ACTA CHEMICA SCANDINAVICA 2 (1948) 669—677

Studies of the Hydrogen Bond

II. Influence of the Polarizability of the Heteroatom

INGA FISCHER and LARS EHRENBERG

Institute of Theoretical Physics and Institute of Organic Chemistry and Biochemistry, University of Stockholm, Stockholm, Sweden

The association of liquids and several solubility phenomena have been explained by the assumption of a hypothetical hydrogen bond [1—4, 5a, 6a, 7]. Some authors have sought to explain these phenomena as an electrostatic attraction between more or less deformed dipoles [8—12]; regarding the smallness of the H atom the X—H partial moments (X being the negative heteroatom) are easily available for an arrangement from which a strong attraction follows [9a]. Hence, an interpretation of the association phenomena on the basis of electrostatic attraction is not excluded, as a rule. The schools maintaining this opinion have been supported by the fact that their calculations agree better with the experimental data than does the attempt to calculate the H bond energy on quantum mechanical basis as a resonance phenomenon [13]. However, Harms [10] and others [11] are forced to assume distances between the dipoles much shorter than those calculated from van der Waals' radii (Table 3) in order to get the right magnitude of the energy. Moelwyn-Hughes [8] bases his calculations on the interaction of dipoles instead of that of separated charges, which is hardly permissible (*cf.* Bauer and Magat [14]). Pauling [6a] interprets the hydrogen bond mainly as an electrostatic attraction of the proton to the two negative atoms linked through the bond. He states that this explanation overbridges the discrepancies between the different interpretations of association. It seems, however, to be rather difficult to draw any definite conclusions without detailed calculations.

The closest agreement with experimental values is obtained by Bauer and Magat [14], who calculate the energy of water association with due consideration to separate charges and polarizability effects. Their method is doubtless adequate so far as it concerns the association of water and other simple molecules, as for instance ammonia (calculations made by van Velden and Ketelaar[16]) and hydrogen fluoride. This method is not opposed to the quantum mechanical one, but is a suitable approximation when the polarizabilities of the groups of atoms in question are known from experiments. Otherwise, the polarizabilities might be calculated, if possible, with the aid of quantum mechanics, or the whole problem might be treated through a direct study of the wave functions involved. However, such calculations have not been made as yet.

Summing up, it may be said that no satisfactory general treatment of the hydrogen bond has been made hitherto.

In the event of association between two molecules, similar or different, both carrying an active H atom the cause of association is difficult to interpret because one or the other or both H atoms might partake in the H bond formation. In the case of association between two molecules, only one of which contains an active H atom there is only one possibility of H bond formation. Gordy *et al.*[15] have studied such simple cases with infrared absorption measurements. Following a similar line we have, in a preceding paper[88], investigated solutions of water in diethyl ether and divinyl ether (solubility, surface tension, partial molar volume, and polarization measurements). The present paper will treat these and some other systems with uni-directional H bond formation, *viz.* the effect of double bond on the water solubilities of ethers, amines, and halides. From this study conclusions concerning the properties which encourage H bond formation can be drawn.

ETHERS

Our experimental data[88] could be explained by the assumption that diethyl ether associates with water, about 50 % of the water molecules in ether solution being present as a (hypothetical) binary complex with $\mu = 2.44$ D, whereas divinyl ether is more like benzene in its ability to dissolve water.

The size of the dipole moment, *cf.* Table 1, and the steric configuration at the oxygen atom of the two compounds being almost the same the different affinity for water cannot be due to a different ability to attract water electrostatically. Regarding physical data of the ethers and their mixtures with indifferent solvents we were able to conclude that the pure liquids are practically uni-molecular and that, *if* there is any association, it is of the same order of magnitude in the two compounds. Their uni-molecularity (*cf.* Harms[10]) is further illustrated by the similarity in boiling points and entropies of vaporization between the ethers and the hydrocarbons of corresponding molecular weight and degree of unsaturation (Table 1, *cf.* also Table 4). Both

Table 1. Physical data of ethers.

