# 351. *The Molecular Complexity of Water as a Solute in Benzene.*

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Measurements of the relation between activity and solubility of water in solution in benzene at 25° indicate absence of polymerisation of the water, contrary to another report.

We have recently begun to study the interactions of water and polar solute molecules in organic media.[1] In order to interpret partition, solubility, and colligative data, we have assumed that water exists solely as the monomer when dissolved in non-polar solvents. Water vapour is virtually ideal near room temperature; hence, we thought it unlikely that water molecules would associate with each other in solvents such as benzene, toluene, carbon tetrachloride, and cyclohexane.

Peterson and Rodebush [2] measured the freezing points of benzene solutions containing varying amounts of water, and found no indication of polymerization. Infrared spectra provide no evidence that water molecules associate in non-polar organic solvents.[3] However, Gordon *et al.*[4] recently concluded from specific-volume and viscosity data that water is highly polymerized in benzene and toluene solutions in the temperature range 60—70°. According to their calculations, at 90% of the saturation concentration at 67°, the average molecular weight of water in benzene solution is ~2·5 times that of the monomer. Ordinarily it is expected that the extent of polymerization in hydrogen-bonding systems will increase as temperature decreases; consequently we decided to study the association of water in benzene at 25° by an independent method. Our results, obtained by a modified

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

[2] Peterson and Rodebush, *J. Phys. Chem.*, 1928, **32**, 709.

[3] Greinacher, Lüttke, and Mecke, *Z. Electrochem.*, 1955, **59**, 23.

[4] Gordon, Hope, Loan, and Roe, *Proc. Roy. Soc.*, 1960, *A*, **258**, 215.

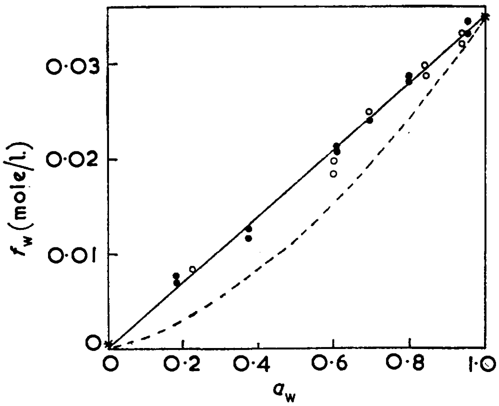
isopiestic method, indicate that no significant association of water molecules occurs in benzene solution at 25°, contrary to the conclusions of Gordon *et al.*

## EXPERIMENTAL AND RESULTS

It is possible to determine whether or not a dissolved species associates in dilute solutions by obtaining the relation between the activity and the concentration of the solute. If a non-linear relation is observed, it may be concluded that the solute does not exist as a single molecular species. A good indicator of water activity is furnished by its partial pressure, since in the vapour phase association is insignificant.

We constructed equilibrators consisting of ordinary wide-mouthed reagent bottles of ~1·5 l. capacity, into which were inserted 100-ml. beakers. Solutions of known partial pressure of water (hence, known activity) were introduced into the beakers, and pure benzene was placed outside them. The equilibrators were tightly capped and immersed in a water-bath held at 25·0° ± 0·1° for at least 2 days. After equilibration, samples of the benzene phase were withdrawn and analyzed for water by the Karl Fischer method (dead-stop end-point).*

Solutions of known water activity introduced into the beakers were of two types: aqueous sulphuric acid and aqueous calcium chloride. Concentrations of the acid were determined by density measurements; the chloride solutions were analyzed by the Mohr method. Water partial pressures (or activities) were inferred from tabular data available in the literature.[5] In one of the equilibrators a water activity effectively equal to zero was maintained by placing anhydrous magnesium perchlorate in the central beaker. Pure water was placed in the beaker in another equilibrator to maintain the partial pressure of water at the saturation value. Densities of the aqueous solutions were checked before and after equilibration to determine whether or not changes had occurred in water activity—in no case was a significant density difference detected. Since benzene is appreciably soluble in concentrated sulphuric acid, all the sulphuric acid solutions employed contained sufficiently high concentrations of water to reduce the benzene solubility to a negligible value.



