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SELF-ASSOCIATION AND HYDRATION OF PHENOL IN ^{SEYCHUEL} ORGANIC SOLVENTS

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SELF-ASSOCIATION AND HYDRATION OF PHENOL IN ^{SEVERAL} ORGANIC SOLVENTS

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TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF ILLUSTRATIONS	viii
Chapter	
I. INTRODUCTION	1
II. OBJECTIVES	10
III. EXPERIMENTAL	11
IV. THEORY	19
V. RESULTS AND CALCULATIONS	25
VI. DISCUSSION	98
BIBLIOGRAPHY	110
APPENDIX A	115
APPENDIX B	153

LIST OF TABLES

Table	Page
1. Beer's Law Data for Phenol in Water at 268 mμ and 274 mμ	34
2. Formal Solubility of Water at Various Water Activities in Carbon Tetrachloride at 25°, using Solute Isopiestic Method. . .	37
3. Formal Solubility of Water at Various Water Activities in Carbon Tetrachloride at 25°, using Partition Method.	38
4. Formal Solubility of Water at Various Water Activities in Cyclohexane at 25°, using Solute Isopiestic Method	39
5. Formal Solubility of Water at Various Water Activities in Benzene at 25°, using Solute Isopiestic Method	41
6. Formal Solubility of Water at Various Water Activities in Benzene at 25°, using Partition Method	42
7. Formal Solubility of Water at Various Water Activities in Benzene at 25°, using the Manual Karl Fischer Titration.	43
8. Formal Solubility of Water at Various Water Activities in Toluene at 25°, using Solute Isopiestic Method	44
9. Formal Solubility of Water at Various Water Activities in 1,1,2,2-Tetrachloroethane at 25°, using Solute Isopiestic Method	46
10. Formal Solubility of Water at Various Water Activities in 1,2-Dichloroethane at 10°, using Solute Isopiestic Method. . . .	49
11. Formal Solubility of Water at Various Water Activities in 1,2-Dichloroethane at 25°, using Solute Isopiestic Method. . . .	50
12. Least Squares Parameter for $f_w^o = \alpha a_w + \beta a_w^m + \gamma a_w^n$	52
13. Solubility and Association Constants of Water in Organic Solvents.	53
14. Partition Data for the System 1,2-Dichloroethane-Water-Phenol at 25°.	55

Table	Page
15. Water Solubility Data for the Phenol-1,2-Dichloroethane System at VARIOUS Water Activities at 25°	56
16. Partition Data for the System Benzene-Water-Phenol at 25°	61
17. Water Solubility Data for the Phenol-Benzene System at Various Water Activities at 25°	62
18. Partition Data for the System 1,1,2,2-Tetrachloroethane-Water-Phenol at 25°	67
19. Water Solubility Data for the Phenol-1,1,2,2-Tetrachloroethane System at Various Water Activities at 25°	68
20. Self-Association and Hydration Constants for Phenol in 1,2-Dichloroethane, 1,1,2,2-Tetrachloroethane and Benzene at 25°	74
21. Partition Data for the System Carbon Tetrachloride-Water-Phenol at 25°	75
22. Water Solubility Data for the Phenol-Carbon Tetrachloride System at Various Water Activities at 25°	77
23. Least Squares Parameters for $f_p^0/C_p^W = \alpha + \beta(C_p^W)^{m-1} + \gamma(C_p^W)^{n-1}$	83
24. Self-Association and Hydration Constants for Phenol in Carbon Tetrachloride.	85
25. Partition Data for the System Carbon Tetrachloride-Water-Phenol at 35°	86
26. Absorbance of Phenol-Carbon Tetrachloride Solutions at the O-H Peak Wavelength of 1.357 μ at 25°	87
27. Absorbance of Phenol-1,2-Dichloroethane at the O-H Peak Wavelength of 1.375 μ at 25°	88
28. Absorbance of Phenol-1,1,2,2-Tetrachloroethane at the O-H Peak Wavelength of 1.385 μ at 25°	89
29. Absorbance of Phenol-Benzene Solutions at the O-H Peak Wavelength of 1.380 μ at 25°	90
30. Solubility Data of Carbon Tetrachloride in Water at 25°, using Vapor Pressure Measuring Device	92
31. Solubility Data of 1,2-Dichloroethane in Water at 25°, using Vapor Pressure Measuring Device	94

Table	Page
32. Solubility Data of Benzene in Water at 25°, using Vapor Pressure Measuring Device	96
33. Solubility of Water in Several Organic Solvents at 25°.	102

LIST OF ILLUSTRATIONS

Figure	Page
1. Beer's Law Plot for Phenol in Water at 268 m μ and 274 m μ	33
2. Solute Isopiestic Apparatus	35
3. Water Equilibration Rate Data at 25° in Benzene and 1,2-Dichloroethane.	36
4. Formal Solubility of Water at 25° in Carbon Tetrachloride and Cyclohexane	40
5. Formal Solubility of Water at 25° in Benzene and Toluene.	45
6. Formal Solubility of Water in 1,2-Dichloroethane at 10° and 25° and 1,1,2,2-Tetrachloroethane at 25°.	51
7. Log-log plot of Formal Solubility of Water at 25° in 1,2-Dichloroethane, 1,1,2,2-Tetrachloroethane, Benzene, Toluene, Carbon Tetrachloride and Cyclohexane as a Function of Various Water Activities.	54
8. Partition Data for System 1,2-Dichloroethane-Water-Phenol at 25°.	59
9. Formal Solubility of Water in Solutions of Phenol in 1,2-Dichloroethane at Various Water Activities.	60
10. Partition Data for System Benzene-Water-Phenol at 25°	65
11. Formal Solubility of Water in Solutions of Phenol in Benzene at Various Water Activities	66
12. Partition Data for System 1,1,2,2-Tetrachloroethane-Water-Phenol at 25°	72
13. Formal Solubility of Water in Solutions of Phenol in Carbon Tetrachloride at Various Water Activities	73
14. Partition Data for the System Carbon Tetrachloride-Water-Phenol.	81

Figure	Page
15. Formal Solubility of Water in Solutions of Phenol in Carbon Tetrachloride at Various Water Activities.	82
16. Absorbance of Phenol Solutions in Benzene, 1,2-Dichloroethane, 1,1,2,2-Tetrachloroethane and Carbon Tetrachloride. . .	91
17. Formal Solubility of Carbon Tetrachloride in Water at 25°, using Vapor Pressure Measuring Device	93
18. Formal Solubility of 1,2-Dichloroethane in Water at 25°, using Vapor Pressure Measuring Device	95
19. Formal Solubility of Benzene in Water at 25°, using the Vapor Pressure Measuring Device.	97

SELF-ASSOCIATION AND HYDRATION OF PHENOL IN ORGANIC SOLVENTS

CHAPTER I

INTRODUCTION

The hydrogen bonding of hydroxyl-containing molecules has been of interest for several decades.^{1,2} Considerable effort has been expended in attempts to deduce and predict the structure and stoichiometry of hydrogen bonded complexes. Numerous techniques have been developed and employed over the years with the objective of elucidating further the nature of the hydrogen bond. Phenol has been subjected to these techniques by many workers in their course of study. Due to the vast amount of literature available on the hydrogen bonding of phenol, a special section (APPENDIX A) has been added listing numerous references.

Although the association of phenol has been studied using a number of media, there is still no agreement among various investigators as to its molecular complexity in dilute solutions. Many investigators have postulated a monomer-dimer equilibrium, while others have proposed the existence of trimers and higher polymers to explain their experimental data. To resolve this confusion a detailed study was made of the solute properties of phenol in several solvents of varying dielectric constant using partition and water solubility techniques.

Historically, the cryoscopic and boiling point elevation methods were among the first techniques used to study the degree of association of phenol. However, these methods do not permit measurements to be made over an arbitrary temperature range, nor do they allow a series of determinations to be made at constant temperature. Available cryoscopic data must be interpreted carefully because phenol forms a solid solution with benzene, the solvent commonly employed.³ Therefore, the results cannot be interpreted meaningfully without some type of adjustment. A summary of cryoscopic data for phenol up to the year 1937 was given by Lassetre.⁴

The partition method has been used extensively to determine the degree of association of hydrogen-bonding molecules. The departure of the distribution ratio from that expected for an ideal solution is usually attributed to the formation of molecular complexes. Rothmund and Wilsmore⁵ and Vaubel⁶ were among the first to study phenol by distributing it between water and organic solvents. They noted that the concentration of phenol in the non-aqueous phases, benzene and carbon tetrachloride, increases more rapidly than the concentration in water, indicating that partial polymerization occurs in the non-aqueous phase. Herz, et. al.,^{7,8,9} also attributed irregularities in the distribution ratios of phenol and other substances between water and organic solvents to polymerization and solvation in the non-aqueous phase. Hirobe¹⁰ and Endo¹¹ concluded that phenol exists as of two types of species, monomers and trimers, in both chlorobenzene and benzene. Endo¹² also distributed phenol between benzene and aqueous salt solutions and concluded that when appropriate phenol activity corrections were made, the data indicated trimer equilibrium in the benzene phase.

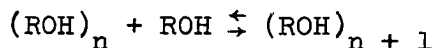
Philip, et. al.,^{13,14} concluded from partition studies that phenol is monomeric in benzene up to 0.02 molar. However, they found at higher concentrations that in addition to a dimer they needed to assume the presence of some higher polymer, such as the trimer, to explain their data. Philbrick,¹⁵ in a careful study of dilute solutions, determined dimerization constants for phenol in several solvents. The dimerization constants for phenol in toluene, chlorobenzene, benzene, and nitrobenzene that he obtained were 0.843, 0.648, 0.575 and 0.196 l/mole, respectively. For concentrations of phenol up to 0.1 molar in carbon tetrachloride he could not detect any change in the distribution ratio. He also noted some abrupt changes in the distribution ratios for the nitrobenzene and toluene systems, which he could not explain. More recently Badger and Greenough¹⁶ have reported that the association of phenol in carbon tetrachloride is greatly promoted by the presence of water. They have concluded from combined partition and infrared studies that in addition to the phenol dimer the predominant hydrated polymer up to 0.3 molar in carbon tetrachloride is a phenol hemihydrate.

Lindenberg and Massin¹⁷ determined the partition coefficients for phenol, m-cresol and p-ethylphenol between water and several solvents. They correlated the change of the coefficients with the concentration in the organic phase and obtained an empirical relation by which they could express the change of the distribution ratio as a linear function of the formal concentration of phenol in the organic phase.

The most common method for determining the association of hydrogen-bonding solutes has been the spectrophotometric measurement of monomer concentration as a function of the total concentration. Since the

development of solution infrared techniques in the early 1930's, numerous studies have been made with phenol. Fox and Martin¹⁸ in 1937 concluded that at moderate concentrations of phenol in carbon tetrachloride an equilibrium exists between single and double molecules.

Wulf and Jones,¹⁹ who studied phenol and its halogen derivatives in the second overtone region, reported a phenol dimerization constant of 1.8 l/mole in carbon tetrachloride at 25°. The equilibrium constants for the higher polymers were represented by a power series. Kempter and Mecke^{20,21} have proposed a dissociation equilibrium scheme for equilibria of the type



where n and $n+1$ refer to complexes of the n th and $(n+1)$ th order. They assumed that the successive dissociation constants were equal for all orders of complexes and thereby obtained

$$K_c = \alpha C / (1 - \sqrt{\alpha})$$

where K_c is the general dissociation constant applicable to each order complex, α is the fraction of unassociated hydroxylated molecules and C is the molar concentration. Their data appeared to support this theory. Later, Coggeshall and Saier²² rejected Kempter and Mecke's hypothesis on the basis of a reinvestigation of phenol in carbon tetrachloride at 25°. They used a separate, distinct constant for dissociation of dimer complexes and a general constant for the dissociation of higher complexes.

Moccia and Califano²³ determined dimer dissociation constants for phenol and several phenol derivatives in carbon tetrachloride by measuring the integrated intensities of the O-H vibration. A value of 0.8 moles/l was obtained for phenol, which compared well with 0.72 moles/l obtained

by Coggeshall and Saier. West, et. al.,^{24,25} also concluded from an infrared study of phenol and some phenol derivatives at several temperatures that the monomeric phenol was in equilibrium with cyclic dimers, in preference to trimers, up to a concentration of 0.2 molar in carbon tetrachloride. They obtained a ΔH of association for the cyclic dimer of 5.12 ± 0.1 Kcal/mole dimer. However, Rea²⁶ in a similar study reported trimer constants for association of phenol in carbon tetrachloride at several temperatures.

The ultraviolet spectrum of phenol has been employed by Ito²⁷ and Rao²⁸ to study the association of phenol. From their data they concluded that the associated aggregates of phenol in n-hexane, cyclohexane and carbon tetrachloride were cyclic dimers in equilibrium with the monomeric form. However, Dearden²⁹ concluded that either monomer-trimer or monomer-polymer equilibrium provided a better explanation for the ultraviolet spectra of solutions of phenol in cyclohexane and he reported a trimer constant of 15.4 (l/mole)^2 at 25° .

Recently nuclear magnetic resonance (NMR) spectroscopy has been used to study hydrogen bonding phenomena. Higgins, et. al.,³⁰ have suggested a monomer-dimer equilibrium to explain their NMR data of phenol in carbon tetrachloride. Saunders and Hyne³¹ have obtained NMR spectra of phenol at much lower concentrations than Higgins, et al., and proposed a monomer-trimer model to explain their chemical shift data. Martin and Quiloeut³² have studied the association of phenol in carbon tetrachloride and chloroform and concluded that the association constants for the formation of the successive phenol polymers are all the same.

Using isopiestic measurements Lassetre and Dickinson³³ have obtained

an anhydrous dimerization constant for phenol in benzene at two temperatures i.e. 0.570 and 0.416 l/mole at 25 and 50°, respectively. Bono,^{34,35} Delvalle³⁶ and Chevalley³⁷ have determined the vapor pressure lowering of phenol-carbon tetrachloride solutions and have interpreted their data in terms of the degree of association of phenol, although no equilibrium constants were deduced from the data. A differential vapor pressure technique has been employed by Coetzee and Lok³⁸ to study the association of certain acids and bases in several non-hydrogen bonding solvents. They have calculated a dimerization constant of 40 l/mole for the association of phenol in 1,2-dichloroethane at 37°.

Obviously there must be some explanation for the discrepancies in the results obtained by the different investigators for the association of phenol. The lack of sensitivity in the techniques employed undoubtedly is responsible for part of the disagreement. However, a major source of error may well arise from neglecting the formation of hydrates. As long ago as 1897, Bödtker³⁹ concluded that the increase in solubility of water in ether containing oxalic acid could best be explained by the formation of a compound between the acid and water in the ethereal solution. Rozsa⁴⁰ in 1911 used cryoscopic data to support the conclusion that strong association occurred in benzene between water and other molecules having a hydroxyl group such as phenol, ethanol and trichloroacetic acid. Lewis and Burrows⁴¹ determined the solubility of urea in ethyl acetate containing various percentages of water. They noted that the presence of water affected the solubility of urea and the increase in solubility was roughly proportional to the amount of water present. Horiba,⁴² in a water-phenol-benzene phase equilibrium study, noted that the presence of phenol

increases the solubility of water in the benzene phase. Staveley, Jeffes and Moy⁴³ also observed an increase in water solubility caused by the presence of a third substance. Cohen, et al.,^{44,45} showed that minute traces of water increased the solubility of salicyclic acid in benzene and chloroform and of nitrobenzoic acid in chloroform. However, they found no influence of water on the solubility of salicyclic acid in carbon tetrachloride. Szyszkowski, et al.,⁴⁶ also demonstrated the effect of water on the solubility of benzoic acid in benzene. These investigators interpreted the increase in solubility of acids in terms of hydration. Bell, et al.,⁴⁷ used cryoscopic data to demonstrate that the mono-, di-, and trichloroacetic acids formed hydrates in benzene.

Hildebrand⁴⁸ proposed that the high solubility of alcohols in water, as compared with organic chlorides and iodides, may be attributed to formation of a water bridge between two alcohol molecules. In review articles on hydrogen bonding Lassettre⁴⁹ and Huggins⁵⁰ indicated that the presence of water may affect the equilibrium of hydrogen bonding molecules.

Arshid, Giles and Jain⁵¹ have proposed the existence of monomer monohydrates and dimer monohydrates to explain refractive index data for both aqueous and non-aqueous solutions of alcohols, aldehydes, carbohydrates, ketones, phenols and quinones. Hardy, Greenfield and Scargill⁵² concluded from infrared and partition data that two nitric acid molecules are bridged by a water molecule to form a dimer monohydrate in benzene, toluene and a number of other organic solvents. Siderov⁵³ and Thompson⁵⁴ have studied the formation of pyridine hydrates in carbon tetrachloride. They concluded from infrared studies that pyridine monomer monohydrates and dimer monohydrates exist in these solutions. Brode, et al.,⁵⁵ have

studied the hydration of dyes in alcoholic solutions and attribute the appearance of a new band in the visible region to the formation of a hydrogen bond between the azo group and water. Recently Mohr, Wild and Barrow⁵⁶ have studied water-base and water-alkylamine halide systems in carbon tetrachloride in the 3μ region. They report a 1:1 complex at low base concentrations; however, at higher base concentrations, bridged complexes involving one water and two base molecules were postulated.

Before hydration constants can be determined from water solubility data, the molecular complexity of water as a solute must be known. Relatively few studies have been reported of the variation of the apparent molecular weight of dissolved water as a function of its formal concentration in dilute solution. Nernst⁵⁷ in 1892 concluded from partial pressure measurements of aqueous ether solutions that water exists predominantly as single molecules in these solutions. Bruni and Amadroi⁵⁸ conducted a series of cryoscopic experiments to determine the average molecular weight of water in a number of solvents including bromoform, ethyl bromide and dimethyl aniline. They concluded that the water tends to associate at higher water concentrations. Roberts and Bury⁵⁹ conducted cryoscopic experiments in which they determined the average molecular weight of water in nitrobenzene at different water activities. They concluded that the data could be explained by assuming approximately 15 per cent association at the saturation concentration. However, using cryoscopic data Peterson and Rodebush⁶⁰ showed that water is primarily monomeric in benzene.

Recently Gordon, et al.,⁶¹ concluded from specific volume and viscosity data that water is highly polymerized in benzene and toluene at

temperatures above 60°. They calculated that dissolved water has an average molecular weight of approximately 2.5 times that of the monomer at 90 per cent of saturation at 67°. Ackermann,⁶² in an infrared study in the same temperature range, also concluded that water is highly polymerized in benzene, toluene and m-xylene at higher water concentrations. From Raman spectral studies Kipling⁶³ concluded that water dimerizes in acetic acid. Hogfeldt and Bolander⁶⁴ in a study of the extraction of nitric acid and water from aromatic solvents concluded that the water is primarily monomeric in benzene and nitrobenzene.

Christian, Affsprung and Taylor⁶⁵ have demonstrated the effect of dissolved water on the association of acetic acid in benzene and have presented a general method for calculating the hydration and association constants from partition and water solubility data. The hydration of trifluoroacetic acid in the vapor phase has been studied by Christian, Affsprung and Ling⁶⁶ using a vapor density apparatus. They concluded that trifluoroacetic acid forms monomer dihydrates in addition to acid dimers in the vapor phase. Lin, Christian and Affsprung,⁶⁷ who have studied the hydration of acetone in 1,2-dichloroethane at 25 and 35°, concluded that acetone forms a 1:1 complex with water over the concentration range investigated.

Techniques developed by Christian, Affsprung, et al.,^{68,69} make it possible to study the hydration of hydrogen-bonding molecules at various water activities. These techniques have been employed to study the nature of the phenol and phenol-water aggregates in several non-aqueous media.

CHAPTER II

OBJECTIVES

The objectives of this research were:

1. To determine the extent of self-association of phenol in several solvents.
2. To develop a method, involving measurement of water solubilities at reduced water activities, for investigating hydration equilibria of polar solutes in non-aqueous media.
3. To determine hydration parameters of phenol in several solvents of varying dielectric constant.
4. To determine the molecular complexity of water as a solute in a number of solvents.

CHAPTER III

EXPERIMENTAL

The phenol was a crystalline product of Allied Chemical Corporation. It was purified by two distillations at reduced pressure; the middle two-thirds being collected each time. To reduce the probability that the phenol might decompose on standing all samples were stored in an evacuated desiccator in the dark and were used within two weeks following preparation.

The solvents, carbon tetrachloride, cyclohexane, toluene, benzene, 1,1,2,2-tetrachloroethane and 1,2-dichlorethane, were purified by distillation through a 30-plate Oldershaw column, using a reflux-ratio of 10:1.

Fisher Certified Reagent Grade Calcium Chloride and Baker and Adamson C.P. Grade Sulfuric Acid were used to prepare solutions of constant water activity.

The partition and water solubility samples were allowed to reach equilibrium in a well-stirred water bath, maintained at a temperature of $25.0 \pm 0.1^\circ$. The bath had auxiliary heating and cooling sources; a 200-watt light bulb activated by a mercury regulator-electronic relay circuit was used as the fine temperature control. Partition samples were contained in 500 ml. glass-stoppered Erlenmeyer flasks; the aqueous phase had a volume of about 100 ml. and the volume of the organic phase was

about 200 ml. Phenol was added from an aqueous stock-solution. The samples were shaken several times during the first 24 hours and then allowed to equilibrate for 2 or 3 days.

All phenol solutions were analyzed spectrophotometrically for total phenol using a Beckman DU Spectrophotometer. The silica cells employed were obtained from the Beckman Corporation. Absorbances were measured at a peak wavelength of 268 m μ , with a slit width of 0.1 mm, for all but the phenol-benzene system, for which a peak wavelength of 274 m μ was used. Figure 1 shows that Beer's law was followed throughout the concentration range 10^{-4} to 10^{-3} moles/l. The molar absorptivities obtained were 1414 l/mole-cm at 268 m μ and 1250 l/mole-cm at 274 m μ . The phenol solutions used for standardization were obtained by diluting two standard solutions which had been prepared separately by weight from purified crystalline phenol. Several of the standards were analyzed independently by bromination titrations.⁷⁰ Concentrations of phenol determined by bromination differed less than 0.2 per cent from those calculated from weight of pure phenol.

In order to analyze the aqueous solutions for total phenol, the samples were diluted with water to a concentration within the range 10^{-4} to 10^{-3} mole/l. To analyze the organic phase for total phenol, aliquots were extracted with sufficient water to give a concentration of phenol within the range needed for ultraviolet analysis. In systems where the distribution ratio is much greater than one it is sometimes necessary to correct for the phenol remaining in the organic phase after water extraction. In the partition experiments, samples were withdrawn from the denser phase in a unique manner. Approximately 30 minutes before sampling a

about 200 ml. Phenol was added from an aqueous stock-solution. The samples were shaken several times during the first 24 hours and then allowed to equilibrate for 2 or 3 days.

