STUDIES IN BINARY SYSTEMS

Part XI. Hydrogen Bond in Benzene

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Introduction

In recent years theories relating to formation of associated molecules in liquid systems due to hydrogen bond have been forthcoming. An atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond.

The assumption that the hydrogen bond was formed by two covalent bonds is not correct because the hydrogen atom can form only one covalent bond. It is now recognised that the hydrogen bond is ionic in character and is formed between the most electronegative atoms.

By the application of quantum mechanical theory of valence Pauling found that a hydrogen atom with only one stable orbital cannot form more than one pure covalent bond and that the attraction of two atoms observed in hydrogen bond formation must be due to ionic forces. According to Pauling, hydrogen bond is a bond by hydrogen between two atoms. Only the most electronegative atoms should form hydrogen bonds, and the strength of the bond should increase with increase in the electronegativity of the two bonded atoms. Thus fluorine, oxygen, nitrogen and chlorine possess this ability in the decreasing order. Fluorine is well known to form very strong hydrogen bonds, oxygen weaker ones and nitrogen still weaker. Chlorine, although it has the same electronegativity as nitrogen, has only a small hydrogen bond forming character which Pauling attributed to its large size relative to nitrogen.

The C-H-Bond.—Although the tendency for hydrogen to act as acceptor is in the order in the series H-F > H-O > H-N > C-H-, the C-H bond plays a very important part in both dilute and concentrated solutions of strong dipoles. Here again we have the series

C-H (halogen compounds) > C-H (unsaturated compounds) > C-H (aromatic) > C-H (aliphatic). The case of C-H in halogen compounds is illustrated by the heats of mixing of chloroform with oxygen and nitrogen compounds studied by Zellhoeffer and co-workers (*vide infra*).

Although the cases of hydrogen attached to oxygen forming a link are well known the case of hydrogen attached to carbon are not so well studied and interpreted. It is usually assumed that in C-H the acceptor properties of hydrogen are quite negligible. Even in the case of saturated hydrocarbon like methane the solid hydrate CH_46H_2O discovered by De Forcrand (*Compt. Rend.*, 1902, **135**, 959) has been explained by assuming van der Waals forces, which seems to be not at all a necessary explanation, if the hydrogen bond is given the property of the co-ordinate link. Pauling (*Nature of the Chemical Bond*) says that no explanation is available for the melting point of methane which is 25° above the expected value even though its boiling point is normal. It has been ascertained by Moore (*Jour. Chem. Soc.*, 1907, **91**, 1373; and 1912, **101**, 1635) that in the case of saturated compounds like paraffins and alkyl groups there is no evidence of co-ordination, but the cases of saturated hydrocarbons forming addition compounds with picric acid are well known. The obvious explanation is that under the strong electrostatic force of the oxygen in water and in picric acid, the hydrogen bond in methane and paraffin compounds exhibits acceptor properties.

The addition compounds of ethylene and aromatic hydrocarbons have not been assigned to definite structures till now, although the possibility of the double links playing a part in the formation of these compounds has been indicated.

The Hydrogen Bond in Benzene

Kablukoff (*Z. Phys. Chem.*, 1889, **4**, 429) found addition product of benzene and hydrogen chloride. This observation could be used to explain the increase in dipole moment of hydrochloric acid in benzene. Also iodine and bromine show an increased polarisation in benzene, that is, they seem to exhibit a dipole moment by the environment of the benzene molecule.

The effect of solvent in determining dipole moments is of special interest. A comparison of the moments of a substance in different media indicates the likelihood of benzene entering into some kind of combination with certain solutes and affecting their moments. Thus iodine has a moment 1.0 in benzene and zero in hexane [Williams (*Physik. Z.*, 1928, **29**, 683); Muller and Sack (*Physik. Z.*, 1930, **31**, 816)]. Aluminium bromide which is non-polar in carbon disulphide has in benzene a moment no less than 4.89 (Nespital, *Z. Electro. Chem.*, 1931, **37**, 559).

Muller (*Trans. Faraday Soc.*, 1934, **30**, 872) suggests that halogen hydrides might form a loosely bound compound and may exhibit a larger moment in solution.

Methylene chloride has a dipole moment of 1.59 in the gas and 1.55 and 1.48 in benzene and carbon tetrachloride. Chloroform has a dipole moment of 1.05 in vapour and in hexane and 1.10 in benzene.

It is obvious that chloroform forms complexes with benzene and the dipole moment determined in benzene refers to the complex. In the case of methylene chloride the effect is slightly negative owing to the effect of hydrogen atoms.

The System C_6H_6-HF.—The system benzene hydrogen fluoride has been shown by Simsons (*J.A.C.S.*, 1931, **53**, 83) to exhibit a large positive deviation from Raoult's law at higher concentrations and a negative deviation at the more dilute solution which latter is a surprising result, which he explained by the electrical field surrounding the highly polar HF molecule. When these molecules are in sufficient concentration to exert an influence upon one another they will be mutually attracted and so tend to be removed from the solution. When the concentration is so low that the distance between the molecules of HF is great enough to make the mutual attraction small, then the electric field around each HF molecule will attract even the slightly polar C_6H_6 molecule, thus cause the vapour pressure to be low.

The System Benzene-Water.—The properties of benzene containing traces of water have been thoroughly studied in connection with the classical researches of Baker on intensive drying. Drying of benzene has shown most remarkable effects and has been the object of study by a large number of workers. The multiple of the molecular weights of wet and dry benzene by the Ramsay and Shield method are 1.28 and 3.39 showing that benzene is associated in liquid state. The molecular weights by vapour density was 102 and by Trouton's constant 136, instead of 78.

Manley (*Nature*, 1929, **123**, 907) has found that the refractivity changed continuously during drying of over a period of six months. On plotting against time benzene showed two distinct portions, one representing removal of mechanically admixed water and other the rate of withdrawal of water in actual combination with benzene. He also obtained evidence of a hydrate of benzene and stated that the drying power of anhydrous benzene is greater than that of phosphorous pentoxide. Although this finding requires further evidence, the fact remains that benzene retains traces of moisture very tenaciously. This is most likely to be due to the hydrogen bond in benzene.

Spectroscopic Evidence.—Benzene should have only one infrared active carbon hydrogen frequency, so the presence of three peaks at 3.232, 3.253 and 3.291 μ calls for some explanation. It has been suggested that splitting takes place because of accidental degeneracy with high states of other frequencies or combinations of other frequencies.

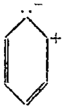
The hydrogens are more highly bound to aromatic carbon than they are to aliphatic carbon.

The Raman spectra of benzene consists of the following lines: 2925, 2940, 3047, 3062, 3164, 3187 cm.^{-1} which are attributable to C-H aromatic vibration. Of these the strongest is 3047, which is due to aromatic C-H bond. No explanation has been offered regarding the origin of the other lines based upon the chemistry of the benzene molecule. Physical explanations such as combination of the lower and higher frequencies are unsatisfactory both on theoretical and practical grounds.

On the basis of our postulate of a weak hydrogen bond in benzene the occurrence of a large number of these C-H frequencies both in the Raman and in the infra-red can be easily explained. The frequencies 2925 may be attributed to the vibration of the weak CH bond in benzene, 2942 to the vibration of a two such *para*-bonds which we have shown to operate in forming complexes.

The presence of one weak hydrogen bond in benzene will give rise to two adjacent hydrogen atoms in the one and two positions with higher energy of bonding, to which the frequencies 3187 and 3164 seem to be appropriate.

The postulate of a weak hydrogen bond in benzene thus seems to account for the numerous frequencies of the benzene molecule observed in the Raman spectra and in the infra-red spectra. It is interesting to note that in mono-chlorbenzene there are just two of the higher frequencies corresponding to the 1 and 2 positions of the hydrogen and in the di-chlorbenzene only one such higher frequency. From these results it is obvious that the combination of frequencies used to explain the large number of lines is fictitious. The following resonant structures of benzene would express the idea of one of the hydrogens of benzene to function as a hydrogen bond. Of these structures C makes a small contribution to the normal state of the molecule (*cf.* Pauling).



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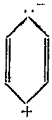

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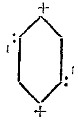


C

In the case of halogenated hydrocarbons it has been found that C-Cl vibration frequency goes on decreasing from methyl chloride to methylene chloride, chloroform and carbon tetrachloride. This would indicate that the C-Cl bond decreases in strength. These results would be in harmony with the capacity of the halogenated compounds in forming complexes with benzene increasing in the order methyl chloride, methylene chloride, chloroform and carbon tetrachloride. It has already been shown that benzene and carbon tetrachloride form a complex which is shown by the freezing point data and anomalous polarisation. Chloroform and benzene also show the presence of the complex in the freezing point but to a minor extent, the complex formed being one chloroform and three benzenes corresponding to the three halogen atoms. The freezing points of methylene chloride-benzene, methyl chloride-benzene apparently have not been studied but the polarisation of methylene chloride in benzene shows slight anomaly. The decreasing frequencies of the C-Cl vibration in the halogenated hydrocarbons can also be explained by their chemical behaviour. Carbon tetrachloride on pyrollysis is more easily decomposed than chloroform and chloroform more easily than methylene chloride.

The most important evidence for the formation of compounds and complexes of benzene with alcohols and halogen compounds is to be found in the study of the dielectric polarisation in benzene as solvent. The classical-example of the increase in the electric moment of ethylene dichloride and ethylene dibromide and the decrease of the moment of alcohols in benzene can be explained on the basis of a complex formation. In concentrated solution the apparent polarisation curves show marked discontinuities at points of molecular compositions. These findings would indicate the dipole moments determined in dilute solutions of benzene owing to the effect of mass law referred to the moment of the complex and not of the solute.

Dielectric Polarisation of Binary Mixtures

Perhaps the most satisfactory evidence for the hydrogen bonding comes from the law of additivity of binary liquid mixtures throughout the range of concentration. Many liquid mixtures do not follow the ideal laws of mixtures. This abnormality is found to be maximum corresponding to definite proportions of the liquids. Many binary mixtures of liquids are shown to form complexes of definite proportions, sometimes more than one by freezing point, polarisation, heats of mixing, vapour pressure, spectroscopic data, etc. The actual cause for the formation of complexes has as yet not been fully brought out.