Dependence of formal solubility of water in benzene on activity. Data obtained by using $H_2SO_4$ solutions (●), $CaCl_2$ solutions (○), anhydrous $Mg(ClO_4)_2$ (*), or pure water (×) in equilibrator. The broken line represents expectation for a dimerisation constant $K = 100$.

In the Figure, formal concentrations of water in benzene, $f_w$, are plotted against activity of water, $a_w$. The standard state chosen is pure water under its saturation vapour pressure at 25°. Although some scatter is observed, $f_w$ appears to vary linearly with $a_w$.

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* We were surprised that, with the equilibrators described, no change in water concentration in the benzene phase was observed after about one day. The rapidity of equilibration is undoubtedly a result of the fact that only relatively small quantities of water must be transferred to saturate the benzene phase. On the other hand, in the usual isopiestic experiment it is necessary to transfer quite large quantities of a volatile solvent at much smaller average differences in activity.

[5] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publns., London, 2nd edn., 1959, pp. 477—478.

## DISCUSSION

The linear dependence of concentration, $f_w$, on activity, $a_w$, lends strong support to the thesis that water molecules do not associate with each other in benzene solutions. It is informative to consider to what extent a moderate amount of association would modify the appearance of the $f_w$–$a_w$ curve.

Let us assume that water partially dimerizes, but undergoes no higher polymerization in benzene. It can then be shown that in these circumstances

$$f_w = f_w^0(a_w + 2Ka_w^2c_{H_2O}^0)/(1 + 2Kc_{H_2O}^0), \tag{1}$$

where $f_w^0$ and $c_{H_2O}^0$ represent the formal and monomer concentrations of water in the saturated benzene solution, and $K$ is the dimerization constant. Suppose, for example, that $K = 100$ (mole$^{-1}$ l.); then, since $f_w^0 = 0{\cdot}0349$M at 25°, $c_{H_2O}^0 = 0{\cdot}0109$M, and equation (1) becomes

$$f_w = f_w^0(a_w + 2{\cdot}2a_w^2)/3{\cdot}2. \tag{2}$$

The broken curve in the Figure shows the predicted dependence of $f_w$ on $a_w$ for $K = 100$ mole$^{-1}$ l. Note that for this hypothetical value of $K$, the effective or average molecular weight of dissolved water in the saturated solution would be about 1·5 times that of the monomer. This corresponds to a degree of association much lower than that calculated by Gordon *et al.* for the 90% saturated solution at 67°. If polymers of higher order than dimer were to be formed, the $f_w$–$a_w$ curve would deviate even more radically from linearity at high values of $a_w$. The solid line in the Figure corresponds to $K = 0$, *i.e.*, to complete absence of association.

There is ample evidence that benzene is not an inert solvent with respect to hydrogen-bonding solutes. The solubility of water in benzene is several times greater than its solubility in carbon tetrachloride and in most alkanes. Further, available data on the heat of solution (calculated from solubilities) indicate that interaction energies between the solvent benzene and the solute water are at least 1—2 kcal./mole greater than those between the solvents carbon tetrachloride or cyclohexane and water.[6] It is likely that the assumption made by Gordon and his co-workers that benzene is inert leads to considerable error in calculating the extent of polymerization from specific-volume data.

We have observed the near-infrared spectra of water dissolved in carbon tetrachloride, over a range of temperatures (15—45°) and concentrations (0—0·015M), and we find no shifts in the relative intensities or frequencies of the water fundamentals at 3650 and 3756 cm.$^{-1}$. From this we conclude that at room temperature water is not significantly associated in carbon tetrachloride solutions. It is improbable that at still higher temperatures water molecules are appreciably polymerized in benzene solutions.

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[6] Seidell, " Solubilities of Organic Compounds," D. Van Nostrand Co., New York, vol. 2, 1941.