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glass tube with a thin bulb on one end was introduced into denser phase of the partition system. To obtain a sample of this phase, the bulb was broken from the inside of the tube with a glass rod; a pipet was then inserted through the tube.

The solute isopiestic apparatus which was developed for performing the hydration studies is shown in Figure 2. It consists of a wide-mouth jar of approximately one liter capacity to which a test tube or a glass tube is attached. The glass tube fits over a vertical rod attached in a constant temperature water bath, so that the jar will float in an upright position and be agitated by the circulation of water. The 150 ml. beaker, A, resting on the bottom of the jar or suspended from the lid, contains a solution or solid of known water activity. Solution B is the phase to be equilibrated at a constant, known water activity. In some cases it may be desirable to interchange the position of the activity solution and the phase to be equilibrated, depending on the expected uptake of water. If the uptake of water will be large the phase to be equilibrated should be placed in the beaker. This allows a large quantity of the activity solution to be used, so that the loss of water to the phase being equilibrated will not affect the constancy of the water activity in the system. The system is closed from the atmosphere with layers of Saran Wrap and aluminum foil. The jar lid, which has a small hole in the top, is placed over the Saran Wrap and aluminum foil. To withdraw a sample, a hole is made through the layers of Saran Wrap and aluminum foil and the pipet is inserted. A piece of tape is temporarily placed over the hole after each sampling to maintain equilibrium until sampling is completed.

Aqueous calcium chloride or sulfuric acid solutions were used as constant water activity sources. A water activity range of 0.3 to 1.0 can be obtained with aqueous calcium chloride, while a range of 0.05 to 1.0 can be obtained with aqueous sulfuric acid at 25°. The choice of water activity source depends upon the nature of the solute which is being studied. For example, sulfuric acid cannot be used if a volatile basic compound is being studied, since a salt will form. Density measurements of the calcium chloride and sulfuric acid solutions were compared with available data to determine the water activity of each solution.⁷¹ The densities were determined using a Westphal density balance standardized with distilled water, taking the specific gravity of water to be 0.9971 at 25°. The reliability of the density measurements were checked by acid and chloride analyses; results indicated that water activities could be determined from density values to within 0.5 per cent.

Water analyses were made primarily with a Beckman KF-3 Aquameter which uses Karl Fischer reagent, a solution of iodine, sulfur dioxide and pyridine in methanol. A stock solution was prepared by dissolving 300 grams of iodine in 946 ml. (2 pt.) of dry pyridine in a 4 liter bottle, 2300 ml. of dry methanol (less than 0.05 per cent water) was then added.⁷² The freshly prepared stock solution was allowed to set for at least one day before any sulfur dioxide was added.

To prepare the reagent for the water analyses, one liter of the stock solution was transferred to the buret reservoir bottle and chilled by placing in a mixture of ice and water. At the same time, 60 ml. of sulfur dioxide was condensed in a cold trap immersed in a carbon dioxide-methanol solution. The liquid sulfur dioxide was then added quickly but

carefully to the chilled stock solution. The buret reservoir bottle containing the active reagent was then stoppered and allowed to come to room temperature after which the pressure was released on the system. The active reagent prepared in this way has a titer of approximately 3.5 milligrams of water per milliliter of reagent. The reagent may be diluted with dry methanol to approximately the desired titer, after which it should be allowed to stand for one day before use.

The Karl Fischer reagent was standardized ordinarily by weighing 200-milligram samples of Fisher Certified Reagent Grade sodium tartrate dihydrate into the titrating vessel and titrating the water present. From the weight per cent of water in the salt the titer was calculated in terms of milligrams of water per milliliter of reagent. The purity of the sodium tartrate dihydrate was checked by measuring the loss of weight of water on heating to 120°; results deviated less than 0.2 per cent from the theoretical weight loss predicted from the formula, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$.

The reagent was also standardized occasionally by titrating a methanol solution of known water content. The water-in-methanol-standard solution was prepared in a 250 ml. glass-stoppered volumetric flask. Water was weighed quantitatively into the flask using a weight buret so that the concentration would be 2 to 3 milligrams of water per milliliter of methanol. The volume was then adjusted with methanol obtained from a stock solution. Samples from the stock reservoir were titrated to determine the amount of water initially present. The titer was calculated after making a correction for the initial water present.

Experiments were conducted to determine the solubility of water in organic solvent as a function of the water activity. Approximately 100

to 200 ml. of the solvent was placed in the solute isopiestic cells at various water activities and then allowed to equilibrate. The time required for equilibration depends upon the amount of water which must be transferred by diffusion through the vapor phase. Figure 3 shows a rate study of the uptake of water in benzene and 1,2-dichloroethane. Note that the time required for equilibration in benzene with a water activity of 0.905 was approximately 8 hours. 1,2-dichloroethane, which dissolves considerably more water, required about 36 hours. Thus, the experimental samples were usually allowed to equilibrate for two or more days.

The dependence of water solubility on the water activity was also studied by distributing water directly between the organic solvents and aqueous calcium chloride solutions. No detectable amount of calcium chloride was extracted into the organic solvents, as determined by silver nitrate tests.

Water analyses were obtained simultaneously with phenol analyses. The sample sizes used for analysis varied depending upon the concentration of water present. 50 ml., 25 ml., and 10 ml. samples were used in the water determinations in carbon tetrachloride and cyclohexane, benzene and toluene, and 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, respectively.

Spectra in the O-H first overtone region of phenol were recorded on a Beckman Model DK-1 Spectrophotometer. The cells employed were Beckman cells with 1 and 2 centimeter pathlengths. The techniques employed were similar to those used by Worley.⁷³ Absorbances were recorded for phenol concentrations of 0.05 to 0.5 mole/l in carbon tetrachloride, benzene, 1,1,2,2-tetrachloroethane and 1,2-dichloroethane. The solutions were dried

in 50 ml. volumetric flasks using a drying cap filled with P_2O_5 . Approximately one day was allowed for equilibration.

The instrument was readjusted each time before the phenol solutions were scanned. The reference and sample cells were filled with dry solvent and the zero and 100% transmittance adjustments were made at the wavelength of the O-H absorption (approximately 1.4 μ). The sample cell was then filled with dry phenol solution using great care to minimize the exposure time to water vapor. Approximately 10 to 15 minutes were allowed for temperature equilibration before each spectrum was recorded. The sensitivity was maximized to give the smallest possible slit width. Each solution was analyzed for total phenol using procedures described earlier.

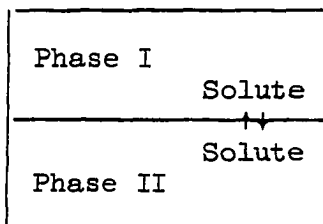
The solubility of benzene, carbon tetrachloride and 1,2-dichloroethane in water was determined using a vapor pressure measuring device similar to the one described by Grigsby⁷⁴ and Taha.⁷⁵ A 200-gram sample of pure water is placed in a flask serving as a reservoir. The apparatus is then evacuated through a Teflon vacuum stop-cock to approximately the vapor pressure of water. Samples of the organic compounds are added through a mercury-sealed sintered-glass, disc, using a micro-pipet or a micro-syringe. After equilibrium is attained, which varies from a few minutes to several hours, the total pressure of the solution is read from the manometer with the aid of a cathetometer. Samples of the organic compounds are added up to and beyond the saturation concentration. An abrupt break appears in a plot of organic concentration versus pressure at the concentration corresponding to the limiting solubility of the organic compound. The micro-pipet or micro-syringe is calibrated by delivering the organic samples into an evacuated weighing bottle which

incorporates the mercury-sealed, sintered-glass disc used in the vapor pressure measuring device.⁷⁶

CHAPTER IV

THEORY

The partition method is a convenient technique for studying the association of phenol. This method involves distributing a solute between water and a second immiscible solvent.



The chemical potential of the solute in phase I may be written as

$$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad \dots(1)$$

and in phase II as

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \quad \dots(2)$$

where a_1 and a_2 are the activities of the solute in the two phases. At equilibrium the chemical potential of the solute in phase I must be equal to the chemical potential of the solute in phase II and since μ_1° and μ_2° are constants at a definite temperature and pressure, then

$$\frac{a_1}{a_2} = \text{Constant} \quad \dots(3)$$

Furthermore, if the solutions behave ideally, in that Henry's and Raoult's laws are obeyed, the activities may be replaced by the respective mole

fractions so that

$$\frac{X_1}{X_2} = \text{Constant} \quad \dots(4)$$

In dilute solutions, solute mole fractions are nearly proportional to concentrations; hence Equation 4 can be written

$$\frac{C_1}{C_2} = \text{Constant} \quad \dots(5)$$

which is the distribution law derived by Nerst⁷⁷ in 1891.

When the solute is assumed to exist in various associated and hydrated forms, it is necessary to relate the formal concentrations of water and the polar solute to the monomer concentrations and various equilibrium constants. In other words, one assumes that the observed deviations from ideality in dilute solutions are due solely to molecular interactions which can be accounted for by appropriate equilibrium constants. One normally works in a solute concentration range in which the solute activity coefficients are equal to unity.

Assuming that the phenol species present in the organic phase are monomer(P), monomer dihydrate(PW₂), dimer monhydrate(P_wW) and trimer(P₃), the formal concentration of phenol can be written as

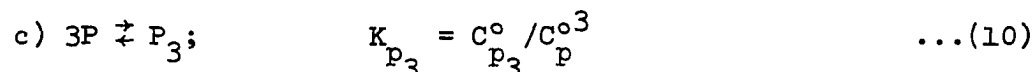
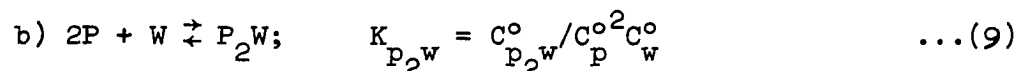
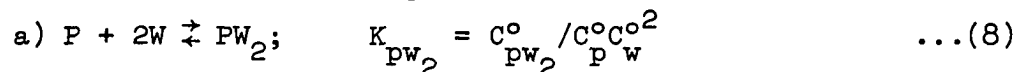
$$f_p^o = C_p^o + C_{pw_2}^o + 2C_{p_2w}^o + 3C_{p_3}^o \quad \dots(6)$$

where C_p^o , $C_{pw_2}^o$, $C_{p_2w}^o$, and $C_{p_3}^o$ represent the respective molarities of the species. If the phenol exists solely as a monomer in the aqueous phase, then the formal concentration is the monomer concentration in that phase. The ratio of the concentration of the monomer in the organic phase to the monomer concentration in the aqueous phase at infinite dilution is the distribution coefficient, K_d , which can be expressed as

$$K_d = C_p^o / C_p^w \quad \dots(7)$$

where C_p^w is the molar monomer concentration in the aqueous phase.

The reactions and equilibrium constants for the formation of the hydrogen bonded species PW_2 , P_2W and P_3 can be written as



where C_w^o is the monomer concentration of water. Substituting into Equation 6 the formation constants and $K_d C_p^w$ for the monomer concentration of phenol in the organic phase, the following expression is obtained

$$f_p^o = K_d C_p^w + K_d K_{PW_2} C_w^{o2} C_p^w + 2K_d^2 K_{P_2W} C_w^o C_p^{w2} + 3K_d^3 K_{P_3} C_p^{w3} \quad \dots(11)$$

Rearranging and dividing through by C_p^w gives

$$f_p^o / C_p^w = K_d (1 + K_{PW_2} C_w^{o2}) + 2K_d^2 K_{P_2W} C_w^o C_p^w + 3K_d^3 K_{P_3} C_p^{w2} \quad \dots(12)$$

If only monomers and dimers of phenol were present, a plot of f_p^o / C_p^w vs. C_p^w would yield a straight line with $K_d (1 + K_{PW_2} C_w^{o2})$ as the intercept and $2K_d^2 K_{P_2W} C_w^o$ as the slope.

If in addition to the phenol hydrates, one assumes the presence of monomers (W) and trimers (W_3) of water, the formal water concentration in the organic phase can be written as

$$f_w^o = C_w^o + 3C_{W_3}^o + 2C_{PW_2}^o + C_{P_2W}^o \quad \dots(13)$$

where C_w^o and $C_{W_3}^o$ are the molar concentrations of the monomer and trimer, respectively. Substituting in the appropriate formation constants for

C_{w_3} , C_{pw_2} and C_{p_2w} , Equation 13 becomes

$$f_w^o = C_w^o + 3K_{w_3} C_w^{o3} + 2K_d K_{pw_2} C_w^{o2} C_p^w + K_d^2 K_{p_2w} C_w^o C_p^w{}^2 \quad \dots(14)$$

Subtracting the terms arising from only monomers and trimers of water from both sides of Equation 14 and dividing by C_p^w yields

$$\frac{f_w^o - (C_w^o + 3K_{w_3} C_w^{o3})}{C_p^w} = \frac{\Delta f_w^o}{C_p^w} = 2K_d K_{pw_2} C_w^{o2} + K_d^2 K_{p_2w} C_w^o C_p^w \quad \dots(15)$$

where $\Delta f_w^o = f_w^o - (C_w^o + K_{w_3} C_w^{o3})$ is the concentration of water in the phenol hydrates.

Subtracting Equation 15 from Equation 11, the following is obtained

$$\frac{f_p^o - \Delta f_w^o}{C_p^w} = K_d(1 - K_{pw_2} C_w^{o2}) + K_d^2 K_{p_2w} C_w^o C_p^w + 3K_d^3 K_{p_3} C_p^w{}^2 \quad \dots(16)$$

Again, if only monomeric and dimeric phenol were present, a plot of

$\frac{f_p^o - \Delta f_w^o}{C_p^w}$ vs. C_p^w would yield a straight line with $K_d(1 - K_{pw_2} C_w^{o2})$ as

the intercept and $K_d^2 K_{p_2w} C_w^o$ as the slope. K_d and K_{pw_2} could then be calculated by determining the first terms in Equations 12 and 16 and solving for the constants simultaneously. The slope of Equation 16 should be one-half the slope of Equation 12 if P_2W was the only hydrated polymer of phenol.

Unfortunately, it is not possible to deduce the number of water molecules in the phenol monomer hydrate from distribution studies at constant water activity; furthermore, the molecular complexity of the free water in the organic solvents cannot be deduced from these experiments.

The solute isopiestic technique provides a method by which the water concentration in the solvent can be determined as a function of water activity. The water monomer concentration at a definite water activity can be expressed as

$$C_w^{\circ'} = C_w^{\circ} a_w \quad \dots(17)$$

where C_w° is a proportionality constant equal to the monomer water concentration at saturation and a_w is the water activity. The activity of water is defined by the relation

$$a_w = p/p^{\circ} \quad \dots(18)$$

where p is the partial pressure of water and p° is the vapor pressure of pure water at the designated temperature. Assuming that monomer-trimer equilibrium is established, the formal concentration at a particular water activity can be expressed as

$$f_w^{\circ} = C_w^{\circ} a_w + 3K_w^{\circ} C_w^{\circ 3} a_w^3 \quad \dots(19)$$

However, if only monomers of water are present then the formal concentration of water will equal $C_w^{\circ} a_w$. If the solute species present are P , PW_2 , P_2W , P_3 , W and W_3 the formal concentration of water in a non-aqueous medium can be expressed as

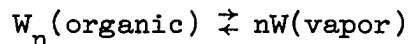
$$f_w^{\circ} = C_w^{\circ} a_w + 3C_w^{\circ 3} K_w^{\circ} a_w^3 + 2K_{pw_2}^{\circ} C_w^{\circ 2} a_w^2 C_p^{\circ} + K_{p_2w}^{\circ} C_w^{\circ} a_w C_p^{\circ 2} \quad \dots(20)$$

and the formal concentration of phenol as

$$f_p^{\circ} = C_p^{\circ} + C_w^{\circ 2} K_{pw_2}^{\circ} a_w^2 C_p^{\circ} + 2C_w^{\circ} K_{p_2w}^{\circ} a_w C_p^{\circ 2} + 3K_{p_3}^{\circ} C_p^{\circ 3} \quad \dots(21)$$

The constants obtained from the partition data can be used in Equations 20 and 21 to determine the consistency of the postulated species with data

obtained at reduced water activities. It could be argued that the water unit in the organic phase is a cluster, rather than the monomer. For example, suppose that the equilibrium



exists, where W_n is a cluster of n water molecules in the organic phase and W is the monomer in the vapor phase. The equilibrium constant might then be written

$$K = \frac{(a_w^v)^n}{a_{w_n}^o} \quad \dots(22)$$

where a_w^v and $a_{w_n}^o$ are the monomer and cluster activities, respectively. In dilute solutions

$$a_{w_n}^o = C_{w_n}^o = f_w^o/n \quad \dots(23)$$

and the equilibrium constant becomes

$$K = (a_w^v)^n / (f_w^o/n) \quad \dots(24)$$

$$\text{or} \quad f_w^o = n(a_w^v)^n / K \quad \dots(25)$$

It can be seen then that if f_w^o varies linearly as a_w^v then n must equal unity. The logarithmic form of Equation 25 is

$$\log f_w^o = \log \frac{n}{K} + n \log a_w^v \quad \dots(26)$$

A plot of $\log f_w^o$ versus $\log a_w^v$ should yield a straight line with the slope equal to the number of water molecules per cluster, provided that a single type of cluster is present.

CHAPTER V

RESULTS AND CALCULATIONS

The water solubility data at various water activities in carbon tetrachloride and cyclohexane at 25° are given in Tables 2 and 4 and are plotted versus water activity in Figure 4. Based on the linearity of the plot, f_w^0 vs. a_w , the data support the conclusion that water dissolves primarily as monomeric units in carbon tetrachloride and cyclohexane. Water solubility data in carbon tetrachloride were obtained by vapor equilibration at different water activities using the solute isopiestic technique and by partitioning water directly between aqueous calcium chloride solutions and carbon tetrachloride. Silver nitrate tests showed that no detectable amount of calcium chloride extracted into the organic phase. Good agreement was obtained by both methods. The limiting solubility at unit activity (saturation) is 0.0087 ± 0.0003 moles/l. The limiting solubility of water in cyclohexane at unit activity is 0.0024 ± 0.0003 moles/l. Considerable difficulty was encountered in titrating the cyclohexane samples for water, since cyclohexane is not sufficiently miscible with methanol, the solvent employed.

The water solubility data at various water activities in benzene and toluene at 25° are given in Tables 5 to 8 and are plotted versus water activity in Figure 5. Earlier solubility for benzene solutions analyzed by manual Karl Fischer titrations are included along with data obtained

with the Beckman KF-3 Aquameter. The aquameter yielded better precision than the manual titration, which employed a dead-stop indication. The water solubilities in benzene solutions were obtained by using both the vapor equilibration and partition techniques. Again good agreement was found for the two methods employed. The data support the conclusion that water dissolves primarily as monomeric units in benzene and toluene; the limiting solubilities at unit water activity are 0.0349 ± 0.0005 and 0.0274 ± 0.0005 moles/l, respectively.

The water solubility data at various water activities in 1,2-dichloroethane at 25° and 10° and in 1,1,2,2-tetrachloroethane at 25° are given in Tables 9 to 11 and are plotted versus water activity in Figure 6. The plots show positive, curvature, indicating some polymerization of water in the organic phases. The data were subjected to least squares analysis in which the formal water solubility was fitted as a function of the water activity. It was found that in all cases that the assumption of monomer-dimer equilibrium gave a poorer fit of the data than the assumption of monomer-trimer or monomer-tetramer equilibrium. The monomer-dimer assumption gave a root mean square deviation 5 to 25% larger than the monomer-trimer equilibrium and 1.5 to 70% larger than the monomer-tetramer equilibrium. While the data are not sufficiently accurate to distinguish between monomer-trimer or monomer-tetramer equilibrium it is believed that the data cannot be explained to within estimated experimental error by assuming monomer-dimer equilibrium. Various combination of three species were also tried, but little improvement in the fit of data was noted. In considering the various combinations of three species in which one of these species was a dimer, the least squares parameter for the dimer was negative

in all cases. Again, this gives support to the conclusion that the dimer is not a major species. A summary of the parameters and root mean square deviations for the various combinations of species considered are given in Table 12. The solid lines in Figure 6 have been calculated using the trimer equilibrium constants obtained from the least squares analysis. The formal water solubility in 1,2-dichloroethane at 25° and 10° and in 1,1,2,2-tetrachloroethane at 25° are 0.1262 ± 0.0014 , 0.0829 ± 0.0010 and 0.1010 ± 0.0012 moles/l, respectively. A summary of the formal water solubilities and equilibrium parameters are given in Table 13 for the organic solvents studied. The tetramer formation constants of water in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane are also given for comparison.

Log-log plots of f_w° vs. a_w are given in Figure 7 for the solvents studied. Assuming that water is essentially monomeric in the vapor phase, the data indicate that the basic water units in the organic phases are monomers. The slope of the solid lines in Figure 7 are unity and the curvature noted in the systems, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane at the higher water activities is interpreted as evidence for the existence of monomer-trimer or monomer-tetramer equilibrium.

The partition data for phenol distributed between 1,2-dichloroethane and water at 25° are given in Table 14. The ratio of the concentration of phenol in the organic phase to the concentration of phenol in the aqueous phase is plotted versus the concentration of phenol in the aqueous phase in Figure 8. The data were subjected to least squares analysis in which the ratio, f_p°/C_p^W was fitted as a function of C_p^W . The assumption of monomer-dimer equilibrium fitted the data better than the monomer-trimer equilibrium and the assumption of monomer-dimer-trimer equilibrium did

not improve the fit significantly. The root mean square deviations and parameters for the assumed species are given in Table 23. Water solubility data were obtained in conjunction with the partition studies and are given in Table 15. The increase in water solubility resulting from the presence of phenol in 1,2-dichloroethane was assumed to be due to the formation of hydrates. The ratio of the difference between the total organic phenol concentration and the bound-water concentration, Δf_w^o , to the concentration of phenol in the aqueous phase is plotted versus the concentration of phenol in the aqueous phase in Figure 8. Water solubility data at various water activities for phenol solutions are given in Table 15. The total concentration of water, f_w^o , is plotted versus the total concentration, f_p^o , in the organic phase in Figure 9. The solid lines in Figures 8 and 9 are calculated using the best set of constants obtained from the least squares analyses and error calculations, assuming the species to be phenol monomer, monomer dihydrates, dimer monohydrates and water monomers and trimers. It was not necessary to assume any self-association of phenol in 1,2-dichloroethane to explain the partition and water solubility data. The partition and water solubility parameters are given in Table 20.

