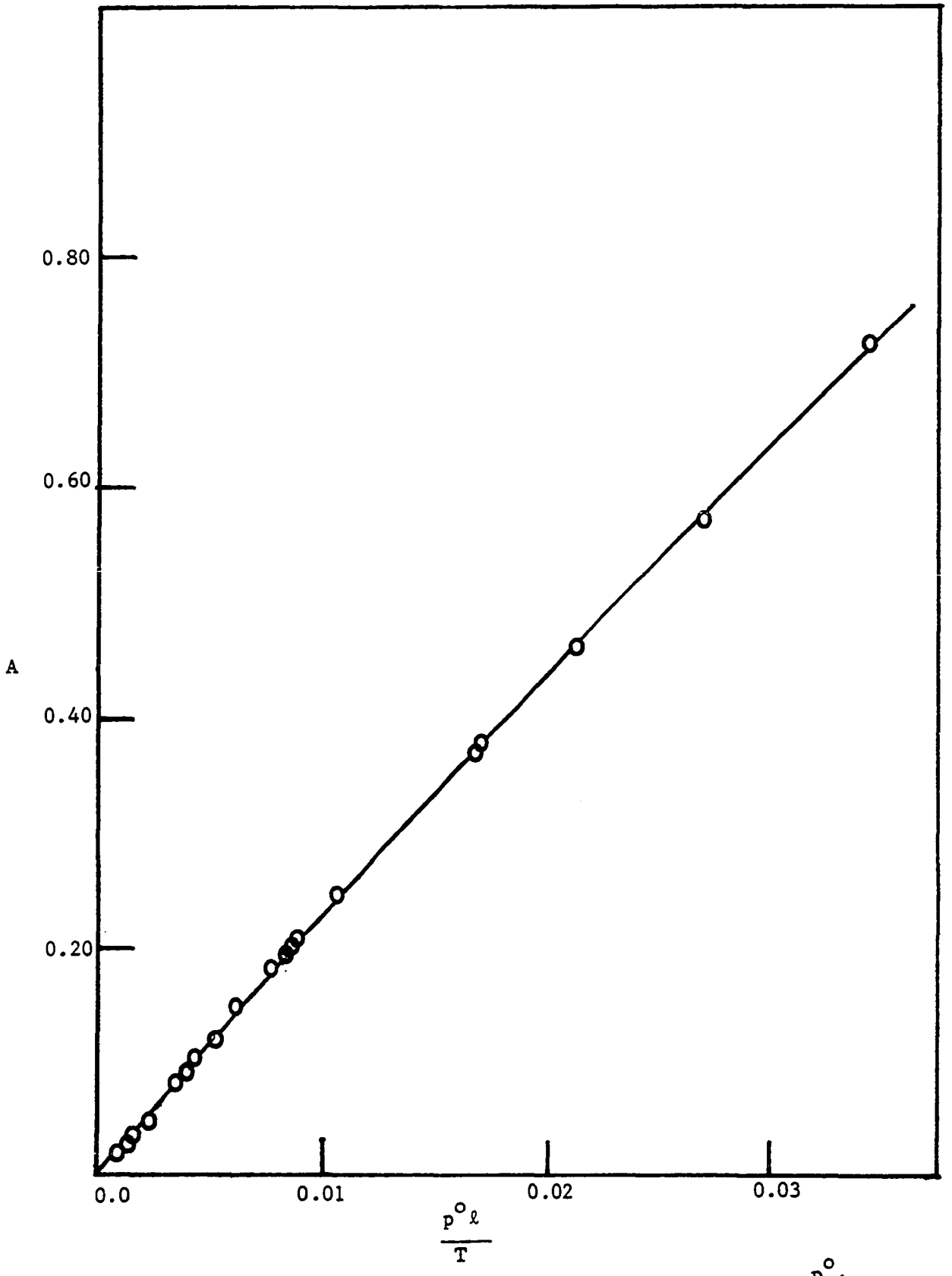


Figure 4. Plots of Vapor Absorbance of Solid Phenol (A) vs. $\frac{p^{o}_{\ell}}{T}$ at 262.6 nm (line is calculated from α, β, and γ values).

$$a = \frac{p}{p^o} = \frac{\frac{p\ell}{T}}{\frac{p^o\ell}{T}} = \frac{\alpha A + \beta A^2 + \gamma A^3}{\frac{p^o\ell}{T}} \qquad (13)$$

where the vapor pressure(p^o)of solid phenol is calculated directly from equation (5). The derived activity data of phenol solutions at three wavelengths at various temperatures are given in Tables 4 to 11. Also included in Tables 4 to 11 are the averaged activities from data at three wavelengths and data at two wavelengths (268.2 nm and 262.6 nm). It is noted that the derived activity data at 268.2 nm and 262.6 nm are in good agreement for all solutions. The derived activity data at 275.1 nm are also in reasonable agreement with those at 268.2 nm or 262.6 nm, except at high absorbances (above 0.5), at which differences in derived activity data (between that at 275.1 nm and that at 268.2 nm or 262.6 nm) are about 3 to 4 percent. The averaged activity data from results obtained at all three wavelengths are used in model fitting.

The changes in phenol concentration due to the temperature variation and the evaporation of solvent and solute from 1 ml solution should be corrected for. The change of concentration with temperature can be estimated from the temperature coefficients of expansion of the pure solvents (1.24×10^{-3} deg^{-1} for CCl_4, 1.1×10^{-3} deg^{-1} for cyclohexane). In correcting for the amount of solvent evaporated from 1 ml solution, it has been assumed that the solvent vapor pressure above the solution is approximately equal to the vapor pressure of pure solvent, the values of which at various temperatures may be obtained from the literature.[72] We further assume that solvent vapor behaves as an ideal gas. The weight of solvents

evaporated from the solutions can be calculated from the volume of the cell and the vapor pressure of solvent at a given temperature with the ideal gas equation. The correction for the evaporation of cyclohexane from 1 ml of solution at 37.7°C is about 2.2 percent and for carbon tetrachloride at 37.8°C is about 2.3 percent.

The correction for the evaporation of solute from 1 ml of solution in the cell was determined point by point in the same way as for the solvent. From the phenol vapor absorbance data above the solution, the vapor pressure can be calculated from equation (6). It should be pointed out that the correction for solute evaporation at low temperatures (13.3°C and 11.85°C) is less than 0.2 percent for all solutions and may be neglected. At the highest temperature, the correction for solute evaporation is no more than 0.7 percent. The concentrations of phenol solutions are all corrected to within 0.2 percent. The formal concentrations of phenol solutions listed in Table 4 to 11 have already been corrected for temperature change and evaporation of solvent and solute.

Association Models for Phenol

In the preceding section, the assumptions were made that Henry's law is obeyed by the phenol monomer and that the ideal gas law is obeyed by phenol vapor; i.e., the self-association of phenol in the vapor phase is nelgigible. Here, we further assume that all deviations from Henry's law are attributable to the formation of specific molecular complexes by hydrogen bonding. From the above assumptions, a linear relationship of monomer concentration (C_M) of phenol with the activity (a) or vapor pressure (p) of phenol can be established as follows:

$$K_p = \frac{a}{C_M} = \frac{\frac{p}{p^o}}{C_M} = \frac{p}{p^o C_M} \tag{14}$$

where K_p is a constant related to Henry's law constant, p^o is the solid phenol vapor pressure. In the limit of very dilute solutions, only monomer phenol exists in solutions. So K_p can be expressed as

$$K_p = \lim_{f_A \to 0} \frac{a}{f_A} = \lim_{f_A \to 0} \frac{p/p^o}{f_A} \tag{15}$$

where f_A is the formal concentration (M) of phenol solution. From equation (15), K_p values may be obtained from the limiting slope in plotting activity vs. formal concentration at low concentration range. If the K_p value is known, the monomer concentration of phenol in each solution can be obtained from the K_p value and activity data by equation (14).

Usually, Henry's law constant is defined as

$$K_x = \frac{p}{X} \tag{16}$$

where p is vapor pressure of solute, X is the mole fraction of solute. For dilute solutions, the relation of molarity (M) with mole fraction may be written as

$$\lim_{f_A \to 0} \frac{f_A}{X} = \frac{\rho^o \times 1000}{M^o} \tag{17}$$

where ρ^o and M^o are density (gram/ml) and molecular weight of solvents, respectively. From equations (15), (16), and (17), K_x can be expressed

in terms of K_p as

$$K_x = K_p \times p^o \times \frac{1000}{M^o} \times \rho^o \qquad (18)$$

If K_x values at several temperatures are known, the enthalpy and entropy changes for the reaction P(monomer in solution) = P(gas) can be expressed as:

$$\frac{d \ln K_x}{d T} = \frac{\Delta H_x^o}{RT^2} \qquad (19)$$

$$\Delta S^o = \frac{\Delta H_x^o - \Delta G^o}{T} \qquad (20)$$

where $\Delta G^o = - RT \ln K$

ΔH_x^o is the molar enthalpy of vaporization of monomeric phenol from solution or, in other words, the negative of the molar enthalpy of transfer of monomeric (gaseous) phenol into solvent at infinite dilution. ΔH_x^o is assumed to be invariant over the temperature range involved.

In principle, K_p (or K_x) values may be obtained from the limiting slope of a plot of activity vs. formal concentration at low concentration range. However, at such low concentration, the measured phenol vapor absorbances above solutions, from which activities are to be obtained, become so small that the limiting slope is difficult to determined with high accuracy, especially at low temperature. In spite of this difficulty, plots of a/f_A vs. f_A have been made for the low concentration range (Fig-

ures (5) and (6)). These plots show that at high temperature the K_p values may be estimated with reasonable accuracy by extrapolating the limiting curve to zero concentration. The K_p values were estimated to be 1.67 M^{-1} for carbon tetrachloride solution at 37.8°C and 4.72 M^{-1} for cyclohexane solution at 37.7°C. The standard errors in such extrapolations are probably less than two percent. Except at 11.85°C for carbon tetrachloride solution and 13.3°C for cyclohexane solution, the K_p values also can be estimated at the other temperatures with fair reliablity from Figures 5 and 6. Another method for obtaining K_p is to consider this constant as an adjustable parameter in model-fitting. This procedure will be discussed in detail later.

In considering the evidence of IR spectra, it has been suggested that the phenol association models limited to dimerization and/or trimerization can be rejected as physically unrealistic, even at concentration of 0.2 M. But we think it is instructive to fit the activity data with the proposed models limited to one or two associated species as well as the more realistic models of multimer species.

For the monomer-dimer model, we can write the equilibrium as

$$2\ P = P_2$$

and equilibrium constant (K_2) as

$$K_2 = \frac{C_2}{C_M^2} \tag{21}$$

where C_M is monomer concentration, C_2 is dimer concentration. The formal concentration of phenol can be expressed as

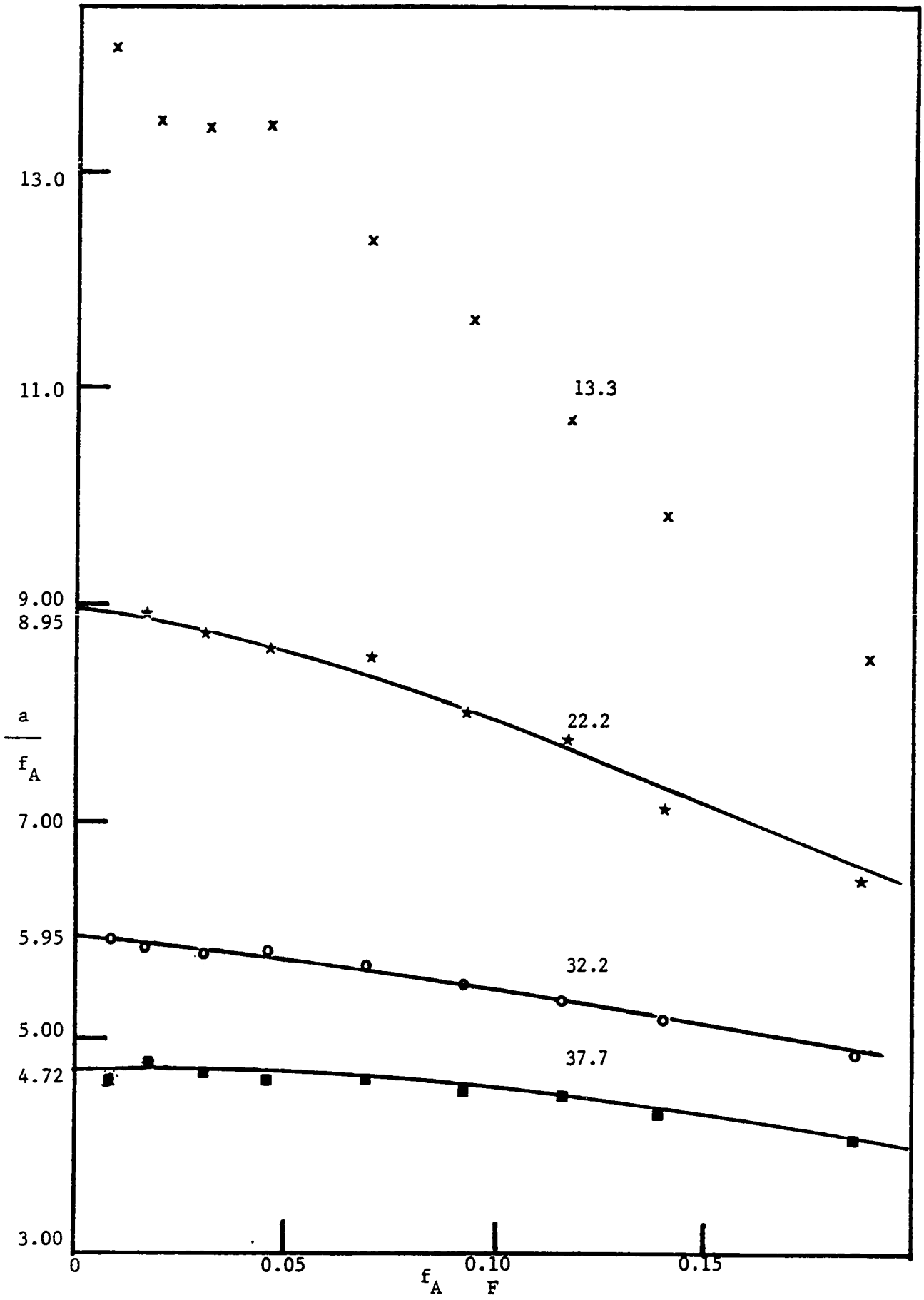


Figure 5. Plots of a/f_A vs. f_A in the Low Concentration Range for Phenol in Cyclohexane Solutions at 37.7, 32.2, 22.2 and 13.3°C.

