412. *The Hydrogen Bonding of Imidazole in Carbon Tetrachloride Solution.*

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Analysis of the concentration-dependence of the infrared spectrum of imidazole in carbon tetrachloride solution at 18° ± 1° indicates that the fundamental N–H stretching band at 3485 ± 10 cm.$^{-1}$ is due to the free end-groups of linear oligomers. The number-average degree of polymerisation of the system increases from 1 to 2·6 in the concentration range 2×10^{-4} to 4×10^{-3}M, and the average number of monomeric units in each oligomer from 2 to 5. The hydrogen-bonding equilibria may be represented quantitatively by a dimerisation constant $\beta_{20} = 234 \pm 15$ l. mole^{-1} and subsequent, successive stepwise association constants K_q $(q \geqslant 3) = 760 \pm 20$ l. mole^{-1}.

THE self-association of pyrazole (I) in carbon tetrachloride solution results in the formation of cyclic, hydrogen-bonded dimers and trimers.[1] Analogous cyclisations for imidazole (II) are impossible on steric grounds. Indeed, a consideration of bond angles suggests that any cyclic oligomer smaller than the decamer will have strained hydrogen bonds. The present study was undertaken to investigate the nature of the oligomers of imidazole which exist in carbon tetrachloride solution.

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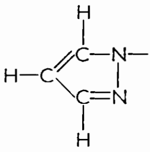
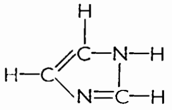
[1] Anderson, Duncan, and Rossotti, *J.*, 1961, 140.

A preliminary infrared spectroscopic examination of dilute solutions showed a fundamental N–H stretching mode at 3485 ± 10 cm.$^{-1}$ with a half-band width of 20 cm.$^{-1}$.



(I)



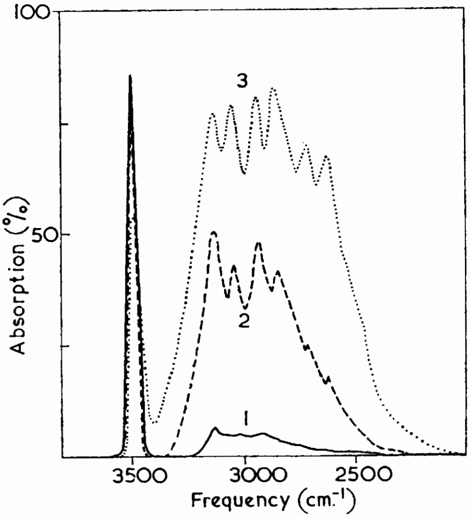
(II)

The intensity of this band decreased with increasing total concentration B of imidazole. Concurrently, a broad, hydrogen-bonded N–H band of increasing intensity appeared in the region 3400—2000 cm.$^{-1}$ (see Fig. 1). This broad band contained six major peaks (3125s, 3040s, 2925s, 2850s, 2705ms, and 2620 ms cm.$^{-1}$). The weak C–H band at 3120 cm.$^{-1}$ was completely masked. A quantitative study was accordingly made of the concentration dependence of the 3485 cm.$^{-1}$ band.

EXPERIMENTAL

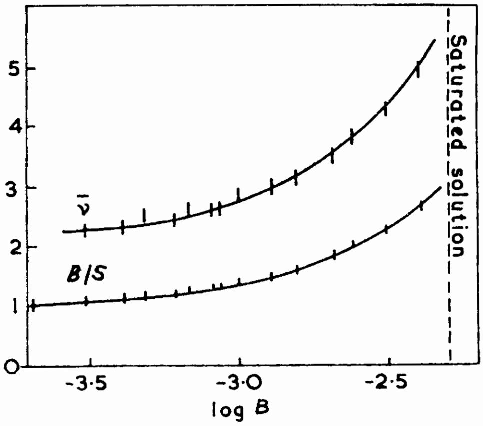
Materials.—Imidazole was recrystallised twice from carbon tetrachloride; it had m. p. 89·5° (lit., 90°). No O–H absorption spectrum was detectable in reagent-grade carbon tetrachloride, which was therefore used without further purification.

FIG. 1. *Infrared absorption spectra in the region 3800—2000 cm.$^{-1}$ for carbon tetrachloride solutions of imidazole at various total concentrations B at* 18°.



