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The
FORMATION CONSTANT OF DIMER OF ACETIC ACID IN DIFFERENT SOLVENTS

By

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M. Saidul Islam

ABSTRACT

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For the determination of Formation Constant of acetic acid dimer (linear and cyclic), a theoretical frame work has been constructed where it is shown that

$$PS = \frac{K}{D} \times \frac{(P_2 - 2PS)^2}{V} + P_1\ ;$$ where P_1, P_2, D, PS, V and K are molar property of monomer, that of dimer, $D = P_2 - 2P_1$, apparent molar property at measured concentrations, ~~and~~ volume V ~~which~~ contain one mole of species and equilibrium constant respectively.

The molar volume and molar polarization were obtained by measurement of specific volume and dielectric constant in solutions of varying concentrations for which PS and V were calculated. An ingenious Graphical methods were employed on the basis of the above relation to obtain P_1, P_2, K/D and finally K.

The results of such investigation in five solvents, such as, CCl_4, benzene, chlorobenzene, high boiling hydrocarbon and cyclohexane have been found to be satisfactory on careful considerations of various effects of solvents and also of their peculiar structures.

$D\ (P_2 - 2P_1)$: Change of molar property.

K_2 or K : Formation constant of dimer

W : Weight fraction

V_f : Volume of the float

W_f : Weight of the float

$\triangle v$: Change of specific volume
(i.e. observed - calculated)

$\triangle \epsilon$: Change of dielectric constant
(i.e. observed - calculated)

Wt. fr. or wt.fraction : Weight fraction

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INTRODUCTION

Chemical Bond and Dissociation Energy

Much of science of chemistry is concerned with making and breaking of chemical bonds. Pauling[1] has defined chemical bond as follows: "There is a chemical bond between two atoms or groups of atom in case that the forces acting between them as such as to lead to the formation of aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species".

The word 'stability' means the 'strength of chemical bond' which is given by bond energies expressed in Kcal/mole. At room temperature, the average translational energy in the direction of one coordinate is ½ RT or .3 Kcal/mole. A simplified expression for the fractional number of molecules possessing translation energy E or greater in two degrees of freedom is $\frac{n_E}{n_0} = \frac{E}{e^{-RT}}$. If two molecules collide, then it is reasonable to assume that the combined translational energy along the line of collision represent translational energy available for chemical reaction (breaking of a chemical bond). Ordinary covalent bonds have enthalpy between 200 — 90 Kcal/mole, whereas the forces that come into operation, which have been recognized as inter-molecular forces, involve energies from less much than 1 to 15 Kcal/mole. We can now look at the stability of "chemical bonds" by computing n_E/n_0 at 300^{0}K for different values of E indicates that at room temperature (300^{0}K) only 1% by molecular collision involve 3 Kcal/mole and a very negligible number of collision, 10^{-42}% have energy equal to or greater than 60 Kcal/mole. Thus it is clear that bond energy involving more than 20 Kcal/mole should have very little measurable dissociation of bond at ordinary temperature.

Inter-Molecular Forces

Six types of inter-molecular forces are generally recognized:

(i) Repulsive forces, due to repulsion effect between closed electron shells which is a very short range interaction;

(ii) Dispersion forces, which are always attractive for molecule or atom in their ground state and arise even between neutral, non-polar molecules or atoms and are due to average interaction of an instantaneous moment of one molecule brought about by charge density fluctuation and the electric moment induced on the other molecule or atom;

(iii) Polarization forces, which arise from the polarization of atom or molecule by an approaching atom or molecule forcing redistribution of charges with concomitant effects on it s permanent electric moment, due to the effect of charges or permanent electric moments of the approaching atom or molecule;

(iv) Orientation forces, due to mutual coloumbic attraction or repulsion of the net charges or electric moments carried by two interacting atoms or molecules, such as interaction between two ions, ion-dipole and dipole-dipole interaction. In a high dielectric medium at a distance of 5 Å E can be nearly 5 Kcal/mole for two unit of charges of opposite signs;

(v) Mulliken charge transfer forces, leading to transfer of an electron from an electron donor molecule to an electron acceptor molecule forming a well defined complex, known as charge transfer complex, with concomitant appearance of a characteristic intense band in the visible or UV spectrum of the region[2]. The thermodynamic parameters for charge transfer complexes are of the same magnitude as for hydrogen-bonded complex and

(vi) Hydrogen bonding, due to involvement of specific H-atom of the proton donor group with a localized site of high electron density in the same or another molecule.

Repulsive, dispersive, polarization and, most of the time, orientation forces are very weak forces and hence are not "stable" enough leading to the formation of an aggregate with sufficient stability to be considered as independent molecular species. On the other hand charge transfer and hydrogen-bonding have bond energies from 30 Kcal/mole down to 4 Kcal/mole or less. The important features of these two types of complexes is that, at ordinary temperature, only a fraction of the molecule are associated and at equilibrium, due to kinetic energy of motion of the molecules, a certain number of new molecules are continually broken while the same number of new complexes are continually formed.

Hydrogen-Bond

Hydrogen-bonds are almost as frequent and almost as important in nature as ordinary chemical bonds and they will probably remain a target for intensive search for many generations to come. Hydrogen-bond formation is a special kind of dipole-dipole interaction. When hydrogen occurs linked to an electronegative element or group, the polarized H-atom permits a close approach to another negative atom having a lone pair, giving rise to a specific bond formation, represented as A — H .... B and termed as H-bond.

The concept of H-bond was first introduced by M. L. Huggins[3] and then Latimer and Rodebush[4] in 1920 during their study about the investigation of the associative nature of the water molecules. Since that time, there has been considerable discussion of a suitable definition of the H-bond[5].

A competent description of the hydrogen-bond has to be able to take into account a number of important properties of H-bonded aggregate for which extensive experimental evidence are available:

(i) Molecules forming H-bonds come much closer than the sum of the vander Waals radii of the nearest atoms would allow. In Figure 1.1 this fact is demonstrated with the aid of two typical H-bonded complexes - $(HF)_2$ and $(H_2O)_2$.

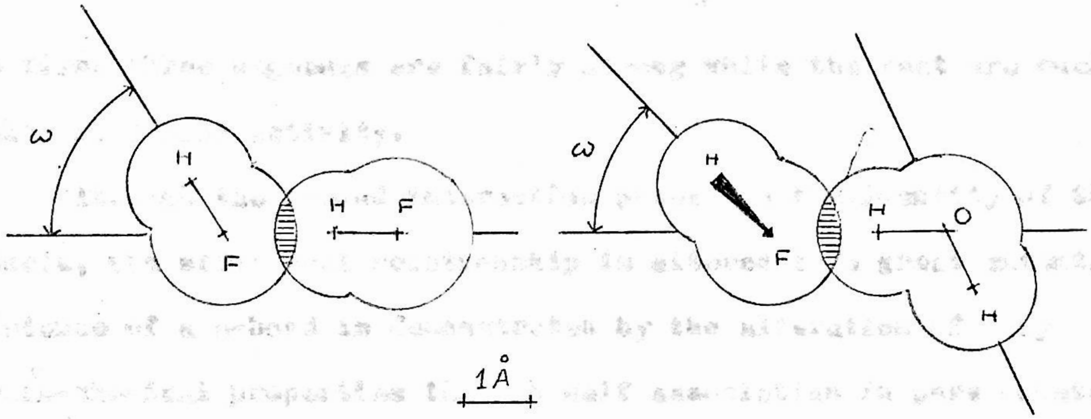


Fig. 1.1. Equilibrium geometry of $(HF)_2$ and $(H_2O)_2$. The circles around the nuclei represent the vander waals radii[6];

(ii) H-bonding increases the polarity of the molecules concerned. The dipole moment of an H-bonded complex is larger than vectorial addition of the monomer moments would suggest;

(iii) As a consequence of H-bonding the lengths of the HX-bonds concerned are somewhat increased, IR stretching frequencies are shifted to smaller wave numbers and larger integral IR intensities of the corresponding absorption bands are found[7] and

(iv) Electron densities at the protons involved in H-bonds are decreased and consequently NMR signals are shifted to lower magnetic fields[8].

The most common H-bond donor segments in the acidic molecule, in order of strength, are F-H, O-H, N-H, [illegible] Cl-H, S-H, P-H and in certain situations C-H (as in chloroform, where C is attached to many negative atoms or in acetylene, where carbon atoms are linked with triple bond rendering the C-atom highly negative in character) can form H-bond. Only the first three segments are fairly strong while the rest are much weaker in H-bond activity.

Although the H-bond interaction preserves the identity of the adducts, the structural relationship is altered to a great extent. The existence of a H-bond is demonstrated by the alteration of many physi~~o~~c-chemical properties through self association in pure substances or by complex formation between donor and acceptor molecules in the mixtures. The following are the causes of such alterations:

(i) Molecular aggregates of two or more come into existence, thereby altering the boiling point, melting point, dielectric constant and the colligative properties;

(ii) As the H-bond interaction is attended with shortening of X ... Y distance, alteration of electronic environment at this zone, the density, refractive index and proton magnetic resonance are also altered and

(iii) As this combination will also alter in many way the vibrational spectra of the uncombined molecules and a face new vibrations should also appear.

If these expectations are fulfilled in any particular situation, then it is assumed that H-bond exists. The effects of the H-bond on self-association or association with a donor molecule on various physico-chemical properties described giving the reasons of such changes in the Table 1.1.

Table 1. 1

Effect of Hydrogen Bonding on Some Physico-Chemical properties of Liquids in Liquid Mixture.

Property	Behaviour of H-bonded compounds relative to non-bonded state	Causes of the behaviour
. Molecular weight (by cryoscopy)	Higher	Number of molecule decreases due to H-bond intermolecularly.
. Density	Higher	Contraction of volume.
. Refractive Index	Higher	Electron density increases at X-H .... Y.
. Dielectric Constant	Mostly higher	Vector addition of moments of adducts.
. Thermal expansion	Lower	Resistance to breakage of H-bond.
. Thermal conductivity	Higher	Protons high vibration freedom facilitate transfer of internal kinetic energy in the bulk.
. Electrical conductivity	Higher	Proton tunneling and rotation of molecule help electrical charge transfer.
. Acoustic conductivity	Higher	Extensive molecular arrangement.
. Viscosity	Much higher	Longer & complex molecular size.
0. Surface tension	Higher	Molecules held together by H-bond.
1. Vapour pressure	Lower	Molecules held together by H-bond.
2. Melting and boiling point	Higher	Resistance to break H-bond holding together many molecules.
3. NMR chemical shift	Shift to lower field generally	Rapid exchange of H-atom between two electronic environment.

Pimentel and McClellan[9] have thoroughly described the uses of these physico-chemical properties in their book. The importance of these properties for investigation of H-bond interaction, in order of frequency of their use, are:

(i) Spectroscopic methods, e.g. U. V., I. R., Raman spectra, and Nuclear magnetic resonance, and

(ii) Nonspectroscopic methods, among these methods, the dielectric properties have been largely preferred over others, mainly due to the relative ease of their quantitative interpretation.

A brief discussion on the spectroscopic manifestations will convince one that H-bonding has all the attributes of a regular chemical bond with some interesting differences.

Spectroscopic Manifestations of Hydrogen Bond

Infrared and Raman spectra reveal the characteristic frequencies of molecular vibrations. Such frequencies are fixed by the masses of the vibrating atoms, the molecular geometry and the restraining forces holding the atoms in their equilibrium position in the molecule. Since the restraining force (force constant) is simply related to chemical bond order, vibrational spectra have been an excellent source of information concerning the H-bond. The different vibrational mode in the H-bonded substances are shown below:

1. ν_s $R - A - H \longrightarrow \cdots B \longrightarrow$ A - H stretch(anti-symmetric)

(3500-2500 cm^{-1}, 3-4 μ)

2. ν_b $R - A - \overset{\curvearrowleft}{\underset{\curvearrowright}{H}} \ldots B$ R - A - H bond (in plane)
(1700 - 1000 cm^{-1}, 6-10 μ)

3. ν_t $R - A - \underset{\curvearrowright}{H} \ldots B$ R - A - H torsion (out of plane)
(900 - 300 cm^{-1} 11-30 μ)

4. ν_σ $R - A - H \ldots \leftarrow B \rightarrow$ A .... B stretch
(250 - 50 cm^{-1}, 40-200 μ)

5. ν_β $R - A - H \ldots \overset{\curvearrowleft}{\underset{\curvearrowright}{B}}$ A-H .... B bend ($<$ 50 cm^{-1}, 200 μ).

The most pronounced changes that occur are (i) A-H stretching frequency (ν_s) is shifted to lower frequency, (ii) the breadth of this frequency increases markedly and (iii) also the intensity is unusually large. This anti-symmetric stretching frequency, ν_s occurs near 3500 cm^{-1} (3 μ) and these changes have properly assumed the importance of qualitative criteria and quantitative indices of the H-bond strength, bond energy and other bond properties. This stretching frequency shows spectacular changes with change of temperature, concentration and to a lesser extent, change of pressure. The increase of temperature reduces the intensity and so does the reduction of concentration, the increase of pressure, on the other hand, has the effect like the increase of concentration. The extreme sensitivity of ν_s to these changes clearly indicates that H-bonding systems involve the non-bonded species and the bonded species in rapid equilibrium. The intensity of IR stretching frequency ($\Delta\nu_s$) is much used for the measurement of equilibrium constant, K of the H-bonding in self-association or of association with another base molecule. The measurement of K at different temperatures permits calculation of the thermodynamic quantities ΔH, ΔS and ΔF.

The shift of stretching frequency ($\Delta \nu_s$), brought about by H-bond formation, has been found to be related to various physico-chemical properties. The first and most important relationship involving $\Delta \nu_s$ was proposed by Badger and Bauer[10] in 1937. Since then, through the works of many other authors[11-18], there has been a general acceptance of the proposal that $\Delta \nu_s / \nu_s$ provides an index of ΔH of H-bond information. Also, various other physical properties have been found to be directly related to $\Delta \nu_s$; such as acid strength[19], base strength[20], reactivity or rate constant[21], Hammett sigma function[22] and Henry's law constant[23].

A technique of rapidly increasing importance in the study of H-bonding is the proton magnetic resonance. H-bonding causes a very large shift to low field of the X-H proton resonance. The position of the proton signal for X-H involved in H-bonding is both temperature and concentration dependent. The H-bonding being essentially dynamic in nature, the formation and breaking of the bond occurs rapidly. Because of the relatively long "observation" time of NMR measurements, only once signal is observed, corresponding to the average environment of the proton distributed between free and complexed state. The frequency of the observed peak is thus the weighed mean of the frequencies of all the components present at the equilibrium[24].

The measurement of the association constant at different temperatures loads to the thermodynamic quantities, ΔH and ΔS. Several workers[25-27] have obtained these quantities from the measurement of chemical shifts. Many workers[28] claim that the change in chemical shift on H-bonding, Δ , is a measure of the strength of the bond. The existence of roughly linear relations between Δ and $\Delta \nu_S$[29], Δ and p^{ka}[30-31] or between Δ and ΔH[24] indicate in a semiquantitative way the linear relationship among $\Delta \nu_S$, Δ , ΔH and b and distance of X ..... Y.

Theory of Hydrogen-Bond

A successful theory of the H-bond has to be able to explain all the properties for which extensive experimental evidences are available. The recent development in theory made it possible to define certain contributions to H-bond energies. Estimate on the relative importance of forces of different origin (coulomb, polarization, dispersion forces etc.) became accessible to various quantum mechanical approach and give a fairly correct description of isolated dimer or in some cases, isolated trimer but fails to deal with larger clusters.

Sometime ago it had already been suggested by Coulson and Danielson[32] and independently by Tsubomura[33] that the main problem in the theory of hydrogen-bond is brought about by a complicated super position of the five men contributions which are of similar magnitude:

(i) Electrostatic or coulomb energy,

(ii) Exchange and repulsion energy,

(iii) Polarization energy,

(iv) Charge transfer energy or covalent contribution and

(v) Dispersion energy.

The efforts of recent calculations meet exactly these ideas. Various methods of application of perturbation theory and M. O. methods to theoretical investigation on H-bond have been described in details in "The Hydrogen Bond", vol.-1(by Schuster, Zundel and Sandorfy)North-Holland publishing company.

All reliable calculations agree in the fact that considerable overlap between the molecule forming the H-bond occurs, and the whole phenomena can be described neither by the electrostatic theory nor by weak covalent bonding alone. A nice example demonstrating the superpoaition of different contribution to the H-bond energy was presented by Kollman[34], who was able to explain the stereo-chemistry of H-bonded structures by superposition of coulomb and charge transfer energy.

Classification of Molecules vis-a-vis Hydrogen-Bonding

All molecules can be conveniently classified into four types with respect to their ability to participate in the hydrogen-bonding(Table-1.2).

Table 1. 2

Classification of Molecules according to Pimentel and McClellan[35].

Type	Description	Examples
I	molecules with one or more donor groups (acids) and no acceptor groups	haloforms, highly halogenated compounds and acetylenes.
II	molecules with one or more acceptor groups (bases) and no donor groups	ketones, ethers, esters, aromatics, tertiary amines, nitriles and isonitriles.
III	molecules with both donor and acceptor groups.	alcohols, water, phenols, inorganic and carboxylic acids, primary and secondary amines.
IV	molecules with neither donor nor acceptor groups.	saturated hydrocarbones, carbon tetrachloride and carbon disulfide.

Hydrogen bonding molecules are divided into types I through III, while molecules incapable of H-bonding form type-IV. The latter includes compounds which are used as the so called inert solvent in studies of H-bonded molecules.

Various H-bonded systems occur when one or more of the three types of molecules are present. The bulk of studies dealing with H-bonded systems have been performed in the liquid phase, and unless otherwise specified we will restrict ourselves to solutions. It is instructive to consider some of the types of H-bonded systems (H-bonded equilibria) formed in solutions of various types of molecules.

Type I plus type II molecules form H-bonded complexes, frequently in a simple 1:1 ratio. The strength of H-bonding depends primarily on the relative acidity of I and the basicity of II. The system chloroform acetone is a typical example:

$$Cl_3C - H + (CH_3)_2\ C = O \rightleftharpoons Cl_3C - H \ldots\ldots O = C(CH_3)_2$$

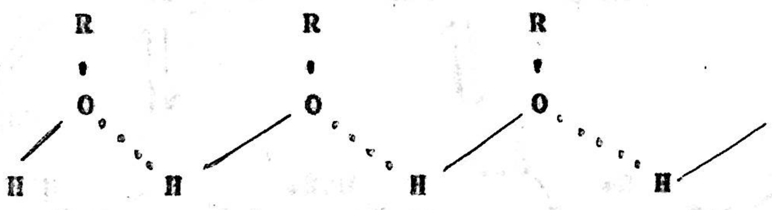
Type III molecules can self-associate by H-bonding with themselves. Two types of H-bonded complexes may be formed:

(i) intermolecular, involving two or more separate molecules; and

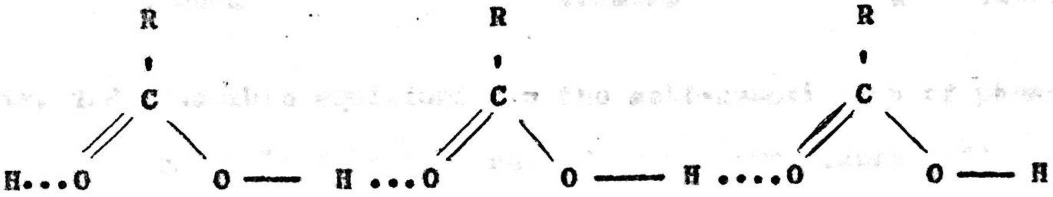
(ii) intramolecular, involving donor and acceptor sites within the same molecule. The strength of H-bonding depends on the relative acidities and basicities of the donor and the acceptor sites and in case of intramolecular H-bonds, on the spatial arrangement of donor and acceptor sites. Self association through intermolecular H-bonds can form a large variety of open (linear) and cyclic (closed) polymers. The exact nature of the H-bonded molecular species present in water, liquid alcohols, and phenols, and in their solutions in inert solvents, remains unclear inspite of a great deal of effort over the last 20 years.

Consequence of Hydrogen Bond Formation

A direct consequence of H-bond formation is the "self-association"[22] of a compound to give dimer, trimer, or higher polymers. Hydrogen bond formation causes water to attach itself to foreign molecules, so that their solubility in water is increased. Multiple bounded arrangements occur in liquid water and in liquid HF and they are common in carboxylic acids, alcohols, phenols, amides, proteins, polypeptides and polyhydroxy organic and inorganic materials. How these alcohols as well as phenols and carboxylic acids form these polymers, are shown below:



(In case of alcohol and phenols)



(In case of carboxylic acids)

Self Association and Equilibrium Constant for Different Self-Associated Species

Many H-bonded molecules contain both donor and acceptor groups and such molecules can self associate through H-bonds in two or more different ways into a number of complex species (polymers, multimers, n-mers) which may co-existsx with one another in a series of complicated equilibria. The most complicated cases of self-association are the ones where the cyclic and linear H-bonded species co-exist. The best known examples are water, alcohols and phenols. Their self-association can be generalized schematically as in Fig. 1.2.

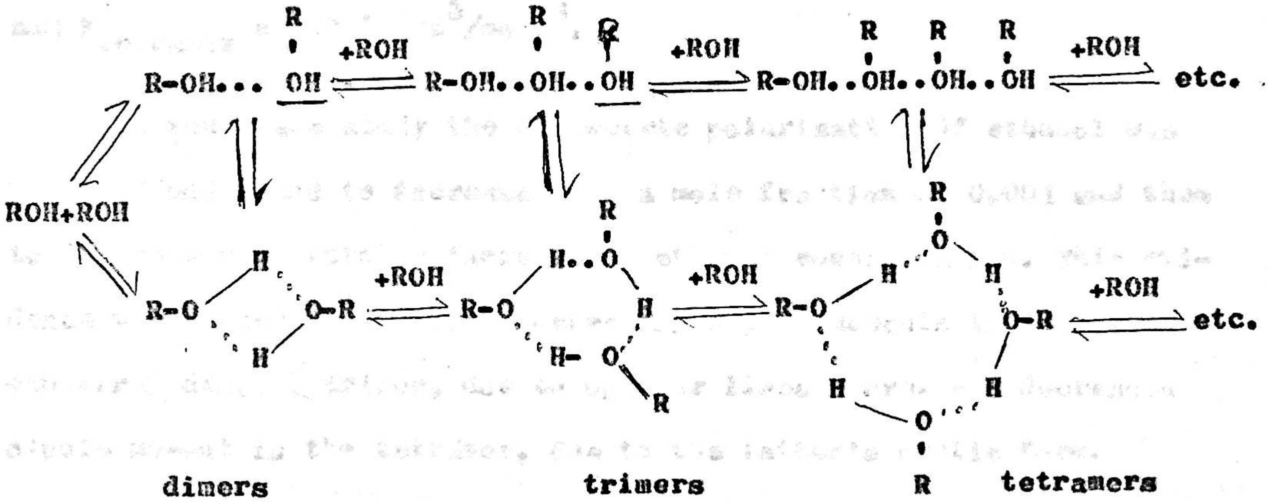


Fig. 1.2 Possible equilibria in the self-association of phenols and alcohols (The terminal OH groups are underlined).

It is obvious that analysis of such systems requires the determination of many equilibrium constants. Rigorous treatments using IR absorption measurements are possible in principle[36], but difficult to carry out in practice.

The usual approach in studies of self-association using IR and PMR techniques has to develop a model which assumes that only a few H-bonded species are present (usually two or three) and then to carry out computations from the experimental data to ascertain whether con-

-sistent values of the association equilibrium constants are obtained. In a typical example, ethanol was assumed to exist in CCl_4 solution as monomer, open dimer and trimer, and cyclic tetramer[37]. This interpretation yielded $K_{dimer} = 0.95$ litre/mole, $K_{trimer} = 95$ litre^2/mole^2 and $K_{tetramer} = 650$ litre^3/mole^3.

In the same study the dielectric polarization of ethanol was measured and found to increase upto a mole fraction of 0.001 and then to decrease with further increase in ethanol concentration. This evidence was judged to indicate increasing dipole moments in the order monomer $<$ dimer $<$ trimer, due to open or linear form, and decreased dipole moment in the tetramer, due to the latter's cyclic form.

Acetic Acid:

It is now clear that a close study of even monomer-dimer equilibria is infested with various formidable complications. The present work was undertaken to study only the monomer-dimer equilibrium of acetic acid in various types of solvents.

Beckman[38] postulated the existence of monomer-dimer equilibrium in order to explain the anomalous freezing point depressions of carboxylic acids in inert solvents. Since this early work acetic acid has been extensively studied[39] and the presence of a monomer-dimer equilibrium has been corroborated.

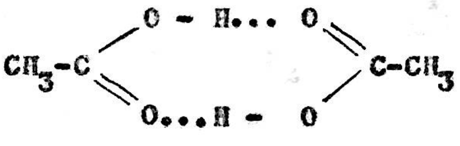
Using electron diffraction Karle and Brockway[40] concluded that in the gas phase acetic acid exists as a cyclic dimer. Based on a model assuming only a simple monomer-dimer equilibrium, several attempts to measure this hydrogen bonding equilibrium constant have resulted in a considerable range of values[41-45].

In the infrared spectroscopy, the extreme sensitivity of the IR stretching frequency(ν_s) indicates that H-bonding systems involve the non-bonded species in rapid equilibrium. The intensity of stretching frequency(ν_s) is much more used for the measurement of equilibrium constant K of the H-bonding in self-association. It is disturbing to note that the magnitude of the equilibrium constant (dissociation of the associated species) obtained from infrared intensity data decreases rapidly with increase of acetic acid concentration[42-44].

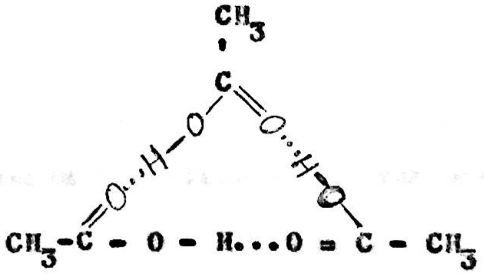
However, the dimerization of acetic acid has been studied extensively and the dimerization constant can be determined by various methods. They include cryoscopy, ebullioscopy at atmospheric and reduced pressure, Isopiestic measurements, absorption spectroscopy (visible, UV and IR) and ultrasonic absorption. Useful summaries of such works upto about 1953 were included in the papers of Lefevre and Vine[46] and Allen and Caldine[39]. Almost all of the recent investigations are limited to IR[47-49], NMR[50], dielectric polarization[51,52] and ultrasonic studies[53].

It is well known that the concentration dependence of the NMR chemical shift can be used to study hydrogen-bonded systems[54]. Huggins, Pimental and Shoolery[55] first studied the NMR chemical shift of acetic acid in CCl_4. This work was extended by Reeves and others[56-58]. Recently the NMR chemical shift of the acid proton of acetic acid in CCl_4 has been investigated by Goldman and Emerson[50]. It was observed that concentration dependence of the acid proton-chemical-shift can not be accounted for quantitatively by a simple monomer-cyclic dimer equilibrium. One must conclude that other hydrogen bonded species are present in solution. The observation of long chain polymers in crystalline acetic acid[59] along with cyclic dimers in the gas phase lead one to postulate that acetic acid in the liquid state can be described as an equilibrium mixture of the gas and solid states. Recently infrared and Raman evidence indicating the presence of chain polymers has been reported[60-62]. Goldman and Emerson[50] explained the observed chemical shift quantitatively by assuming that acetic acid is present as an equilibrium mixture of monomers, cyclic dimers, linear dimers and linear polymers.

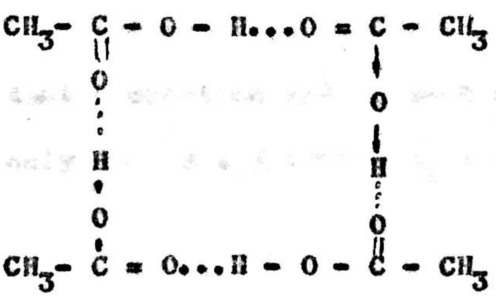
The structure of acetic acid dimer, trimer and tetramers as represented by Ritter and Simons[63] is given in the following:



dimer



trimer



tetramer

As we now see, even monomer-dimer equilibrium of acetic acid in solvents is not without problems. Let us look at the following equilibriums occuring simultaneously,

$$\begin{tikzcd}
A + A \arrow[r, shift left, "K_1"] & A_2 \arrow[l, shift left] \arrow[d, shift left, "K_3"] & \text{(open chain or linear)} \\
\text{and} & & \\
A + A \arrow[r, shift left, "K_2"] & A_2^* \arrow[l, shift left] \arrow[u, shift left] & \text{(cyclic chain)}
\end{tikzcd}$$

where,

$$K_1 = \frac{[A_2]}{[A][A]}$$

and

$$K_2 = \frac{[A_2^*]}{[A][A]}$$

$$K_3 = \frac{K_1}{K_2} = \frac{[A_2]}{[A_2^*]}$$

Therefore, it appears that in a simultaneous formation of linear and cyclic dimer, the ratio of concentration of two forms remain in a constant proportion and in such a case, this will appear one interaction only as $A + A \rightleftharpoons (A_2 + A_2^*)$; where a different equilibrium constant, K_4 appears.

Thus,

$$K_4 = \frac{\left[(A_2 + A_2^*)\right]}{\left[A\right]\left[A\right]} = K_1 + K_2.$$

These pictures are applicable to ideal solutions only. The solvent effect frequently complicates physico-chemical studies in solution; of which we get ample evidence in the present work. For this reason we must take into account the factor which may distort the equilibria of the interactions.

Finally it will be of interest to look at the table below. It is seen that the value of K (association) cover a very wide range of values from 27.7 to 5550 litre/mole.

Table 1. 3

Solvent	Temp. (°C)	$K_{\text{Association}}$ (litre/mole)	Method	References
CCl_4	25	5,550-3200	IR	42
	25	1,000-2,650	IR	43
	31	63.57 (linear)	NMR	50
	31	181 (cyclic)	NMR	50
	25	1800	IR	47
Benzene	30	370	D.C	84
	25	116.3 (polar)	D.C	85
	25	45.45 (non-polar)	D.C	85
	20	27.70	IR	86
	28	500	IR	87

The lower values seem to be more reasonable. The lowest value, as seen here for acetic acid and benzene system, 27.7 litre/mole compares well with the results of this work. The reasons for such divergence of results are due to experiments at different concentration ranges, use of different theoretical frame work and disregard of other interactions exhibited by different solvent effects. Unfortunately most of these reported works do not give the experimental data. For this reason their comparison in the same theoretical frame work could not be possible.

Solvent Effects

The closest approximation to a truely ideal system is the vapour phase. In liquid state no completely neutral solvent can exist since dissolving take place only through some interaction between solvent and solute molecules. In his original development of the method for the determining dipole moment through measurement of dilute solution, Debye[88] gives due consideration to the question of whether the values so obtained would be independent of the nature of the solvent and identical with the moments derived from the measurements on the vapour. In 1929 he suggested that, as the internal forces which control the interatomic distances in a molecule are of electrical origin, one might expect small difference, which would increase with increasing dielectric constant of a solvent. The existence of a "solvent effect" was not given full credence until attention was drawn to the matter by Muller[89][40] in 1933. The first attempt to evaluate solvent effect theoretically was by Weigle[90] who distinguished three possible factors which may contribute to the effects which are observed. These are,

(a) An extra contribution to the (apparent) dipole moment, acting in the same direction as the latter, through the orientation of solvent molecules by the field around the dipole;

(b) The change in the mean polarizability of the molecules under the influence of an external field due to the orientation produced by the dipole and

(c) The induced moment produced in the medium through the asymmetric geometrical form of the dipolar molecule.

Since 1933 there have been innumerable attempts to derive equations relating to the apparent dipole moment of the substance in solution with the dielectric constant of the medium, with the eventual aim of permitting the calculation of the true moment of the isolated molecule from measurement on solution. The theories and emperical equation so far attempted in pure liquid state interms of their distortion polarization and dipole moment have not been completely successful. It has been generally realized that Debye theory, developed for gases and vapour and latter extended to dilute solution, where the polar molecules are relatively far apart, is inadequate to cover the strong interactions which must occur between polar molecules in the pure liquids, and therefore the treatment of the problem suggested involved drastic modifications. None of the theories have been thought satisfactory; nevertheless they have made important contributions to the understanding of the subject. A full discussion on the subject have been excellently reviewed by Smith.[91] The important types of interaction that take place between solvent and solute may be classified as:

(i) Dipole - dipole interaction where both solute and solvent are polar;

(ii) Solute permanent dipole - solvent induced dipole interaction where the former is polar and the latter is not;

(iii) Solvent permanent dipole - solute induced dipole interaction for the reverse case;

(iv) Dispersion interaction between the solute transition - dipole and the dipole induced in the solvent;

(v) Specific interactions such as hydrogen - bonding, charge transfer - complex formation, etc. and

(vi) Solvent - cage compression effects on the solute where the solute occupies a volume larger than the site in the solvent quasi - lattice.

