1. Self-association and Hydration of Phenol in Carbon Tetrachloride.

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Measurements have been made of the distribution of phenol between water and carbon tetrachloride and the solubility of water in solutions of phenol in carbon tetrachloride at various water activities at 25°. The results support the following conclusions:

(a) Species of phenol having a molecular weight greater than that of the dimer exist in substantial concentrations in the carbon tetrachloride solutions investigated. The trimer is almost certainly one of the major species.

(b) The monomer monohydrate and the trimer monohydrate are probably the major hydrated species present at formal concentrations of phenol in carbon tetrachloride less than about 0·15 formal weight per litre. At higher concentrations of phenol, hydrated species are present in which more than one water molecule is attached to an aggregate of phenol molecules.

Self-association and hydration equilibrium constants are reported for the reactions occurring in the organic phase.

IN recent reports from this laboratory [1-3] methods have been described for studying the hydration and self-association of polar solutes in organic solutions, using both partition data and water solubility data obtained at arbitrary water activities. We have applied these techniques in a study of the system carbon tetrachloride–water–phenol at 25°, with the object of elucidating further the nature of phenol aggregates and hydrates which exist in the carbon tetrachloride phase.

EXPERIMENTAL AND RESULTS

The partition of phenol between water and carbon tetrachloride at 25·0 ± 0·1° was studied with techniques similar to those described previously.[2] The phenol was purified by two distillations at reduced pressure; the middle fraction was collected each time. To reduce the probability that the phenol might decompose on standing, all samples were stored in the dark and used within four weeks following preparation. Carbon tetrachloride was purified by distillation through a 30-plate Oldershaw column.

All solutions were analysed spectrophotometrically for total phenol. Absorbance at the peak wavelength, 268 mμ, was measured with a Beckman DU Spectrophotometer, using 1 cm. cells and a slit width of 0·1 mm. Beer's Law dependence was observed for spectral measurements obtained throughout the concentration range 10^{-4} to 10^{-3} mole/l. Solutions of phenol of known concentration were prepared by dilution of two standard solutions which had been prepared separately by weight from purified crystalline phenol. The solutions were standardized independently by a bromination analysis.[4] Concentrations of phenol determined by bromination differed less than 0·2% from those calculated from the weights of the pure components.

[1] Christian, Affsprung, and Johnson, *J.*, 1963, 1896.

[2] Christian, Affsprung, and Taylor, *J. Phys. Chem.*, 1963, **67**, 187.

[3] Christian, Affsprung, Johnson, and Worley, *J. Chem. Educ.*, 1963, **40**, 419.

[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 5th edn., 1939, p. 2253.

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In the partition experiments, samples of each phase were diluted to concentrations in the range 10^{-4} to 10^{-3} mole/l. Samples were withdrawn from the carbon tetrachloride phase in a unique manner. Approximately 30 min. before sampling, a glass tube having a thin bulb on one end was introduced into the partition system, with the bulb resting on the bottom of the flask, in the carbon tetrachloride phase. To obtain a sample of the denser phase, the bulb was broken from the inside with a glass rod, and a pipette was inserted through the tube.

Equilibrations of the phenol-carbon tetrachloride solutions at reduced water activities at $25 \cdot 0 \pm 0 \cdot 1°$ were made as described earlier.[3] The concentration of water in the carbon tetrachloride phase was determined by means of a Beckman KF-3 Aquameter; in all instances, 50 ml. samples were analysed. The Karl Fischer reagent was standardized with Fisher Certified Grade sodium tartrate dihydrate. The purity of the standard tartrate was checked by measuring the loss of weight of the compound on heating to 120°; results deviated less than 0·2% from the theoretical weight loss predicted from the formula, $Na_2C_4H_4O_6,2H_2O$.

Fig. 1 represents partition data for the system carbon tetrachloride-water-phenol at 25°; the ratio of the formal concentration of phenol in carbon tetrachloride, f_P^0, to the concentration
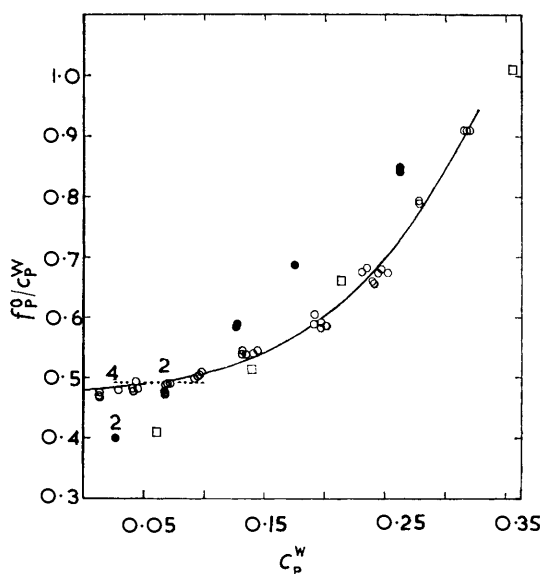

FIG. 1. Partition data for the system carbon tetrachloride–water–phenol. Curve is calculated; points are experimental.

