STUDIES IN BINARY SYSTEMS

PART VIII.—SYSTEM BENZENE—CARBON TETRACHLORIDE

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In the previous parts it was shown from a study of both physical properties and selective adsorption measurements that complexes were formed between a polar and a non-polar liquid. It was interesting to study the behaviour of mixtures of two non-polar liquids benzene and carbon tetrachloride which are known to form a definite compound.

The freezing point of binary mixtures of carbon tetrachloride and benzene were investigated by Baud (*Ann. de Chem. and de Phys.*, 1913, **VIII**, 29, 124) who found the formation of 1 : 1 complex as indicated by the freezing point-composition curve. Williams and Krchma (*J. Amer. Chem. Soc.*, 1927, **49**, 2408) showed that the polarization varied directly with concentration. The frequency used in the measurement of the dielectric constant was of the order of 10^6 cycles.

B. S. Rao (*J. Phys. Chem.*, 1932, **36**, 616) obtained a 'U' type of curve for the system benzene carbon tetrachloride and *silica gel*, only one mixture having been studied between zero and 50% of carbon tetrachloride and no mixtures were studied near 65% composition corresponding to the formation of 1:1 compound.

E. Heymann and E. Boye (*Kolloid Z.*, 1933, **63**, 154-65) obtained an 'S' type curve which showed a zero selectivity at 0·2 moles of carbon tetrachloride by adsorption on *silica gel*, corresponding to CCl_4 $4C_6H_6$ complex. The selectivity curve was flat in the region 0·4 to 0·6 moles which is in agreement with the results of the authors.

Venkatnarsimhachar and Doss (*Ind. Acad. Sci.*, 1937, **6**, 33), found zero selectivity at about 65% carbon tetrachloride which corresponds to 1 : 1 complex when *alumina gel* was used. A study of their results when *ferric oxide* gel was used, however, indicated that the curve was of the usual U-type with a maximum between 70 – 80% carbon tetrachloride. The authors explained their results on the basis of the assumption of attraction between the alumina and chlorine atoms of the adsorbed liquid and suggested that the S-type curve is probably caused by the preferential adsorption of the latter. They mentioned similar findings in the case of the system pyrindine-water-silica gel.

The adsorption of this system on carbon does not appear to have been studied previously. In the present investigation the authors have studied the dielectric constant of different mixtures of benzene

System Benzene-Carbontetrachloride

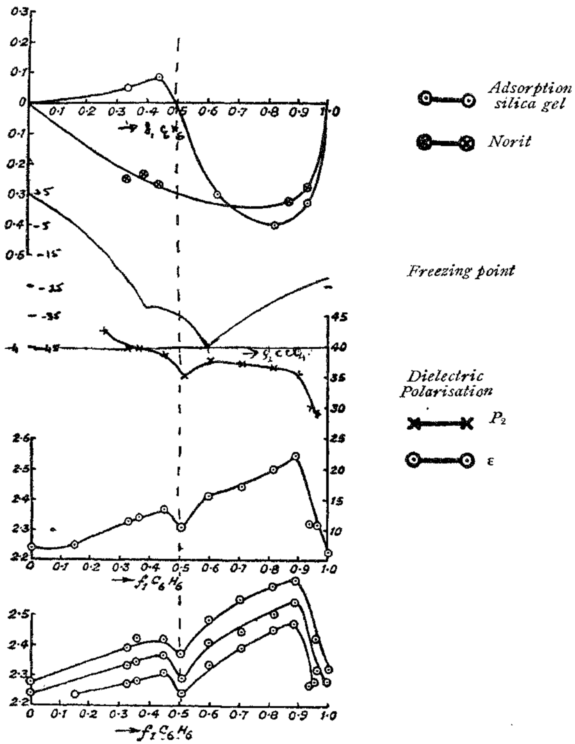


FIG. I

and carbon tetrachloride at different frequencies and also the selective adsorption of the components by silica gel and carbon.

EXPERIMENTAL

(*a*) In the present investigation the authors have carried out the dielectric constant measurements at a number of frequencies from 23·6 to 10,000 Kcs.