(i - iv) may be classified as general electrostatic solvent effects and much of the theoretical work on solvent shifts involves these interactions. However, where present, (v) and (vi) are likely to dominate the solvent - solute interaction and are generally treated as strong interactions leading to complex formation. But the other effects (i) - (iv) can not be avoided by choice. The effects of solvents on charge transfer complex have been extensively discussed in " Molecular Association " Vol. I, by K. M. C. Davis, (Page 150-204), Academic Press, 1975. The H-bond complexes are not immune from such effects. We will have more on these points in our discussion on the results of the present investigation.

About this Work

In the present work an investigation on only monomer-dimer association equilibrium in five solvents of diverse nature by measurement of specific volume and dielectric constant have been undertaken. The five solvents are:

(i) Carbon tetrachloride,

(ii) Benzene,

(iii) Chlorobenzene,

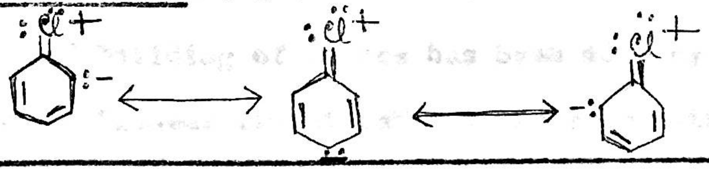
(iv) Cyclohexane and

(v) High boiling hydrocarbon (HBH) (150°C - 200°C).

__Carbon tetrachloride:__ Although it is ordinarily thought that this solvent is inert and have very little effect on solute molecules, it is to be noted that Sharpe and Walker have published several papers concerning interactions of carbontetrachloride with alkyl and heterocyclic amines, ethers and sulphides[64-66]. In general the interaction of poly halogenated alkanes with a variety of lone-pair donors are no longer in doubt[67].

__Benzene:__ This solvent is widely known to be a π-electron donor[68] which readily form a weak H-bond, ---H-OAc with highly polarized H-atom such as alcohol, carboxylic acids etc.

__Chlorobenzene:__ The structure of chlorobenzene is given as,

* 

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* Taken from "Physical Chemistry" by W. J. Moore, page-706, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1972.

See also,

"Electric Dipole Moments" by Smith, Page-200, London Butterworths Scientific Publications, 1955.

Thus we have two most important sites, (i) positively polarized Cl-atom and (ii) donor ring orbital for interactions. We will find profound effects of these sites in our present investigation.

Cyclohexane and HBH: Although, in chemical sense, these two solvents should be 'inert' in comparison to all other kinds. We have here a new kind of effect which will be called "solute - hole interaction".

In this work it is proposed that, at first, a very detailed picture of variations of a measured property should be build up (in our case specific volume and dielectric constant), by very accurate and careful experiment approaching from very high dilution to more concentrated solution; so that it is visibly evident that some kind or other interactions are most probably taking place within the range. The importance of finding the ranges of various interactions is that the variations of property with changing concentration can be examined analytically so that it become pertinent to subject them to particular calculation of important parameters. The measurement specific volume has been done by "Magnetic Float Densimeter" and dielectric constant by "Dipole Meter" using a very large cell; the examination of error of data and building of curves has been done by a powerful graphical method known as "Linear Transform" and the examination of these variations of property have been done by a new formulation of variation of apparent molar properties with the change of concentration.

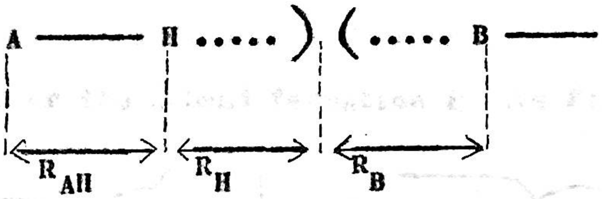
CHAPTER-2

THEORETICAL DISCUSSION

THEORETICAL DISCUSSION

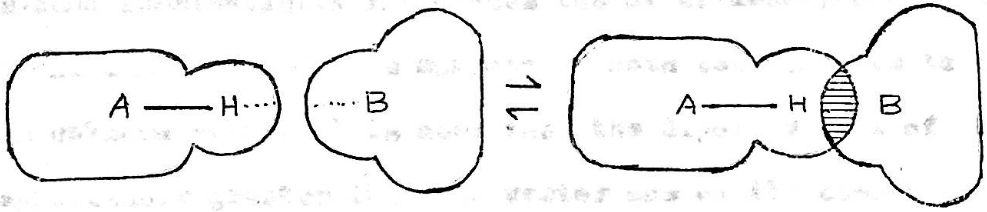
Volume Changes on Hydrogen-Bonding

In the absence of H-bonding, therefore, the distance between A and B should be as represented in the following diagram:



where R_{AH} is the covalent bond distance of A —— H, R_H is the vander waal's radius of the H-atom and R_B is the vandar waal's radius of the B-atom. Therefore, the closest distance between A and B in absence of any interaction should be equal to ($R_{AH} + R_H + R_B$). Therefore, the observed distance between A and B when subtracted from this calculated distance, gives the contraction of A .... B distance on H-bond formation, denoted by δ(A....B), and similarly the H....B distance is less than $R_H + R_B$ by an amount δ(H....B). It is to be noted that δ(A....B) is not exactly equal to δ(H....B) and which indicates that the H-bonding is never without an effect on the length of the original covalent A-H bond. This effect seems to be the expansion of this bond under some sort of an attractive force on the H-atom.

The study made on the over-lapping of vander waal's radii of H and B and the position of H-atom with relation to A and B by Barman and Rahim is worth-noting[6], where it is indicated that H-bond formation not only shortens the H....B distance but also leaves an overall shortening of A....B distance of comparable in magnitude and which must cause an overall volume contraction. Thus, there is an excellent possibility of detecting the H-bond formation by measuring the volume contraction of the reacting species. We may represent the geometry of the molecules before and after the H-bond formation in the following manner:



Overlapping zone, indicated by the shaded portion, represents the volume contraction consequent to the shortening of H....B distance. Therefore, the important postulates are:

(i) There is a net definite volume contraction for the formation of particular molecular complex, and

(ii) The shorter is the H-bond interaction the greater is the volume contraction.

Dielectric Changes on Hydrogen-Bonding

The formation of a H-bond A-H....B leads to an increased polarity of the bond A-H and hence, to a large d. c. and greater dipole moment. The d. c. (permitivity) is proportional to μ^2. Thus, the two dipole A-H, each of moment μ, associate to form a structure - A-H.... A-H of moment 2 μ, the increase of permitivity is proportional to an increase of $2\mu^2$ to $(2\mu)^2$. This has been viewed for basic reason for the abnormally large permitivity of water.

Mutual polarization of the donor and acceptor molecule involving H-bond substantially influences the d. c. measurement. These polarizations change the dipole moments of both the partners in the complex by an unknown amount it is seen that the dipole moment of the complex is appreciably greater than the vector sum of the components. The use of permitivity measurements in the study of intermolecular H-bonding in solutions is exemplified by the isomers of octanol by Dannhauser and his collaborators[69]. It is possible to distinguish linear and cyclic self-association of various alcohols.

When the complexes studied dissociate strongly we have specific design of experiment and specific design of mathematical processing for the different physical methods. There are general approaches for studying weak intermolecular reaction some of which are graphical interpolation method which are widely used and can be termed "Linearization of relation with insufficient number"[70].

Theoretical Treatment

Present work utilizes a new theoretical frame work developed by Rahim[71]. The ingeneous way it has been developed is presented in the following:

1. The molar property of a pure substance is calculated by multiplying the specific property by its molar volume and the molar property of a solution is calculated by multiplying specific propetty of the mixture by its molar volume, which can be expressed as :

$$P_m = p x V_m \quad \ldots\ldots\ldots\ldots\ldots \quad 2.\ 1,$$

V_m here is the volume in which $\sum x_i = 1$, where x_i, the mole fraction of ith species and thus molar volume is calculated by $V_m = \vartheta \sum x_i M_i$ in which ϑ is the specific volume of the solution[72].

There are various molar properties which are found to be structurally additive (vectorically or otherwise, such as, molar volume, molar refraction and molar polarization). These properties seem to follow simple additivity rule in mixtures where no appreciable interaction between species is expected; the additivity rule can be expressed as,

$$P_i = \sum p_i x_i \quad \ldots\ldots\ldots\ldots\ldots \quad 2.\ 2,$$

where, P_i, p_i and x_i are the molar property, specific property and mole fraction of ith species. Whenever there is a deviation of the observed molar property P_m from P_i, an interaction between species are taken into consideration. This rule holds fairly well so that this deviation of molar properties are widely used in the studies of various molecular interaction in solution[73-80].

Suppose we have x_A mole of a substance A, which remain in solution in various polymeric forms, such as, monomer, dimer, trimer etc., designated as A_1, A_2, A_3, ... in a solvent B, then the molar property would be $P = \sum p_i x_i + P_B\, x_B$ (2.3) where P_B and x_B denote molar property and mole fraction of the solvent B. Let us divide both sides of equation (2.3) by x_A, the mole fraction of substance A and we have the equation (2.4)

$$\frac{P}{x_A} = \sum p_i \frac{x_i}{x_A} + P_B \frac{x_B}{x_A} \quad \ldots\ldots\ldots\ldots \quad 2.4.$$

The equation (2.4) can be expressed as,

$$\overline{P} = \sum p_i X_i + S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.5$$

Where, $\overline{P} = P/x_A$ and $S = \dfrac{P_B x_B}{x_A}$ and X_i is the mole fraction of ith species which is equal to x_i/x_A. Please note that the mole fraction, X_i is now calculated only in terms of species A alone and solvent species is kept apart being calculated on the basis on its actual presence per mole of substance A.

Thus $\overline{P} - S = p_i X_i$ 2. 6

Note that $\overline{P}$-S is the apparent molar volume of substance A, now designated as PS.

Suppose one mole of A is dissolved in X_s mole of solvent B in which only monomer and dimer exist. In that case, the equation (2.6) becomes $PS = P_1X_1 + P_2X_2$ .... 2.7, showing that the appafent molar property is dependent on the relative presence of monomer and dimer.

Remembering that two molecules of monomer join to form one molecule of dimer and that the total monomer , either as dimer or monomer, must be equal to one mole,

We have,

$$X_1 + 2X_2 = 1$$

$$X_1 = 1 - 2X_2 \quad \text{.................} \quad 2.8$$

Therefore, $PS = P_1(1-2X_2) + P_2X_2$

Or, $PS = P_1 + X_2(P_2 - 2P_1)$.

Finally, $PS - P_1 = X_2(P_2 - 2P_1)$

$$PS - P_1 = X_2D \quad \text{................} \quad 2.9;$$

where $D = P_2 - 2P_1$, which is the change of molar property due to formation of 1 mole of dimer from two moles of monomer. Therefore, we write, from equation (2.9)

$$\boxed{X_2} = \frac{PS - P_1}{D} \quad \text{...................} \quad 2.10$$

$$x_1 = 1 - \frac{2(Ps - P_1)}{D} = \frac{D - 2PS + 2P_1}{D}$$

$$= \frac{P_2 - 2\cancel{P_1} - 2Ps + 2\cancel{P_1}}{D}$$

Now, substituting $D = P_2 - 2P_1$ in the relation (2.8), which is

$X_1 = 1 - 2X_2$, we have

$X_1 = 1 - 2(PS - P_1)/D$

$$\text{Or, } X_1 = \frac{D - 2(PS - P_1)}{D} \quad \ldots\ldots\ldots\ldots \quad 2.11.$$

$\rightarrow P_2 - 2\cancel{P_1} - 2PS + 2\cancel{P_1}$

$$X_1 = \frac{P_2 - 2PS}{D}$$

2. If in a solution species A are in different polymeric forms A_1, A_2, A_3 etc. which remain in equilibrium as follows:

$$A_1 + A_1 \rightleftharpoons A_2$$

$$A_2 + A_1 \rightleftharpoons A_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.12$$

$$A_{n-1} + A_1 \rightleftharpoons A_n$$

which is expressed in mathematical form,

$$K_2 = \frac{[A_2]}{[A_1]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.13$$

$$K_3 = [A_3]/[A_2][A_1]$$

$$K_4 = [A_4]/[A_3][A_1]$$

$$\text{Or, } K_5 = [A_3]/[A_1]^3$$

$$K_6 = [A_4]/[A_1]^4$$

Where, $K_5 = K_2K_3$ and $K_6 = K_2\,K_3\,K_4$; $[A_1]$, $[A_2]$, $[A_3]$ refer to concentration in mole/litre of particular species and K with subscripts refer to different equilibrium constants. It is obvious that when solution of A in B is very dilute the higher species tends to decrease.

Suppose, the concentration is so low that only monomer and dimer are in sufficient quantity to have perceptible effect on the observed properties of the mixture, then the equation (2.11) and (2.13) become useful. The equation (2.13) is now written in the following form:

$$K_2 = \frac{X_2 \cdot V}{(X_1)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.14$$

because, $[A_1] = \frac{X_1}{V}$ and $[A_2] = \frac{X_2}{V}$

On substituting the values of X_1 and X_2 from equation (2.10) and (2.11) into the equation (2.14) we write,

$$K_2 = \frac{\left(\frac{PS - P_1}{D}\right) V}{\left(\frac{P_2 - 2PS}{D}\right)^2}$$

$$PS = -\sqrt{\frac{D}{4K}}\sqrt{\nabla V} + P_2/2$$

$$\text{or,}\quad K_2 = \frac{D(PS - P_1)\,V}{(P_2 - 2PS)^2}$$

For simplicity we write $K_2 = K$ and then transposing we have,

$$\frac{K}{D} \times \frac{(P_2 - 2PS)^2}{V} = (PS - P_1) \quad \ldots\ldots\ldots\ldots\ldots \quad 2.15 .$$

Again transposing, $PS = -\frac{K}{D} \times \frac{(P_2 - 2PS)^2}{V} + P_1$ .... 2.16 .

In this equation observable are only PS and V and there are three unknowns in an involved form, A direct solution of this equation is not possible.

3. When the solution is very dilute the monospecies predominate; this means, PS tend towards P_1 and therefore $\overset{2PS - P_2}{P_2 - 2PS}$ becomes nearly equal to $P_2 - 2P_1$ i.e., equal to D. Thus, by approximation, we arrive to relation from equation(2.16):

$$PS \approx -\frac{K}{D} \cdot \frac{D^2}{V} + P_1$$

$$(PS \longrightarrow P_1)$$

$$\text{Or,} \quad PS \approx \frac{KD}{V} + P_1 \quad \text{............} \quad 2.17$$

$$(V \longrightarrow \infty)$$

$V.PS = P_1 V + KD$

we can also write,

$$V.\ PS \approx KD + P_1 V \quad \text{.............} \quad 2.18\ .$$

Here we arrive at two most important relation~~s~~, equation(2.17) and (2.18). Equation (2.17) shows that PS plotted against 1/V give a straight line, in which a dimer association interaction is taking place, whose slope give KD and intercept give P_1. The plot PS versus 1/V has utilized to obtain P_1. There should be no doubt that the plot of PS versus 1/V should give only one straight line in absence of any association interaction; this should be evident by the following reasoning. Equation (2.5) give the relation,

$$\overline{P} = \sum P_i X_i + S$$

$$\text{or, } \overline{P} - S = \sum P_i X_i$$

Therefore, $PS = P_1 X_1$ when only one kind of species is present in the solution when without doubt $X_1 = 1$.

$$\text{Thus } PS = P_1$$

This shows that PS remain constant and is also true in equation (2.17) when $KD = 0$, giving a straight line parallel straight line to axis, 1/V. In practice, the zero (0) slope is never realized because of the presence of some kind or other interaction between solvent and solute and the extrapolated volue of P_1 thus obtained, indicate the molar property of the monomer species in the environment of the dominant solvent atmosphere.

There are possibilities of two kinds of dimer formation, (i) open chain dimer and (ii) cyclic dimer. These two types of interaction take place in the same solvent, but either as simultaneous or consecutive interaction, i.e., at first one of the kind is formed and after it reaching a point the next one begins to be formed. In these cases, we should

? have two linear portions in plot, PS versus 1/V (or V.PS versus V plot). In case of simultaneous interaction in which both the kind appear in solution following their own equilibrium conditions. We should have only one linear section related to dimer interaction because they will appear as one interaction. Although the reason for this has already been discussed in the Introduction, yet here it is:

Let $K_{(1)} = \frac{[A_2]}{[A]^2}$ and $K_{(2)} = \frac{[A_2^*]}{[A]^2}$

where, $K_{(1)}$ and $K_{(2)}$ are for open chain or cyclic dimer equilibrium in simultaneous interaction of the type shown below:

(i) $A + A \rightleftharpoons -A_2-$ (open chain)

and

(ii) $A + A \rightleftharpoons A_2^*$ (cyclic)

$$\therefore \quad \frac{K_{(1)}}{K_{(2)}} = \frac{[A_2-]}{[A_2^*]}$$

$$\therefore \quad [A_2-] = \frac{K_{(1)}}{K_{(2)}} \cdot [A_2^*]$$

Thus substituting this relation in either of the two equilibrium equation

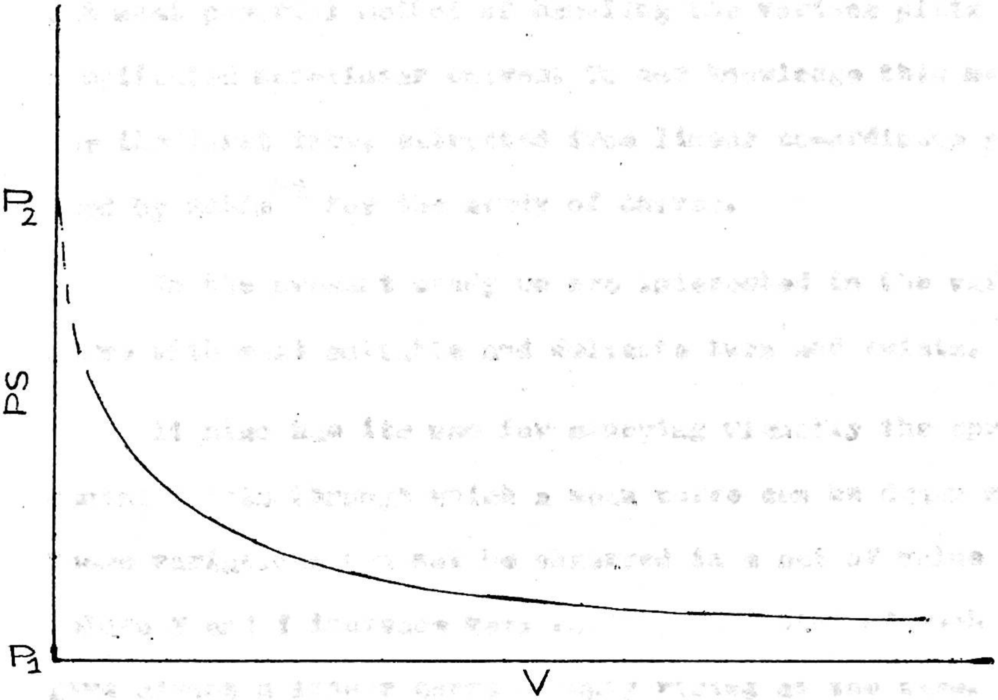
$$K_1 = \frac{K_{(1)}}{K_{(2)}} \cdot [A_2^*] / [A]^2 \qquad \therefore \quad K_2 = \frac{[A_2^*]}{[A]^2}$$

This means that both the species, open and closed dimer appear in this solution in a constant ratio to each other and they appear to be only one interaction which is simply an interaction of dimer mixture of constant ratio. (Equation(2.18) has its usefulness because the KD appear as intersect which is far more easier to determine. It does not mean the equation(2.17) and its plot can not be used for finding KD, appearing in the slope of the linear portion of the curve; but the determination of any slope value is always, for that matter, subject to some confusion and error.)

Thus, finding PS and V from experiments in very dilute solutions and using the relation(2.17) and (2.18) we can find, at least approximately the value of KD and also P_1. But unless we find the value of D, which is equal to $P_2 - 2P_1$, we can not find K. Thus, the problem now is to find the value of P_2.

4. Consider the following aspects of PS versus V plot. It is obvious that when V is made bigger and bigger i.e. when the solution is progressively diluted, PS must and being be almost equal to P_1 and on the other hand when the volume V is continuously made smaller i.e., the solution is progressively made concentrated then PS approaches slowly towards P_2. We have calculated PS and V by using a suitable computer programme. Using the equation (2.15) for a system in which only one

dimer is formed, whose P_1 = 55 c.c., P_2=2X60 c.c. and K = 100 l/m. The plot of PS versus V presented in the following Figure:



In this curve it appears that a careful extrapolation to V=0 we can get a reasonable value of P_2 which should help us to find an acceptable value of K and D. It must be noted that in various methods that have been used at different lines using various properties the procedure for finding P_1 and P_2 is always extrapolation. The difficulties of separating D from KD has always been recognized at least in weak interactions. It must be said at this point that the procedure that has been developed here is no worse, if not better than others.

Thus finally, we find KD from the slope of the plot PS vs. $\frac{1}{V}$ (refer equation 2.17) and already we have P_1 and P_2 as discussed above; therefore we can obtain K knowing that $D = 2P_1 - P_2$.

Linear Transform

But before closing this chapter let us discuss an unfamiliar but most powerful method of handling the various plots which give complicated non-linear curves. To our knowledge this method has been for the first time, extracted from linear co-ordinate geometry and used by Rahim[81] for the study of curves.

In the present study we are interested in the variations of a curve with most suitable and delicate turn and twists.

It also has its use for studying visually the spread of experimental points through which a mean curve can be drawn most conveniently. These variations can not be observed in a set of value when both of values X and Y increase very rapidly. The plot of such a set of data give almost a linear curve steeply rising at the time. If there be some small variations, even a plotting on a very big graph sometimes are not of much use. In these cases"Linear transform" is very helpful.

Suppose we have a curve which is, in reality, an interconnection of ~~g~~ two straight lines at a very wide angle of very nearly of 180^o whose equations are(a) $Y=a_1x + b_1$ and (b) $Y=a_2x + b_2$ and whose common point, of course, is at $x = \frac{b_1 - b_2}{a_1 - a_2}$. Now let us transform this equation with reference to another straight line which passing very closely to these straight lines whose equation is $Y = a_3x + b_3$. Let us calculate

Y_1 at a value x by this equation and subtract it from the values of Y, obtained for either equation (a) or (b) to obtain $\triangle Y=Y-Y_1$, then we have, for straight line of equation (a), $\triangle Y=(a_1-a_3)\ x+(b_1-b_3)$ and for the other equation (b), $\triangle Y=(a_2-a_3)\ x+(b_1-b_3)$. These two again, as we can see, are straight line equations whose common point, of course, is at $x=(b_1-b_2)/(a_1-a_2)$. Thus we see that $\triangle Y$ versus x give a curve whose intersection point in reference to x remain unchanged and the angle become comparatively acute. Thus it is evident that by suitable choice of straight line equation as a reference, the transformed value of Y, $\triangle Y$ versus x can give a kind of plot which is not only equivalent to using a very large graph but also the increase of sharp and more acute bending of curve give a far greater insight into nature of the curve. These findings will convincingly be clear in our first example of study on acetic acid in CCl_4 system.

This method of studying curves, help to find accurately the slope and determining intercepts by linear extrapolations, has been extensively used in the present work.

CHAPTER-3

EXPERIMENTAL

EXPERIMENTAL

Description of the Magnetic Float Densimeter

The magnetic float densimeter used in the present investigation is similar to one developed by Barman and Rahim[82] which is based on the principle to the one developed by Lamb and Lee[83] with one important modification.

A float made of glass bulb in which a permanent magnet is fixed at the lower end. The weight of the float is so adjusted that it just floats when immersed in a liquid (whose density is to be measured) within a glass vessel. A solenoid is attached at the base of this vessel. When a large amount of current is passed through the solenoid the magnetic field so produced drags the float down to the bottom. When the current is decreased slowly a point is reached when the magnetic float just begins to float. At that point the current is measured, termed as the "equilibrium current". Then the weight of the liquid displaced by the completely immersed float must be equal to the sum of the actual weight of the float and a weight which is equivalent to the magnetic attraction between the solenoid field and the magnet. As the magnetic attraction is directly proportional to the applied current, we can write,

$$w_f = k_i' + v_f \cdot d$$

where,

w_f = the weight of the float

v_f = volume of the float

d = density of the experimental liquid

i = the minimum current required to hold the float bottom

k' = weight equivalent of the current.

The magnetic float densimeter consists of the following assembly:

(i) A thermostatic air-bath (Fig. 3.2) in which the densimeter is placed (Fig. 3.1) with the help of a clamp and stand. The different components of the densimeter are,

(ii) A magnetic float(C) which is immersed in the liquid in the container;

(iii) Solution container,(A) in which liquid is taken whose density is to be measured. A quickfit lid(E) is to cover the mouth of the container;

(iv) A micro-meter syringe(MS) by which one of the components is dropped to the container to vary the concentration of the solution in the container, and a syringe(PS) is attached with a suction arrangement for homogeneous mixing of the mixture and

(v) Contact thermometer(CT) (Fig. 3.2), fans (F_1, F_2), electric bulb (L) is for monitoring the temperature of the air-bath.

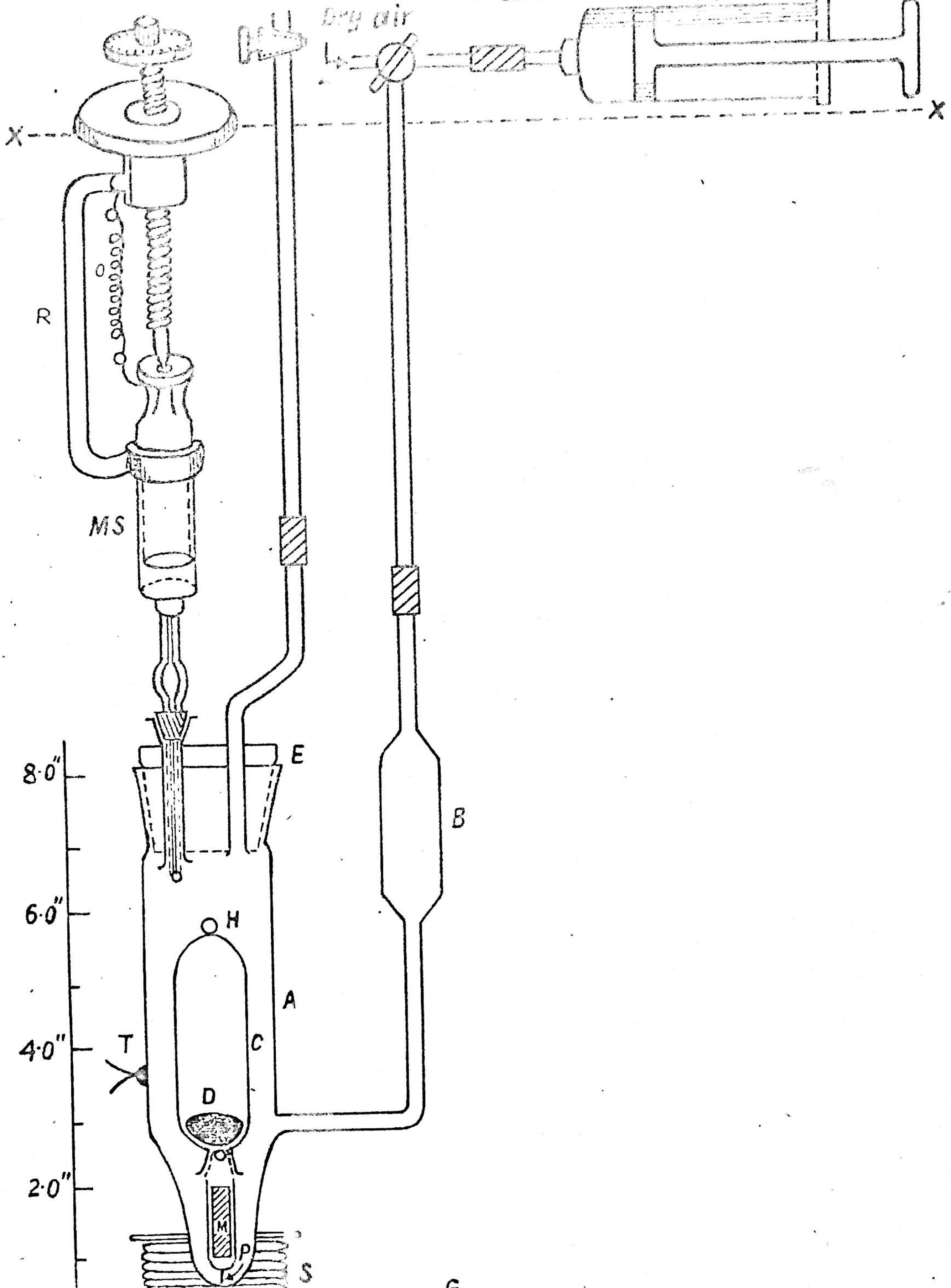


Fig.-3.1 Schematic of the Magnetic float densitometer. A - solution container, B - Bulb, E - Quickfit lid, C - Magnetic float, D - Mercury, M - Magnet, P - Platinum tip, H - Platinum ring, T - Thermistart, S - Solenoid, G - Spirit level, MS - Micrometer syringe, PS - 20 cc. syringe, R - Brass frame, X .... X - Surface of the thermostatic air bath showing the [illegible]

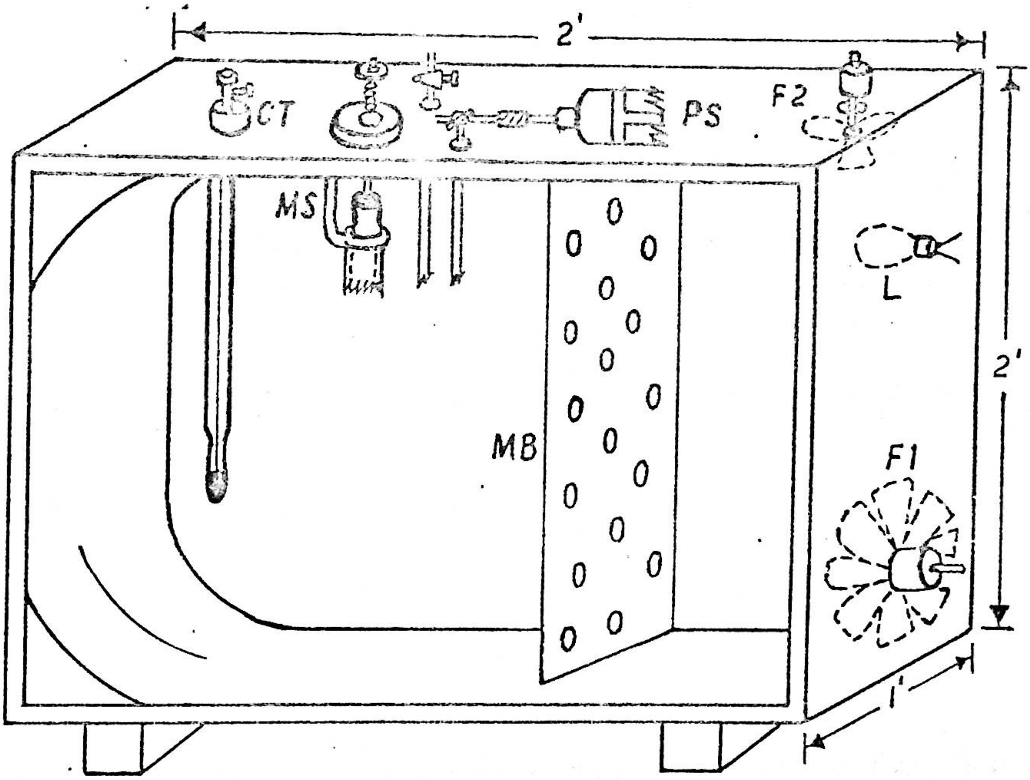


Fig.-3.2 Thermostatic air bath. CT - Contact thermometer, MS - Micrometer syringe, PS - 20 cc. syringe, F1 - and F2 - Fans, L - 60 watt bulb, MB - A thin metal foil barrier with perforations.(Electric bulb and contact thermometer are connected to an electronic relay).

