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DIPOLE ATTRACTION AND HYDROGEN BOND FORMATION IN THEIR RELATION TO SOLUBILITY*

By Professor JOEL H. HILDEBRAND

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THE germ of the idea of a hydrogen bond may be seen in some of the formulas of Werner involving covalent linkage; however, he avoided committing himself concerning the nature of this linkage, which was little more than a dotted line, and very different from its modern significance of a definite electron pair bond. Moore and Winmill,¹ in 1912, wrote formulas containing light and heavy lines to account for the weakness of trimethyl amine in aqueous solution, $(\text{CH}_3)_3 \equiv \text{N}-\text{H}-\text{OH}$, as compared with tetramethyl ammonium hydroxide, $(\text{CH}_3)_4 \equiv \text{N}-\text{OH}$. The former may be interpreted as the first definite repre-

sentation of a hydrogen band. In the following year Pfeiffer² suggested as an explanation of the weakness of o-hydroxyanthraquinone that the hydrogen atom is "coordinately" bound to the oxygen atom of the adjacent carbonyl group. The first recognition of the hydrogen bond as a general phenomenon we owe to Latimer and Rodebush.³ They called attention to the effects of hydrogen bond formation, such as the high dielectric constant of water, which ordinary dipoles do not show. Lewis⁴ cited the existence of HF_2^- but not F_2^{--} as offering direct evidence of a hydrogen bond. The unusual properties of ammonia, water

* Address of the vice-president and chairman of the Section of Chemistry, American Association for the Advancement of Science, St. Louis, December, 1935.

¹ T. S. Moore and T. F. Winmill, *Jour. Chem. Soc., London*, 101: 1675, 1921.

² P. Pfeiffer, *Ann.*, 398: 137, 1913.

³ W. M. Latimer and W. H. Rodebush, *Jour. Am. Chem. Soc.*, 42: 1419, 1920.

⁴ G. N. Lewis, "Valence," p. 109, Chemical Catalog Company, 1923.

and hydrogen fluoride have come to be regarded largely as the effects of their hydrogen bonds. The lattice structure currently attributed to ice and to water assumes the hydrogen atoms to be placed on lines joining pairs of oxygen atoms,⁵ and similar evidence exists for methanol.⁶ The extraordinary stability of double molecules of acetic acid and of, apparently, six-fold polymers of hydrogen fluoride in the gaseous state⁷ presents evidence of the strength which such bonds may assume. Kumler⁸ has pointed out abnormalities in polarization which accompany hydrogen bond formation. The writer, in his studies of solubility, has discovered a number of solutions whose behavior is highly anomalous if the explanations are based upon dipole moment alone, but which become quite "reasonable" if account is taken of hydrogen bonds. The purpose of this paper is to present a few of the most striking of these cases.

Table 1 gives the solubilities of several organic liquids in water, together with their dipole moments. (The data quoted in this paper are available, except as noted, in the International Critical Tables.) The first four liquids, benzene, nitrobenzene, aniline and phenol, become rapidly more soluble in water in the order named. If ordinary "polarity" were responsible

TABLE 1
SOLUBILITY OF LIQUIDS IN WATER, 20°

	Per cent.	$\mu \times 10^{18}$
Benzene	0.06	0.
Nitrobenzene	0.19	4.19
Aniline	3.49	1.51
Phenol	8.2	1.70
Ethyl iodide	0.40	1.66
Ethyl alcohol	∞	1.70
Propyl chloride	0.27	2.0
Propyl iodide	0.11	1.6
Propyl alcohol	∞	1.7
Water	...	1.85

we should expect to find nitrobenzene, with by far the highest dipole moment as well as the highest dielectric constant, to be the most soluble in water; however, this is far from being the case, for it is only three times as soluble as the non-polar benzene, whereas phenol, with a much smaller moment, is 137 times as soluble. The molecular fields of the non-polar portion of these four molecular species must be nearly identical so that hydrogen bond formation appears to offer the only explanation. This is stronger in water than in ammonia, as shown, for example, by their boiling points, and we should expect phenol to associate with water

⁵ J. D. Bernal and R. H. Fowler, *Jour. Chem. Phys.*, 1: 515, 1933. S. Katzoff, *Jour. Chem. Phys.*, 2: 841, 1934.

