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The Intermolecular Hydrogen Bonding between Methanol and Triethylamine in Various States

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The intermolecular hydrogen bond energy between methanol and triethylamine was determined by infrared studies in the vapor state and in solutions. It was also found that, with an increase in the dielectric constant, ε, of the solvents, the free O–H stretching band of methanol shifts to a lower frequency, the molar absorptivity of this band increases, and the hydrogen bond energy of this system decreases. As is well known, the hydrogen-bonded system is mainly stabilized by the contribution of two resonating structures, the non-bonded structure and the charge-transfer structure. It seems probable that the weight of the latter for a relatively weak hydrogen-bonded complex is small. Therefore, if the energies for both resonating structures are assumed to be mainly determined by the electrostatic interaction, the hydrogen bond energy may be expected to be reciprocal to the dielectric constant of the environment. This is actually true within the limits of experimental error in a few solutions. It was also found, however, that the relation cannot be extrapolated to the case of $\varepsilon=1$, i. e., to the case of vapor.

While a considerable number of infrared studies of hydrogen bonding in solutions have been reported, little attention has been paid to the vapor state. It seems that it would be interesting to

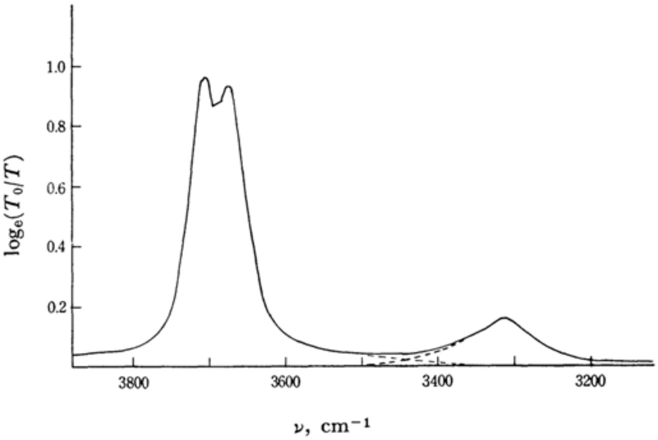

Fig. 1. The infrared spectrum of the O–H stretching band for methanol and the complex in the vapor.

Table I. Hydrogen bond energy in the vapor

Molar fraction of methanol	Total pressure mmHg at 0°C	Temp., °C	I_h, cm^{-1}	$-\Delta E$, kcal./mol.
0.324	30	19.0 33.6	21.1 10.6	8.4
0.318	28	22.2 34.8	20.5 12.4	7.1
0.322	25	20.0 34.4	17.1 9.43	7.4
				mean : 7.6

Spectral slit width : $S=4.46\,\text{cm}^{-1}$ at $3313\,\text{cm}^{-1}$

study the hydrogen bonding in the vapor state as well as in solutions for the same substances in order to obtain information about the effect of environment on the hydrogen bonding.

For this study methanol and triethylamine have been chosen as the proton donor and the proton acceptor respectively, and the intermolecular hydrogen bond energy will be measured spectroscopically in the vapor state and in solutions.

Experimental

Materials.—Methanol, triethylamine, carbon tetrachloride, chlorobenzene, dichloromethane, and chloroform were purified by the usual methods[1]; for each substance only that fraction was used which distilled at a constant temperature.

Infrared Spectra.—For the measurements in the vapor state, two thin glass ampules, in which methanol and triethylamine had been sealed separately, were broken in a three-liter spherical, vacuumed flask; the two vapors were thus mixed. The quantity of each substance should be adequately adjusted so as to make each vapor pressure less than its own saturated vapor pressure in the flask. After prolonged mixing, the mixture was expanded into a one-meter vacuumed gas cell for infrared studies.

For the measurements in solutions, a 3.0 mm. fixed cell was used throughout this study.

The spectra were measured over the range from 3000 to 3900 cm^{-1} with a Perkin-Elmer Model 112 Infrared Spectrometer equipped with a lithium fluoride prism for both states.

The temperature of the samples was measured by a copper-constantan thermocouple.

Measurements of the Integrated Intensities.—An infrared spectrum of a mixed vapor of methanol and triethylamine is shown in Fig. 1. The band near 3683 cm^{-1} is due to the hydroxyl stretching vibration of the free methanol molecules, while the band near 3313 cm^{-1} can be assigned to that of the hydrogen-bonded complex of methanol and triethylamine, for this band disappears in the spectrum of pure methanol vapor.