(i) Thermostatic air-bath: The densimeter assembly is placed inside a thermostatic air-bath. It is a double walled hardboard box of 60X30X60 cm. The external surface of the bath has been heavily insulated with polyurethane foam sheet. The corners of the left wall of the box have been made round. The front wall of the box is the door, which is made of glass and covered with insulating materials on both sides, keepinga ~~a~~portion bare for observing the dessimeter assembly. The thermostatic system consists essentially of two fans, a 60W electric bulb, a contact thermometer, and an electronic relay as shown in(Fig. 3.2). The electrical connections of the control system are shown schematically in (Fig. 3.3).

There is a metallic barrier containing a few holes separating the heater and fans from the densimeter assembly for fair mixing of hot and cold air. For the maintenance of a nonfluctuating and uniform temperature around the liquid container and micrometer syringe, these two are placed inside a replaceable metallic enclosure. The metallic enclosure has been provided with a transparent window for viewing the movements of the float within the solution container.

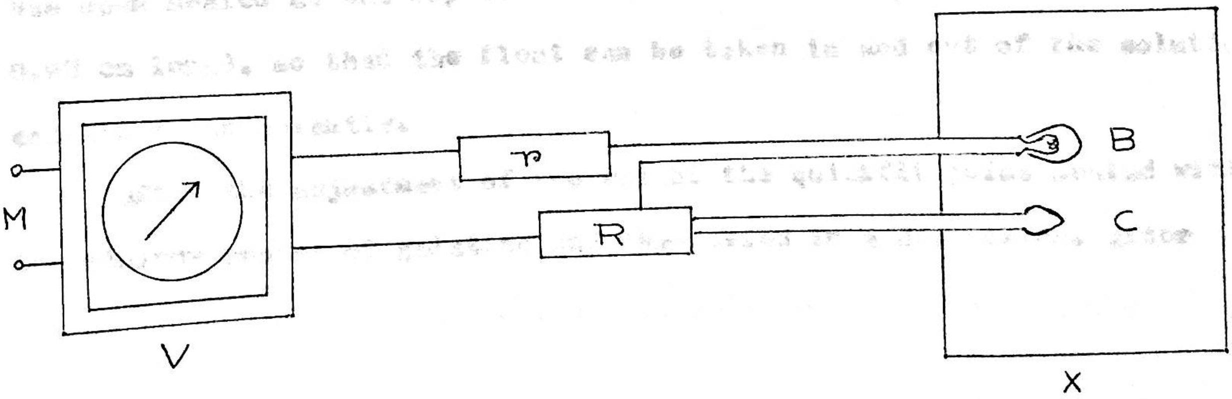


Fig. 3.3. Electronic connection of the Control System.

drying, it is immersed in dry and pure CCl_4. Before starting work the float is rubbed with a piece of dry cloth and then weighed.

(iii) Solution Container: The solution container, A, (Fig. 3.1) of about 100 c.c. capacity (diam. 1.8" and height 7"), is provided with a side tube having a bulb, B. The top of the container is fitted with a quickfit lid, E. This lid consists of two narrow holes: one being pressure outlet and another for dropping one of the components of the mixture from a micrometer syringe, MS. The solution container is fitted with a solenoid, S, at the bottom. The solenoid of length 3.0 cm. consists of 11500 turns of 42 gauge enamelled copper wire wound on a plastic former and its resistance is about 2000 ohms.

There is a bakelite base fixed below the solenoid. A spirit level, G, fixed on the base, is used for getting a definite position of the solenoid relative to those of magnet in the float and earth's magnetic field.

The solution container can be held in position by clamp and stand arrangement (not shown in the figure). Only non-magnetic materials have been used in the construction of the stand. The spirit level below the solenoid can be adjusted by screw legs in the base of the stand.

(iv) Micrometer Syringe, MS: The micrometer syringe is a clinical syringe, MS, of 5 ml. capacity, which is attached to the brass frame R (Fig. 3.1). The piston of the syringe can be moved by means of a micrometer, and a spring G, which are attached with the brass frame. It has a long glass needle (8.75 cm long) with a small bulb at the middle.

The micrometer syringe is calibrated in situ by dropping purified kerosene of known density (on turning a certain number of terns) from the micrometer syringe into a small weighed conical flask and weighing the conical flask with kerosene.

The composition of the mixture in the solution container can be varied by decopping one of the components from the micrometer syringe. The resulting solution can be made homogeneous by stirring it with the help of up and down movements of the float and also by transferring some liquid in the side tube, B, with the help of the suction arrangement attached to one of the tube through the lid of solution container (Fig. 3.1). The float can be danced if the current passing through the solenoid is followed by a sudden cut.

(v) <u>Temperature Monitoring Device:</u> The temperature of the experimental liquid has been monitored by a bead type thermistor (F22, standard Telephone and Cable Co.) whose resistance is about 125 ohms. at 30°C having temperature coefficient approximately 4% per °C. The thermistor has been fixed on the glass surface of the liquid container at T (Fig. 3.1) and it is used as an arm of a wheatstone resistance bridge as shown in (Fig. 3.4). The other three arms of the resistance bridge, each about 125 ohms. have been made of high resistance Nichrome wire and these are placed inside the thermostatic air-bath. The e.m.f.

across the bridge is maintained at 1.3 volts. and a sensitive galvanometer is connected to the bridge. Wheatstone bridge circuit containing the thermistor gives a balance in the galvanometer at a definite temperature (30°C ± .005°C). The necessary measurements for density data are made when the spot of the galvanometer remain within - 0.1 cm. to + .01 cm. of the scale.

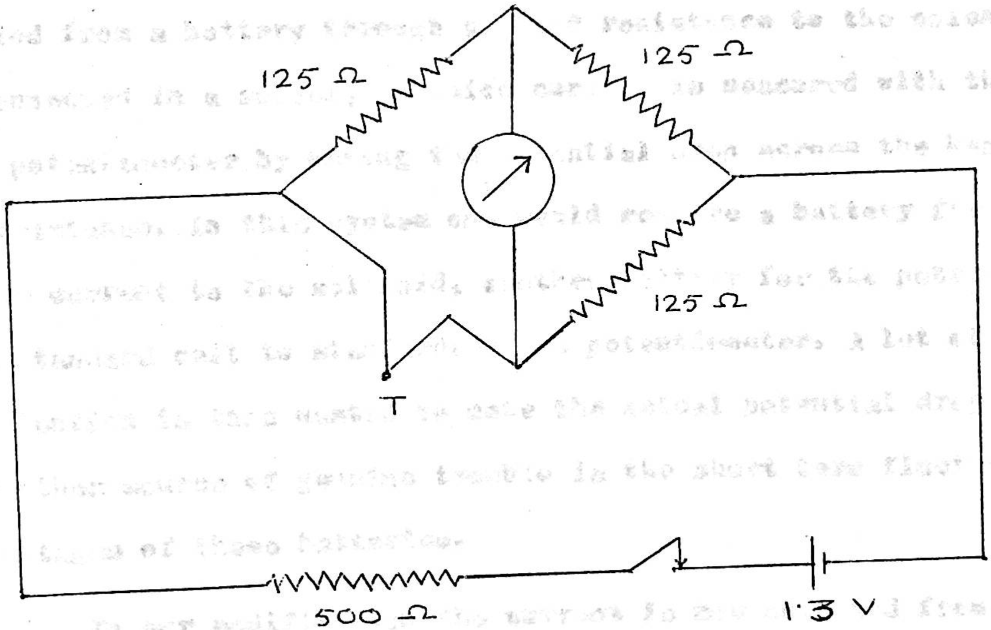


Fig. 3.4 Wheatstone bridge circuit.

A thermistor is attached on the glass of the solution container. It is covered thickly with wax so that the short term temperature fluctuation in the air-bath may not have serious effect on it and the temperature of the solution can easily pass through the glass to the thermistor for monitoring.

System for the Measurement of Current through Solenoid

In Barman and Rahim's[82] system the equilibrium current is supplied from a battery through a fixed resistance to the solenoid, all connected in a series, in which current is measured with the help of a potentiometer by noting the potential drop across the known fixed resistance. In this system one would require a battery for supplying the current to the solenoid, another battery for the potentiometer and a standard cell to standardize the potentiometer. A lot of time and attention is thus wasted to note the actual potential drop each time. Another source of genuine trouble is the short term fluctuation of voltages of these batteries.

In our modification the current is now supplied from a stabilized voltage source. Thus the use of potentiometer and batteries are altogether despensed with and the equilibrium current is obtained from the reading on decade resistance box, RD (Fig. 3.5).

The circuit diagram is shown below:

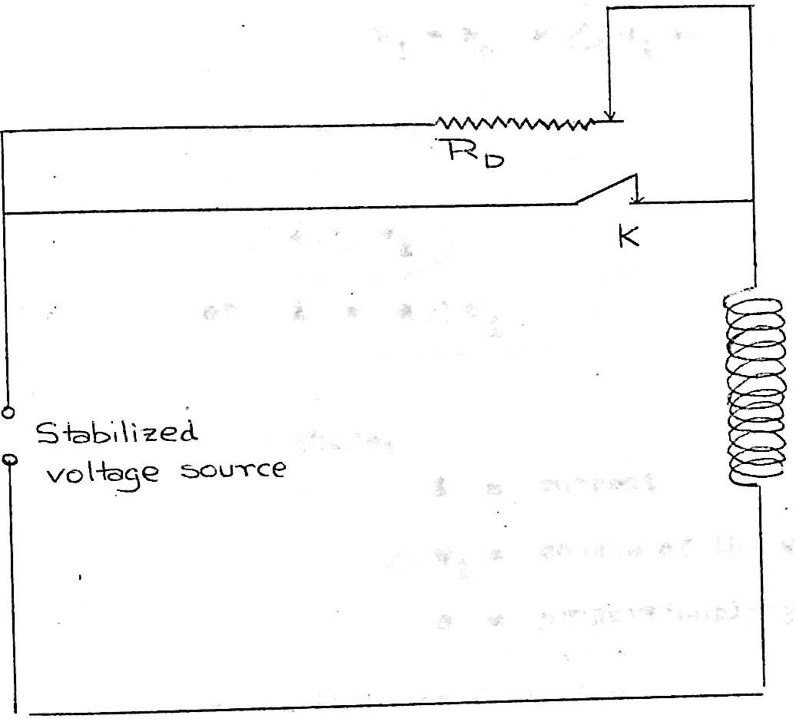


Fig. 3.5. Circuit diagram of current measuring system.

(R) fixed resistance solenoid

where,

RD —— Decade resistance (variable resist-)ance

K —— key

E ~~S~~ —— stabilized voltage source.

Calibration and Calculation of the Densimeter

To establish a relation for the calculation of the specific volume, the weight of the float is so adjusted that when it is immersed in a solvent in the solution container the equilibrium current is zero. Suppose that the weight of the float at that condition is w_o and the resistance is r_o. Again suppose the weight of the float is increased to w_1 and w_2 for which the resistances obtained are r_1 and r_2 respectively.

Therefore, the equilibrium current passing through the solenoid across the fixed resistance(R) (Fig. 3.5) must be directly proportional to the change of the weight of the float i. e.,

$$w_1 - w_0 = \triangle w_1 = ik$$

Therefore, we can write,

$$i \propto w_1$$

or $i = a \triangle w_1$

Where,

i = current

$\triangle w_1$ = change of the weight of the float ($w_1 - w_0$)

a = proportionality const.

Again, from the Ohm's law

$$i = \frac{\overset{E}{S}}{R+r} \qquad i = \frac{E}{R+r}$$

Where,

S = voltage

R = fixed resistance

r = variable resistance.

Therefore, from the above relation,

$$\frac{\overset{E}{S}}{R + r_1} = a \triangle w_1 \qquad \text{..............} \qquad 3.\ 1$$

and

$$\frac{\overset{E}{S}}{R + r_2} = a \triangle w_2 \qquad \text{..............} \qquad 3.\ 2$$

Where,

$$\triangle w_2 = w_2 - w_o$$

and

r_1 and r_2 are variable resistance for w_1 and w_2 respectively.

From equation (3.1) and (3.2)

$$R = \frac{\triangle w_1 r_1 - r_2 \triangle w_2}{\triangle w_2 - \triangle w_1} \quad \text{and} \quad S/a = \triangle w_1 \, (R+r_1)$$

$$\text{or, } \triangle w_2 \, (R+r_2) \, .$$

At equilibrium current the equivalent weight ,

$$w_i = \frac{S/a}{R + r}$$

Knowing the value of w_i, specific volume can be calculated from the following equation:

$$\text{Specific volume} = \frac{\text{volume of the float}}{\text{weight of the float} + w_i} \quad \ldots\ldots\ldots\ldots\ldots \quad 3.3$$

Results and Calculations

Weight of float	Resistance
w_o = 22.56056	r_o = 7713
w_1 = 22.56695	r_1 = 7769
w_2 = 22.57105	r_2 = 7834

The value of R and S/a is calculated and the value is $R = -7935.29$ and $S/a = -1.06256$

Volume of the float is found out from the relation (3.3) by a solvent of known specific volume and it is found $V_f = 25.9976$ c.c.

Hence, specific volume can easily be calculated by reading the resistance from the resistance box.

A detail Description of the Working of Magnetic Float Densimeter

(i) A stoppered dropping funnel is filled with the purified and dried solvent and weighed. Then the solvent is poured into the solution container(A) (Fig. 3.1), close the lid(E) and weigh the funnel again. The difference of the weight gives the weight of the solvent taken in the container. The volume of the solvent in the container should be such that the float can completely sink in the liquid when pulled down by magnetic force.

(ii) The adjusted float (described in the magnetic float heading) is then immersed in the liquid of the container by opening the lid(E) (Fig. 3.1) and close it again.

(iii) By screw adjustment the spirit level is brought into proper position.

(iv) The container is enclosed in the replaceable metallic enclosure (described earlier in the heading thermostatic air-bath). The micrometer syringe(MS) is filled with the mixture of accurately known composition (acetic acid and solvent, usually 6%) and introduced into the solution container.

(v) The door is closed and the instrument is switched on and the thermostatic air-bath is allowed to attain equilibrium temperature which takes over an hour, which is indicated by the galvanometer of the thermistor circuit (Fig. 3.4). During this time the liquid in the container is stirred at intervals of 5 - 10 mins. by up and down movements of the float and also by transferring some liquid in the side tube B (Fig. 3.1)(as described earlier).

(vi) Then the resistance, r is read from the decade resistance box. Special care should be taken to take the final reading. At first by trial and error reading is taken which is say 3236Ω. Next time to start with the resistance is fixed at 2000Ω. The float dragdown to the bottom of the container by "hold down current[*] ". After sometime the resistance is increased by one thousand, then by one hundred at each step and then by 10Ω till it reaches 3230. Then by care and caution the

---

[*] When a large amount of current is passed through the solenoid across the fixed resistance (R), it drags down the float to the bottom of the container. This current is termed as hold down current.

resistance is increased by one thousand, and then by one hundred at each step and then by 10Ω till it reaches 3230. Then by care and caution the resistance is increased by oneΩ and allow some time to increase by anotherΩ till the float just begins to rise up. This is done as the current gradually reaches to the equilibrium current the hold down current becomes zero. The float may begin to rise before equilibrium current is reached due to the agitation or mobility of the liquid.

Two or three readings are taken and the mean value is recorded. It should be remembered that temperature control is the most important factor for obtaining a good result. When the reading is noted the care should be taken that the spot of the galvanometer remain within ± 0.1 cm of the scale.

(vii) The concentration of the liquid in the container is now varied by adding a desired amount of mixture from the micrometer syringe followed by homogeneous mixing by the method described earlier. The system is again brought to the equilibrium temperature and the resistance for equilibrium current is recorded. Thus, by repeating this process, data for several concentrations which lie very close to each other within a particular section are obtained. At last the float is removed from the container, it is dried by rubbing with the cloth and kept in dry CCl_4 solvent.

The float can be readjusted and used for other system.

Dipolemeter

The dipolemeter, type DM-01, represents a precision instrument for measurement of the dielectric constant of a pure liquid or mixture measurable upto the 5th place of decimal with measuring sensitivity $(4-8)X10^{-5}$ depending upon the cell used.

This instrument operates on the superposition method, by which the oscillations of two high frequency oscillators are brought to superposition in a mixing section. After subsequent amplification, the resulting beats are brought to the screen of a cathode ray tube as the indicator. By this method it is thus possible to observe even fractions of a 1HZ(cycle) beat frequency.

The sample holding cell, with the liquid dielectric to be measured, and the variable measuring condenser connected in parallel to it are parts of one of the oscillators. By changing the measuring condenser the sum of both the capacitance values is set so that the same frequency results as by the other oscillator (zero beat).

The double geared, precision scale, with 4500 divisions(scale length about 33 ft (10 meters)) permits determination of the measuring condenser position with the required reading accuracy.

Types of Cell used: The sample holding cells used in connection with the apparatus for dielectric constant measurements are cylindrical condensers. These are of DFL types.

All the sample holding cells are provided with a water jacket for maintaining the constant temperature of the experimental solution. The surface of the electrodes of DFL type cells are gold plated.

The sample volume of the DFL-2 is 4 c.c. ceramic is used for the insulation of the inner cylinder. Teflon is used for the gaskets. The sample volume of the DFL-1 is 20 c.c. Both the types have a threaded cover, which can be unscrewed. These types have ground glass joint inlets. The DFL-1 type has a bottom outlet drain fittings. The DFL-2 has in addition a teflon stopcock at the bottom. The DFL-2 does not have any drain.

Measuring Range for DFL-1 and DFL-2 Type Cells: A specific cell can be used for the measurement of dielectric constant of a certain range. The measuring range for DFL-1 and DFL-2 type cells are shown below -

Sample holding cell	Switch position		
	D_1	D_2	M_1
DFL-2	2.0-4.7	4.2-6.9	1.0-3.7
DFL-1	1.0-2.4	2.0-3.4	- -

By using the cell DFL-1, scale reading is obtained in the range switch at D_1 and D_2. For the cell DFL-2, the reading is obtained at all the three positions of the switch.

Calibration of the Cell DFL-1 and DFL-2: The calibration curves with scale divisions against dielectric constant for the cell MFL-1, supplied by the company. The curve is a straight line and the equation of the curve has been found to be:

dielectric constant(d.c.) = 0.0018375X scale reading(at M_1 position) + 1.50706.

With the help of this calibration curve, cell DFL-1 and DFL-2 have calibrated and verified by the pure liquid of known dielectric constant. The equation for these calibration curves are,

For DFL-1

d. c. = 0.0008555186X scale reading (at D_1) + 1.59220.

and

For DFL-2

i) d. c. = 0.0004783X scale reading (at D_1) + 0.72567.

ii) d.c. = 0.0018677X scale reading (at D_2) + 3.40968

Measurement

The dipolemeter is plugged into the 220 volts A. C. line. The instrument is turned on. The internal thermostat of the lower housing should also be turned on. (The panel lamp above the switch indicates that the heaters of the built in thermostat are operating). After about 30 minutes, during which the thermostat and its panel lamp should often turn on and off, the instrument is ready for operation.

Focus and intensity of the cathode ray tube can be adjusted by the two small knobs on the upper panel below the screen. With the range switch at the Korr. position, the measuring oscillator is brought into resonance with the reference oscillator by means of the correction knob. In the Korr. setting of the range switch the position of the measuring condenser has no influence upon the resonance point. By turning the correction knob, the horizontal line on the cathode ray tube broadens vertically and wave forms become evident. Lissajous figures are formed between the beat frequency and the cathode ray tube scanning frequency 50c/s, which at ± 50c/s change over into the well known circle or ellipse.

At exact resonance the line remains still, moving up and down with very small changes. The number of up and down movements per second indicates the beats per second. By further divergence from resonance, these up and down movements again become Lissajous figures. After the zero beat has been adjusted in Korr. position, the instrument is ready for measuring. The correction knob must not be disturbed once the adjustment has been made as this will destroy the resonance.

Working Procedure

(i) A range of solution from pure solvent to 0.4% by weight have been prepared by the following procedure,

A flat bottom flask of capacity 100 ml. is cleaned, dried and weighed. A quantity of acetic acid is taken in it by a syringe and again weighed. The difference between the two weights gives the weight of acetic acid. The pure and dry solvent is then added and weighed again. The difference between 3rd weight and first weight gives the total weight of the solvent and AcOH. The concentration in weight percentage is then given by

$$w_s = \frac{w_1}{w_2} \times 100.$$

where,

w_1 = weight of acid taken.

w_2 = Total weight of solvent and AcOH.

w_s = weight percentage of the solution.

This solution is termed as stock solution. Solutions of low concentrations are prepared from this stock solution. Next another flask (already cleaned and dried) is weighed. Then the stock solution is poured into it and weighed again. The difference between these two weights gives the weight of stock solution. Then pure and dry solvent is added and weighed. The difference between this last weight and first weight gives the weight of solvent and stock solution. Hence concentration of dilute solution is computed by,

$$w = \frac{w_s \cdot w_3}{w_4},$$

where,

w_3 = weight of stock solution.

w_4 = total weight of solvent and stock solution.

In this way a series of solutions are prepared for measurement. All these operations excepting weighing is done in a moisture free box containing P_2O_5.

(ii) The measuring cell to be used is kept for several hours at 120°C in the drying chamber after being washed with distilled water and acetone and finally allowed to cool in a dessicator. Now this cell is inserted into the co-axial connection at the upper right side of the instrument. This cell is leveled to avoid spillage, with its central axis perpendicular to the table top. After starting the measurement the cell is not removed from, moved or turned in its connector in order to avoid errors due to slight change in electrical contact. The constant temperature of the cell is maintained by circulating water from constant temperature bath (described latter). The reading of the empty cell is taken by operating the range switch at M_1 and D_1 or D_2, as required by the sample holding cell used and by turning the measuring condenser resonance (Zero beat) is again established. Then the cell is filled with the liquid (or mixture) and reading is taken in the same way. In each case three readings are taken, and the average value is taken as the valid figure. After measurement of a sample is completed, the range switch is turned to Korr. position.

Constant Temperature Bath used in Dielectric Measurement

The thermostatic water bath is equipped with a GallenKamp thermostirrer(Cat.No. TM 860) which controls the temperature of the water bath at $30^{\circ}C \pm .01^{\circ}C$. The control of temperature at $30 \pm .01^{\circ}C$ is achieved by maintaining the main voltage to 180 volts by a variac transformer and connecting an extra resistance in series with the thermostat-heater. An extra heater is also used to cut the initial heating period. Although, it has been written in the catalogue that the temperature monitors at $30^{\circ}C \pm .01^{\circ}C$, we have observed that it maintains the temperature at $30^{\circ}C \pm .002\text{-}3^{\circ}C$.

Reagents and Their Purification

Acetic Acid

E. Merck acetic acid is dried by shaking with P_2O_5 in cold and allowing to stand for several hours; then the liquid is drained off and distilled. The distilled liquid is frozen in an ice-bath. When half portion of acid is transformed into fine fibrous crystal, the remaining acid is transferred into another flask. This procedure of fractional crystallization is repeated several time and is finally kept in an air-tight flask placed in a dessicator containing P_2O_5. A stock can be used for about one and half month in dry season and 15 days in rainy season. Each time acetic acid is needed for a set of experiment it is frozen, the liquid part is separated and the crystals are taken.

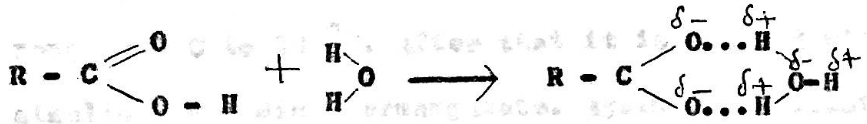
Purification of Solvents

Generally, at first the solvents are dried by P_2O_5, and then Na-threads are dropped into the liquid to remove the traces of water in the solvent. But this method does not remove sufficiently the traces of water. We adopt the following method.

After the treatment with P_2O_5, the solvent is distilled and is treated with Na-threads. After several hours the liquid is distilled and treated with a little fceshly purified acetic acid (.06 gms acid is added in 100 gms of solvent) followed by Na-threads. Na-threads are added till the reaction is complete. Then it is finally distilled and a centre cut of constant boiling point is taken.

In support of this procedure we have to state the following:

In our earlier work in acetic acid - CCl_4 system it was found that even after drying with Na-threads, the dielectric constant progressively decreased from that of pure solvent upto a point, from which again, dielectric constant increased with increasing concentration of acetic acid. It was thought that addition of acetic acid to CCl_4, dielectric constant should, on no account, be less than that of solvent. To account for this strange behaviour we concluded that there are traces of H_2O in CCl_4 which form addition compound with acetic acid, which most probably, has the following symmetrical structure with very little dipole,



Thus, it was concluded that the last traces of H_2O remain inside interstices of the solvent from which it is difficult to be removed by interaction with sodium. If pure dry acetic acid in trace quantity (.6 gm in 1000 gm of solvent) is added, will react with H_2O to form the addition compound; which is, as a whole a strong acid. This compound will therefore react strongly at once it come in contact with

CHAPTER-4

RESULTS

RESULTS

System: Acetic Acid in Carbontetrachloride.

Results of Specific Volume Measurement and Obtaining Refined Values

The specific volume of solution of acetic acid in CCl_4 was measured by magnetic float densimeter in the range between pure solvent and .002 weight fraction following the procedure described in the previous chapter. The data obtained by such experiment is given in the Appendix-A.1, along with the linear transform of specific volume (referred to as $\triangle v$) by a reference line, $v_{cal} = .634985 + .30303 \times w$, where w is the weight fraction of acid. The plot of the $\triangle v$ versus w is shown in the Fig. 4.1 curve(a).

It is to be noted in this curve that there are three distinct changes of direction. These inflections could not be observed without the help of this linear transform plotting. Here we see that the mean deviation no where is more than 2×10^{-6} c.c/gm. There is a curvature from 0.0 to about .0012 weight fraction showing a gradual increase of specific volume and then again there is a sharp decrease of specific volume upto .0015 weight fraction and from that point there is again a sharp increase of specific volume upto the highest measured point. A

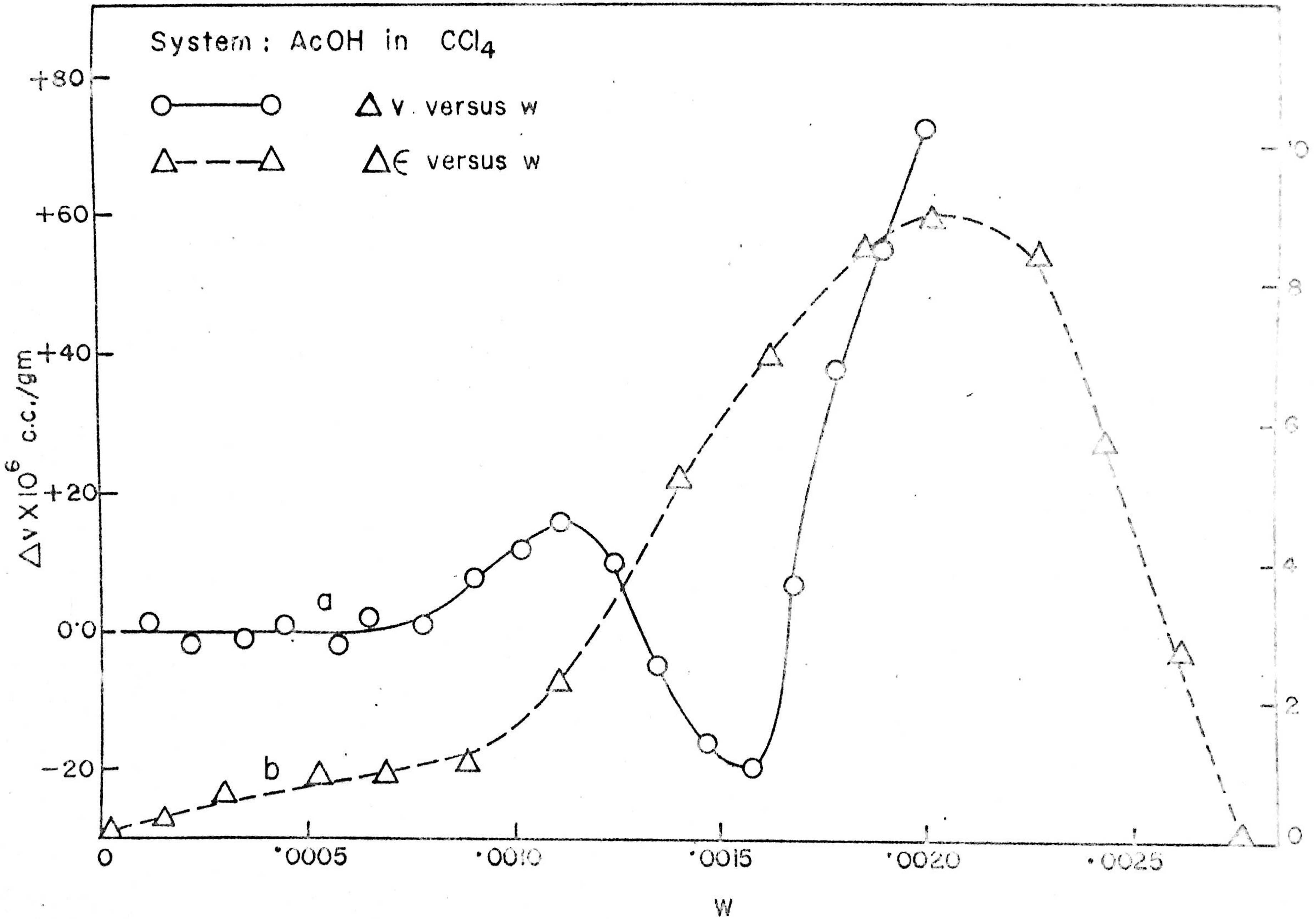

System : AcOH in CCl_4
Δv versus w
$\Delta \epsilon$ versus w
+80
+60
+40
+20
0·0
-20
$\Delta v \times 10^6$ c.c./gm
a
b
0
·0005
·0010
·0015
·0020
·0025
w
0
2
4
6
8
10
$\Delta \epsilon \times 10^4$

Fig. 4·1

sample calculation from the line of the curve shows that the standard deviation is ± $1 X 10^{-6}$ c.c/gm. Thus, we can say that the precision of the measurement are highly satisfactory.

Results of the Dielectric Measurement

The data of dielectric measurement of solutions of acetic acid in CCl_4 between 0.0 to .0027 weight fraction is recorded in the Appendix-A.1, along with the linear transform, $\triangle\epsilon$ from the straight line of equation, $\epsilon_{cal} = 2.251207 + 1.21415Xw$, whose plot is shown in Fig. 4.1 curve(b). The transform plot shows that the mean deviation of the experimental data from the drawn line is $2X10^{-5}$ c.c/gm, the percentage deviation of course is of the same order of as that of specific volume. This means that dielectric measurement also has a high precision. The curve shows a number of inflections keeping in line with the inflections shown in the specific volume - wt. fraction curve.