Substance	Boiling point °C	Entropy of vaporization cal · T^{-1} · mol^{-1}	Solubility in water mol · l^{-1}	Dipole moment 10^{18} e. s. u.	r_D cm^3	Exaltation of MR_D cm^3	Heat of hydrogenation cal · mol^{-1}
Diethyl ether	34.6 [33]	20.7 [37]	1.010 (20°) [41b] 0.632 (38°) [41a] 1.2 (25°) [35b]	gas: 1.14 [44—46] 1.10 [47] benzene soln: 1.22 [48—50] 1.15 [51] 1.27 [52] 1.23 [88]	0.3041 [53]	+ 0.22	—
Ethylvinyl ether	35.7 [34]		scarcely soluble [42]				26740 [34] *
Divinyl ether	28.3 [87]	20.8 [38]	0.11 (25°) [35b] 0.056 (37°) [43]	benzene soln: 1.06 [87, 88]	0.3130 [87]	+ 0.56	57236 [34] *
Cyclopropyl-ethyl ether	68 [35 a]		0.25 (27°) [35a] 0.23 (25°) [35b]				
Cyclopropyl-vinyl ether	67 [36]		0.08 (25°) [36]				
Diethyl methane	36.2 [33]	20.0 [39]	0.005 (16°) [25]	0 [75, 82]	0.3504 [75]	0	
Divinyl methane	26.0 [33]	21.0 [40] (isoprene)					

the low heat of hydrogenation and the high specific refraction, r_D, of divinyl ether show that the electron configuration of this compound is similar to those of molecules with conjugated double bonds. Electrons from the oxygen atom must be involved in the conjugation. Hence, the electron cloud around the O atom becomes less polarizable than in diethyl ether which is the possible cause of the diminished miscibility with water.

Table 1 contains also data to show that the diminished attraction for water molecules seems to be a general property of ethers with a double bond in the vicinity of the oxygen atom. Gordy *et al.*[15] have found a smaller frequency shift of the O—D bond in the system CH_3OD-ether in the cases of phenetol and β, β-dichloroethyl ether compared to diethyl ether. They assume a diminished negativity of the oxygen to be the cause.

---

* *Cf.* allyl alcohol: 31458 cal . mol^{-1} [34].

Table 2. Physical data of heterocyclic compounds.

Substance	Boiling point °C	Entropy of vaporization cal · T^{-1} · mol^{-1}	Solubility in water at 20° C mol · l^{-1}	Dipole moment (benzene solution) 10^{18} e. s. u.
Furan	31.3 [87]	20.8 [55]	insoluble [58]	0.63 [68]; 0.67 [54]; 0.71 [87]
Tetrahydrofuran	64.1 [87]		∞ (22°) [59]; 4.2 (25°) [60]	1.68 [54]; 1.71 [87]
Thiophene	84 [54]		0.002—0.005 [61]	0.54 [54]; 0.63 [69]
Tetrahydrothiophene	120 [54]		insoluble [62]	1.87 [54]
Pyridine	115 [33]	22.0 [37]	∞ [63]	2.11 [49, 50]; 2.26 [70]; 2.21 [71]
Piperidine	106 [33]	19.9 [56]	∞ [64]	1.17 [70]
Pyrrole	131 [33]		insoluble [22]	1.80 [54]
Pyrroline	90 [33]		very soluble [65]	1.42 [54]
Pyrrolidine	88.5 [33]		∞ [66]	1.57 [54]
Trimethyl amine	2.9 [33]		∞ [63]	gas: 0.60 [72]; 0.82 [73]
Triethyl amine	89.4 [33]	22.5 [57]	1.41 [67]; ∞ ($<$ 18.6°) [67]	gas: 0.76 [74]; 0.82 [73]

HETEROCYCLIC COMPOUNDS

A similar difference as to the ability to associate with water is found in a comparison between furan and tetrahydrofuran, Table 2. In this case the involvement of the oxygen electrons of furan is even more marked because of the aromatic structure. This will lead to an electron displacement towards the centre of the molecule, which is a probable cause of the diminished dipole moment. The small dipole moment of furan cannot account for the insolubility of the compound, because molecules (the tertiary amines of Table 2) with the same dipole moment, about the same molecular weight, about the same cohesion in the pure liquid (entropy of vaporization, boiling point), the same or greater steric hindrance, and a somewhat larger radius of the negative atom * (Table 3) are very soluble in water. A comparison between thiophene and tetrahydrothiophene shows the same peculiarities of dipole moment and electron displacement, but since the sulphur atom does not form H bonds to

Table 3. Van der Waals' radii of atoms [6b].