⁶ Warren, *Phys. Rev.*, 44: 969, 1933.

⁷ J. Simons and J. H. Hildebrand, *Jour. Am. Chem. Soc.*, 46: 2183, 1924.

⁸ W. D. Kumler, *ibid.*, 57: 600, 1935.

in this way more strongly than does aniline, as is indeed the case.

The ethyl and propyl halides and alcohols given in Table 1 differ but little from each other in their dipole moments, hence, if their solubilities in water were due simply to electrostatic dipole attractions their solubilities should be of the same order of magnitude. Propyl chloride and iodide have solubilities paralleling their dipole moments, but the alcohols, which can form hydrogen bonds with the water, mix with it in all proportions.

Table 2 gives the per cent. deviation of the total vapor pressure curves of carbon disulfide solutions from Raoult's law. The first three liquids show deviations such as might be expected from their dipole moments, but methyl alcohol, with a much smaller moment than acetone, shows a much larger deviation, due, we may assume, to the hydrogen bonds in the alcohol which have the effect of enhancing the intermolecular forces and resisting penetration by the non-polar carbon disulfide.

TABLE 2
PER CENT. DEVIATION OF TOTAL VAPOR PRESSURE CURVE
FROM RAOULT'S LAW. 20°

Carbon disulfide with	Dipole moment $\mu \times 10^{18}$ e.s.u.	Per cent. deviation
Ethyl ether	1.1	17
Chloroform	1.1	15
Acetone	2.8	59
Methyl alcohol	1.7	>70 (2 liq.)

Table 3 gives solubilities in eight liquids of the non-polar gases hydrogen and nitrogen, and the polar, hydrogen-bond forming ammonia. We see again here that dipole moment alone is of little significance. Ether, in spite of its moment of 1.14, is a better solvent for the non-polar gases than benzene. The ether dipole is sufficiently buried to do little more than enhance the molecular field, but not enough to "squeeze out" the non-polar solute. Aniline, although much less polar than nitrobenzene, is a poorer solvent, because, we believe, it "associates" with itself through the hydrogen bond. The increase in such association as we proceed through ethanol and methanol to water sharply reduces the solvent power. With ammonia as solute, the order is the reverse, since ammonia is

TABLE 3
SOLUBILITY OF GASES. MOL PER CENT.

	$\mu \times 10^{18}$ e.s.u.	H ₂ 20°	N ₂ 20°	NH ₃ 0°
Ether	1.14	0.061	0.124	7.9
Toluene	0.4	0.037	0.053	0.26
Benzene	0.	0.025	0.043	...
Nitrobenzene ..	4.08	0.015	0.026	...
Aniline	1.51	0.012	0.011	...
Ethanol	1.70	0.021	0.033	39.8
Methanol	1.68	0.015	0.022	43.9
Water	1.85	0.0015	0.0013	48.1

able to form these bonds very strongly and thus penetrate the "associated" water molecules.

Fig. 1 shows a plot of the logarithm of the solubility

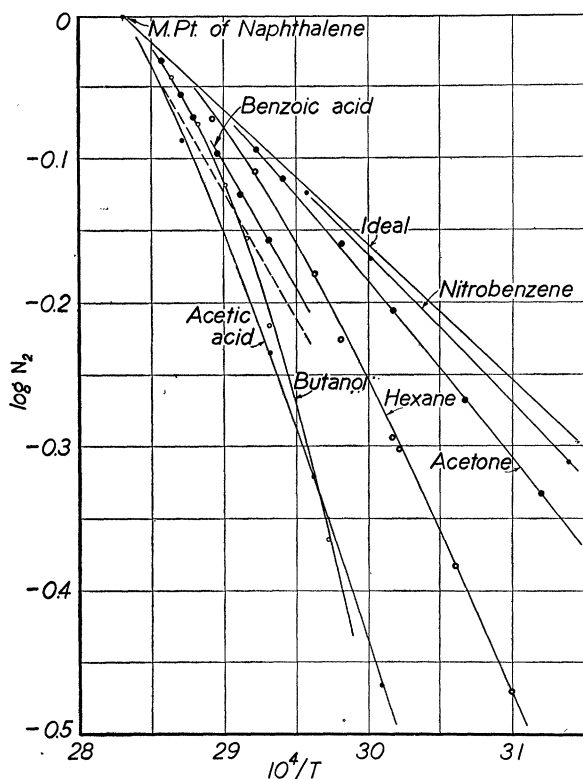


FIG. 1. Freezing point lowering of naphthalene caused by various liquids.