Calculation of S and V and the Plot of VS against V

Using the following relations, V and VS is calculated:

$$V = \frac{v}{w} X M; \quad S = v_s X \left(\frac{1 - w}{w} \right) X M \text{ and } VS = V-S .$$

Reading out carefully the value of $\triangle v$ from linear transform curve and calculating back to "refined "value" of specific volume as described a

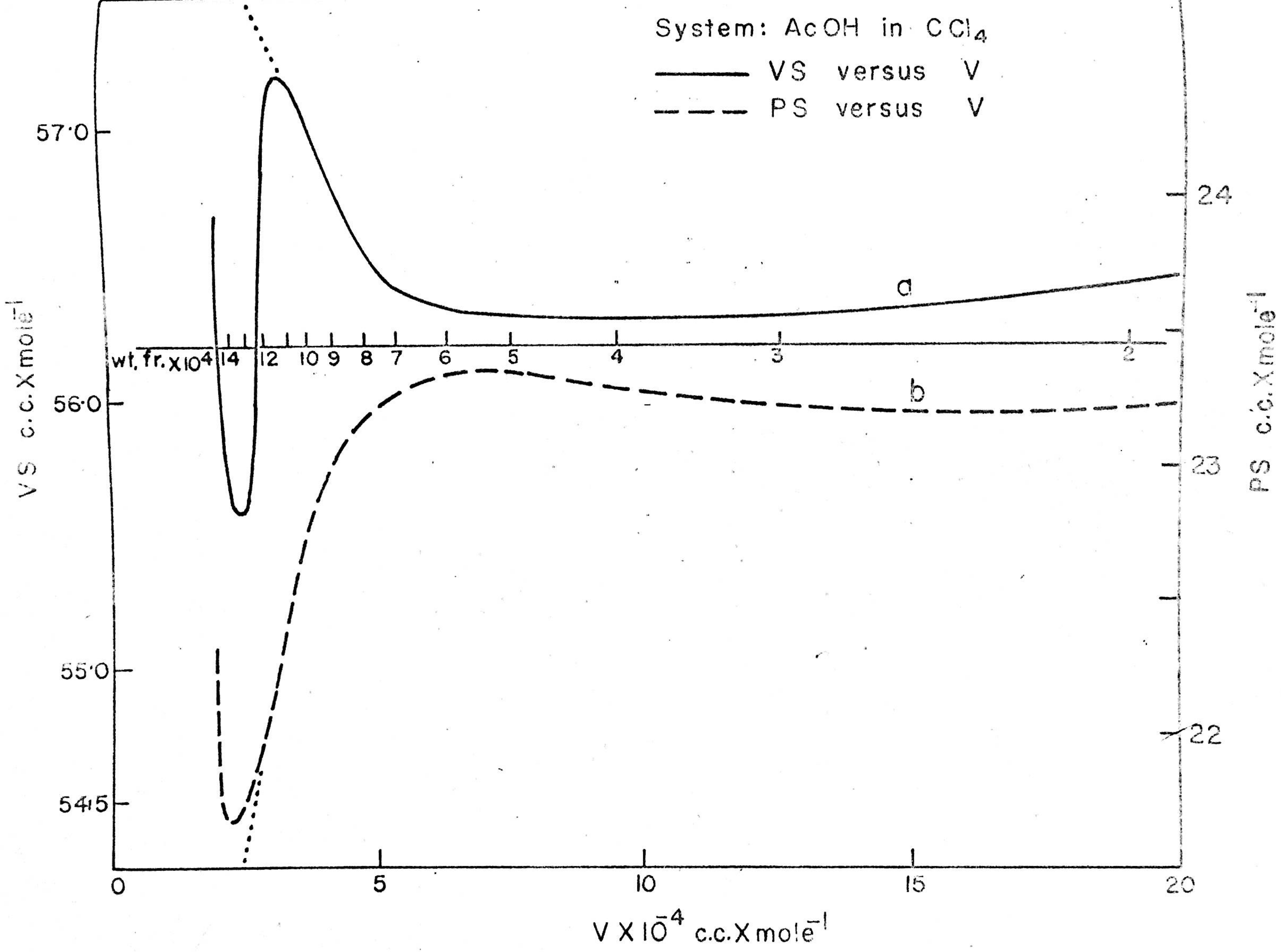

System: AcOH in CCl$_4$
VS versus V
PS versus V
a
b
wt. fr. x10^4
14
12
10
9
8
7
6
5
4
3
2
57·0
56·0
55·0
54·5
VS c.c. X mole^{-1}
24
23
22
PS c.c. X mole^{-1}
0
5
10
15
20
V X 10^{-4} c.c. X mole^{-1}

Fig. 4·2

"refined specific volume" already calculated and tobulated at these points previously.

The P, S and PS are calculated using the following relations:

$$P = \frac{p}{w} X M ;$$

$$S = p_s X M \left(\frac{1-w}{w} \right) ;$$

and $$PS = P-S;$$

The plot of PS versus V is shown in Fig. 4.2 curve(b).

PS – V

A Comparative study of VS and PS Curves

In Fig. 4.2 the curve(a) and (b) show the variation of VS and PS versus V. The straight line at the middle of the graph, with marking from 2 to 14 is given to indicate the weight fraction composition of the mixture at which such values are obtained, to compare with other systems, interpret and compare these curves more intelligently and to speculate about the regions at which different kinds of interaction takes place. Let us start our inspection from the right side of the curves whose V is very high. It is seen that VS and PS both attain nearly a constant value between mark 2 to 6 (i.e. wt. fraction .0002 to .0006). Then there is a rise of VS and on the other hand, a fall of PS upto about .0012 wt. fraction. From this point onward, there is a fall of

VS and rise of PS. Thus, it appears that from .0002 to .0006 wt. fraction PS and VS change very little which indicate that only monomer predominate at this region; and, after .0006 wt. fraction the increase of VS and decrease of polarization indicate the formation of cyclic dimer. To obtain the value of molar polarization of dimer, P_2 and V_2, the molar volume of this dimer has to be obtained by extrapolation of the curve between 6 to 12 mark (i.e. .0006 to .0012 wt. fraction). By this method, we obtain,

P_2 = 2X 19.19 c.c/mole

V_2 = 2X 59.08 c.c/mole

The value of V_1 and P_1 can be obtained from these curves by rough extrapolation. But we have a better method; according to equation(2.17), the extrapolation of the plot (Fig. 4.3) PS (or VS) versus $\frac{1}{V}$, should give P_1 or V_1 as the case may be . By that method, we obtain,

P_1 = 23.10 c.c/mole

V_1 = 56.26 c.c/mole

$\therefore$ D for molar volume = 5.64 c.c/mole

D for molar polarization = – 7.82 c.c/mole.

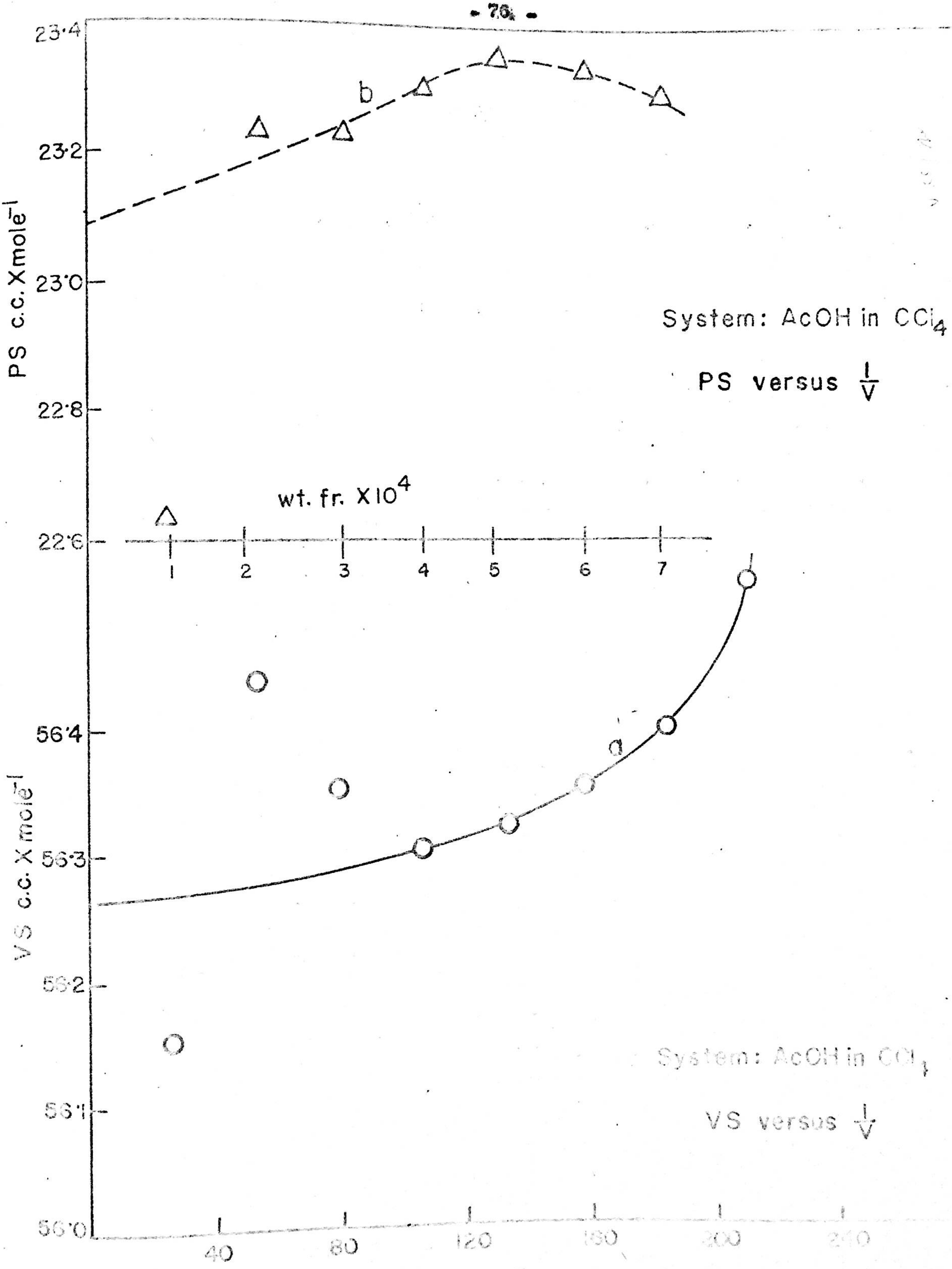
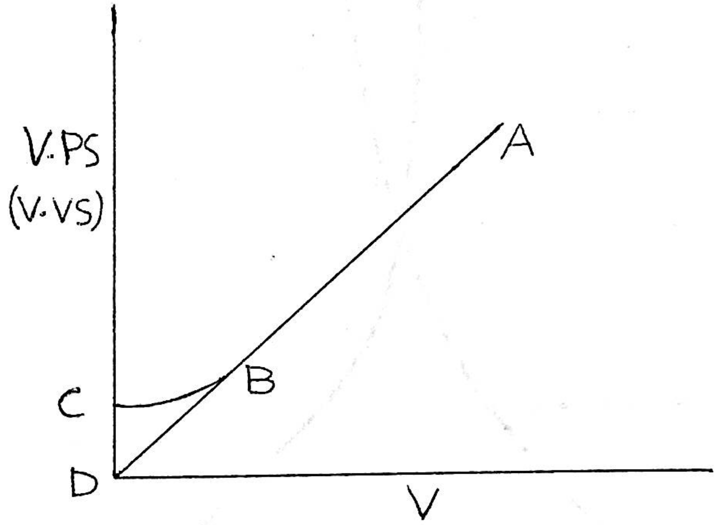

PS c.c. X mole^{-1}
23·4
23·2
23·0
22·8
22·6
b
System: AcOH in CCl$_4$
PS versus $\frac{1}{V}$
wt. fr. X10^4
1
2
3
4
5
6
7
a
VS c.c. X mole^{-1}
56·4
56·3
56·2
56·1
56·0
System: AcOH in CCl$_4$
VS versus $\frac{1}{V}$
40
80
120
160
200
240
$\frac{1}{V}$ X10^7 mole X c.c.$^{-1}$

Fig. 4·3

The Plot of V. PS(or V. VS)Versus V and Calculation of KD and K

V. PS (or V.VS) versus V plot give a curve is not satisfactory for convenient estimation of KD. The following figure shows an exaggeration of such a plot.



The part of the curve AB shows that at this region only monomer exit . As we have already shown, if only monomer existed althroughout then the line should have been ABD. Here CD is the intersection of ABC curve. In ordinary plotting actually it falls very near to zero. Therefore, V. PS or V. VS versus V have been transformed by the straight line ABD, whose slope is equal to P_1(or V_1) and intersection is zero. Thus, $\triangle$(V.PS) and $\triangle$(V.VS) have been calculated and given in Appendix- A.1 . The plots are shown in Fig. 4.4.

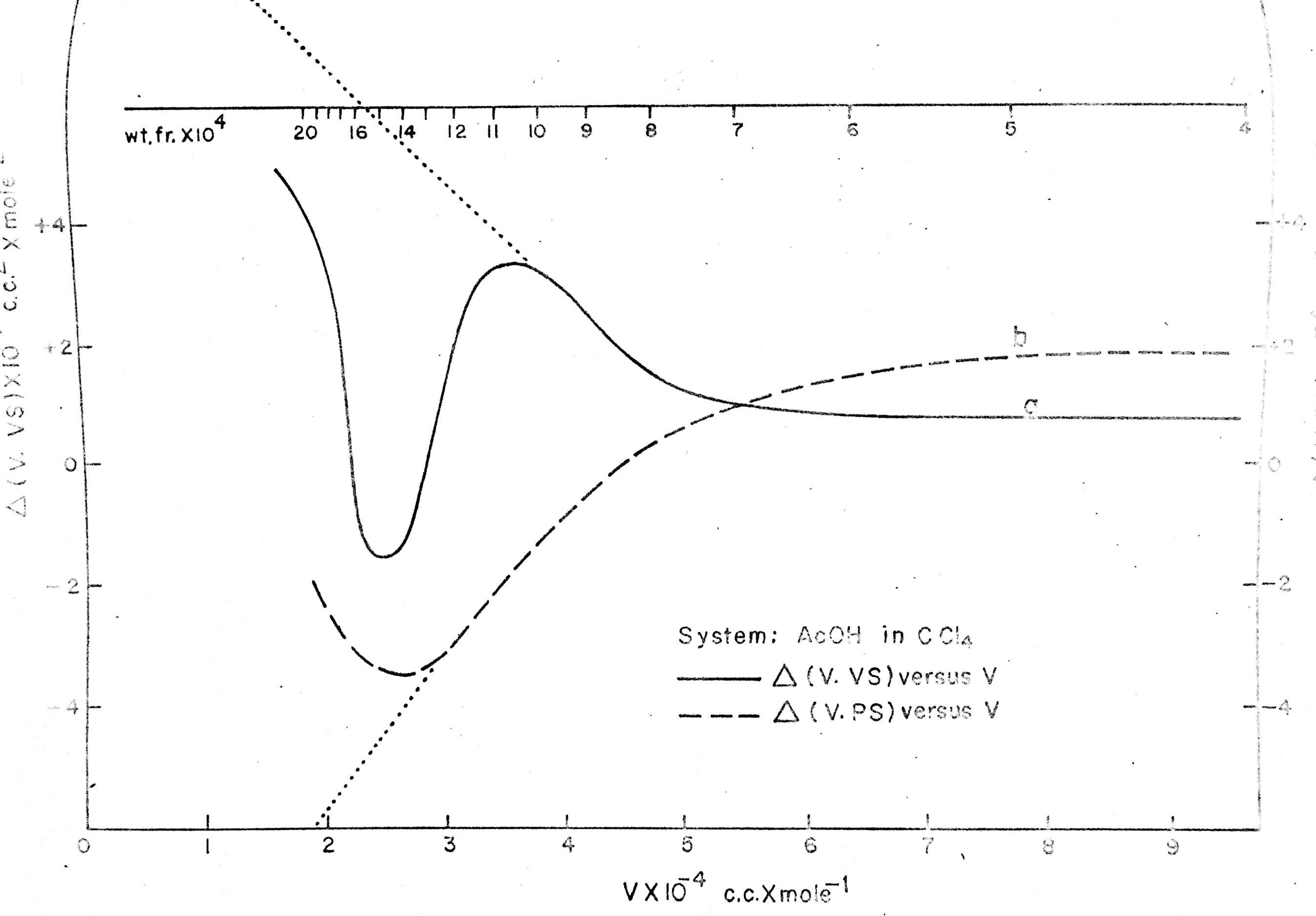

wt.fr. X10^4
20
16
14
12
11
10
9
8
7
6
5
4
Δ (V. VS) X10^{-4} c.c.^{2} X mole^{-2}
+4
+2
0
-2
-4
+4
+2
0
-2
-4
b
a
System: AcOH in C Cl$_4$
Δ (V. VS) versus V
Δ (V. PS) versus V
0
1
2
3
4
5
6
7
8
9
V X 10^{-4} c.c. X mole^{-1}

Fig. 4·4

It is to be noted that from high dilution to .0006 wt. fraction in both cases shows a flat portion. This part is obviously concerned with existence of monomer and weak interaction of this monomer with solvent. In V.VS then rise upto .0012 wt. fraction and in case of polarization V.PS fall down. This region indicate the equilibrium reaction of dimer formation. The linear extrapolation of these curves leads the following values of KD.

For molar volume, KD = 100600 $c.c^2/mole^2$

For molar polarization, KD = - 105000 $c.c^2/mole^2$

But we have D for molar volume = 5.64 c.c/mole

and D for molar polarization = - 7.82 c.c/mole.

Therefore, K are 17.84 l/mole and 13.43 l/mole for specific volume and polarization respectively. The results are tabulated in the Table 4.1 .

TABLE 4.1

Molar property	Monomer (c.c/mole	Dimer (c.c/mole	KD ($c.c^2/mole^2$)	K (l/mole)
Volume	56.26	59.08X2	100600	17.84
Polarization	23.10	19.19X2	—105000	13.43

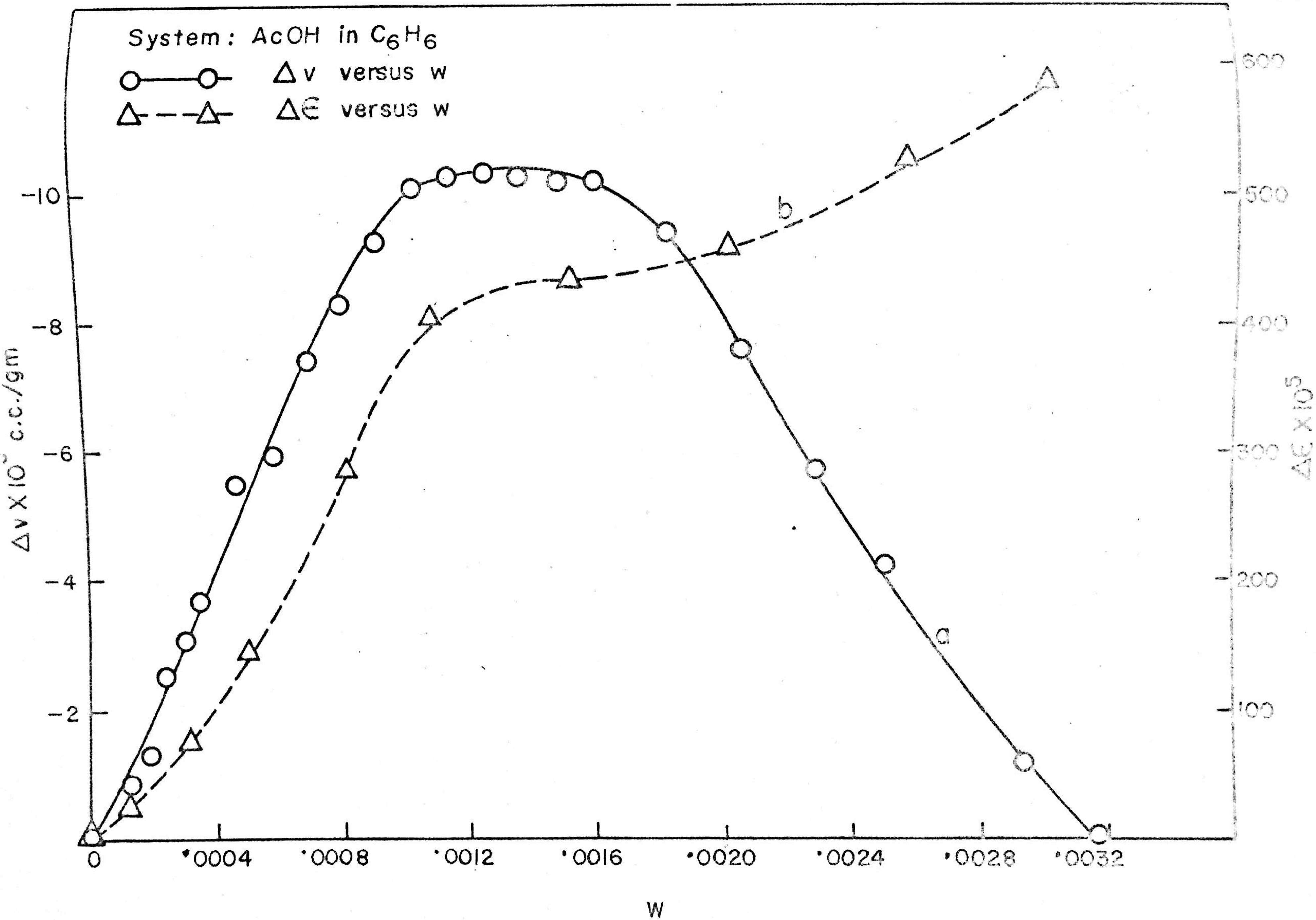

System: AcOH in C_6H_6
Δv versus w
$\Delta\epsilon$ versus w
$\Delta v \times 10^5$ c.c./gm
$\Delta\epsilon \times 10^5$
-10
-8
-6
-4
-2
600
500
400
300
200
100
0
·0004
·0008
·0012
·0016
·0020
·0024
·0028
·0032
a
b
w

Fig. 4·5

in the case of CCl_4) to calculate S, P, V, Vs, Ps etc. at equally spaced chosen points of composition.

Plot of VS and PS Against V

Vs (and PS) versus V are plotted and shown in Fig. 4.6 curve(a) and (b). The curves in the figure show the variation of Vs and PS versus V. (The straight line at the middle of the graph marking from 2 to 20 has been given to indicate the wt. fractions of acid in the solution). From .0002 to .0008 wt. fraction there is an increase of PS and decrease of VS. The increase of PS shows that a species is continuously forming with the increase of concentration has higher polarization than the monomer, supposed to exist abundantly in the dilute solution. In VS we observed that there is a weak but definite tendency of VS falling down indicating that the species is formed with a little contraction of volume on the combination of two monomers. So, we are led to consider the formation of open chain dimer in this concentration range. Then after the solution has attained the concentration .0009 and goes on increasing, we find that PS decrease and VS increase. This section strongly indicate the formation of cyclic dimer, as we know, the formation of which is always attended the increase of volume and decrease of polarization. Thus, we have calculated the important parameters for

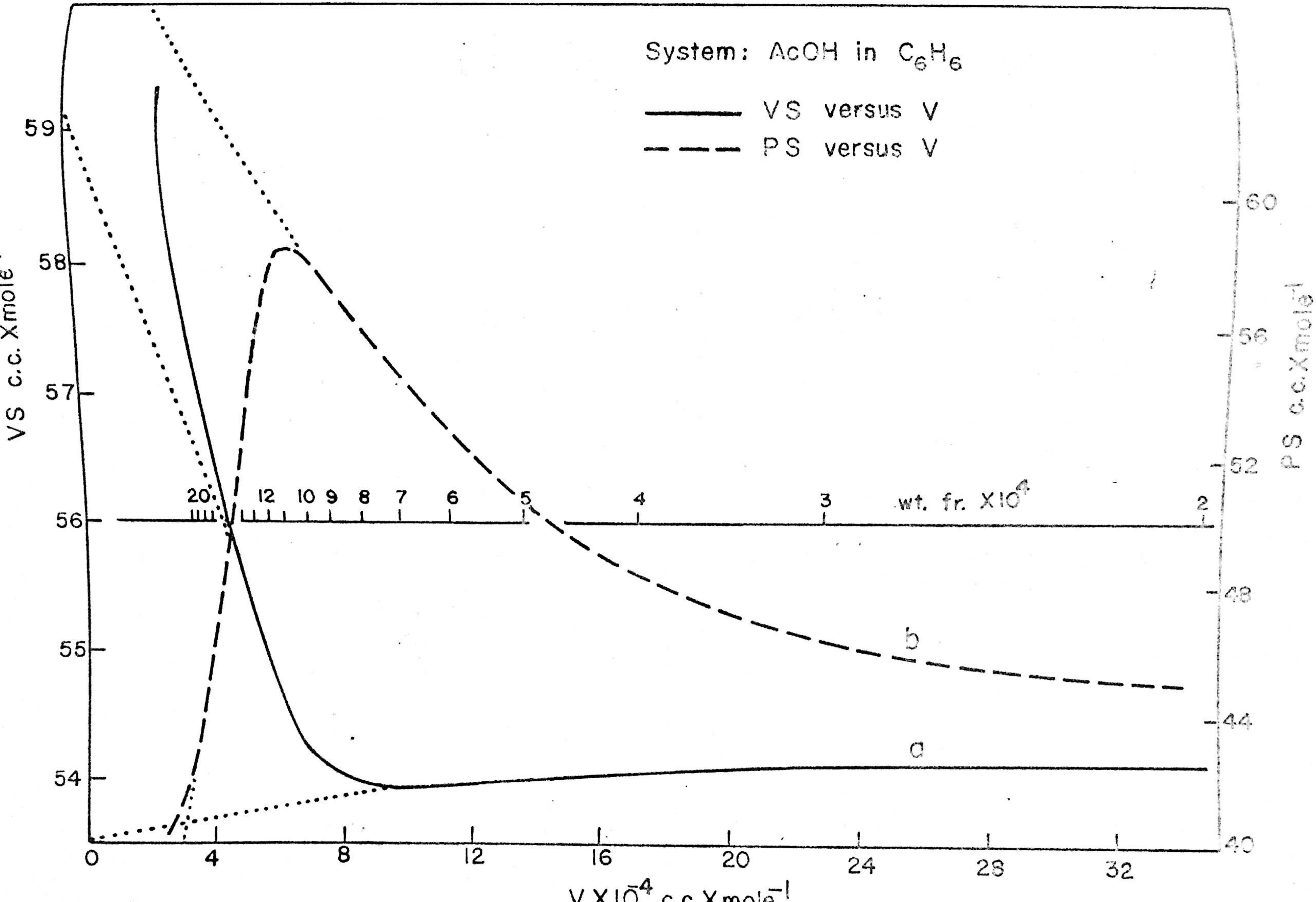

System: AcOH in C_6H_6
VS versus V
PS versus V
VS c.c. Xmole^{-1}
59
58
57
56
55
54
PS c.c.Xmole^{-1}
60
56
52
48
44
40
wt. fr. X10^4
20
12
10
9
8
7
6
5
4
3
2
b
a
0
4
8
12
16
20
24
28
32
V X10^{-4} c.c.Xmole^{-1}

Fig. 4·6

two distinct interaction, in succession:

(a) $A + A \rightleftharpoons A - A$ (open chain dimer)

and

(b) $A + A \rightleftharpoons \binom{A}{A}$ (closed chain dimer)

The justification of such a supposition will be perfectly clear when we examine $\triangle(V.PS)$ and $\triangle(V.VS)$ variation with the variation of volume.

The molar volume of dimer, open chain and cyclic have been obtained by extrapolation of these curves according to the procedure already laid down. The values obtained by such operations are shown below:

V_2 (open) = 2X52.53 c.c/mole, P_2(open) = 2X72.57 c.c/mole

V_2 (cyclic) = 2X59.13 c.c/mole, P_2 (cyclic) = 2X16.17 c.c/mole.

The determinations of V_1 and P_1 was carried out by VS (and PS) versus 1/V plot and extrapolation to 1/V = 0(not shown in figure). From these operations we obtained the value V_1 = 54.18 c.c/mole and P_1 = 40.20 c.c/mole. Thus, the values of P_1, V_1, P_2, V_2 and D obtained are shown in the Table 4.2.

Table 4.2

V_1 = 54.18 c.c/mole;

P_1 = 40.20 c.c/mole.

Molar properties	Open chain (c.c./mole)	Closed chain (c.c./mole)
V_2	2X53.53	2X59.13
D (volume)	- 1.3	9.9
P_2	2X69.60	2X16.17
D (Polarization)	58.80	- 48.06

△ (V. VS) and △ (V.PS) Plots

The △(V. VS) and △ (V.PS) versus V are shown in Fig. 4.7. In both the curves there are two clear sections: (a) from most dilute to .0008 wt. fraction a straight line nearly, but not exactly, parallel to the V-axis, and (b) another linear section from .0010 to .0017 wt. fraction.

The first portion at dilute region could be very well a weak interaction just, as in the case of CCl_4 or the formation of open chain dimer.

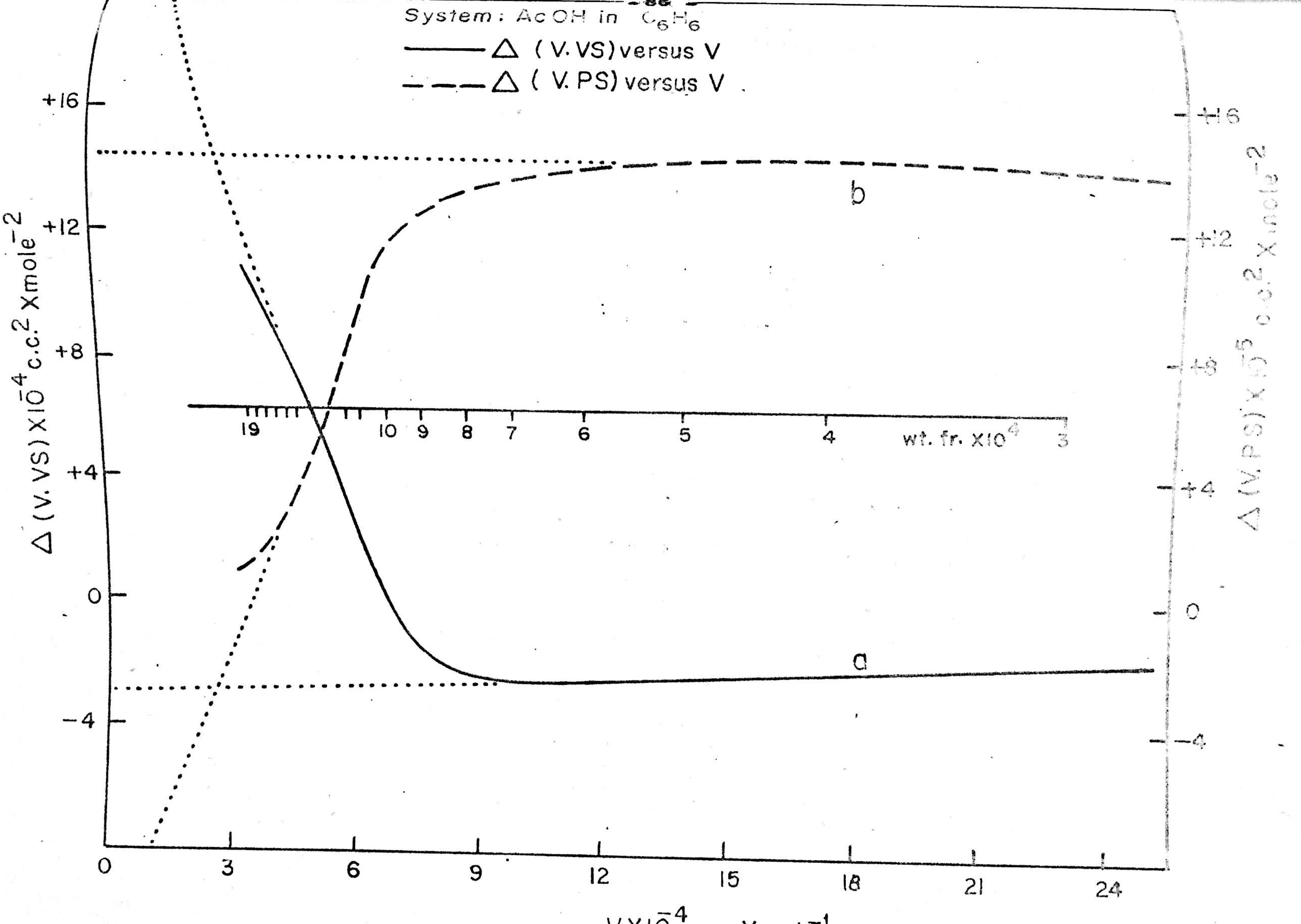

System : AcOH in C_6H_6
—— Δ (V. VS) versus V
– – – Δ (V. PS) versus V
Δ (V. VS) X 10^{-4} c.c.^{2} X mole^{-2}
+16
+12
+8
+4
0
−4
Δ (V. PS) X 10^{-5} c.c.^{2} X mole^{-2}
+16
+12
+8
+4
0
−4
b
a
19
10
9
8
7
6
5
4
3
wt. fr. X10^4
0
3
6
9
12
15
18
21
24
V X 10^{-4} c.c. X mole^{-1}

Fig. 4·7

Here the indication by comparison with VS (and PS) versus V plot we are convinced of an interaction and the second portion of interaction line of closed chain dimer. The extrapolation of these relevant line leads to the following results:

Table 4.3

	Open chain		Closed chain	
	Vol.	Pol.	Vol.	Pol.
KD($c.c^2/mole^2$)	- 30000	1440000	260000	- 1120000
K (l/mole)	23.08	24.49	26.26	23.30

System: Acetic Acid in C_6H_5Cl

The specific volume and dielectric constant of the system has been measured from pure solvent upto .0025 wt. fraction. The data is given in the Appendix A.3, along with the other parameters (S, P, V, $\Delta\epsilon$, Δv, VS, PS etc.). The linear transform equation for specific volume is $v_{cal.} = .912825 + 0.24650 \times w$ and for dielectric constant is $\Delta\epsilon = \epsilon_{cal} - 5.610160$. The plot of Δv and $\Delta\epsilon$ are shown in the Fig. 4.8 curve (a) and (b). The plots show clearly the spread of error of measurements

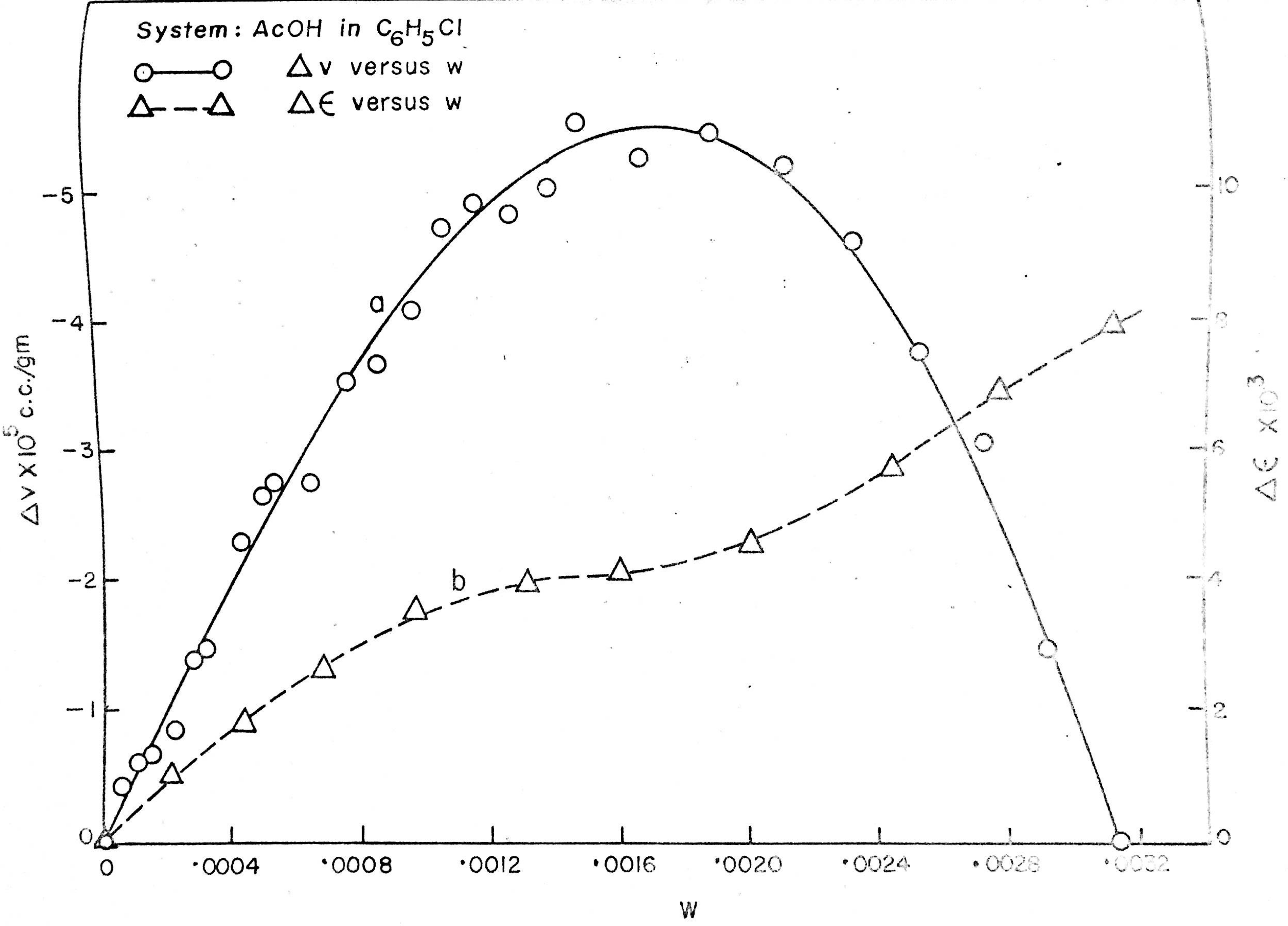
System: AcOH in C_6H_5Cl
Δv versus w
$\Delta\epsilon$ versus w
a
b
$\Delta v \times 10^5$ c.c./gm
$\Delta\epsilon \times 10^3$
0
-1
-2
-3
-4
-5
0
2
4
6
8
10
0
·0004
·0008
·0012
·0016
·0020
·0024
·0028
·0032
w

Fig. 4·8

which are as usual within reasonable limits. The variations of the properties due to interaction are also evident. The mean lines are drawn very carefully from which refined and acceptable values have been specified and chosen for calculations of other important parameters.