H	N	|O	F	P	S	|Cl
1.2 Å	1.5	1.40	1.35	1.9	1.85	1.80

---

* It might be supposed, *cf.* pyrrole [17], that the oxygen atom of furan were positive. From the dipole moment of furfural, 3.61 D [18], the moment of the aromatic aldehyde group, — 2.95 D [19], and the bond angles of furan from electron diffraction measurements [20] the oxygen atom of furan is shown to be negative.

Table 4. Physical data of halides.

Substance	Boiling point[33] °C	Entropy of vaporization cal · T^{-1} · mol^{-1}	Solubility in water at 20° C mol · l^{-1}	Dipole moment 10^{18} e. s. u.
Ethyl fluoride	—37.7		0.09 (14°)[33]	1.92[80]
Vinyl fluoride	—51		insoluble[76]	
Ethyl chloride	12.2	20.9[84]	0.089[77, 25]	2.02[81]
Vinyl chloride	—13.9		0.014[33a]	1.44[27]
Ethyl bromide	38	21.1[85]	0.083[78]; 0.088 (17.5°)[25]	2.02[80]
Vinyl bromide	15.8		insoluble[33]	1.48[74]; 1.41[27]
Ethyl iodide	72.2	20.6[37]	0.026[78]; 0.025 (22.5°)[25]	1.90[80]
Vinyl iodide	56		insoluble[33]	1.26[27]
Butane	— 0.6		0.007 (17°/772 mm)[33]	0
1,3-Butadiene	— 3	21.6[86]	0.011 (25°/520 mm)[79]	0[83]

any appreciable extent[5b] (larger atomic radius, Table 3) both compounds are clearly insoluble. In the case of pyridine and piperidine both are very soluble in water. The polarizability of the unshared electron pair of the nitrogen atom is not much changed in the aromatic state: like amines, pyridine can easily donate an electron pair in proton addition, forming the pyridonium ion. A similar proton addition to furan leads to a breakdown of the molecule. In his interesting work, Gordy[15] has found a relation between basicity constants of amines and frequency shifts of the O—D band (see above). The importance of this relation has also been regarded by Bernal[21].

In the pyrrole series the aromatic compound carries no unshared electron pair. Accordingly, pyrrole cannot act as electron donor in a supposed H bond and is, compared to its hydrogenated derivatives, very slightly soluble. Like furan it is incapable of forming a stable positive ion through proton addition. Naturally, pyrrole might be a proton donor in an H bond (*cf.* Harada *et al.*[22], Ingold *et al.*[23], and Gordy *et al.*[24]). The high solubilities in water of di-, tri-, and tetrazoles are understood on similar grounds[17].

ETHYL AND VINYL HALIDES

Unsubstituted alkanes are incapable of H bond formation and, consequently, are not very soluble in water[25], the solubility being chiefly due to dispersion forces (*cf.* London[26]). In this case the introduction of double bonds will increase the molecular polarizability and the mutual solubility (*cf.* butane-butadiene, Table 4; as to the solubility of water in hydrocarbons, see the recent measurements by Black *et al.*[89]). This is a common effect, though immeasurably small when the solubility is dominated by the presence of a heteroatom capable of H bond formation. In the latter case the introduction of a double bond in the vicinity of the heteroatom will have the opposite effect on the water solubility. The unshared electrons of the heteroatom become partly involved in interaction with the π-electrons of the $C = C$ bonds.

The halides show the same solubility peculiarities as the ethers. In this case, too, the decreased availability of the electrons of the heteroatom might be responsible for the decreased solubility of the unsaturated compounds (Table 4). In comparison to ethers, a more marked electron displacement occurs in the halides [27—30], *cf.* their dipole moments.