The change in the relative intensities of these bands with the temperature was measured. As the two bands overlap near 3500 cm^{-1}, the observed curve of absorbances was divided into two smooth curves so that their sum was equal to the observed value, as is shown in Fig. 1. The ambiguity in dividing these bands does not seem to have any noticeable influence on the results. The area intensities were obtained by the graphical integration of the absorbances by using a planimeter, since the contours of the bands were not so simple for the vapor. The integrations were carried out from 3150 to 3480 cm^{-1} and from 3500 to 3865 cm^{-1} for the two bands respectively. This sufficiently covers a range of about four times the half-intensity width for each band. The integration outside this

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1) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," Interscience Publishers, New York (1955), p. 445, p. 413 (by the method of Günther et al.), p. 408 (by the method of McAlpine and Smyth), p. 409 (by the method of Maryott et al.), and p. 411 (by the method of Morgan and Lowry).

interval may be neglected without noticeable influence on the evaluation of the relative intensities, because their absorbances at these limits are smaller than one-fifteenth of those at the peaks. The correction for finite slit widths can be neglected for the vapor, because of the breadth of the bands. The results obtained for the vapor are shown in Table I.

For the studies of solutions it did not seem that it would be accurate to determine the concentration of the complex by measuring the intensity of the hydrogen-bonded O-H stretching band, because both O-H stretching bands shift to lower frequencies in solutions than in the vapor and the hydrogen-bonded O-H band overlaps with the C-H stretching bands at the wing. Therefore, the concentration of the complex was estimated by measuring the decrease in the intensity of the free O-H stretching band. For this the intensity of the free O-H stretching band in solutions should be studied first. The methanol solutions used for this purpose were so dilute that the spectra showed no evidence of the band characteristic of the hydrogen bonding. In the solvent of carbon tetrachloride or dichloromethane, the free O-H band was represented by Lorentz's equation. Although in the solvent of chlorobenzene the shape of the band was asymmetric, each side of the band could be represented by the equation. Therefore, the true integrated absorption intensity per mole (the true molar absorptivity), a, corrected for finite slit widths, was calculated by the equation:

$$a = K(1/CL)\log_e(T_0/T)_{max}\Delta\nu^a_{1/2}$$

where the letters have their usual meanings.[2] The values of K were obtained from Ramsay's table.[2] For the non-polar solvent of carbon tetrachloride, the area intensity of this band is independent of the temperature. However, for the polar solvent of chlorobenzene or dichloromethane the intensity decreases slightly with an increase in the temperature. The results obtained are shown in Table II and should be used for the evaluation of the concentration of the complex shown in Table III.

The infrared spectra of the mixture of methanol and triethylamine in carbon tetrachloride or dichloromethane also have these bands, of which one is due to the free molecule and the other to the hydrogen-bonded complex. In chlorobenzene, however, the band due to the hydrogen-bonded complex cannot be detected because the band is masked by an absorption of the solvent.

Results and Discussion

The change in the internal energy, ΔE, which is equal to the hydrogen bond energy in its absolute magnitude, can be evaluated by the van't Hoff equation:

$$\mathrm{d}\log_e K_c/\mathrm{d}T = \Delta E/\boldsymbol{R}T^2$$

The equilibrium constant, K_c, is given by:

$$K_c = C_X/(C_D - C_X)(C_A - C_X),$$

where C_D is the initial concentration of methanol, C_A that of triethylamine, and C_X the concentration of the hydrogen-bonded complex.

In the vapor, the area intensity, I_f, of the free O-H stretching band at 20°C and that of that at 35°C were almost the same, within the limits of experimental error. Therefore, it may be a good approximation to take $(C_D - C_X)$ and $(C_A - C_X)$ as constant over this temperature range, since the values of C_X were shown to be very small compared with those of C_D and C_X. On the other hand, the area intensity, I_h, of the O-H stretching band of the complex markedly decreases with a rise in the temperature, as is shown in Table I. Therefore, by measuring this change with the temperature, the ratio of C_X's at two temperatures could be obtained. The fact that the intensity of the band is very sensitive to small variations in the concentration of the complex is due to the marked increase in the molar absorptivity of the O-H stretching band when hydrogen bonding occurs. The evidence for this may be seen in Table IV for the case of the dilute carbon tetrachloride solution. The suffixes f and h refer to the values of the free molecule and of the complex respectively.

The hydrogen bond energy in the vapor can then be evaluated by:

$$\log_e\frac{(K_c)_1}{(K_c)_2} = \log_e\frac{(C_X)_1}{(C_X)_2} = \log_e\frac{(I_h/a_h)_1}{(I_h/a_h)_2} = \frac{-\Delta E}{\boldsymbol{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The suffixes 1 and 2 refer to the values at the temperatures T_1°K and T_2°K respectively. The values of molar absorptivity, a_h, were cancelled in this equation, because of its independence of the temperature.