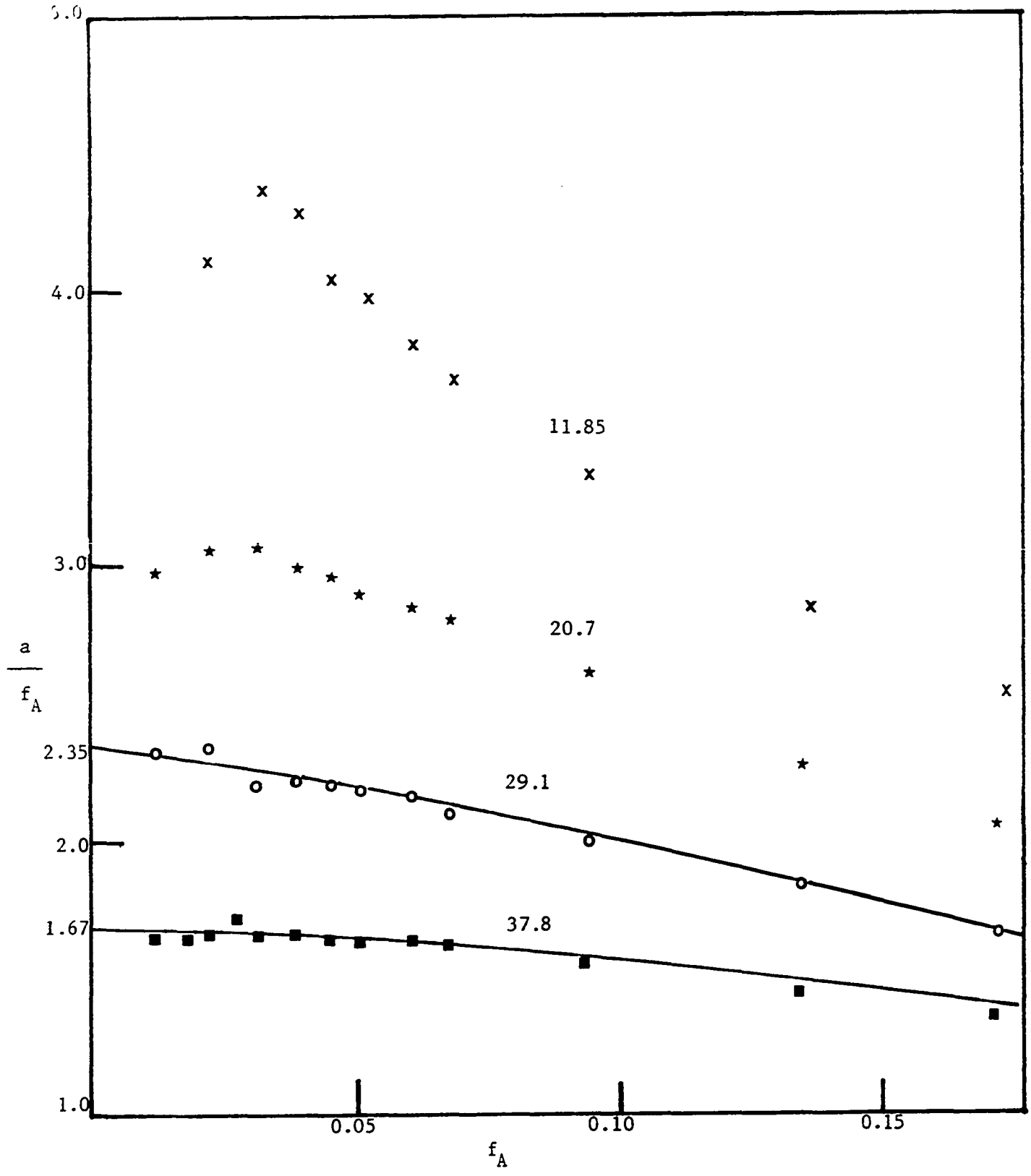


Figure 6. Plots of a/f_A vs. f_A in the Low Concentration Range for Phenol in Carbon Tetrachloride Solution at 37.8, 29.1, 20.7 and 11.85°C.

$$f_A = C_M + 2C_2 \tag{22}$$

Combing equations (21) and (22), we find

$$f_A = C_M + 2K_2C_M^2 \tag{23}$$

However, the monomer concentration can be estimated from the activity and K_p values by

$$C_M = \frac{a}{K_p} \tag{24}$$

From equations (23) and (24), we obtain

$$f_A = \left(\frac{a}{K_p}\right) + 2\,K_2\,\left(\frac{a}{K_p}\right)^2 \tag{25}$$

Similarly, for the monomer-trimer model the formal concentration can be expressed as:

$$f_A = \left(\frac{a}{K_p}\right) + 3K_3\left(\frac{a}{K_p}\right)^3 \tag{26}$$

and for the monomer-dimer-trimer model, we can write

$$f_A = \left(\frac{a}{K_p}\right) + 2K_2\left(\frac{a}{K_p}\right)^2 + 3K_3\left(\frac{a}{K_p}\right)^3 \tag{27}$$

For the multimer association models, the chemical equilibrium may be expressed as

$$n\,P = P_n \quad (n=2,3,4,5\ \cdots\cdots)$$

and the equilibrium constants as

$$K_n = \frac{C_n}{C_M^n} \qquad (n=1,\ 2,3,4\cdots\cdots) \tag{28}$$

where C_n is the concentration of n-mer, K_n is equilibrium constant for the equilibrium between monomer and n-mer. And the formal concentration of phenol solution can be represented as the sum of concentration of monomer and polymers

$$f_A = C_M + 2C_2 + 3C_3 + 4C_4 + \cdots\cdots + nC_n \tag{29}$$

Combining equations (28) and (29), we can write

$$f_A = C_M + 2K_2C_M^2 + 3K_3C_M^3 + 4K_4C_M^4 + \cdots + nK_nC_M^n \tag{30}$$

The above equation can be expressed in terms of activity as

$$f_A = \left(\frac{a}{K_p}\right) + 2K_2\left(\frac{a}{K_p}\right)^2 + 3K_3\left(\frac{a}{K_p}\right)^3 + \cdots\cdots + nK_n\left(\frac{a}{K_p}\right)^n \tag{31}$$

Obviously, if several terms are required in fitting data to equation (31), it will be difficult to determine reliable values of the required parameters from a given set of data. It is therefore necessary to make some simplifying assumptions. Coggeshall and Saier[42] have used two equilibrium constants for polymer formation; a unique equilibrium constant for the formation of dimer and a constant for the formation of all higher polymers in stepwise fashion. Assuming dimer to be the first important associated species, their model leads to:

$$2P = P_2$$

$$K_2 = \frac{C_2}{C_M^2} \tag{32}$$

and $$P_{n-1} + P = P_n \qquad (n=3,4,5,\ \cdots)$$

$$K_\infty = \frac{C_n}{(C_M)\ (C_{n-1})} \qquad (33)$$

It is assumed that K_∞ is identical for all values of n greater than 2. The relation of K_n in equation (28) with K_2 and K_∞ can be written as:

$$K_n = K_2 K_\infty^{n-2} \qquad (\ n>2\ )$$

Now the equation (31) can be represented as

$$f_A = (\frac{a}{K_p}) + 2K_2(\frac{a}{K_p})^2 + 3K_2K_\infty(\frac{a}{K_p})^3 + \cdots + nK_2K_\infty^{n-2}(\frac{a}{K_p})^n \qquad (34)$$

$$\text{or} \quad f_A = (\frac{a}{K_p}) + K_2(\frac{a}{K_p})^2(\ 2 + 3K_\infty(\frac{a}{K_p}) + \cdots + nK_\infty^{n-2}(\frac{a}{K_p})^{n-2}) \qquad (35)$$

Equation (35) may be transformed into closed form with some simple mathematical operations:

$$f_A = (\frac{a}{K_p}) + \frac{K_2(\frac{a}{K_p})^2(2 - K_\infty(\frac{a}{K_p}))}{(\ 1 - K_\infty(\frac{a}{K_p}))^2} \qquad (36)$$

However, Tucker and Becker[68] have provided some evidence that trimers rather than dimers, are the smallest self- associated species of importance in solutions of tert-butanol in n-hexadecane, using vapor pressure, IR, and PMR methods. In such a case, equation (35) may be changed to

$$f_A = (\frac{a}{K_p}) + 3K_3(\frac{a}{K_p})^3 + 4K_3K_\infty(\frac{a}{K_p})^4 + \cdots + nK_3K_\infty^{n-3}(\frac{a}{K_p})^n \qquad (37)$$

where $K_n = K_3K_\infty^{n-3}$ (n>3). Using similar mathematical operations, equat-

ion (37) is transformed into the closed form:

$$f_A = \left(\frac{a}{K_p}\right) + \frac{K_3\left(\frac{a}{K_p}\right)^3\left(3 - 2K_\infty\left(\frac{a}{K_p}\right)\right)}{\left(1 - K_\infty\left(\frac{a}{K_p}\right)\right)^2} \qquad (38)$$

Equations (36), (38) as well as equations (25), (26), (27) can be analyzed by least squares method. A modified version of a non-linear least squares program developed by Marquardt[73] was used to obtain the best values of association constants or K_p values. The algorithm of the Marquardt program is based on a maximum neighborhood method, and the program performs an optimum interpolation between the Taylor series method and the gradient method. Thus the program not only has ability to converge from an initial guess value which may be outside the region of convergence of other methods (e.g. the gradient method), but also it can close in on the converged values rapidly after the vicinity of the converged values has been reached (the Taylor series method). Since experimental errors in activity are greater than those of formal concentration, it is preferred to fit activity as a function of formal concentration. Thus, deviations in activity, instead of formal concentration, are minimized in seeking the best least squares values of association constants and K_p. The Newton-Raphson method[74] has been used to obtain the calculated activity data corresponding to the values of formal concentration and parameters. The root mean square deviation, RMSD, which is minimized is defined as

$$\text{RMSD} = \left\{\frac{\sum_{i=1}^{n}\left(a_i^{\text{obs.}} - a_i^{\text{calc.}}\right)^2}{n - p}\right\}^{1/2}$$

where $a_i^{obs.}$ and $a_i^{calc.}$ are, respectively, the observed and calculated values of activities for the ith data point; n is the total number of points; and p is the number of adjustable parameters. The adjustable parameters for a specific model were systematically varied in a search for a minimum in the RMSD for a given data set. The standard errors in the association constants at the minimum RMSD were taken as the uncertainties in these parameters.

The activity data have been treated in two ways in the least squares model fitting. (1) The K_p values, which were obtained from the plots of a/f_A vs. f_A, were kept constant and only the association constants were considered as adjustable parameters. This was tested at the two highest temperatures. The association constants and RMSD resulting from such fitting are given in Tables 13 and 14. The analysis shows that the 1-3-∞ model has the best fit for both carbon tetrachloride and cyclohexane solutions. The RMSD values for this model are within the experimental errors, whereas the 1-2, 1-3, and 1-2-3 models provide significantly poorer fits for the activity data. A physically unrealistic negative dimer constant was obtained for the 1-2-3 model. The 1-2-∞ model does not fit as well as the 1-3-∞ model except at 29.1°C for carbon tetrachloride solution, where the RMSD values of the 1-2-∞ and 1-3-∞ models are comparable. (2) The K_p values are considered as adjustable parameters along with the association constants in model fitting. Since the 1-3-∞ and the 1-2-∞ models seemed to be more physically realistic, these two models were tested with the activity data over the whole range of temperatures. The 1-2, 1-3, and 1-2-3 models were fitted only at one or two temperatures for the purpose of comparison. Tables 15 and 16 give

TABLE 13

RMSD AND ASSOCIATION CONSTANT VALUES FOR PHENOL IN CARBON TETRACHLORIDE

(K_p values are derived from limiting intercepts and kept constant)

Model	Temperature(^oC)	$K_p(M^{-1})$	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
1-3-∞	37.8	1.67	-	2.63±0.09	1.81±0.05	0.002579
	29.1	2.35	-	5.76±0.25	2.11±0.08	0.003893
1-2- ∞	37. 8	1.67	0.54±0.03	-	2.33±0.05	0.004576
	29.1	2.35	0.94±0.03	-	2.82±0.04	0.003920
1-2-3	29.1	2.35	-1.65±0.37	18.8 ±1.3	-	0.01201
1-3	29.1	2.35	-	13.4 ±0.5	-	0.01695
1-2	29.1	2.35	4.34±0.31	-	-	0.04555

TABLE 14

RMSD AND ASSOCIATION CONSTANT VALUES FOR PHENOL IN CYCLOHEXANE

(K_p values are derived from limiting intercepts and kept constant)

Model	Temperature(^{o}C)	$K_p(M^{-1})$	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
1-3- ∞	37.7	4.72	-	7.88±0.11	4.27±0.02	0.002148
	32.2	5.95	-	12.9±0.3	4.84±0.04	0.003681
1-2- ∞	37.7	4.72	0.95±0.04	-	4.78±0.05	0.007249
	32.2	5.95	1.33±0.06	-	5.47±0.06	0.009264
1-2-3	32.2	5.95	-7.30±1.10	94±7	-	0.03225
1-3	32.2	5.95	-	55±3	-	0.05475
1-2	32.2	5.95	10.1±1.0	-	-	0.01121

TABLE 15

RMSD, ASSOCIATION CONSTANT, AND HENRY'S LAW CONSTANT VALUES FOR PHENOL IN CARBON TETRACHLORIDE

(K_p is considered as an independent parameter in model fitting)

Model	Temperature(°C)	$K_p(M^{-1})$	K_x(torr/X)*	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
1-3-∞	37.8	1.67±0.02	17.9±0.2	-	2.58±0.19	1.79±0.05	0.00241
	29.1	2.24±0.03	11.3±0.1	-	4.38±0.32	2.18±0.05	0.00293
	20.7	3.06±0.03	7.12±0.07	-	6.25±0.37	2.96±0.04	0.00284
	11.85	4.28±0.06	4.20±0.06	-	10.2±0.9	3.66±0.07	0.00500
1-2-∞	37.8	1.81±0.03	19.4±0.3	0.79±0.07	-	2.34±0.04	0.00313
	29.1	2.49±0.04	12.5±0.2	1.20±0.09	-	2.87±0.04	0.00309
	20.7	3.42±0.06	7.95±0.13	1.46±0.11	-	3.73±0.05	0.00359
	11.85	4.91±0.09	4.82±0.09	2.14±0.16	-	4.58±0.06	0.00412
1-2-3	29.1	1.73±0.10		-2.52±0.17	10.2±1.2	-	0.00855
	20.7	2.08±0.16		-3.52±0.18	14±2		0.01269
1-3	29.1	2.70±0.17		-	22±5	-	0.01513
	20.7	3.97±0.40		-	49±2	-	0.02279
1-2	29.1	10±7		$105\pm1.5\times10^2$	-	-	0.03188
	20.7	17±20		$256\pm6.5\times10^2$	-	-	0.04433

* X represents mole fraction

TABLE 16

RMSD, ASSOCIATION CONSTANT, AND HENRY'S LAW CONSTANT VALUES FOR PHENOL IN CYCLOHEXANE

(K_p is considered as an independent parameter in model fitting)

Model	Temperature(°C)	$K_p(M^{-1})$	K_x(torr/X)*	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
1-3-∞	37.7	4.72±0.03	44.8±0.3	-	7.83±0.28	4.27±0.02	0.00219
	32.2	5.90±0.06	35.0±0.3	-	12.3±0.7	4.83±0.04	0.00370
	22.2	9.00±0.09	21.6±0.2	-	26.0±1.4	6.62±0.06	0.00399
	13.3	13.97±0.12	14.2±0.1	-	45.6±2.6	9.73±0.09	0.00321
1-2-∞	37.7	5.30±0.08	49.7±0.8	1.47±0.10	-	5.08±0.06	0.00415
	32.2	6.66±0.16	39.5±0.9	2.07±0.19	-	5.88±0.10	0.00650
	22.2	10.38±0.14	24.9±0.5	3.41±0.28	-	8.18±0.14	0.00597
	13.3	15.49±0.31	15.8±0.3	3.54±0.16	-	11.80±0.16	0.00533
1-3	32.2	10±2		-	$314±1.8\times10^2$	-	0.04336
	22.2	18±4		-	$1059±8.5\times10^2$	-	0.05490
1-2	22.2	85±35		$1956±2\times10^4$	-	-	0.1100

* X represents mole fraction

the results of this least squares fitting. The results clearly indicate that in general the 1-3-∞ model provides the best fit for the activity data for both solutions. It is also encouraging to find that the best least squares values of K_p obtained for the 1-3-∞ model at 37.8°C and 37.7°C are in excellent agreement with the values extrapolated from the plots of a/f_A vs. f_A in Figures 5 and 6. Although the RMSD values of the 1-2-∞ model at 37.8°C (in CCl_4) and 37.7°C (in cyclohexane) are not unreasonably large, the K_p values from the 1-2-∞ model are in considerable disagreement with those from the plots. The 1-2, 1-3, and 1-2-3 models all provide a poor fit of the activity data. The calculated activity data and derived monomer concentrations of phenol solutions for the 1-3-∞ and 1-2-∞ model fits are given in Table 17 to Table 24. The plots of observed and calculated activity data vs. formal phenol concentration are presented in Figures 8a and 8b. For clarity, some points at low concentration are omitted.

Also included in Tables 15 and 16 are the best least squares values of Henry's law constants (K_x) calculated from K_p values by equation (18). From equations (19) and (20), the molar enthalpies ($-\Delta H_x$) and entropies ($-\Delta S_x$) of transfer of gaseous phenol can be obtained for carbon tetrachloride and cyclohexane solutions by a linear least squares method and are given in Table 25. The van't Hoff plots of K_x are also given in Figure 7.

The usual van't Hoff equation as shown in equation (19) has been used by some authors to obtain enthalpies for association reactions without considering the concentration units of the solution. However, it has been noted[30] that the values of association constants expressed in terms of different concentration units lead to differing values of the enthalpy of association. The correct way to use the van't Hoff equation is for the

standard states on which the association constant is based to be independent of temperature (such as molality and mole fraction). If molarity units are employed (as in most hydrogen bonding studies), the following form of the van't Hoff equation should be used.

$$\Delta H = RT^2 \left(\frac{d \ln K_c}{d T}\right) + RT^2 (1 - n) \alpha \qquad (40)$$

where K_c is expressed in terms of molarity, α is the coefficient of thermal expansion of the solvent and n is number of monomers associated. For carbon tetrachloride solution with n=3 (trimer) at 25°C, RT^2 (1-n) α = -430 cal/mole ($\alpha \doteq 1.23 \times 10^{-3}$), while for cyclohexane solution, $RT^2(1-n)\alpha$= -380 cal/mole ($\alpha \doteq 1.1 \times 10^{-3}$). So the difference in enthalpy of trimerization derived from equation (40) and equation (19) is about 0.4 Kcal/mole. For convenience in comparison, both values of ΔH_2, ΔH_3, and ΔH_∞ derived from conventional van't Hoff equation and equation (40) for the 1-3-∞ model and the 1-2-∞ model are given in Table 25.