With the refined values at specified points the V, P and S are calculated from which we obtained PS and VS versus V. The plot of VS (and PS) versus V are shown by two curves in the Fig. 4.9 curve (a) and (b).

There are two distinct sections:

(a) from extreme dilution to 0.0005 wt. fraction and (b) from 0.0005 to 0.0019 wt. fraction, revealed in the PS versus V plot. In VS versus V plot the second section can not be clearly marked out and this is because of the fact that there is a continuous increase of volume with the increase of acetic acid and this must be due to formation of such complexes in succession which have greater molar volume than its predecessor. This feature is distinctly different from those two systems we have already studied, which will be discussed later.

In $\triangle$(V.VS) and $\triangle$(V. PS) versus V plot there are two distinct sections Fig. 4.10 : (i) from dilute to 0.0015 wt.fraction, at which range both polarization and volume of species formed, is attended with increase of volume and polarization; which shows something unusual; (ii) in the next portion, from 0.0015 wt. fraction upward, volume increases and polarization decreases. We will presently find that

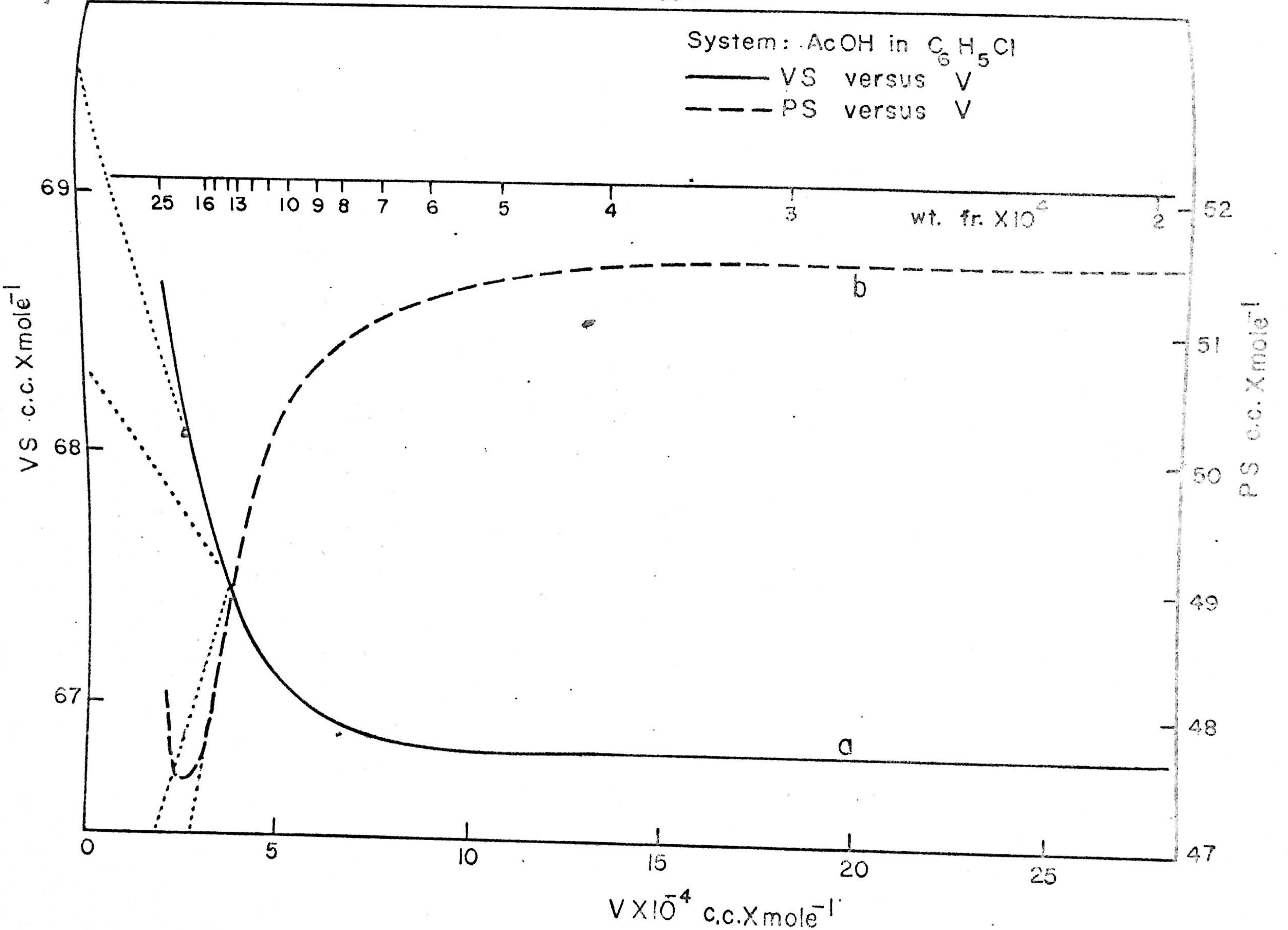

System: AcOH in C_6H_5Cl
VS versus V
PS versus V
wt. fr. X10^4
25
16
13
10
9
8
7
6
5
4
3
2
b
a
69
68
67
VS c.c. X$mole^{-1}$
52
51
50
49
48
47
PS c.c. X$mole^{-1}$
0
5
10
15
20
25
V X10^{-4} c.c.X$mole^{-1}$

Fig. 4·9

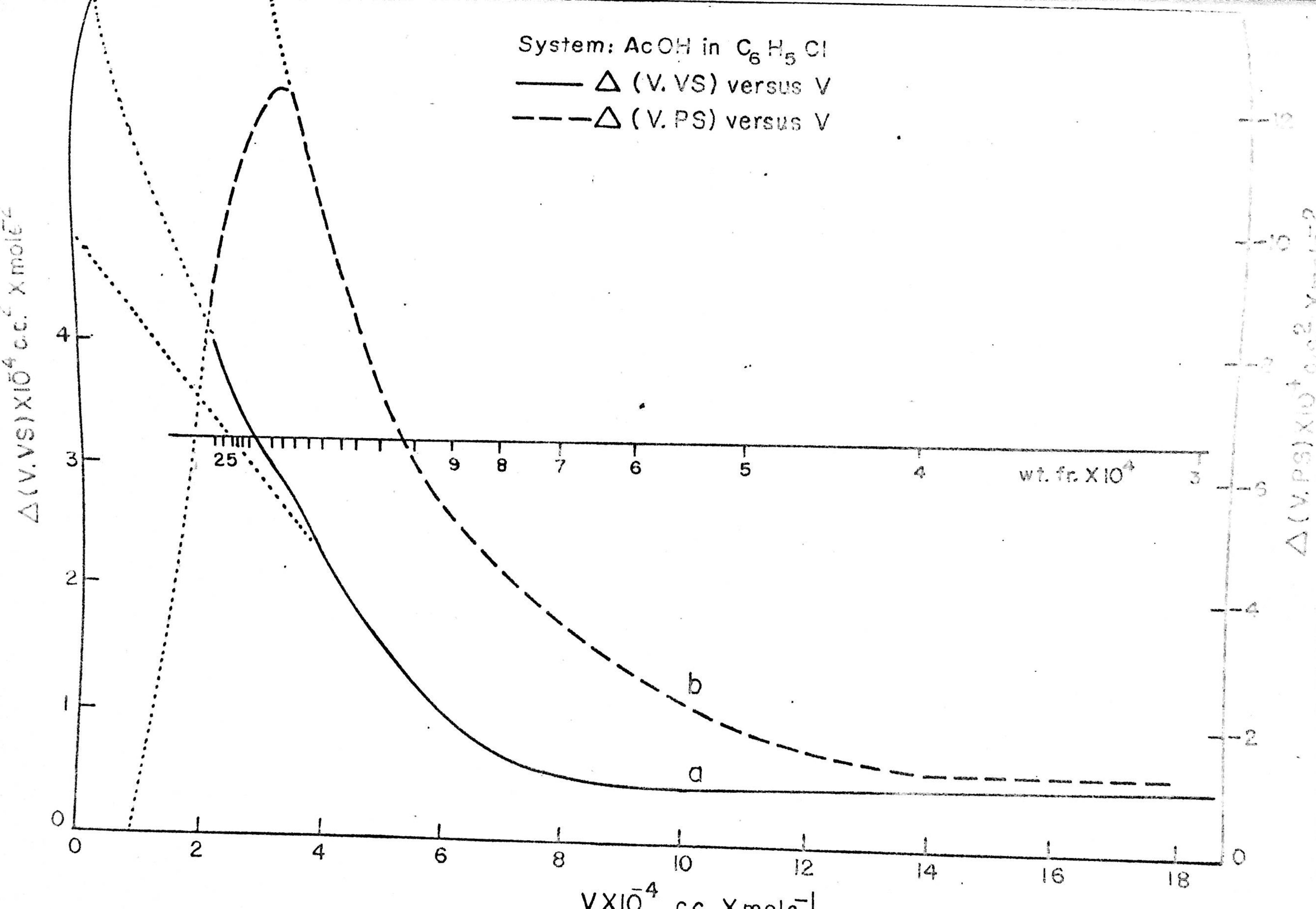

System: AcOH in C_6H_5Cl
—— Δ (V. VS) versus V
– – –Δ (V. PS) versus V
Δ(V.VS)X10⁻⁴ c.c.² X mole⁻²
Δ(V.PS)X10⁴ c.c.² X mole⁻²
0
1
2
3
4
2
4
6
10
12
wt. fr. X10⁴
25
9
8
7
6
5
4
3
a
b
0
2
4
6
8
10
12
14
16
18
VX10⁻⁴ c.c. X mole⁻¹

Fig. 4·10

this section does not conform to any monomer-dimer equilibrium. All these will be explained at a latter part of this work.

Following the usual procedure the parameters have been estimated which is given in the following Table. V_1 and P_1 were found out by extrapolation of 1/V = 0 from VS or PS versus 1/V plot (not shown in Figure).

Table 4.4

Molar proper-ties	Monomer (c.c/mole)	Dimer open chain (c.c/mole)	Dimer cyclic (c.c/mole)	D open chain (c.c/mole)	D cyclic (c.c/mole)	KD open chain ($c.c^2/mole^2$)	KD cyclic ($c.c^2/mole^2$)	K open chain (l/mole)	K cyclic (l/mol
Volume	66.81	2X68.3	2X69.47	2.98	5.32	48500	68000	16.28	12.78
Polari-zation	51.56	2X45.46	2X42.88	-12.2	-17.36	-230000	92000	18.85	-5.30

Here again we see an unexpected thing, the value of V_1 is higher than expected.

There is another section which invites our attention, is from 0.0016 to 0.0024 wt. fraction. Here the PS shows down ward movement with clear linear section and its counterpart in VS also shows upward movement of clear linear section. Does it indicate another dimer interaction ? The extrapolation of PS gave KD is + 92×10^3 c.c^2/$mole^2$ and D for polarization is -17.36 c.c/mole which gives K = - 5.30 l/mole. As K can not be a negative value, this clearly indicate that this can not be indicative of a dimer interaction. The speciality of association interaction of acetic acid in this solvent has been discussed in the section dealing with interpretation of results.

Solvent Behaviour of high Boiling Hydrocarbon and Cyclohexane to Acetic Acid.

High boiling hydrocarbon (HBH) and cyclohexane are universally accepted as "inert" solvents, at least more inert than CCl_4. Inspite of being so, we have trouble ahead. We have very strong indications of solute solvent interaction of a very unusual kind. This came to our notice in this laboratory a few years back. It was found that in very dilute solution of both cyclohexane and HBH acetic acid molecule(most probably monomer) looses a great part of its volume which is very surprising and quite inesplicable. A work* was undertaken to investigate this aspect more thoroughly. The result of such investigation was very interesting. It was found that the apparent molar volume of acetic acid

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* A project "Equilibrium Interaction of Solute species entering into the holes of a solvent body" was undertaken by Mr. Zillur Rahim, Associate Professor of Chemistry, in the year 1977, in which the present author was a research Fellow. The Final report was submitted in the year 1980.

molecule, VS attained 40 c.c at very high dilution in HBH and 10 c.c in cyclohexane, which gradually increase with increasing concentration. The variation of the apparent molar volume(VS) of acetic acid in these solvents was explained assuming holes in the solvent. It was proposed that the solvents have a number of "holes" within the solvent body in which the species enter and looses its own volume; but this entry and exit follows a dynamic process which can be expressed by a dynamic equilibrium in the following:

$$A + O \rightleftharpoons \textcircled{A}$$

free Solute hole solute in hole

where,
$$K = \frac{[\textcircled{A}]}{[A] \times [O]} \text{ ; in}$$

which $[\textcircled{A}]$, $[A]$ and $[O]$ indicate the concentrations of $\textcircled{A}$, A and the holes.

It must be emphasized that the law of mass action is essentially statistical in nature. Hence, the above formulation is not altogether illogical. The important point is whether this formulation can stand the test. The result of such investigation is given in the Appendix-B which amply show that in the dilute part of acetic acid in HBH and cyclohexane behave very differently whose dominant characteristic is an interaction of the type termed as "solute - solvent hole" interaction.

This interaction is followed in case of HBH acetic acid systems upto 0.0006 wt. fraction and in cyclohexane upto 0.0008 wt. fraction. Thus, this part of the solution has been relegated to "solute hole" interaction and when we present the results of our present investigation for determination of monomer-dimer equilibrium we will find its pronounced effects.

System: Acetic Acid in High Boiling Hydrocarbon (150°C - 200°C)

The results of specific volume and dielectric constant along with the calculations of other parameters (V, P, S, VS, Ps etc.) are given in the Appendix A.4. The plot of linear transform of specific volume and dielectric constant (by the reference lines quoted in the Appendix A.4) given in the Fig. 4.11 . The errors in the measurement are of the same dimension as in the other cases. From the carefully drawn curves the relevant values have been read out at properly spaced specific points, from which P, S, VS, PS and other parameters have been calculated. The PS and VS versus V plots are given in the Fig. 4.12 . Both the curve show some abnormal features in the most dilute part of the system. The VS, which shows the ~~x~~ apparent molar volume of the species, at very dilute solution is about 40 c.c, which ultimately rise to a value of 60 c.c and PS showing the apparent molar polarization of the species at first rise from the low value 30 c.c to about 58 c.c at

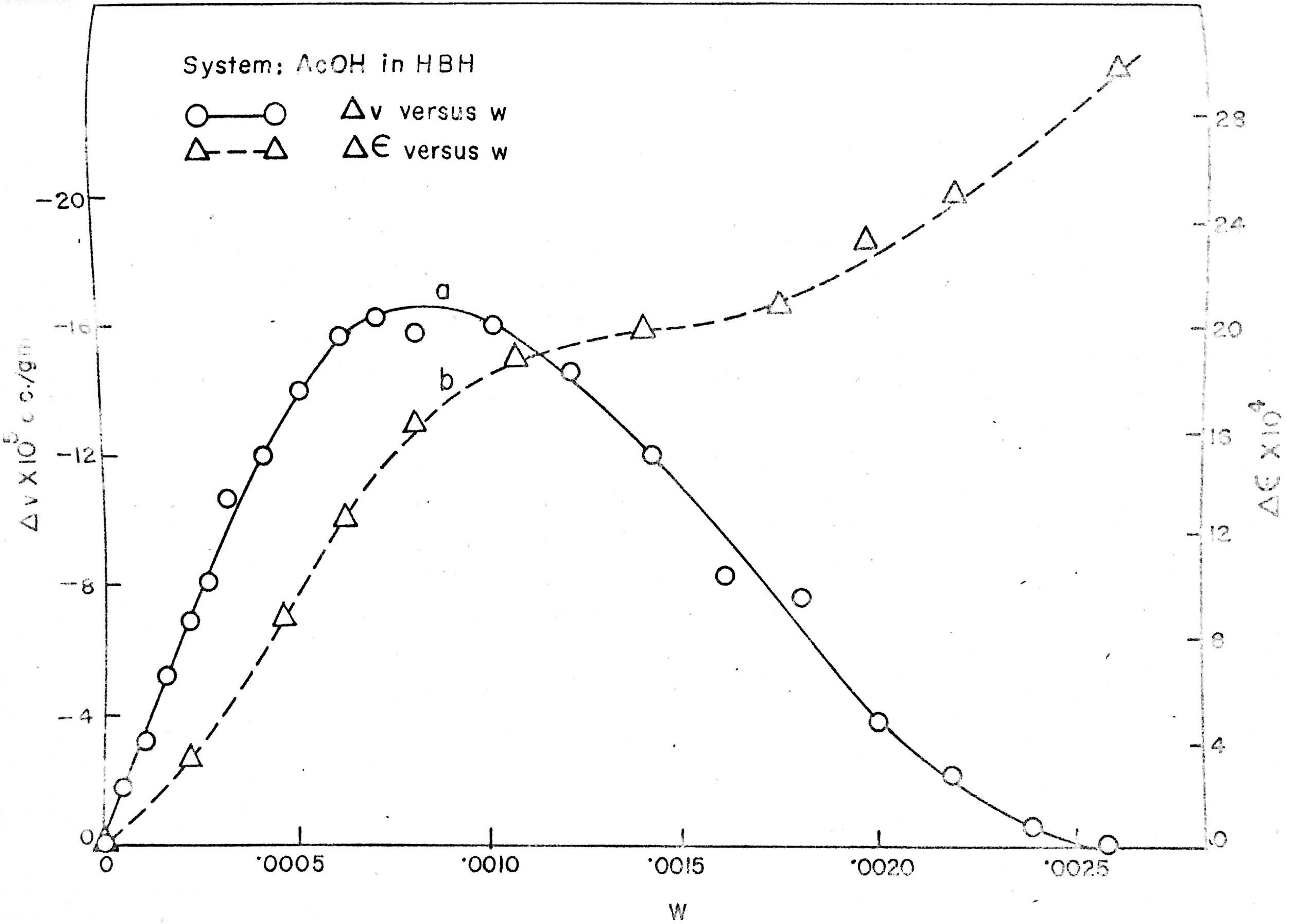

System: AcOH in HBH
Δv versus w
Δϵ versus w
a
b
Δv X10⁵ c.c./gm
-20
-16
-12
-8
-4
0
ΔϵX10⁴
28
24
20
16
12
8
4
0
0
·0005
·0010
·0015
·0020
·0025
w

Fig. 4·11

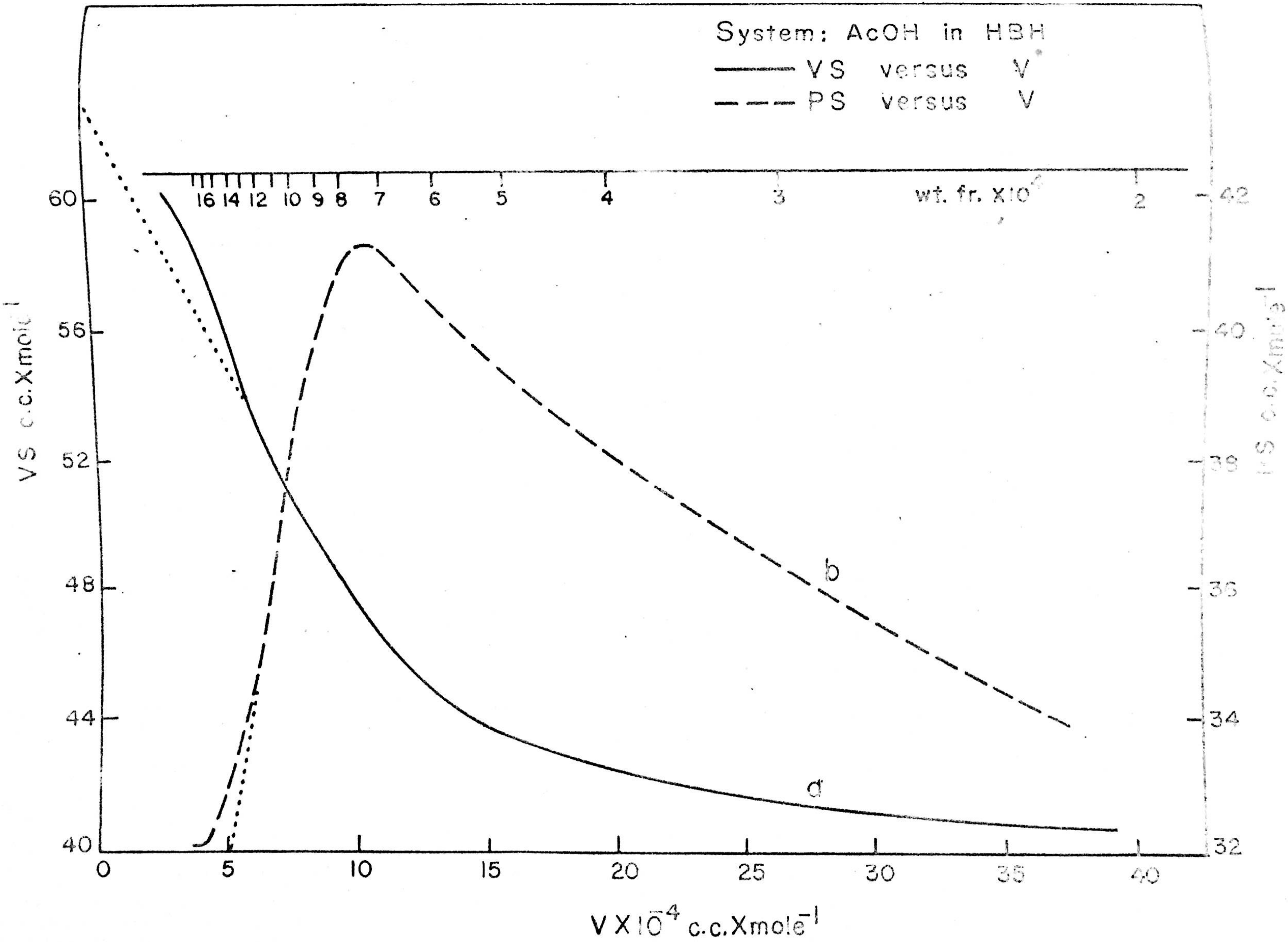

System: AcOH in HBH
VS versus V
PS versus V
wt. fr. X10^4
16 14 12 10 9 8 7 6 5 4 3 2
VS c.c.Xmole^-1
60 56 52 48 44 40
PS c.c.Xmole^-1
42 40 38 36 34 32
b
a
0 5 10 15 20 25 30 35 40
V X 10^-4 c.c.Xmole^-1

Fig. 4·12

0.0007 wt. fraction and then begins to fall continually to a very low value. It has been assumed on the ground of our previous investigation on "solute - hole interaction" that the section of the curve from most dilute to 0.0008 wt. fraction must be mostly relegated to solvent solute interaction and it is also assumed that after this section the solute in monomeric form are comparitively free to participate in the monomer dimer equilibria whose structure is suspected to be cyclic. V_2 and P_2 for dimer have been obtained by plotting VS and PS versus V on a larger graph. The values obtained are $P_2 = 2X19.99$ c.c and $V_2 = 2X63.40$ c.c. In case of polarization P_1 was obtained by extrapolation to $1/V = 0$ in PS versus 1/V plot. But in case of V_1, although we can get by such a proceeding, the value, 39.0 c.c which seem to be of dubious nature; because V_1 under these circumstances, is an ill defined quantity, varying continuously with the change of concentration under the influence of "solute-hole interaction".

$\triangle$ (V.VS) and $\triangle$(V.PS) against V are plotted and shown in the Fig. 4.13. The effect of "solute hole interaction" is evident at dilute solution upto .0007 wt. fraction. From .0007 to about.0014 wt. fraction we find, in both the curve linear sections clearly indicating the monomer dimer equilibrium. In case of molar volume we have a slight difficulty in ascertaining the slope within this sections; however, the points at .0005 to .0009 wt. fraction have been extended to get the intersection

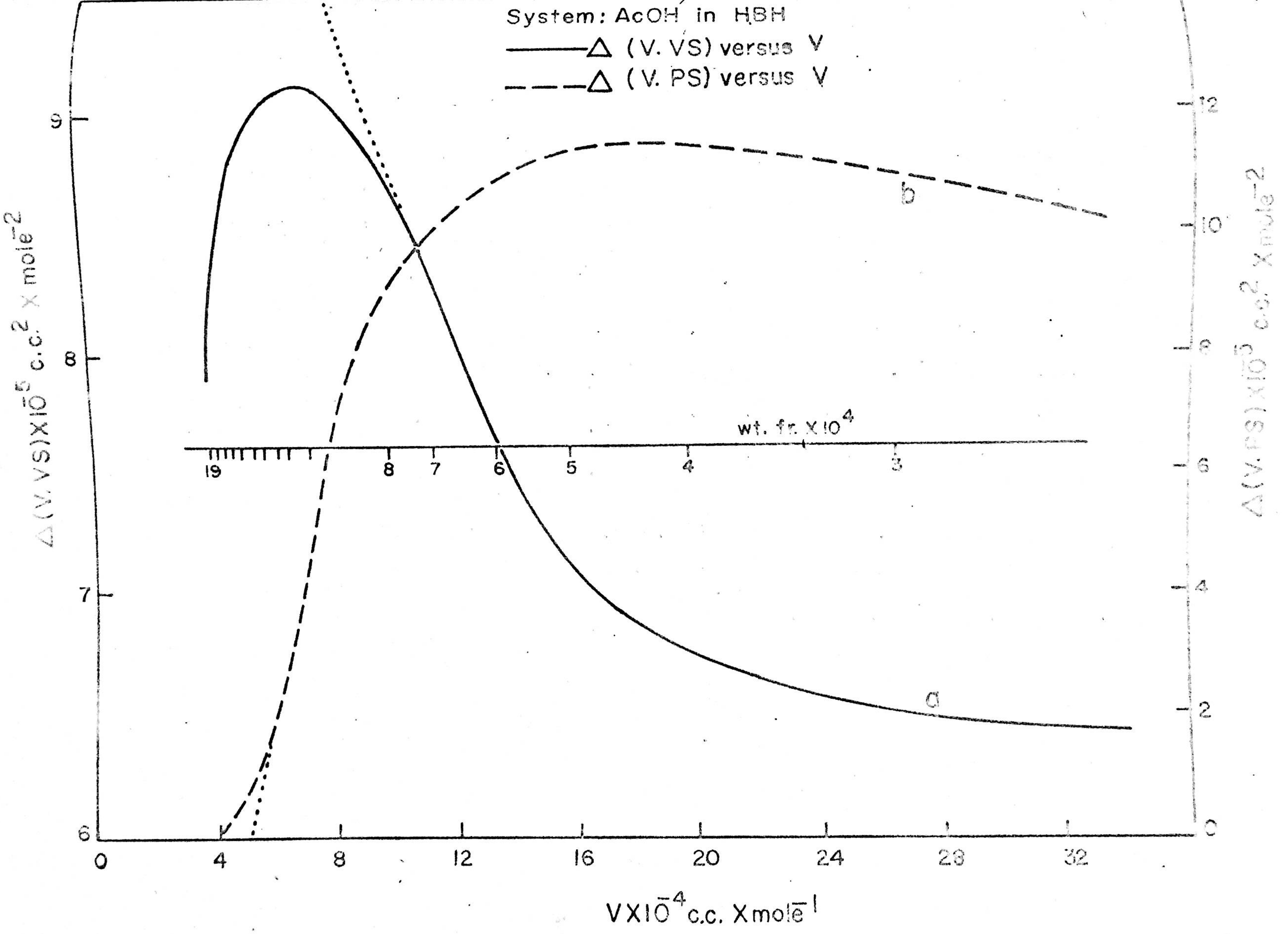

System: AcOH in HBH
—— Δ (V. VS) versus V
– – – Δ (V. PS) versus V
Δ(V. VS)X10^{-5} c.c.^{2} X mole^{-2}
9
8
7
6
Δ(V. PS)X10^{-5} c.c.^{2} X mole^{-2}
12
10
8
6
4
2
0
wt. fr. X10^4
19
8
7
6
5
4
3
a
b
0
4
8
12
16
20
24
28
32
VX10^{-4}c.c. Xmole^{-1}

Fig. 4·13

for KD value. In case of polarization the fall of PS indicate the formation of cyclic dimer. The finding of the intersection for KD is not a problem. We can find V_1 or K for volume property by using the values obtained in polarization study.