The apparatus used for the measurement of the dielectric constant of the system benzene-carbon tetrachloride at various frequencies was similar to that described in part VI. Piezo-electric quartz oscillators whose frequencies were known very accurately were used during these experiments.

The values of the measurements of the dielectric constants at different frequencies and the polarization P_2 of benzene calculated from the dielectric constants at 473 kc are given in the following tables: (Tables I and II) and represented in fig. I.

TABLE I

Dispersion of Dielectric constants of mixtures of Benzene and Carbontetrachloride

Kc. f_1 Benzene	23·6	49·47	473	1350	1841·5	1829	3644	3750	7155	10000
0·0	—	—	2·24	2·17	2·20	—	2·21	—	2·28	2·24
0·15	2·24	2·24	2·25	2·27	2·26	2·28	2·27	—	2·46	2·33
0·33	2·27	2·27	2·33	2·24	2·33	2·37	2·33	—	2·39	2·38
0·36	2·28	2·28	2·34	2·33	2·33	—	2·33	—	2·42	2·40
0·45	2·31	2·31	2·37	2·34	2·41	2·41	2·35	—	2·42	2·40
0·51	2·24	2·24	2·29	2·30	2·29	—	2·29	—	2·37	2·42
0·60	2·34	2·34	2·41	2·38	2·46	2·46	2·42	2·41	2·48	2·45
0·71	2·39	2·39	2·44	2·42	2·48	—	—	2·47	2·55	2·49
0·82	2·45	2·45	2·50	2·49	2·53	—	2·49	—	2·59	2·55
0·89	2·47	2·47	2·54	2·51	2·56	—	—	2·55	2·61	—
0·94	2·27	2·27	2·32	2·33	2·38	—	2·33	2·33	2·40	2·37
0·96	2·28	2·28	2·32	2·54	2·38	—	—	—	2·42	2·37
1·0	—	—	2·28	2·24	—	—	2·11	2·34	2·32	2·18

With increase in the percentage composition of carbon tetrachloride the dielectric constant rises and falls to a minimum at about 10% and then rises to a sharp maxima at 20% carbon tetrachloride where the complex $CCl_4\ 4C_6H_6$ might exist. With further increase in concentration, dielectric constant decreases linearly with composition until a sharp minima is reached at the composition $C_6H_6\ CCl_4$. On further addition of carbon tetrachloride dielectric constant again rises and falls down as the value for pure carbon tetrachloride is reached. The minima in the dielectric constant at 0·5 mole and also that reached at 10% concentration may be due to the fact 1:1 complex which exists in those solutions has least polarization. The effect of frequency on the dielectric constant is the same at all frequencies in the range studied.

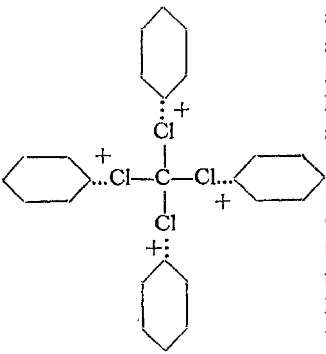
TABLE II

Polarization of the system Benzene—Carbon tetrachloride

f_1 (C_6H_6)	Dielectric Constant (473 K.c.)	P_{12}	P_2 (C_6H_6)
0·0	2·24	27	43
0·15	2·25	29	40
0·33	2·33	31	90
0·36	2·34	31	39
0·45	2·37	32	35
0·51	2·29	31	38
0·60	2·41	33	37
0·71	2·44	34	37
0·82	2·50	35	35
0·89	2·54	35	30
0·94	2·32	30	29
0·96	2·32	29	...
1·0	2·28	27	...

The increase in the polarization of benzene at high concentrations in carbon tetrachloride is due to the compound formation. A similar result has been observed for the dipole moment of *S* trinitro-benzene in benzene for which a difinite moment $0{\cdot}8 \times 10^{-18}$ is observed. This would mean that two molecules unite to form a highly polar compound because of the introduction of an additional semi-bond, which contribute to the dipole moment of the molecule. We shall take up this matter in a later communication.