DISCUSSION

The examples mentioned above demonstrate that attraction between dipoles is not solely responsible for the water solubility of polar compounds (*cf.* Hildebrand [4]). This is shown most clearly in a study of the pair diethyl ether-divinyl ether. Hence, the interpretation of association phenomena on the basis of electrostatic attraction between dipoles is not sufficient.

The present examples show that the availability of unshared electrons at the heteroatom is greatly significant for the water solubility.

This fact has been mentioned casually by several authors [6c, 15] but it has not been regarded in the interpretation of the phenomena in question. It should be mentioned that this view as to »H acceptor atoms» is contrary to that of Huggins [31], who states that decreased electron availability means increased strength of the H bond, generally.

An involvement of the electrons of the heteroatom through conjugation or displacement, *i. e.* a decreased polarizability of the electron cloud around the heteroatom, will diminish the attraction of molecules with an active H atom. Consequently, data make it fitting to explain association phenomena with the concept of a hydrogen bond.

The energy of the hydrogen bond has been calculated by several authors [13, 14, 31, 32] using more or less modified Morse functions. This treatment seems, as a rule, to give the right order of magnitude of the energy, but it is to coarse for any estimations of such properties as those concerned in solubility and similar phenomena. Probably, experimental facts might be sufficiently accounted for only through more refined calculations of the energy of the system on the basis of quantum mechanics with due consideration to the change of the electronic orbitals effected partly by the rest of the molecule and partly by the contiguity of the other molecule of the complex. Such calculations will be tried on the case of associates between water and different ethers.

SUMMARY

The water solubilities of ethers, tertiary amines, and halides are treated. Unsaturated or aromatic compounds, where the electron cloud of the heteroatom is less polarizable (through conjugation or displacement), are less soluble in water. It is fitting to explain the association phenomena studied with the concept of a hydrogen bond, for the formation of which the availability of unshared electrons at the heteroatom is important.

Acknowledgement: Thank you, Brother Arrhenius, for a cup of coffee and a good discussion!

LITERATURE

1. Latimer, W. M., and Rodebush, W. H. *J. Am. Chem. Soc.* **42** (1920) 1419.
2. Rodebush, W. H. *Chem. Revs.* **19** (1936) 55.
3. Huggins, M. L. *J. Org. Chem.* **1** (1936) 407.
4. Hildebrand, J. H. *Science* **83** (1936) 21.
5. Lassettre, E. N. *Chem. Revs.* **20** (1937) a: 259 ff., b: 267.
6. Pauling, L. *The nature of the chemical bond* 2nd ed. Ithaca (1940) a: 284 ff., b: 189, c: 289.
7. Hoyer, H. *Z. Elektrochem.* **49** (1943) 97.
8. Moelwyn-Hughes, E. A. *J. Chem. Soc.* (1938) 1243, (1940) 850.
9. Wolf, K. L. a: *Z. physik. Chem.* **B 43** (1939) 20, b: *Theoretische Chemie* Part 3. Leipzig (1943).
10. Harms, H. *Z. physik. Chem.* **B 43** (1939) 257.
11. Briegleb, G. *Z. physik. Chem.* **B 51** (1941) 9.
12. Prigogine, I. *Bull. soc. chim. Belg.* **52** (1943) 1.
13. Gilette, R. H., and Sherman, A. *J. Am. Chem. Soc.* **58** (1936) 1135.
14. Bauer, E., and Magat, M. *J. phys. radium* [7] **9** (1938) 319.
15. Gordy, W., and Stanford, S. C. *J. Chem. Phys.* **8** (1940) 170.
16. van Velden, P. F., and Ketelaar, J. A. A. *Chem. Weekblad* **43** (1947) 401.
17. Jensen, K. A., and Friediger, A. K. *Danske Videnskab. Selskab Math.-fys. Medd.* **20** (1943) no. 20.
18. Shott-L'vova, E. A., and Syrkin, Ya. K. *J. Phys. Chem. (USSR)* **12** (1938) 479 from *Chem. Abstr.* **33** (1939) 4839.
19. Coomber, D. I., and Partington, J. R. *J. Chem. Soc.* (1938) 1444.
20. Beach, J. Y. *J. Chem. Phys.* **9** (1941) 54.
21. Bernal, J. D. *Trans. Faraday Soc.* **36** (1940) 912.
22. Harada, M., and Titani, T. *Bull. Chem. Soc. Japan* **11** (1936) 465.
23. Ingold, C. K., and Wilson, C. L. *Z. Elektrochem.* **44** (1938) 62.
24. Gordy, W., and Stanford, S. C. *J. Am. Chem. Soc.* **62** (1940) 497.