The partition data of phenol distributed between benzene and water at 25° are given in Table 16. The water solubility at unit water activity and partition data are plotted in Figure 10 as f_p^o/C_p versus C_p^w and $\frac{f_p^o - \Delta f_w^o}{C_p^w}$ vs. C_p^w . For comparison the phenol data of Philbrick are also included in the plot. The data of Philbrick agree very well with the present data. It appears that his data scattered somewhat less than the present data.

The larger errors reported here might be attributed to the problem encountered in the analysis of phenol in the benzene phase. Normally a small aliquot of the organic phase was diluted with water and the aqueous phase was analyzed for the total phenol extracted. However, water saturated with benzene absorbs significantly at 268 μ , which is the wavelength used for the analysis. Therefore, the partition samples were prepared in such a way that the total phenol concentrations were known. After equilibrium had been attained the aqueous phases were analyzed in the usual manner and the concentration in the benzene phases were determined by difference. It was found later that one could analyze for the phenol in water saturated with benzene by using the peak wavelength 274 μ , since benzene does not seem to absorb significantly at this wavelength. This wavelength was used to analyze for the total phenol present in later experiments. The water solubility data are given in Table 17 and the data are plotted as f_w^o , the total concentration of water, versus f_p^o , the total phenol concentration, in Figure 11. It was necessary to assume the presence of phenol trimers in addition to phenol monomers, monomer dihydrates and dimer monohydrates and water monomers to explain the partition and water solubility data. The solid lines in Figures 10 and 11 are calculated using the best constants for the assumed species obtained from the least squares analyses and error calculations given in Table 20.

The partition data for phenol distributed between 1,1,2,2-tetrachloroethane and water at 25° are given in Table 18. The water solubility data at unit water activity and the partition data are plotted in Figure 12 as f_p^o/C_p^w vs. C_p^w and $\frac{f_p^o - \Delta f_w}{C_p^w}$ vs. C_p^w . The water solubility data at various

water activities are given in Table 19, and are plotted in Figure 13 as f_w^o versus f_p^o . It was found from the least squares analyses and error calculations that the data could best be explained by assuming phenol monomers, monomer dihydrates, dimer monohydrates, trimers and water monomers and trimers. The solid lines in Figures 12 and 13 are calculated using the constants given in Table 20.

The partition data of phenol distributed between carbon tetrachloride and water at 25° are given in Table 21. The data are plotted as f_p^o/C_p^w vs. C_p^w in Figure 14. The partition data of Badger and Greenough at 28° and Herz and Rathmann at 25° are also included in the plot. The positive curvature of the plot f_p^o/C_p^w vs. C_p^w indicated that associated species having higher molecular weights than the dimer are present in the carbon tetrachloride phase. Judging from the limiting slope, the concentration of the dimeric units is not very great. While it is not possible to say that the limiting slope is zero, as it would be if the dimeric units were absent, it is worth noting that Philbrick could not detect any systematic change of the ratio f_p^o/C_p^w over the organic concentration range of 0.02 to 0.1 molar. Least square analyses assuming various combinations of two and three parameters were obtained and are given in Table 23. The partition data could be fitted quite well over the concentration range by assuming phenol monomers, trimers, and hexamers. The water solubility data are given in Table 22 and are plotted versus the formal phenol concentration in Figure 5. In fitting the water solubility data it was necessary to assume the presence of phenol monomer monohydrates and trimer monohydrates to explain the data up to phenol concentrations less than 0.15 molar for all activities. However, it was necessary to postulate hydrated species

having more than three phenol molecules to explain all the solubility data at all water activities. The data could be explained by assuming the important hydrate species to be either (a) PW , P_3W and P_6W_4 or (b) PW , P_3W , P_3W_2 and P_6W_3 . Although combination (a) has one less hydrated species than combination (b), the latter was chosen as being physically more plausible. The lines in Figures 14 and 15 are calculated using the constants given in Table 24.

The partition data for phenol at 35° distributed between carbon tetrachloride and water are given in Table 25. Least squares analyses of the plot shows that the assumption of phenol monomer-trimer-hexamer fitted the data as well as any of the other combinations. No water solubility data were obtained for the phenol solutions in carbon tetrachloride at 35°.

The infrared peak absorbances for the O-H first overtone for anhydrous phenol solution- in 1,2-dichloroethane, benzene, 1,1,2,2-tetrachloroethane and carbon tetrachloride are given in Tables 26 to 29. The free hydroxyl stretching frequencies in the first overtone region occur approximately at 1.380 μ for benzene, at 1.375 μ for 1,2-dichloroethane, at 1.360 μ for 1,1,2,2-tetrachloroethane and at 1.357 μ for carbon tetrachloride. It was noted that the O-H peak for phenol in benzene has a split peak; this has been interpreted by Mecke, et. al., as arising from intermolecular hydrogen bonding of the O-H group with benzene molecules.

The absorbance data are plotted versus the formal phenol concentration in Figure 16. The infrared data in the O-H overtone region indicate that phenol associates little, if any at all in 1,2-dichloroethane, benzene and 1,1,2,2-tetrachlorethane for concentrations up to 0.5 molar; however, the data indicate that phenol is highly associated in carbon tetrachloride.

It was possible to fit the absorbance data using the self-association constants obtained from partition studies and a single unknown parameter, the extinction coefficient (equal to 0.332 l/mole-cm).

Solubility data for 1,2-dichloroethane, benzene and carbon tetrachloride in water at 25° are given in Table 30 to 32. These data, obtained using the vapor pressure-measuring device, are plotted as a function of the partial pressure of the organic compound in Figures 17 to 19. The limiting solubility of 1,2-dichloroethane, benzene and carbon tetrachloroethane in water at 25° are 0.0895, 0.022 and 0.0051 moles/l, respectively.

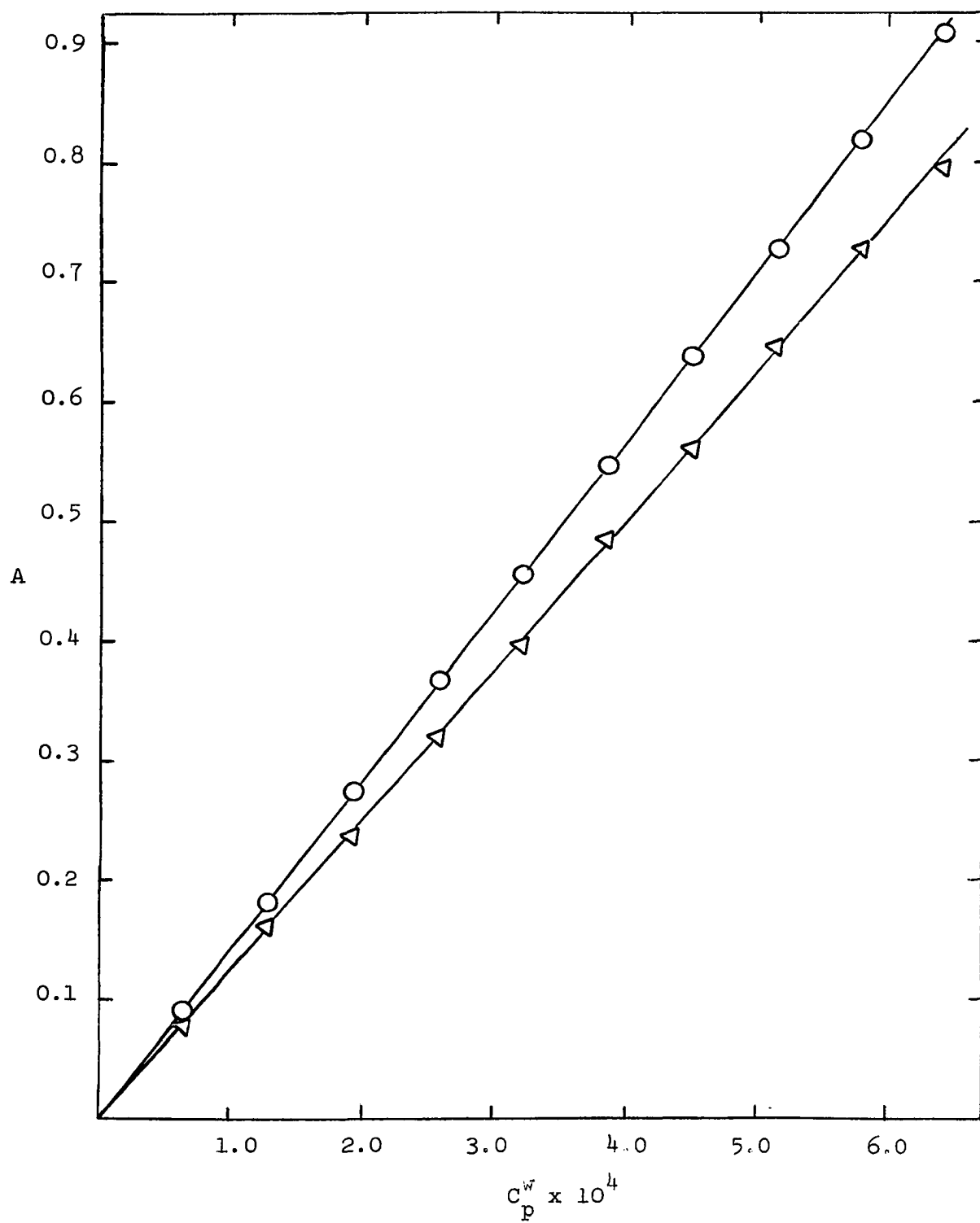


Figure 1. Beer's law plot for phenol in water at 268mμ and 274mμ.

TABLE 1

BEER'S LAW DATA FOR PHENOL IN WATER AT 268m and 274m

$C_p^w \times 10^4$ (moles/liter)	A (268m)	A (274m)
0.643	0.092	0.078
1.286	0.182	0.162
1.929	0.274	0.236
2.572	0.367	0.321
3.215	0.456	0.398
3.858	0.549	0.487
4.501	0.638	0.563
5.144	0.728	0.647
5.787	0.820	0.728
6.430	0.908	0.796

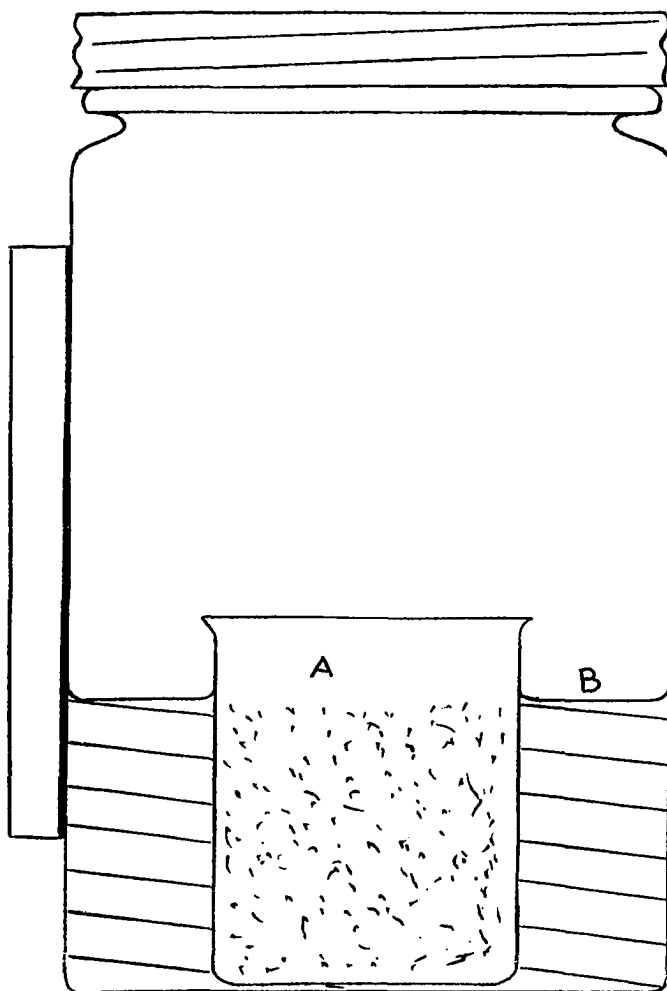


Figure 2. Solute isopiestic apparatus.

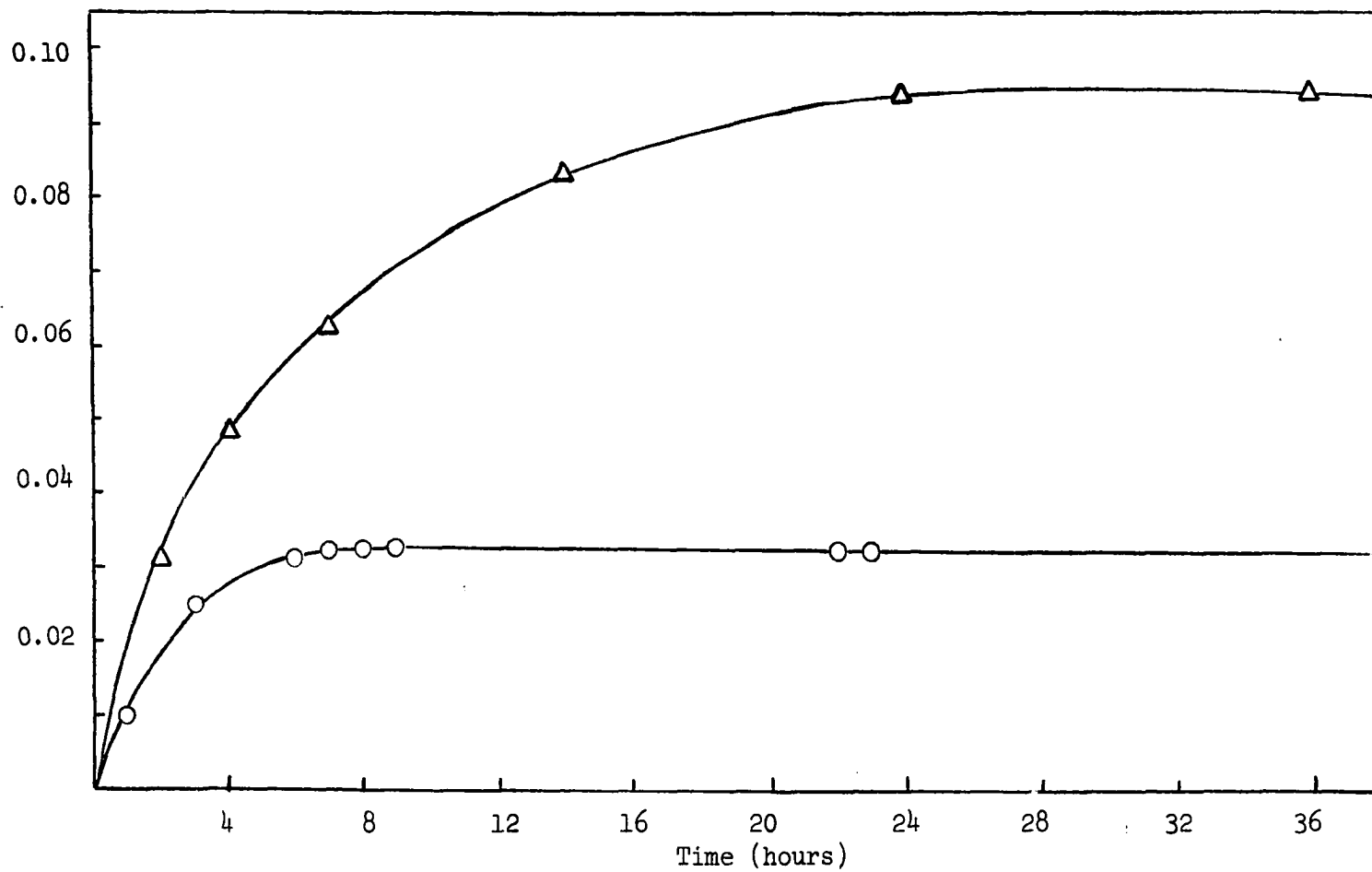


Figure 3. Equilibration rate data at 25°; $\circ$, Benzene at $a_w = 0.9$, Δ , 1,2-Dichloroethane at $a_w = 0.808$.

TABLE 2

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
CARBON TETRACHLORIDE AT 25°, USING SOLUTE ISOSPIESTIC METHOD.

f_w° (moles/liter)	a_w
0.0021	0.26
0.0024	
0.0022	
0.0039	0.47
0.0041	
0.0041	
0.0062	0.69
0.0063	
0.0083	0.89
0.0083	
0.0085	0.945
0.0085	
0.0087	1.0
0.0091	
0.0084	
0.0088	
0.0088	

TABLE 3

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
CARBON TETRACHLORIDE AT 25°, USING PARTITION METHOD.

f_w^o (moles/liter)	a_w
0.0046	0.52
0.0058	0.65
0.0069	0.78
0.0075	0.85
0.0082	0.95
0.0092	1.0
0.0090	

TABLE 4

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES
IN CYCLOHEXANE AT 25°, USING SOLUTE ISOPIESTIC METHOD.

f_w° (moles/liter)	a_w
0.0009	0.434
0.0009	
0.0016	0.616
0.0015	
0.0022	0.85
0.0020	
0.0023	1.0
0.0022	
0.0024	
0.0024	
0.0022	

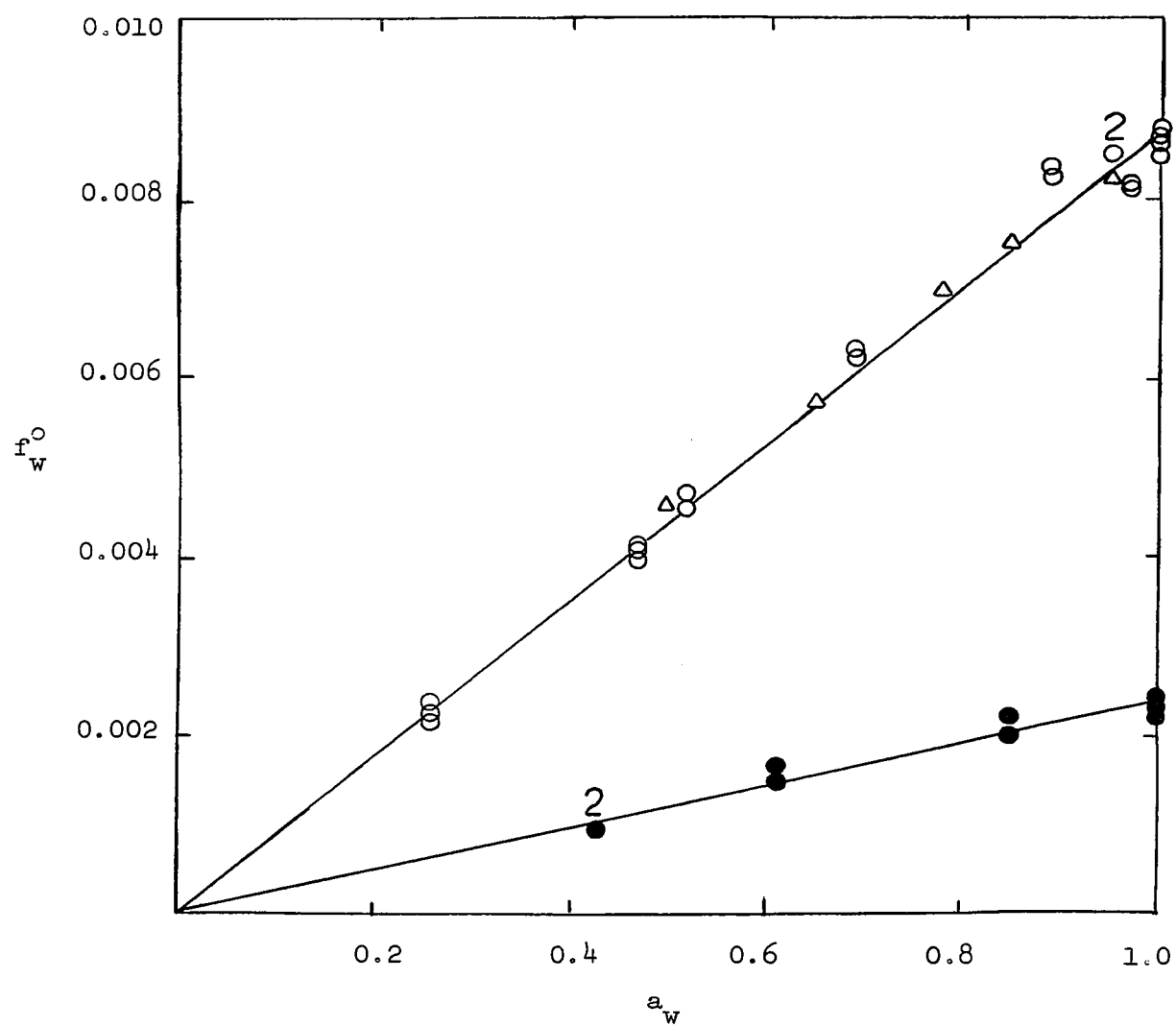


Figure 4. Formal solubility of water at 25° in: Δ , carbon tetrachloride, using the partition method; $\bigcirc$, carbon tetrachloride, using solute isopiestic method; $\bullet$, cyclohexane, using the solute isopiestic method.

TABLE 5

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES
IN BENZENE AT 25°, USING SOLUTE ISOPIESTIC METHOD.

f_w° (moles/liter)	a_w
0.0062	0.175
0.0065	
0.0066	
0.0091	0.256
0.0147	0.434
0.0150	
0.0154	
0.0208	0.616
0.0212	
0.0212	
0.0263	0.756
0.0261	
0.0279	0.808
0.0280	
0.0309	0.89
0.0317	
0.0349	1.0
0.0350	
0.0349	
0.0349	
0.0351	
0.0352	
0.0352	
0.0351	

TABLE 6

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES
IN BENZENE AT 25°, USING PARTITION METHOD.

f_w° (moles/liter)	a_w
0.0179 0.0181	0.52
0.0226 0.0224	0.65
0.0271 0.0272	0.78
0.0300 0.0299	0.85
0.0330 0.0333	0.95
0.0350 0.0354	1.0

TABLE 7

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
BENZENE, AT 25° USING THE MANUAL KARL FISCHER TITRATION.