Smyth (*Dielectric Constant and Molecular Structure*) has discussed in detail some of the causes for molecular association in pure liquids. He attributes the formation of associated molecules to sharing of electrons or possibly of hydrogen bonds between their structure and also due to van der Waals forces and other stray forces.

Debye (*Polar Molecules*) has shown that three types of polarisation curves are possible for dilute solutions of polar substances in non-polar solvents. He has illustrated them by the curves of ethyl alcohol-benzene, ethyl ether-benzene and nitrobenzene-benzene. Benzene is assumed to be the non-polar substance.

The various forms of the polarisation curves are given in Fig. 1

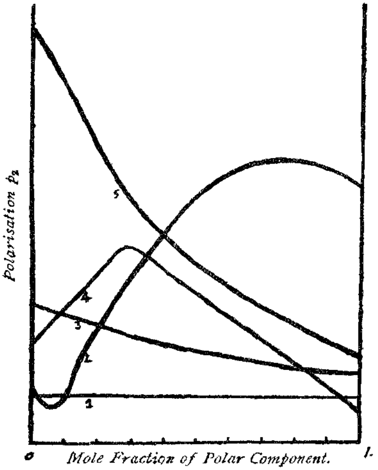


FIG. 1

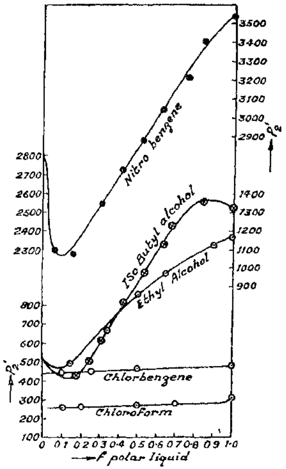
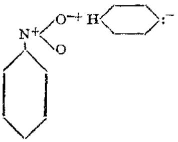


FIG. 2

In the first type of curve the polarisation goes on decreasing with concentration of the polar component. To this type belong the curves (5) of polarisation of nitro-benzene in benzene and acetone in carbon tetrachloride.

The cause for the decrease of the polarisation of nitrobenzene in benzene in concentrated solutions is attributed by Sidgwick (*Covalent Link in Chemistry*) to mutual attraction of the dipole than to any chemical combination or co-ordination. Sidgwick explains rapid change of the association with increase in concentration of nitrobenzene as due to the orientation of the dipoles under the influence of their mutual attraction indicating that the molecules are farther apart, and he also concluded from a comparison of the polarisation of nitrobenzene in different solvents, that the association factor is greater in solvents of higher dielectric constant.

The probable explanation for this curvature of polarisation (P_2) of nitrobenzene in benzene is the formation of the complex formed by the attachment of the benzene ring to the oxygen in the nitro group, the co-ordination increasing the dipole moment.



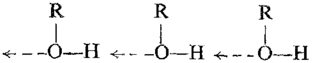
The polarisation curve of acetone is similar to that of nitrobenzene and the same explanation holds.

The second type of curve is represented by the polarisation P_2 ethyl ether in benzene (Curve No. 1). The polarisation remains constant in the entire range of concentration. This kind of curve is the one that is expected for ideal mixtures.

There are two varieties of curves belonging to the third type of polarisation P_2 curve. One is represented by the polarisation P_2 of ethyl alcohol in benzene and the other by ethyl alcohol in hexane, heptane and carbontetrachloride and *n*-octyl alcohol in heptane. These are illustrated by curves 2 and 4.

Smyth (*Dielectric Constant and Molecular Structure*) has studied the polarisation P_2 of ethyl alcohol in solution in heptane and hexane at different temperatures. The values of P_2 of ethyl alcohol increase with temperature instead of decreasing as required by theory in the absence of inter-molecular action. At room temperature the curve goes through a minimum for very dilute solutions of alcohol, then goes through a maximum at about 0.4 mol alcohol and then gradually comes down to the value of alcohol. Smyth explains this result as due to associated molecules of alcohol.

Debye has illustrated the polarisation curve of ethyl alcohol in benzene. The curve starts with a value of 72 c.c. for infinite dilution, rises to 95 c.c. at about 0.3 mol alcohol and then comes down to the value of 52 c.c. in pure alcohol. But no explanation for this kind of behaviour has been offered by Debye. Sidgwick (*Covalent Link in Chemistry*) attributes this change of polarisation as due to associated molecules of alcohol in the pure state, in the following manner:—



$$\leftarrow\text{-}\text{-}\text{-}\overset{\displaystyle R}{\overset{|}{O}}\text{—}H \leftarrow\text{-}\text{-}\text{-}\overset{\displaystyle R}{\overset{|}{O}}\text{—}H \leftarrow\text{-}\text{-}\text{-}\overset{\displaystyle R}{\overset{|}{O}}\text{—}H$$

The association increases with concentration with consequent rise in polarisation. Since the formation of more complex molecules by co-ordination will not proceed without limit, it will be opposed by the thermal agitation of the molecules and so at still greater concentrations of the alcohol, the normal orientation of these highly polar polymerised molecules will begin to prevail and will ultimately cause a fall of the polarisation curve.

In a liquid system the probability of chain polymers existing will be less than that of cross polymers. A liquid forming polymerised molecules will have a very small proportion of free molecules. The polarisation of alcohol goes on increasing from 1.0 to 0.3 mol alcohol due to dissociation of the alcohol molecules. But the free alcohol molecules formed will begin to form a complex with the benzene molecule through hydrogen bonding causing the polarisation value to decrease.

The formation of the complex between the hexane and heptane molecule with ethyl alcohol through hydrogen bonding, and between carbon tetrachloride and alcohol through C-Cl bonding, can be postulated to account for the shape of the second type of curve observed for ethyl alcohol. In very dilute solutions of alcohol, all the alcohol molecules will go to form the complex with the solvent. Since no molecules of alcohol will be left, the polarisation drops. But as the concentration of alcohol is increased, the system will consist of the solvent, the complex and alcohol molecules. Thus from here onwards the polarisation goes on increasing and the same argument holds for the shape of the curve from this point as that given for the polarisation curve of ethyl alcohol in benzene.

In the dilute region the system will consist of the non-polar solvent and the complex. If the complex does not dissociate the polarisation P_2 curve in that region will remain constant, if the complex dissociates then the polarisation will increase thus accounting for the shape of the curve observed in the case of ethyl alcohol in benzene; the U-shape of the curve in the dilute region is thus explained.

Theoretically the equation of the polarisation curve, as can be shown easily, is of the third degree, when a complex is formed in a binary system. The shape of the third degree equation curve will be similar to that given by the system ethyl alcohol in hexane, heptane and carbon tetrachloride.

In addition to these the authors obtained polarisation curves which showed a distinct dip usually at 0.5 mol. This drop in the polarisation value is attributed to the presence of a complex formed between the solvent and the solute through hydrogen bonding.

Hückel and Schneiden (*Z. Phy. Chem.*, B, 1940, **47**, 227) have measured the polarisation of *iso*-propyl alcohol in benzene, hexane, etc., and the curve is similar to that illustrated in the figure for ethyl alcohol in hexane.

The polarisation P_2 value obtained for *iso*-butyl alcohol both in heptane and hexane are very nearly the same, showing that the effect of orientation is the same in these two solvents.

Hückel and Schneiden (*loc. cit.*) have studied the dielectric polarisation of *tert.* butyl alcohol in benzene, hexane, etc. They explain the decrease in the polarisation as due to steric hindrance. The polarisation-concentration curve when there is no steric hindrance is explained by assuming the presence of both chain, double and quadruple molecules.

A similar phenomenon is observed for *iso*-amyl alcohol in non-polar solvents. Smyth explains the maxima and the minima observed in the polarisation curve as due to the presence of two isomers of the amyl alcohol used.

The authors have studied the polarisation of *iso*-amyl alcohol in benzene and carbon tetrachloride and also the selective adsorption of this binary system on silica gel and carbon. A minima in the polarisation value at about 0.3 mol *iso*-amyl alcohol in benzene, and in carbon tetrachloride at 0.5 mol were attributed to the presence of the complex AmOH 2 C_6H_6 and AmOH CCl_4 respectively. (*This Jour.*, 1942, **24A**, 23).

The dielectric constant and polarisation of all forms of octyl alcohol has been given by Smyth. The values are found to differ for each type depending on the location of both of the hydroxyl group and of the branching of the chain.

According to Thompson (*Chemistry and Industry,* 1938, **52,** 512) the organic molecular complexes in solution are held together purely by physical forces or by definite co-ordinate linkages according as the polarisation is *less* than the sum of the two components for the former and *more* in the latter. Also he points out that 1 : 1 complex formation are most usual when both components are monomolecular.

The usual way of calculating the polarisation of a binary system of a polar liquid in a non-polar one by the Debye equation

$$P_{12} = \frac{f_1 m_1 + f_2 m_2}{d} \quad \frac{\epsilon - 1}{\epsilon + 2} \tag{1}$$

where f_1 and f_2 are the mole fractions of the components and ε is the dielectric constant. The above formula holds only when the molecules are not associated. The authors have shown elsewhere that this equation is inapplicable for both pure liquids and concentrated solutions. The New Equation is:

$$\epsilon - 1 \, \frac{(f_1 m_1 + f_2 m_2)}{d} = P'_{12} \tag{2}$$

from which P_2' and P_0' the molar electric susceptibility, are calculated in the usual way (*cf.* p. 20).

A graph of the molal susceptibility calculated by the New Equation is shown in Fig. 2. The polarisation of the systems benzene-chloroform and chlorobenzene are nearly linear functions of composition and nitrobenzene and alcohols show anomaly at either end of concentration curves which are understandable on the basis of formation of complexes. The latter will lead to an equation of third degree for polarisation-concentration.