$\bigcirc$, Badger and Greenough; $\square$, Herz and Rathmann; – – – –, Philbrick.

of phenol in water, c_P^W, is plotted against c_P^W. For comparison, partition data at 28° reported by Badger and Greenough [5] and the results of Philbrick [6] and of Herz and Rathmann [7] at 25° are plotted in the same Figure. In the discussion that follows it is assumed that phenol exists solely as the un-ionized monomer in the aqueous solution; consequently, the symbol c_P^W represents both the formal concentration of phenol and the concentration of the monomer in the water-rich phase. Throughout, the symbol f will be used to denote formal concentration of a compound (in formula weights/l.) and c will indicate the concentration of an individual species (in mole/l.). Philbrick's measurements are represented by a broken line, rather than by points, since he reported only a single value of the ratio, f_P^0/c_P^W, which he observed to be constant to within 1% throughout the range of concentrations included in his investigation.

Fig. 2 illustrates the dependence of the formal concentration of water in the carbon tetrachloride phase, f_W^0, on f_P^0 at several water activities, a_W. Water solubility data reported by Badger and Greenough for solutions of phenol in carbon tetrachloride at 28° are included in the Figure. In Fig. 3, the solubility of water in pure carbon tetrachloride is plotted against a_W.

[5] Badger and Greenough, *J. Phys. Chem.*, 1961, **65**, 2088.
[6] Philbrick, *J. Amer. Chem. Soc.*, 1934, **56**, 2581.
[7] Herz and Rathmann, *Z. Elektrochem.*, 1913, **19**, 553.

DISCUSSION

The association of phenol in carbon tetrachloride has been investigated by numerous workers.[5,8-14] However, there is no general agreement concerning the molecular complexity of associated phenol species in solution. Several investigators have postulated monomer–dimer equilibrium [5,8-11,14] and others have proposed monomer–trimer equilibrium [12,13] to explain spectral, colligative and partition data for dilute solutions.

Badger and Greenough [5] have shown that the formal solubility of water in carbon tetrachloride increases markedly as the concentration of phenol increases. They report partition and spectral data to support the argument that hydrated and unhydrated phenol dimers are the major associated species present in carbon tetrachloride solutions at phenol concentrations less than about 0·3 formal.

The positive curvature of the plot in Fig. 1 indicates that associated phenol species of higher molecular weight than the dimer are present throughout most of the concentration range represented. While it is not possible to assert that the slope of the f_P^0/c_P^W curve approaches zero at low values of c_P^W (as would be required were the dimer completely absent) it is evident that the limiting slope of the curve is considerably smaller than slopes corresponding to c_P^W values in excess of 0·1 molar. In this connexion, it is worth noting that Philbrick could detect no systematic variation in the ratio f_P^0/c_P^W throughout the concentration range $0·02 < c_P^W < 0·10$ mole/l.; in fact, he was inclined to disbelieve his data because the distribution ratio did not vary with concentration as in the systems benzene–water–phenol, toluene–water-phenol and other partition systems which he had studied.

We were able to fit the partition data quite well over the entire range of concentration by assuming that only monomers, trimers and hexamers of phenol exist in the carbon tetrachloride phase. The solid curve in Fig. 1 has been calculated from the relation

$$f_P^0/c_P^W = 0·481 + 2·53 \, c_P^{W^2} + 55·2 \, c_P^{W^5} \tag{1}$$

which is a least squares equation representing experimental values of the ratio f_P^0/c_P^W, with a standard deviation of 0·0109. Least squares constants were calculated for other possible combinations of the exponents in equations of the form

$$f_P^0/c_P^W = \alpha + \beta \, (c_P^W)^{m-1} + \gamma \, (c_P^W)^{n-1} \tag{2}$$

Table 1 lists the standard deviation of experimental f_P^0/c_P^W values and the least squares coefficients for several choices of the exponents m and n.

It is obvious that no satisfactory fit of the data in Fig. 1 can be obtained unless a value greater than 3 is selected for at least one of the exponents m and n. The dimer does not appear to be an important species, inasmuch as the monomer–dimer–trimer combination requires a negative value for β, and the monomer–dimer–tetramer combination leads to a fit of the data not significantly superior to that given by the monomer–tetramer combination. In fact, using the parameters in Table 1 for the m = 2, n = 4 combination, it can be calculated that the formal dimer concentration is less than 5% of f_P^0 throughout the range of concentrations studied. All of the combinations monomer–tetramer, monomer–trimer–tetramer, monomer–trimer–pentamer and monomer–trimer–hexamer lead to standard deviations compatible with the scatter of partition data estimated graphically. However, the combination monomer–trimer–hexamer was selected as being the most plausible physically.