The existence of the complex C_6H_6 CCl_4 is born out by cryoscopic measurement. The complex between benzene and carbon tetrachloride has been made evident from negative fluidity deviation, a small volume contraction and also a small heat of adsorption. The formation of a complex between one molecule of carbon tetrachloride and 4 of benzene is probable on structural grounds as shown in the following figure. The high polarization may as well be due to close packing of the molecules at that particular composition with Van-der-Waal forces, or due to a degeneracy of the hydrogen bond in benzene if as is well known benzene possesses a weak CH frequency as revealed by light scattering which may form a loose linkage with each of the chlorine atom of the carbon tetrachloride.



(*b*) *Adsorption.*—Definite amounts of the various mixtures of carbontetrachloride and benzene were shaken with 3% of the adsorbent and the mixtures were kept for over 4 hours for attaining equilibrium and then centrifuged. The adsorption was calculated by measuring the change in the refractive index on a Pulfrich Refractometer, the usual precautions being taken. The results are given in the following table and shown graphically in fig I.

It can be seen that both the dielectric constant-composition curve and the polarization-concentration curve reach a maximum at about 0·1 mole fraction of carbon tetrachloride. The curves show a maximum on one side of the composition diagram on account of the fact that the formation of the complex is complete near that composition owing to the effect of mass law a conclusion which the authors have arrived at also by a study of adsorption from binary system.

TABLE III

Norit		Silica gel	
Cf	$C_0-C\%$	Cf	$C_0-C\%$
·94	−0·28	·94	−0·33
·87	−0·32	·82	−0·40
·44	−0·27	·63	−0·3
·39	−0·24	·44	+0·08
·34	−0·25	·34	+0·05

The shape of the adsorption curve at either end of the concentration axis are modified not by existence of any polymers of the components which are both non-polar but more by the formation of perhaps more than one complex in the system which appear to be preferentially adsorbed than either of the components. Thus in the case of both norit and silica gel the minima in the selective adsorption at about 0·25 moles fraction carbon tetrachloride would appear to indicate the formation of the complex CCl_4 $4C_6H_6$ as one of the points falls on the other side of the curve at about 0·2 moles fraction carbon tetrachloride. It would be interesting to confirm this by conducting a careful measurement of the other physical properties of this binary system. It is significant to point out that the measurement of dielectric constant of this system have also shown anomalies similar to those mentioned above.

Silica gel shows a zero adsorption at 0·5 mole carbon tetrachloride as in the case of alumina gel investigated by Venkatnarsimhachar and Doss (*loc. cit.*) while carbon shows a flat maximum in the same region. At about 0·33 moles carbon tetrachloride corresponding to the formation of $2C_6H_6$ CCl_4, the curves for both silica gel and carbon pass through a minimum.

Thus the anomalous nature of the adsorption from the binary mixtures of two entirely non-polar liquids is due certainly to the formation of the complex of the molecular composition, and polarization (P_2) curve is in agreement with the finding from the freezing point diagram.

In dilute solutions of carbon tetrachloride, the selective adsorption curves for both silica gel and carbon pass through a steep negative maxima and show that benzene is more polar compared to carbon tetrachloride. The shape of the curve from 0·3 to 0·6 moles fraction carbon tetrachloride is rather complicated and is difficult to explain by the nature of the adsorbents. As pointed out above, it may be due to the formation of complexes. After this region the curve is smooth and the selective adsorption decreases for the same reason given for other cases like benzene-acetic acid. (*Cf.* next part.)

SUMMARY

Although benzene and carbon tetrachloride are both non-polar substances, in binary liquid mixtures they appear to form co-ordination compound CCl_4 C_6H_6 (I) and CCl_4 $4C_6H_6$ (II), the hydrogen bond being degenerate CH linkage which is revealed in light scattering. The complex (I) is shown by the cryoscopic study. Molar polarization P_{12} and polarization P_2 showed a sharp minimum at the compsition 1 : 1.

The selective adsorption curve by silica gel indicates that benzene is adsorbed in moderate concentrations and carbon tetrachloride in concentrated solutions, the curve passing through zero selective adsorption at 0·5 moles composition (I).

The complex (II) appears to be indicated by maxima in the selective adsorption of carbon tetrachloride by both norit and silica gel and by maxima in the dielectric constant curves at different frequencies.

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