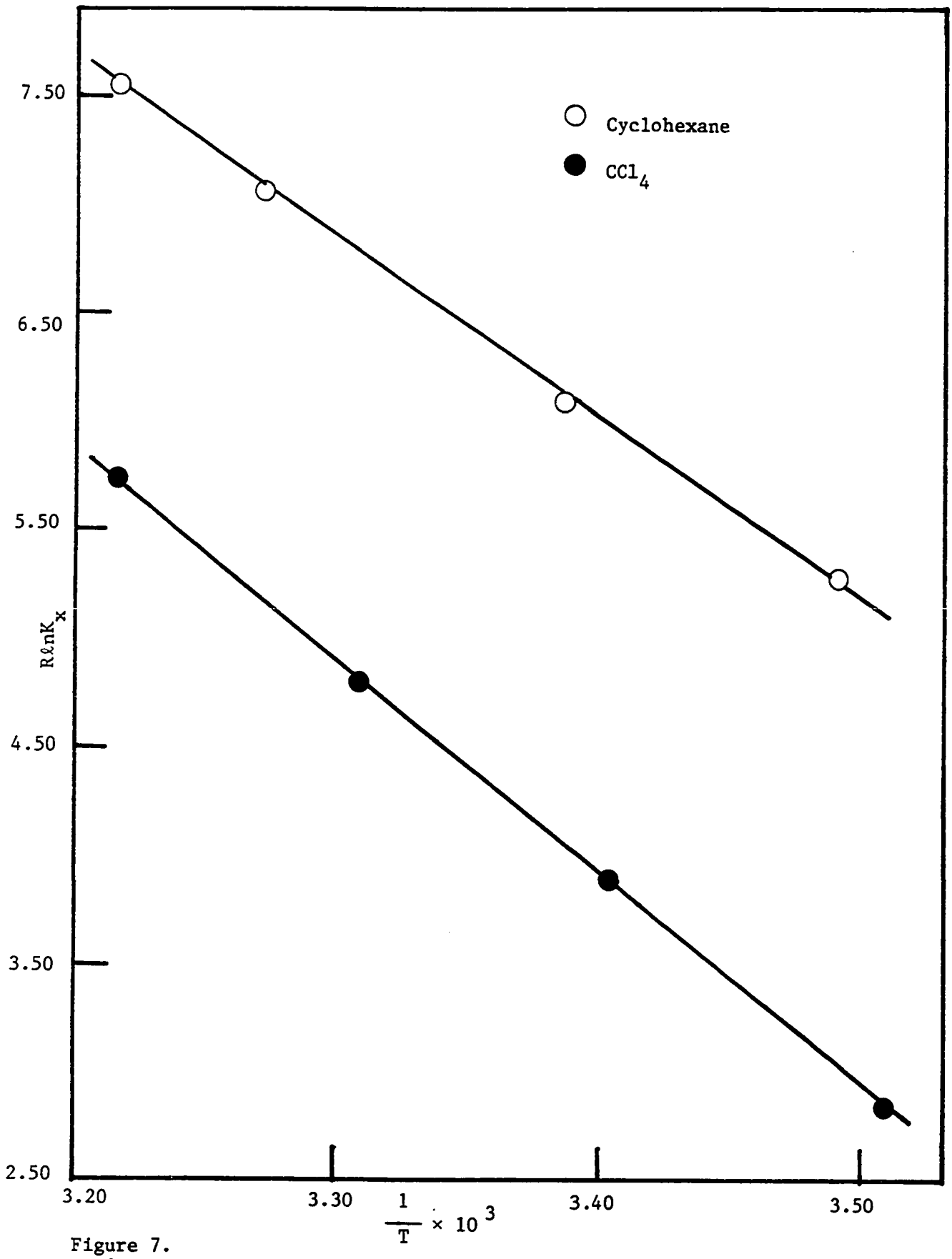


Figure 7.
Van't Hoff Plots of the Temperature Dependence of Henry's Law Constants (K_x values are derived from the 1-3-∞ model) for Phenol in Cyclohexane and CCl_4.

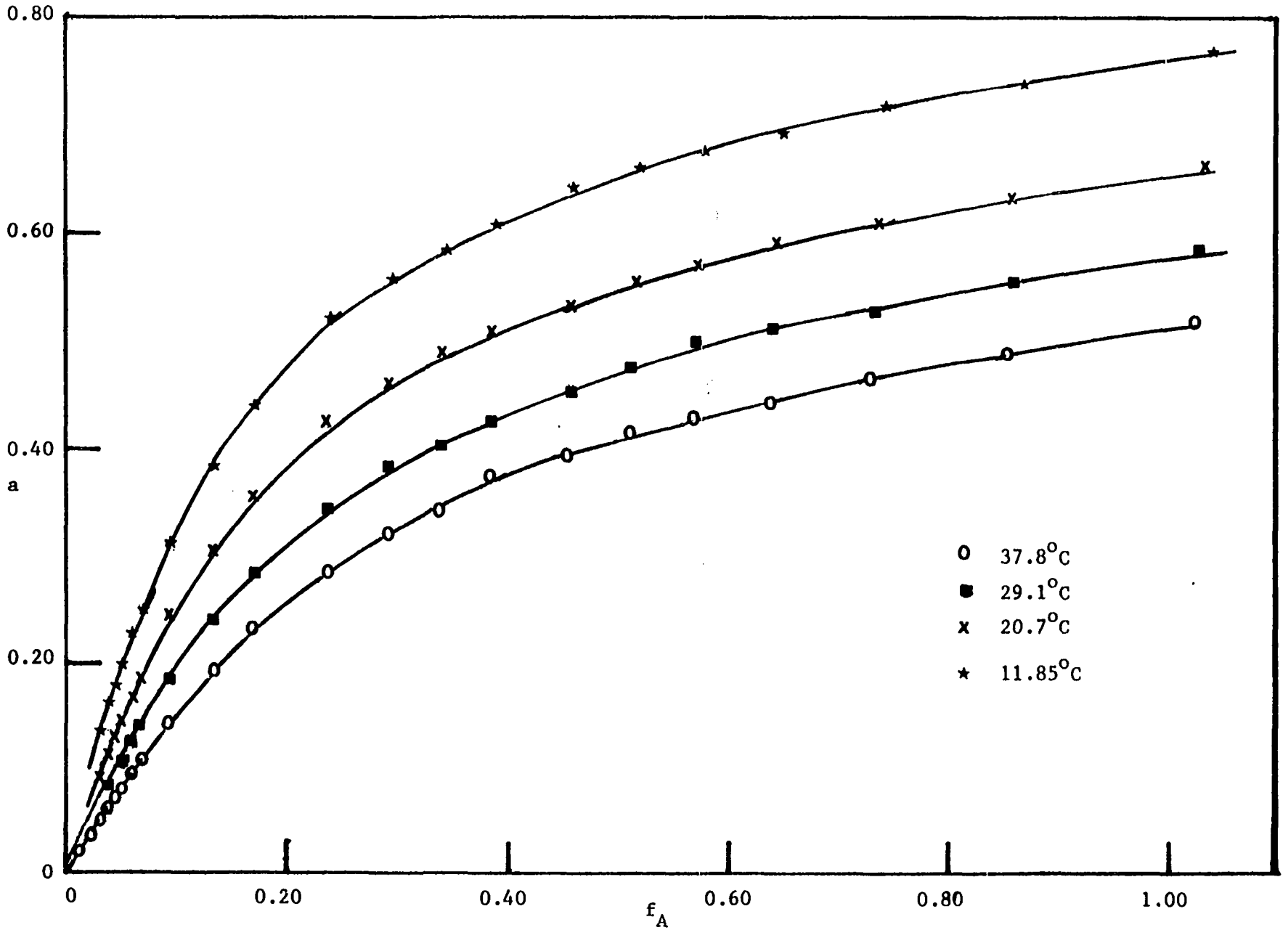


Figure 8a. Plots of Phenol Activity(a) vs. Formal Concentration(f_A) in Carbon Tetrachloride at Various Temperatures (lines are calculated).

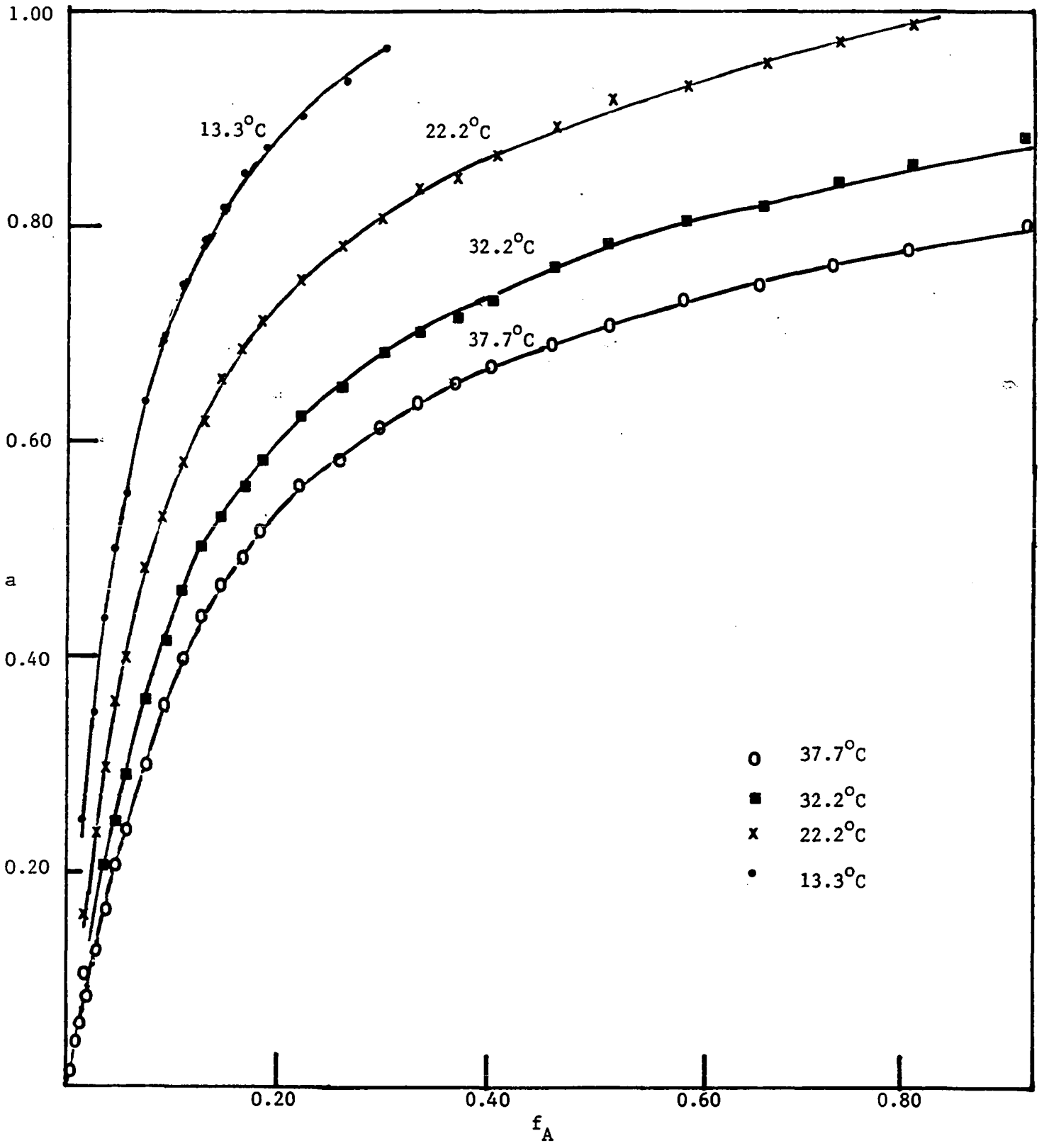


Figure 8b. Plots of Phenol Activity(a) vs. Formal Concentration(f_A) in Cyclohexane at Various Temperatures (lines are calculated).

TABLE 17

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CARBON TETRACHLORIDE AT 37.8°C

	1 - 3 - ∞		1 - 2 - ∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
1.02413	.5165	.3087	.5129	.2829
.85347	.4906	.2932	.4898	.2702
.73151	.4681	.2798	.4689	.2587
.64008	.4481	.2678	.4497	.2481
.56892	.4301	.2570	.4321	.2384
.51206	.4137	.2472	.4157	.2293
.45521	.3951	.2361	.3968	.2189
.38405	.3676	.2197	.3685	.2033
.34141	.3484	.2082	.3485	.1922
.29262	.3228	.1929	.3218	.1775
.23661	.2873	.1717	.2849	.1572
.17082	.2336	.1396	.2303	.1270
.13389	.1956	.1169	.1927	.1063
.09319	.1453	.0868	.1442	.0795
.06695	.1079	.0645	.1085	.0599
.05951	.0967	.0578	.0977	.0539
.05021	.0823	.0492	.0838	.0462
.04463	.0735	.0439	.0752	.0415
.03825	.0632	.0378	.0651	.0359
.03090	.0513	.0307	.0533	.0294
.02232	.0372	.0222	.0390	.0215
.01217	.0203	.0122	.0216	.0119
.02736	.0455	.0272	.0474	.0262
.01785	.0298	.0178	.0314	.0173

TABLE 18

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CARBON TETRACHLORIDE AT 29.1°C

	1 - 3 - ∞		1 - 2 - ∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
1.02819	.5840	.2604	.5800	.2331
.85686	.5569	.2483	.5558	.2234
.73441	.5333	.2378	.5340	.2146
.64262	.5124	.2285	.5141	.2066
.57117	.4936	.2201	.4958	.1993
.51410	.4766	.2125	.4789	.1925
.45702	.4572	.2039	.4594	.1846
.38557	.4288	.1912	.4302	.1729
.34276	.4087	.1822	.4094	.1645
.29378	.3821	.1704	.3815	.1534
.23731	.3447	.1537	.3425	.1376
.17150	.2875	.1282	.2835	.1140
.13443	.2455	.1095	.2415	.0971
.09356	.1873	.0835	.1851	.0744
.06721	.1417	.0632	.1418	.0570
.05975	.1275	.0569	.1284	.0516
.05041	.1091	.0487	.1109	.0446
.04480	.0977	.0436	.0999	.0402
.03840	.0844	.0376	.0870	.0350
.03102	.0686	.0306	.0716	.0288
.02241	.0499	.0223	.0528	.0212
.01222	.0274	.0122	.0295	.0119

TABLE 19

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CARBON TETRACHLORIDE AT 20.7°C

	1 - 3 - ∞		1 - 2 - ∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
1.03327	.6589	.2154	.6542	.1916
.86109	.6332	.2070	.6314	.1849
.73804	.6106	.1996	.6106	.1788
.64580	.5903	.1930	.5919	.1732
.57399	.5719	.1870	.5740	.1681
.51664	.5551	.1815	.5576	.1633
.45928	.5359	.1752	.5385	.1577
.38748	.5073	.1659	.5096	.1492
.34446	.4870	.1592	.4887	.1431
.29524	.4596	.1503	.4603	.1348
.23849	.4207	.1375	.4195	.1228
.17218	.3592	.1174	.3554	.1041
.13496	.3125	.1022	.3079	.0901
.09393	.2448	.0800	.2412	.0706
.06754	.1889	.0617	.1878	.0550
.06004	.1709	.0559	.1708	.0500
.05066	.1471	.0481	.1484	.0434
.04503	.1322	.0432	.1342	.0393
.03859	.1145	.0374	.1174	.0343
.03117	.0935	.0306	.0969	.0284
.02252	.0682	.0223	.0719	.0211
.01228	.0375	.0122	.0404	.0118

TABLE 20

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CARBON TETRACHLORIDE AT 11.85°C

	1 - 3 - ∞		1 - 2 - ∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
1.04140	.7707	.1802	.7656	.1560
.86787	.7432	.1738	.7410	.1510
.74384	.7189	.1681	.7188	.1464
.65088	.6972	.1630	.6984	.1423
.57851	.6774	.1584	.6796	.1384
.52070	.6594	.1542	.6620	.1349
.46289	.6388	.1494	.6417	.1307
.39053	.6081	.1422	.6109	.1245
.34717	.5862	.1371	.5886	.1199
.29756	.5569	.1302	.5583	.1137
.24036	.5150	.1204	.5145	.1048
.17353	.4483	.1048	.4448	.0906
.13602	.3970	.0928	.3918	.0798
.09467	.3202	.0749	.3151	.0642
.06801	.2532	.0592	.2508	.0511
.06045	.2309	.0540	.2298	.0468
.05100	.2007	.0469	.2015	.0410
.04534	.1814	.0424	.1834	.0374
.03886	.1582	.0370	.1615	.0329
.03139	.1230	.0304	.1347	.0274
.02267	.0953	.0223	.1009	.0206