[8] Coggeshall and Saier, *J. Amer. Chem. Soc.*, 1951, **73**, 5414.
[9] Kempter and Mecke, *Z. phys. Chem.*, 1940, B**46**, 229.
[10] Thiel, Becker, and Pimentel, *J. Chem. Phys.*, 1957, **27**, 95.
[11] Huggins, Pimentel, and Shoolery, *J. Phys. Chem.*, 1956, **60**, 1311.
[12] Saunders and Hyne, *J. Chem. Phys.*, 1958, **29**, 1319.
[13] Rea (private communication), Pimentel and McClellan, " The Hydrogen Bond," W. H. Freeman and Co., San Francisco, 1960, p. 432.
[14] Maguire and West, *Spectrochim. Acta*, 1961, **17**, 369.

TABLE 1.

Least squares parameters for equation (2).

Postulated species	m	n	α	β	γ	Standard deviation
Monomer–dimer	2	—	0·416	1·15	—	0·0467
Monomer–trimer	3	—	0·467	3·89	—	0·0226
Monomer–tetramer	4	—	0·489	13·25	—	0·0131
Monomer–pentamer	5	—	0·504	43·6	—	0·0232
Monomer–dimer–trimer	2	3	0·499	−0·60	5·74	0·0174
Monomer–dimer–tetramer ...	2	4	0·479	0·127	12·0	0·0124
Monomer–trimer–tetramer ...	3	4	0·485	0·624	11·2	0·0126
Monomer–trimer–pentamer ...	3	5	0·483	2·03	22·0	0·0114
Monomer–trimer–hexamer ...	3	6	0·481	2·53	55·2	0·0109

It was assumed in all calculations that the free water present in the organic phase exits solely as monomers. In a previous communication [1] we claimed that water dissolves in benzene primarily as the monomer. This contention was supported by the observed
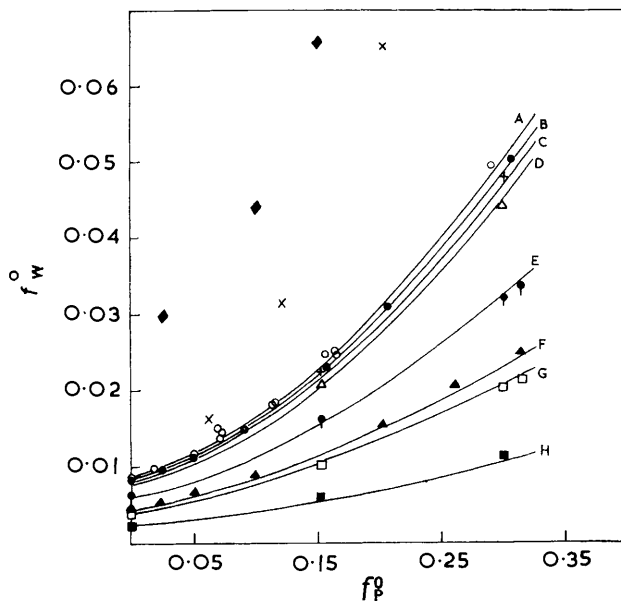

FIG. 2. Formal solubility of water in solutions of phenol in carbon tetrachloride at various water activities. Curves are calculated, points are experimental. Data at: A: $a_W = 1·0$; B: $a_W = 0·97$; C: $a_W = 0·945$; D: $a_W = 0·89$; E: $a_W = 0·69$; F: $a_W = 0·52$; G: $a_W = 0·47$; H: $a_W = 0·26$. Data of Badger and Greenough: spectral, ×; turbidity measurement, ◆.

linearity of a plot of formal concentration of water in benzene against water activity. The apparent linearity of the plot in Fig. 3 indicates that water is also primarily monomeric when dissolved in carbon tetrachloride.

In computing hydration constants from the water solubility data represented in Fig. 2, we attempted to postulate the minimum number of hydrate species required to reproduce the data.* It was sufficient to assume the existence of the phenol monomer monohydrate, PW, and the trimer monohydrate, P_3W, to explain the f_W^0 *vs.* f_P^0 data corresponding to phenol concentrations less than 0·15 formal at all water activities. However, in order to explain the water solubilities at the higher water activities and phenol concentrations, it

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* Note that the form of equation (1) is consistent with the assumption that the only hydrated species of phenol present in carbon tetrachloride are the monomer, trimer and hexamer. The choice of exponents in equation (2) other than m = 3, n = 6 would, of course, lead to a different set of assumed hydrate species and hydration equilibrium constants.

was necessary to postulate the existence of hydrated phenol species containing more than three phenol molecules. Excellent agreement with data could be obtained by assuming the important hydrate species to be either (a) PW, P_3W and P_6W_4 or (b) PW, P_3W, P_3W_2 and P_6W_3. Although combination (a) involves one less hydrate species than combination (b), the latter combination was selected as being physically more plausible.