(1) $B = 10^{-4}$M. (2) $B = 10^{-3}$M. (3) $B = 5 \times 10^{-3}$M.

FIG. 2. *The number-average degree of polymerisation of the system B/S, and the average number of monomers per oligomer, $\bar{\nu}$, as a function of* log B. *The curve passing through the experimental points B/S,* log B *is calculated by substituting values of the stability constants obtained from eqns.* (15) *and* (16) *into eqns.* (3) *and* (5).



Infrared Measurements.—A Hilger H800 double-beam spectrophotometer fitted with a quartz prism was used. Operating conditions, calibration, and the precision of the frequency and intensity measurements were the same as reported previously.[1] A pair of carefully matched 4·00 cm. Unicam quartz cells was used for measurements in the concentration range $10^{-4} \leqslant B \leqslant 10^{-3}$M. A matched pair of cells of variable path-length, set at 5·000 ± 0·005 mm., and fitted with rock-salt windows, was necessary for more concentrated solutions.

Imidazole solutions of concentration $B > 4 \times 10^{-4}$M were prepared by semi-micro-weighing. More dilute solutions were prepared by dilution of a $1{\cdot}022 \times 10^{-3}$M-stock solution. Solutions were kept at 18° ± 1° throughout the measurement.

Procedure.—It was impossible to confirm that the intensity of the fundamental N–H stretching band of the free monomer conformed to Beer's law, as the most dilute solutions ($B \sim 10^{-4}$M) that could be studied were still slightly ($\sim$5%) hydrogen-bonded. The optics of the system were checked by confirming that the intensity of the 3485 cm.$^{-1}$ band adhered to Lambert's law. Solutions with $10^4B = 8{\cdot}176$, $8{\cdot}743$, and $10{\cdot}22$M were used in conjunction with the 4·00 and 0·500 cm. cells. The results conformed to Lambert's law within ± 1%.

The concentration dependence of the intensity of the 3485 cm.$^{-1}$ band was then investigated. Details of the fifteen solutions used ($10^{-4} \leqslant B \leqslant 4 \times 10^{-3}$M) are listed in Table 1.

TABLE 1. *Infrared absorbancies at* 3485 *cm.*$^{-1}$ *of associated imidazole in carbon tetrachloride at* 18° ± 1° *and concentration variables derived therefrom.*

10^4B	$\log I_0/I$	10^4S	$\log b$	10^4B	$\log I_0/I$	10^4S	$\log b$	10^4B	$\log I_0/I$	10^4S	$\log b$
2·044	0·174	1·941	−3·718	6·800	0·495	5·523	−3·325	15·59	0·111 *	9·937	−3·138
3·066	0·252	2·810	−3·584	8·176	0·578	6·455	−3·271	20·62	0·130 *	11·57	−3·102
4·088	0·325	3·628	−3·483	8·743	0·607	6·777	−3·255	24·10	0·139 *	12·37	−3·086
4·857	0·374	4·170	−3·430	10·22	0·670	7·473	−3·223	31·19	0·157 *	14·00	−3·060
6·132	0·462	5·158	−3·350	12·78	0·098 *	8·750	−3·174	40·22	0·173 *	15·41	−3·043

* 5·000 mm. cells: other results refer to 4·00 cm. cells.

INTERPRETATION OF THE DATA

Calculation of Concentration Variables.—The value of the apparent molar extinction coefficient ε_1 of the monomer at 3485 cm.$^{-1}$ was obtained graphically as $\lim\limits_{B \to 0} (\log I_0/I)/Bl$, where I_0 and I are the intensities of the incident and transmitted radiation, and l is the cell length. Only a short extrapolation was necessary to obtain the precise value $\varepsilon_1 = 224 \pm 2$.

The free N–H band in associated solutions might be due to free monomer only or to the free end-groups of linear oligomers. In the pyrazole system,[1] it was possible to distinguish between these possibilities by an argument based on the law of mass action. This rigorous approach cannot be applied to the imidazole system owing to the more extensive hydrogen bonding. However, a qualitative argument will show that the absorption is due to the end-groups of the oligomers. As compared with the pyrazole system, where the free N–H absorption is due to free monomer only,[1] the intensity of the broad, bonded N–H band of imidazole increased, as B increased, far more markedly than the intensity of the free N–H band decreased (compare Fig. 1 with Fig. 1 in ref. 1). Moreover, no bands or shoulders were detectable between the 3485 cm.$^{-1}$ band and the first bonded N–H band at 3125 cm.$^{-1}$, even for saturated solutions ($B \sim 5 \times 10^{-3}$M).