TABLE 21

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CYCLOHEXANE AT 37.7°C

	1-3-∞		1-2-∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
.92258	.7959	.1688	.7910	.1513
.80609	.7779	.1650	.7749	.1482
.73313	.7647	.1622	.7630	.1459
.66187	.7499	.1591	.7495	.1433
.58882	.7324	.1553	.7331	.1402
.51569	.7117	.1509	.7135	.1365
.46175	.6936	.1471	.6962	.1331
.40346	.6707	.1422	.6737	.1289
.36694	.6539	.1387	.6571	.1257
.33127	.6353	.1347	.6384	.1221
.29501	.6134	.1301	.6161	.1178
.25810	.5871	.1245	.5892	.1127
.22100	.5553	.1178	.5561	.1064
.18430	.5162	.1095	.5154	.0986
.16657	.4936	.1047	.4919	.0941
.14752	.4658	.0988	.4631	.0886
.12982	.4259	.0925	.4324	.0827
.11090	.3985	.0845	.3944	.0754
.09243	.3551	.0753	.3511	.0671
.07430	.3041	.0645	.3014	.0577
.05556	.2412	.0512	.2413	.0461
.03682	.1674	.0355	.1709	.0327
.01834	.0857	.0182	.0906	.0173
.04607	.2052	.0435	.2070	.0395
.02764	.1277	.0271	.1324	.0253
.01229	.0577	.0122	.0619	.0118
.00670	.0316	.0067	.0343	.0066
.00351	.0165	.0035	.0182	.0035

TABLE 22

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CYCLOHEXANE AT 32.2°C

	1-3-∞		1-2-∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
.92631	.8764	.1482	.8686	.1304
.80935	.8550	.1448	.8512	.1278
.73610	.8406	.1424	.8384	.1259
.66455	.8247	.1397	.8239	.1237
.59120	.8059	.1365	.8064	.1211
.51725	.7835	.1327	.7854	.1179
.46315	.7643	.1295	.7671	.1152
.40468	.7400	.1254	.7435	.1116
.36805	.7223	.1224	.7261	.1090
.33261	.7030	.1191	.7067	.1061
.29590	.6799	.1152	.6834	.1026
.25889	.6526	.1106	.6556	.0984
.22167	.6197	.1050	.6125	.0933
.18486	.5796	.0982	.5797	.0870
.16707	.5565	.0943	.5555	.0834
.14796	.5281	.0895	.5258	.0789
.13008	.4973	.0842	.4938	.0741
.11123	.4590	.0778	.4545	.0682
.09271	.4139	.0701	.4089	.0614
.07445	.3597	.0609	.3554	.0533
.05573	.2910	.0493	.2893	.0434
.03693	.2061	.0349	.2089	.0314
.01839	.1071	.0181	.1132	.0170
.04621	.2501	.0424	.2506	.0376
.02773	.1586	.0269	.1636	.0246
.01232	.0723	.0122	.0779	.0117
.00672	.0396	.0067	.0435	.0065
.00352	.0208	.0035	.0231	.0035

TABLE 23

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CYCLOHEXANE AT 22.2°C

	1-3-∞		1-2-∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
.81264	.9855	.1096	.9794	.0943
.73909	.9709	.1080	.9664	.0931
.66725	.9546	.1061	.9518	.0917
.59360	.9354	.1040	.9343	.0900
.51988	.9127	.1015	.9134	.0880
.46551	.8932	.0993	.8951	.0862
.40674	.8685	.0966	.8716	.0840
.36992	.8506	.0946	.8542	.0823
.33396	.8307	.0924	.8348	.0804
.29710	.8074	.0898	.8116	.0782
.25994	.7798	.0867	.7839	.0755
.22257	.7465	.0830	.7500	.0723
.18543	.7058	.0785	.7079	.0682
.16758	.6824	.0759	.6835	.0658
.14857	.6539	.0727	.6537	.0630
.13061	.6226	.0692	.6209	.0598
.11158	.5832	.0649	.5797	.0558
.09299	.5363	.0597	.5311	.0512
.07468	.4785	.0532	.4722	.0455
.05584	.4012	.0446	.3958	.0381
.03704	.2974	.0331	.2971	.0286
.01845	.1612	.0179	.1684	.0162
.04635	.3527	.0392	.3493	.0336
.02781	.2340	.0260	.2377	.0229
.01236	.1098	.0122	.1177	.0113
.00674	.0604	.0067	.0668	.0064

TABLE 24

THE CALCULATED ACTIVITY AND MONOMER CONCENTRATION FOR PHENOL IN CYCLOHEXANE AT 13.3°C

	1-3-∞		1-2-∞	
f_A	$a^{calc.}$	$C_M^{calc.}$	$a^{calc.}$	$C_M^{calc.}$
.29954	.9642	.0690	.9592	.0619
.26207	.9382	.0672	.9357	.0604
.22440	.9066	.0649	.9065	.0585
.18695	.8673	.0621	.8693	.0561
.16895	.8446	.0605	.8474	.0547
.14963	.8164	.0585	.8197	.0529
.13155	.7854	.0562	.7887	.0509
.11238	.7458	.0534	.7486	.0483
.09366	.6979	.0500	.6993	.0451
.07522	.6373	.0456	.6364	.0411
.05624	.5527	.0396	.5489	.0354
.03731	.4301	.0308	.4257	.0275
.01857	.2459	.0176	.2486	.0161
.04669	.4971	.0356	.4924	.0318
.02801	.3480	.0249	.3461	.0223
.01245	.1698	.0122	.1753	.0113
.00679	.0942	.0067	.1000	.0065
.00356	.0496	.0036	.0537	.0035

TABLE 25

THERMODYNAMIC PARAMETERS FOR SOLUTION AND ASSOCIATION OF PHENOL

IN CARBON TETRACHLORIDE AND CYCLOHEXANE

	CARBON TETRACHLORIDE		CYCLOHEXANE	
	1-3-∞ model	1-2-∞ model	1-3-∞ model	1-2-∞ model
$-\Delta H_x^a$(Kcal/mole)	-9.8±0.1	-9.5±0.1	-8.4±0.1	-8.3±0.1
$-\Delta S_x^a$(e.u./mole)	-37.3±0.1	-36.3±0.1	-34.5±0.4	-34.5±0.3
ΔH_2^b(Kcal/mole)	- -	-6.3±2.3 (-6.1)	-	-7.2±1.7 (-7.0)
ΔS_2^b(e.u./mole)	-	-20.1±7.5	-	-21.6±5.6
ΔH_3^b(Kcal/mole)	-9.5±0.5 (-9.1)	-	-13.4±0.7 (-13.0)	-
ΔS_3^b(e.u./mole)	-27.4±1.8	-	-37.7±2.2	-
ΔH_∞^b(Kcal/mole)	-5.2±0.4 (-5.0)	-5.0±0.5 (-4.8)	-6.0±0.4 (-5.8)	-6.3±0.2 (-6.1)
ΔS_∞^b(e.u./mole)	-15.0±0.4	-13.6±0.6	-15.9±1.3	-16.4±0.7

a Thermodynamic quantities for transfer from 1 atm ideal gas to unit mole fraction ideal dilute solution state.

b Thermodynamic quantities for reactions for the unit molarity ideal dilute solution standard state (obtained from Equation(40)). Values in () are without correction for thermal expansion of solvents

CHAPTER V

DISCUSSION AND CONCLUSION

The Empirical Relation of the Vapor Absorbance of Solid Phenol vs. Concentration

Because the Beer-Lambert law is not obeyed by phenol vapor, an empirical equation (6) has been used to obtain the relation of vapor absorbance vs. vapor concentration. The quantity p^o/T ($= nV^{-1}R$) on the left hand side of equation (6) actually corresponds to a given concentration of phenol. The precision of thermodynamic results of this work depends not only on good vapor absorbance measurements above phenol solutions, but also on good fitting of equation (6), from which all activity data of solutions are derived. It may be instructive to discuss the validity of equation (6) before any thermodynamic results are mentioned. In the least squares method, the χ^2 values have been used as an indication of the goodness of fitting. A smaller χ^2 value represents a better fitting when the errors assigned to the measured quantities are the same. Table 12 gives the χ^2 values for fitting equation (6) at three wavelengths. These values are comparable to the expected χ^2 value (26.3). The Table also shows that the absorbance data at 268.2 nm and 262.6 nm provided a better fit of equation (6) than that at 275.1 nm,

because χ^2 values at 268.2 nm and 262.6 nm are only one-half of that at 275.1 nm and that of the expected value. The relative goodness of fitting is also demonstrated in Figures 2 to 4, where the points are experimental and the lines are calculated from the α. β. γ values. Another criterion to use in judging the goodness of fitting is to compare the activity data derived for each solution at the three wavelengths. Tables 4 to 11 indicate that the derived activity data at the three wavelengths are generally in good agreement except for a few points of high absorbance (above 0.5), at which a sizable difference (3% to 4%) in derived activity data is observed between that from the 275.1 nm data and that from the 268.2 nm or 262.6 nm data. However, the derived activity data at 268.2 nm and at 262.6 nm are in excellent agreement throughout the whole absorbance range. The relatively large deviation in activity data derived from high absorbances probably can be attributed to the fact that the 275.1 nm band is narrower than the other two bands, and therefore deviations from linearity in the absorbance vs. concentration plot at 275.1 nm are more pronounced at the fixed slit width (0.2 mm) used in this study. The difference in the averaged activity data between those of two wavelengths (268.2 nm and 262.6 nm) and those of three wavelengths at high absorbance points is always less than one percent. Their effect on the model fitting is thus very slight and will be discussed later (see Tables 31 and 32). In this work the averaged activity data at three wavelengths are used to infer all thermodynamic parameters. The discussion leads us to the conclusion that, in spite of the difficulty arising from deviations from the Beer-Lambert law and the limited availability of optical cells, a good empirical correlation of phenol vapor absorbance with the

phenol vapor concentration has been determined, from which it is possible to derive activity data and other thermodynamic quantities with considerable accuracy.

Henry's law constants, K_x or K_p

In addition to the precise measurements of activity data, the accurate determination of Henry's law constants at various temperatures is of primary importance in this work, because the concentrations of phenol monomer in solution are calculated from K_p values and activity data. So far no K_p or K_x values for phenol in carbon tetrachloride or cyclohexane solution have been reported. The only quantity related to K_x or K_p is the molar enthalpy of transfer of monomeric (gaseous) phenol into solvents (cyclohexane, carbon tetrachloride, and benzene) at infinite dilution which was calculated by Woolley and Hepler[60] from enthalpies of solution of phenol and the enthalpy of sublimation of phenol. The enthalpies of transfer of gaseous phenol ($-\Delta H_x$) were estimated to be -8.8 and -10.1 Kcal/mole for cyclohexane and carbon tetrachloride solutions, respectively. However, no corresponding entropies or free energies of transfer of gaseous phenol were derived, so it was not possible to calculate Henry's law constants from previous thermodynamic data. As has been mentioned, Henry's law constants may be directly estimated from the limiting slopes of plots of activity vs. concentration in the dilute solution range. But only at high temperatures can the K_p values be estimated with good accuracy. Another method used in this work was to consider K_p as an adjustable parameter to be found by fitting all of the activity data (see Tables 15 and 16).

A third alternative is to calculate the K_p values at various temperatures using the enthalpies of transfer of gaseous phenol of Woolley and Hepler[60] and one K_p value at high temperature from this work (at 37.7°C for cyclohexane, at 37.8°C for CCl_4). The K_p and K_x values thus obtained are given in Table 26 along with the derived association constants for the 1-2-∞ and the 1-3-∞ models. It is noted that the K_p values derived from the 1-3-∞ model are in reasonable agreement with those of the plots in Figures 5 and 6 except at 13.3°C for cyclohexane solution and at 11.85°C for carbon tetrachloride solution; at these two temperatures, the data points are too scattered to evaluate the K_p values from the plots However, the K_p values derived from the 1-2-∞ model are incompatible with those from the plots at all temperatures. The K_p values obtained as adjustable parameters for the 1-2-∞ model and the 1-3-∞ model are given in Table 15 and Table 16. These results show that the K_p values derived from the 1-3-∞ model at 37.7°C (for cyclohexane) and 37.8°C (for CCl_4) are in excellent agreement with those of the plots. The K_p values derived from the 1-3-∞ model at 29.1°C, 20.7°C (CCl_4) and 32.2°C, 22.2°C (cyclohexane) are also compatible with those of the plots and those calculated from the enthalpies of transfer of gaseous phenol (see Table 26). However, the K_p values obtained as adjustable parameters from the 1-2-∞ model are incompatible with those of the plots and those calculated from the enthalpies of transfer of gaseous phenol. Figure 7 shows the van't Hoff plots of K_x derived from the 1-3-∞ model for cyclohexane and carbon tetrachloride solutions. The least squares values of enthalpies and entropies of transfer of gaseous phenol for both solvents are given in Table 25. As compared to -10.1 Kcal/mole and -8.8 Kcal/mole for transfer

TABLE 26

RMSD, ASSOCIATION CONSTANT VALUES FOR PHENOL SOLUTIONS OBTAINED USING THE K_p VALUES DERIVED FROM ΔH_x OF WOOLLEY AND HEPLER AND ONE VALUE OF K_p FROM THE PLOTS OF THIS WORK

Model	Temperature(°C)	$K_p(M^{-1})$	K_x(torr/X)*	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
			IN CCl_4				
1-3-∞	29.1	2.22	11.2	-	4.07±0.14	2.19±0.05	0.002941
	20.7	2.96	6.90	-	5.22±0.18	2.96±0.05	0.003523
	11.85	4.10	4.03	-	8.10±0.38	3.64±0.07	0.005868
1-2-∞	29.1	2.22		0.72±0.04	-	2.76±0.06	0.006079
	20.7	2.96		0.80±0.06	-	3.48±0.07	0.008296
	11.85	4.10		1.04±0.08	-	4.22±0.09	0.01130
			IN CYCLOHEXANE				
1-3-∞	32.2	5.85	34.7	-	11.7±0.2	4.81±0.04	0.003707
	22.2	8.85	21.2	-	24.1±0.5	6.56±0.05	0.004111
	13.3	13.1	13.3	-	31.1±1.5	9.67±0.18	0.006859
1-2-∞	32.2	5.85		1.24±0.04	-	5.41±0.07	0.01012
	22.2	8.85		1.92±0.09	-	7.31±0.09	0.01175
	13.3	13.1		1.65±0.15	-	10.86±0.24	0.01387

* X represents mole fraction

of gaseous phenol into carbon tetrachloride and cyclohexane, respectively, obtained by Woolley and Hepler,[60] the values of -9.8 Kcal/mole for carbon tetrachloride and -8.4 Kcal/mole for cyclohexane in this work are only about 3% and 4.5% different. The ΔH_x values obtained from the 1-2-∞ model in carbon tetrachloride and cyclohexane solutions (9.5 Kcal/mole and 8.3 Kcal/mole) are also comparable to those obtained from Woolley and Hepler. However, these latter ΔH_x values are derived from K_p values which do not agree with the limiting intercepts of plots in Figures 5 and 6. It should be noted that ΔH_x values of Woolley and Hepler do not pertain to any association model.

Tables 15 and 16 also give some K_p values derived as adjustable parameters for the 1-2, 1-3, and 1-2-3 models fitting. These values can be rejected immediately as being unreasonble, and they result in poor fitting and unrealistic association constants.

The smaller magnitude of the enthalpy of transfer of gaseous phenol into cyclohexane provides strong evidence that cyclohexane is more nearly an inert solvent than carbon tetrachloride. It has been suggested[58,77] that carbon tetrachloride may form weak hydrogen bonds with alcohols. However, it seems more reasonable simply to state that solute-solvent interactions, including both specific and nonspecific effects,[75] are stronger for carbon tetrachloride solutions.

The Self-Association Models

The results of model fitting will be discussed as follows: First, the fitting of the activity data of this work with various association models will be treated without referring to the results of other

techniques. The best model for the phenol association in cyclohexane and carbon tetrachloride will be determined solely from fitting the activity data. Second, the results of this work will be compared with the results obtained by other techniques, such as IR, NMR, calorimetry, distribution method and total vapor pressure method. Third, the possible structure of associated species in cyclohexane and carbon tetrachloride will be discussed. Fourth, the effect of errors in experimental data on the results will be analyzed.

(1) Tables 15 and 16 present the association constants and the RMSD values obtained for various models when K_p is considered as an adjustable parameter. Here at least two criteria can be used to determine the goodness of fitting for a model: (A) the RMSD values for a fit should be small and within the experimental errors; (B) the best least squares values of K_p obtained as an adjustable parameter should be consistent with those of the plots in Figures 5 and 6. Only a model fulfilling these two criteria will be considered satisfactory.

