Jahns[10] for the Type II double hydrates. No such correlation was observed with the front reflexion data but it was possible that a small effect had been masked by the error of measurement (σ = 0.03 to 0.10 A). Accordingly, more precise lattice parameters were obtained by taking back-reflexion photographs of new samples. A linear trend was observed when the lattice parameters were plotted against melting points, an observation interesting in itself. Once again there is no marked correlation with van der Waals diameters although it is probably significant that TMO and E, the hydrates of which differ from the others have, respectively, the smallest and largest diameters.

The two sets of measurements at 110 and 135°K yield rough values for the mean coefficient of expansion $\alpha = \Delta a / a \Delta T$. The values lie in the range 30–150 $\times$ 10^{-6} with an average value of 80 as compared to values of 23 $\times$ 10^{-6} ($\|C$) and 32 $\times$ 10^{-6} ($\perp C$) for ice at 110°K.[15] The variation in values is probably due to the low accuracy of the values at 110°K. Using an average value of 17.34 A for clathrate hydrates at 273°K,[7] one derives α = 75 $\times$ 10^{-6} for the range 110–273°K.

Conclusions

The hydrates of THF, DHF, CB, PO, DO, and TMO are all Type II. In the TMO–H$_2$O system there is a second hydrate. In the E–H$_2$O system the hydrate is not Type II. These differences between TMO and E and the other hydrates studied probably account for the differences in dielectric behavior observed by Davidson.[3–6]

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Hydration of Benzoic Acid in Diphenylmethane

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In previous communications from this laboratory, it has been reported that carboxylic acid molecules interact with water to form hydrated species in nonpolar solvents and in the vapor phase.[1–3] Partition and water solubility data have been analyzed to show that monomers of acetic and benzoic acids form hydrates in dilute solutions in benzene, but that the dimers of the acids show less tendency to associate with water. In order to obtain additional information about the stoichiometry and stability of hydrates of carboxylic acid species, we decided to investigate the interaction of water with a nonvolatile acid dissolved in a nonvolatile solvent; the solute chosen was benzoic acid and the solvent was diphenylmethane, which is quite similar in solvent properties to benzene and toluene. We report here water solubilities, partial pressures, and partition data for solutions of benzoic acid in diphenylmethane at 25°.

Experimental Section

Technical grade diphenylmethane was vacuum distilled through a 12-plate Oldershaw column. A constant-boiling fraction amounting to about the middle half of the sample was collected. The compound had a melting point of 24.6° under a vacuum and a refractive index of 1.5756 at 25°.

The vapor pressure apparatus and technique have been described previously.[4] Approximately 100 ml of a solution of benzoic acid in diphenylmethane was added initially to the 250-ml Florence flask serving as the solvent reservoir. Successive 0.010-ml samples of pure water were introduced through the mercury-covered sintered-glass disk inlet valve into the evacuated system, using a 0.2000-ml precision microburet (manufactured by Roger Gilmont Industries, Inc.), which was found to deliver 0.0100 ml to within ±0.0002 ml. After equilibrium was established (within 4 to 12 hr), the pressure indicated on the closed-end mercury manometer was measured with a cathetometer. Formal concentrations of benzoic acid in the reservoir were varied from 0 to approximately 0.3 M; the entire apparatus was immersed in the constant temperature water bath at 25.0 ± 0.1°.

In addition, the solubility of benzoic acid in diphenylmethane at 25° was determined at both zero and unit water activity. Samples of the solid acid were equilibrated with diphenylmethane in isopiestic cells of the type described previously.[5] Distilled water or solid

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desiccant was placed in a beaker suspended above a mixture of 100 ml of diphenylmethane and an excess of solid benzoic acid. The cell was closed from the atmosphere and submerged in a constant temperature bath for a period of about 14 days, during which time the solution was stirred intermittently. The dissolved acid was determined by titration with KOH.

A series of samples of benzoic acid was distributed between diphenylmethane and 1 M aqueous sodium benzoate at 25° in order to obtain partition ratios for the acid. The sodium benzoate served the dual purpose of repressing the ionization of the acid in the aqueous phase and increasing the rate of separation of the two phases after equilibrium.

