The Infrared Absorption Spectrum of Water and Alcohols in Nonpolar Solvents

The vapor-like behavior of the electric moment of water dissolved in carbon tetrachloride and the colligative properties of the alcohols dissolved in nonpolar solvents are usually regarded as evidence for the existence, in the solution, of essentially vapor-like molecules. If this view is correct the infrared absorption spectra of water and the alcohols dissolved in carbon tetrachloride and carbon disulfide should be vapor-like. This point was investigated by studying the absorption in the 1.0–2.5μ region of water dissolved in carbon disulfide and of some of the alcohols dissolved in carbon tetrachloride. Preliminary results are shown in Fig. 1. The curves, representing the galvanometer deflections as ordinates and wave-lengths in μ as abscissae, show *A* the absorption of a thin cell of liquid water, *B* the absorption of 1 meter of carbon disulfide saturated with water at room temperature, *C* the radiation of the source containing the atmospheric water-vapor bands, *D* the absorption of 96 cm of methyl alcohol vapor at room temperature, *E* the absorption of liquid methyl alcohol and *F* the absorption of a solution of methyl alcohol in carbon tetrachloride. The solution and liquid cell lengths were chosen in each case so that the radiation traveled through approximately the same number of molecules. The bands marked W and OH, which occur in approximately these positions in all compounds containing the OH group, including water, with small variations in wave-length, are the ones to be noted. Curve *C* for the liquid alcohol shows the characteristic broad OH band of any alcohol at 1.45–1.65μ, cut by a water vapor band of the atmosphere on its short wave-length slope. Curve *F* shows, among others, a remarkably sharp band which appears very near the vapor position as shown in Curve *D*. In this set of curves the fact that the OH bands in solution are the sharpest of the three states of vapor, liquid and solution is even more apparent than in the case of water. Another fact appears significant. The bands marked CH which occur in approximately these positions whenever carbon-hydrogen groups are present, and which therefore are due to vibrations essentially characteristic, in the alcohol case, of the methyl group, are weak in the vapor and practically unchanged in the passage from the liquid to the solution state.

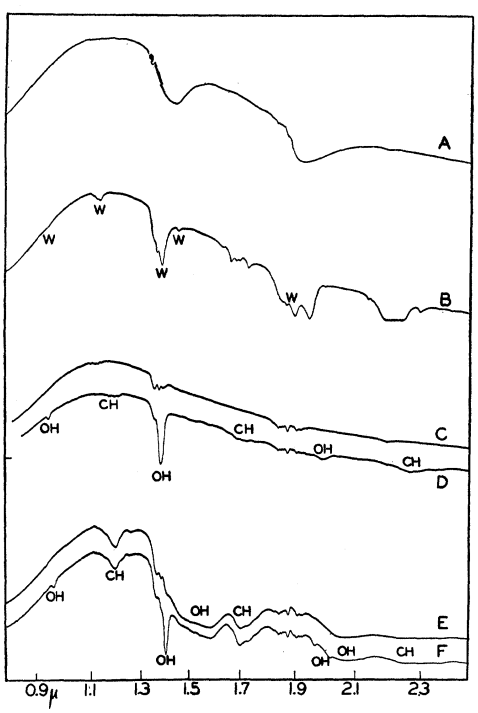

FIG. 1. *A*, 0.15 mm of water. *B*, 1 meter of water+carbon disulfide, ratio of numbers of molecules, 1 : 300. Water bands marked W. *C*, Intensity distribution, showing atmospheric water vapor bands. *D*, 96 cm of methyl alcohol vapor. *E*, 2 mm of methyl alcohol liquid. *F*, 4 cm of methyl alcohol+carbon tetrachloride, 1 : 7.9.

These observations are in agreement with the view that the interaction, whatever its nature, that occurs between molecules in the liquid is very much weakened, if not destroyed, in the solution state. They show also that the interaction affects, relatively, only the polar part of the molecule, for perhaps the most striking thing in the figure is the vast difference between the behavior of the so-called "OH" and "CH" bands of the alcohol when dissolved in carbon tetrachloride. Whether definite polymers consisting of double, triple or multiple molecules exist and produce the vapor-liquid differences, or whether indefinite aggregates held together by dipole forces which, acting upon a single molecule shift and broaden its absorption bands, is an open question.

But whatever view is taken, the existence of violent disturbances in the structure of the OH group must be recognized. Such disturbances may be due to strong dipole interaction between the OH ends of the alcohol, or in the case of water between two or more entire molecules, which results in the destruction of sharp quantization and the consequent production of broad absorption maxima for the OH bands, and for these alone. Another type of interaction however may be possible. The strong disturbing forces which arise may be caused by an interchange of protons between the OH groups in the manner postulated by Bernal and Fowler[1] to account for the high mobility of the H and OH ions in water solution. The existence of such a resonance phenomenon in liquid water and liquid alcohols in which the probability of occurrence would depend upon the proximity of neighboring molecules could easily account for the destruction of sharp quantization. The diffuse nature of the Raman bands in liquid water would also be a consequence of this interaction. It is evident however that a choice between these two views cannot be made at the present time.

Studies of these effects in the 3μ region are being made, and it is hoped that they may be carried out also under high resolving power and dispersion.

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[1] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).