Table 15 shows that the activity data of carbon tetrachloride solutions at 37.8, 29.1, and 20.7°C are best fit by the 1-3-∞ model. Their RMSD values are all within experimental errors. However, the 1-2-∞ model gave the best fit of the activity data at 11.85°C. It also shows that the models limited to dimer and/or trimer gave poor fits of the activity data. The 1-2-3 model even gave negative values of K_2, which is physically unrealistic. So the 1-2, 1-3, and 1-2-3 models are not seriously considered as possible models for phenol solutions. Although it seems that the 1-3-∞ model is fitted somewhat better than the 1-2-∞ model, the RMSD values of the two models are comparable with

each other and generally within the experimental errors. Therefore, it is difficult to judge which model is prefered just from a statistical treatment of data. However, when the least squares values of K_p for the 1-3-∞ model are compared with those for the 1-2-∞ model, a significant difference in the K_p values arises between the two models. (It should be noted that, for the same solutions at the same temperature, the Henry's law constants are definite thermodynamic quantities, although different models applied to the same set of data may yield different calculated values of these constants.) When the least squares values of K_p for the 1-2-∞ and the 1-3-∞ models are compared with those from the plots in Figure 6, it can be seen that the K_p values of the 1-3-∞ model at the three highest temperatures are compatible with those from the plots, while the K_p values from the 1-2-∞ model are significantly different from those of the plots. At 11.85°C, no comparison can be made because of scatter in the plots. Some results of model fitting for data at 37.8°C using the K_p value from the plot are given in Table 13. These results show that the RMSD value of the 1-2-∞ model is 80% larger than that of the 1-3-∞ model. The preceding discussion leads us to the conclusion that the 1-3-∞ model is best for carbon tetrachloride solutions. The van't Hoff plots of K_3 and K_∞ for the 1-3-∞ model are given in Figures 9 and 10. The least squares values of -9.5 Kcal/mole and -5.2 Kcal/mole were obtained for ΔH_3 and ΔH_∞, respectively (Table 25).

Table 16 presents the results of the model fitting for cyclohexane solution. It shows that the 1-3-∞ model fits the activity data better than the 1-2-∞ model at all temperatures. The RMSD values for the 1-2-∞ model are 60% to 80% larger than those of the 1-3-∞ model. Table 16 also

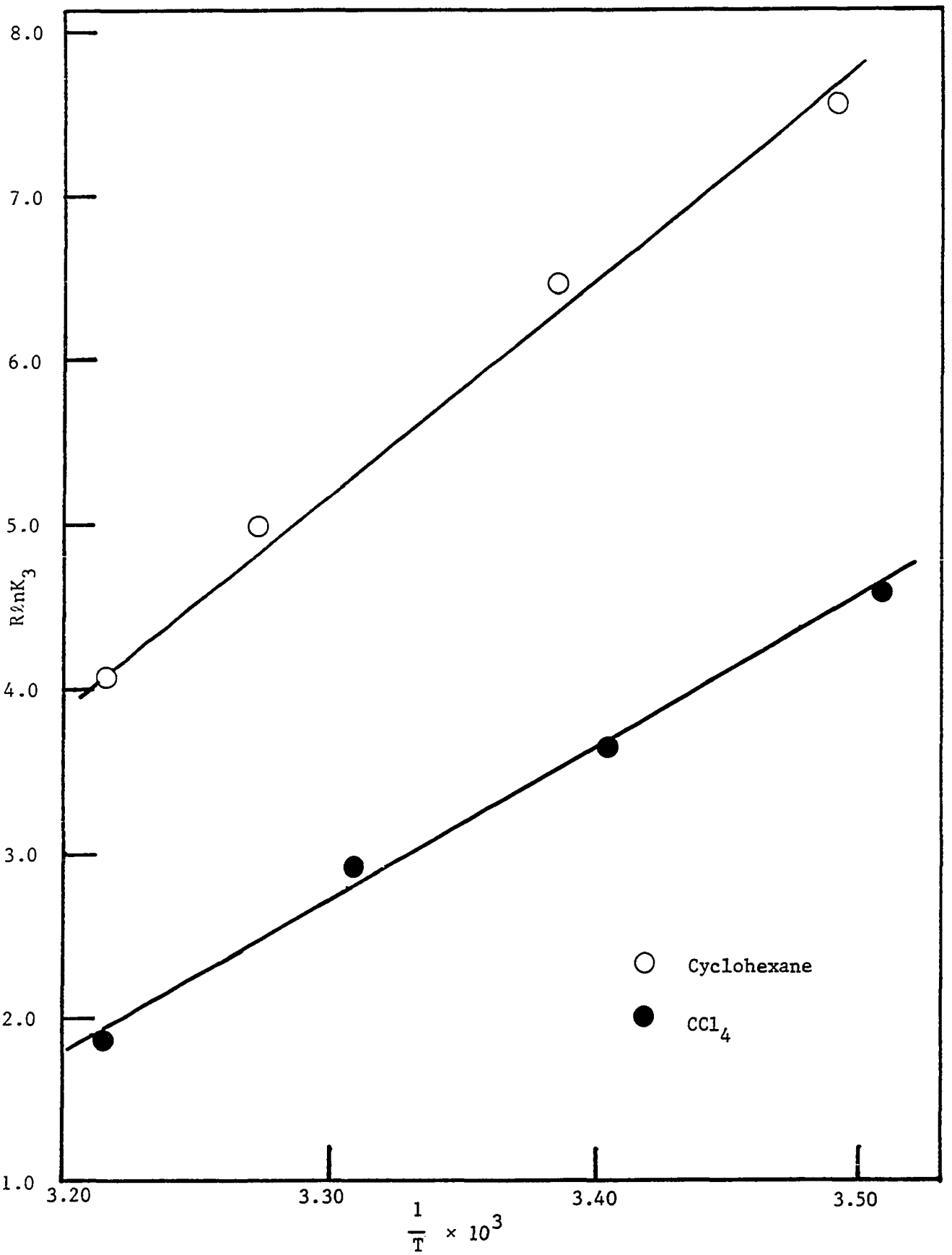


Figure 9. Van't Hoff Plots of the Temperature Dependence of the Trimer Association Constants(K_3) for Phenol in Cyclohexane and CCl_4

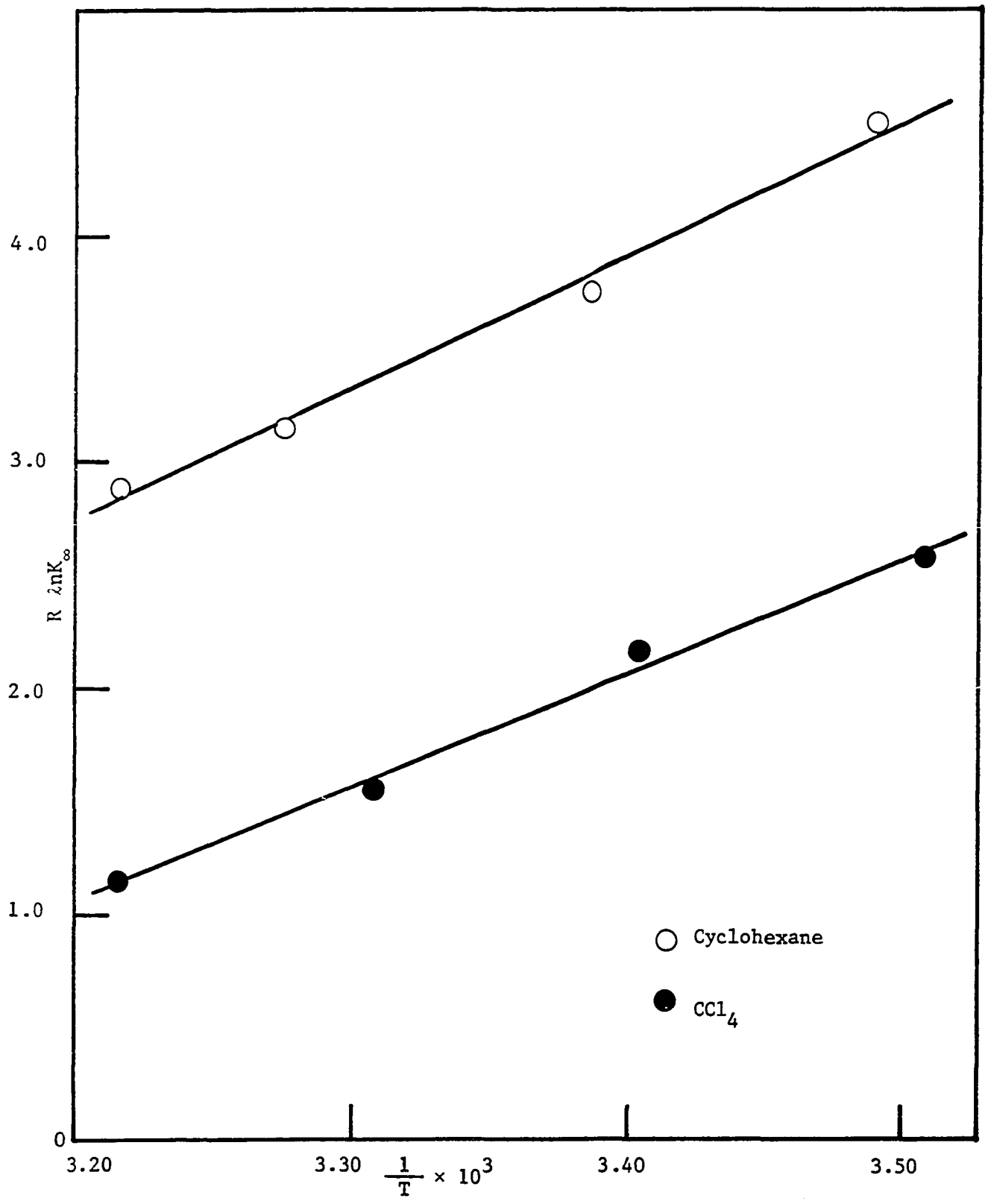


Figure 10. Van't Hoff Plots of the Temperature Dependence of the K_∞(1-3-∞ model) for Phenol in Cyclohexane and CCl_4.

indicates that the RMSD values of the 1-2-∞ model are larger than the experimental errors. We can conclude from the RMSD values that the 1-3-∞ model is statistically a better model. Further examining the K_p values, we find that the K_p values of the 1-3-∞ model are in good agreement with those of the plots, while the K_p values of the 1-2-∞ model are not. The results of model-fitting using the K_p values of the plots at 37.7 and 32.2°C also indicate that the RMSD values of the 1-2-∞ model are larger than those of the 1-3-∞ model by a factor of 2.5. The van't Hoff plots of K_3 and K_∞ for the 1-3-∞ model are shown in Figures 9 and 10. The values of K_3 and K_∞ vary with temperature in a regular manner. The best least squares values of ΔH_3 and ΔH_∞ for the 1-3-∞ model in cyclohexane solutions are estimated to be -13.4 Kcal/mole and -6.0 Kcal/mole, respectively.

The results of model fitting of activity data lead us to the conclusion that the solutions of phenol for both carbon tetrachloride and cyclohexane up to about 1 M are best interpreted in terms of the 1-3-∞ model.

It may be instructive to fit the activity data with the 1-2-∞ and the 1-3-∞ models using the K_p values calculated from the ΔH_x values obtained by Woolley and Hepler, and one K_p value (at 37.7°C for cyclohexane and 37.8°C for carbon tetrachloride) from the plots (Figures 5 and 6) in this work. Table 26 gives the results of such fitting. It also shows from the RMSD values that the 1-3-∞ model provides the better fit for both solutions. As compared to Tables 15 and 16, it was observed that a small difference in K_p values between two methods causes big deviations in the K_3 values from the model fitting, especially at 11.85°C for carbon

tetrachloride solution and 13.3°C for cyclohexane solution. For example, about a 4% difference in the K_p values (4.10 vs. 4.28) at 11.85°C for carbon tetrachloride solution produces a 20% deviation in the K_3 values (8.1 vs. 10.2), while for phenol in cyclohexane at 13.3°C, a 6.5% difference in the K_p values (13.1 vs. 13.97) makes about a 30% deviation in the K_3 value (31.1 vs. 45.6). Considering the strong dependence of the K_3 value on the K_p value in model fitting, it is apparent that a reliable K_p value is very important in this work. The K_p values obtained as an adjustable parameters vary with temperature in a regular manner; the standard errors in ΔH_x are only about 1% for both solutions. Furthermore, the K_3 and K_∞ values derived also vary regularly with temperature. The standard errors in ΔH_3 are about 5% for both solutions. A small change in the value of K_p has no marked effect on the corresponding K_∞ value. Although the enthalpies of transfer of gaseous phenol ($-\Delta H_x$) obtained by Woolley and Hepler[60] are only 3 - 4.5% different from those of this work, the K_p values calculated from these ΔH_x at low temperatures (11.85°C and 13.3°C) are 4 - 6% different from the least squares values of K_p (Tables 15 and 16). Furthermore, the temperature dependence of K_3 values obtained from these K_p values (Table 26) is not as satisfactory as that of K_3 values derived from the least squares fits (Tables 15 and 16). There is no evidence to show whether the ΔH_x values of this work are better or worse than those of Woolley and Hepler, but we do think the standard errors in ΔH_x obtained by Woolley and Hepler should be at least 2%. Therefore, the derived K_p values at low temperature may be in error by more than 3% and the derived K_3 values (obtained from the present data using these K_p values) could be 15% in error. Considering the good behavior of the K_p,

K_3, and K_∞ values obtained by three-parameter fitting with temperature, the use of ΔH_x obtained by Woolley and Hepler, and one K_p value of this work appears not to be a practical way to calculate the K_p values at various temperatures.

(2) The results of this work are qualitatively consistent with the IR spectral evidence which indicates that more than one associated species is present in phenol solutions in carbon tetrachloride and cyclohexane solvents. The previous IR data on the self-association of phenol were interpreted in terms of the 1-2-∞ model, with either one formation constant[39,40] or two formation constants.[42,46] However, the present research gives no support to the assumption made in previous infrared studies (e.g. the near-IR study of Whetsel and Lady and the IR-fundamental study of Coggeshall and Saier) that the phenol dimer is present in significant amounts in organic solutions. According to the activity results, the first important associated species appears to be the trimer. A similar observation was also reported by Tucker and Becker for the association of tert-butanol in n-$C_{16}H_{34}$ (and n-$C_{16}D_{34}$) combining the results of the vapor pressure, IR, and PMR techniques.[68] In order to make a comprehensive comparison of the results of this work with those of the near-IR study of Whetsel and Lady, the near-IR absorbance data were tested with the 1-3-∞ model (without end OH group correction). The results are listed in Tables 27 and 28 along with the results of the 1-2-∞, 1-2, 1-3, and 1-2-3 model fitting obtained by Whetsel and Lady. It is interesting to note that the 1-3-∞ model fitting of near-IR absorbance data is generally better than the 1-2-∞ model. Table 27 clearly shows from the RMSD values that the absorbance data for carbon tetrachloride

TABLE 27

RMSD AND ASSOCIATION CONSTANT VALUES FOR PHENOL IN CARBON TETRACHLORIDE OBTAINED USING THE NEAR-IR DATA OF WHETSEL AND LADY (WITHOUT END GROUP CORRECTION)

Model	Temperature(°C)	ε(liter/mole-cm)	$K_2(M^{-1})$	$K_3(M^{-2})$	$K\ (M^{-1})$	RMSD
1-3-∞	46.0	3.427	-	2.31±0.05	1.19±0.03	0.00355
	37.8	3.447	-	3.01±0.04	1.60±0.02	0.00291
	29.1	3.453	-	4.52±0.05	2.03±0.01	0.00257
	20.7	3.453	-	7.25±0.06	2.49±0.01	0.00245
	11.9	3.462	-	11.02±0.08	3.33±0.01	0.00239
	2.5	3.460	-	20.7±0.3	4.21±0.03	0.00490
1-2-∞	46.0	3.427	0.557	-	1.73	0.0011
	37.8	3.447	0.713	-	2.06	0.0031
	29.1	3.453	0.894	-	2.55	0.0042
	20.7	3.453	1.30	-	2.99	0.0047
	11.9	3.462	1.70	-	3.80	0.0066
	2.5	3.460	2.60	-	4.75	0.0089
1-2-3	20.7		-5.01	36.8	-	0.0171
1-3	20.7		-	20.0	-	0.0318
1-2	20.7		5.75	-	-	0.0610

Note: The association constants for the 1-2-∞, 1-2-3, 1-3 and 1-2 models were obtained by Whetsel and Lady, while those for the 1-3-∞ model were obtained by the present author's fitting of their data.