(1) System Benzene-Carbon Tetrachloride

Baud (*Ann. der Chem. und der Phys.,* 1913, **8,** 29, 124, 6) found that the freezing point of this system clearly indicated the formation of the complex of one molecule of benzene with one of carbon tetrachloride.

The other physical properties like dielectric constant, density, polarisation, etc., as studied by Williams and Krchma (*Jour. Amer. Chem. Soc.*, 1927, **49,** 2408) indicated no divergency from the usual law of mixtures.

Dolezalek (*Z. Phy. Chem.*, 1908, **64**, *727*) accounted for the positive deviations observed for this system in the application of Raoult's law by assuming CCl_4 to be associated, the degree of association being derived from the law of mass action for the equilibrium constant $K = 0.207$. But it is, however, shown that even large values of K are insufficient to account for deviations from Raoult's law.

Pesec, Tuozzi and Evdokimoff (*Chim. Ital.*, 1940, **70**, 721) have carried out refractometric, density and volume changes in mixing benzene with carbon tetrachloride. The deviations from linearity with respect to volume were found to be negative while the refractive index deviations positive.

The anomalous dispersion of dielectric constant, the dielectric polarisation and the selective adsorption by carbon and silica gel in the entire range of concentration of this system have been studied by us previously (*This Jour.*, 1942, **24A**, 27).

Even though both the components used are known to be classical examples of non-polar substances the properties studied indicated formation of complexes between the two components. The complexes formed are CCl_4 C_6H_6 and CCl_4 $4C_6H_6$ as concluded in the paper (*loc. cit.*). The formation of these compounds was explained by assuming a degeneracy of one of the hydrogen bonds in benzene which may form a loose linkage with each of the chlorine atom of the carbon tetrachloride. In the present investigation the authors have studied the selective adsorption by activated coconut shell charcoal and silica gel and also the electronic polarisation and molecular electric susceptibility have been calculated.

EXPERIMENTAL

(1) *Adsorption.*—The activated coconut shell charcoal used for the adsorption experiments was taken from a portion of the charcoal prepared for gas masks.

The silica gel used was prepared by disgesting nickel silicate with hydrochloric acid. The nickel silicate was prepared by precipitating from a solution of nickel nitrate by sodium silicate. The silica gel thus prepared was powdered to 40 mesh, dried again in an oven for a day and used for the experiments.

The adsorption measurements were carried out on a Pulfrich refractometer as described before (*This Jour.*, 1942, **24A**, 11). The selectivity of the two adsorbents were calculated in the usual way.

The results of the various experiments are given in Table I and represented in Figs. 3 and 4.

TABLE I

1939			1942		
f_{CCl_4}	Silica gel $C_0 - C_1\%$	Norit $C_0 - C_1\%$	f_{CCl_4}	Silica gel $C_0 - C_1\%$	Carbon $C_0 - C_1\%$
0·067	0·508	0·275	0·895	−0·126	0·315
0·130	0·357	0·440	0·748	−0·063	0·231
0·178	0·253	−0·220	0·632	0·525	0·294
0·270	0·096	0·110	0·564	0·189	0·252
0·347	0·308	0·123	0·506	−0·021	0·252
0·362	−1·333	0·495	0·388	0·462	0·210
0·371	0·143	0·151	0·337	0·126	−1·134
0·560	0·158	0·341	0·282	0·273	−0·231
0·610	0·399	0·385	0·110	0·126	0·189
0·660	0·116	0·440	..	..	..

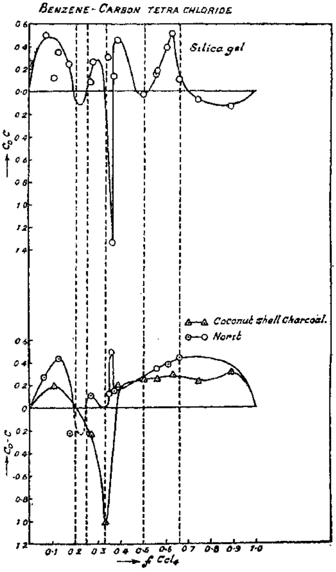


FIG. 3

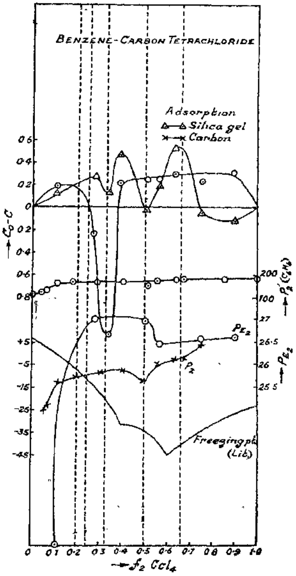


FIG. 4

Discussion.—The two sets of results for silica gel have been measured at intervals of three years both of which confirm the anomalous nature of the adsorption. It has been shown previously that whenever there is the possibility of compound formation in liquid state, the adsorption curve is characterised by a sharp change in the slope. Thus silica gel shows a sharp maxima in the adsorption at .66 mol of carbon tetrachloride ($2\ CCl_4C_6H_6$), zero adsorption at .5 mol ($CCl_4C_6H_6$). A sharp negative adsorption at .33 ($CCl_42C_6H_6$), zero adsorption at .25 ($CCl_43C_6H_6$) and at .20 ($CCl_44C_6H_6$).

In the case of Norit the latter two compounds are indicated in the curve as having zero adsorption and the 1 : 2 compound by a maximum, 1 : 1 by zero, and 2 : 1 by a maximum; in the case of coconut shell carbon, 3 to 1 is indicated by zero and 2 to 1 by a sharp negative maxima and 2 to 1 by a very flat maxima. The highly anomalous nature of the adsorption of this binary system has been confirmed by the authors by carrying out two sets of results at the interval of three years.

These results are in harmony with the ideas of the authors that carbon tetrachloride can form addition compounds with 1, 2, 3 and 4 of benzene, the various complexes being preferentially adsorbed leaving the compositions of the mixtures at these points unchanged.

(2) *Polarisation.*—The electronic polarisation P_{E_2} of carbon tetrachloride in benzene at various concentrations, was calculated from the refractive angles observed while determining the adsorption. The results are given in Table II and shown in Fig. 4 on an enlarged scale.

TABLE II

f_2	$d_{25/4}$	n_{546}	$P_{E_{12}}$	P_{E_2}
0·895	1·5148	1·4642	26·61	26·60
0·748	1·4164	1·4704	26·58	26·58
0·564	1·2892	1·4782	26·54	26·47
0·506	1·2473	1·4805	26·54	26·98
0·282	1·0854	1·4958	26·75	27·09
0·110	0·9669	1·4963	26·11	22·00

The curve starts with a value of 22 c.c. at 0.11 mol carbon tetrachloride and rises steeply to a value of about 27 c.c. at 0.28 mol in which region the formation of hydrogen bond decreases the electronic polarisation. After this it remains constant up to 0.5 mol. The curve again falls here and comes down to a value of 26.5 c.c. after which it remains sensibly constant.

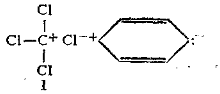
(3) *Electric Susceptibility.*—The P_2' values of benzene in carbon tetrachloride were calculated by making use of the dielectric constant and density values determined previously by using the New Equation. The results are given in Table III.

TABLE III

$f_{C_6H_6}$	ϵ_{25}	P_{12}'	P_2'
0·00	2·24	114	183
0·15	2·25	124	180
0·33	2·33	134	176
0·36	2·34	136	175
0·45	2·37	140	171
0·51	2·29	133	151
0·60	2·41	147	168
0·71	2·44	151	166
0·82	2·50	157	166
0·89	2·54	157	162
0·94	2·32	129	130
0·96	2·32	126	126
1·00	2·28	114	114

The molecular suceptibility of benzene in carbon tetrachloride decreases with concentration passing through a slight kink at 0.5 mol at which point the electronic polarisation measured recently on different samples showed marked kink. The rapid fall from 0.25 CCl_4 has its counterpart in each of the curves showing that the fall in the susceptibility curve is almost entirely due to change in the electronic polarisation of the complex $4C_6H_6\ CCl_4$.

The various compounds of benzene and carbon tetrachloride may be represented as:



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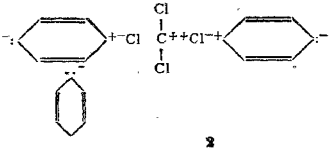

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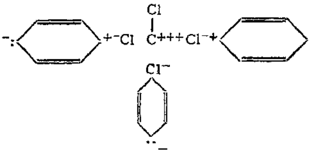

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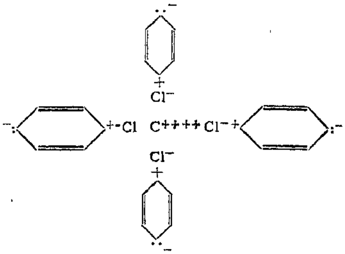


4

(2) System Benzene-Chloroform

Linebarger (*Amer. Chem. Jour.*, 1896, **15**, 429) has measured the densities of the mixtures of benzene and chloroform at different concentrations. He finds the calculated specific gravities to be less than the observed ones. He attributes this behaviour to some specific action between the molecules of the liquids mixed.

Williams and Krchma (*Jour. Amer. Chem. Soc.*, 1927, **49**, 1676) have studied the refractive index, dielectric constant and molar polarisation in the entire range of concentration. They find that the P_2 (molar polarisation) curve is not a straight line and explain it as belonging to one of the types of curves described by Debye (polar molecules).

The freezing point of the system benzene-chloroform has been investigated by Wyatt (*Trans. Faraday Soc.*, 1928, **24**, 429). Even though the curve does not show any complex formation, the two portions of the curves from the pure components to the eutectic point are concave towards the concentration axis, and according to the freezing point curve given in Timmermann's book (*Les solutions concentrees,* p. 184) the existence of the complex $3CHCl_3\ C_6H_6$ is clearly indicated.