C_w	a_w
0.0331	0.94
0.0298	0.84
0.0242	0.695
0.0184	0.60
0.0083	0.225
0.0321	0.94
0.0288	0.84
0.0249	0.695
0.0199	0.60
0.0331	0.96
0.0285	0.798
0.0213	0.605
0.0127	0.375
0.0071	0.181
0.0348	1.0
0.0345	0.96
0.0283	0.798
0.0209	0.605
0.0117	0.375
0.0078	0.181
0.0350	1.0

TABLE 8

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES
IN TOLUENE AT 25°, USING SOLUTE ISOPIESTIC METHOD.

f_w° (moles/liter)	a_w
0.0048	0.175
0.0044	
0.0043	
0.0070	0.256
0.0068	
0.0075	
0.0117	0.434
0.0114	
0.0167	0.616
0.0165	
0.0204	0.756
0.0205	
0.0219	0.808
0.0219	
0.0246	0.89
0.0246	
0.0276	1.0
0.0274	
0.0276	
0.0276	

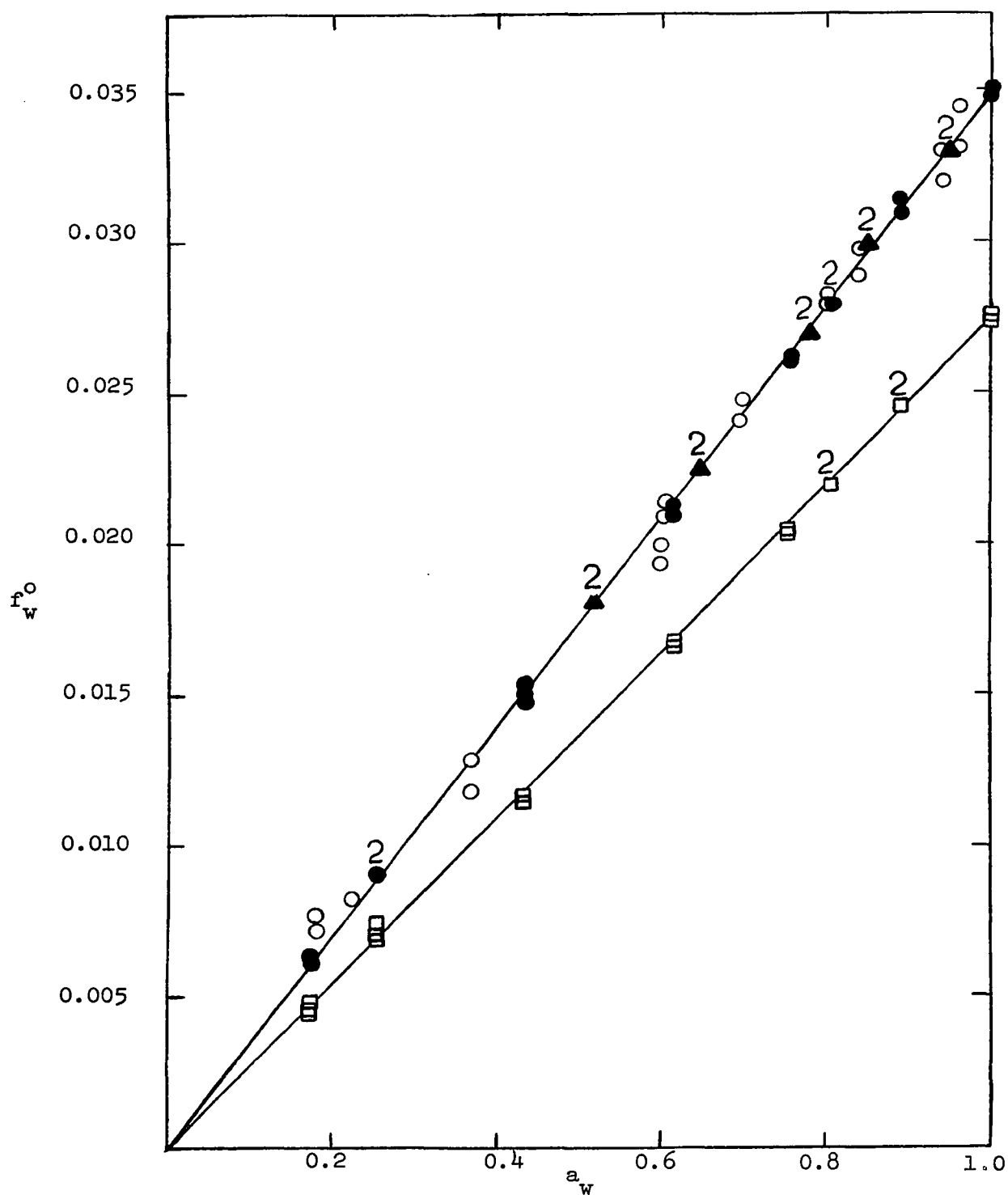


Figure 5. Formal solubility of water at 25° in: ●, benzene using the solute isopiestic method; ▲, benzene using the partition method; ○, benzene, earlier data; □, toluene using the solute isopiestic method.

TABLE 9

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
1,2-DICHLOROETHANE AT 25°, USING SOLUTE ISOPIESTIC METHOD.

f_w^o (moles/liter)	a_w
0.0193	0.175
0.0193	
0.0201	
0.0185	
0.0186	
0.0280	0.250
0.0279	
0.0283	
0.0280	
0.0280	
0.0404	0.35
0.0397	
0.0397	
0.0452	0.395
0.0447	
0.0438	
0.0485	0.434
0.0491	
0.0489	
0.0516	0.47
0.0516	
0.0517	
0.0532	
0.0520	
0.0515	
0.0610	0.54
0.0607	
0.0607	
0.0625	0.55
0.0625	

TABLE 9 ...continued

f_w^o (moles/liter)	a_w
0.0715	0.615
0.0709	
0.0707	
0.0717	0.616
0.0720	
0.0814	0.693
0.0807	
0.0794	
0.0806	
0.0800	
0.0874	0.74
0.0876	
0.0874	
0.0885	0.756
0.0895	
0.0890	
0.0981	0.808
0.0981	
0.0981	
0.0940	
0.0946	
0.0986	
0.0978	
0.1048	0.85
0.1047	
0.1055	0.89
0.1063	
0.1057	
0.1100	
0.1110	
0.1139	0.90
0.1118	
0.1111	

TABLE 9 ...continued

f_w^o (moles/liter)	a_w
0.1129	0.94
0.1136	
0.1133	
0.1127	
0.1160	0.945
0.1158	
0.1147	
0.1175	0.95
0.1162	
0.1165	
0.1168	
0.1265	1.0
0.1267	
0.1268	
0.1261	
0.1264	
0.1266	
0.1274	
0.1268	
0.1270	
0.1285	
0.1279	
0.1261	
0.1276	
0.1267	
0.1273	
0.1262	

TABLE 10

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
1,2-DICHLOROETHANE AT 10°, USING SOLUTE ISOPIESTIC METHOD.

f_w°	a_w
0.0168	0.242
0.0318	0.461
0.0501	0.682
0.0677	0.882
0.0734	0.944
0.0829	1.00
0.0105	0.160
0.0163	0.238
0.0292	0.418
0.0422	0.603
0.0589	0.800
0.0819	1.0

TABLE 11

FORMAL SOLUBILITIES OF WATER AT VARIOUS WATER ACTIVITIES IN
1,1,2,2-TETRACHLOROETHANE AT 25°, USING SOLUTE ISOPIESTIC METHOD.

f_w^o (moles/liter)	a_w
0.0187	0.175
0.0194	
0.0178	
0.0252	0.256
0.0250	
0.0250	
0.0410	0.434
0.0410	
0.0588	0.616
0.0588	
0.0660	0.693
0.0660	
0.0720	0.756
0.0720	
0.0786	0.808
0.0787	
0.0883	0.89
0.0884	
0.0945	0.945
0.0945	
0.1010	1.0
0.1014	
0.1020	
0.1020	
0.1014	

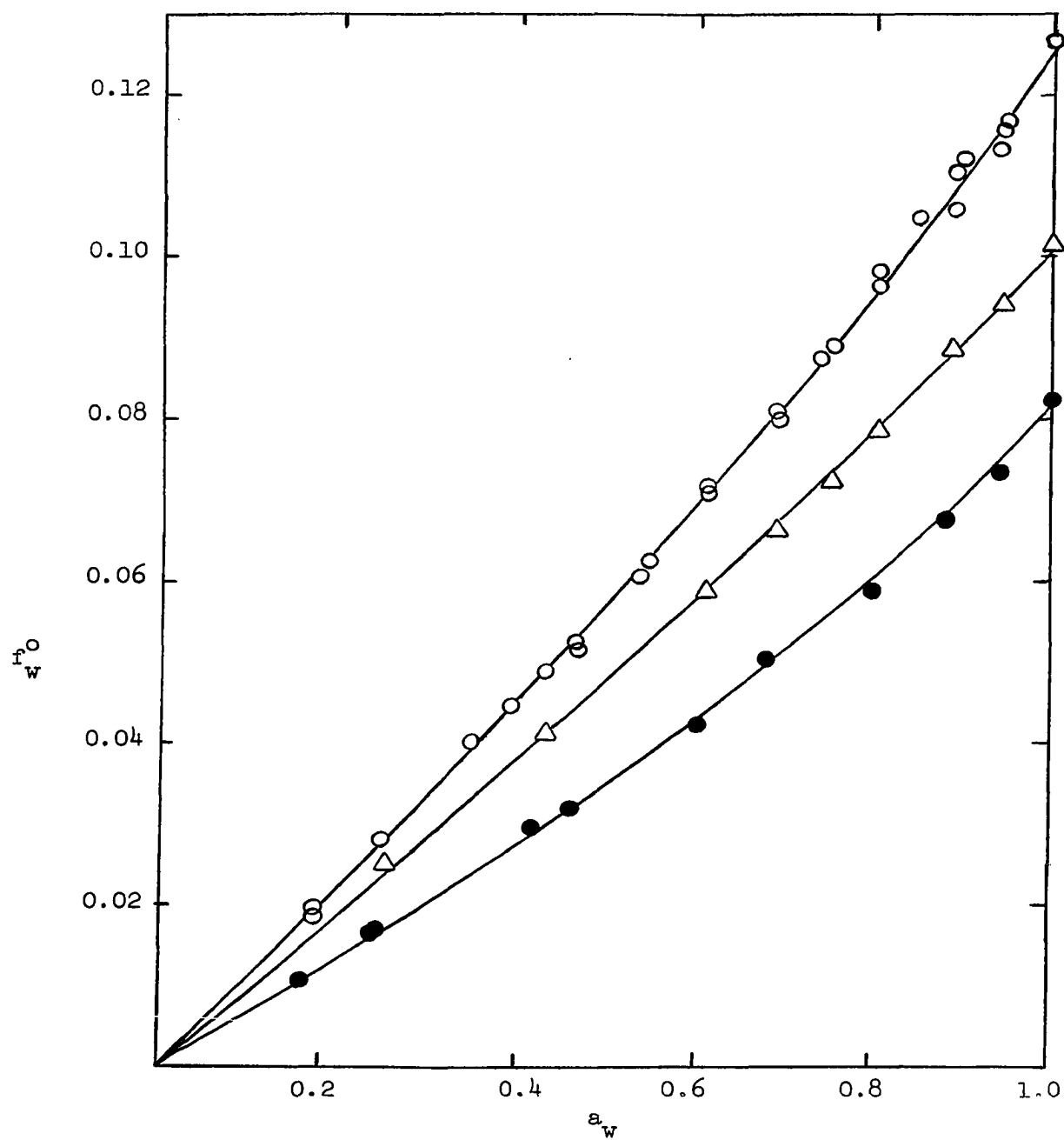


Figure 6. Formal solubility of water in: O, 1,2-dichloroethane at 25°; Δ, 1,1,2,2-tetrachloroethane at 25°; ●, 1,2-dichloroethane at 10°. Each point represents an average of 2 or 3 measurements.

TABLE 12

LEAST SQUARE PARAMETER FOR $f_W^o = \alpha a_W + \beta a_W^m + \gamma a_W^n$

SOLVENT	POSTULATED SPECIES	m	n	α	β	ROOT MEAN SQUARE	
						γ	DEVIATION
1,2-dichloroethane (25°)	monomer-dimer	2	-	0.102	0.0224	-	0.00139
	monomer-trimer	3	-	0.109	0.0161	-	0.00132
	monomer-tetramer	4	-	0.112	0.0141	-	0.00137
	monomer-dimer-trimer	2	3	0.1095	-0.0006	0.0164	0.00135
	monomer-dimer-tetramer	2	4	0.1070	-0.0102	0.00784	0.00136
	monomer-trimer-hexamer	3	6	0.1088	0.0172	-0.00101	0.00135
1,2-dichloroethane (10°)	monomer-dimer	2	-	0.0584	0.0222	-	0.00149
	monomer-trimer	3	-	0.0650	0.0162	-	0.00110
	monomer-tetramer	4	-	0.0675	0.0142	-	0.00087
	monomer-dimer-trimer	2	3	0.0740	-0.028	0.0353	0.00089
	monomer-dimer-tetramer	2	4	0.0708	-0.0076	0.0186	0.00081
	monomer-trimer-hexamer	3	6	0.0689	0.0024	0.01067	0.00080
1,1,2,2,-tetrachloro-ethane (25°)	monomer-dimer	2	-	0.0897	0.0109	-	0.00143
	monomer-trimer	3	-	0.0925	0.00848	-	0.00120
	monomer-tetramer	4	-	0.0937	0.00755	-	0.00105
	monomer-dimer-trimer	2	3	0.1088	-0.0473	0.0404	0.00059
	monomer-dimer-tetramer	2	4	0.104	-0.0224	0.0198	0.00065
	monomer-trimer-hexamer	3	6	0.0978	-0.0082	0.0121	0.00083

TABLE 13

SOLUBILITIES AND ASSOCIATION CONSTANTS OF WATER IN ORGANIC SOLVENTS

SOLVENT	f_w^o (mole/l)	c_w^o (mole/l)	K_3 (1/mole) ²	c_w^o (mole/l)	K_4 (1/mole) ³
1,1,2,2-Tetrachloroethane(25°)	0.1010 $\pm$ 0.0012	0.0925 $\pm$ 0.0009	3.6 $\pm$ 0.6	0.0937 $\pm$ 0.0007	24.5 $\pm$ 3.5
1,2-Dichloroethane (25°)	0.1262 $\pm$ 0.0014	0.1083 $\pm$ 0.0007	4.6 $\pm$ 0.3	0.1113 $\pm$ 0.0005	24.5 $\pm$ 1.5
1,2-Dichloroethane (10°)	0.0812 $\pm$ 0.0010	0.0650 $\pm$ 0.0006	20 $\pm$ 3	0.0670 $\pm$ 0.0005	172 $\pm$ 24
Benzene (25°)	0.0349 $\pm$ 0.0005				
Toluene (25°)	0.0274 $\pm$ 0.0005				
Carbon Tetrachloride (25°)	0.0087 $\pm$ 0.0003				
Cyclohexane (25°)	0.0024 $\pm$ 0.0003				

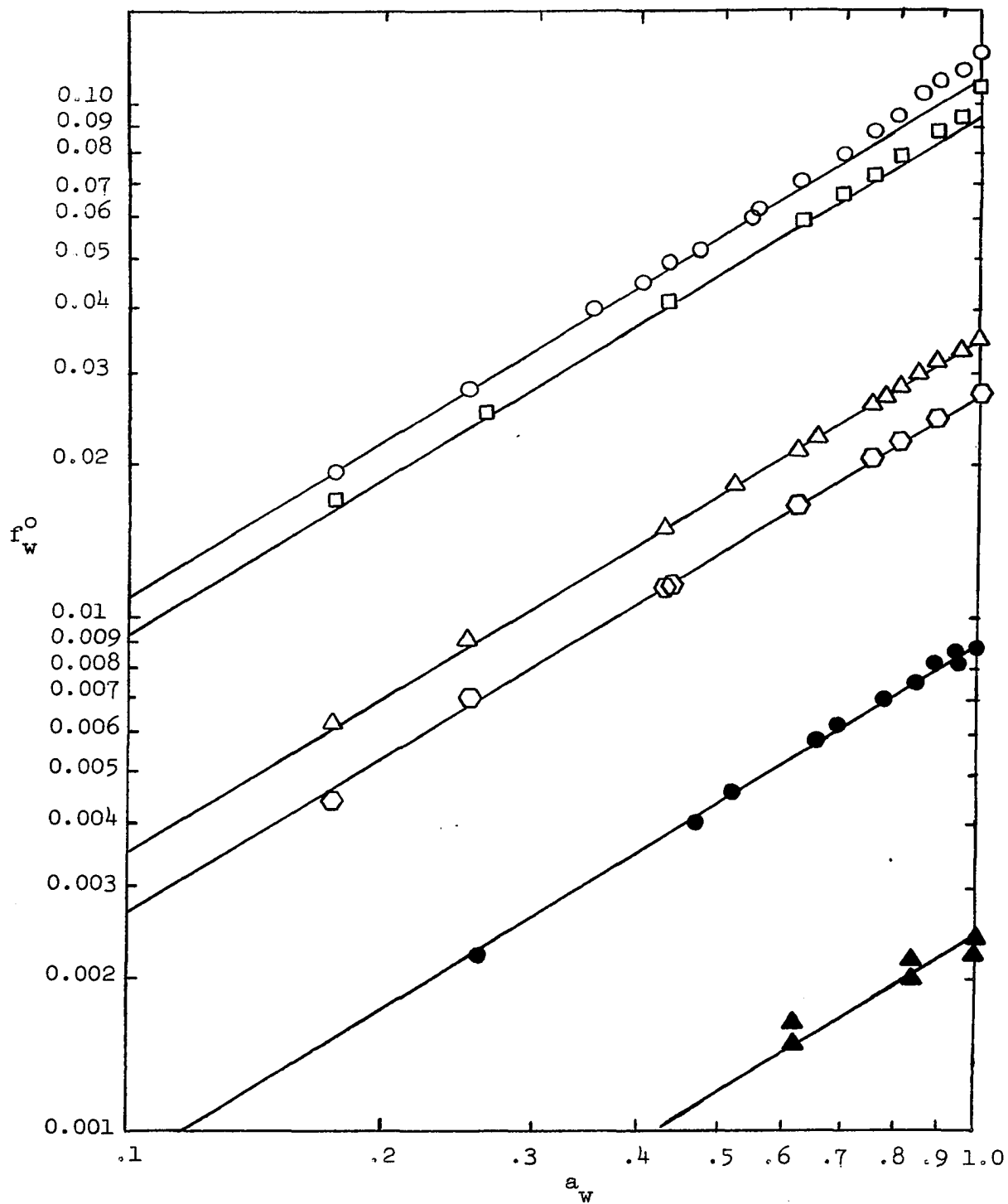


Figure 7. Formal solubility of water at 25° in: O, 1,2-dichloroethane; □, 1,1,2,2-tetrachloroethane; △, Benzene; ◇, Toluene; ●, Carbon tetrachloride and ▲, cyclohexane at various water activities.

TABLE 14

PARTITION DATA FOR THE SYSTEM 1,2-DICHLOROETHANE-WATER-PHENOL AT 25°.

f_p^o (moles/liter)	C_p^w (moles/liter)	f_p^o/C_p^w
0.0084	0.0020	4.211
0.0259	0.0060	4.332
0.0495	0.0115	4.315
0.1026	0.0230	4.457
0.1574	0.0350	4.500
0.2077	0.0443	4.694
0.2562	0.0536	4.779
0.3176	0.0657	4.836
0.3904	0.0781	5.000
0.4483	0.0877	5.116
0.4854	0.0934	5.199
0.0813	0.0182	4.463
0.0904	0.0202	4.486
0.0867	0.0195	4.448
0.1314	0.0286	4.554
0.2421	0.0510	4.747
0.2782	0.0582	4.779
0.3125	0.0639	4.888
0.3835	0.0767	4.999
0.3785	0.0760	4.980

TABLE 15

WATER SOLUBILITY DATA FOR THE PHENOL-1,2-DICHLOROETHANE
SYSTEM AT VARIOUS WATER ACTIVITIES AT 25°.

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.0084	0.1319 0.1312 0.1300 0.1314	1.0
0.0259	0.1367 0.1355 0.1352	1.0
0.0495	0.1407 0.1411 0.1407	1.0
0.1026	0.1556 0.1559 0.1556	1.0
0.1574	0.1686 0.1698 0.1690	1.0
0.2077	0.1834 0.1846 0.1846	1.0
0.2562	0.2007 0.1995 0.1995	1.0
0.3176	0.2206 0.2194 0.2194	1.0
0.3904	0.2427 0.2446 0.2443	1.0
0.4483	0.2673 0.2681	1.0

TABLE 15---continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.4854	0.2810 0.2817	1.0
0.1146	0.1251 0.1218 0.1229	0.85
0.2546	0.1580 0.1575	0.85
0.3472	0.1846 0.1852	0.85
0.3946	0.1931 0.1931	0.85
0.00	0.1031 0.1031	0.85
0.1174	0.0974 0.0986	0.70
0.2546	0.1246 0.1234	0.70
0.3593	0.1439 0.1444	0.70
0.3982	0.1507 0.1504	0.70
0.00	0.0819 0.0821	0.70
0.1253	0.1025 0.1018	0.70
0.2458	0.1272 0.1257	0.70
0.3642	0.1487 0.1484	0.70
0.4887	0.1755 0.1757	0.70

TABLE 15 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.00	0.0819 0.0822	0.70
0.1167	0.0753 0.0758	0.55
0.2546	0.0945 0.0938	0.55
0.3564	0.1074 0.1085	0.55
0.3904	0.1153 0.1150	0.55
0.00	0.0617 0.0612	0.55

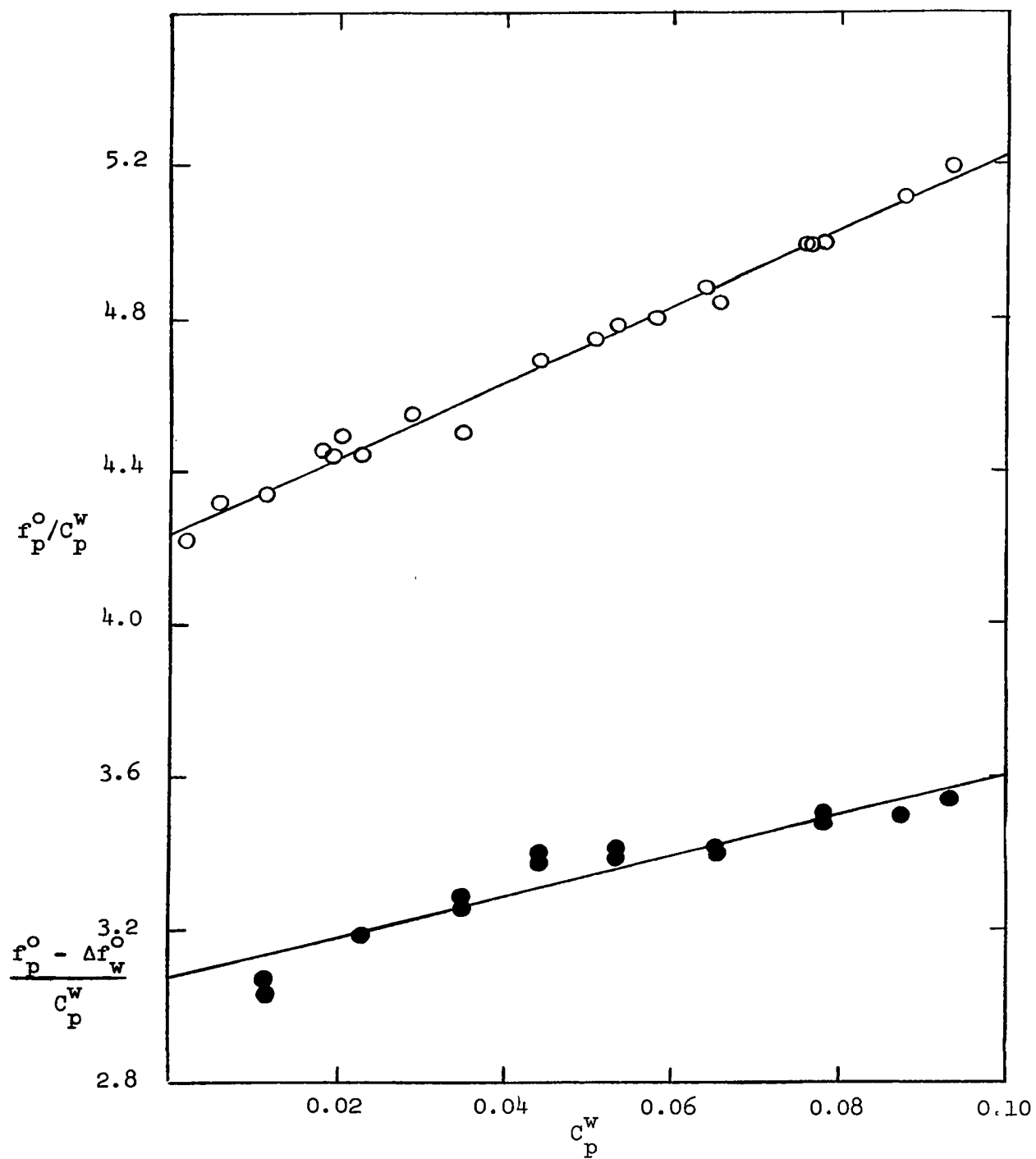


Figure 8. Partition data for system 1,2-dichloroethane-water-phenol at 25°. Curve is calculated; points are experimental.