Now if we assume that K = 46.68 l/mole (polarization), then deviding KD (1018627.5 c.c^2/mole^2 for volume) by 46.68 l/mole (i.e., 46680 c.c/mole), we obtain D = 21.82 c.c/mole. But $2V_1 = V_2 - 21.82$ c.c/mole and therefore, we have finally, $V_1 = 52.49$ c.c/mole. This is an excellent finding; because in case of CCl_4 and benzene we get $V_1 = 56.26$ c.c/mole and 54.18 c.c/mole respectively. Thus, we can claim that KD obtained by both the studies agree well with each other as there is a clear linear section between .0008 and .0014 wt. fraction. The result of such investigation is given below:

Table 4.5

Molar property	Monomer (c.c/mole)	Dimer (c.c/mole)	KD (c.c^2/mole^2)	K (l/mole)
Volume	—	2X63.4	1018627.4	—
Polarization	32.2	2X19.99	1140000	46.68

System: **Acetic Acid in Cyclohexane**

The results of specific volume and dielectric constant measurement and other subsequent calculations have been given in the Appendix-A.5 . The plot of linear transformation of specific volume and dielectric constant have been given in the Fig. 4.14 . The results are excellent as regards the mean deviation and standard deviation. From the carefully drawn lines, values of specific volume and dielectric constant have been read out at the properly spaced specific points from which VS, PS, P,S etc. have been calculated PS and VS both have been plotted against V and are given in the Fig. 4.15 .

We observe that VS, apparent molar volume keeps on a very low value, 8-9 c.c upto .0004 wt. fraction and then upto .0007 wt. fraction it reaches to 13 c.c, from that point there is a continuous rise of this value to highest point (.0030 wt. fraction) to 44 c.c. This clearly indicates that there is a tremendous loss of volume of the species, acetic acid all throughout this range. This shows that a very unusually strong solute-solvent interaction of the type 'solute hole interaction' is taking place.

In PS versus V plot (curve (b)) also, we find a similar variation. Upto .0007 wt. fraction the solute in the solvent have a very low apparent molar polarization, 17.5 c.c and from that point it slowly rises

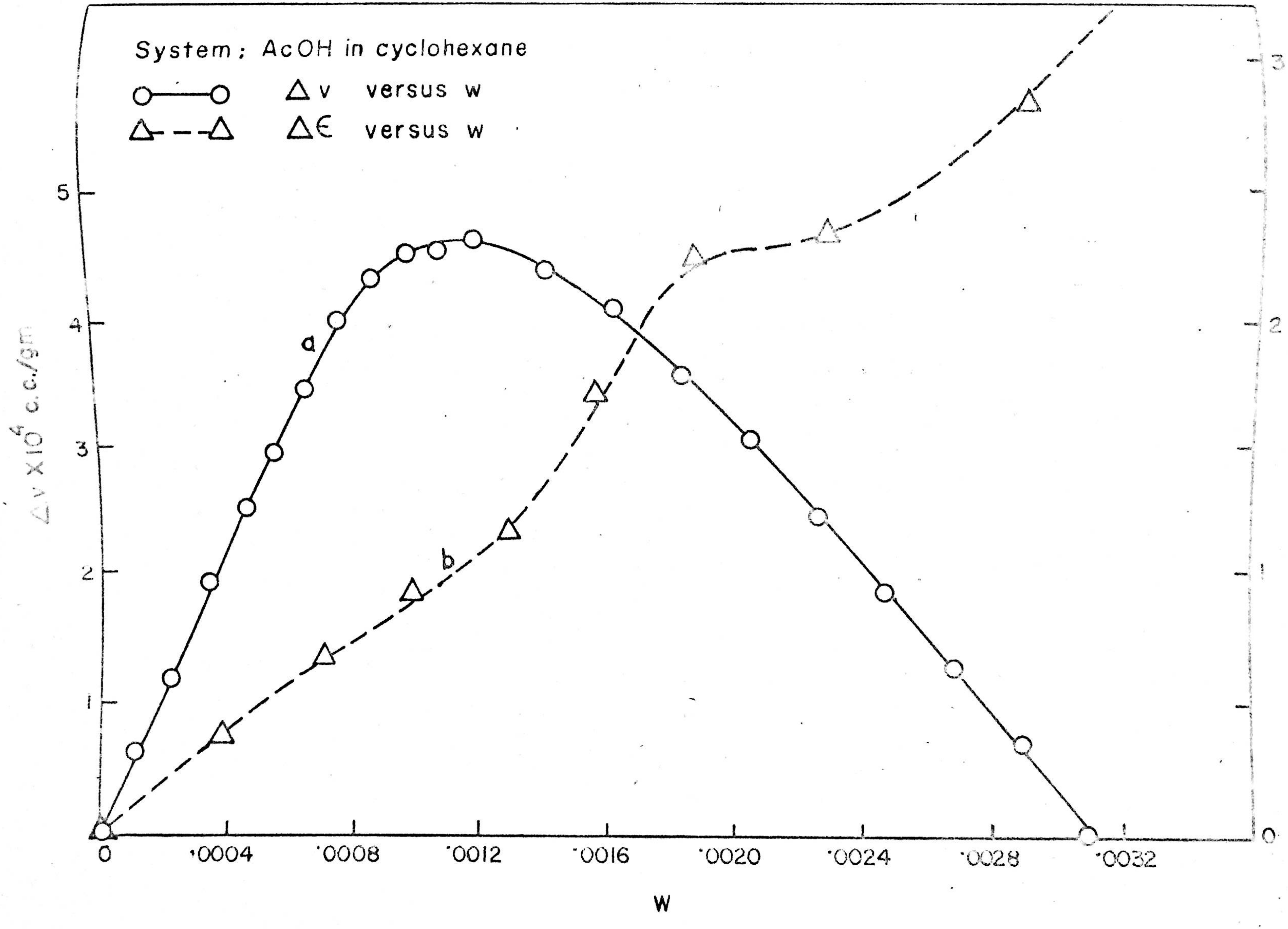

System ; AcOH in cyclohexane
○—○ Δv versus w
Δ- - -Δ Δϵ versus w
a
b
Δv X 10^4 c.c./gm
Δϵ X 10^3
w
0
·0004
·0008
·0012
·0016
·0020
·0024
·0028
·0032
1
2
3
4
5
0
1
2
3

Fig. 4.14

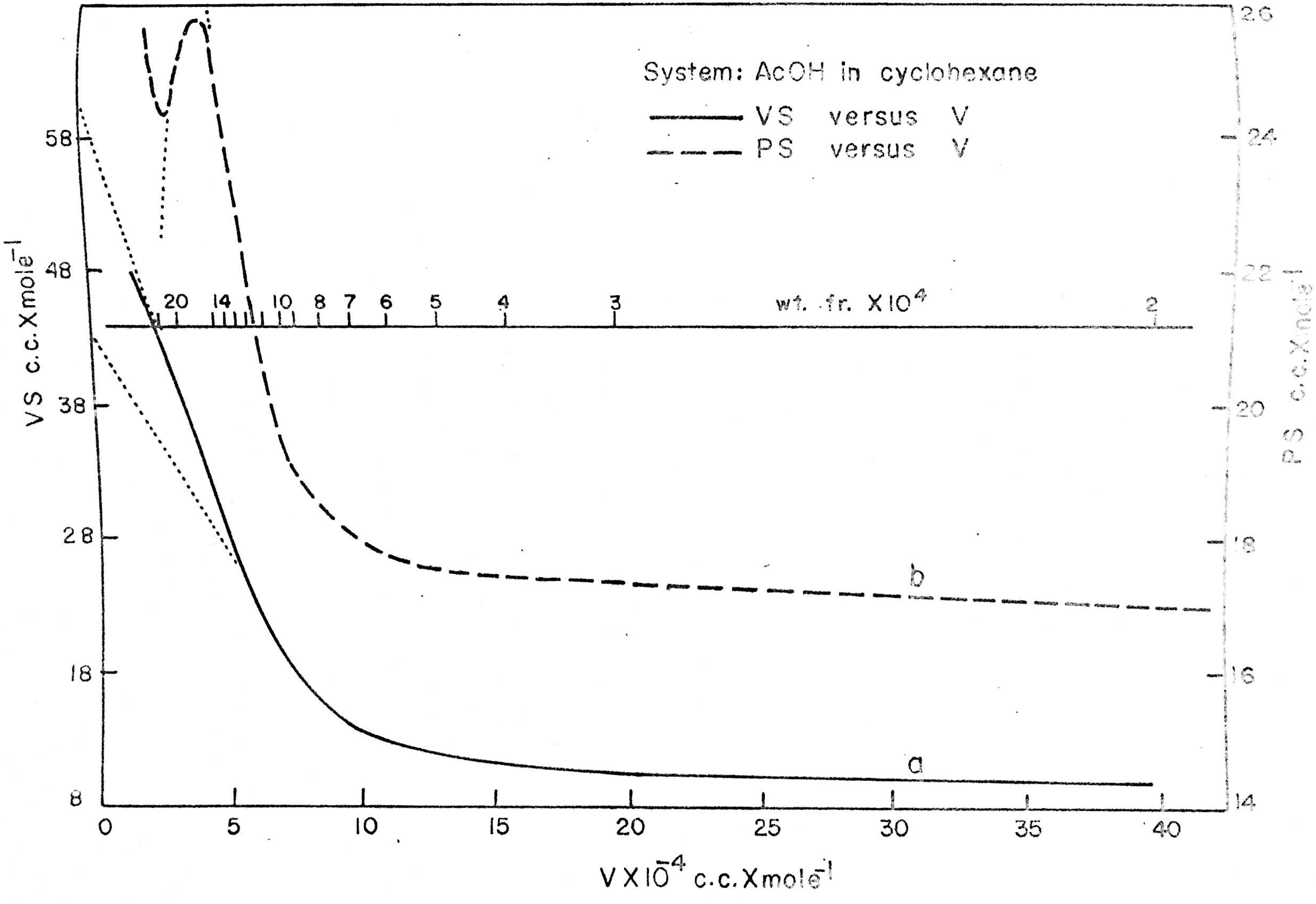

System: AcOH in cyclohexane
VS versus V
PS versus V
VS c.c.Xmole^{-1}
PS c.c.Xmole^{-1}
V X 10^{-4} c.c.Xmole^{-1}
wt. fr. X10^{4}
20
14
10
8
7
6
5
4
3
2
58
48
38
28
18
8
2.6
24
22
20
18
16
14
0
5
10
15
20
25
30
35
40
a
b

Fig. 4·15

upto .0010 wt. fraction and then there is a swift rise to 26 c.c. at .0018 wt. fraction. From this point upto .0024 wt. fraction there is a fall of this value and then again a rise. These indicate a number of interaction with the variation of concentration. These will be indicated very clearly in the next plots, △(V. VS) and △(V. PS) against V in Fig. 4.16 curve (a) and (b).

In these curves (a & b) in Fig. 4.16 we identify two linear sections in each of the curves:

(i) From .0008 to .0014 wt. fraction in molar volume curve and from .0011 to .0018 wt. fraction in molar polarization curve;

(ii) From .0018 to .0024 wt. fraction in both molar polarization and volume curves. The open chain dimer is identified by increase of molar volume and decrease of molar polarization (the lower part of the curve, i.e., .0008 wt. fraction down to more dilute solution the curve indicate the solvent-solute interaction as has already been indicated as 'solute hole interaction'.). The linear portions as indicated in the two curves have been extrapolated to obtain the intercept for the value of KD for the molar volume and molar polarization.

P_2 and V_2 obtained by extrapolation of the curves, PS and VS against V plot (Fig. 4.15) at proper sections of the curve P_1 was obtained by PS against 1/V plot, extrapolation to $1/V = 0$. As we have

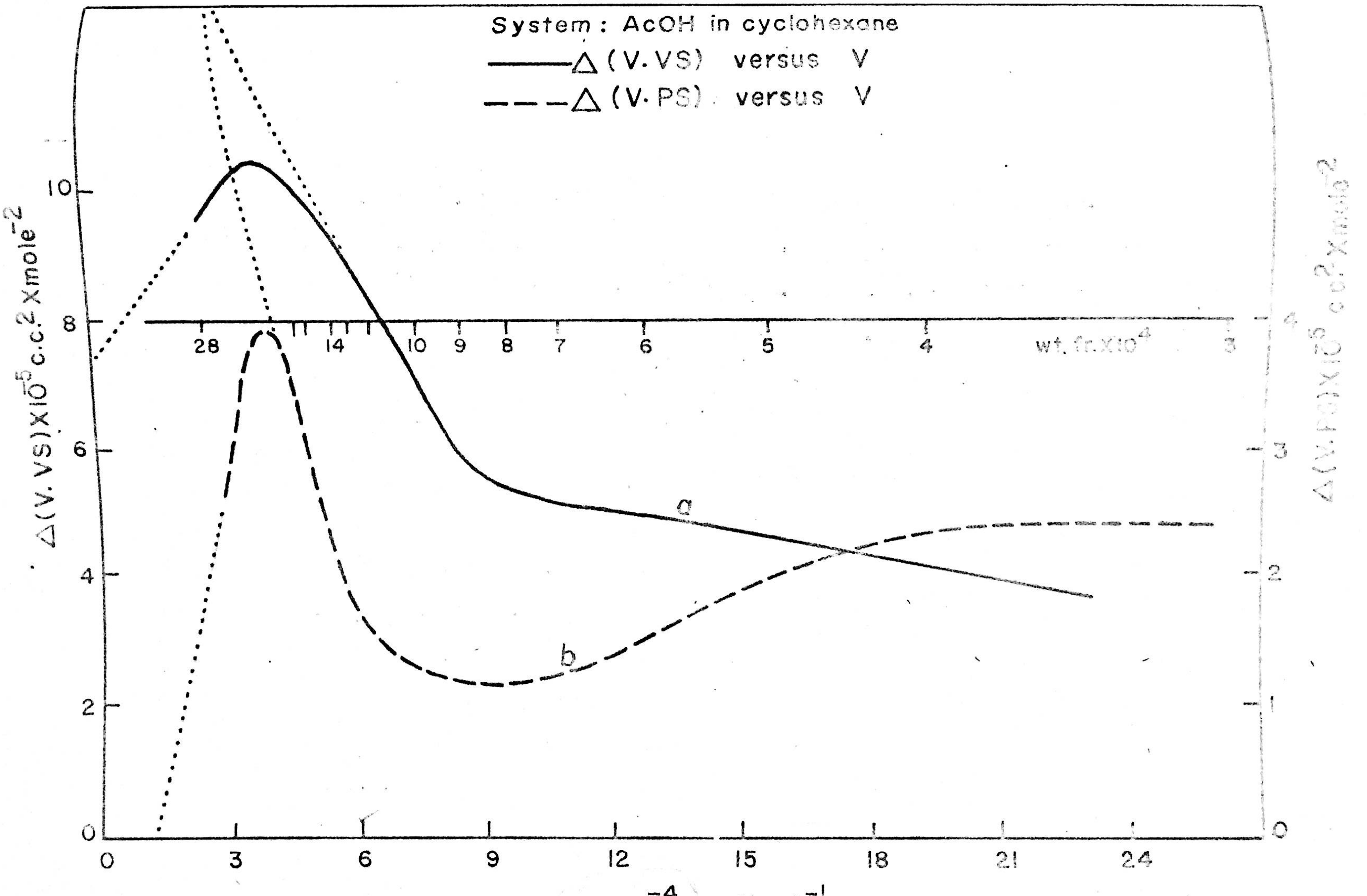


Fig. 4·16

$\frac{60000}{V} \times 10^{-4} = 6$

already discussed in the case of HBH that V_1 obtained by VS against 1/V plot give a value, 8.2 c.c/mole which is not to be taken very seriously, because with the continuous variation of the apparent molar volume of the monomer varies continuously with the change of concentration at this region. However, the results of such investigation is tabulated below:

Table 4.6

Molar property	Monomer (c.c/mole)	Dimer (c.c/mole		KD(c.c^2/mole^2)		K (l/mole)	
		open	cyclic	open	cyclic	open	closed
Volume	—	43X2	60X2	1580000	750000	—	—
Polarization	16.40	36.8X2	11.2X2	1100000	260000	26.96	25.0

We see that we can confidently obtain K values for both types of interactions - open chain dimer and closed chain dimer association interaction by polar method because molar polarization remain uneffected by solute-hole interaction, because the volume effect have been incorporated properly in specific polarization calculation. But in the case of molar volume the effect of 'solute-hole interaction' largely remains.

Thus, the calculation V_1 (although we obtain by usual method to be 8.2 c.c/mole) is not useful for determination of values of K for both these interactions. One way of finding V_1 would be to calculate them by using the values of K from polar data. Thus, we obtain the V_1 values for open and closed chain dimer as follows:

$$\text{Open chain} : \frac{1580000}{26960} = 58.60/2 = 13.7 \text{ c.c/mole}$$

$$\text{Closed chain} : \frac{750000}{25000} = 45 \text{ c.c/mole} .$$

Thus we find $V_1 \approx 14$ c.c. at a stage of interaction when open chain dimer is formed. That means only few of the added solute are out of "holes". Then again $V_1 \approx 45$ c.c/mole when cyclic dimer begins to form. This would mean that quite a large number of solute molecules are outside the "hole" at this stage. It is to be noted with some satisfaction that V_2 for cyclic dimer in CCl_4 and C_6H_6 are about 2X59 c.c/mole; where as, in HBH is found to be 2X63 c.c/mole and cyclohexane 2X60 c.c/mole. This close agreement is quite remarkable. Note in the case of chlorobenzene the cyclic dimers have V_2 = 2X69.47 c.c/mole. The reasons will be discussed in the next chapter.

The results of all the five systems are given in the table 4.7.

Table 4.7

Consolidated Results, of the Systems of AcOH with Different Solvents.

System: AcOH in	Molar property	Monomer (c.c/mole)	Dimer (c.c/mole)		K (l/mole)	
			Opem	Cyclic	Open	Cyclic
CCl_4	Volume	56.26	-	118.16	-	17.84
	Polarization	23.10	-	38.38	-	13.43
C_6H_6	Volume	54.18	107.06	118.26	23.08	26.26
	Polarization	40.20	139.20	32.34	24.49	23.30
C_6H_5Cl	Volume	66.81	-	136.60		16.28†
	Polarization	51.56	-	90.92		18.85†
HBB	Volume	52.49*	-	126.8	**	**
	Polarization	32.2	-	39.98	-	46.68
Cyclohexane	Volume	13.7 45.0 } *	86.0	120.0	**	**
	Polarization	16.4	73.6	22.4	26.96	25.00

* Calculated values.

** The value could not be calculated since D was not known.

† Most probably a distinct complex of linear dimer-chlorobenzene is formed.

CHAPTER-5

DISCUSSION

DISCUSSION

Molar Volume

Monomer: If is encouraging to note that the molar volume obtained in CCl_4, benzene and HBH are 56.26 c.c., 54.18 c.c. and 52.49 c.c. respectively, which can be considered very close to each other. The reasons for slight variations among them are not very difficult to find on the basis of various solvents effects noted in the Introduction (page-22).

Carbontetrachloride possibly form a weak charge - transfer complex,

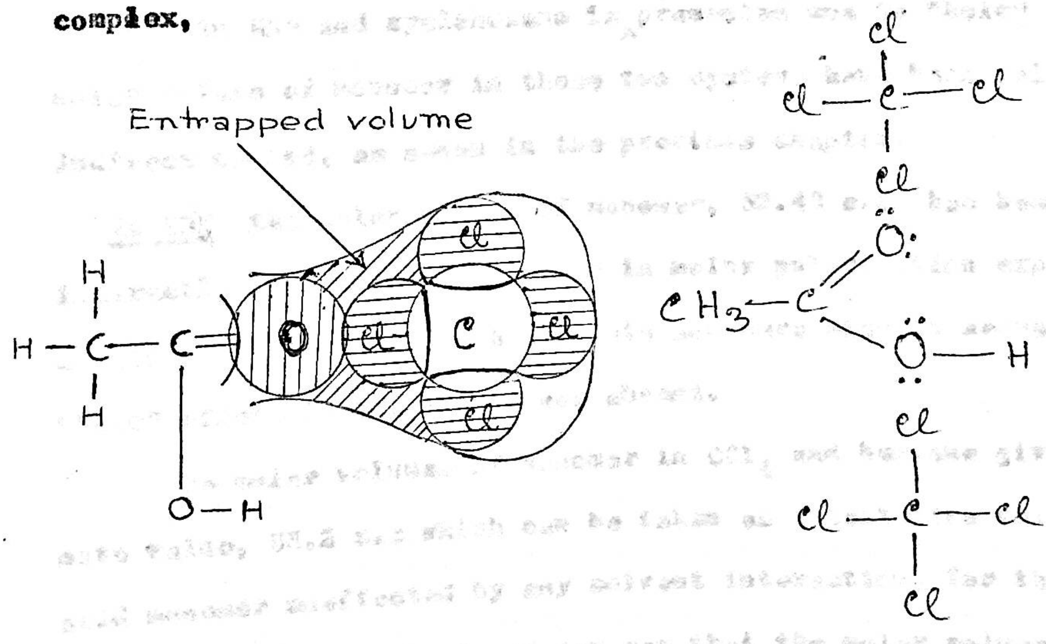
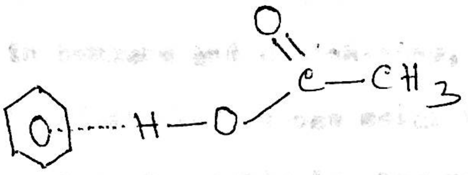


Fig. 5.1

causing a slight overall expansion of volume of acetic acid monomer due to entrapped volume within adducts despite a small volume contraction, if any, due to oxygen-chlorine interaction as shown in Fig. 5.1 .

Benzene forms a well known type of H-bonding[68] with acetic acid as shown,



which causes volume contraction.

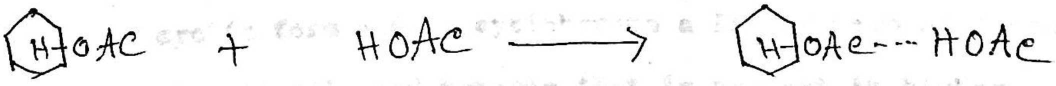
The straight forward determination of apparent molar volume of monomer in HBH and cyclohexane is not presented due to "hole" effect. The molar volume of monomer in these two systems have been calculated by indirect method, as shown in the previous chapter.

In HBH the molar volume of monomer, 52.49 c.c. has been obtained indirectly from K-value obtained in molar polarization experiment. This should be taken as a rough estimate and here also it seems that the "hole" effect is not altogether absent.

The molar volumes of monomer in CCl_4 and benzene give an approximate value, 55.2 c.c which can be taken as a tentative value for acetic acid monomer uneffected by any solvent interaction, for the purposes of comparison. On this basis we can say that the molar volume expansion in

CCl_4 and volume contraction in benzene is about 1 c.c., while in HBH the volume loss of the monomer species is about 2.5 c.c. - a negligible amount; and in cyclohexane volume loss is about 10 c.c. which is considerably high.

Dimer: Only in benzene and cyclohexane, as already stated, linear dimer could be identified, whose molar volume are found to be 107.06 c.c. and 86.00 c.c. respectively. The molar volume of dimer should be double that of monomer plus (or minus) the volume contraction (or expansion) due to structural changes and bond formation. The molar volume of monomer in benzene being 54.18 c.c., we have here a volume contraction due to linear dimer formation of 1.3 c.c . But more careful calculation should be on the following basis,



54.18 c.c   55.2 c.c   107.06 c.c

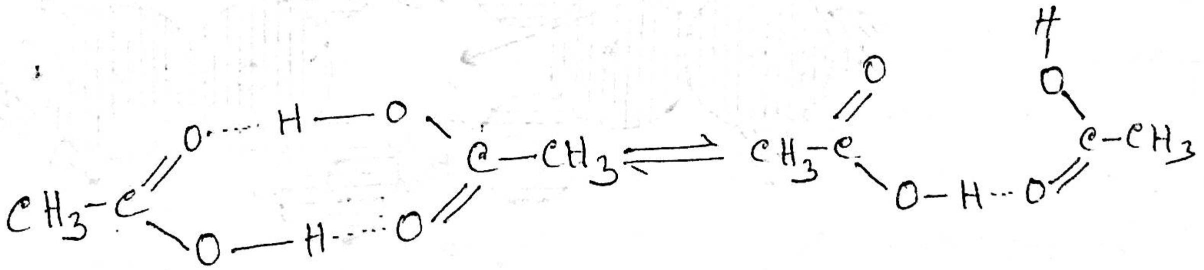
Therefore, D = 54.18 + 55.2 - 107.06 = 2.32 c.c, where D is the volume contraction.

In case of cyclohexane, the molar volume of monomer being approximately 45.0 c.c,D for linear dimer formation should be as follows:

D = 2X45.0 - 86.0 = 4 c.c;

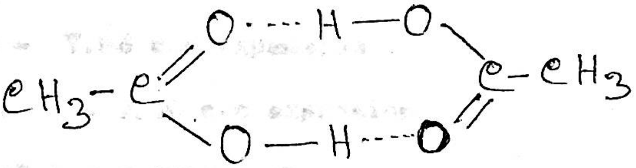
which seem to be a little higher than expected. But considering that 45.0 c.c is only an approximate (obtained indirectly), we can say that the method employed here give a value not far off from the mark. Here we find that the "hole" effect on linear dimer is as strong as on the monomer.

In CCl_4, benzene, cyclohexane and HBH the molar volume of dimer have been found to be 118.16, 118.26, 120.0 and 126.80 c.c respectively. The first two values are remarkably closer to each other; the value in cyclohexane is not far off; and in HBH a slightly higher value is obtained. If we take into account of the fact that in each case, the presence of different amount of linear dimer is likely to be present along with the cyclic form, then these values should be considered quite satisfactory. Thinking in these line we can say that in HBH dimer may consist mostly of cyclic form and in cyclohexane a little more of linear form is present, while in CCl_4 and benzene that is present in higher quantities due to an equilibrium of,

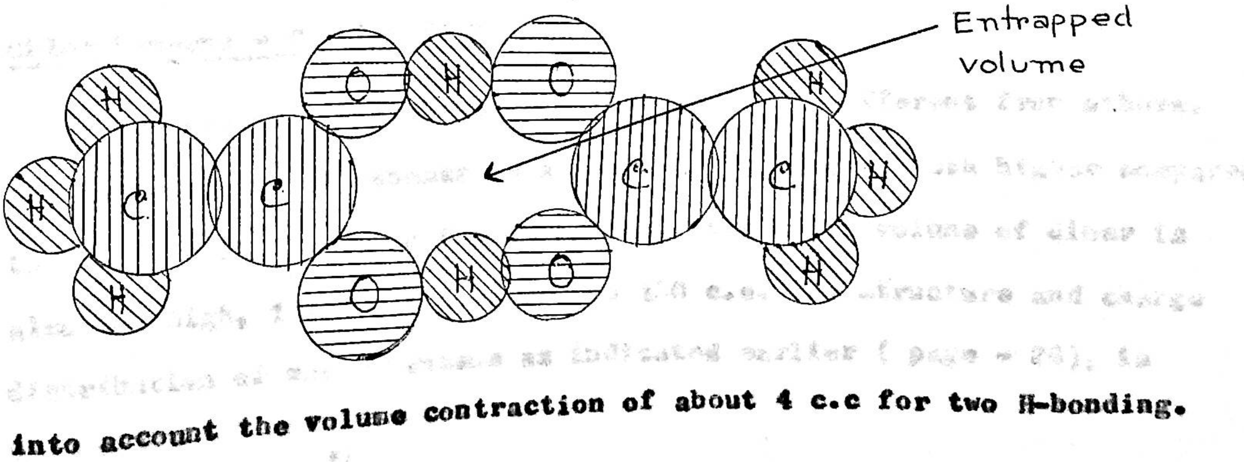


As we have indicated that due to interaction of solvents with monomer and linear dimer, the linear form should be present to a greater extent in CCl_4 and benzene.

The cyclic form has the following structure,



This closed structure should have some special characteristics, such as, low dipole moment (consequent to which it should have lower dielectric constant), less solvent effects, such as, weak charge-transfer and other dipole- dipole interactions and large volume expansion due to cyclic structure. A model calculation on volume effect, as shown in the following figure, give a net volume expansion of about 9-10 c.c, taking



into account the volume contraction of about 4 c.c for two H-bonding.

The volume expansion is due to "entrapped" volume inside the ring as shown in figure.

We find the following values of D, by the following relation,

$D = 55.2 \times 2$ - molar volume of dimer;

D in CCl_4 - 7.76 c.c expansion

Benzene - 7.86 c.c expansion

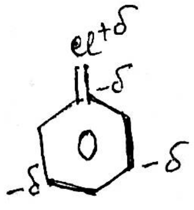
Cyclohexane - 9.60 c.c expansion

HBH - 15.6 c.c expansion

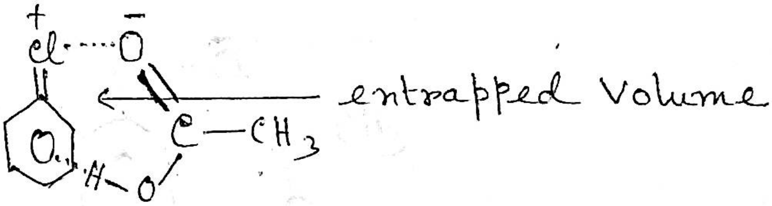
The value obtained in HBH seem to be a little too high and that may be due to progressively increasing formation of cyclic trimer, which also has smaller dipole, with the increase of concentration of the solution. This is very likely, in non-polar solvent the dissolved species tend to become as much non-polar as possible by induction effect or structural change by self-association or some other changes within the structure.

Chlorobenzene - Complex Formation

The case of chlorobenzene system is quite different from others. The molar volume of monomer is as high as 66.81 c.c (much higher compared to 55.2 c.c in HBH), on the other hand, the molar volume of dimer is also too high, 136.6 c.c compared to 120 c.c. The structure and charge distribution of chlorobenzene as indicated earlier (page - 26), is like

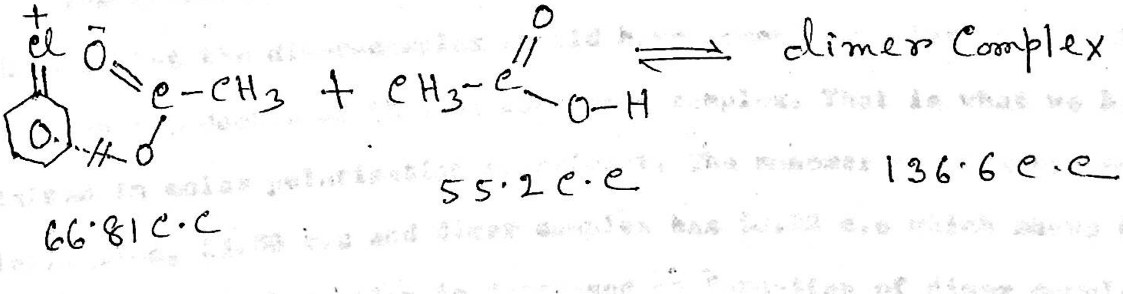


It is obvious that C=O group of acetic acid can form a good charge - transfer complex with Cl-atom and on the other hand, the H-atom of OH group of ACOH will tend to form a π-H-bond complex much more strongly than benzene, forming a complex like,



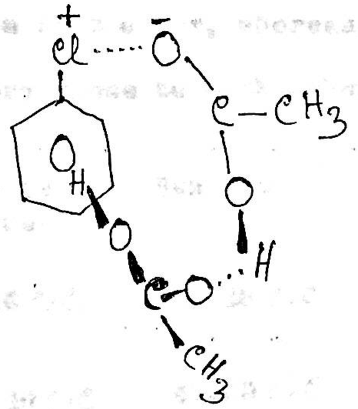
(chlorobenzene - acetic acid complex)

Thus D for molar volume change, shows an expansion of volume of 11.61 c.c. This is not unreasonable, when we look at entrapped volume within structure of the chlorobenzene - acetic acid complex. We should calculate D for dimer formation on the following basis:



$$D = 66.81 + 55.2 - 2.3 - 136.60 = 16.89 \text{ c.c.}$$

This means that another, 16.89 - 11.61 = 5.28 c.c. expansion is attended on attachment of second monomer to chlorobenzene - acetic acid complex. We must then seek a structure which can justify this second volume expansion. This can be achieved by the following proposed structure.