Giovanni Bottecchia (*C. A.*, 1936, 4063) has carried out dilatometric measurements of benzene and chloroform at 16° and 140° and shows that the maximum increase in volume occurs at 27 per cent. $CHCl_3$ corresponding to a ratio $CHCl_3 : C_6H_6 :: 1 : 4$.

Linebarger (*Amer. Chem. Jour., IV,* 1936, 2, 331) has measured the viscosity of mixtures of benzene and chloroform at different concentrations. The difference between the calculated and the observed viscosities are so slight, the author attributed the differences to experimental errors.

EXPERIMENTAL

(1) *Polarisation.*—The dielectric constant measurements were carried out on an apparatus described previously (*This Jour.,* 1942, **24A**, 17).

Piezoelectric quartz crystals whose frequencies were determined very accurately were connected between the grid and filament of a tuned anode valve circuit using a LP_2 valve and 40 volts on the anode. In this circuit the plate current will vary very rapidly with increase in capacity in the circuit in a certain region. It will first fall slowly when the oscillations start and then more rapidly until it reaches a minimum after which a very small rise in capacity will stop the circuit from oscillating and the anode current will jump up. This stopping point is used to adjust the setting rather than the point for the same current as usually done. Measurements could be carried out very rapidly by changing the anode coils to suit different crystals from 23 kcs. to 7,100 kcs. As the circuit stops oscillating at the critical setting the dielectric constant is measured at high frequency damped but sinusoidal waves.

For some of the crystals the sudden increase on the plate current was very sharp, while for some crystals it was found to change very slowly which made the reading unreliable. To start the crystal oscillating, it was found that the condenser had to be set back behind the point where the current rises sharply, and even then a switching arrangement had to be devised to start the crystal oscillating. The condenser is set just beyond the critical value sufficient for the sudden rise in the plate current, and then the filament would be switched off and on when the crystal began to oscillate. It was also found very essential to clean the crystals with a fine cloth wetted with alcohol, as moisture sticking to the sides of the crystals would affect the oscillation properties of the crystal, and on rainy days the readings could not be got as sharp as on a dry day.

In the present investigation, the oil-bath for the measuring condenser was surrounded by a water-bath which in turn was placed in a wooden box to keep the temperature steady. The space between the water-bath and the wooden box was packed with saw dust. An electric heater and a stirrer were immersed in the water-bath. In the oil-bath only a hand stirrer was used. When the temperature of the water-bath was just 0.1°-0.2° higher than the required temperature the heater would be put off, and only the stirrer kept in action. This was sufficient to keep the oil-bath steady at the required temperature. If the temperature rose more than what was required in the oil-bath, it could be brought down by adding a few pieces of ice to the water-bath. This arrangement was found to work very satisfactorily especially as measurements were made near room temperature 25° C. or 30° C.

The values of the various physical properties of this system are given in Table IV and represented in Fig. 5.

TABLE IV

Polarisation of Chloroform in Benzene

f_{CHCl_3}	ϵ_{25}	$d_{25/4}$	D.C.M.				New Law	
			P_{12}	P_2	P_{E_2}	P_0	P_{12}'	P_2''
0·80	4·25	1·336	..	..	..	..	291	..
0·75	4·04	1·3101	41·92	47·49	21·53	25·96	253	299
0·70	3·88	1·2713	41·24	48·10	21·80	26·30	243	299
0·65	3·68	1·2399	39·96	47·90	21·85	26·05	227	288
0·51	3·29	1·1556	37·16	48·70	21·60	26·10	197	276
0·50	3·30	1·1483	37·32	49·45	22·70	26·75	198	282
0·45	3·10	1·1029	36·03	49·30	21·95	27·35	184	269
0·34	2·86	1·0560	33·25	49·60	21·60	28·0	162	261
0·26	2·74	1·0135	32·16	52·00	21·00	31·00	152	262
0·25	2·72	1·0118	31·78	51·60	20·95	30·65	150	256
0·24	2·57	1·0033	30·21	46·12	20·95	25·17	138	213
0·21	2·61	0·9890	30·34	49·25	20·94	28·30	140	238
0·12	2·50	0·9446	27·68	45·57	20·20	25·37	125	208
0·10	2·40	0·8338	26·13	34·60	18·80	13·80	115	120

The polarisations have been calculated by the usual Debye Clausius Mosotti equation (D.C.M.) (P_2) and by the application of the New Equation of the authors (P_2').

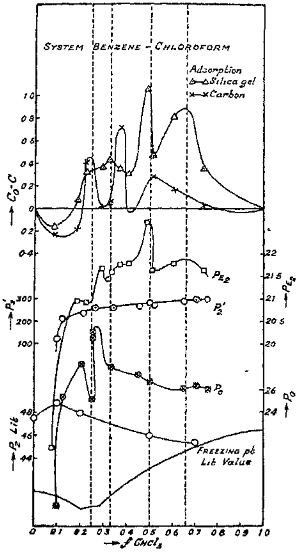


FIG. 5

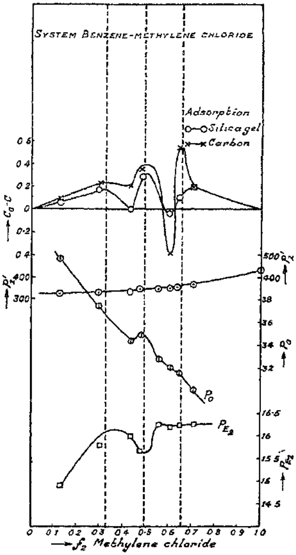


FIG. 6

Discussion.—Williams and Krchma (*Jour. Amer. Chem. Soc.*, 1927, **49**, 1676) found that the polarisation (D.C.M.) goes on increasing in the dilute solutions of chloroform from 47.5 c.c. at 1 mol benzene to 48.8 c.c. at 0.1 mol chloroform, afterwards the curve shows a gradual depression in value to 45 c.c. in 1 mol chloroform, whereas the authors get a complicated type of curve in different concentrations of chloroform. The curve starts with a much lower polarisation than that found by Williams and Krchma, then goes on increasing till 0.21 mol chloroform, when the polarisation value suddenly drops. Again the curve begins to ascend sharply at 0.25 mol chloroform. From here onwards the curve takes a cup-shaped form with a convexity towards the concentration axis. Again from 0.5 mol. chloroform the curve becomes convex towards the axis. This shape of the curve was confirmed by determining the polarisation of number of mixtures of benzene and chloroform at small differences of concentrations of mixtures. The polarisation curve of Williams and Krchma has very few points. And from a comparison of their curve with the authors' it is noticeable that Williams and Krchma have no values for polarisation in the region where the authors get the peculiar curvatures. And also if a curve is drawn through the points from the authors', values corresponding to compositions determined by Williams and Krchma both the curves of the authors and Williams and Krchma are found to be parallel.

To allow for the influence of polarisation due to electronic polarisation, the latter was calculated from the refractive indices of the mixtures studied and the molecular electronic polarisation calculated from the formula

$$P_{E_{12}} = f_1 P_{E_1} + f_2 P_{E_2}$$

was subtracted from the molecular polarisation P_2 thus giving P_0. This is represented in Fig. 5. Even though the scale of the curve is exaggerated the general outline of the curve is very similar to that of the molar polarisation curve. The sudden change of the slopes at 0.25, 0.3 and 0.5 mol. chloroform is very much marked. These points correspond to the composition of the complexes $CHCl_3$ $3C_6H_6$, CHl_3, $2C_6H_6$ and $CHCl_3C_6H_6$. As already pointed out the presence of the first complex has been borne out by freezing point determinations.

The difference in value of the electric moment of chloroform obtained in the gaseous state and in benzene can be explained on the basis of a co-ordinate linkage between chloroform and benzene. In dilute solutions the moment measured is that of the complex which has a higher moment than the free molecule owing to the decrease of the influence of one C-Cl bond on the other.

Polarisation was also calculated by applying the New Equation $\frac{(\epsilon - 1)M}{d} = 4\pi N \mu^2/kT$. The molar susceptibility P_2' of chloroform was calculated from the formula $P_{12} = f_1 P'' + f_2 P_2'$. The P_{12}' was calculated from the formula,

$$P_{12}' = (\epsilon - 1)\frac{f_1 m_1 + f_2 m_2}{d}.$$

The values of P_2' are represented in Fig. 5. The curve rises with concentration in the dilute region and remains constant in the concentrated region. The P_2' has been also calculated from the values given in Landolt Börnstein and the results are in agreement except at lower concentrations.

Adsorption.—The adsorption measurements were carried out in the manner described previously, the same sample of silica gel and activated coconut shell charcoal were used as absorbents. The results of the adsorption measurements for various mixtures studied are given in Table V and represented in Fig. 5.

TABLE V

System Benzene-Chloroform

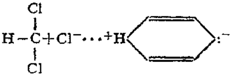
f_{CHCl_3}	Silica gel $C_0 - C$	Carbon $C_0 - C$
0·74	0·36	−0·02
0·60	0·81	0·17
0·50	0·47	0·27
0·49	1·05	..
0·41	0·30	−0·04
0·37	0·36	0·72
0·34	..	0·06
0·33	0·43	−0·04
0·30	0·37	0·02
0·23	0·33	0·41
0·19	0·08	−0·18
0·09	−0·16	−0·22

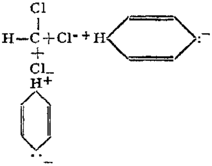
The adsorption curves take very complicated forms and they are twisted about the axis for silica gel, the curve goes through a negative direction up to 0.18 mol chloroform after which for a short concentration range of chloroform the adsorption increases, then the value becomes almost flat and suddenly drops in value at about 0.4 mol chloroform. The adsorption after this reaches a maximum at about 0.5 mol comes down and goes up and then decreases in value with concentration of chloroform.

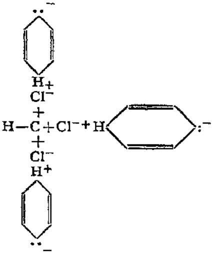
The abrupt change in the slope of the curve corresponds to definite compositions of complexes that might be present in the systems. That is the change at 0.25, 0.33 and 0.5 mol chloroform might be due to $CHCl_3\ 3C_6H_6$, $CHCl_3\ C_6H_6$ and $CHCl_3C_6H_6$.