of naphthalene, expressed as mol fraction, in a selected list of solvents. It may be regarded as expressing the "freezing point lowering" of naphthalene. This substance has zero moment but it nevertheless forms nearly ideal solutions with nitrobenzene in spite of the high moment of the latter. Both have molecular fields about equally enhanced over that of benzene, so that their behavior indicates that the nitrobenzene molecules show but little electrostatic dipole association. Acetone with a smaller moment shows, nevertheless, a larger deviation on account of a weaker molecular field. Hexane, with a still weaker field, deviates still more, but the difference in field strengths, substituted in the approximation formula for solubility,⁹ reproduced the solubility almost exactly, giving the smooth curve running through the points. Acetic acid appears to form definite dimers, doubtless through two hydrogen bonds, accordingly, its curve in dilute solutions—concentrated in naphthalene, approaches the dotted curve drawn on the assumption of complete formation of a dimer which obeys Raoult's law. Its

⁹ J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, 1: 817, 1933; J. H. Hildebrand, *J. Am. Chem. Soc.*, 57: 866, 1935.

deviation lower down accords with the difference in field strength of the hydrocarbon portions of the two species. Benzoic acid, as might be expected, forms a weaker dimer with field strength nearer to that of naphthalene. Butanol associates through the formation of hydrogen bonds, but it forms less definite polymers than the acids, and these break down more readily as they are diluted with naphthalene. The striking fact to note here is the enormous difference between butanol and acetone. The former not only has a larger hydrocarbon portion to the molecule but a much lower dipole moment, both of which should, operating alone, make it a better solvent for naphthalene. That the contrary is the case seems to admit of no other explanation than that the strength of its hydrogen bonds renders it inhospitable to naphthalene.

The difference between association due to hydrogen bonds and that due simply to dipole attraction is strikingly illustrated by Fig. 2, giving variations in

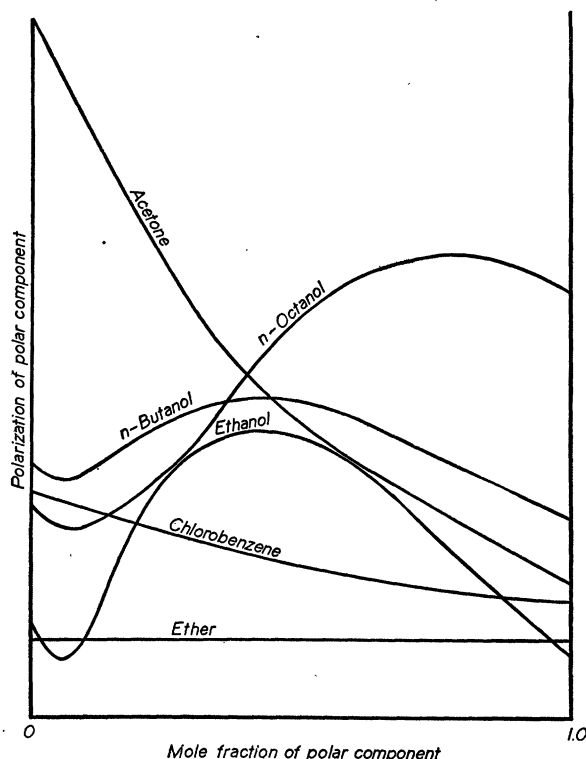


FIG. 2. Variation of molar polarization with concentration.

molar polarization with concentration in solutions with non-polar components.¹⁰ It is evident that the alco-

¹⁰ Data from J. Krehma and J. W. Williams, *Jour. Am. Chem. Soc.*, 49: 1676, 2408, 1927; C. P. Smyth and W. N. Stoops, *ibid.*, 42: 1419, 1920. An excellent discussion of association is given by C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, 1931, Chap. IX. Cf. also C. Hennings, *Z. physik. Chem.*, B 28: 267, 1935.