In this structure one end of the linear dimer i.e. CO group attaches itself to $Cl^{+\delta}$ atom while the free acidic H-atom attached itself to π electron of the ring.

The consideration of vector addition of moment of this structure indicate that the dimer-complex should have moment or molar polarization less than the double of that of monomer - complex. That is what we have obtained in molar polarization experiment. The monomer complex has molar polarization, 51.56 c.c and dimer complex has 90.92 c.c which shows that 12.2 c.c molar polarization is decreased on formation of dimer complex.

Thus this probable structure satisfy two observable molar properties V_2 and P_2 and D for molar volume and polarization.

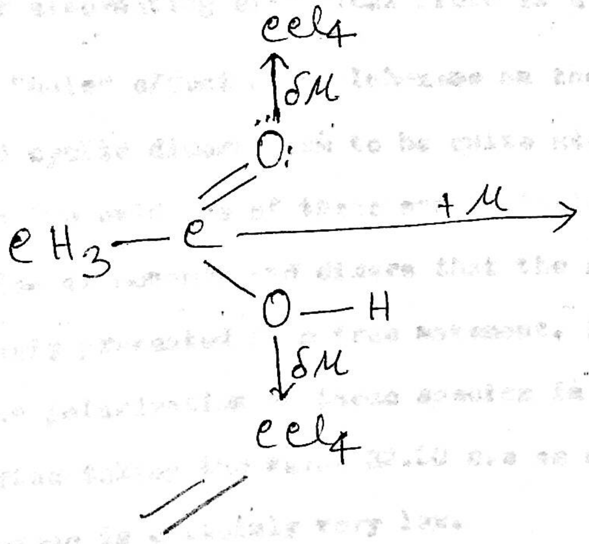
Molar Polarization

Molar polarization of monomer obtained in different solvents are widely apart from each other, whereas, we have in three solvents the molar volume, very close to each other, as shown in the following:

	Carbon tetra chloride	Benzene	HBH	Cyclohexane	C_6H_5Cl
Molar volume	56.26 c.c	54.18 c.c	52.49 c.c	45.0 c.c	66.81 c.c
Molar polarization	23.10 c.c	40.20 c.c	32.20 c.c	16.4 c.c	51.56 c.c

We have already known that small effects like weak H-bonding, weak charge - transfer complex and dipole - dipole interactions can lead to change of volume from less than 1 c.c to about 5 c.c. This explains the close resemblance of molar volumes of acetic acid monomer in CCl_4, benzene and HBH. The somewhat larger departure of molar volume of acetic acid monomer in cyclohexane and C_6H_5Cl has been shown to be due to "hole" effect and a complex formation respectively. Here in case of molar polarization we are confronted with the problem of solvent effects of various kinds.[88,92,93] Thus a conformity of results of molar polarization of monomer acetic acid, which is a very highly polar molecule, in different solvent ~~is~~ can be expected. But we can discuss each case very carefully on the basis of interactions we have already identified.

i) In Carbon Tetrachloride the formation of a weak complex have been suggested by the Fig. 5.1 . The main dipole is along the C - C bond and the induced dipole by CCl_4 molecules on both the oxygen attached carbon are along the right angle to it in opposite directions, as shown below:



This explains why the monomer acetic acid should have lower moment and consequently molar polarization in CCl_4. Had the adduct joined along the main axis the moment would have increased.

ii) The formation of π-H-bond complex with benzene along the axis of main dipole of acetic acid obviously increase the dipole of the complex and the highest value obtain in benzene compared to those in CCl_4, HBH and cyclohexane is thus satisfactorily explained. The molar polarization of linear dimer in benzene is also very high for the same reason.

iii) The value obtained in HBH, it seems to us, can be taken as the "true" value for monomer unaffected by any"solvent effect". The reason for such assignment is quite simple. Although there is a "hole" effect which cause a little volume loss the monomer can freely orientate itself under alternating electrical field in a dielectric measurement.

iv) The "hole" effect in cyclohexane on the monomer, as well as linear and cyclic dimers seem to be quite strong. We are lead to believe on the evidence of these surprisingly low values of molar polarization of monomer and dimers that the species in the "hole" are very strongly prevented from free movement. Hence the contribution of orientation polarization of these species in the "hole" are bound to be less. Thus taking the value 32.20 c.c as normal (in HBH), 16.4 c.c in cyclohexane is certainly very low.

The value for linear dimer is only 73.6 c.c whereas it should have been somewhat less than 139.20 cc which is the value for linear dimer in benzene. Again we find that the even the cyclic dimer in this solvent have a very low value compared to others. All these indicate that "hole" has restrictive effect on the free movement of the species in such a condition.

v) The cyclic dimer in solvents should have much less molar polarization than monomer and linear dimer is obvious due to its symmetrical structure. They seem to be less effected by solvent effects. In CCl_4, benzene and HBH the values are 38.38, 32.34 and 39.98 c.c respectively. The small differences between them is not easy to explain. But we advocate that the value obtained in HBH should be taken as a reasonable value because of the possibility that it is less effected by the solvent interactions. The smaller value in cyclohexane is already discussed above.

vi) The interaction of monomer and linear dimer with chlorobenzene lead to the formation of complexes and has already been shown. A careful explanation of this structure shows that they should have higher molar polarization compared to others. It has already been shown in the experimental results that cyclic dimer in chlorobenzene can not exist. The explanation is simple. The complex formation with monomer and linear form is so strong that the cyclic form is broken up as readily as its formed.

Equilibrium Constant

In the present investigation, in each set of experiments we have determined three unknown quantities, molar properties of monomer and dimer of AcOH and the equilibrium constant related to particular type of association (linear or cyclic). Looking at the Table 4.7 we find tolerably closer values of some of these quantities. Most remarkable conformity or closeness of values are found in the values of equilibrium constants. There are two sets of values:

(i) 17.84, 13.43 and 16.28, 18.85 l/mole

(for CCl_4 and chlorobenzene)

and

(ii) 23.08, 26.26, 24.49, 23.30 and 26.96, 25.0 l/mole

(for benzene and cyclohexane).

The values in CCl_4 and chlorobenzene are much lower than those of benzene and cyclohexane, while the value in HBH is still higher than those and stand apart. It is also interesting to note that the equilibrium constants for linear and cyclic dimer association in benzene and cyclohexane are nearly equal to each other. We have equilibrium constant in HBH for only cyclic form which is nearly the sum of equilibrium constants for linear and cyclic dimers in benzene or cyclohexane.

In two types of association linear and cyclic, we find in the processing of results that they occur in stages and not simultaneously, contrary to expectation according to the scheme of interactions presented earlier (page- 20). The explanation of this effect is not easy. In case of benzene system acetic acid monomer has greater tendency to form a H-bonding with ring π-electrons of benzene and so does the linear dimer. It indicates that in such a system dimer will remain more in open form than cyclic ~~x~~ so long the concentration of acetic acid monomer and linear dimer are not too high to be able to remain engaged in H-bonding with π- electron of benzene. But in case of cyclohexane the explanation will not be easy until the "hole" mistry of this solvent is fully understood.

In two sets of values, the higher values, including that of HBH, are associated with hydrocarbon nature of the solvent, i.e. non-polarizability of the atoms, while the lower values of equilibrium constant is associated with chloro-compounds in CCl_4 and chlorobenzene. In these two latter solvents we have indicated that Cl-atom can form charge-transfer complex with C=O group. This complexation virtually remove, or in other words, inactivate the donor property of C=O which consequent lead to formation of lesser quantity of dimers by self association which obviously must lower the equilibrium constant of the association interaction.

In conclusion we are to remark that our equilibrium constant values are the lowest so far obtained and it nearly conform to the value obtained by Simamura[86]. The method developed in this work has a general importance in the fact that this proceedings can be applied to any other chemical species which can have self-associations. Thus it is expected that the method described therein will receive serious attention it deserves.

CHAPTER-6

SUMMARY

SUMMARY

1. A discussion on the problems associated with the determination of Formation Constant of Hellgand acetic acid dimer in different solvents in the Introduction show that (i) various associated species - dimer (linear and cyclic), trimer (linear and cyclic) and higher polymer of the various types should exist simultaneously in equilibrium and (ii) different solvents should have various "solvent effects" including the possibility of formation of distinct complexes. At a suitably chosen dilute region, it is expected that only the first association i. e. dimer formation, can exist with the effective exclusion of others and the investigation can be conducted at this region to study this particular association interaction.

2. A theoretical frame work has been constructed for the study of the variation of "apparent molar property", such as molar volume and molar polarization, whereby it is shown that the "apparent molar property", PS is related linearly to volume, V which contain one mole of the added species, as follows:

$$PS = \frac{K}{D} \times \frac{(P_2-2PS)^2}{V} + P_1$$; where the symbols has the usual significants according to list of symbols. How this relation has been used, to determine P_1, P_2 and KD graphically and finally D and K, is explained.

3. (i) A description of the method for the determination of specific volume of liquid solution with the help of a Magnetic Float Densimeter

is presented along with the details of the construction and manipulation of the device. (ii) The method for the determination of dielectric constant with the help of a Dipole meter has been described with full particulars. (iii) The details of purification and particularly, careful dehydration have been fully described. (iv) Finally, how the variation of concentration of solution have been accomplished is reported.

4. For five systems of acetic acid solutions, in CCl_4, Benzene, Chlorobenzene, cyclohexane and high boiling hydrocarbon (HBH), the specific volumes and dielectric constants have been measured. The linear plots of these quantities against weight fractions have been carefully scrutinized to obtain finally a minimum - error-free values at regularly spaced weight fractions. From these " refined values" the various parameters, P, V, PS, VS etc, have been calculated; from which various plots have been constructed related to various equations to obtain P_1, P_2 and KD. The results of such efforts have been presented in the Table 4.7 .

5. (i) In CCl_4 and chlorobenzene the equilibrium constants for the formation of dimer is obtained between values 13.43 to 18.85 litre/mole. (ii) In benzene and cyclohexane the value is between 23.08 to 26.96 litre/mole. (iii) The value in HBH is 46.68 litre/mole. The lower value of equilibrium constant in (i) has been explained as due to weak charge-transfer interaction between Cl-atom of solvent with

C=O group of the acid. In case of benzene and cyclohexane two types of dimer, linear and cyclic form, the K values are nearly same in both cases; whereas in HBH only cyclic form is observable, in which case K value is almost equal to the sum of the values for linear and cyclic form in benzene and cyclohexane.

6. (i) The molar volume of cyclic dimer obtained in different solvents are found to be very close to each other— 118.16 c.c in CCl_4, 118.26 c.c in benzene, 120 c.c in cyclohexane and 126.8 c.c in HBH. It is suggested that the closed structure of cyclic dimer form is likely to be least affected by solvents and they should have very similar values. The formation of cyclic form is attended with volume expansion of about 10-14 c.c which is accounted for by considering the entrapped volume in the closed structure. (ii) The linear dimer in benzene have molar volume 107.06 c.c which is attended with volume contraction of 2.32 c.c - this value is reasonable for one H-bond considering the contraction of volume of about 1 c.c for π-H-bond formation with the end H-atom of the linear dimer. The molar volume of this form in cyclohexane is much less than expected and is explained by the loss of volume due to the "hole" effect. The calculation shows that the formation of this type, as expected, is attended with volume contraction of 4 c.c - this value seem to be a little higher, although not unexpected. (iii) The range of values obtained for molar volume of monomer (excepting in chlorobenzene where complex formation takes place and in HBH and cyclohexane where the "hole" effect is strong) are quite

close to each other, between 54.18 to 56.26 c.c.

7. (i) The molar polarization of monomer have been found to be different in different solvents. It has been pointed out that the various effects of solvents including complex formation and "hole" effect, would always have profound effect on the measured molar polarization. (ii) The molar polarization of linear dimer in benzene have a higher value due to linear alignment of two monomers. This is found to be true in case of cyclohexane if the molar polarization of monomer in this solvent is taken into account. (iii) The molar polarization of cyclic form have much less values than that of monomer and linear dimer as can be expected on the symmetrical structure.

It has been pointed out that the molar polarization of monomer, linear dimer and cyclic dimer in cyclohexane are always much less than the corresponding values of these species in other solvent. It has been argued that the species in "hole" of the cyclohexane solvent have a profound restrictive effect on their free movement which consiquently keeps the orientation polarization low.

In conclusion, it is hoped that the method developed in this work will be considered to be applicable to any other monomer-dimer equilibrium system for investigation and evaluation of different parameters.

APPENDIX I

APPENDIX

System: Acetic acid in CCl_4

Table 1. Experimental results of specific volume

Weight fraction(w)(1)²	Observed specific volume(v) c.c./gm.	Difference in specific volume, v (obs. - cal.)×10⁵ c.c./gm.
0.0	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		

$v_{cal.}$ = [illegible]

APPENDIX- A.1

System: Acetic Acid in CCl_4

Table 1. Experimental results of specific volume

Weight fraction(w)X10^2	Observed specific volume(v)c.c./gm.	Difference in specific volume, $\triangle v$ (obs.- cal.)X10^6 c.c./gm.
0.0	0.635001	+16
0.011489	0.635021	+ 1
0.022936	0.635053	- 2
0.034343	0.635088	- 1
0.045709	0.635125	+ 1
0.057034	0.635156	- 2
0.066765	0.635189	+ 2
0.079564	0.635227	+ 1
0.090769	0.635268	+ 8
0.101934	0.635306	+12
0.113059	0.635344	+16
0.124140	0.635371	+10
0.135190	0.635390	- 5
0.146200	0.635411	-17
0.157169	0.635441	-20
0.168100	0.635501	+ 7
0.178990	0.635565	+38
0.189840	0.635615	+55
0.200660	0.635666	+73

$$v_{cal.} = 0.634985 + 0.30303 X w.$$

Table 2. Experimental result of dielectric constant.

(Weight fraction)X10^2	Observed d.c (ϵ)	$\Delta\epsilon$(obs.-cal.)X10^6
0.0	2.251207	0.0
0.01520	2.251372	- 20
0.03040	2.251516	- 60
0.05167	2.251749	- 85
0.06951	2.251957	- 94
0.08780	2.252164	-109
0.11073	2.252328	-223
0.14176	2.252404	-524
0.16232	2.252478	-699
0.18413	2.252596	-847
0.20150	2.252756	-898
0.22627	2.253121	-833
0.24311	2.253589	-569
0.26097	2.254107	-269
0.27583	2.254556	0.0

$$\epsilon_{cal.} = 2.251207 + 1.21415X_w .$$

Table 3. Refined values of specific volume and dielectric const.

Weight fraction	Specific volume (c.c./gm.)	d. c.	Specific polarization (c.c/gm.)
0.0	0.634986	2.251207	0.186888
0.0001	0.635015	2.251306	0.186907
0.0002	0.635046	2.251410	0.186928
0.0003	0.635076	2.251526	0.186948
0.0004	0.635106	2.251636	0.186968
0.0005	0.635136	2.251744	0.186989
0.0006	0.635167	2.251855	0.187009
0.0007	0.635198	2.251954	0.187029
0.0008	0.635230	2.252035	0.187047
0.0009	0.635265	2.252108	0.187065
0.0010	0.635300	2.252162	0.187081
0.0011	0.635333	2.252200	0.187095
0.0012	0.635362	2.252255	0.187109
0.0013	0.635381	2.252316	0.187121
0.0014	0.635399	2.252417	0.187137
0.0015	0.635421	2.252479	0.187150
0.0016	0.635451	2.252556	0.187167
0.0017	0.635512	2.252547	0.187184
0.0018	0.635570	2.252565	0.187203
0.0019	0.635617	2.252654	0.187226
0.0020	0.635664	2.252745	0.187250

Table 4. Calculated parameters from refined data.

Weight fraction	V(c.c/mole)	VS(c.c/mole)	PS(c.c/mole)	$\triangle$(V.VS)cc^2/mole^2	$\triangle$(V.PS) c.c^2/mo
0.0001	381326.51	56.15	22.63	-22880.0	- 179223.40
0.0002	190672.56	56.44	23.23	+43855.0	+ 24787.40
0.0003	127121.05	56.35	23.23	+17796.9	+ 16525.70
0.0004	95345.29	56.30	23.30	+ 8581.1	+ 19069.10
0.0005	76279.89	56.32	23.35	+ 8390.8	+ 19070.00
0.0006	63569.63	56.35	23.33	+ 8899.7	+ 14621.00
0.0007	54490.91	56.40	23.30	+ 10353.3	+ 10898.20
0.0008	47681.95	56.52	23.15	+ 14781.4	+ 2384.10
0.0009	42386.29	56.81	23.04	+ 25431.8	- 2543.17
0.0010	38149 .77	57.05	22.83	+ 32045.8	- 10300.44
0.0011	34683.41	57.08	22.54	+ 33643.0	- 19422.74
0.0012	31794.57	56.99	22.27	+ 24799.8	- 26389.49
0.0013	29349.71	56.42	21.99	+ 6163 .5	- 32578.18
0.0014	27254.08	55.89	21.90	- 8721.3	- 32704.89
0.0015	25438.02	55.58	21.72	- 16026.0	- 35104.47
0.0016	23849.27	55.62	21.68	- 14071.1	- 33865.96
0.0017	22448.53	56.75	21.68	+ 12122.2	- 31876.91
0.0018	21203.32	57.65	21.73	+ 30532.7	- 29048.55
0.0019	20088.84	58.10	21.91	+ 37968.0	- 23905.72
0.0020	19085.81	58.52	22.09	+ 44088.3	- 19276.67

Table 5. Parameters VS,,PS and 1/V .

Weight fraction$\times 10^4$	$1/V \times 10^7$ (mole/c.c)	VS(c.c/mole)	PS(c.c/mole)
1	26.22	56.15	22.63
2	52.44	56.44	23.23
3	78.66	56.35	23.23
4	104.88	56.30	23.30
5	131.09	56.32	23.35
6	157.30	56.35	23.33
7	183.51	56.40	23.30
8	209.72	56.52	23.15

APPENDIX- A.2

System: Acetic Acid in Benzene

Table 1. Experimental results of specific volume

(Weight fraction)X10^2	Observed specific volume (v) (c.c/gm)	Difference in specific volume, $\triangle v$(obs.-cal.)X10^5 (c.c/gm.)
0.0	1.151490	0.0
0.01189	1.151464	− 0.81
0.01782	1.151450	− 1.31
0.02373	1.151429	− 2.52
0.02964	1.151415	− 3.02
0.03553	1.151400	− 3.63
0.04728	1.151464	− 5.46
0.05899	1.151341	− 5.99
0.07065	1.151309	− 7.42
0.08226	1.151282	− 8.37
0.09383	1.151255	− 9.32
0.10536	1.151230	− 10.07
0.11684	1.151211	− 10.24
0.12827	1.151193	− 10.31
0.13966	1.151176	− 10.29
0.15101	1.151160	− 10.17
0.16231	1.151142	− 10.26
0.18478	1.151117	− 9.37
0.20709	1.151101	− 7.59
0.22922	1.151086	− 5.75
0.25118	1.151068	− 4.23
0.27298	1.151052	− 2.53
0.29461	1.151033	− 1.16
0.31608	1.151012	0.0

$$V_{cal.} = 1.151490 + (- 0.1512) w .$$

Table 2. Experimental results of dielectric constant

(Weight fraction)X10^2	D. C.
0.0	2.295660
0.0110	2.295901
0.0302	2.296421
0.0490	2.297120
0.0819	2.298539
0.1095	2.299750
0.1541	2.300009
0.2016	2.300232
0.2582	2.300910
0.3021	2.301509
0.3496	2.302381

$$\Delta\epsilon = \epsilon_{cal} - 2.295660.$$

Table 3. **Refined values of specific valume and dielectric constant.**

Weight fraction	Specific volume(c.c/gm.)	D. C.	Specific polarizatio (c.c/gm.)
0.0	1.151490	2.295660	0.347313
0.0001	1.1514~~4~~65	2.295871	0.347345
0.0002	1.151440	2.296173	0.347395
0.0003	1.151414	2.296461	0.347440
0.0004	1.151389	2.296802	0.347496
0.0005	1.151364	2.297182	0.347560
0.0006	1.151333	2.297610	0.347630
0.0007	1.151311	2.298041	0.347705
0.0008	1.151287	2.298480	0.347780
0.0009	1.151263	2.298983	0.347866
0.0010	1.151241	2.299431	0.347943
0.0011	1.151223	2.299749	0.347997
0.0012	1.151207	2.299901	0.348020
0.0013	1.151191	2.299952	0.348025
0.0014	1.151176	2.300000	0.348030
0.0015	1.151161	2.300000	0.348025
0.0016	1.151147	2.300000	0.348021
0.0017	1.151134	2.300031	0.348023
0.0018	1.151122	2.300049	0.348023
0.0019	1.151113	2.300101	0.348030
0.0020	1.151105	2.300199	0.348046
0.0021	1.151098	2.300298	0.348062
0.0022	1.151092	2.300401	0.348079
0.0023	1.151086	2.300521	0.348100
0.0024	1.151079	2.300650	0.348122
0.0025	1.151070	2.300772	0.348142

Table 4. Calculated parameters from refined data.

Weight fraction	V(c.c/mole)	VS(c.c/mole)	PS(c.c/mole)	△(V.VS) (c.c^2/mole^2)	△(V.PS) (c.c^2/mole^2)
0.0001	691454.73	54.14	40.08	- 27644.0	- 82975
0.0002	345719.82	54.10	45.48	- 27657.0	1825401
0.0003	230474.62	54.09	46.27	- 20742.0	1398691
0.0004	172852.33	54.03	48.40	- 22471.2	1417388
0.0005	138278.80	54.00	50.52	- 24890.3	1427037
0.0006	115229.29	53.95	52.59	- 26502.9	1427690
0.0007	98766.05	53.90	54.48	- 27654.5	1410378
0.0008	86418.45	53.88	55.92	- 25925.6	1358498
0.0009	76814.83	54.01	57.69	- 13058.4	1243491
0.0010	69132.01	54.18	58.67	- 0.30	1276868
0.0011	62846.29	54.55	58.20	+ 23253.1	1131233
0.0012	57608.30	54.97	56.25	+ 45510.4	9246134
0.0013	53176.18	55.34	53.74	+ 61684.2	720005
0.0014	49377.22	55.68	51.59	+ 74066.3	562406.8
0.0015	46084.82	55.99	49.36	+ 83413.5	482137.3
0.0016	43203.97	56.26	47.42	+ 89864.0	311932.5
0.0017	40662.10	56.56	45.92	+ 96775.5	232587.6
0.0018	38402.71	56.87	44.53	+ 103303.2	166284.1
0.0019	36381.22	57.23	43.50	+ 110962.6	120058
0.0020	34561.92	57.58	42.85	+ 117510.2	91588.9
0.0021	32915.91	57.93	42.27	+ 123435.0	68136.5
0.0022	31419.58	58.29	41.76	+ 129134.2	49014.9
0.0023	30053.35	58.59	41.39	+ 132535.5	35763.4
0.0024	28800.95	58.86	41.09	+ 134788.60	25632.9

APPENDIX A. 3

System: Acetic Acid in C_6H_5Cl .

Table 1. Experimental results of specific volume

(Weight fraction) X 10^2	Observed specific volume (v) (c.c/gm.)	Difference in specific volume $\triangle v$(obs.-cal.) X 10^5 (c.c/gm.)
0.0	0.912825	0.0
0.0055	0.912834	-0.45
0.0110	0.912846	-0.61
0.0156	0.912857	-0.64
0.0221	0.912871	-0.84
0.0280	0.912880	-1.40
0.0332	0.912892	-1.48
0.0443	0.912911	-2.31
0.0509	0.912924	-2.64
0.0553	0.912934	-2.73
0.0662	0.912961	-2.71
0.0773	0.912908	-3.55
0.0880	0.913005	-3.69
0.0998	0.913030	-4.10
0.1088	0.913046	-4.71
0.1197	0.913071	-4.90
0.1298	0.913097	-4.79
0.1401	0.913120	-5.03
0.1502	0.913140	-5.52
0.1710	0.913194	-5.25
0.1918	0.913243	-5.47
0.2130	0.913298	-5.20
0.2329	0.913353	-4.60
0.2530	0.913411	-3.76
0.2729	0.913467	-3.06
0.2927	0.913532	-1.45
0.3131	0.913597	0.0

$$v_{cal.} = 0.912825 \underset{+}{-} 0.2465 \times w$$

Table 2. Experimental results of dielectric constant.

(Weight fraction)X10^2	D. C. (ϵ)
0.0	5.610160
0.0201	5.611201
0.0440	5.611962
0.0681	5.612769
0.0985	5.613710
0.1321	5.614149
0.1610	5.614230
0.2021	5.614701
0.2461	5.615889
0.2795	5.617109
0.3122	5.618120
0.3413	5.618951

$$\Delta\epsilon = \epsilon_{cal.} - 5.610160$$

Table 3. Refined values of specific volume and dielectric constant.

Weight fraction	Specific volume (c.c/gm.)	D. C.	Specific polarization (c.c/gm.)
0.0	0.912825	5.610250	0.552985
0.0001	0.912845	5.610701	0.553018
0.0002	0.912865	5.611029	0.553046
0.0003	0.912884	5.611429	0.553076
0.0004	0.912905	5.611800	0.553106
0.0005	0.912925	5.612171	0.553136
0.0006	0.912942	5.612549	0.553164
0.0007	0.912965	5.612870	0.553193
0.0008	0.912986	5.613171	0.553220
0.0009	0.913007	5.613472	0.553247
0.0010	0.913029	5.613750	0.553274
0.0011	0.913051	5.613901	0.553294
0.0012	0.913073	5.614050	0.553315
0.0013	0.913095	5.614149	0.553333
0.0014	0.913118	5.614200	0.553349
0.0015	0.913142	5.614232	0.553365
0.0016	0.913166	5.614251	0.553380
0.0017	0.913190	5.614361	0.553397
0.0018	0.913215	5.614379	0.553416
0.0019	0.913239	5.614519	0.553437
0.0020	0.913265	5.614650	0.553459
0.0021	0.913290	5.614852	0.553484
0.0022	0.913317	5.615101	0.553512
0.0023	0.913345	5.615380	0.553542
0.0024	0.913373	5.615669	0.553573
0.0025	0.913402	5.616000	0.553606

Table 4. Calculated parameters from refined data.

Weight fraction	V(c.c/mole)	VS(c.c/mole)	PS(c.c/mole)	△(V.VS) (c.c^2/mole^2)	△(V.PS)(c.c^2/mole^2)
0.0001	548163.48	66.89	53.26	43853.0	+ 931877
0.0002	274087.71	66.83	51.52	5482.0	- 10964
0.0003	182728.97	66.84	51.50	5482.0	- 10963.7
0.0004	137049.87	66.84	51.47	4110.9	- 12334.4
0.0005	109642.31	66.85	51.39	4385.7	- 18639.2
0.0006	91370.25	66.86	51.13	4568.5	- 39289.2
0.0007	78319.34	66.89	51.06	6265.5	- 39159.6
0.0008	68531.02	66.91	50.90	6853.1	- 45230.4
0.0009	60917.84	66.95	50.70	8528.5	- 52389.4
0.0010	54827.39	67.07	50.56	14255.1	- 54827.4
0.0011	49844.26	67.13	50.08	15950.1	- 73769.5
0.0012	45691.71	67.24	49.72	19647.4	- 84072.7
0.0013	42177.98	67.31	49.28	21089.0	-96165.8
0.0014	39166.24	67.39	48.83	22716.5	- 106923.9
0.0015	36556.11	67.50	48.42	25223.7	- 114786.2
0.0016	34272.26	67.61	48.05	27417.8	- 120295.7
0.0017	32257.09	67.71	47.78	29031.4	- 121931.8
0.0018	30465.86	67.82	47.59	30770.5	- 120949.5
0.0019	28863.17	67.91	47.52	31749.5	- 116607.2
0.0020	27420.77	68.01	47.44	32904.9	- 112973.6
0.0021	26115.75	68.12	47.48	34211.6	- 106552.2
0.0022	24929.41	68.26	47.61	36147.7	- 98471.1
0.0023	23846.24	68.39	47.75	37677.1	-90854.2
0.0024	22853.36	68.53	47.92	39307.8	- 83186.2
0.0025	21939.91	68.67	48.12	40808.3	- 75473.3

APPENDIX-A.4

System: Acetic Acid in High Boiling Hydrocarbon(HBH) (150°-200°C).

Table 1. Experimental results of specific volume.

(Weight fraction)X10^2	Observed specific volume (ϑ) c.c/gm	Specific volume difference $\Delta\vartheta$ (obs.-cal.)X10^5(c.c/gm)
0.0	1.323345	0.0
0.0050	1.323312	- 1.69
0.0103	1.323280	- 3.20
0.0152	1.323245	- 5.20
0.0207	1.323210	- 6.90
0.0260	1.323181	- 8.10
0.0310	1.323139	- 10.70
0.0413	1.323092	- 12.10
0.0515	1.323039	- 14.10
0.0617	1.322990	- 15.70
0.0718	1.322951	- 16.29
0.0819	1.322923	- 15.83
0.1021	1.322855	- 16.13
0.1221	1.322805	- 14.69
0.1419	1.322768	- 12.01
0.1615	1.322742	- 8.30
0.1811	1.322685	- 7.69
0.2004	1.322660	- 3.98
0.2197	1.322615	- 2.26
0.2388	1.322571	- 0.51
0.2577	1.322515	0.0

$$v_{cal} = 1.323345 + (-0.32207)X_w$$

Table 2. Experimental results of dielectric constant.

(Weight fraction)X10^2	D. C.
0.0	2.063891
0.0225	2.064240
0.0461	2.064789
0.0625	2.065141
0.0810	2.065511
0.1082	2.065692
0.1422	2.065790
0.1765	2.065971
0.1989	2.066210
0.2205	2.066391
0.2603	2.066849
0.3015	2.067890

$$\Delta\epsilon = \epsilon_{cal} - 2.063891$$

Table- 3.. Refined values of specific volume and dielectric constant.

Weight fraction	Sp.volume(c.c/gm)	D. C.	Sp.polarization (c.c/gm.)
0.0	1.323345	2.063891	0.346440
0.0001	1.323279	2.064040	0.346459
0.0002	1.323216	2.064204	0.346482
0.0003	1.323155	2.064419	0.346517
0.0004	1.323099	2.064640	0.346555
0.0005	1.323045	2.064862	0.346594
0.0006	1.322998	2.065079	0.346635
0.0007	1.322959	2.065321	0.346682
0.0008	1.322923	2.065482	0.346711
0.0009	1.322891	2.065601	0.346732
0.0010	1.322862	2.065660	0.346739
0.0011	1.322835	2.065692	0.346739
0.0012	1.322810	2.065720	0.346739
0.0013	1.322789	2.065739	0.346739
0.0014	1.322771	2.065780	0.346744
0.0015	1.322754	2.065831	0.346751
0.0016	1.322737	2.065880	0.346759
0.0017	1.322719	2.065939	0.346768
0.0018	1.322700	2.066001	0.346778
0.0019	1.322681	2.066100	0.346797
0.0020	1.322661	2.066202	0.346815
0.0021	1.322639	2.066300	0.346834
0.0022	1.322615	2.066399	0.346851
0.0023	1.322592	2.066479	0.346864
0.0024	1.322567	2.066619	0.346891
0.0025	1.322539	2.066740	0.346913

Table 4. Calculated Parameters from refined data.

Wt. fraction	V(c.c/mole)	VS(c.c./mole)	PS(c.c/mole)	△(V.VS) (c.c^2/mole^2)	△(V.PS) (c.c^2/mole^2
0.0001	794629.03	39.83	32.04	659542.0	- 127140.0
0.0002	397295.60	40.74	33.40	691294.0	476755.0
0.0003	264851.52	41.44	36.34	646237.0	1096485.0
0.0004	198630.23	42.53	38.19	701164.7	1189795.0
0.0005	158897.70	43.44	39.37	705505.7	1139296.0
0.0006	132410.04	44.74	40.33	760033.6	1076493.0
0.0007	113490.94	46.43	41.29	843237.7	1031632.0
0.0008	99301.93	48.81	41.19	874850.0	892724.3
0.0009	88266.24	49.19	40.28	899433.0	713191.2
0.0010	79437.86	50.46	38.74	910357.9	519523.6
0.0011	72214.75	51.61	37.11	910628.0	354574.4
0.0012	66195.60	52.68	35.79	931895.8	237642.2
0.0013	61102.69	53.80	34.61	904319.8	147257.5
0.0014	56737.44	54.86	33.83	899855.8	92482.0
0.0015	52954.25	55.81	33.25	890160.9	55602.0
0.0016	49643.97	56.65	32.77	876216.1	28297.0
0.0017	46723.09	57.35	32.40	857368.7	9344.7
0.0018	44126.75	57.96	32.08	836643.2	5295.2
0.0019	41803.69	58.50	32.09	815171.9	4598.4
0.0020	39712.90	58.93	32.08	791478.0	4765.5
0.0021	37821.17	59.28	32.07	767013.3	4916.7
0.0022	36101.37	59.54	32.03	741522.1	6137.3
0.0023	34531.15	59.81	31.87	718593.2	11395.3
0.0024	33091.73	60.00	32.09	694926.4	3640.1
0.0025	31767.39	60.11	32.17	670609.6	953.0

APPENDIX- A.5

System: Acetic Acid in Cyclohexane

Table 1. Experimental results of Specific volume.