For coconut shell charcoal the curve lies below the concentration axis till about 0.22 mol and then suddenly rises to a positive maximum at 0.25 mol chloroform, corresponding to $CHCl_3\ 3C_6H_6$. The curve from this point again comes down passing through zero adsorption at about 0.3 mol chloroform corresponding to $CHCl_3\ 2C_6H_6$. Again the adsorption value rises, goes through a maximum, comes down once more to zero value at 0.4 mol chloroform and then again to a maximum at 0.5 mol corresponding to $CHCl_3\ C_6H_6$.

On the basis of $CH \leftarrow Cl$ bonding the structure of the possible complexes can be represented in the following way:







(3) System Benzene-Methylene Chloride

EXPERIMENTAL

(1) *Polarisation.*—The dielectric constant measurements were carried out in the manner described before. The density, dielectric constant, polarisation P_2, electronic polarisation P_{E_2} and molar susceptibility P_2' are given in Table VI. P_{E_2} and $(P_2 - P_{E_2}) = P_0$ and P_2' are represented in Fig. 6.

TABLE VI

Dielectric Polarisation

f_2	ϵ_{25}	d_{25}	D.C.M.			New Law		
			P_{12}	P_2	P_{E2}	P_0	$P_{12}\bar{l}$	$P_2\bar{l}$
1·00	7·70	1·3054	44·93	..	..	..	436	420
0·71	5·16	1·1645	41·37	47·40	16·28	30·12	296	370
0·65	4·76	1·1353	40·40	47·83	16·26	31·57	273	359
0·61	4·54	1·1172	39·81	48·24	16·20	32·04	260	354
0·56	4·28	1·0906	39·19	49·07	16·25	32·82	246	350
0·48	3·94	1·0551	38·15	50·64	15 67	34·97	227	350
0·44	3·72	1·0387	37·10	50·45	16·02	34·43	212	337
0·30	3·21	0·9806	34·63	53·33	15 80	37·53	180	334
0·13	2·65	0·9170	30·52	56·69	14·92	41·77	142	330
0·00	2·27	0·8734	26·61	..	..	..	..	324

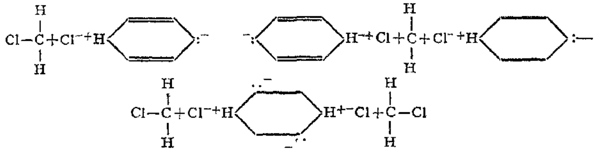
The P_{E_2} curve for methylene chloride rises with concentration up to 0.4 mol methylene chloride, then goes through a minimum at 0.5 mol after which the value remains almost constant. The P_0 values decrease with concentration but go through a slight kink at 0.5 mol. Even the molar susceptibility P_2' curve denotes appreciable change of slope at 0.6 and 0.66 mole methylene chloride plotted on 1/50th the scale. Whereas the D.C.M. equation shows a fall with concentration the susceptibility shows a rise. The former is difficult to explain as methylene chloride is not an associated liquid and formation of compounds or complexes should decrease the polarisation which is given only by the susceptibility equation. All the curves show the kinks at molar compositions. The dipole moment calculated from the polarisation in concentrated solutions will be discussed later.

(2) *Adsorption.*—The adsorption measurements (Table VII, Fig. 6) both for silica gel and activated coconut shell charcoal gave similar results. In both the cases the selective adsorption goes on increasing with concentration up to 0.3 mol methylene chloride, then comes down to zero at 0.43 mol for silica gel and a minimum for charcoal. The curves again rise to a maximum at 0.5 mol and drop in value and again rise to a maximum at O.66 mol methylene chloride. These compositions correspond to the complexes 1 : 2, 1 : 1

TABLE VII

$f_2 CH_2Cl_2$	Silica gel $C_0 - C$	Carbon 1 $C_0 - C$	Carbon 2 $C_0 - C$
0·71	0·18	0·20	0·16
0·65	0·11	0·54	0·44
0·61	−0·05	−0·38	−0·38
0·56	0·23	0·35	0·27
0·48	0·29	0·36	0·42
0·44	0·00	0·21	0·16
0·30	0·17	0·22	0·10
0·13	0·06	0·10	0·06

and 2:1 respectively. The various compounds may be given the following structures:—



(4) System Benzene *tert.* Butyl Chloride

(1) *Polarisation.*—The dielectric constant measurements were determined as described previously. The calculation of the molecular electronic polarisations by the D.C.M. equation and molar susceptibility by the New Equation are given in Tables VIII and IX and represented in Fig. 7.

TABLE VIII

f_2	ϵ_{25}	$d_{25/4}$	D.C.M.		New Law	
			P_{12}	P_2	P_{12}'	P_2'
0·13	2·83	0·8688	36·02	99·2	171	576
0·26	3·82	0·8637	48·84	111·4	284	768
0·43	4·74	0·8588	54·48	91·1	367	702
0·50	5·45	0·8552	59·56	92·5	444	774
0·55	5·84	0·8537	62·16	91·8	487	792
0·61	6·25	0·8515	64·91	89·7	536	806
0·67	6·60	0·8497	67·30	87·0	579	808
0·86	8·30	0·8406	64·21	70·1	661	750
1·00	9·65	..	..	..	945	..

The P_{E_2} values for *tert.* butyl chloride decreases rapidly with concentration in the dilute region going through a minimum at about 0.33 mol *tert.* butyl chloride. The value rises slightly and comes down again at about 0.5 mol and afterwards remains appreciably constant. The P_0 values go through a maximum at 0.3 mol *tert.* butyl chloride and then again pass through a slight maximum at 0.5 mol after which the value goes on decreasing with concentration.

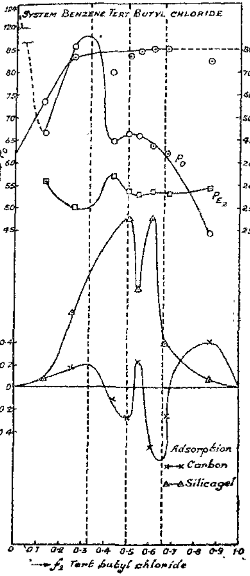


FIG. 7

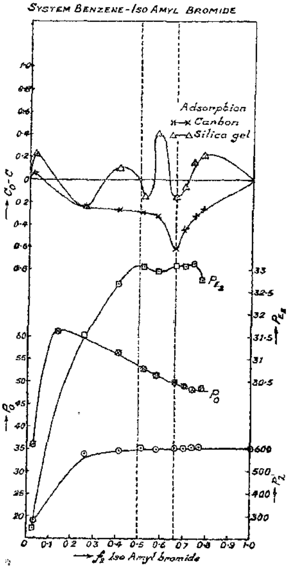


FIG. 8

TABLE IX

f_2	n_{546}	P_{E12}	P_{E2}	P_0
0·86	1·39786	26·00	25·9	44·21
0·67	1·419522	26·11	25·8	62·18
0·61	1·426004	26·14	25·8	63·78
0·55	1·432372	26·14	25·8	65·98
0·50	1·438222	26·20	25·8	66·60
0·43	1·450347	26·40	26·2	64·88
0·26	1·466602	26·27	25·5	85·89
0·13	1·487162	26·47	26·1	..

The P_2' values rise steeply in the dilute region and then the values remain almost constant in the concentrated region. The value of the dipole moment calculated for this steady value of P_2' is 2.10.

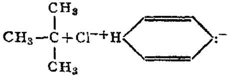
(2) *Adsorption.*—The adsorption of this system was also carried as before using the same adsorbents. The selective adsorption values calculated for the entire range of concentration of *tert.* butyl chloride in benzene is given in Table X and represented in Fig. 7.

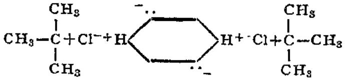
TABLE X

f_2	Carbon $C_0 - C_1$	Silica gel $C_0 - C_1$
0·13	0·08	0·08
0·26	0·17	0·67
0·43	−0·11	..
0·50	−0·27	1·51
0·55	0·23	0·88
0·61	−0·53	1·51
0·67	−0·25	0·39
0·86	+0·41	0·06

For silica gel the values go through very high values compared with charcoal with a maxima at 0.5 and 0.6 mol *tert.* butyl chloride and from 0.6 mol the curve comes down. For charcoal the curve is of a complicated nature passing through a positive maxima at 0.33 and negative maxima at 0.5 and 0.66 and again positive at 0.85 mol *tert.* butyl chloride.

The two possible compounds may be represented by the following structures:—





(5) System Benzene-*iso*-Amyl Bromide

(1) *Polarisation.*—The dielectric constant measurements were carried out in the apparatus described previously. The dielectric constants, polarisation and densities of the different mixtures studied are given in Table XI.

TABLE XI

Dielectric Polarisation of iso-*Amyl Bromide in Benzene*

f_2	ϵ_{25}	$d_{25/4}$	D.C.M.		New Law	
			P_{12}	P_2	P_{12}'	P_2'
1·00	5·94	..	..	..	..	605
0·777	5·28	1·1478	69·0	81·1	502	611
0·741	5·11	1·1338	67·3	81·5	479	607
0·70	4·97	1·1332	65·5	82·1	456	603
0·66	4·87	1·1114	64·0	83·1	439	606
0·577	4·57	1·0876	60·0	84·4	394	597
0·521	4·38	1·0681	57·5	85·9	367	601
0·408	3·91	1·0315	52·3	89·6	309	590
0·256	3·37	0·9772	43·7	93·2	234	575
0·028	2·32	0·8848	27·6	63·2	119	580
0·00	2·28	0·873	..	..	114	604

The polarisation P_2 was calculated by the D.C.M. equation. Using P_{E_2} values from Table XII, P_0 was calculated and the results are shown in Fig. 8. P_0 rises with dilution showing marked change of slope at 0.66 mol bromide (1 : 2 compound). The rapid drop at low concentration is shown both by P_0 and P_{E_2} curves. The latter (plotted on a large scale) brings out kinks at 0.5 mol and 0.66 mol, and emphasizes the decrease in electronic polarisation in dilute solutions contrary to usual assumptions.