TABLE 28

RMSD AND ASSOCIATION CONSTANT VALUES FOR PHENOL IN CYCLOHEXANE OBTAINED USING THE NEAR-IR DATA OF WHETSEL AND LADY (WITHOUT END GROUP CORRECTION)

Model	Temperature(^{o}C)	ε(liter/mole-cm)	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
1-3-∞	68.5	4.47	-	2.43±0.04	1.86±0.02	0.00379
	59.5	4.56	-	3.17±0.06	2.37±0.02	0.00581
	50.0	4.67	-	6.05±0.07	2.56±0.02	0.00163
	40.8	4.79	-	7.56±0.07	3.76±0.01	0.00272
	32.3	4.87	-	12.6±0.3	4.88±0.01	0.00247
	22.2	5.00	-	26.2±0.3	6.18±0.02	0.00305
	13.3	5.10	-	53.3±1.1	8.11±0.08	0.00120
1-2-∞	68.5	4.47	0.63	-	2.24	0.00130
	59.5	4.56	0.77	-	2.69	0.0038
	50.0	4.67	0.98	-	3.35	0.0040
	40.8	4.79	1.39	-	4.13	0.0054
	32.3	4.87	1.60	-	5.44	0.0019
	22.2	5.00	2.45	-	7.04	0.0036
	13.3	5.10	2.96	-	9.97	0.0013
1-2-3	22.2		-19.0	255.3	-	0.0212
1-3	22.2		-	124.9	-	0.0350
1-2	22.2		17.35	-	-	0.0584

Note: The association constants for the 1-2-∞, 1-3, 1-2-3, and 1-2 models were obtained by Whetsel and Lady, while those for the 1-3-∞ model were obtained by the present author's fitting of their data.

solutions are better fit by the 1-3-∞ model except at a temperature of 46.0°C. Similarly, the 1-3-∞ model for cyclohexane solution is also fitted better than the 1-2-∞ model except at 68.5°C, 59.5°C, and 32.3°C. However, the RMSD values for the two models are comparable (especially for cyclohexane solutions) and within the experimental errors. It is hard to judge which model is prefered solely from near-IR data. However, the results of activity data presented in the preceding section give strong evidence that trimers rather than dimers are the most important lowest molecular weight aggregate in both solutions. The presence of phenol dimers in solutions at ambient temperature has been assumed rather than experimentally proven by previous workers.

It is instructive to make a quantitative comparison of the results obtained by applying the 1-3-∞ model to both activity data and near-IR absorbance data. The values of 12.34 M^{-2} and 4.83 M^{-1} for K_3 and K_∞ derived from activity data for cyclohexane solution at 32.2°C are in excellent agreement with values of 12.64 M^{-2} and 4.88 M^{-1} obtained from near-IR data at 32.3°C. The K_3 and K_∞ values at 37.7°C and 22.2°C (Table 16) obtained in this work are also in good agreement with those obtained from the near-IR data at 40.8°C and 22.2°C (Table 28). However, a significant difference in K_3 and K_∞ at 13.3°C (about 16%) is observed between the two techniques. For phenol in carbon tetrachloride solution, the values of K_3 and K_∞ derived from the activity data are in reasonable agreement with those from the near-IR data at all four temperatures (Tables 15 and 27). The enthalpy of trimerization (ΔH_3) of -9.5 Kcal/mole for phenol in carbon tetrachloride solution is in good agreement with the value of -9.3 Kcal/mole derived from the near-IR data (Table 29). The enthalpy

TABLE 29

THERMODYNAMIC PARAMETERS FOR ASSOCIATION OF PHENOL OBTAINED USING THE NEAR-IR DATA OF WHETSEL AND LADY (WITHOUT END GROUP CORRECTION)

	CARBON TETRACHLORIDE		CYCLOHEXANE	
	1-3-∞ model	1-2-∞ model	1-3-∞ model	1-2-∞ model
ΔH_2(Kcal/mole)		(-6.1±0.2)[a]		(-5.63±0.2)[a]
ΔS_2(e.u./mole)		(-20.2±0.7)[a]		(-17.4±0.7)[a]
ΔH_3(Kcal/mole)	-9.3±0.3	-	-11.3±0.5	-
ΔS_3(e.u./mole)	-26.3±0.9	-	-30.0±1.7	
ΔH_∞(Kcal/mole)	-5.2±0.2	(-4.07±0.06)[a]	-5.5±0.3	(-5.22±0.13)[a]
ΔS_∞(e.u./mole)	-15.2±0.7	(-11.7±0.2)[a]	-14.2±0.8	(-13.7±0.4)[a]

a: Thermodynamic quantities obtained by Whetsel and Lady without correction for thermal expansion of solvents, while those for the 1-3-∞ model were obtained by the present author's fitting of their data.

Note:All thermal quantities are based on the unit molarity ideal dilute solution standard state.

of formation for higher polymers (ΔH_∞) derived from both techniques has the same value of -5.2 Kcal/mole. Excellent agreement of the values of ΔS_3 and ΔS_∞ are also observed for carbon tetrachloride solution. For phenol in cyclohexane solution, an enthalpy of trimerization of -13.4 Kcal/mole was obtained in this work, while a value of -11.3 Kcal/mole was derived from near-IR data; this is the largest discrepancy between results from the two studies. The enthalpy of formation of -6.0 Kcal/mole of this work for higher polymer (ΔH_∞) in cyclohexane solution is comparable with the value of -5.3 Kcal/mole derived from the near-IR data. It is interesting to note that the values of K_2 and K_∞ derived from activity data for the 1-2-∞ model are not in as good agreement with those of the near-IR data, especially in the case of cyclohexane solutions.

One of the important quantities derived from this work which can be directly compared with those of the near-IR data is the monomer phenol concentration. All association models which have been used to describe phenol polymerization should be reducible, directly or indirectly, to monomer versus total concentration curves. The concentration of phenol monomer derived from the near-IR absorbance data is independent of the association model. Its value is directly determined from the absorptivity of very dilute solutions (only phenol monomer exists in sufficiently dilute solution). Theoretically, the monomer concentration also can be directly determined from the activity data and Henry's law constant (K_p) in this work. Actually, since it is difficult to obtain the precise value of the Henry's law constant from the limiting intercepts of plots of a/f_A vs. f_A for dilute solutions (especially at low temperature), the Henry's law constants of this work have to be considered as parameters

to be inferred from fitting data to the various association models. Tables 17 to 24 list calculated activities and monomer concentrations of phenol as a function of phenol concentration for the 1-2-∞ and 1-3-∞ models. These results show that the monomer concentrations derived from the 1-2-∞ model are significantly smaller than those from the 1-3-∞ model. Figures 11 to 18 present the plots of the formal concentration of phenol vs. the monomer concentration determined from this work, near-IR measurements, and other techniques. In the low concentration range the monomer concentrations of phenol obtained from the near-IR data are in good agreement with those derived from the 1-3-∞ model of this work, but in disagreement with those derived from the 1-2-∞ model. However, at higher concentrations a small difference in derived monomer concentration between the two independent techniques (the 1-3-∞ model fit of this work) was observed at temperatures of 11.85, 20.7, and 29.1°C for carbon tetrachloride solution and at temperatures of 13.3 and 22.2°C for cyclohexane solution. At those temperatures, the monomer concentrations of phenol derived from the near-IR data are slightly higher than those from activity data. A similiar phenomenon was also observed by Tucker and Becker[68] in their comparison of monomer concentrations of tert-butanol in hexadecane derived from fundamental infrared data and vapor pressure data as functions of formal tert-butanol concentration. They attributed the higher monomer concentrations measured by the fundamental-IR method to the absorbance of the end hydroxyl group of linear trimers at the monomer band. The present work thus may be interpreted as giving evidence that the end hydroxyl group interference is of some importance in phenol solutions. However, the magnitude of the interference for phenol solutions (in the overtone region) is smaller than

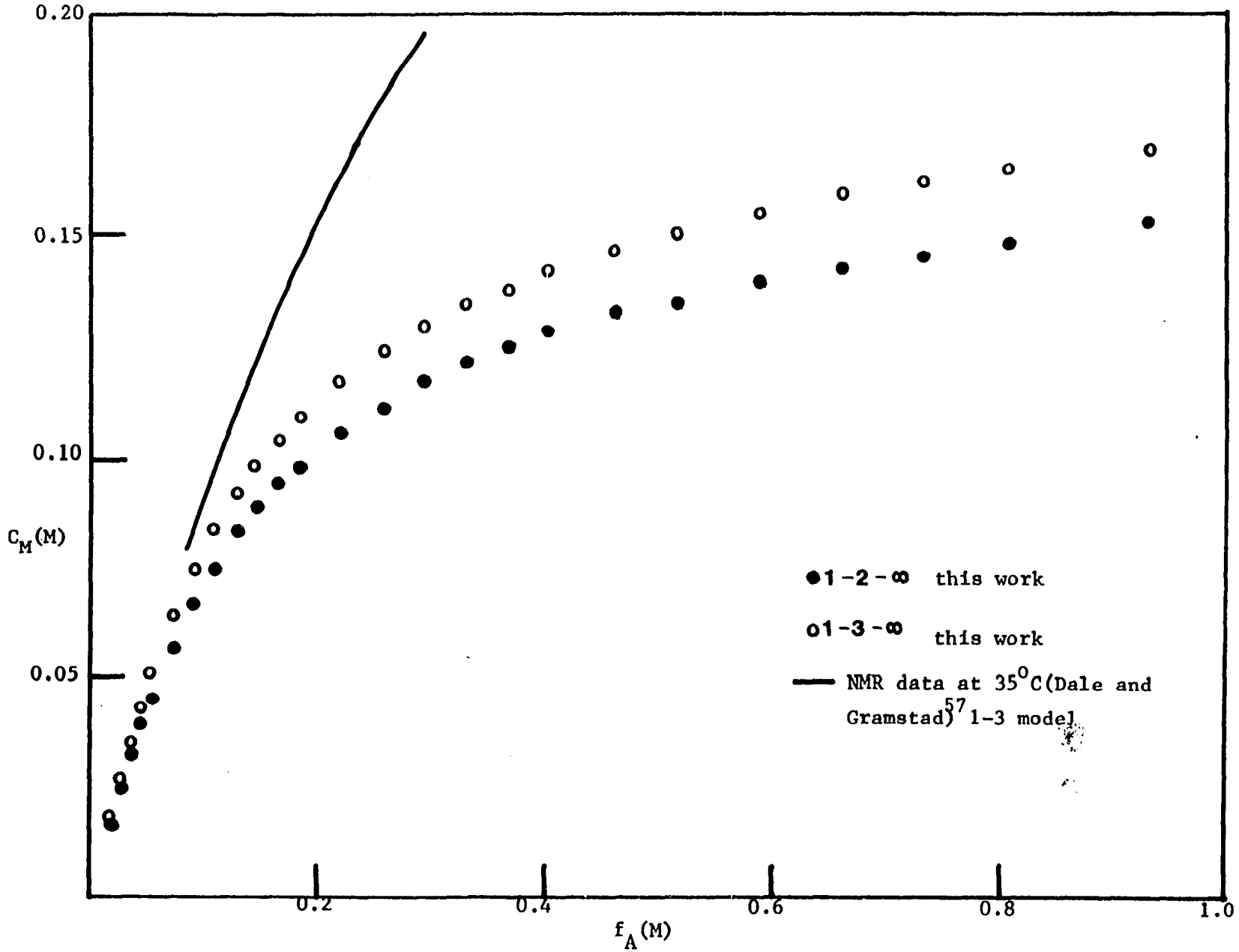


Figure 11. Phenol Monomer Concentration (C_M) as a Function of Formal Concentration (f_A) in Cyclohexane (37.7°C for this work).

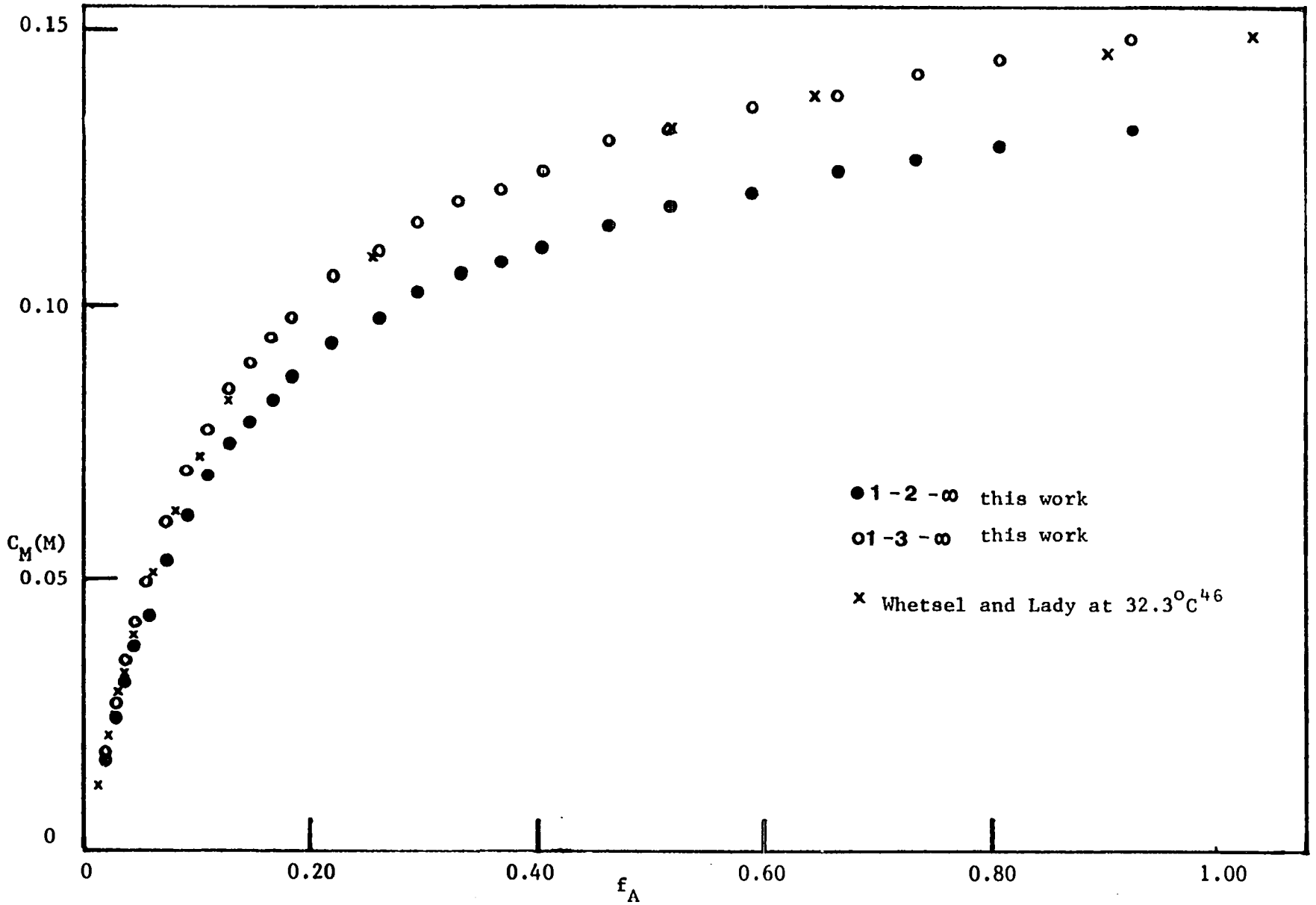


Figure 12. Phenol Monomer Concentration(C_M) as a Function of Formal Concentration(f_A) in Cyclohexane (32.2°C for this work)

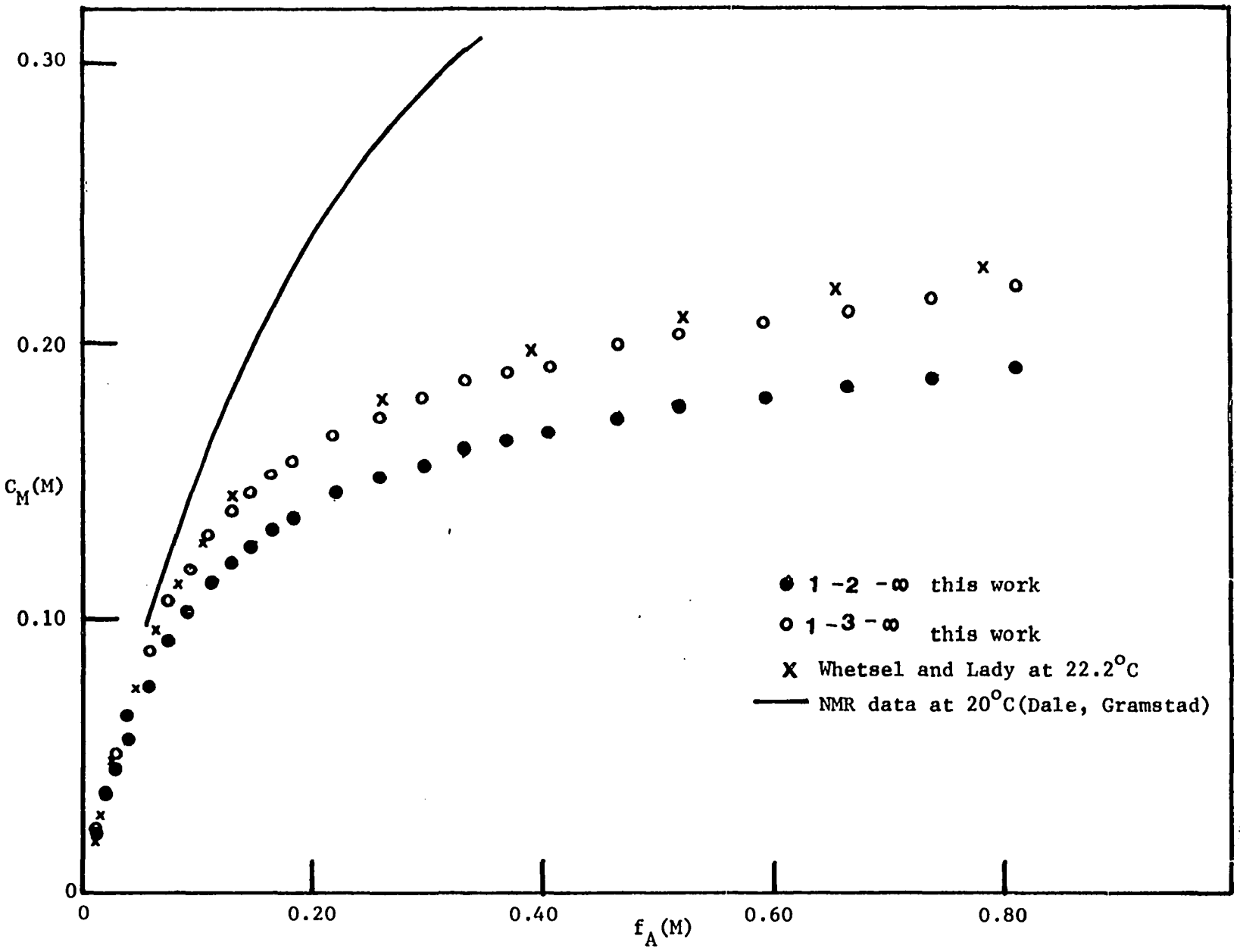


Figure 13. Phenol Monomer Concentration (C_M) as a Function of Formal Concentration (f_A) in Cyclohexane (22.2°C for this work).