Accordingly, at 3485 cm.$^{-1}$, we may write

$$\log I_0/I = l\sum_1^Q \varepsilon_q B_q, \tag{1}$$

where ε_q is the apparent molar extinction coefficient of the qth oligomer B_q (concentration B_q), and Q is the maximum value of q in the system. On the further reasonable assumption that all values of the extinction coefficients are approximately equal, we may transform eqn. (1) into

$$(1/\varepsilon_1 l) \log I_0/I = \sum_1^Q B_q = S \tag{2}$$

and use eqn. (2) to calculate the end-group concentrations, S. These are given in Table 1. The total concentration B of imidazole is related to the free monomer concentration b by the equation

$$B = \sum_1^Q qB_q = \sum_1^Q q\beta_{q0}b^q \tag{3}$$

where the self-association constants are defined by

$$\beta_{q0} = B_q b^{-q} \tag{4}$$

Similarly,

$$S = \sum_{1}^{Q} \beta_{q0} b^q \qquad (5)$$

B, *S*, and *b* are simply interrelated by Jannik Bjerrum's integral [2]

$$\log b/b_1 = (1/2{\cdot}303) \int_{S_1}^{S} (1/B)\mathrm{d}S \qquad (6)$$

Hence, values of *b* may be calculated from the experimental data (B^{-1}, *S*) without any assumptions about the equilibria, provided that a value S_1, of *S*, corresponding to a known value b_1 of the monomer concentration can be selected. A point (S_1, b_1) was found by the following method suggested by Rossotti and Rossotti.[3] In sufficiently dilute solutions, where the dimer is the sole oligomer, eqns. (3), (4), and (5) may be combined to

$$\log (B - S) = \log \beta_{20} + 2 \log (2S - B) \qquad (7)$$

The plot of log ($B - S$) against log ($2S - B$) tended to a straight line of slope 2 as $S \longrightarrow B$. A point (B_1, S_1) was found by solution of eqn. (7), and the corresponding value of b_1 by substitution into the equation

$$b_1 = (2S_1 - B_1)$$

Values of *b*, obtained by graphical integration using eqn. (6), are also included in Table 1.

The Degree of Polymerisation of the System.—By combining eqns. (3) and (5), we obtain [4]

$$B/S = \sum_{1}^{Q} qB_q / \sum_{1}^{Q} B_q = \sum_{1}^{Q} M_q B_q / M_1 \sum_{1}^{Q} B_q = \overline{M}_n / M_1,$$

where M_1, M_q, and $\overline{M}_n$ are the monomeric molecular weight, the molecular weight of the *q*th oligomer, and the number-average molecular weight respectively. The ratio *B*/*S* is clearly the number-average degree of polymerisation of the system, and may be obtained directly from the infrared measurements. In the restricted concentration range available to experiment, its value increases from unity to 2·6 (see Fig. 2). A better indication [3,5] of the nature of the oligomers present in solution is obtained by subtracting the monomeric term and calculating $\bar{\nu}$, the average number of monomers per oligomer. Values of $\bar{\nu}$, calculated by using the equation

$$\bar{\nu} = (B - b)/(S - b) = \sum_{2}^{Q} qB_q / \sum_{2}^{Q} B_q,$$

increase from ~2 to ~5, and increase sharply as saturation is approached (see Fig. 2). Consequently, at least the first six oligomers of the series B_q coexist in carbon tetrachloride solution.

Calculation of the Stability Constants.—*Successive extrapolations.* An attempt was made to obtain independent values of the self-association constants by a method of successive extrapolations.[3,4] Rearrangement of eqn. (3) gives

$$F_t = Bb^{-t} - \sum_{1}^{t-1} q\beta_{q0} b^{q-t} = t\beta_{t0} + (t + 1)\beta_{t+1,0} b + \sum_{t+2}^{Q} q\beta_{q0} b^{q-t} \qquad (8)$$

where *t* is an integer such that $2 \leqslant t \leqslant Q$. Values of $t\beta_{t0}$ and $(t + 1)\beta_{t+1,0}$ may be obtained as the intercept and limiting slope of the plots $F_t(b)$. Equation (5) may be treated similarly to give values of β_{t0} and $\beta_{t+1,0}$. The best set of parameters β_{q0} was found by alternate extrapolations of the functions *B*(*b*) and *S*(*b*). As is usually the case,[3-5] the precision of the experimental

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[2] J. Bjerrum, *Kem. Maanedsblad*, 1943, **24**, 21.