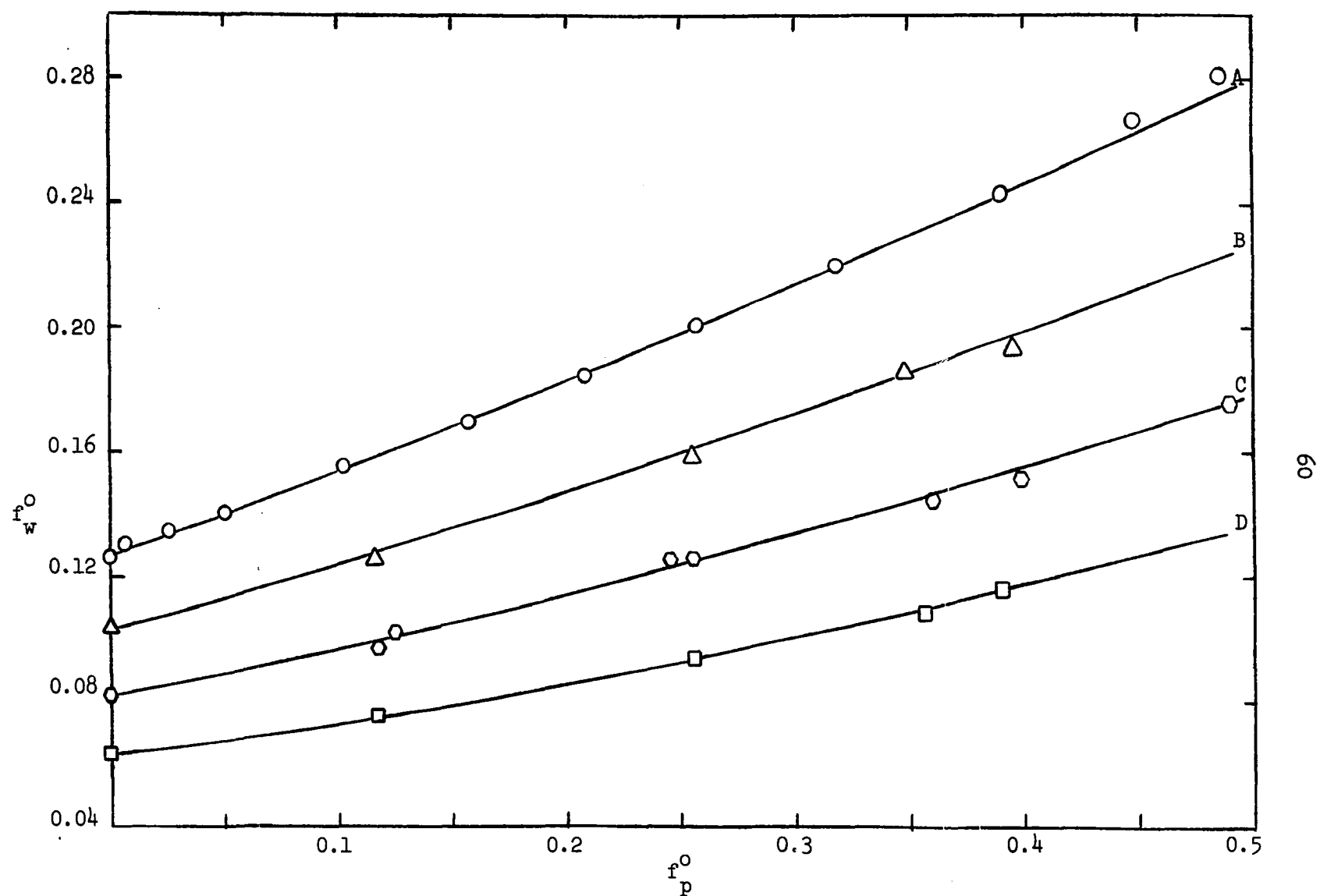


Figure 9. Formal solubility of water in solutions of phenol in 1,2-dichloroethane at various water activities. Curves are calculated, points are experimental. Data at: A: $a_w = 1.0$; B: $a_w = 0.85$; C: $a_w = 0.70$; D: $a_w = 0.55$.

TABLE 16

PARTITION DATA FOR THE SYSTEM BENZENE-WATER-PHENOL AT 25°.

f_p^o (moles/liter)	C_p^w (moles/liter)	f_p^o/C_p^w
0.0254	0.0111	2.286
0.0541	0.0228	2.373
0.1109	0.0446	2.487
0.1357	0.0535	2.536
0.2077	0.0785	2.647
0.2473	0.0899	2.751
0.2297	0.1050	2.854
0.3469	0.1190	2.899
0.3895	0.1304	2.987
0.4455	0.1418	3.143

TABLE 17

WATER SOLUBILITY DATA FOR THE PHENOL-BENZENE
SYSTEM AT VARIOUS WATER ACTIVITIES AT 25°.

f_p° (moles/liter)	f_w° (moles/liter)	a_w
0.0254	0.0392 0.0382	1.0
0.0541	0.0412 0.0434 0.0416	1.0
0.1109	0.0519 0.0516	1.0
0.1357	0.0555 0.0549	1.0
0.2077	0.0695 0.0689	1.0
0.2473	0.0769 0.0767 0.0766	1.0
0.2997	0.0882 0.0879	1.0
0.3469	0.0983 0.0981	1.0
0.3895	0.1088 0.1085	1.0
0.4455	0.1220 0.1217	1.0
0.0909	0.0367 0.0364	0.75
0.1939	0.0498 0.0490 0.0498	0.75

TABLE 17 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.2744	0.0629 0.0634	0.75
0.384	0.0801 0.0803	0.75
0.00	0.0263 0.0271 0.0279 0.0263	0.75
0.1022	0.0350 0.0350	0.70
0.2064	0.0474 0.0477	0.70
0.3024	0.0615 0.0620	0.70
0.4064	0.0777 0.0782	0.70
0.00	0.0245 0.0252 0.0240 0.0245	0.70
0.1040	0.0332 0.0340 0.0335	0.69
0.2060	0.0452 0.0465 0.0457	0.69
0.3040	0.0585 0.0585	0.69
0.4070	0.0739 0.0742	0.69
0.00	0.0244 0.0249	0.69

TABLE 17 ... continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.1024	0.0272 0.0273	0.55
0.2036	0.0367 0.0367	0.55
0.3064	0.0479 0.0474	0.55
0.4088	0.0608 0.0598	0.55
0.00	0.0194 0.0192	0.55
0.0900	0.0214 0.0208	0.434
0.1939	0.0282 0.0281	0.434
0.2816	0.0354 0.0354	0.434
0.3888	0.0445 0.0445	0.434
0.00	0.0156 0.0158 0.0153	0.434
0.1030	0.0205 0.0207	0.39
0.2060	0.0260 0.0257	0.39
0.3160	0.0334 0.0325	0.39
0.4070	0.0431 0.0429	0.39
0.00	0.0124 0.0127 0.0135	0.39

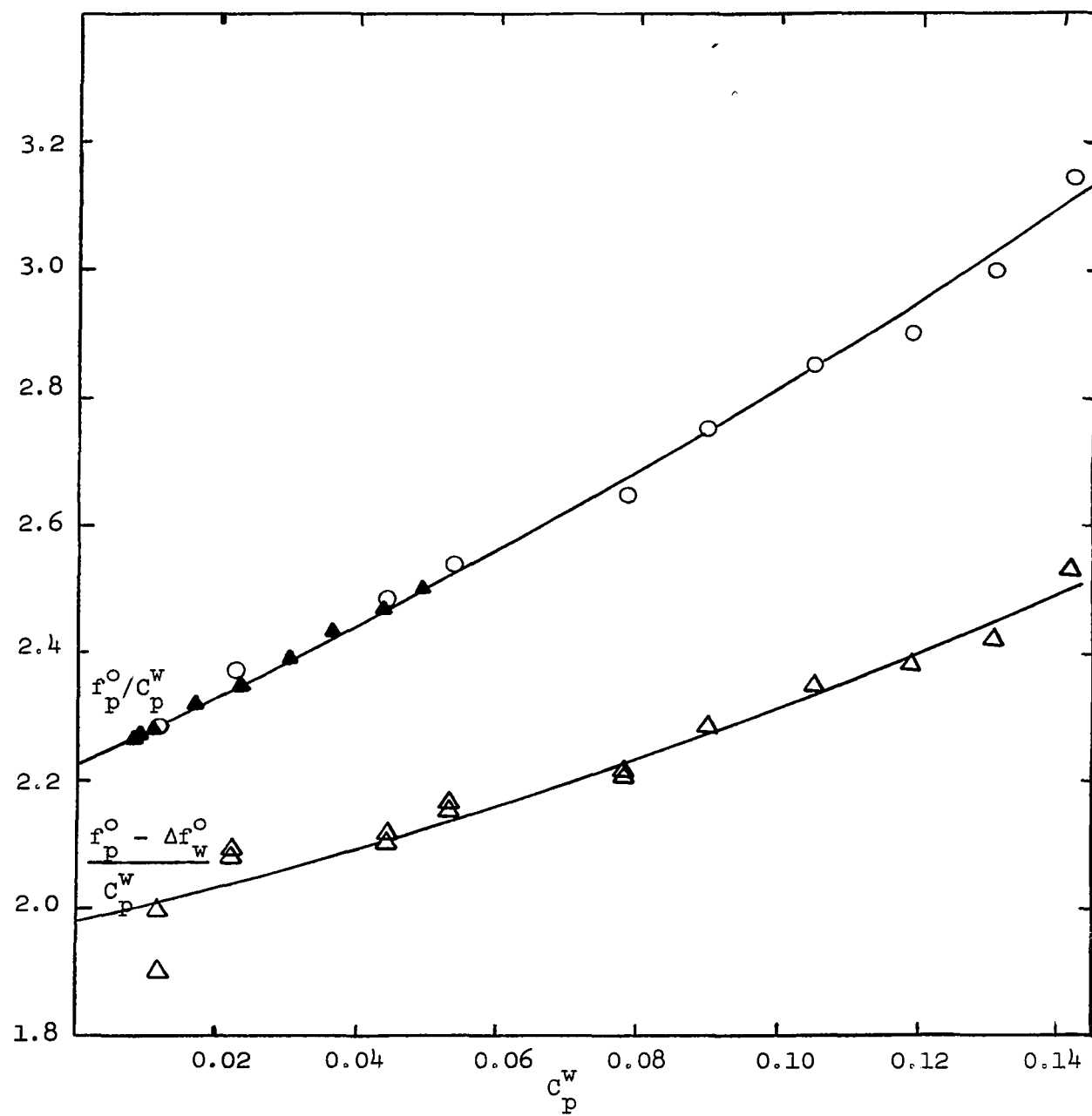


Figure 10. Partition data for system Benzene-water-phenol at 25°. Curves are calculated; points are experimental. ▲, Philbrick.

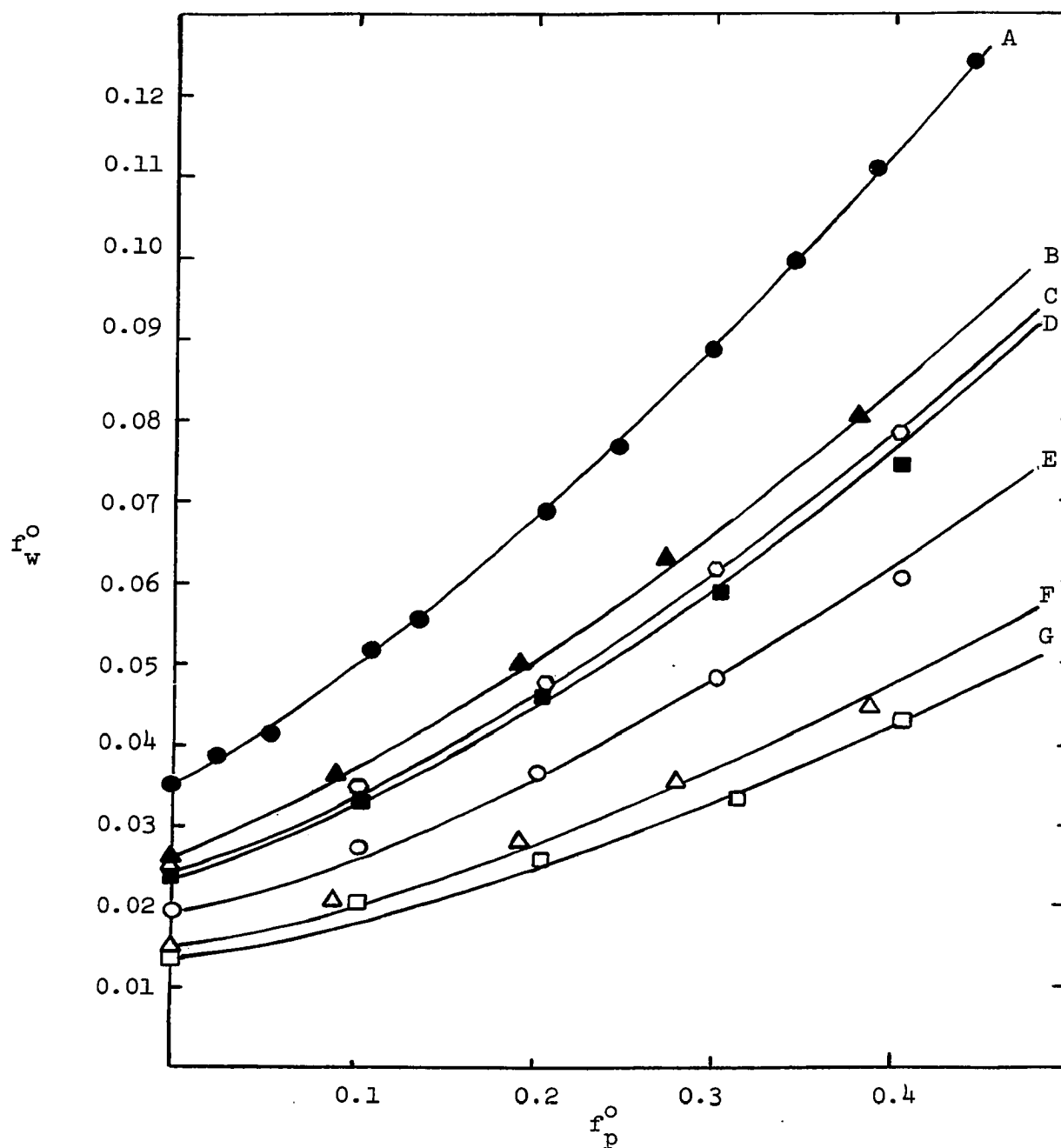


Figure 11. Formal solubility of water in solutions of phenol in benzene at various water activities. Curves are calculated; points are experimental. Data at: A: $a_w = 1.0$; B: $a_w = 0.75$; C: $a_w = 0.70$; D: $a_w = 0.69$; E: $a_w = 0.55$; F: $a_w = 0.434$; G: $a_w = 0.39$.

TABLE 18

PARTITION DATA FOR THE SYSTEM
1,1,2,2-TETRACHLORETHANE-WATER-PHENOL AT 25°.

f_p^o (moles/liter)	C_p^w (moles/liter)	f_p^o/C_p^w
0.0163	0.0058	2.817
0.0536	0.0186	2.888
0.0816	0.0275	2.967
0.1129	0.0364	3.106
0.1482	0.0468	3.165
0.1800	0.0562	3.206
0.2185	0.0661	3.308
0.2599	0.0757	3.425
0.3006	0.0839	3.584
0.3479	0.0938	3.710
0.3911	0.1035	3.779
0.4441	0.1137	3.906
0.0148	0.0054	2.740
0.0146	0.0054	2.700
0.0513	0.0176	2.910
0.0782	0.0256	3.059
0.1081	0.0349	3.100
0.1414	0.0444	3.184
0.1743	0.0535	3.260
0.2129	0.0632	3.368
0.2521	0.0726	3.474
0.2912	0.0818	3.565
0.1828	0.0559	3.272
0.2196	0.0659	3.332
0.2606	0.0761	3.424
0.3423	0.0929	3.685
0.3840	0.1023	3.754
0.4385	0.1122	3.908

TABLE 19

WATER SOLUBILITY DATA FOR THE PHENOL-1,1,2,2-TETRACHLOROETHANE
SYSTEM AT VARIOUS WATER ACTIVITIES AT 25°.

f_p° (moles/liter)	f_w° (moles/liter)	a_w
0.0163	0.1053 0.1037 0.1040	1.0
0.0536	0.1125 0.1125	1.0
0.0816	0.1192 0.1173 0.1174	1.0
0.1129	0.1260 0.1264	1.0
0.1482	0.1326 0.1332 0.1340	1.0
0.1800	0.1449 0.1432 0.1436	1.0
0.2185	0.1532 0.1557 0.1544	1.0
0.2599	0.1663 0.1651	1.0
0.3006	0.1763 0.1766	1.0
0.3479	0.1939 0.1923	1.0
0.3911	0.2066 0.2073	1.0
0.4441	0.2282 0.2234 0.2237	1.0

TABLE 19 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.014	0.1051 0.1046	1.0
0.0513	0.1124 0.1136	1.0
0.0782	0.1187 0.1188	1.0
0.1081	0.1260 0.1254	1.0
0.1414	0.1345 0.1348	1.0
0.1743	0.1441 0.1440	1.0
0.2129	0.1542 0.1534	1.0
0.2521	0.1646 0.1650	1.0
0.2914	0.1765 0.1767	1.0
0.1188	0.0847 0.0860 0.0855	0.70
0.2426	0.1067 0.1062 0.1057	0.70
0.3656	0.1305 0.1287 0.1284	0.70
0.4123	0.1337 0.1342	0.70
0.00	0.0679 0.0682 0.0674	0.70

TABLE 19 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.1188	0.0857	0.70
0.2426	0.1046 0.1047	0.70
0.3656	0.1254 0.1256	0.70
0.4123	0.1363 0.1367	0.70
0.00	0.0675 0.0677	0.70
0.1136	0.0826 0.0828	0.69
0.2132	0.0966 0.0962	0.69
0.3359	0.1178 0.1170	0.69
0.3939	0.1233 0.1242	0.69
0.00	0.0667 0.0668	0.69
0.1188	0.0602 0.0596 0.0601	0.51
0.2426	0.0751 0.0751	0.51
0.3656	0.0922 0.0912	0.51
0.4123	0.0969 0.0979	0.51
0.00	0.0483 0.0481 0.0486	0.51

TABLE 19 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.1188	0.0592 0.0601	0.51
0.2426	0.0738 0.0742	0.51
0.3656	0.0899 0.0904	0.51
0.4123	0.0970 0.0966	0.51
0.00	0.0492 0.0483	0.51
0.1072	0.0439 0.0435	0.39
0.2192	0.0567 0.0580 0.0542 0.0542	0.39
0.3359	0.0633 0.0633	0.39
0.3939	0.0713 0.0706	0.39
0.00	0.0350 0.0350	0.39

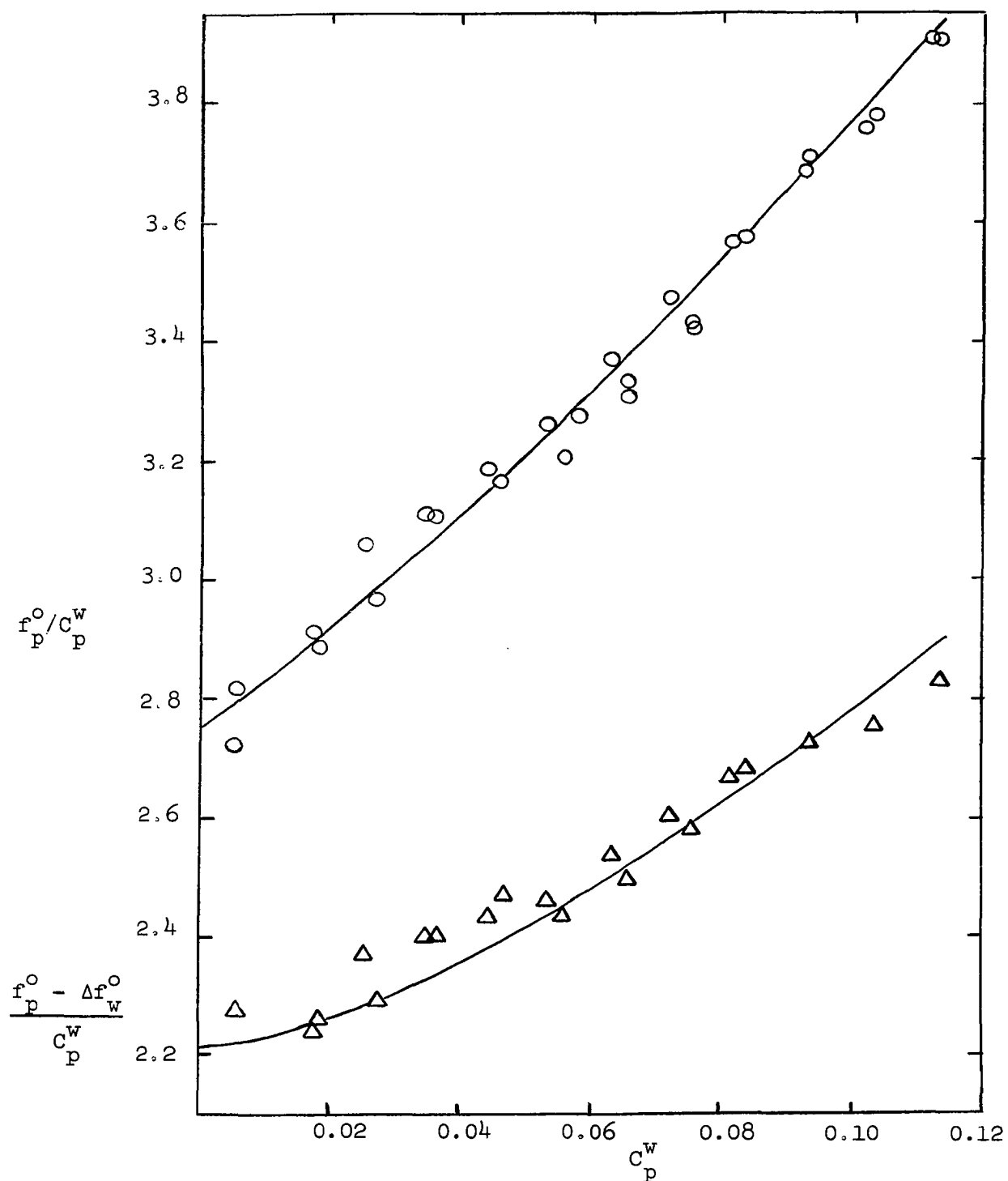


Figure 12. Partition data for system 1,1,2,2-tetrachloroethane-water-phenol at 25°. Curves are calculated; points are experimental.