TABLE XII

Electronic Polarisation of iso-Amyl Bromide

f_2	n_{546}	$P_{E_{12}}$	P_{E_2}	P_0
0·777	1·444772	31·19	32·52	48·6
0·741	1·452152	31·44	33·15	48·4
0·70	1·453951	31·12	33·08	49·0
0·66	1·455942	30·86	33·09	50·1
0·577	1·46004	30·25	32·97	51·5
0·521	1·463416	29·94	33·07	52·9
0·408	1·470159	29·16	32·96	56·6
0·256	1·498929	27·82	31·54	61·7
0·028	1·498929	26·56	27·25	35·9

P_2' values remain fairly constant (604 c.c.) up to 0.5 mol concentration and then decrease. These results will be discussed later.

(2) *Adsorption.*—The adsorption of this system on silica gel and activated carbon was carried out in the way described previously. The results are given in Table XIII and represented in Fig. 8.

TABLE XIII

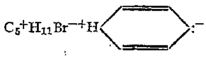
Adsorption

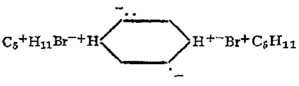
f_2	Silica gel $C_0 - C_1$	Carbon $C_0 - C_1$
0·777	0·21	−0·26
0·741	0·15	−0·32
0·700	−0·06	−0·43
0·660	−0·15	−0·61
0·577	0·40	−0·32
0·521	−0·15	−0·29
0·408	0·11	−0·26
0·256	−0·23	−0·23
0·028	0·23	−0·06

The adsorption curve for silica gel is of a very complicated shape starting with a positive value at 0.02 mol *iso*-amyl bromide. The curve passes through zero adsorption at 0.1 mol to a negative maximum value at 0.25 mol after which the curve again rises to a positive value at 0.4 mol bromide. Again the curve goes to a negative maximum value at 0.5 mol, going to a positive maximum once more at 0.6 mol and after this the curve smoothly joins the concentration curve at 1 mol *iso*-amyl bromide.

For activated carbon the curve starts with a positive value at 0.02 mol and the rest of the curve lies on the negative side. At 0.66 mol *iso*-amyl bromide the curve goes to a sharp negative maxima.

The two possible compounds may be represented as follows:—





(6) System Benzene-Chlorbenzene

(1) *Polarisation.*—L. Klemm, W. Klemm and Schiemann (*Z. Phy. Chem.*, 1933, **165**, 379) have determined the freezing points in the entire range of concentrations of benzene with mono halogenated derivatives of benzene.

The freezing point curve for the system fluorbenzene-benzene indicates the existence of a complex by a slight dent in the curve. For chlorbenzene-benzene the curve is concave towards the concentrations axis with an eutectic. The curves for brom- and iodobenzene with benzene are normal. It may be said that the affinity of the halogen bond with the C-H bond in benzene, decreases in the order fluorine, chlorine, bromine and iodine as expected.

Williams and Krchma (*Jour. Amer. Chem. Soc.*, 1927, **49**, 1676) have determined the refractive index and polarisation of this system. They get a smooth curve, but have no points in the region where the authors get discontinuities in the curve. The curve obtained by Williams and Krchma comes under one of the types of curves explained by Debye.

Smyth, Morgan and Boyce (*Jour. Amer. Chem. Soc.*, 1928. **50**, 1536) have measured the polarisation of chlorbenzenes in benzene, and have shown that the departure from linearity of both the dielectric constant and density curves depends upon the character not only of the polar substance but also of the non-polar. The decrease in the polarisation with concentration is explained as due to the molecules of chlorbenzenes tending to orient themselves in such a way that neighbouring doublets oppose one another, thereby decreasing the polarisation. The effect is greater, greater the concentration.

Smyth and Morgan (*Jour. Amer. Chem. Soc.*, 1928, **50**, 1547) have measured the dielectric constants of solutions of ethyl bromide, chloroform and chlorbenzene in hexane over the entire range of concentration. As expected, they found that the molecules affect one another more strongly in concentrated solutions, at lower temperatures and when their moments are high. Thus the P_{12} curve for chloroform which has the smallest moment of the three polar substances studied, is nearly a straight line in the dilute region and the curve for 60° shows only a small departure from linearity, but this departure increases as the temperature is lowered. Chlorbenzene which has a larger moment shows a noticeable change throughout all the curves, but the slope of the curvature increases with decreasing temperature and increasing concentrations. The curve for ethyl bromide, which has the largest moment of the three, passes through a maximum.

Experimental.—The dielectric constant measurements of this system were carried out in the manner described previously (*Jour. Ind. Inst. Sci.*, 1942, p. 16). The results (except the dispersions) are given in Table XIV and represented in Fig. 9.

TABLE XIV

Dielectric Polarisation of the System Chlorbenzene-Benzene

f	ϵ_{25}	$d_{25/4}$	D.C.M.				New Law	
			P_{12}	P_2	P_{E2}	P_0	P_{12}	P_2
1·00	5·39	1·1000	60·21	60·21	31·11	29·10	445	414
0·92	5·15	1·0941	58·18	60·90	31·12	29·78	416	442
0·54	3·97	1·0049	47·82	65·75	31·01	34·74	285	431
0·49	3·88	0·9928	46·69	67·84	31·11	36·78	275	443
0·44	3·70	0·9830	44·88	67·85	31·08	36·77	256	436
0·38	3·50	0·9672	42·73	69·28	31·03	38·25	235	432
0·34	3·33	0·9574	40·91	69·05	27·69	41·36	218	421
0·27	3·11	0·9420	38·23	69·19	30·84	38·35	195	415
0·20	3·04	0·9268	37·01	79·64	29·90	49·74	187	479

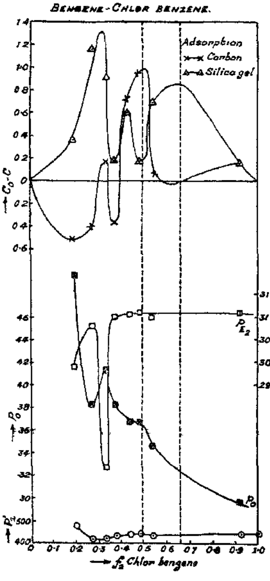


FIG. 9

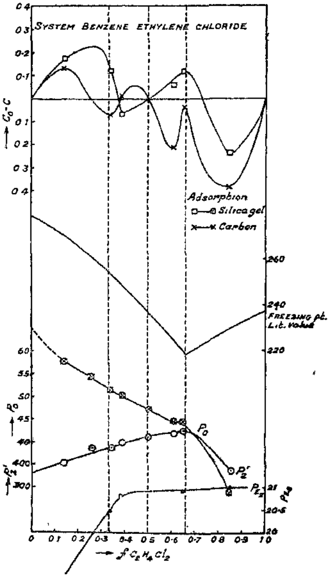


FIG. 10

The curve for the molar polarisation of chlorobenzene drops at two steps—one at 0.33 and another at about 0.5 mol chlorobenzene. These two points correspond to the composition of the complexes $C_6H_5Cl\ 2C_6H_6$ and $C_6H_5Cl\ C_6H_6$ respectively, the former is characterised by a sharp drop in P_{E_2} value. The general tendency of the decrease in P_{E_2} is also in common with the results for other systems. The results of refractive dispersion are given later. The polarisability calculated by the New Equation is fairly constant although the anomalies at 0.3 and 0.5 mol persist. The results will be discussed in a later paper.

(2) *Adsorption.*—The adsorption measurements were conducted as described previously, using silica gel and activated coconut shell charcoal as adsorbents. The results are given in Table XV and represented in Fig. 9.

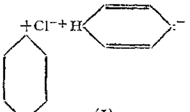
TABLE XV
Adsorption

f_2	Carbon $C_0 - C_1$	Silica gel $C_0 - C_1$
0·920	0·15	0·15
0·542	0·17	0·70
0·487	2·38	0·18
0·443	0·73	0·62
0·378	−0·37	0·18
0·337	0·18	0·92
0·273	−0·40	1·17
0·196	−0·51	0·37

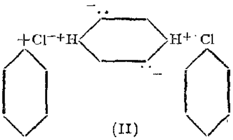
For silica gel, the selective adsorption curve lies above the concentration axis with a number of maxima and minima the curve having a zig-zag form. The curve goes through maxima at 0.33 mol, 0.44 and again at 0.66 mol chlorbenzene, and passes through minima at 0.37 and 0.5 mol chlorbenzene. The maximum and minimum points correspond to $C_6H_5Cl\ 2C_6H_6$ and $C_6H_5Cl\ C_6H_6$.

For activated coconut shell charcoal the curve lies on both sides of the concentration axis. In lower concentrations of chlorbenzene the curve passes through negative values and from 0.28 mol the curve rises and goes to the positive side till 0.33 mol chlorbenzene is reached. Again the curve comes down to a negative value at 0.38 mol C_6H_5Cl goes to a positive maximum with a sharp slope at 0.5 mol chlorbenzene after this the curve comes down sharply to 0.54 mol chlorbenzene.

The presence of the compounds $C_6H_5Cl\ 2C_6H_6$, and $C_6H_5Cl\ C_6H_6$ which are markedly shown to exist both by polarisation and adsorption curves, can be explained in the following way: The hydrogen opposite to the chlorine atom will have an induced charge opposite in sign to that of the chlorine atom. One of the benzene will form a link with the chlorine and another with the hydrogen opposite to the chlorine, thus making possible the existence of the complex $C_6H_5Cl\ 2C_6H_6$.