25. Führer, H. *Ber.* **57** (1924) 510.
26. London, F. *Z. Physik* **63** (1930) 245.
27. Hugill, J. A. C., Coop, I. E., and Sutton, L. E. *Trans. Faraday Soc.* **34** (1938) 1518.
28. Ketelaar, J. A. A. *Rec. trav. chim.* **58** (1939) 311.
29. Brockway, L. O., Beach, J. Y., and Pauling, L. *J. Am. Chem. Soc.* **57** (1935) 2693.
30. Walsh, A. D. *Trans. Faraday Soc.* **41** (1945) 35.
31. Huggins, M. L. *J. Phys. Chem.* **40** (1936) 723.
32. Cross, P. C., Burnham, J., and Leighton, P. A. *J. Am. Chem. Soc.* **59** (1937) 1134.
33. *Handbook of chemistry and physics.* 29th ed. Cleveland (1945), a: 1207.
34. Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., Smith, E. A., and Vaughan, W. E. *J. Am. Chem. Soc.* **60** (1938) 440.
35. a: Krantz, J. C. Jr., Carr, C. J., Evans, W. E. Jr., Forman, S. E., and Wollenweber, H. L. *J. Pharmacol. Exptl. Therap.* **72** (1941) 233; b: Cone, N. M., Forman, S. E., and Krantz, J. C. Jr. *Proc. Soc. Exptl. Biol. Med.* **48** (1941) 461.
36. Krantz, J. C. Jr., Evans, W. E. Jr., Forman, S. E., and Wollenweber, H. L. *J. Pharmacol. Exptl. Therap.* **75** (1942) 30.
37. Mathews, J. H. *J. Am. Chem. Soc.* **48** (1926) 562.
38. Miles, F. T., and Menzies, A. W. C. *J. Phys. Chem.* **37** (1933) 425.
39. Griffiths, E., and Awbery, J. H. *Proc. Phys. Soc. (London)* **44** (1932) 121.
40. Landolt-Börnstein *Physikalisch-Chemische Tabellen* 5th ed. Erg. II : 2. Berlin (1931) p. 1489.
41. a: Klobbie, E. A. *Z. physik. Chem.* **24** (1897) 615, see p. 620, b: Schuncke, J. *Z. physik. Chem.* **14** (1894) 334.
42. *Beilstein's Handbuch d. org. Chemie* **I** (1918) 433.
43. Ruigh, W. L., and Erickson, A. E. *Anesthesiology* **2** (1941) 546.
44. Sänger, R. *Physik. Z.* **31** (1930) 306.
45. Stuart, H. A. *Z. Physik* **51** (1928) 490.
46. Fuchs, O. *Z. Physik* **63** (1930) 824.
47. Sänger, R., and Steiger, O. *Helv. Phys. Acta* **2** (1929) 136.
48. Williams, J. W., and Krchma, I. J. *J. Am. Chem. Soc.* **49** (1927) 1676.
49. Lange, L. *Z. Physik* **33** (1925) 169.
50. Rolinski, J. *Physik. Z.* **29** (1928) 658.
51. Meyer, L. *Z. physik. Chem.* **B 8** (1930) 27, see p. 45.
52. Hassel, O. *Z. Elektrochem.* **36** (1930) 735.
53. Voellmy, H. *Z. physik. Chem.* **127** (1927) 305.
54. de Vries Robles, H. *Rec. trav. chim.* **58** (1939) 111.
55. Mathews, J. H., and Fehlandt, P. R. *J. Am. Chem. Soc.* **53** (1931) 3212.
56. Werner, A. *Z. anorg. Chem.* **15** (1897) 1.
57. Timmermans, J., and Hennaut-Roland, Mme. *J. chim. phys.* **29** (1932) 529.
58. a: Koizumi, M., and Titani, T. *Bull. Chem. Soc. Japan* **13** (1938) 95; b: Limpricht, H. *Ann.* **165** (1873) 253, see p. 281; c: Koch, E. M., and Cahan, M. H. *J. Pharmacol. Exptl. Therap.* **26** (1925/26) 281.
59. Klapproth, H. *Nova Acta Leopoldina* **9** (1940) 305.
60. Stoughton, R. W., and Robbins, B. H. *J. Pharmacol. Exptl. Therap.* **58** (1936) 171.
61. Östergren, G., and Levan, A. *Hereditas* **29** (1943) 496.
62. Grischkewitsch-Trochimowski, E. *J. Russ. Phys. Chem. Soc.* **48** (1916) 901, from: *Chem. Zentr.* (1923) I, 1502.
63. Pickering, S. U. *J. Chem. Soc.* **63** (1893) 141.