Results and Discussion

In Figure 1, the partial pressure of water, p, is plotted against the formal concentration of water in solution, f_W, corresponding to various formal concentrations of benzoic acid, f_A. It is observed that the curve for which $f_A = 0$ is approximately linear, indicating that the primary water species in pure diphenylmethane is the monomer. Recent work performed in this laboratory indicates that small concentrations of associated water species are present at the higher water activities, but it is not believed that a correction for self-association is warranted with the data reported

Table I: Partition Data at 25° (Mole/Liter)

$C_A{}^W$	f_A	$C_A{}^W$	f_A	$C_A{}^W$	f_A
0.0126	0.0410	0.0242	0.1329	0.0321	0.2277
0.0126	0.0407	0.0245	0.1336	0.0320	0.2278
0.0191	0.0865	0.0284	0.1792	0.0352	0.2744
0.0191	0.0859	0.0284	0.1792	0.0352	0.2749

here. The p vs. f_W curves corresponding to increasing concentrations of benzoic acid are progressively lower; this implies that a considerable fraction of the dissolved water is involved in complexes with the acid.

The partition data, given in Table I, can be represented by the relation

$$f_A/C_A{}^W = 0.668 + 200.6 C_A{}^W \qquad (1)$$

with a root-mean-square deviation of 0.054 in $f_A/C_A{}^W$, where $C_A{}^W$ is the concentration of the acid in the aqueous phase (assumed to be present primarily as the monomer). The form of eq 1 is consistent with the assumption that only monomeric and dimeric benzoic acid species, both hydrated and unhydrated, are present in the organic phase.

In attempting to fit the data shown in Figure 1, various possible choices of hydrate species were proposed. The curvature of the p vs. f_W plots for $f_A > 0$ suggests that at least one hydrate species involving more than one water molecule must be present. Further, in order to explain the data, it is necessary to assume the presence of a hydrate of an associated species of benzoic acid. A reasonable fit of the data may be achieved by assuming that the only hydrate species present are the monomer dihydrate (AW_2) and the dimer monohydrate (A_2W). It is interesting to note that the root-mean-square deviation in f_W is not significantly reduced by assuming the monomer monohydrate (AW) to be present as well. It has been assumed that the acid monomer (A) and dimer (A_2) and the water monomer (W) are the only additional solute species present in the solutions investigated.

If Henry's law is obeyed by each solute species individually for the entire range of concentrations involved in this study, the relations

$$f_W = kp + K_{A_2W}c_A{}^2kp + 2K_{AW_2}c_A(kp)^2 \qquad (2)$$

and

$$f_A = c_A + 2K_{A_2}c_A{}^2 + K_{AW_2}c_A(kp)^2 + \\ 2K_{A_2W}c_A{}^2kp \qquad (3)$$

must be valid, where c_A is the concentration of the acid monomer and k is the reciprocal of the Henry's law constant for the water monomer in diphenylmethane. From the dependence of p on f_W in the solution containing no benzoic acid, the value $k = (1.12 \pm 0.01) \times 10^{-3}$ mole/(l. mm) is calculated; this leaves three unknown equilibrium constants (K_{A_2}, K_{AW_2}, and K_{A_2W}) in eq 2 and 3. However, the partition data represented by eq 1 provide an independent relation among the three equilibrium constants, and are particularly valuable in determining the value of K_{A_2}. It is possible to choose a tentative value of K_{A_2} and fit the solubility data by means of eq 2 and 3 to obtain values of K_{AW_2} and K_{A_2W}. This procedure can be repeated with other choices of K_{A_2} until the set of three constants best fitting all the solubility and partition data is obtained.

Methods for obtaining least-squares values of equilibrium constants have been described previously.[6,7] Given any trial set of values of K_{A_2}, K_{A_2W}, and K_{AW_2}, it is possible to calculate a value of c_A from eq 3 for each data set. Using these values of c_A, the root-mean-square deviation of f_W may be computed cor-
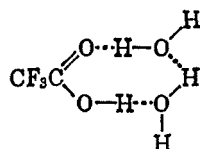
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responding to the selected values of the constants. The least-squares solution is obtained by minimizing the root-mean-square deviation with respect to both K_{A_2W} and K_{AW_2}; standard deviations of the equilibrium constants are calculated from the dependence of the root-mean-square deviation on variation of the constants in the vicinity of the absolute minimum. The solid curves in Figure 1 have been calculated using the least-squares values $K_{A_2} = 370 \pm 10$ l./mole, $K_{AW_2} = 483 \pm 21$ l.^{2}/mole^2, and $K_{A_2W} = 890 \pm 55$ l.^{2}/mole^2. The root-mean-square deviation in f_W for this set of constants is 0.000363 mole/l.; the constants are forced to be consistent with eq 1.