(I)



(II)

(7) System Benzene-Ethylene dichloride

Stearn and Smyth (*Jour. Amer. Chem. Soc.*, 1934, **56**, 1667), Muller (*Phy. Z.*, 1933, **34**, 689), Smyth, Dornte and Wilson (*Jour. Amer. Chem. Soc.*, 1931, **53**, 4242) have found an abnormally high value for the dipole moment of ethylene chloride in benzene as compared with its values in other solvents. Formation of complex between the solvent and solute has been suggested as the cause.

Hugo Huettig Jr. and C. Smyth (*Jour. Amer. Chem. Soc.*, 1935, **57**, 1523) have determined the freezing point of this system but found no evidence of any compound formation. It may be mentioned that while freezing point investigations (*Jour. Amer. Chem. Soc.*, 1935, **57**, 1324) give no evidence of the presence of a complex in the system, they do not necessitate the abandonment of the idea of the possible loose complex between the two components, which seems to offer an explanation for the high dipole moment observed in benzene and of the relative intensities of certain lines in its Raman spectrum in benzene solution.

Kubo (*Bull. Inst. Phys. Chem. Research, Tokyo,* 1934, **13**, 1221) has explained the electric polarisation values on the assumption of 1:1 compound of benzene and ethylene dichloride. In the present paper the dielectric dispersion of ethylene dichloride in benzene have been measured over the entire range of concentration from which the molar polarisation of ethylene dichloride is calculated both by the D.C.M. equation and New Law. The adsorption of the system on silica gel and activated coconut shell charcoal has been also determined with a view to give additional evidence for the existence of complexes between the solvent and the solute.

EXPERIMENTAL

(1) *Polarisation.*—The dielectric constant measurements were carried out as described previously. The physical properties are given in Table XVI and represented in Fig 10. The dispersion results will be given in a separate paper.

TABLE XVI

Ethylene dichloride-Benzene

f_2	e_{25}	$d_{25/4}$	D.C.M.				New Law	
			P_{12}	P_2	P_E	P_0	P_{12}'	P_2'
·85	5·23	1·1879	46·4	50·1	20·8	29·1	336	375
·65	5·91	1·1050	50·8	64·6	20·7	44·68	402	557
·61	5·55	1·0874	49·7	65·4	20·6	44·56	375	542
·51	4·83	1·0487	46·8	67·97	47·0	47·02	320	525
·39	4·08	1·0052	43·1	71·1	20·6	50·28	262	494
·34	3·77	0·9880	41·0	71·7	20·3	51·2	237	475
·26	3·40	0·9615	38·4	75·0	..	54·45	207	472
·14	2·78	0·9171	32·6	78·0	18·9	59·0	156	413

The molar polarisation P_0 which is obtained after the subtraction of P_{E_2} the electronic molar polarisation from P_2 of ethylene chloride in benzene, decreases linearly with concentration up to about 0.66 mol ethylene dichloride then the value comes down more rapidly in concentrated solution.

The electronic polarisation remains sensibly constant between 0.4 to 1.0 mol and drops rapidly in lower concentrations. The molar susceptibility P_2' calculated from the New Formula increases with concentration up to 0.7 mol ethylene dichloride and then decreases.

The authors believe that the polarisation of ethylene dichloride should decrease in dilute solutions if complexes with benzene are formed owing to law of mass action. The latter also shows itself in concentrated region as expected.

Adsorption.—The selective adsorption measurements of this system in the entire range of concentration on silica gel and activated coconut shell charcoal was carried out on a Pulfrich Refractometer as already described. The results are given in Table XVII and represented in Fig. 10.

TABLE XVII

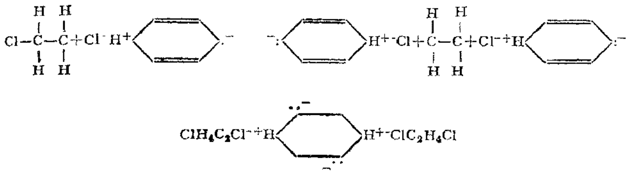
Adsorption

$C_{C_6H_6}$	$f_{2C_2H_4Cl_2}$	Silica gel $C_0 - C$	Carbon 1 $C_0 - C$	Carbon 2 $C_0 - C$
12·14	0·85	−0·235	−0·387	−0·41
30·15	0·65	+0·123	−0·035	−0·06
33·97	0·61	+0·06	−0·21	−0·176
55·9	0·39	−0·06	+0·017	−0·017
61·07	0·34	+0·123	0·0	−0·07
83·7	0·14	+0·176	+0·14	+0·017

A zig-zag curve is obtained for coconut shell charcoal passing through a positive maximum at 0.15 mol ethylene chloride then through negative maxima at 0.33 and zero at 0.5, and again through negative maxima at 0.6 and minima at 0.66 and maxima at 0.85 mol ethylene dichloride.

For silica gel also the curve goes through a positive maxima at 0.25 mol and through zero at 0.5 mol and again positive maxima at 0.66.

The complexes prominently shown to exist by the curve are C_6H_6-$C_2H_4Cl_2$ and $2C_6H_6$-$C_2H_4Cl_2$. These complexes might be formed through the C-H ← Cl bonding since benzene is shown to possess a weak hydrogen bond. The formation of 1 : 1 compound will explain the rise in the moment of the value of C-Cl bond. Since there are two chlorine atoms in ethylene dichloride capable of bonding with two hydrogen atoms the most probable complex formed between benzene and ethylene dichloride will be $C_2H_4Cl_2$ $2C_6H_6$. The structures of the possible complexes are:



(8) System Benzene-Ethylene dibromide

Ethylene dibromide and ethylene dichloride are found to have comparable properties. Just as the moment of ethylene dichloride was found to give considerably high value in benzene when compared to those in other solvents like hexane, heptane, etc., ethylene dibromide was also found to behave in a similar manner (Smyth and Kamerling, *Jour. Amer. Chem. Soc.*, 1931, **53**, 2988).

Dahms (*Wied. Ann.*, 1895, **54**, 486) has carried out the freezing point determinations of this system over the entire range of concentration. As in the case of ethylene dichloride-benzene here also the freezing point diagram indicates no compound formation in the system. But both the freezing point curves for ethylene dichloride-benzene and ethylene dibromide-benzene are not ideal, *i.e.*, the line joining the freezing points of the pure components to the eutectic point is not a straight line but is convex. Perhaps this is due to the presence of loose complexes present in the system which may not appreciably alter the freezing points.

The molar polarisation and selective adsorption measurements of this system have been carried out to give additional evidence for the presence of complexes in the system.

EXPERIMENTAL

(1) *Polarisation.*—The dielectric constant measurements of this system were carried out in the manner described previously. The dielectric dispersion values will be given later. The polarisation calculated from steady values of dielectric constants are given in Table XVIII (*a* and *b*). The molar polarisation for ethylene dibromide is represented in Fig. 11.

TABLE XVIII

Polarisation : System Ethylene Dibromide-Benzene

$f_{C_2H_4Br_2}$	ϵ_{25}	$d_{25/4}$	D.C.M.				New Law	
			P_{12}	P_2	P_{E_2}	P_0	P_{12}'	P_2'
			(*a*) *New Results*					
0·81	4·13	1·9114	44·5	48·99	26·8	21·93	273	310
0·65	3·74	1·7058	41·9	51·04	26·6	24·10	241	309
0·58	3·52	1·6050	40·4	51·55	26·8	23·61	223	302
0·47	3·30	1·4396	39·1	54·73	26·5	26·93	207	313
0·33	3·00	1·2869	35·5	56·42	26·4	29·72	178	306
0·24	2·80	1·1563	33·3	60·12	25·9	33·95	159	308
0·12	2·54	10·151	30·3	69·30	25·8	43·21	137	309
0·07	2·46	0·9568	29·4	82·43	26·1	55·00	131	340
			(*b*) *Preliminary Results*					
0·61	3·60	1·6607	40·5	50·31	26·7	23·61	226	299
0·50	3·37	1·4880	39·4	53·81	26·9	26·9	212	309
0·38	3·05	1·3373	36·3	54·52	26·9	27·62	..	..
0·24	2·81	1·2883	33·7	50·17	26·8	23·37	..	..
0·22	2·71	1·1469	32·1	56·36	26·3	30·06	151	282
0·15	2·56	1·0710	30·2	58·33	26·2	32·13	138	271

The D.C.M. polarisation curve starts with a value of 83 c.c. in infinite dilute solution of ethylene dibromide and comes down to the value of 70 c.c. at about 0.1 mol ethylene dibromide. The curve takes a convex shape towards the concentration axis with a slight dent at about 0.5 mol $C_2H_4Br_2$. The electronic polarisation curve $P_{E_{12}}$ goes through a maximum point at 0.5 mol $C_2H_4Br_2$.

The P_0 curve represented in Fig. 11 shows rapid fall in polarisation with concentration and dents in the values at 0.5 and 0.66 mol. The electronic polarisation P_{E_2} of ethylene dibromide goes through a maximum at 0.5 mol.

The molar susceptibility P_2' (calculated by the application of the New Equation) curve is a straight line parallel to the concentration axis from 0.25 mol forwards. The curve takes a cup-shaped form in the region 0.1 to 0.25 mol. And from 0.1 the P_2' value increases steeply with dilute concentration of ethylene dibromide, owing to the failure of the New Equation in this region where D.C.M. equation probably holds good and to the formation of complex between the solvent and the solute.

(2) *Adsorption.*—Adsorption measurements of this system on activated coconut shell charcoal and silica gel were carried out in the same manner as described in the previous parts. The results are given in Table XIX and represented in Fig. 11.