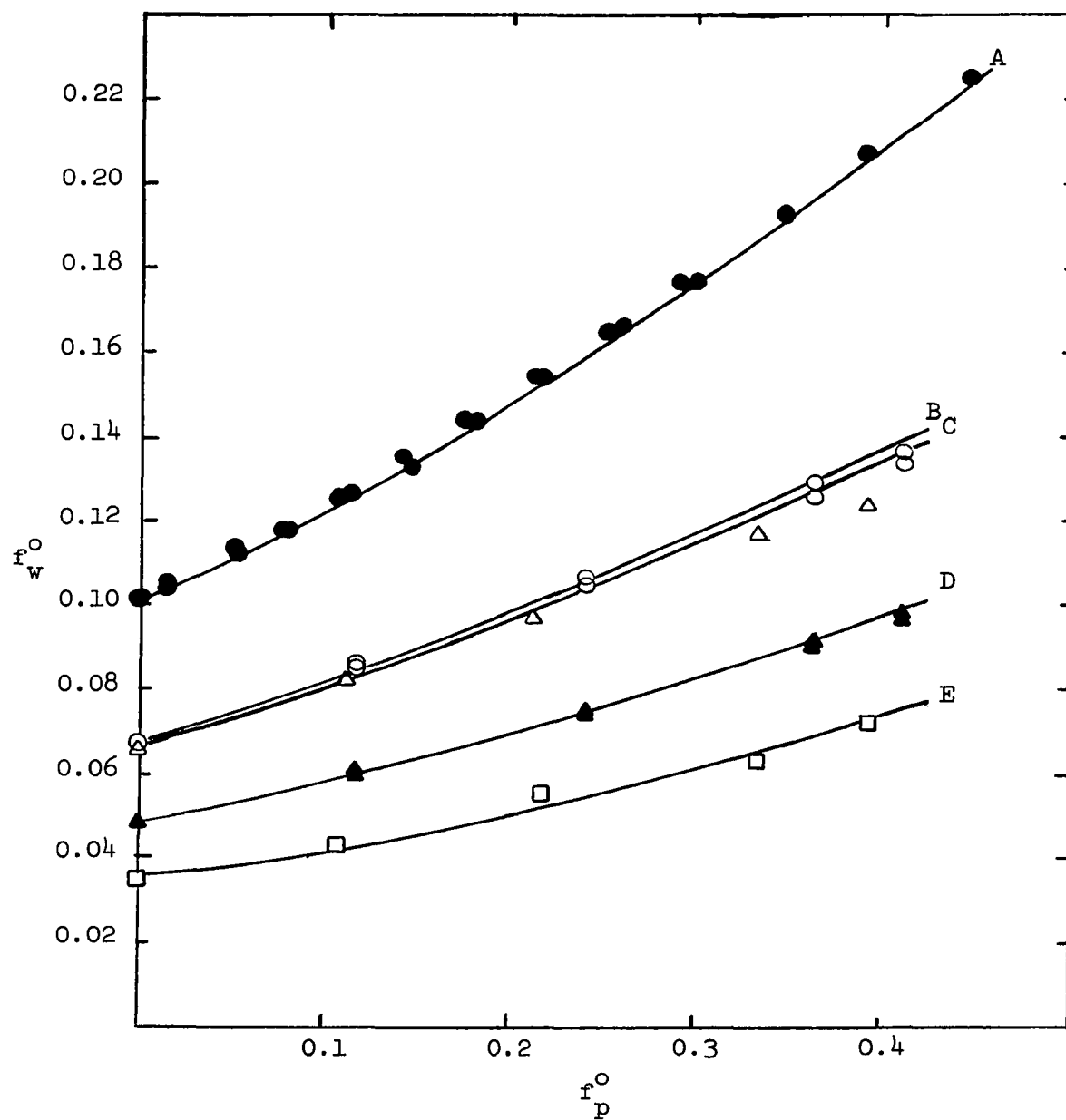


Figure 13. Formal solubility of water in solutions of phenol in 1,1,2,2-tetrachloroethane at various water activities. Curves are calculated; points are experimental. Data at: A: $a_w = 1.0$; B: $a_w = 0.70$; C: $a_w = 0.69$; D: $a_w = 0.51$; E: $a_w = 0.39$.

TABLE 20

SELF-ASSOCIATION AND HYDRATION CONSTANTS FOR PHENOL IN
1,2-DICHLOROETHANE, 1,1,2,2-TETRACHLOROETHANE AND BENZENE AT 25°.

SOLVENT	K_D	$K_{PW_2} (1/\text{mole})^2$	$K_{P_2} (1/\text{mole})^2$	$K_{P_3} (1/\text{mole})^2$	$C_W^o (\text{mole/l})$	$K_{W_3} (1/\text{mole})^2$
1,2-dichloro-ethane	3.68 ± 0.01	12.97 ± 0.12	3.37 ± 0.10	---	0.1083 ± 0.0007	4.6 ± 0.3
*	3.68 ± 0.01	12.97 ± 0.23	3.31 ± 0.14	0.002 ± 0.029	0.1083 ± 0.0007	4.6 ± 0.3
1,1,2,2-tetra-chloroethane	2.46 ± 0.01	13.79 ± 0.43	6.99 ± 0.26	0.477 ± 0.060	0.0925 ± 0.0009	3.6 ± 0.6
Benzene	2.11 ± 0.01	50.03 ± 1.86	15.74 ± 0.26	0.263 ± 0.043	0.0349 ± 0.0005	---

* Best fit assuming monomer-dimer-trimer equilibrium.

TABLE 21

PARTITION DATA FOR THE SYSTEM CARBON TETRACHLORIDE-WATER-PHENOL AT 25°.

f_p^o (moles/liter)	C_p^w (moles/liter)	f_p^o/C_p^w
0.0217	0.0448	0.4849
0.0218	0.0445	0.4902
0.0335	0.0684	0.4900
0.0337	0.0680	0.4958
0.0475	0.0945	0.5023
0.0473	0.0935	0.5061
0.0797	0.1458	0.5464
0.0797	0.1460	0.5457
0.1181	0.2013	0.5867
0.1178	0.1991	0.5916
0.1703	0.2527	0.6739
0.1709	0.2509	0.6811
0.0068	0.0142	0.4775
0.0137	0.0283	0.4824
0.0219	0.0440	0.4968
0.0335	0.0675	0.4968
0.0463	0.0925	0.5007
0.0770	0.1428	0.5389
0.1147	0.1970	0.5822
0.1683	0.2477	0.6795
0.0069	0.0146	0.4718
0.0068	0.0146	0.4669
0.0136	0.0282	0.4810
0.0136	0.0282	0.4817
0.0201	0.0418	0.4796
0.0202	0.0420	0.4810
0.0486	0.0959	0.5066
0.0484	0.0959	0.5060

TABLE 21 ...continued

f_p^o (moles/liter)	C_p^W (moles/liter)	f_p^o/C_p^W
0.0718	0.1331	0.5395
0.0726	0.1331	0.5453
0.1127	0.1916	0.5882
0.1132	0.1920	0.5896
0.1583	0.2416	0.6552
0.1583	0.2405	0.6582
0.0069	0.0146	0.4733
0.0136	0.0283	0.4816
0.0205	0.0422	0.4848
0.0353	0.0718	0.4909
0.0495	0.0971	0.5100
0.0732	0.1360	0.5385
0.1143	0.1984	0.5890
0.1653	0.2463	0.6711
0.1156	0.1920	0.6050
0.1563	0.2316	0.6748
0.2869	0.3144	0.9125
0.1598	0.2355	0.6786
0.1598	0.2366	0.6754
0.2912	0.3194	0.9117
0.2912	0.3176	0.9168

TABLE 22

WATER SOLUBILITY DATA FOR THE PHENOL-CARBON TETRACHLORIDE
SYSTEM AT VARIOUS WATER ACTIVITIES AT 25°.

f_p° (moles/liter)	f_w° (moles/liter)	a_w
0.0199	0.0095 0.0095	1.0
0.0495	0.0114 0.0114	1.0
0.0702	0.0153 0.0152	1.0
0.1156	0.0183 0.0184	1.0
0.1563	0.0249 0.0247	1.0
0.2912	0.0496 0.0497	1.0
0.0205	0.0095 0.0096	1.0
0.0495	0.0111 0.0112	1.0
0.0732	0.0144 0.0146 0.0132 0.0135	1.0
0.1143	0.0180 0.0179	1.0
0.1653	0.0249 0.0246	1.0
0.0258	0.0095 0.0094 0.0094 0.0096	0.97

TABLE 22 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.0502	0.0110 0.0111 0.0109	0.97
0.0908	0.0153 0.0150 0.0150	0.97
0.1552	0.0233 0.0234	0.97
0.2066	0.0314 0.0315	0.97
0.3062	0.0505 0.0505	0.97
0.00	0.0081 0.0081	0.97
0.1525	0.0228 0.0226 0.0229	0.945
0.3001	0.0482 0.0482	0.945
0.00	0.0085 0.0085	0.945
0.0217	0.0095	0.90
0.0534	0.0119 0.0106	0.90
0.1050	0.0168 0.0165	0.90
0.2110	0.0288 0.0290	0.90
0.2982	0.0438 0.0433	0.90

TABLE 22 ...continued

f_p^o (moles/liter)	f_w^o (moles/liter)	a_w
0.1525	0.0166 0.0161 0.0162	0.69
0.3001	0.0321 0.0320	0.69
0.3140	0.0337 0.0336	0.69
0.00	0.0062 0.0069	0.69
0.1525	0.0107 0.0109 0.0108	0.47
0.3001	0.0205 0.0205	0.47
0.3141	0.0215 0.0216	0.47
0.00	0.0039 0.0041 0.0040	0.47
0.1525	0.0218 0.0215	0.89
0.3001	0.0435 0.0434	0.89
0.00	0.0083 0.0083	0.89
0.0256	0.0055 0.0054	0.52
0.0520	0.0069 0.0067 0.0071	0.52
0.1030	0.0086 0.0086	0.52

TABLE 22 ...continued

f_p° (moles/liter)	f_w° (moles/liter)	a_w
0.2033	0.0149 0.0153 0.0152	0.52
0.2639	0.0211 0.0206 0.0207	0.52
0.3141	0.0254 0.0257 0.0255	0.52
0.00	0.0051 0.0051 0.0048 0.0046	0.52
0.1525	0.0063 0.0061 0.0061	0.26
0.3001	0.0114 0.0113 0.0114	0.26
0.00	0.0021 0.0024 0.0022	0.26

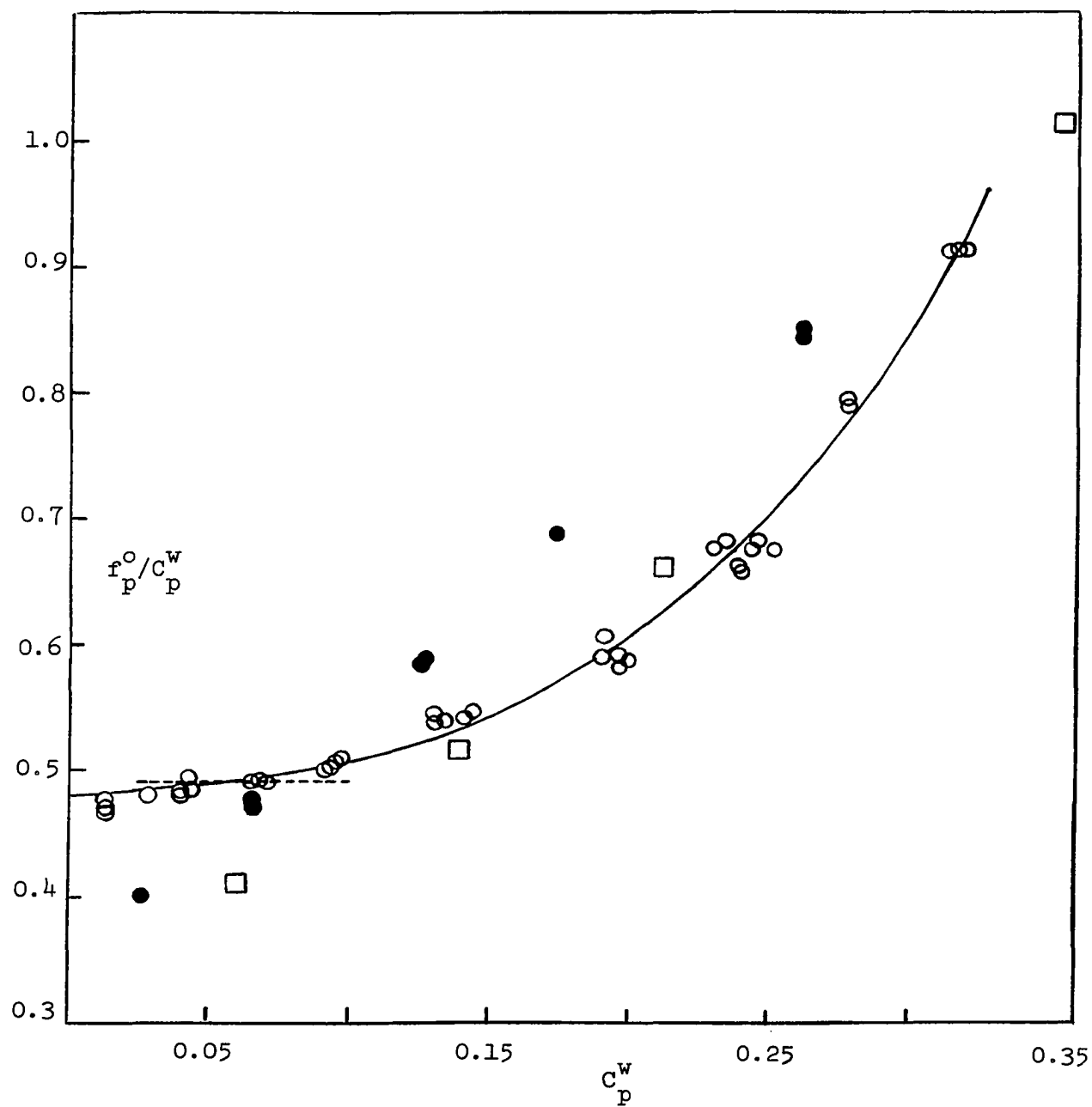


Figure 14. Partition data for the system carbon tetrachloride-water-phenol. Curve is calculated; points are experimental. ●, Badger and Greenough; □, Herz and Rathmann; ----, Philbrick.

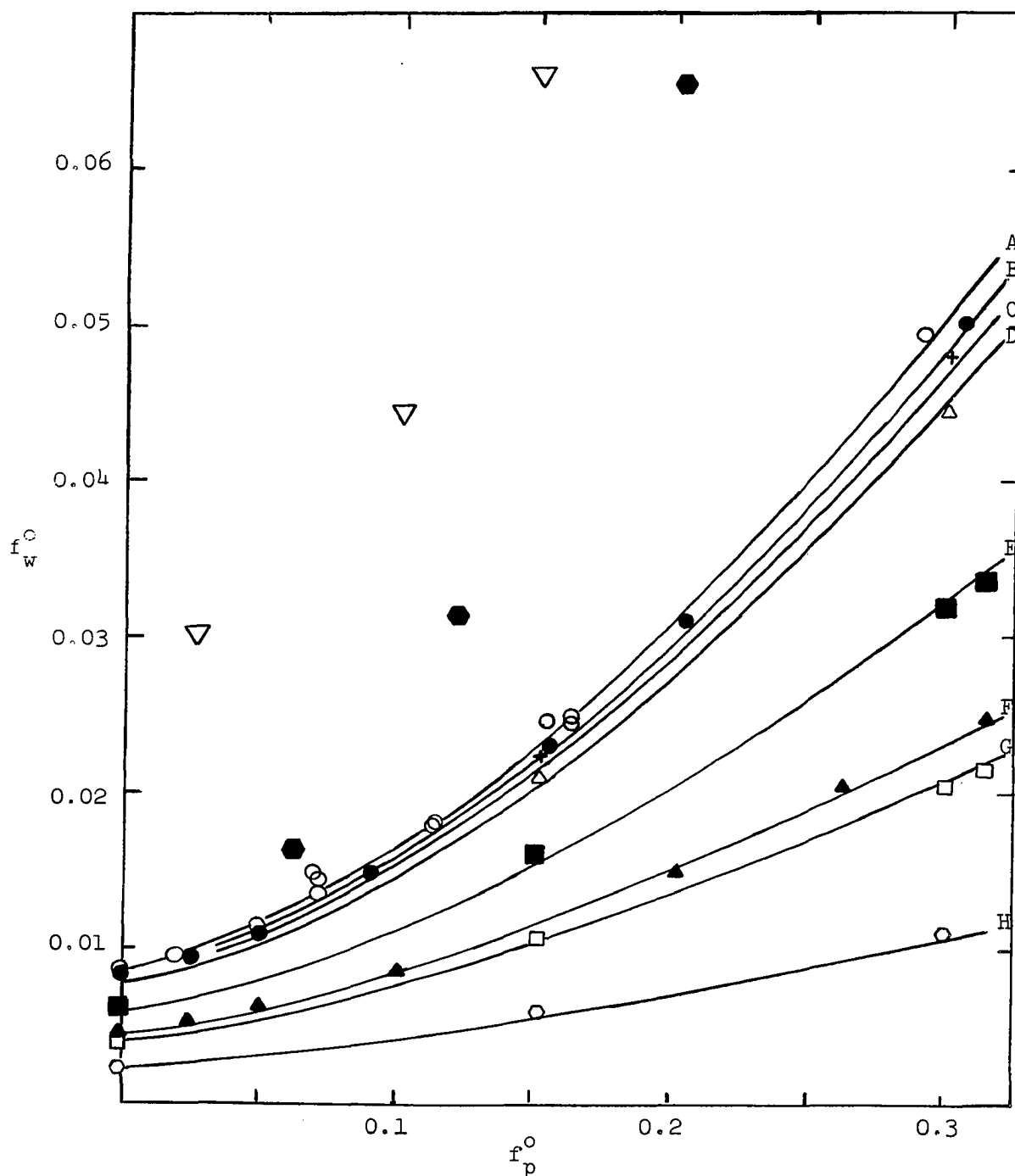


Figure 15. Formal solubility of water in solutions of phenol in carbon tetrachloride at various water activities. Curves are calculated, A: $a_w = 1.0$; B: $a_w = 0.97$; C: $a_w = 0.945$; D: $a_w = 0.89$; E: $a_w = 0.69$; F: $a_w = 0.52$; G: $a_w = 0.47$; H: $a_w = 0.26$. Data of Badger and Greenough: w_{spectral} , $\bullet$; $w_{\text{turbidity measurement}}$, ∇ .