The values thus obtained are shown in the last column of Table I. The values of $|\Delta E|$ is larger by about 2.9 kcal./mol. than that for the methanol - ethyl ether complex in the vapor reported by Inskeep et al.[3] This result agrees with the expectation in that the frequency shift of the O-H stretching band, $\Delta\nu_{\mathrm{OH}} = (\nu_{\mathrm{OH}})_f - (\nu_{\mathrm{OH}})_h$, is larger for the former than the latter.

In solutions the C_D and C_A concentrations were obtained by weighing. The C_X concentration could be evaluated by:

$$C_X = C_D - (I_f/a_f L)$$

where I_f is the area intensity of the free O-H stretching band. The equilibrium constants at various temperatures thus obtained are listed in Table III. From these data the hydrogen bond energy* can be calculated; the results are shown in Table V, together with the changes in the free energy and the entropy.

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[2] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[3] R. G. Inskeep, F. E. Dickson and J. M. Kelliher, *J. Mol. Spectroscopy*, **4**, 477 (1960).

* For solutions the difference between ΔE and the change in the enthalpy can be neglected.

TABLE II. MOLAR ABSORPTIVITY OF THE O-H STRETCHING BAND OF METHANOL IN SOLUTIONS

Solvent : CCl_4
Spectral slit width : $S=4.75\ \mathrm{cm}^{-1}$ at $3642\ \mathrm{cm}^{-1}$

Temp. °C	Concn. 10^{-2} mol./l.	$\log_e(T_0/T)_{max}$	$\Delta\nu^a_{1/2}$ cm^{-1}	K	a_f 10^3 darks
31.0	2.50	0.867	27.5	1.56	5.01
	1.98	0.715	25.6	1.56	4.83
					mean : 4.9
10.5	2.22	0.795	26.8	1.56	4.99
	2.04	0.805	23.6	1.56	4.81
					mean : 4.9

Solvent : C_6H_5Cl
Spectral slit width : $S=6.39\ \mathrm{cm}^{-1}$ at $3633\ \mathrm{cm}^{-1}$

Temp. °C	Concn. 10^{-2} mol./l.	$\log_e(T_0/T)_{max}$	$\Delta\nu^a_{1/2}$ cm^{-1}	K	a_f 10^3 darks
24.0	2.01	1.20	14.1 and 12.7	1.56	8.30
	2.22	1.23	17.0 and 12.5	1.56	8.47
					mean : 8.4
6.0	2.05	1.30	13.2 and 14.1	1.56	9.01
	2.26	1.48	13.2 and 15.2	1.56	9.88
					mean : 9.5

Solvent : CH_2Cl_2
Spectral slit width : $S=7.92\ \mathrm{cm}^{-1}$ at $3628\ \mathrm{cm}^{-1}$

Temp. °C	Concn. 10^{-2} mol./l.	$\log_e(T_0/T)_{max}$	$\Delta\nu^a_{1/2}$ cm^{-1}	K	a_f 10^3 darks
20.0	2.15	1.29	29.5	1.56	9.20
	2.26	1.46	27.5	1.56	9.23
					mean : 9.2
0.0	2.23	1.43	29.1	1.56	9.70
	2.34	1.46	31.5	1.56	10.2
					mean : 10

TABLE III. EQUILIBRIUM CONSTANTS FOR THE METHANOL-TRIETHYLAMINE COMPLEX IN SOLUTIONS

Solvent : CCl_4

Temp. °C	C_D 10^{-2} mol./l.	C_A 10^{-2} mol./l.	I_f/L $10^2\ \mathrm{cm}^{-2}$	C_D-C_X 10^{-2} mol./l.	K_c l./mol.
31.0	2.05	4.71	0.780	1.59	6.9
	1.42	4.49	0.557	1.14	5.9
	1.97	4.95	0.721	1.47	7.6
					mean : 6.8
10.5	2.03	4.74	0.620	1.27	15
	2.19	4.76	0.690	1.41	14
	2.03	5.08	0.626	1.28	14
					maen : 14

Solvent : C_6H_5Cl

Temp. °C	C_D 10^{-2} mol./l.	C_A 10^{-2} mol./l.	I_f/L $10^2\ \mathrm{cm}^{-2}$	C_D-C_X 10^{-2} mol./l.	K_c l./mol.
24.0	2.21	4.96	1.47	1.76	5.8
	1.80	4.92	1.20	1.42	5.9
	2.01	4.90	1.32	1.57	6.3
					mean : 6.0
6.0	2.25	5.06	1.45	1.53	10.8
	1.84	5.02	1.23	1.30	9.3
	2.05	5.00	1.40	1.47	8.9
					mean : 9.7

Solvent : CH_2Cl_2

Temp. °C	C_D 10^{-2} mol./l.	C_A 10^{-2} mol./l.	I_f/L $10^2\ \mathrm{cm}^{-2}$	C_D-C_X 10^{-2} mol./l.	K_c l./mol.
24.0	2.26	4.88	1.58	1.72	7.2
	2.19	4.96	1.57	1.71	6.3
					mean : 6.8
−1.0	2.34	5.06	1.56	1.56	11
	2.27	5.14	1.55	1.55	11
					mean : 11