holds represent a class very different from the other liquids, acetone, chlorobenzene and ether. (Nitrobenzene shows a curve similar to that of acetone but much steeper.) Any simple treatment based upon dipole attraction that might apply to the latter group would obviously not apply to the former. Indeed the enthusiasm with which dipole moments have been applied to all such problems should be strongly tempered by a realization of their inadequacy to deal with, first, molecules associated through hydrogen bonds, second, molecules of zero moment but containing vectorially opposed polar groups,¹¹ and, third, the intermolecular forces to the neglect of van der Waals forces. So far as this last is concerned, London¹² has calculated the magnitude of the components of the potential between molecules of HCl and of HBr. These components

are, first, the van der Waals potential due to the "dispersion effect," or interaction of the electron systems, second, the interaction potential of the permanent dipoles, third, the interaction of the moments induced in each by the permanent dipole of the other. The potentials due to the induced moments are nearly negligible compared to the others. By far the largest component is the "dispersion effect." Although the dipole moment of HCl is 1.03×10^{-18} e.s.u., the potential due thereto is only about one fourth of the dispersion potential, and with HBr, with a moment of 0.78×10^{-18} , the dipole potential is only about seven per cent. of the dispersion effect. It should be evident from this that all attempts to deal with the interaction of polar molecules on the basis of their dipole forces alone are doomed to failure.

WOMEN IN SCIENCE¹

By Dr. FLORENCE R. SABIN

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH

President Park: I can not express adequately to you and to your committee the pleasure I feel in receiving this prize, for there is distinction to an honor which bears the name of M. Carey Thomas.

I confess at once that any award for work in science must awake a certain sense of timidity; for one can never be sure that research will stand. How often have the supposed facts and theories of the very ablest been reversed by new evidence! In the case of my own work, I can see with great clarity how far it is from reaching its goal.

But why does an honor from Bryn Mawr touch so deep a sense of gratification? It is because of the traditions of this place and all that they have meant for scholarship and for women. I remember so vividly getting the essential quality of this spirit on the occasion, now thirteen years ago, when Miss Thomas retired from the presidency of the college. There was not a person who spoke at that time, former members of the faculty and former students alike, who did not bring out that the influence of Miss Thomas had been in a quite unique manner toward fostering high standards of work. This is what she has bequeathed to the college. What a gratification it must be to her, President Park, that you have the same feeling for scholarship and that you have carried on and extended the high traditions of Bryn Mawr.

It seems to me fitting that I should speak of certain

points concerning the influence of Miss Thomas on education in science. As is well known, the greatest function of the president of any institution of learning is the choosing of a faculty. Moreover, real ability for this function consists in having the insight to select scholars while they are still young, before they have demonstrated their full power. To use only one example, but that one striking enough, the early faculty of Bryn Mawr College included three young men who became our most distinguished biologists. Edmund B. Wilson, Thomas Hunt Morgan and Jacques Loeb have given American biology world-preeminence. It was, I think, Professor Wilson who first won from Europe full recognition for American biological research. In 1911 he was invited by the editor of the *Archiv für mikroskopische Anatomie* to republish in a foreign journal his work on the X-chromosome in relation to sex. It is interesting to recall that in this article he gave full credit to the work of Netty Stevens, who had independently and at the same time made the same discovery. As you well know, Miss Stevens did her work here and she had here a research position with almost no obligations for teaching, such as is seldom held in our universities except by the professor emeritus. Such a group of scientists as was and is still assembled here depends, of course, on the presence of the graduate school which was established at Bryn Mawr from the start along with the undergraduate department.

I want next to dwell on the influence which Miss Thomas exerted on medical education. The opening of the Johns Hopkins Medical School in 1893 was made possible by a fund raised by a group of women

¹¹ J. H. Hildebrand and J. M. Carter, *Proc. Nat. Acad. Sci.*, 16: 285, 1930.

¹² F. London, *Z. Physik*, 63: 245, 1930.

¹ Response on receiving the M. Carey Thomas Prize on the occasion of the fiftieth anniversary of the founding of Bryn Mawr College.