64. Ewert, M. *Bull. soc. chim. Belg.* **46** (1937) 90.
65. Ciamician, G. L., and Dennstedt, M. *Ber.* **16** (1883) 1536.
66. Gabriel, S. *Ber.* **24** (1891) 3231.
67. Rothmund, V. *Z. physik. Chem.* **26** (1898) 433.
68. Hunter, E. C. E., and Partington, J. R. *J. Chem. Soc.* (1931) 2062.
69. Hassel, O., and Naeshagen, E. *Tids. Kjemi Bergvesen* **10** (1930) 81.
70. Rau, M. A. G., and Narayanaswamy, B. N. *Z. physik. Chem.* **B 26** (1934) 23.
71. Bergmann, E., Engel, L., and Meyer, H. *Ber.* **65** (1932) 446.
72. Steiger, O. *Physik. Z.* **32** (1931) 425.
73. Ghosh, P. N., and Chatterjee, T. P. *Phys. Rev.* **37** (1931) 427.
74. Höjendahl, K. *Physik. Z.* **30** (1929) 391.
75. Dornte, R. W., and Smyth, C. P. *J. Am. Chem. Soc.* **52** (1930) 3546.
76. Swarts, F. *Bull. acad. roy. Belg.* (1901) 383, from: *Chem. Zentr.* (1901) II, 804.
77. van Arkel, A. E., and Vles, S. E. *Rec. trav. chim.* **55** (1936) 407.
78. Rex, A. *Z. physik. Chem.* **55** (1906) 355.
79. McBain, J. W., and O'Connor, J. J. *J. Am. Chem. Soc.* **63** (1941) 875.
80. Smyth, C. P., and McAlpine, K. B. *J. Chem. Phys.* **2** (1934) 499.
81. Sänger, R. *Helv. Phys. Acta* **3** (1930) 162.
82. Fuchs, O., and Wolf, K. L. *Dielektrische Polarisation, Hand- u. Jahrb. d. chem. Physik* **6 I B** Leipzig (1935).
83. Hannay, N. B., and Smyth, C. P. *J. Am. Chem. Soc.* **65** (1943) 1931.
84. Yates, G. W. C. *Phil. Mag.* [7] **2** (1926) 817.
85. Wirtz, K. *Wied. Ann. Physik Chem.* **40** (1890) 438, see p. 446.
86. Vaughan, W. E. *J. Am. Chem. Soc.* **54** (1932) 3863, see p. 3874.
87. Smyth, C. P., and Walls, W. S. *J. Am. Chem. Soc.* **54** (1932) 3230.
88. Ehrenberg, L., and Fischer, I. *Acta Chem. Scand.* **2** (1948) 657.
89. Black, C., Joris, G. G., and Taylor, H. S. *J. Chem. Phys.* **16** (1948) 537.

Received July 16, 1948.