The solubility of benzoic acid in diphenylmethane at 25° increased from 0.377 ± 0.004 mole/l. at zero water activity to 0.412 ± 0.004 mole/l. at unit water activity. Based on values of K_{A_2} and the hydration constants reported above, the unit water activity value of the acid solubility is predicted to be 0.407 ± 0.004. Hence, the solubility data support the interpretation of the vapor pressure and partition results.

It is worth noting that a significant fraction of the complexed water is accounted for by the species AW$_2$, which becomes increasingly important at high water activities. Previously,[2] it was reported that trifluoroacetic acid interacts with water in the vapor phase to form the dihydrate, $CF_3COOH \cdot 2H_2O$, with a proposed structure

It is not unlikely that a similar cyclic dihydrate of benzoic acid is present in the solutions investigated in this study.

One somewhat surprising result of the calculations is the conclusion that the benzoic acid monomer monohydrate (AW) is apparently not an important species over the concentration range investigated. It might have been expected that the monomer hydration constant would be of the same order of magnitude as the equilibrium constant for the reaction $A_2 + W = A_2W$, which is $K_{A_2W}/K_{A_2} = 2.4$ l./mole, based on the analysis of data presented here. However, the acid monomer concentration does not exceed 0.019 M in any of the solutions investigated, and if K_{AW} were equal to 2.4 l./mole, the maximum concentration of AW would not exceed 0.0012 mole/l. at the highest water activities.

The value of K_{A_2} determined from the analysis of data (370 l./mole) is approximately equal to values
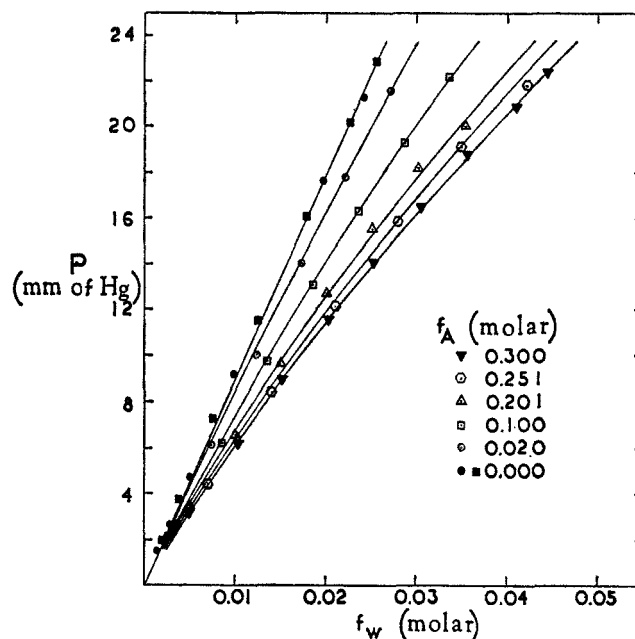

Figure 1. Partial pressure–solubility data.

previously reported for benzoic acid in benzene, most of which range from 490 to 625 l./mole at 25°.[3,8,9] This is an indication that diphenylmethane is a suitable nonvolatile analog of benzene with respect to its interaction with hydrogen-bonding solutes.

The solute vapor pressure method applied in the present study has several important advantages over vapor pressure and colligative property methods commonly used to investigate hydrogen bonding. In effect, the method is an "inverse" vapor pressure lowering technique. The activity of a solute is measured directly, rather than calculated indirectly from the change in solvent activity as in colligative methods. Excellent precision is attainable even with extremely dilute solutions, particularly for systems in which the solute has a low solubility and a relatively high volatility. Currently, several nonvolatile solvents are being employed in this laboratory as media for association reactions; a particularly promising solvent is hexachloro-1,3-butadiene, which is closely analogous to CCl$_4$ in its solution properties and is an excellent spectral solvent throughout most of the near-infrared region.

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