(Weight fraction)X10^2	Observed specific volume, v (c.c/gm)	Difference in specific volume Δ v(obs.-cal.)X10^4 (c.c/gm)
0.0	1.299916	0.0
0.01122	1.299790	- 0.63
0.02241	1.299673	- 1.18
0.03355	1.299536	- 1.92
0.04465	1.299413	- 2.54
0.05571	1.299307	- 2.98
0.06673	1.299195	- 3.48
0.07770	1.299080	- 4.02
0.08864	1.298986	- 4.35
0.09953	1.298908	- 4.53
0.11039	1.298842	-4.58
0.12119	1.298775	- 4.65
0.14270	1.298680	- 4.40
0.16404	1.298589	- 4.12
0.18523	1.298525	- 3.58
0.20625	1.298460	- 3.05
0.22713	1.298401	- 2.48
0.24785	1.298347	- 1.86
0.26842	1.298290	- 1.29
0.28384	1.298235	- 0.70
0.30911	1.298192	0.0

$$v_{cal} = 1.299916 + 0.5577XW$$

Table - 2. Experimental results of dielectric constant.

(Weight fraction)X10^2	D. C.
0.0	2.012330
0.0380	2.012701
0.0701	2.013009
0.0984	2.013250
0.1303	2.013489
0.1572	2.014052
0.1884	2.014581
0.2287	2.014680
0.2889	2.015162
0.3199	2.015620
0.3462	2.016359

$$\Delta \epsilon = \epsilon_{cal} - 2.012330.$$

Table-13. Refined values of specific volume and dielectric constant.

Weight fraction	Specific volume (cc/gm)	D. C.	Specific polarization (c.c/gm.)
0.0	1.299916	2.012330	0.327974
0.0001	1.299800	2.012425	0.327968
0.0002	1.299689	2.012513	0.327961
0.0003	1.299578	2.012613	0.327958
0.0004	1.299463	2.012725	0.327956
0.0005	1.299360	2.012820	0.327953
0.0006	1.299256	2.012913	0.327949
0.0007	1.299155	2.013013	0.327948
0.0008	1.299057	2.013093	0.327942
0.0009	1.298972	2.013175	0.327941
0.0010	1.298903	2.013255	0.327943
0.0011	1.298842	2.013325	0.327945
0.0012	1.298786	2.013400	0.327949
0.0013	1.298731	2.013518	0.327963
0.0014	1.298685	2.013675	0.327990
0.0015	1.298644	2.013875	0.328028
0.0016	1.298603	2.014100	0.328072
0.0017	1.298573	2.014300	0.328113
0.0018	1.298540	2.014463	0.328144
0.0019	1.298511	2.014588	0.328166
0.0020	1.298482	2.014650	0.328174
0.0021	1.298451	2.014675	0.328172
0.0022	1.298422	2.014675	0.328165
0.0023	1.298395	2.014675	0.328158
0.0024	1.298367	2.014700	0.328157
0.0025	1.298341	2.014775	0.328169
0.0026	1.298316	2.014862	0.328184
0.0027	1.298288	2.014950	0.328198
0.0028	1.298261	2.015063	0.328218
0.0029	1.298234	2.015175	0.328238
0.0030	1.298209	2.015313	0.328265

Table 4. . Calculated parameter from refined data

Wt. fraction	V(c.c/mole)	VS(c.c/mole^2)	PS(c.c/mole)	Δ(V.VS) (c.c/mole^2)	Δ(V.PS) (c.c/mole^2)
0.0001	780529.90	8.41	18.50	163991.3	1639113.0
0.0002	390231.62	9.91	16.99	667296.1	230236 .7
0.0003	260132.19	10.40	17.29	574892.8	231517.6
0.0004	195081.88	10.06	17.59	362853.0	232147.4
0.0005	156053.13	11.28	17.65	480643.7	195066.4
0.0006	130033.86	12.01	17.59	495429.0	154740.2
0.0007	111448.93	12.89	17.47	522695.5	119250.4
0.0008	97510.46	13.58	17.59	524606.3	116037.4
0.0009	86670.30	15.08	17.76	596291.7	117871.6
0.0010	77999.13	17.23	18.08	704332.2	131038.5
0.0011	70904.96	19.43	18.33	796262.7	136846.6
0.0012	64993.41	21.51	18.64	865062.3	145585.2
0.0013	59991.38	23.32	19.37	907069.6	178174.4
0.0014	55704.31	25.26	20.56	950315.5	231730.0
0.0015	51989.05	27.14	22.02	984672.6	292178.4
0.0016	48738.19	28.78	23.52	1003032.0	347015.9
0.0017	45870.18	30.63	24.75	1028868.0	383016.0
0.0018	43320.74	32.16	25.50	1037964.0	394218.7
0.0019	41039.78	33.66	25.89	1044872.0	389467.6
0.0020	38986.92	35.01	25.82	1045239.0	367256.8
0.0021	37129.52	36.17	25.48	1038512.0	337136.0
0.0022	35441.02	37.29	25.02	1030979.0	305501.6
0.0023	33899.40	38.35	24.61	1022066.0	278314.0
0.0024	32486.22	39.30	24.27	1010321.0	255666.5
0.0025	31186.15	40.23	24.38	998890.8	248865.4
0.0026	29986.11	41.11	24.55	986842.8	244386.8
0.0027	28874.89	41.86	24.66	971928.8	238506.5
0.0028	27843.06	42.57	24.93	956966.0	237501.3

APPENDIX-B

Equilibrium Interaction of the Solute Species Entering into the Holes of a Solvent Body.

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Theory

With the discovery of interstitial compounds and various other observations along with the advancement of theories on the nature of solvents one is lead to suspect the presence of ordered structure of liquids having some unoccupied spaces which is referred to in this paper as "holes". It is possible that very minute quantity of solute species of tolerably small size temporarily occupy some of these "holes". The duration of such occupation may be attended with some distortions of both solvent "holes" and the solute species depending on the polarizability and structural differences of the components. One of the logical treatments that can be conceived on the basis of law of mass action (which is essentially statistical in nature) take the following form:

$$\text{Species} + \text{holes} \rightleftharpoons \text{"species in hole"}$$

$$\text{and} \quad K = \frac{[\text{species in hole}]}{[\text{species}] \times [\text{hole}]} ;$$

where bracket indicate the concentration in terms of number of species as well as "holes" per unit volume.

Testing of this "model of interaction" can be based on the assumption that species entering into the "holes" lose a part or whole of its

$V = S + (1-\alpha)V_1 + \alpha V_2$

$VS = V_1 - \alpha(V_1 - V_2) = V_1 - \alpha D$

$\therefore \alpha = \frac{V_1 - VS}{D} \quad \ldots\ldots\ldots\ldots (1)$

$$\frac{K(\beta S - \alpha)}{V} = \frac{\alpha}{1-\alpha} = \frac{V_1 - VS}{VS - V_2}$$

$$K\beta - \frac{K\cancel{\beta}}{D}\frac{(V_1 - VS)}{\cancel{S}V} = \frac{V_1 - VS}{VS - V_2} \longmapsto VS - V_2 = -\frac{DV}{K}$$

$$\beta - \frac{V_1 - VS}{D\cancel{S}V} = \left(\frac{V_1 - VS}{VS - V_2}\right)\frac{1}{K\cancel{\beta}}$$

$$\frac{\beta D\cancel{V} - V_1 + VS}{D\cancel{S}V} = \frac{1}{K\cancel{\beta}}\left(\frac{V_1 - VS}{VS - V_2}\right)$$

$$\beta D\cancel{V} - V_1 + VS = \frac{D\cancel{V}}{K\cancel{\beta}}\left(\frac{V_1 - VS}{VS - V_2}\right)$$

~~Can we think DV much greater than $VS - V_1$ at V_∞~~
~~Then~~

~~$\beta DV = \frac{DV}{K\beta}\frac{(V_1 - VS)}{(VS - V_2)}$~~

~~$\therefore K\beta(VS - V_2) = V_1 - VS$~~

~~$VS(1 + K\beta) = V_1 + K\beta V_2$~~

~~$VS_\infty = V_1 + K\beta V_2$ if K & β are very small.~~

~~$(VS - V_2)^2 = \frac{1}{K\beta} D(V_1 - VS)$~~

$$VS + \beta DV = \frac{DV}{K}\left(\frac{V_1 - VS}{VS - V_2}\right) + V_1$$

if $V_1 = VS$ at any point then

(1) $VS = -\beta DV + V_1$

or (2) $\beta\cancel{K} = \frac{V_1 - VS}{VS - V_2} \quad \therefore \beta K VS - \beta K V_2 = V_1 - VS$

$Vs(1 + \beta K) = \beta K V_2 + V_1$

volume, if calculated on the basis of simple additivity rule*. If V is expressed as the volume which contain one mole of A, of which α fraction has entered into the "holes" and each c.c of solvent have only β moles of "holes" (i.e. $10^{23} \times 6.06 \times \beta$ holes per c.c.) then

$$K = \frac{\alpha V}{(1-\alpha)(\beta S-\alpha)}$$; where S express the actual volume of the solvent, initially added to make the mixture.

Now, the volume, V contain solvent S and free A, while the rest of A remain inside the "hole" without contributing its volume to the bulk, thus,

$$V = S + (1-\alpha)\, V_1$$

where, V_1 is the molar volume of A .

Hence we can write,

$$V - S = VS = (1-\alpha)\, V_1$$

Or, $$1-\alpha = \frac{VS}{V_1}$$

Or, $$\alpha = \frac{V_1 - VS}{V_1}$$

---

* $v = w_1 v_1 + w_2 v_2$; where v is specific volume of the mixture, v_1 and v_2 are that of solute and solvent, and $1 = w_1 + w_2$.

Now, putting $Z = V_1 - VS$, we get,

$$\alpha = \frac{Z}{V_1} \quad \text{and} \quad \frac{\alpha}{1 - \alpha} = \frac{Z}{VS} .$$

$$\therefore \quad K = \frac{ZV}{VS(\beta S - Z/V_1)}$$

$$\text{Or,} \quad K = \frac{Z\,V\,V_1}{VS(\beta V_1 S - Z)}$$

$$\therefore \quad \frac{K}{V_1} = \frac{(\beta V_1 S - Z)}{Z} = \frac{V}{VS}$$

$$\text{Or,} \quad \frac{V}{VS} = \frac{K\beta S}{Z} - \frac{K}{V_1}$$

Putting back $Z = V_1 - VS$, finally we have the relation,

$$\frac{V}{VS} = K\beta \frac{(S)}{V_1 - VS} - \frac{K}{V_1} \quad \text{.....................} \quad 7.1$$

Therefore, a plot of $\frac{V}{VS}$ against $\frac{S}{V_1 - VS}$ will give a straight line at the lower end of concentrations. The slope of this plot gives $K\beta$ and the intersection give K/V_1. Molar volume of AcOH monomer known to be about 55.2 (average V_1 value in CCl_4 and Benzene), β and K can be found.

Results

In the present work of two systems, (i) acetic acid - Kerosene (HBH) and (ii) acetic acid - cyclohexane, acetic acid as the solute species have investigated for the "solute - hole equilibrium effect."

It must be noted that extremely accurate and precise measurement of density (or specific volume) is needed to investigate the emperical basis of such a construct. The measurement of specific volume have been carried out by magnetic float densimeter, as described in the main body of this thesis (page-43). V and S have been calculated by the relations described already (Appendix- A.4 and A.5). Molar volume of acetic acid monomer is about 55.2 c.c(obtained by indirect method shown previously). Now V/VS and S/V_1-VS for both the systems (HBH and cyclohexane) have been calculated and given in Table 7.1 and 7.2 respectively and the plots of V/VS versus S/V_1-VS are shown in Fig. 7.1 and ~~7.2~~ 1.2 respectively. The results of K and β are given in Table 7.3 . These results were obtained by using a much bigger graph which is shown in the Fig. ~~7.1~~ 1.1 and 7.2 1.2 in a smaller scale. The intersections are in the negative which rightly conform to the equation (7.1). The slopes and intersection so obtained were used to calculate β and K.

$V =$

$S =$

$V - S = VS$

$V_1 =$

Table ~~7.1~~ ١٫١

System: Acetic Acid in HBH

(Wt. fraction)X10^4	$\frac{V}{VS}$	$\frac{S}{V_1 - VS}$
1	19950.52	51697.41
2	9751.98	27472.67
3	6391.20	19244.92
4	4670.36	15673.85
5	3657.87	13508.02
6	2959.54	12654.43
7	2444.35	12935.52
8	2077.01	13430.87

Table ~~7.2~~ 1.2

System: Acetic Acid in Cyclohexane

(Wt. fraction)X10^4	$\frac{V}{VS}$	$\frac{S}{V_1 - VS}$
1	92809.74	16681.37
2	39377.56	8616.07
3	24980.68	5807.59
4	19391.84	4321.48
5	13834.50	3552.87
6	10827.13	3010.46
7	8646.15	2633.80
8	7180.45	2342.55
9	5747.37	2159.90
10	4526.94	2053.78

Results

Table ~~7.3~~ 1.3

Solvent	K/V_1	K (litre/mole)	βK	β (mole/litre)
HBH (High Boiling hydrocarbon)	1.8×10^3	220.8	0.4151	0.00418
Cyclohexane	4.0×10^3	99.36	5.0322	0.0227

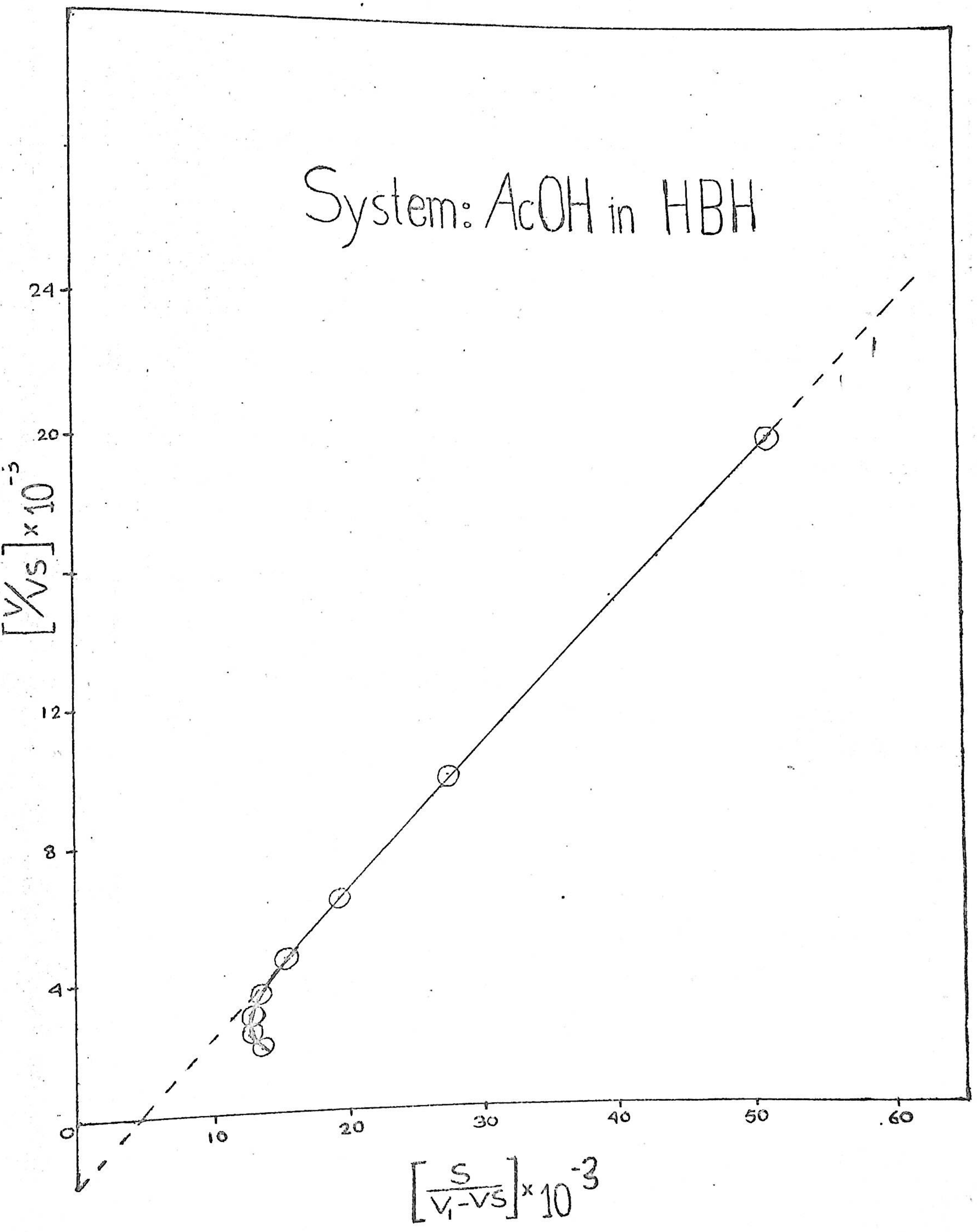
System: AcOH in HBH
24
20
12
8
4
0
10
20
30
40
50
.60
$\left[V/Vs\right] \times 10^{-3}$
$\left[\frac{S}{V_1 - VS}\right] \times 10^{-3}$

Fig. ~~7·1~~ 1·1

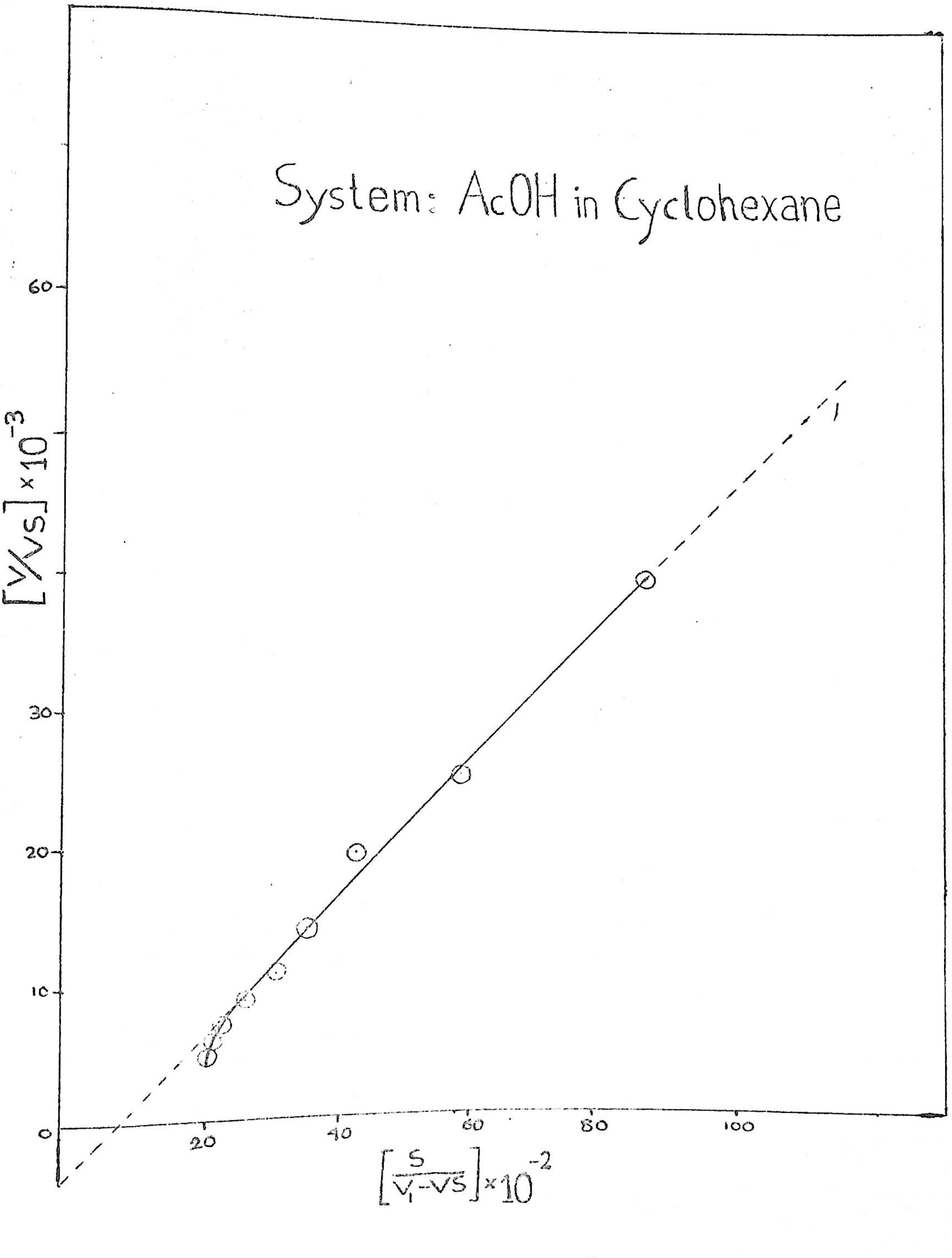
System: AcOH in Cyclohexane
$[V/V_S] \times 10^{-3}$
60
30
20
10
0
20
40
60
80
100
$\left[\frac{S}{V_1 - V_S}\right] \times 10^{-2}$

Fig. ~~7·2~~ 1·2

Discussion

Fig. ~~7.1~~ 1.1 and ~~7.2~~ 1.2 show that the equation 1.1 (7.1) very closely represent the variation of the parameters from near zero concentration upto about .0006 wt. fraction solution. The equilibrium constants are neither too high nor too low. Similarly the number of "holes" are within reasonable value. A sample calculation for cyclohexane system indicate that only one "hole" of the size of one molecule of acetic acid monomer exist per 450 molecules of cyclohexane. In HBH such calculation is not possible as the molecular weight is not known but the molecular "holes" exist only one - fifth times that of cyclohexane.

References

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BIBLIOGRAPHY

BIBLIOGRAPHY

1. Pauling, L : "The Nature of the Chemical Bond", P-6, Third Edition, Oxford and IBH Publishing Co., 1975 (Indian print - New Delhi).

2. Mulliken and Pearson : "Donor - Acceptor Complexes", Ann. Rev. Phys. Chem. 13, 107 (1962); "Molecular Association", Volume I, Academic Press, 1975.

3. Huggins, M. L : Angew. Chem. internat. Edit., 10, 147 (1971), No. 3.

4. Latimer and Rodebush : J. Am. Chem. Soc., 42, 1419 (1920).

5. Blinc and Hadzi : "Hydrogen Bonding", (Pergamon, 1959); London Abstracted in Angew. Chem., 69, 755 (1957).

6. Barman and Rahim : Acta Cryst., A34, 761 (1978).

7. Schuster, Zundel and Sandorfy : "The Hydrogen Bond", P-28, Vol. I, North Holland Publishing Company, 1976.

8. Schuster, Zundel and Sandorfy : "The Hydrogen Bond", P-81, Vol.1, North Holland Publishing Company, 1976.

9. Pimentel and Mc Clellan : "The Hydrogen Bond", P-51, Freeman and Co., 1960.

10. Badger and Bauer : J. Chem. Phys., 29, 1193 (1937).

11. Albert and Badger : J. Chem. Phys., 29, 1193 (1958).

12. Badger, G. M : J. Chem. Phys., 8, 288 (1940).

13. Herman, R. C : J. Chem. Phys., 8, 252 (1940).

14. Fox and Martin : Proc. Roy. Soc., (London) 162 A, 419 (1937).

15. Gordy and Stanford : J. Chem. Phys., 9, 204 (1941).

16. Searles and Tamres : J. Am. Chem. Soc., 73, 3704 (1951).

17. Tamres, M : J. Am. Chem. Soc., 74, 3375 (1952).
18. Barrow, G. M, et al. : J. Am. Chem. Soc., 75, 71 (1953).
19. Barrow, G. M : J. Phys. Chem., 59, 1129 (1955).
20. Fermer, Hardie and Thomson : J. Chem. Phys., 8, 3600 (1959).
21. Gordy and Stanford : J. Chem. Phys., 8, 170 (1940).
22. Josien, M. L : Compt. rend., 237, 175 (1953).
23. Josien and Sourisseau: Compt. rend., 238, 2525 (1954).
24. Eyman and Drago : J. Am. Chem. Soc., 88, 1617 (1966).
25. Becker, Riddle and Shoolery : J. Mol. Epect. P-211 (1958).
26. Takahashi and Li : J. Phys. Chem. 68, 2136 (1964).
27. Cresswell and Altred : J. Am. Chem. Soc., 68, 2136 (1964).
28. Bystrov : Opt. Spekt., 16, 430 (1964).
29. Eyaman and Drago : J. Am. Chem. Soc., 88, 1617 (1966).
30. Suhr : Ber. Beuseu. Phys. Chem., 17, 1104 (1967)
31. Socrates : Trans. Farad Soc., 63, 1063 (1967).
32. Coulson, C. A. and Danielson, U : Arkiv Fysik 8, 205 (1955).
33. Tsubomura, M : Bull. Chem. Soc., Japan, 27, 445 (1954).
34. Kollman, P. A. and Allen, L. C : Chem. Rev. 72, 283 (1972).
35. Pimentel and Mc Clellan : "The Hydrogen Bond", P-39, Freeman& Co., 1960.
36. Vinogradov : J. Chim. Phys., 63, 239 (1966).
37. Ibbitson and Moore : J. Chem. Soc.,(B), 80 (1967).

38. Beckman, E : J. Phys. Chem., 6, 444 (1890)

39. Allen, G. and Caldin, E. F : Quart. Rev. 7, 255 (1953) and references therein.

40. Karle, J. and Brockway, L. O : J. Am. Chem. Soc., 66, 574 (1944).

41. Taylor, M. D : J. Am. Chem. Soc., 73, 315 (1951).

42. Harris, J. T. Jr. and Hobbs, M. E : J. Am. Chem. Soc., 76, 1419 (1954).

43. Barrow, G. M. and Yerger, E. A : J. Am. Chem. Soc., 76, 5248 (1954).

44. Wenegred, J. and Sprurr, R. A : J. Am. Chem. Soc., 79, 9844 (1957).

45. Fredman, E : J. Chem. Phys., 21, 1784 (1953).

46. Le Fevre, R. J. W. and Vine, H : J. Chem. Soc., 1795 (1938).

47. Coburn, W. C. Jr.and Grunwald, E : J. Am. Chem. Soc., 80, 1318 (1958).

48. De. Tar, DeLos, Novak, R. W : J. Am. Chem. Soc., 92, (5), 1361 (1970).

49. Mathows, D. M. and Sheets, R. W : J. Chem. Soc.,(A), 2203 (1969).

50. Goldman, M. A. and Emerson, M. T : J. Phys. Chem., 77, (19), 2295 (1973).

51. Jenkins, J. O. and Smith, J. W : J. Chem. Soc.,(B), 1538 (1970).

52. Liszi, Janos : Acta Chem. 67(1), 5-14,(1971)(Cf. Chem. Abs. 103756h), 74 (1971).

53. Corsaro, Robert, D., et al. : J. Chem. Phys. 54 (9), 4090 (1971).

54. Arnold, J. T. and Packard, N. N : J. Chem. Phys.,19, 1608 (1951).

55. Huggins, Pimentel, G.C. and Shoolery, J.N. : J. Phys. Chem., 60, 1311 (1956).

56. Reeves, L. W. and Schneider, W. G : Trans. Farad. Soc., 54, 314 (1958).

57. Reeves, L. W : Trans. Farad. Soc., 55, 1684 (1959).

58. Davis, J. C. Jr. and Pitzer, K. S : J. Phys. Chem., 64, 886 (1960).

59. Jones, R. E. and Templeton, D. H : Acta cryst., 11, 484 (1958).

60. Lascombe, J. et al. : J. Chem. Phys., 59, 1233 (1962)

61. Bellamy, L. et al. : Spectro Chim. Acta., 19, 443 (1963)

62. Hauric, M. et al. : C. R. Acad. Sci. Rev. C, 264, 694(1967).

63. Ritter, H. L. and Simons, J. H : J. Am. Chem. Soc., 67, 757 (1945) and references therein.

64. Sharpe, A. N. and Walker, S : J. Chem. Soc., 2974 (1961).

65. Sharpe, A. N. and Walker, S : J. Chem. Soc., 157 (1962).

66. Sharpe, A. N. and Walker, S : J. Chem. Soc., 2340 (1964).

67. Kulevsky, N : "Molecular Association", P-144, Volume 1, Academic Press, 1975.

68. Vinogradov : "Hydrogen Bonding", P-14, Van Nostrand Reinhold Company, 1971.

69. Johari and Dannhauser : J. Phys. Chem., 72, 2373 (1968).

70. Cantacuzene : J. Bull. Soc. Chim., Fr., No. 4, 747 (1962); (Cf. Donor Acceptor Bond, E.N. Gur'yanova, et al. John Wiley & sons, New York, Toronto, 1975).

71. Rahim, Z : Private Communication (Associate Professor of Chemistry, Rajshahi University).

72. Glasstone, S : "Text Book of Physical Chemistry", P-531, MacMillan and Co. Ltd., 1969.

73. Smyth : "Dielectric Behaviour and Structure", P-401, (Mc. Graw).

74. Smyth : J. Am. Chem. Soc., 51, 1734 (1949).

75. Baur, M.E., Horsma, D. A, Knobler, C.M. and Perez, P : J. Phys. Chem., 73, 641 (1969).

76. Baur, M.E, Knobler, C.M, Horsma, D.A. and Perez.P : J. Phys. Chem., 74, 4594 (1970).

77. Voronkov, M.G. and Deich, A.Y. Teor. i Eksperim. Khim. : Akad. Nauk Ukr. SSr (Eng.Trans.), 1, 443 (1965).

78. Voronkov, M.G, Deich, A.Y. and Akatova, E.V. Khim. Geterotsikl. Soedin. : Akad. Nauk Lat.SSR (Eng. Trans.), 2, 5 (1966).

79. Kulevesky, N : "Molecular Association", P-115, Vol.1, Academic Press, 1975.

80. Guryanova, E. N. et al. : "Donor-Acceptor Bond", P-59, John Wiley & Sons, New York. Toronto, 1975.

81. Rahim, Z : Private Communication (Associate Professor of Chemistry, Rajshahi University).

82. Barman and Rahim : Rev. Sci. Instrument, 48, 1695 (1977).

83. Lamb, A. B. and Lee, R.E : J. Am. Chem. Soc., 35, 1666 (1913).

84. Pohl, Hobbs and Gross : J. Chem. Phys., 9, 408 (1941).

85. Buckingham, A.D. and Raab, R. E : Trans. Faraday Soc., 55, 377 (1959).

86. Nagai and Simamura : Bull. Chem. Soc., Japan, 35, 132(1962).

87. Satchel, D. P. N. and Wardell, J. L : Trans. Faraday Soc., 61, 1199 (1965).

88. Dobye, P : Polar Molecules, Page-54, New York, 1929

89. Müller, F. H. : Phys. Z., 34, 689 (1933).

90. Weigle, J. : Helv. Phys. Acta, 6, 68 (1933).

91. Smith, J. W. : "Electric Dipole Moments", Page-127-167 London Butterworths Scientific Publications, 1955.

92. Müller, F. H. : Trans. Faraday Soc., 30, 729 (1934).

93. Müller, F. H. : Phys. Z., 35, 346 (1934).

N. B. : References 64-66 and 75-79 were cited in "Molecular Association", volume 1, Edited by R. Foster. Academic Press, 1975; Reference~~s~~ 80 was obtained from "Donor-Acceptor Bond", John Wiley & Sons, New York. Toronto, 1975 and References 88-90 and 92, 93 were obtained from "Electric Dipole Moments", by Smith, London Butter worths Scientific Publications, 1955.