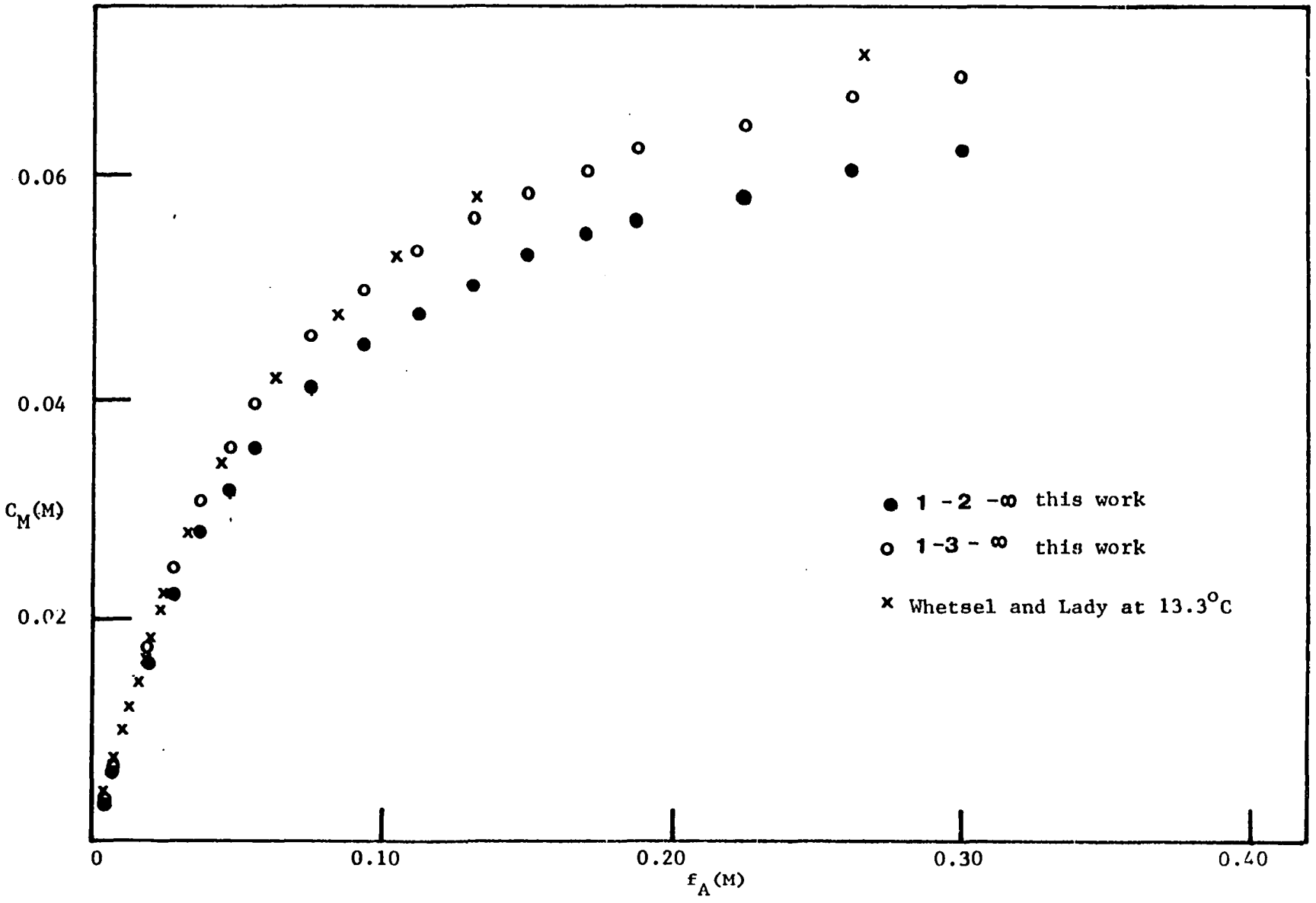


Figure 14. Phenol monomer Concentration(C_M) as a Function of Formal Concentration(f_A) in Cyclohexane (13.3°C for this work)

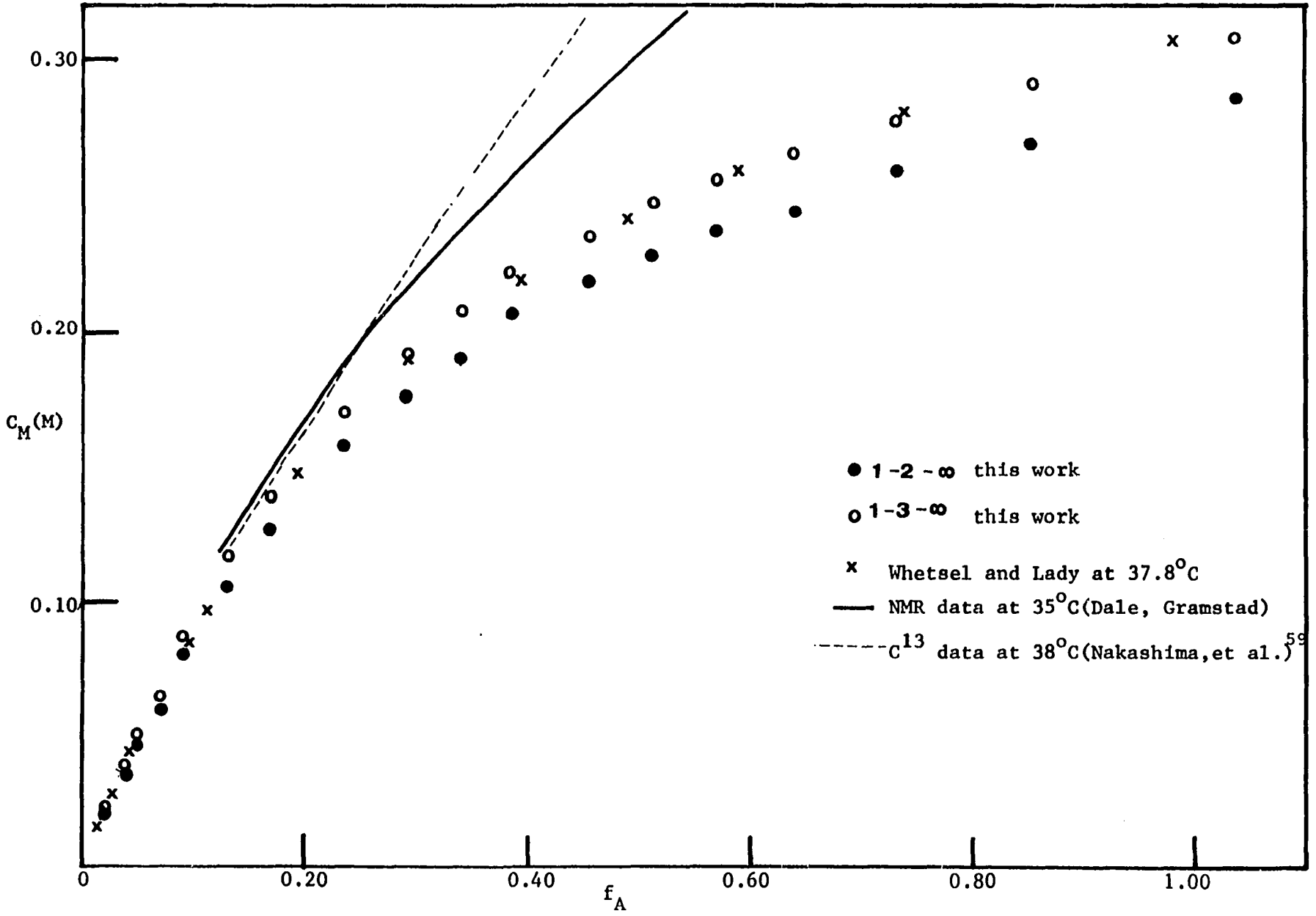


Figure 15. Phenol Monomer Concentration(C_M) as a Function of Formal Concentration(f_A) in Carbon Tetrachloride (37.8°C for this work).

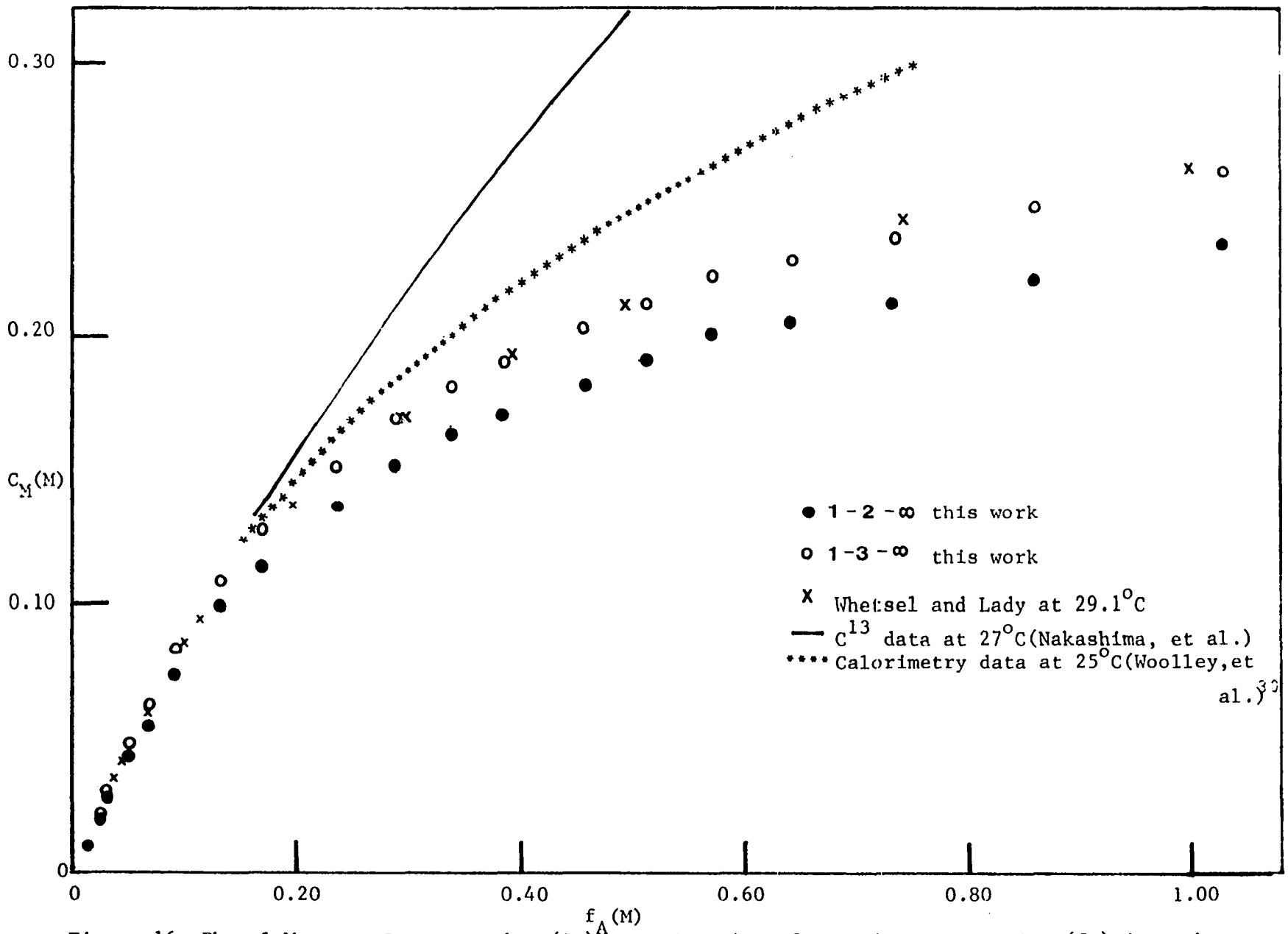


Figure 16. Phenol Monomer Concentration (C_M) as a Function of Formal Concentration (f_A) in Carbon Tetrachloride (29.1°C for this work).

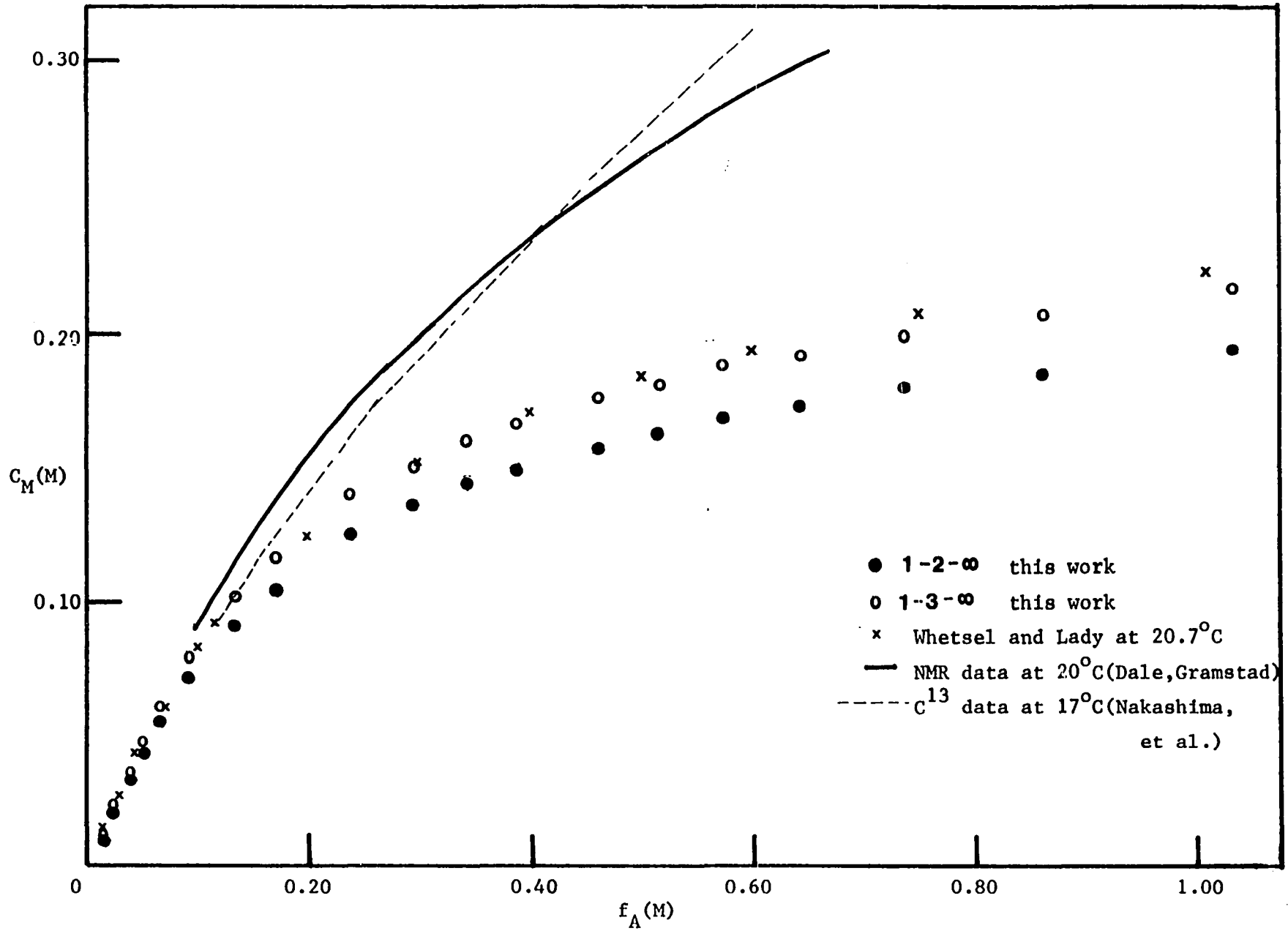


Figure 17. Phenol Monomer Concentration(C_M) as a function of Formal Concentration (f_A) in Carbon Tetrachloride (20.7°C for this work).