TABLE 23

LEAST SQUARES PARAMETERS FOR $f_p^o/c_p^w = \alpha + \beta(c_p^w)^{m-1} + \gamma(c_p^w)^{n-1}$

SOLVENT	POSTULATED SPECIES	m	n	α	μ	γ	ROOT MEAN SQUARE DEVIATION
1,2-dichloroethane (25°)	monomer-dimer	2	-	4.237	9.91	-	0.0366
	monomer-trimer	3	-	4.402	100.26	-	0.0749
	monomer-dimer-trimer	2	3	4.248	9.19	7.69	0.0372
Benzene* (25°) *(includes Philbrick's data (J. Am. Chem. Soc. <u>56</u> , 2581 (1934))	monomer-dimer	2	-	2.218	6.02	-	0.0232
	monomer-trimer	3	-	2.350	40.89	-	0.0552
	monomer-dimer-trimer	2	3	2.242	4.85	8.34	0.0198
1,1,2,2-tetrachloro- ethane (25°)	monomer-dimer	2	-	2.701	10.37	-	0.0423
	monomer-trimer	3	-	2.930	84.34	-	0.0899
	monomer-dimer-trimer	2	3	2.728	9.009	11.78	0.0413
Carbon tetrachloride (25°)	monomer-dimer	2	-	0.416	1.15	-	0.0467
	monomer-trimer	3	-	0.467	3.89	-	0.0226
	monomer-tetramer	4	-	0.0489	13.25	-	0.0131
	monomer-pentamer	5	-	0.504	43.6	-	0.0232
	monomer-dimer-trimer	2	3	0.499	-0.60	5.74	0.0174
	monomer-dimer-tetramer	2	4	0.479	1.27	12.0	0.0124
	monomer-trimer-tetramer	3	4	0.485	0.624	11.2	0.0126
	monomer-trimer-pentamer	3	5	0.483	2.03	22.0	0.0114
	monomer-trimer-hexamer	3	6	0.481	2.53	55.2	0.0109

TABLE 23 ...continued

SOLVENT	POSTULATED SPECIES	m	n	α	β	γ	ROOT MEAN SQUARE DEVIATION
Carbon Tetrachloride (35°)	monomer-dimer	2	-	0.519	1.140	-	0.0444
	monomer-trimer	3	-	0.564	3.71	-	0.0148
	monomer-tetramer	4	-	0.583	11.77	-	0.0188
	monomer-dimer-trimer	2	3	0.576	-0.25	4.46	0.0128
	monomer-dimer-tetramer	2	4	0.563	0.31	8.98	0.0104
	monomer-trimer-tetramer	3	4	0.571	2.22	4.80	0.0113
	monomer-trimer-hexamer	3	6	0.567	3.02	23.33	0.0110

TABLE 24
SELF-ASSOCIATION AND HYDRATION CONSTANTS FOR PHENOL IN CARBON TETRACHLORIDE

REACTION	EQUILIBRIUM CONSTANT
$P \text{ (aqueous phase)} = P \text{ (CCl}_4 \text{ phase)}$	$K_D = 0.458$
$P + W \text{ (CCl}_4 \text{ phase)}$	$K_{PW} = 5.75 \text{ (l./mole)}$
$3P \text{ (CCl}_4 \text{ phase)} = P_3 \text{ (CCl}_4 \text{ phase)}$	$K_P = 4.1 \text{ (l./mole)}^2$
$3P + W \text{ (CCl}_4 \text{ phase)} = P_3W \text{ (CCl}_4 \text{ phase)}$	$K_{P_3W} = 443 \text{ (l./mole)}^3$
$3P + 2W \text{ (CCl}_4 \text{ phase)} = P_3W_2 \text{ (CCl}_4 \text{ phase)}$	$K_{P_3W_2} = 9900 \text{ (l./mole)}^4$
$6P \text{ (CCl}_4 \text{ phase)} = P_6 \text{ (CCl}_4 \text{ phase)}$	$K_{P_6} = 432 \text{ (l./mole)}^5$
$6P + 3W \text{ (CCl}_4 \text{ phase)} = P_6W_3 \text{ (CCl}_4 \text{ phase)}$	$K_{P_6W_3} = 8.6 \times 10^8 \text{ (l./mole)}^8$

TABLE 25

PARTITION DATA FOR THE SYSTEM
CARBON TETRACHLORIDE-WATER-PHENOL AT 35°.

f_p^o (moles/liter)	C_p^w (moles/liter)	f_p^o/C_p^w
0.0071	0.0126	0.5634
0.0126	0.0222	0.5663
0.0228	0.0394	0.5794
0.0232	0.0405	0.5732
0.0553	0.0929	0.5952
0.0790	0.1262	0.6260
0.1275	0.1915	0.6658
0.1748	0.2336	0.7483
0.3085	0.3242	0.9515
0.0070	0.0125	0.5627
0.0127	0.0219	0.5772
0.0224	0.0387	0.5783
0.0229	0.0399	0.5741
0.0546	0.0914	0.5966
0.0780	0.1236	0.6313
0.1252	0.1847	0.6778
0.1705	0.2282	0.7470
0.3049	0.3156	0.9661

TABLE 26

ABSORBANCE OF PHENOL-1,2-DICHLOROETHANE AT
THE O-H PEAK WAVELENGTH OF 1.375μ AT 25° .

f_p° (moles/liter)	A/l (Absorbance per cm pathlength)
0.0467	0.030
0.0945	0.071
0.1420	0.115
0.1916	0.153
0.2405	0.193
0.2850	0.231
0.3310	0.266
0.3798	0.300

TABLE 27

ABSORBANCE OF PHENOL-1,1,2,2-TETRACHLORETHANE AT
THE O-H PEAK WAVELENGTH OF 1.385μ AT 25° .

f_p° (moles/liter)	A/l (Absorbance per cm pathlength)
0.0426	0.047
0.0854	0.100
0.1296	0.155
0.1722	0.211
0.2192	0.258
0.2595	0.316
0.3034	0.360
0.3458	0.410
0.3910	0.450
0.4321	0.510

TABLE 28

ABSORBANCE OF PHENOL-BENZENE SOLUTIONS AT
THE O-H PEAK WAVELENGTH OF 1.380μ AT 25° .

f_p° (moles/liter)	A/l (Absorbance per cm pathlength)
0.0069	0.004
0.0124	0.009
0.0247	0.017
0.0692	0.042
0.0346	0.024
0.0692	0.048
0.1038	0.071
0.1522	0.104
0.2076	0.137
0.2420	0.172
0.2760	0.190
0.3460	0.232

TABLE 29

ABSORBANCE OF PHENOL-CARBON TETRACHLORIDE SOLUTIONS
AT THE O-H PEAK WAVELENGTH OF 1.357μ AT 25° .

f_p° (moles/liter)	A/l (Absorbance per cm pathlength)
0.0564	0.163
0.1123	0.288
0.1676	0.386
0.2238	0.456
0.2822	0.515
0.3373	0.550
	0.545
0.3981	0.593 ?
	0.572

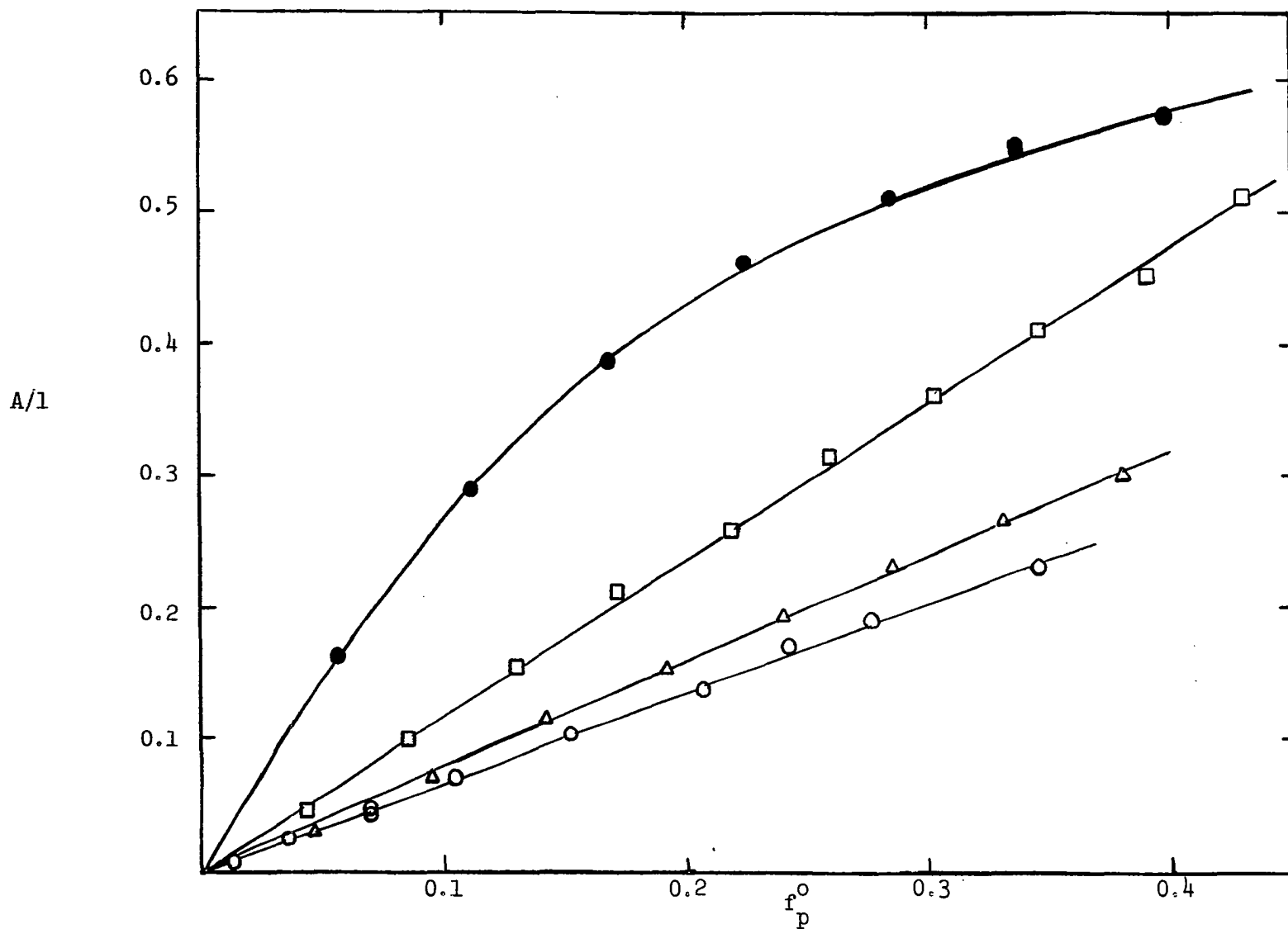


Figure 16. Absorbance of phenol solutions: O, Benzene at 1.380μ ; Δ , 1,2-dichloroethane at 1.375μ ; $\square$, 1,1,2,2-tetrachloroethane at 1.360μ ; and $\bullet$, Carbon tetrachloride at 1.357μ .

TABLE 30

SOLUBILITY DATA OF CARBON TETRACHLORIDE IN WATER AT 25°, USING VAPOR PRESSURE MEASURING DEVICE.

Total grams	P_T (mm)	ΔP (mm)	Grams in Vapor	Grams in Solution	f_o^w (moles/liter)
0.0	26.61	---	---	---	---
0.0382	45.12	18.51	0.0135	0.0247	0.0008
0.0764	63.50	36.89	0.0269	0.0485	0.0016
0.1146	82.10	54.49	0.0397	0.0749	0.0025
0.1528	99.08	72.47	0.0528	0.1000	0.0033
0.1910	117.40	90.79	0.0662	0.1248	0.0041
0.2292	135.66	109.05	0.0795	0.1497	0.0049
0.2674	140.00	113.39	0.0826	0.1848	0.0060
0.3820	140.74	114.13	0.0832	0.2988	0.0097

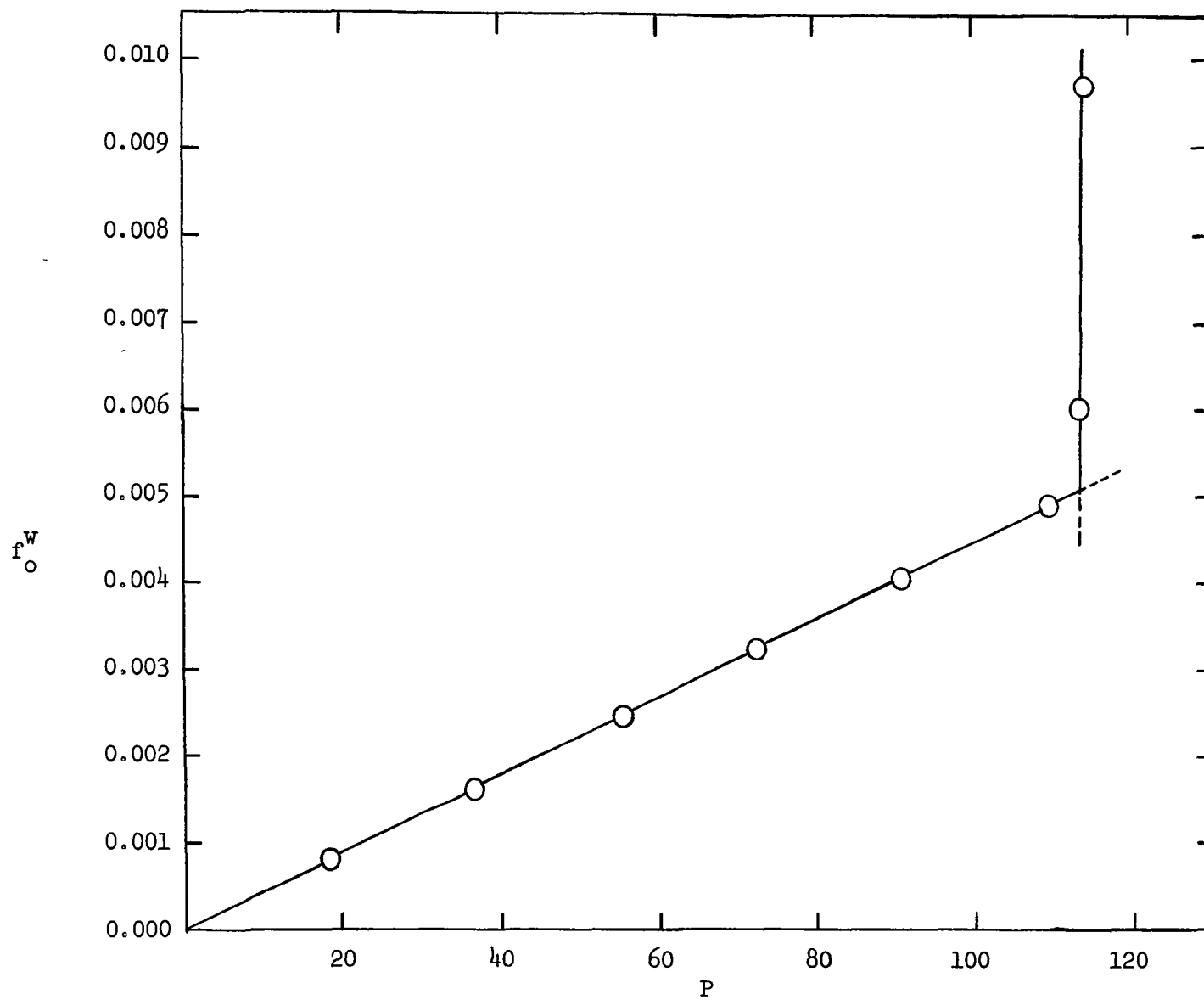


Figure 17. Formal solubility of carbon tetrachloride in water at 25°, using vapor pressure measuring device.

TABLE 31

SOLUBILITY DATA OF 1,2-DICHLOROETHANE IN WATER AT 25°, USING VAPOR PRESSURE MEASURING DEVICE.

Total Grams	P_T (mm)	ΔP (mm)	Grams in Vapor	Grams in Solution	f_o^W (moles/liter)
0.0	26.28	---	---	---	---
0.1207	31.77	5.49	0.0005	0.1152	0.0058
0.3017	39.24	12.96	0.0013	0.3004	0.0152
0.4827	47.91	21.63	0.0022	0.4805	0.0243
0.6637	55.99	29.71	0.0030	0.6607	0.0334
0.8447	63.84	37.56	0.0038	0.8409	0.0425
1.0257	71.82	44.54	0.0044	1.0213	0.0516
1.2067	79.82	53.54	0.0053	1.2014	0.0607
1.3877	87.67	61.39	0.0061	1.3816	0.0698
1.5687	95.48	69.20	0.0069	1.5618	0.0789
1.7497	103.35	77.07	0.0077	1.7420	0.0880
1.9307	105.01	78.73	0.0079	1.9228	0.0971
2.1117	105.73	79.45	0.0079	2.1038	0.1063
2.2927	105.67	79.39	0.0079	2.2848	0.1154
2.4737	105.75	79.47	0.0079	2.4658	0.1246
2.6547	105.88	79.60	0.0080	2.6467	0.1337

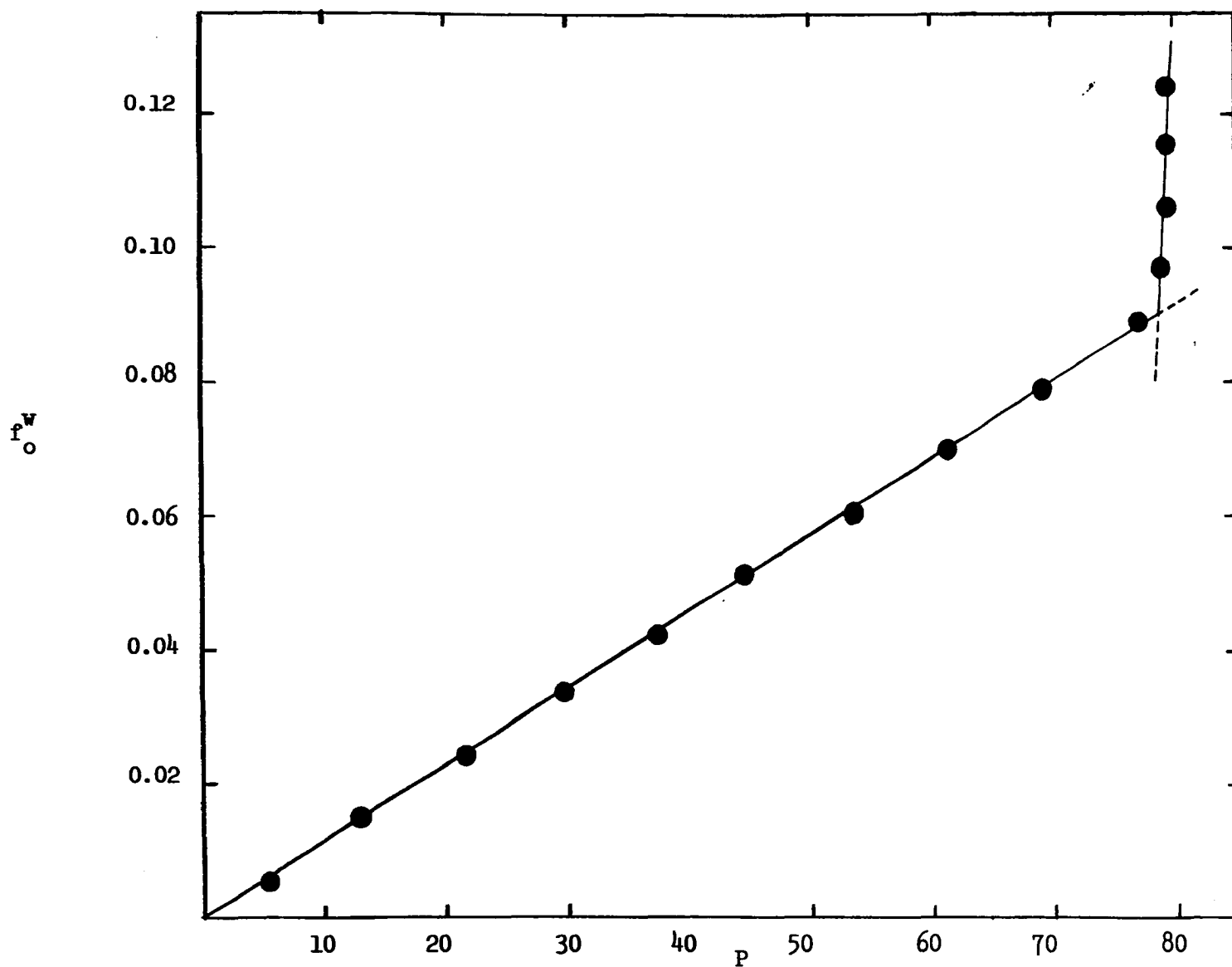


Figure 18. Formal solubility of 1,2-dichloroethane in water at 25°, using vapor pressure measuring device.

TABLE 32

SOLUBILITY DATA OF BENZENE IN WATER AT 25°, USING VAPOR PRESSURE MEASURING DEVICE.

Total Grams	P _T (mm)	ΔP(mm)	Grams in Vapor	Grams in Solution	f _O ^W (moles/liter)
0.0	25.05	---	---	---	---
0.0416	35.98	10.92	0.0045	0.0371	0.0025
0.0832	46.87	21.82	0.0090	0.0742	0.0050
0.1248	57.80	32.75	0.0014	0.1113	0.0075
0.1664	69.60	44.55	0.0018	0.1480	0.0100
0.2080	79.32	54.21	0.0022	0.1857	0.0125
0.2496	90.29	65.24	0.0027	0.2227	0.0150
0.2912	100.95	75.90	0.0031	0.2599	0.0175
0.3328	111.63	86.58	0.0036	0.2971	0.0200
0.3744	119.72	94.67	0.0039	0.3354	0.0226
0.4160	120.00	94.95	0.0039	0.3769	0.0254
0.4576	120.11	95.06	0.0039	0.4181	0.0282
0.4992	120.18	95.13	0.0039	0.4601	0.0310
0.5824	120.44	95.39	0.0039	0.5432	0.0366
0.7072	120.66	95.61	0.0039	0.6679	0.0450

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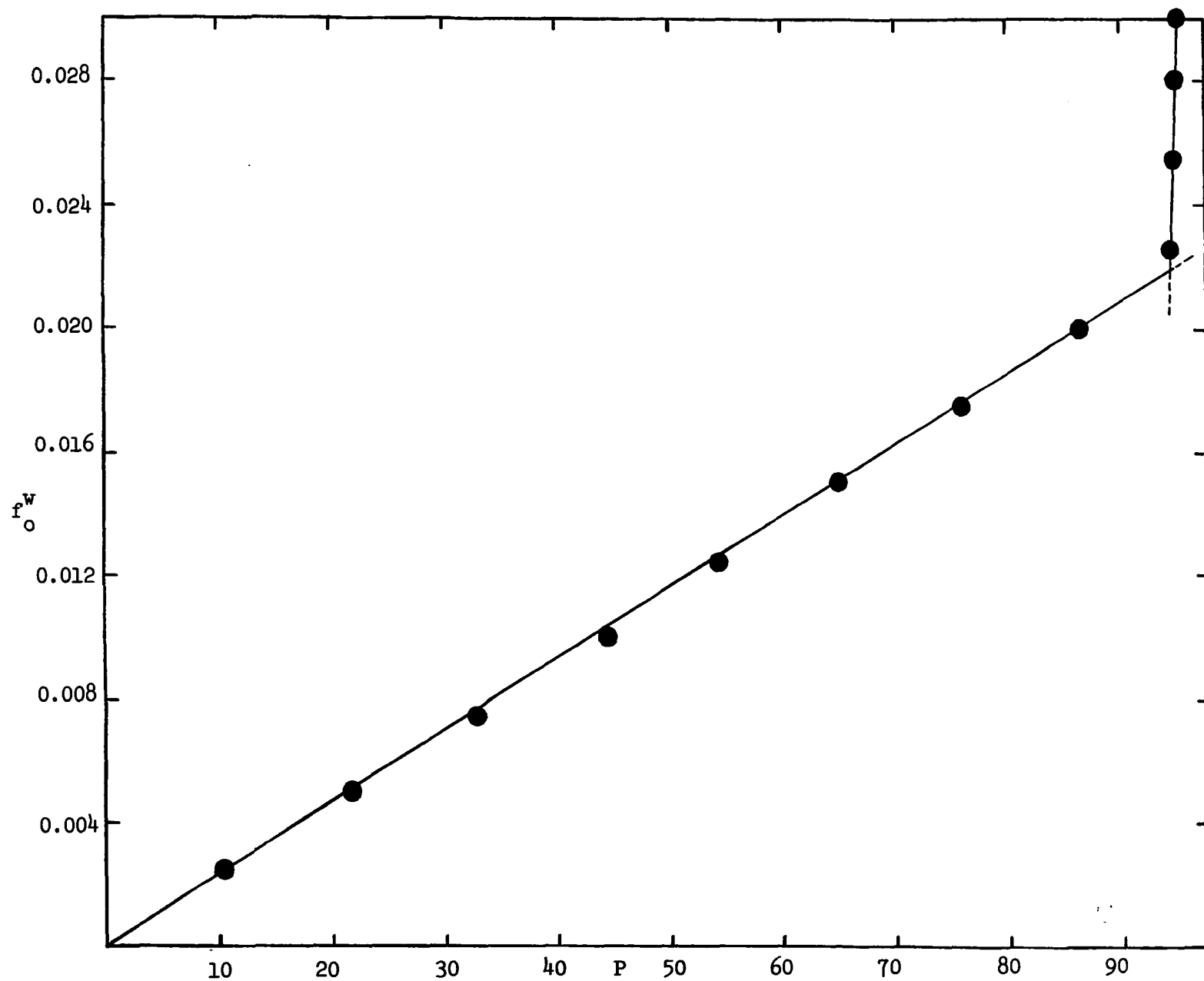


Figure 19. Formal solubility of benzene in water at 25°, using the vapor pressure measuring device.