Table IV. Molar absorptivity of the hydrogen bonded O–H stretching band in the CCl_4 solution

C_D 10^{-2} mol./l.	C_A 10^{-2} mol./l.	I_h/L 10^2 cm^{-2}	I_f/L 10 cm^{-2}	C_X 10^{-3} mol./l.	a_h 10^4 darks
2.01	4.77	4.13	6.23	7.4	5.6
2.16	4.76	3.77	6.90	7.6	5.0
					mean : 5.3

By using the value of a_f shown in Table II, $a_h/a_f=11$.

Table V. The properties of the intermolecular hydrogen bonding between methanol and triethylamine

State	Solvent	ε	$(\nu_{OH})_f$ cm^{-1}	$\Delta\nu_{OH}$ cm^{-1}	a_f 10^3 darks	$-\Delta E$ kcal./mol.	$-\Delta F$ kcal./mol.	$-\Delta S$ ca.l/mol.·deg.
Vapor		1	3683	370	—	7.6	—	—
Soln.	CCl_4	2.24	3642	430	4.9	6.0	1.2(31°C)	15 (31°C)
	C_6H_5Cl	5.71	3633	—	8.3	4.3	1.1(24°C)	10 (24°C)
	CH_2Cl_2	9.08	3628	328	9.2	3.0	1.1(24°C)	6.4(24°C)

It can be seen from Table V that the free O–H stretching band shifts to a lower frequency and that the molar absorptivity, a_f, of the band increases with an increase in the dielectric constant of the solvents. This fact indicates that the ionic character of the free O–H bond increases with an increase in the dielectric constant of the solvents.

As is well known, the hydrogen-bonded system is mainly stabilized by the contribution of two resonating structures, the non-bonded structure, $-\mathrm{O{-}H\cdots N}\lessdot$, and the charge-transfer structure, $-\mathrm{O^-\cdots H{-}{}^+N}\lessdot$. Because the energy of the non-bonded structure is mainly due to the electrostatic interaction, the energy may be reciprocal to the dielectric constant, ε, of environment. As for the charge-transfer structure, it seems to be hard to estimate the effects of a solvent on its energy. However, it seems probable that the weight of the charge-transfer structure for such a relatively weak hydrogen-bonded complex is small[4] and that even for this structure the main part of energy is due to the electrostatic interaction. Therefore, if the energies for both resonating structures are considered to be mainly determined by the electrostatic interaction, the hydrogen bond energy may be expected to be a linear function of $1/\varepsilon$.

It is well known that, with an increase in the strength of hydrogen bonding, the O–H stretching bands in linear hydrogen bonds are progressively lowered in frequency.[5] Therefore, the $\Delta\nu_{OH}$ shift may be considered to be a measure of the strength of the hydrogen bonding.

The data of $\Delta\nu_{OH}$ shown in Table V and the value of $\Delta\nu_{OH}$, 360 cm^{-1}, obtained in the chloroform solution ($\varepsilon=4.81$) are plotted against $1/\varepsilon$ in Fig. 2-(a). The values for the solutions are represented by a straight line, which is in agreement with the expectation mentioned above.

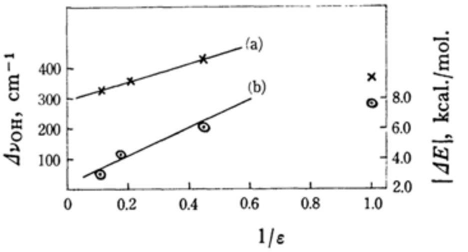

Fig. 2. (a) $\Delta\nu_{OH}$ vs. $1/\varepsilon$
(b) $\Delta E|$ vs. $1/\varepsilon$

Furthermore, since a direct measure of the strength of the hydrogen bonding is the value of $|\Delta E|$, the values of $|\Delta E|$ are also plotted against $1/\varepsilon$ in Fig. 2-(b). Because of the possibility of experimental error in the evaluation of $|\Delta E|$, it is not conclusive; nevertheless it is very probable that the values of $|\Delta E|$ for the solutions can also be represented by a straight line.

The values of $\Delta\nu_{OH}$ or $|\Delta E|$ for the vapor phase do not fall on the straight line extrapolated from those obtained in the solutions. This fact may be taken as showing that the mechanism of the hydrogen bonding is somewhat different in the vapor from that in the solutions.

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[4] C. A. Coulson, "Hydrogen Bonding," Ed. by D. Hadži, Pergamon Press, London (1959), p. 67.

[5] See, e. g., N. Sheppard, ibid., p. 87.