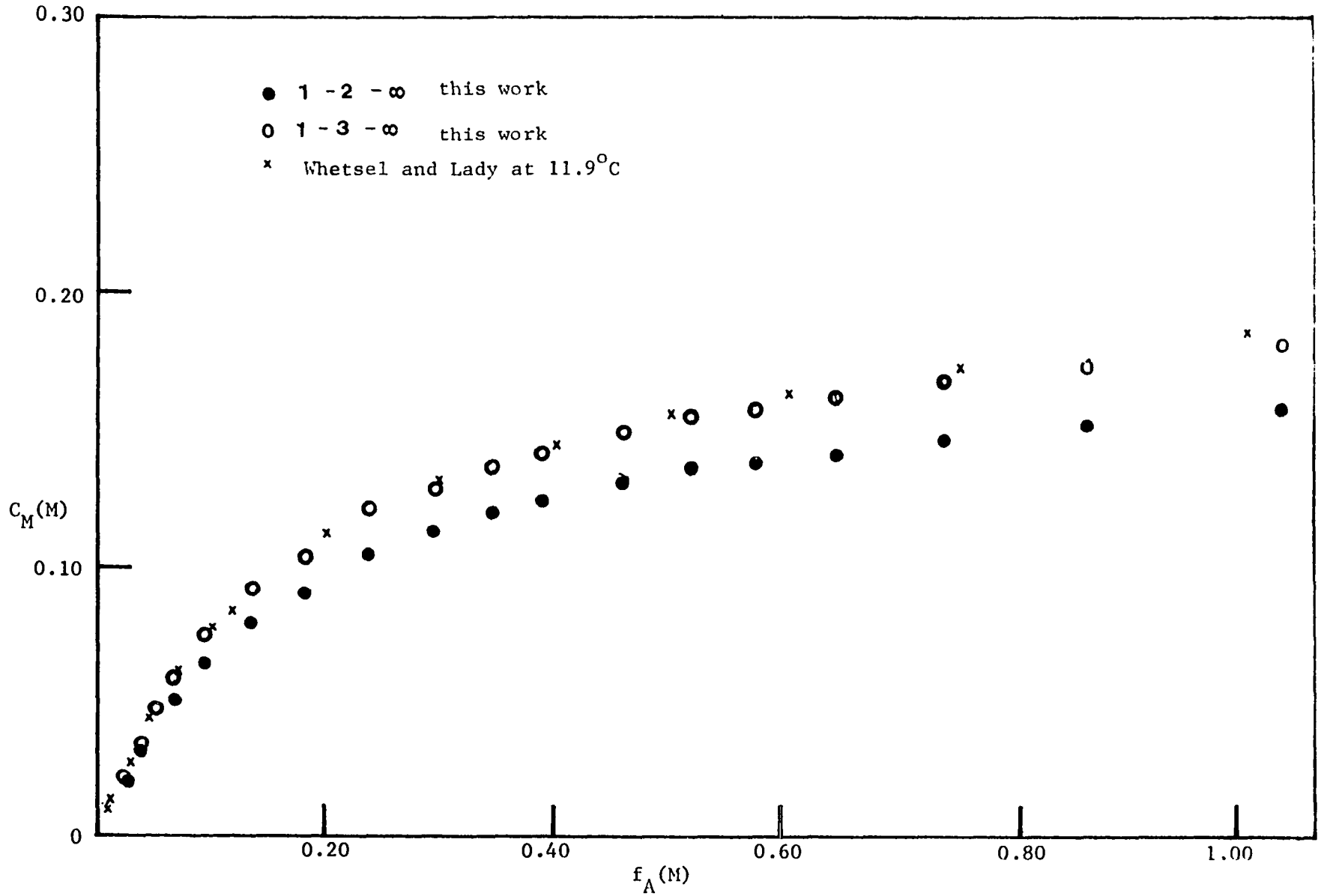


Figure 18. Phenol Monomer Concentration(C_M) as a Function of Formal Concentration(f_A) in Carbon Tetrachloride (11.85°C for this work).

in the case of tert-butanol (in the fundamental region). This may be an argument for saying that a significant portion of the phenol trimer or other polymers exists in cyclic forms; however, the extent of overlap between monomer and polymer bands may be relatively smaller in the overtone region. At 37.8°C for carbon tetrachloride solution and at 32.2°C for cyclohexane solution, the monomer concentrations of phenol derived from the two techniques are almost identical within the experimental errors. Therefore, the present research supports the conclusion of Whetsel and Lady that the end-group interference is relatively weak in both solutions. The above discussion can lead to the conclusion that the concentrations of phenol monomer derived from this work and those of Whetsel and Lady are upper limiting values.

In most of the NMR studies of the self-association of phenol, the data have been interpreted in terms of one associated species, e.g., dimer or trimer. Huggins, et al.,[50] and Nakashima, et al.,[58] found that the monomer-dimer model can account satisfactorily for the phenol association data. However, Saunders and Hyne,[51] Ahlf and Platthaus,[55] Dale and Gramstad,[57] and Bogachev, et al.,[58] argued that a model containing a monomer-trimer equilibrium provided the best fit of their NMR data. Although Rao, et al.,[54] interpreted their PMR data of phenol in carbon tetrachloride in terms of monomer-dimer-polymer, no thermodynamic parameters were reported. The best way to compare the results of NMR measurements with those of activity data is to compare the monomer concentration of phenol as a function of phenol formal concentration. Some of the monomer concentration vs. formal concentration results deduced from the association constants of Nakashima, et al., and Dale and Gramstad, are also plotted in Figure 11 through Figure

18. It should noted that, except in the low concentration range, the NMR data lead to a calculated phenol monomer concentration which increases much too rapidly with total phenol concentration to be consistent with the activity or IR measurements. It should be emphasized that the monomer concentrations of phenol should be the same within experimental errors for a given solution at a given temperature regardless of which technique is used. There are generally two distinct disadvantages of NMR measurements for calculations of association constants; (1) no measurable quantity directly related to the monomer concentration may be obtained from NMR data; (2) almost twice as many parameters are required for NMR data in model fitting as compared to IR or vapor pressure techniques.

Figure 16 also shows the plot of the concentration of phenol monomer vs. formal phenol concentration derived from the calorimetric results of Woolley, et al.[30] As in the case of the NMR plot, the monomer concentration increases too rapidly with formal phenol concentration. The disadvantages of obtaining association constants from calorimetric data are similar to those of NMR data. However, the concentrations of phenol monomer derived from partition-water solubility data[27,28] and from total vapor pressure measurements[34] on phenol-carbon tetrachloride solutions are in reasonable agreement with those from activity measurements.

The marked discrepancies among the curves derived from various techniques as shown in Figures 11 to 18 clearly indicate that not all of the results obtained are meaningful. In view of the direct relation between thermodynamic activity values and the concentrations of phenol monomer in solution, it is essential that any association model for phenol solutions be consistent with reliable activity results. This restriction

arises from the basic assumption, made in all spectral and classical studies of phenol association, that Henry's law is obeyed by each of the individual phenol species. Under this assumption, values of the concentration of phenol monomer obtained from various association models should vary linearly with the thermodynamic activity. The concentration of monomer phenol calculated from the near-IR data generally varies nearly linearly with the activity values, although at higher phenol concentrations the near-IR results lead to somewhat higher monomer concentrations (probably due to the end-OH-group absorption of polymers). In any case, monomer concentrations derived from activity data or near-IR data should represent upper limiting values; other spectral and thermodynamic results should be expected to yield monomer concentrations no larger than these.

The above discussion leads us to the conclusion that phenol association models limited to dimerization and/or trimerization can be rejected as being physically unrealistic except in quite restricted ranges of phenol concentration. After a careful numerical analysis of the near-IR data of Whetsel and Lady and consideration of the present activity results, we believe that the 1-3-∞ model is the best model proposed to date for representing the association of phenol in carbon tetrachloride and cyclohexane.

(3) Possible Structures of the Associated Species: The activity method used in this work, like other vapor pressure methods, gives no direct structural information. However, by comparing the concentrations of phenol monomer derived from this work with those of the near-IR method, the possible structure of the trimer or higher polymers may be suggested. The higher monomer concentration derived from near-IR data probably indicates that end-OH-group absorption by the linear trimer or higher polymers

occurs at the monomer band. There are still arguments[76] as to whether the end OH groups and free OH groups absorb at the same frequency and with the same intensity, or whether the end OH groups only slightly interfere at the frequency of the monomer band. Whetsel and Lady have estimated that the absorptivities of the end OH group at the free OH frequency in the overtone are less than 30% of the free OH group absorptivities. There is still no unambiguous way to determine the fraction of linear trimer in solution using the absorprivity data. The results of this work seem to indicate that both cyclic and linear trimer are present in solutions. The larger enthalpy of trimerization for phenol in cyclohexane obtained in this work (-13.4 Kcal/mole vs. -6.0 Kcal/mole for K_∞) might be explained by the fact that a substantial fraction of cyclic trimers exists.

(4) Error Analysis: In order to assess the reliability of experimental results, it is desirable to analyze the effects of errors in activity data on the association constants and Henry's law constants. Although the RMSD values of model fitting are expressed in terms of activity, which is not directly measured, the dependence of activity on directly measured quantities (phenol vapor absorbances) can be estimated at various temperatures. For example, for carbon tetrachloride solution, an error of 0.005 in activity at 11.85°C corresponds to an error of about 0.001 in averaged absorbance at the three wavelengths, while an error of 0.003 in activity at 37.8°C is equal to an error of 0.0035 in averaged absorbance. Similar relations at other temperatures may be deduced from the results in Table 4 to Table 11. Except for the low concentration solutions, observed activity values always differ by less than 1% from calculated values listed in Table 17 to Table 24. Two sets of synthetic data have been used to study

the effect of errors in activity on the association constants and Henry's law constant for the 1-3-∞ model. Such results are given in Table 30. Random, normally distributed errors (σ=0.003) were introduced into all activity values in order to simulate a set of measured activities with errors. This produced standard errors of 1.1%, 7%, and 1.5% for K_p, K_3, and K_∞, respectively, for the first set of data. Random, normally distributed errors (σ=0.004) resulted in standard errors of 1.2% in K_p, 7% in K_3, and 1.0% in K_∞ for the second set of data. The standard errors of fit of this work for the 1-3-∞ model are approximately the same size as those derived from the synthetic data. Therefore, the standard errors of the experimental values of K_p, K_3, and K_∞ can probably be estimated to be within ±1.5%, ±10%, and ±2.0%, respectively.

Finally, it may be instructive to compare the thermodynamic parameters derived from the averaged activity data at the three wavelengths (Tables 15 and 16) with those derived from the averaged activity data at 268.2 nm and 262.6 nm (Tables 31 and 32). This comparison shows that the differences in association constants and thermodynamic parameters derived from the different two sets of activity data are within the standard errors mentioned above.

Summary

A new technique has been developed to investigate the self-association of phenol in organic solutions. By utilizing this technique, the activity of phenol in cyclohexane and carbon tetrachloride solutions at various temperatures was determined from absorbance measurements in the ultraviolet region on phenol vapor above the solution. Deviations of

TABLE 30

ERROR STUDY FOR THE 1-3-∞ MODEL USING SYNTHETIC DATA

First Data Set (20 Points)

	K_p	K_3	K_∞	Standard Error
Synthetic Data	3.06	6.25	2.96	0.000
Random Error of 0.003 in Activity	3.060±0.034	6.28±0.43	2.96±0.05	0.00303

Second Data Set (24 Points)

	K_p	K_3	K_∞	Standard Error
Synthetic Data	9.0	26.1	6.62	0.0
Random Error of 0.004 in Activity	8.98±0.11	25.9±1.50	6.60±0.06	0.00389

TABLE 31

RMSD, ASSOCIATION CONSTANT AND HENRY'S LAW CONSTANT VALUES FOR PHENOL IN CARBON TETRACHLORIDE AND CYCLOHEXANE OBTAINED USING AVERAGED ACTIVITY DATA AT 268.2 nm AND 262.6 nm (K_p is considered as an adjustable parameter in model fitting)

Model	Temperature(°C)	$K_p(M^{-1})$	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_\infty(M^{-1})$	RMSD
			In Carbon Tetrachloride			
1-3-∞	37.8	1.67±0.02	2.66±0.21	2.66±0.21	1.81±0.05	0.00264
	29.1	2.26±0.03	-	4.65±0.33	2.18±0.05	0.00282
	20.7	3.08±0.03	-	6.53±0.39	2.99±0.04	0.00288
	11.85	4.32±0.07	-	10.8±1.0	3.68±0.08	0.00542
1-2-∞	37.8	1.81±0.03	0.79±0.07	-	2.34±0.04	0.00313
	29.1	2.51±0.04	1.26±0.09	-	2.90±0.04	0.00292
	20.7	3.45±0.06	1.51±0.11	-	3.78±0.05	0.00365
	11.85	4.98±0.01	2.26±0.18	-	4.72±0.07	0.00446
			In Cyclohexane			
1-3-∞	37.7	4.70±0.03	-	8.01±0.29	4.31±0.02	0.00219
	32.2	5.89±0.05	-	12.5±0.6	4.86±0.04	0.00347
	22.2	8.99±0.09	-	26.5±1.4	6.64±0.05	0.00388
	13.3	14.07±0.13	-	48.4±2.8	9.75±0.10	0.00326
1-2-∞	37.7	5.22±0.08	1.49±0.09	-	5.13±0.05	0.00393
	32.2	6.66±0.15	2.01±0.18	-	5.92±0.10	0.00609
	22.2	10.39±0.22	3.46±0.26	-	8.22±0.13	0.00574
	13.3	15.65±0.32	3.73±0.33	-	11.90±0.16	0.00527

TABLE 32

THERMODYNAMIC PARAMETERS FOR SOLUTION AND ASSOCIATION OF PHENOL OBTAINED USING THE AVERAGED ACTIVITY DATA AT 268.2 nm AND 262.6 nm

	IN CARBON TETRACHLORIDE		IN CYCLOHEXANE	
	1-3-∞ model	1-2-∞ model	1-3-∞ model	1-2-∞ model
$-\Delta H_x^a$(Kcal/mole)	-9.4±0.5	-9.4±0.1	-8.3±0.1	-8.2±0.1
$-\Delta S_x^a$(e.u./mole)	-36.0±1.6	-36.1±0.2	-34.3±0.4	-34.3±0.3
ΔH_2^b(Kcal/mole)	-	-6.8±0.8	-	-7.5±1.5
ΔS_2^b(e.u./mole)	-	-21.4±2.7	-	-22.4±5.1
ΔH_3^b(Kcal/mole)	-9.6±0.7	-	-13.6±0.5	-
ΔS_3^b(e.u./mole)	-27.6±2.4	-	-38.3±1.7	-
ΔH_∞^b(Kcal/mole)	-5.2±0.5	-5.0±0.2	-6.0±0.4	-6.3±0.3
ΔS_∞^b(e.u./mole)	-15.0±1.7	-13.7±0.7	-15.7±1.4	-16.3±0.8

a: Thermodynamic quantities for transfer from 1 atm ideal gas to unit mole fraction ideal dilute solution state.

b: Thermodynamic quantities for reactions for the unit molarity ideal dilute solution standard state(obtained from Equation (40)).

activity data from Henry's law were attributed to the formation of specific hydrogen-bonded complexes. A non-linear least squares program was employed to fit the activity data with various association models. The Henry's law constants and association constants for various models have been inferred as the results of data analysis.

The results of this study indicate that a model with a unique association constant for trimerization and another for the successive association to higher polymers (monomer-trimer-stepwise-n-mers) provided the best fit for the activity data of phenol solutions. The importance of the dimer as the first associated species is not supported by the activity data. A careful numerical analysis of the near-IR data of Whetsel and Lady also indicates that the monomer-trimer-stepwise-n-mers model in general is better fitted than the monomer-dimer-stepwise-n-mers model. The association constants derived from both experimental techniques for the monomer-trimer-stepwise-n-mers model are compatible. The concentrations of phenol monomer obtained from the activity data are also in good agreement with those of the near-IR data of Whetsel and Lady, but incompatible with those of PMR, ^{13}C NMR and calorimetry data. The latter lead to concentrations of calculated phenol monomer which increase too rapidly with formal phenol concentration to be consistent with the activity measurements. The models limited to dimer and/or trimer are not adequate to fit activity data. The activity results confirm that end hydroxyl group interference is present in phenol solutions, but only to a small extent.

By studying the temperature dependence of association constants, the enthalpies and entropies of the association reactions were determined. The enthalpies and entropies of transfer of gaseous (monomeric) phenol

into solvents at infinite dilution were also obtained from the van't Hoff plots of Henry's law constants.

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