CHAPTER VI

DISCUSSION AND CONCLUSIONS

a) Water complexity

The molecular complexity of water as a solute in non-aqueous media must be known in order to determine the stoichiometry and equilibrium constants for polar hydrates. The apparent linear dependence of concentration f_w^o , on activity, a_w , supports the conclusion that water dissolves primarily as monomeric units in carbon tetrachloride, cyclohexane, toluene and benzene at 25°. Peterson and Rodebush⁶⁰ using cryoscopic data also showed that water was primarily monomeric in benzene. However, Grodon, et al.,⁶¹ using specific volume and viscosity data calculated the average molecular weight of dissolved water in benzene to be 2.5 times that of the monomer at 90 per cent of the saturation concentration at 67°. Ackermann⁶² also concluded from near-infrared spectral data that water was highly associated in benzene, toluene and m-xylene at temperatures above 60°. It is not obvious why one should observe molecular association of water in benzene at high temperatures but not at low temperatures since normally one would expect larger degrees of association and higher numerical values for the equilibrium constants at the lower temperatures. However, the mass action phenomenon is working for the association at the higher temperatures since considerably more water dissolves. Thus,

the net effect may be towards increased association because of the predominance of mass action at higher temperatures. On the other hand, it is possible that the model Gordon, et al., used may lead to considerable error in calculating the degree of association from specific-volume data since they assumed that benzene and toluene are "inert" solvents. The data obtained by Ackermann using differentail spectral techniques are difficult to interpret quantitatively because of the high absorbance of these aromatic solvents.

The departure from linearity of plots of f_w^0 vs. a_w supports the conclusion that water is polymerizing in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane at activities above 0.6. While the data are not sufficiently accurate to distinguish between monomer-trimer or monomer-tetramer equilibrium, it is shown that the assumption of monomer-dimer equilibrium does not fit the experimental data to within estimated errors. That is, based on least squares analysis of the data, it appears that the dimer is not an important species, since in considering various combinations of assumed species the dimer did not improve the fit of the data significantly. Thus, it might be argued that the important polymerized solute species are cyclic. For, if chain polymers were forming, significant concentrations of the dimers should exist along with trimers and tetramers. In conjunction with this, Holmes, Kevelson and Drinkard⁷⁹ have used a cyclic trimer model to explain a proton exchange mechanism in a number of organic solvents.

From the trimerization constants determined for water in 1,2-dichloroethane at 10 and 25° an enthalpy of association of approximately -16 Kcal/mole is calculated. Assuming the water trimer to be cyclic, an individual

hydrogen bond enthalpy of approximately -5 Kcal/mole is obtained, which is comparable with values for association found for similar molecules.

An explanation for the tendency of water to associate in the chlorinated solvents while existing primarily as the monomer in the four solvents of lower dielectric constant, is in order. One might attribute this effect to the lower solubility of water in cyclohexane, carbon tetrachloride, toluene and benzene. Thus, even if the trimer formation constant had a value of 100 (l/mole)^2 in carbon tetrachloride, the f_w^0 vs. a_w curve would not differ detectably from linearity. Similarly, in benzene, a trimer constant as large as 20 (l/mole)^2 would produce only a slight departure from linearity. In other words, mass action is more important in promoting the association of water in these chlorinated solvents than in solvation effective in preventing it.

It might be argued that the basic unit of water dissolved in organic solvents is a cluster having a definite number of water molecules and that the association noted in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane is an association of these clusters. If it is assumed that water is monomeric in the vapor phase, which is a reasonably good assumption, the number of water molecules per cluster can be determined from the slope of a log-log plot of f_w^0 vs. a_w . The slope obtained from such plots for the six systems studied (Figure 7) is unity; thus, the basic water unit in the organic phase is a monomer.

A number of water solubilities found in the literature are compared with results obtained from the present studied in Table 33. Högfeltdt and Bolander⁶⁴ determined the solubility of water in a number of aromatic solvents and also tabulated available literature values. They used density measurements to convert the solubilities to a common unit of

molarity; a number of these values are given in Table 33. The water solubilities obtained in the present work are in general somewhat larger than those given in the literature. It is interesting to note that the ratio of the solubility values reported here for water in benzene and toluene is essentially the same as that reported by Högfeldt and Bolander. They claimed that due to their technique of adding the samples to the Karl Fischer apparatus, a small correction for the water coming from the air, adsorbed on the pipet, etc., was needed and was obtained from blank determinations. In the present work no such corrections were made since the water-in-methanol standardization (where blanks were determined) and the sodium tartrate dihydrate method both gave essentially the same titer for the Karl Fischer reagent used.

The value of 0.0220 moles/l for the solubility of benzene in water at 25° obtained using the vapor pressure-measuring device agrees well with the values, 0.0223 and 0.0229 moles/l reported by Andrews and Keefer⁹⁰ and Bohon and Claussen,⁹¹ respectively. The values, 0.0895 and 0.0051 moles/l obtained for the solubility of 1,2-dichloroethane and carbon tetrachloride in water at 25° also compare favorably with the values, 0.0895 and 0.0051 moles/l reported in the literature.^{92,93} The technique described here is convenient for determining the solubility of volatile organic compounds in water.

b) Phenol complexity

The partition and water solubility data for solutions of phenol in 1,2-dichloroethane, benzene and 1,1,2,2-tetrachloroethane have been interpreted in terms of phenol and phenol-water aggregates. The phenol data can be explained by assuming the existence of phenol monomers,

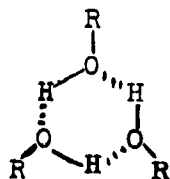
TABLE 33

SOLUBILITY OF WATER IN SEVERAL ORGANIC SOLVENTS AT 25°.

SOLVENTS	C _w ^o (1/mole)	REFERENCE	EXPERIMENTAL WORK
Benzene	0.026	80	Water displaced by air dried and absorbed in CaCl ₂
	0.0343	81	Cloud point
	0.0350	82	Solubility of AgClO ₄
	0.032 ± 0.001	64	Karl Fischer
	0.025	83	Tritium tracer
	0.0240	84	Vapor pressure
	0.033	85	Gasometric with CaH ₂
	0.033	43	Cloud point
	0.031	86	Cloud point
	0.0365±0.002	87	Karl Fischer
	0.031	88	Tritium tracer
	0.0349±0.0005	This work	Karl Fischer
Cyclohexane	0.0043 (20°)	86	Cloud point
	0.0043 (20°)	89	Tritium tracer
	0.0024±0.0003	This work	Karl Fischer
Carbon			
Tetrachloride	0.0087 (24°)	88	Water displaced by air dried and absorbed in CaCl ₂
	0.0070 (20°)	85	Gasometric with CaH ₂
	0.0087±0.0003	This work	Karl Fischer
1,2-Dichloroethane	0.1262±0.0014	This work	Karl Fischer
1,1,2,2-Tetrachloroethane	0.1010±0.0012	This work	Karl Fischer
Toluene	0.0260±0.001	64	Karl Fischer
	0.0240	85	Gasometric with CaH ₂
	0.022	86	Cloud point
	0.019	88	Tritium tracer
	0.0274±0.0005	This work	Karl Fischer

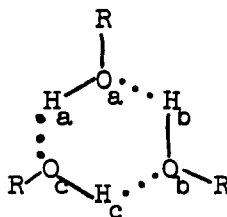
monomer dihydrates, dimer monohydrates and a small amount of trimers in the organic phase. The values for the phenol monomer dihydrate constants, 50.03 ± 1.86 , 13.79 ± 0.43 and 12.97 ± 0.12 (1/mole)² in benzene, 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, respectively, at 25° are compatible with the solvent order (inertness) based on their dielectric constant. Similarly, the values for the dimer monohydrate constants, 15.74 ± 0.26 , 6.99 ± 0.26 and 3.37 ± 0.1 (1/mole)² in benzene, 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, respectively, follow the same criterion. However, the values for the trimerization constants, 0.263 ± 0.04 and 0.477 ± 0.06 (1/mole)² for phenol in benzene and 1,1,2,2-tetrachloroethane, respectively, are in the reverse order from the expected. The "best" trimerization constant obtained for the association of phenol in 1,2-dichloroethane was 0.002 ± 0.029 (1/mole)², i.e., the value of the constant is over-shadowed by the probable error in its determination. Thus, in this solvent the data can be explained by assuming only the existence of hydrated aggregates. Using differential pressure techniques, Coetzee and Lok³⁸ obtained a dimerization constant of 40 1/mole in 1,2-dichloroethane at 37° but did not mention the drying procedures employed or the water content of their reagents.

While it is not possible to determine the exact nature of the structure of these phenol and phenol-water aggregates, plausible structures can be postulated. Since these aggregates are composed of three monomer units, a cyclic model is proposed to explain the stability of the aggregates



where R can be either a hydrogen atom or a phenol group.

Cohen and Reid⁹⁴ have suggested that the cyclic trimer or tetramer is more stable than the dimer. They argued that the polarization of the "unshared pair" electrons of O_b as it approaches H_c allows the O-H bond of molecule c to become much more polar than in the isolated state. This means that because of the increased electron density on O_c its unshared pair of electrons becomes more polarizable and c can form a stronger hydrogen bond with molecule a than was present in the dimer.



It is argued that if one of the hydrogen bonds is broken, the cyclic trimer or tetramer will tend to break up completely. Thomas⁹⁵ has also proposed the cyclic trimer model for the association of alcohols and phenol to explain the observed entropy changes for several systems.

Schringer, et al.,^{96,97} have studied the structure of crystalline phenol using x-ray techniques and found that phenol crystallizes in the monoclinic system ($C_2^2 - P2_1$, $a = 6.05$, $b = 9.24$, $c = 15.29\text{\AA}$, $\gamma = 90^\circ$) with 6 molecules per unit cell. The phenol molecules are connected in infinite chains by hydrogen bonds with cyclic phenol trimers in a screw-like position in the chains. While it is dangerous to draw conclusions concerning the structure of phenol aggregates in solution from their structure in the crystalline state, a qualitative correlation may be suggested.

The partition data for phenol distributed between benzene and water agree quite well with the data of Philbrick.¹⁵ He calculated a dimer-

zation constant of 0.575 l/mole; however, his interpretation did not include the formation of hydrates. There is no obvious explanation for the discrepancy between the results of Lassettre and Dickinson³³ and those of the present work. They calculated a dimerization constant of 0.570 l/mole at 25° for phenol in anhydrous benzene solutions using isopiestic measurements. The partition study of Endo¹¹ was conducted over a larger concentration range (up to 1 molar in the organic phase) and he interpreted the data in terms of a monomer-trimer equilibrium without considering the formation of hydrates.

It was not possible to fit the data for phenol in carbon tetrachloride using the same species assumed in benzene, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane. Phenol appears to polymerize to a greater extent in carbon tetrachloride; the data could be explained by assuming monomers, trimers and hexamers. However, the data could also be explained assuming tetramers instead of hexamers. Since least squares analysis indicated that the total formal dimer concentration is less than 5 per cent of the total throughout the concentration range studied, the dimer does not seem to be an important species.

The value of the trimerization constant, 4.1 (l/mole)^2 , obtained in the present work agrees reasonably well with 4.78 (l/mole)^2 at 21° reported by Saunders and Hyne³¹ and with 13.6 and 8.9 (l/mole)^2 at 20 and 30°, respectively, given by Rea.²⁶ Hoffman⁹⁸ and Raczy⁹⁹ calculated for phenol in carbon tetrachloride trimerization constants of 5.31 and 0.8 (l/mole)^2 at 25 and 21.5°, respectively, in addition to 1.13 and 1.1 l/mole given for the dimerization constants. The general interpretation given by the investigations above is that the phenol trimer is cyclic.

The partition and water solubility data of Badger and Greenough¹⁶ do not agree with the present work. There is no obvious explanation for the discrepancy; however, their water solubility data are not of sufficient accuracy to justify a detailed analysis.

The infrared data for phenol in the first overtone region in anhydrous benzene, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane indicate that phenol is not associated to a very large extent in these solvents at 25°. On the other hand, the data indicate that phenol is highly polymerized in carbon tetrachloride.

From the present work it is concluded that the association of phenol in organic solvents is greatly affected by the presence of water. The interaction of phenol with water in 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and benzene could be explained by the formation of monomer dihydrates and dimer monohydrates. It is to be emphasized that the partition method is inadequate for determining equilibrium constants for self-association of polar molecules without accompanying water solubility data. However, it is believed that meaningful results can be obtained using a combination of partition and water solubility techniques.

c) Error Calculations

The error calculation for water in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane is a two-parameter problem. The data were fitted using the function

$$f_w^o = C_w^o a_w + nK_n (C_w^o a_w)^n$$

where f_w^o is formal concentration of water, C_w^o is a proportionality constant equal to monomer concentration at saturation, a_w is the water activity, n is the number of water molecules per aggregate, and K_n is the association constant. Since the water activity is known more

accurately than the water concentration, the error was placed in the concentration variable rather than the activity. The root mean square deviations were obtained using

$$f(C_w^o, K_n) = \left[\frac{\sum_{i=1}^N [f_{w,i}^o - f_{w,i}^{o,calc.}(C_w^o, K_n)]^2}{N-2} \right]^{1/2}$$

where $f_{w,i}^o$ is the observed value for the formal concentration of water for the i th data set and N represents the number of measured values.

The standard errors in the parameters were obtained with the aid of a computer using a graphical least squares method.¹⁰⁰ From a plot of C_w^o vs. K_n , the errors can be obtained from the location of the horizontal and vertical tangents drawn to the error contour,

$$r_s = r_m \left(1 + \frac{1}{N-2} \right)$$

where r_s is the standard error and r_m is minimum error.

The error calculations for data on solutions of phenol in 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and benzene were obtained using the weighted average root mean square deviations of partition and water solubility data. The partition data were fitted using the equation

$$f_p^o/C_p^w = K_d(1 + K_{pw_2} C_w^{o2} C_a^{o2}) + 2K_d^2 K_{p_2w} C_w^o C_a C_p^w + 3K_d^3 K_{p_3} C_p^{w2}$$

The error was placed in the ratio of the phenol concentration in the organic phase to the concentration in the aqueous phase, since it is believed that the relative errors in the determined phenol concentrations in the two phases are approximately equal. The water solubility data were fitted using the equation

$$\Delta f_w^o = 2K_{pw_2} C_w^{o2} C_a^{o2} C_p^o + K_{p_2w} C_w^o C_a C_p^{o2}$$

Again it was assumed that all the error resides in the water concentration. The "best" constants were obtained from partition data and independently from Water solubility data. By combining the errors obtained from both sets of data, a weighted average was used to obtain the errors in the constants.¹⁰¹

No error calculations were performed for the phenol in carbon tetrachloride due to the large number of parameters used. Except for the phenol monomer-monohydrate and trimerization constants, the equilibrium constants reported for this system should be considered as order of magnitude values.

d) Suggested studies

Several experiments might be proposed for extending the present study of the molecular complexity of water and phenol in dilute solutions.

The accurate determination of the solubility of water in benzene and the other solvents as a function of water activity at higher and lower temperatures than 25° would provide much needed information concerning its molecular complexity as a solute. Also water solubility studies are needed in solvents which dissolve much more water than 1,2-dichloroethane to determine whether monomer-trimer or monomer-tetramer equilibrium is favored. The vapor pressure-measuring device offers a convenient method to determine the solubility of water as a function of its partial pressure or activity in organic solvents, especially in solvents which have low volatility.

To gain more information on the molecular complexity of phenol in organic solvents, especially in carbon tetrachloride, partition experiment in which phenol is distributed between aqueous salt solutions and

the organic solvents would be most useful. It is believed that one can obtain the distribution ratios with greater accuracy than the water solubility measurements and thus, with appropriate equations the constants of association can be calculated. Preliminary experiments indicate some difficulty arising in using calcium chloride as the salt in the aqueous phase. It is possible that some type of interaction occurs between phenol and calcium ions; thus a salt is needed which will not interact with phenol and which will at the same time give a large range of water activity.

Many investigators have given evidence for the association of solutes in aqueous phase.^{12,102} The association of phenol in the aqueous phase can be studied by measuring the absorbance in the ultraviolet region (268 mμ) of phenol vapor in equilibrium with the aqueous solutions. Preliminary experiments indicate that such a study is feasible at 25° using 10 cm. cells. By observing the absorbance of phenol vapor as a function of phenol concentration in the aqueous phase, the complexity can be determined, provided it is assumed that the phenol vapors are not significantly associated.

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APPENDIX A

Introduction

This section contains a list of references encountered during the course of a literature survey on the hydrogen bonding properties of phenol. The survey was conducted by using Chemical Abstracts and by cross-referencing articles dealing with hydrogen bonding. This list is reasonably complete through the year 1964.

The arrangement is alphabetical according to first author. The title of the article is included so that a judgment can be made on the context.

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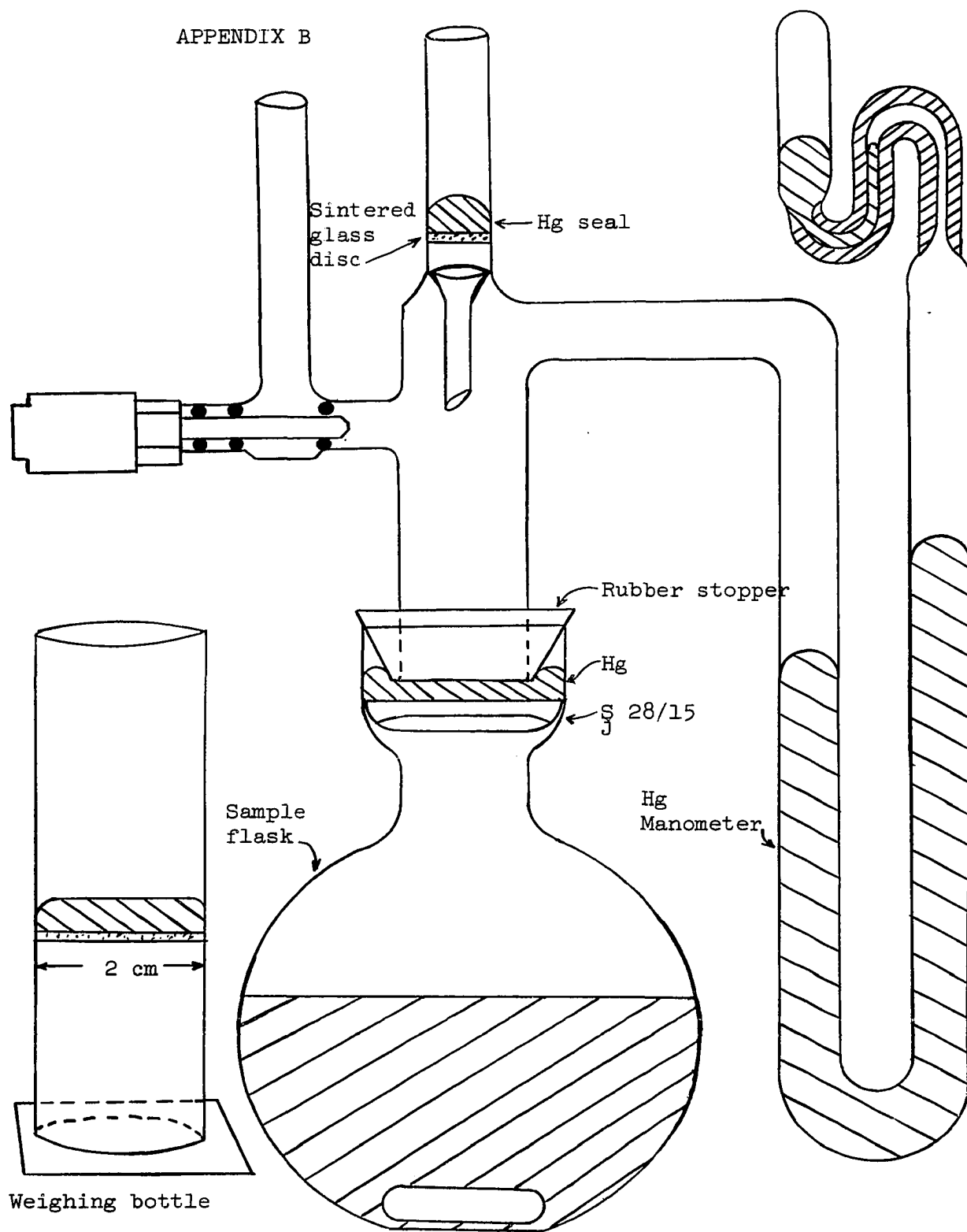
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APPENDIX B



Vapor Pressure-measuring apparatus.