

Possible Formation of Hydrogen Bonds in Liquid Mixtures

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Citation: [The Journal of Chemical Physics](#) **5**, 202 (1937); doi: 10.1063/1.1750010

View online: <http://dx.doi.org/10.1063/1.1750010>

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Possible Formation of Hydrogen Bonds in Liquid Mixtures

In a recent communication¹ the writer suggested that some results obtained by him on the infrared absorption of certain binary liquid mixtures might possibly be interpreted as indicating the formation of hydrogen bonds between the two liquids. When liquids containing the hydroxyl group, such as alcohol or water, which probably are already associated through hydrogen bonds, were mixed with some other liquids, such as acetone or methyl cyanide, which contain the strongly electronegative atoms, oxygen or nitrogen, having unshared electron pairs, the fundamental band of the hydroxyl group was found to be shifted to the shorter wave-lengths. There has arisen some question as to whether, in a mixture of liquids in which hydrogen bonds are formed between the liquids, the hydroxyl band would appear at shorter wave-lengths than it would in the pure liquid. Buswell, Deitz, and Rodebush² have suggested that one may predict an opposite effect, a shift to the longer wave-lengths of this band. Indeed, such a prediction would be justified were it not likely that the formation of hydrogen bonds in the pure water or alcohol has already shifted the hydroxyl band to the longer wave-lengths and that these bonds are probably broken if and when the H of the hydroxyl group is employed in forming a bond between a molecule of alcohol or water and a molecule of some other liquid. If the molecules of the pure liquid, XOH, are linked in some manner so that both the O and the H of a single hydroxyl group participate in the formation of bonds, as would be the case if large aggregates of molecules are formed, a possibility suggested by Latimer and Rodebush,³

or if two molecules are joined through a pair of hydrogen bonds, as $\text{XO}-\text{H}$, it would seem that one may anticipate a



greater shift to the longer wave-lengths of the hydroxyl band than if only the H of the group participated in the bond formation, as it would if the liquid were linked with some other liquid, say a ketone $\text{RC}=\text{O}$, as $\text{XO}-\text{H}-\text{O}=\text{CR}$. This view should explain the resulting shorter wave-length shift of the hydroxyl band in liquid mixtures of this type, and should certainly account for the longer wave-length shift of the $\text{C}=\text{O}$ band of the second liquid. However, the results would require that in a 1 : 1 mixture of the above-mentioned liquids only a relatively small number of the molecules unite to form the complex, $\text{XO}-\text{H}-\text{O}=\text{CR}$. It is possible that in a given mixture complexes of this type together with polymerized and also unassociated molecules of XOH exist in dynamical equilibrium. This may be the explanation of the broadness and also of the variation with concentration of the hydroxyl band.

I cannot see how the above interpretation would conflict with the one given by Buswell, Deitz, and Rodebush to their results. I recognize, however, that there may be other explanations and that more experimental data is needed before the question can be decided.

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February 8, 1937.

¹ Walter Gordy, J. Chem. Phys. 4, 749 (1936).

² A. M. Buswell, V. Deitz and W. H. Rodebush, J. Chem. Phys. 5, 84 (1937).

³ W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. 42, 1419 (1920).