Table 2 lists self-association and hydration constants used in calculating all the solid curves in Figs. 1 and 2. This set of constants is sufficient to explain the entire collection of partition and water solubility data reported here.

To calculate the theoretical curves in Figs. 1 and 2, it is convenient to use the following equations:

$$f_P^0 = c_P^0 + K_{PW}c_P^0 c_W^0 + 3K_{P_3}c_P^{03} + 3K_{P_3W}c_P^{03}c_W^0 + 3K_{P_3W_2}c_P^{03}c_W^{02} + 6K_{P_6}c_P^{06}$$
$$+ 6K_{P_6W_3}c_P^{06}c_W^{03}$$

and

$$f_W^0 = c_W^0 + K_{PW}c_P^0 c_W^0 + K_{P_3W}c_P^{03}c_W^0 + 2K_{P_3W_2}c_P^{03}c_W^{02} + 3K_{P_6W_3}c_P^{06}c_W^{03}.$$

A value of a_W is selected, and the corresponding value of c_W^0 is calculated from the expression $c_W^0 = 0.0087\ a_W$ (moles/l.). Arbitrary values of c_P^0 are selected, and simultaneous values of f_P^0 and f_W^0 are computed, using the constants in Table 2.

FIG. 3. Formal solubility of water in carbon tetrachloride as a function of water activity.
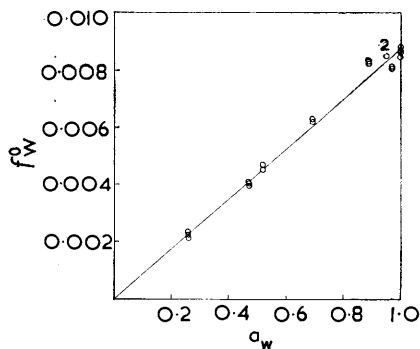
The trimerization constant, $K_{P_3} = 4.1$ (mole/l.)$^{-2}$, obtained in the present study agrees reasonably well with the values 4.78 (mole/l.)$^{-2}$ at 21° reported by Saunders and Hyne,[12] and 13.6 and 8.9 (mole/l.)$^{-2}$ at 20 and [30°, respectively, given by Rea.[13] The reported monomer hydration constant, $K_{PW} = 5.75$ (mole/l.)$^{-1}$, is of the same order of magnitude as equilibrium constants previously reported for the formation of many 1 : 1 hydrogen-bonded complexes in non-polar solvents.[15]

TABLE 2.

Self-association and hydration constants for phenol in carbon tetrachloride.

Reaction	Equilibrium constant
P (aqueous phase) = P (CCl$_4$ phase)	$K_D = 0.458$
P + W (CCl$_4$ phase) = PW (CCl$_4$ phase)	$K_{PW} = 5.75$ (l./mole)
3P (CCl$_4$ phase) = P$_3$ (CCl$_4$ phase)	$K_{P_3} = 4.1$ (l./mole) [2]
3P + W (CCl$_4$ phase) = P$_3$W (CCl$_4$ phase)	$K_{P_3W} = 443$ (l./mole) [3]
3P + 2W (CCl$_4$ phase) = P$_3$W$_2$ (CCl$_4$ phase)	$K_{P_3W_2} = 9900$ (l./mole) [4]
6P (CCl$_4$ phase) = P$_6$ (CCl$_4$ phase)	$K_{P_6} = 432$ (l./mole) [5]
6P + 3W (CCl$_4$ phase) = P$_6$W$_3$ (CCl$_4$ phase)	$K_{P_6W_3} = 8.6 \times 10^8$ (l./mole) [8]

We believe that the experimental methods applied here to the system carbon tetrachloride–water–phenol may be applied profitably to many other systems involving polar species which form hydrates in an organic medium. With the simple and inexpensive water equilibration apparatus used in this study,[3] organic solutions can be brought to a

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[15] Reference (13), Appendix C, pp. 365—386.

known water activity in a matter of a few hours. Partition data for a polar solute can be interpreted meaningfully, provided that water solubility data are available for a range of water activities. However, in the absence of water solubility data, we believe the partition method is virtually worthless as a technique for obtaining self-association constants for hydrogen-bonding solutes.

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