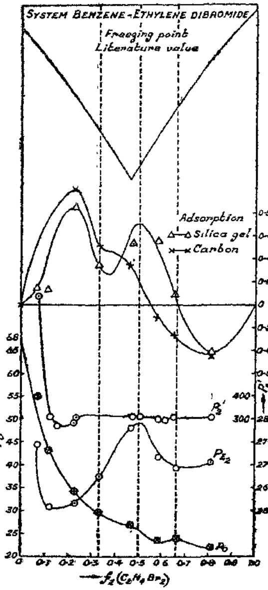


Fig. 11

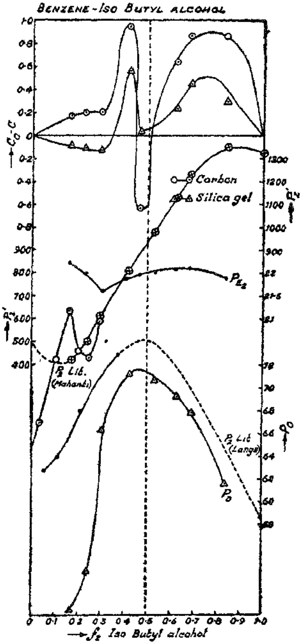


Fig. 12

The selective adsorption curves for both silica gel and activated carbon are of twisted shape. For silica gel, the curve passing through almost a constant value up to 0.1 mol reaches a maximum value at 0.23 mol. The value suddenly drops from here to 0.33 mol after which the curve takes a 'S'-shaped form passing through zero adsorption of 0.66 mol ethylene dibromide.

TABLE XIX

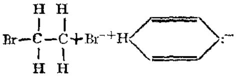
Adsorption

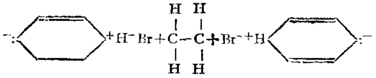
System Benzene Ethylene Dibromide

New Results			Preliminary Results		
$f_{C_2H_4Br_2}$	Sample 1 $C_0 - C_1$	Sample 2 $C_0 - C_1$	$f_{C_2H_4Br_2}$	Sample 1 $C_0 - C_1$	Sample 2 $C_0 - C_1$
		(*a*) *Activated Coconut Shell Charcoal*			
0·81	0·00	−0·45	0·61	−0·47	−0·30
0·65	−0·16	−0·26	0·50	−1·13	+0·20
0·58	−0·47	−0·12	0·38	−0·41	−0·53
0·47	−0·88	0·35	0·34	−0·35	−0·03
0·33	0·85	0·51	0·22	0·00	−0·75
0·23	0·00	1·02	0·15	0·26	..
0·12	0·40	..			
0·07	0·21	..			
		(*b*) *Silica Gel*			
0·81	−0·44	..	0·61	−0·03	..
0·65	+0·08	..	0·50	0·41	..
0·58	0·55	..	0·38	0·44	..
0·47	0·53	..	0·34	−0·35	..
0·33	0·34	..	0·22	0·00	..
0·23	0·85	..	0·15	0·35	..
0·12	0·13	..			
0·07	0·15	..			

The curve for activated carbon, rises steadily in dilute solutions $C_2H_4Br_2$ up to about 0.23 mol, then comes down. A change of slope is observed at about 0.5 mol and 0.66 mol, the curve being similar to that of silica gel.

The possible structures of the compounds are given below:—





(9) System Benzene-*iso*-Butyl Alcohol

The measurements of dielectric constant of the system benzene *iso*-butyl alcohol have been carried out by Lange (*Z. Phys.*, 1925, **33**, 169) and by Mahanti (*Jour. Ind. Chem. Soc.*, 1929, **6**, 743). Lange finds that the polarisation varies linearly with concentration in dilute solutions. No measurements have been carried out between 0.35 and 1.00 alcohol in which region the authors find the polarisation value decreasing with concentration. Lange obtains a value of 58 c.c. (P_2) for pure alcohol, showing that the P_2 values in concentrated solutions would decrease.

The molecular polarisation P_2 was calculated by the authors from the dielectric polarisation P_{12} from Mahanti's values for *iso*-butyl alcohol. The values in the very dilute region rise first, then drop and then rise again in the region studied from 0.0 mol to 0.3 mol alcohol. The polarisation curve of the authors lie between the curves obtained by Lange and by Mahanti. The discrepancy in the values by the different authors might be due to the molecular polarisation P_1 assigned to benzene. The deviation from the linear law of molecular polarisation has been explained by Mahanti as due to associated molecules.

EXPERIMENTAL

(1) *Polarisation.*—The dielectric constants of various mixtures of *iso*-butyl alcohol in benzene was carried in a way similar to that explained in a previous part at 25° C. The refractive index of mixtures was measured and P_E calculated is given in the Table XX, the polarisation values are given in Table XXI and the molecular polarisation P_2 represented graphically in Fig. 12.

TABLE XX

f_2	n_{546}	$d_{25/4}$	P_{E12}	P_{E2}
0·840	1·40610	0·8087	22·67	21·9
0·683	1·42639	0·8195	23·55	22·1
0·626	1·43241	0·8238	23·78	22·1
0·532	1·44193	0·8301	24·18	22·0
0·470	1·44845	0·8314	24·44	22·0
0·423	1·45334	0·8377	24·63	21·9
0·304	1·46630	0·8472	25·11	21·6
0·238	1·47420	0·8486	25·52	22·0
0·168	1·48184	0·8577	25·69	22·3

The polarisation P_2 curve rises linearly with concentration upto about 0.4 mol alcohol, after which the curve comes down. The electronic polarisation P_{E_2} calculated from the refractive index of mixtures remains sensibly constant but shows marked deviation, at about 0.3 mol alcohol.

TABLE XXI

^{2}*iso*-BuOH	ϵ_{25}	$d_{25/4}$	D.C.M.			New Law	
			P_{12}	P_2	P_0	P'_{12}	P'_2
1·00	15·5	..	..	..	..	.	1328
0·840	13·54	0·8087	74·47	83·58	61·67	1157	1356
0·683	10·53	0·8195	69·85	89·91	67·79	875	1233
0·626	9·24	0·8238	67·18	91·41	69·33	755	1131
0·532	7·27	0·8301	61·81	92·76	70·73	573	980
0·423	5·43	0·8377	54·79	93·21	71·30	407	812
0·304	3·92	0·8472	44·70	86·08	64·44	265	617
0·238	3·28	0·8486	39·20	79·49	53·97	207	502
0·168	2·85	0·8577	34·39	72·85	50·59	167	426

The same results when calculated by the New Equation give a different type of curve. The polarisation remains constant in concentrated region and drops linearly with dilution in the region where D.C.M. procedure gives a maxima. The anomalous nature of the alcohols will be discussed in a later paper.

(2) *Adsorption.*—The selective adsorption measurements of this system by silica gel and activated coconut shell charcoal were carried out in the manner described previously. The values of the apparent selective adsorption are given in Table XXII.

TABLE XXII

f_2	Silica gel $C_0 - C_1$	Carbon $C_0 - C_1$
0·84	−0·30	−0·87
0·683	0·45	0·87
0·626	0·24	0·64
0·470	0·03	−0·62
0·423	0·56	0·95
0·304	−0·12	0·21
0·238	−0·11	0·21
0·168	−0·08	0·08

The selective adsorption for silica gel is negative and zero at 0.33 mol and at 0.5 mol respecting. The curve rises to a maximum at about 0.75 mol alcohol.

For carbon the curve starts with positive values which sharply rise at about 0.34 mol. dropping sharply to negative value at 0.5 mol. The broad maxima in the region of 0.75 mol is noteworthy.

The adsorption by both silica gel and carbon taken along with the results of polarisation show the possibility of formation of compounds of benzene and *iso*-butyl alcohol in the ratio 2 : 1, 1 : 1 and 1 : 2 or 3 either in the binary liquid system or on the surface of the adsorbent, or both.

Summary

According to Pauling (*The Nature of the Chemical Bond*, p. 267), only the most electronegative atoms form hydrogen bonds. The strength of the bond increases with the increase in the electronegativity of the two bonded atoms.

The electronegativity of phenyl group should make one of the hydrogen bonds positive, which should thus be capable of forming a bond with oxygen and halogens. In the present paper the authors have presented data to show the formation of complexes or definite compounds of benzene, with alcohols and halogenated compounds, giving a strong indication that one or two of the hydrogens in benzene is or are of bridge-forming character.

The most important evidence for the formation of compounds and complexes of benzene with alcohols and halogen compounds is to be found in the study of the dielectric polarisation and the electronic polarisation in benzene as solvent. The classical example of the increase in the electric moment of ethylene dichloride and ethylene dibromide and the decrease of the moment of alcohols in benzene can be explained on the basis of a complex formation. In concentrated solution the apparent polarisation curves show marked discontinuities at points of molecular compositions. These findings would indicate that the dipole moments determined in dilute solutions of benzene owing to the effect of mass law, referred to the moment of the complex and not of the solute.

The molecular polarisation P_2 and the electronic polarisation P_{E_2} of the polar component, selective adsorption by silica gel and activated coconut shell charcoal, in the entire range of concentration have been studied with a view to throw light on the problem. The systems investigated are:—(1) Benzene-Carbon tetrachloride, (2) Benzene-Chloroform, (3) Benzene-Methylene dichloride, (4) Benzene-Ethylene dichloride, (5) Benzene-Ethylene dibromide, (6) Benzene-Chlorbenzene, (7) Benzene-*tert.* Butyl chloride, (8) Benzene-*iso*-Amyl bromide, and (9) Benzene-*iso*-Butyl alcohol.

It has been found that highly anomalous apparent polarisation P_2 in concentrated solutions goes hand in hand with the still more marked anomalous selective adsorption at compositions corresponding to the possible molecular complexes.

The indirect confirmation of the complexes of molecular composition comes from the study of the adsorption from the binary mixtures in the region where complexes are formed. The apparent selective adsorption curve shows very marked change in the slope of the curve. Most of the curves are of 'S'-type and are highly anomalous. It would appear that the surface of the adsorbent by its property of exhibiting oriented adsorption forms highly favourable seat for forming molecular complexes.

The apparent selective adsorption curves indicate all the possible ways by which the C-H and the halogen bonds can unite.

The authors explain these results by postulating a C-H-aromatic-C-halogen or oxygen bonding. The fact that the infra-red spectra in benzene shows a frequency in the region of 2900 $cm.^{-1}$ corresponding to C-H bond, the normal frequency of which is about 3050 $cm.^{-1}$ indicated by its Raman and infra-red spectra, indicates a weak hydrogen bond in benzene.

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