[3] Rossotti and Rossotti, *J. Phys. Chem.*, in the press.

[4] Rossotti and Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961.

[5] Rossotti and Rossotti, *J. Phys. Chem.*, in the press.

data was only sufficient to allow the first three self-association constants to be determined. Their values are given in Table 2.

Curve fitting. When the precision of experimental data does not permit the determination of $(Q - 1)$ independent stability constants, a quantitative description of the data is often possible in terms of one, two, or three independent parameters. These parameters may conveniently be determined by comparing suitable plots of the experimental data with normalised curves.[4,5]

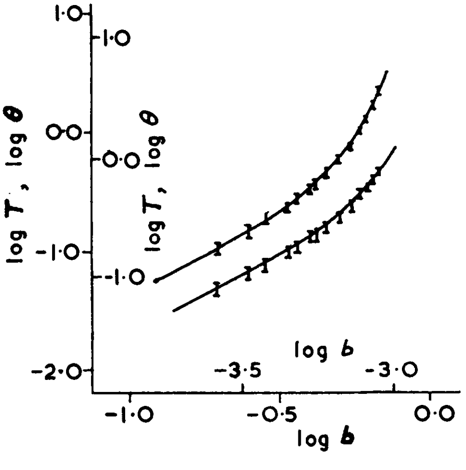

FIG. 3. *The experimental data* $\log T$ ($\log b$) *and* $\log \theta$ ($\log b$) *superimposed in the position of best fit on normalised curves calculated by using eqns.* (17) *and* (18).

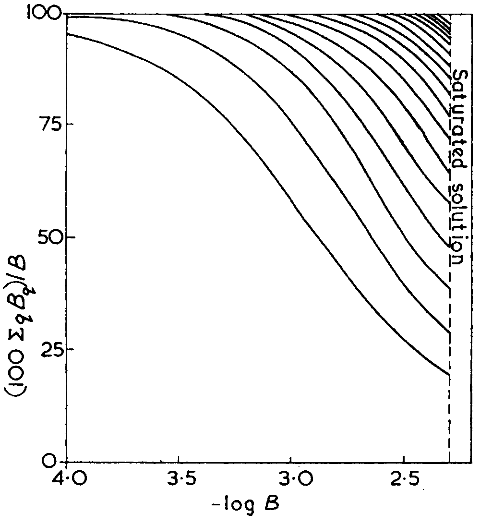

FIG. 4. *The percentage distributions* $(100\Sigma q B_q)/B$ *of the imidazole species* B_q *in carbon tetrachloride at* 18° *plotted as a function of* $\log B$. The curves are for B_1, B_2, B_3, etc., from lowest curve upwards.

Two auxiliary concentration variables are defined by

$$T = (B - b)b^{-1} \tag{9}$$

and

$$\theta = (S - b)b^{-1} \tag{10}$$

and the experimental data plotted in the form $\log T$ ($\log b$) and $\log \theta$ ($\log b$) with common co-ordinate axes. These functions were compared with various pairs of normalised curves $\log \mathbf{T}$ ($\log \mathbf{b}$) and $\log \boldsymbol{\theta}$ ($\log \mathbf{b}$), calculated by Rossotti and Rossotti[4,5] for a number of models. The experimental curves were found to be of the same shape as a pair of normalised curves calculated on the assumptions described in ref. 5 as " Hypothesis I " (see Fig. 3). Hence, this hypothesis provides a valid description of the imidazole system in carbon tetrachloride solution.

On the simple model of " Hypothesis I," the stepwise association constants for the reactions

$$B_{q-1} + B \rightleftharpoons B_q \quad (q \geqslant 3)$$

are all assumed to be equal and to have a value K. Hence

$$\beta_{q0} = \beta_{20} K^{q-2} \tag{11}$$

and by combining eqns. (3), (5), and (11)

$$T = \sum_{2}^{Q} q \beta_{20} K^{q-2} b^{q-1} \tag{12}$$

and

$$\theta = \sum_{2}^{Q} \beta_{20} K^{q-2} b^{q-1} \tag{13}$$

The analogous normalised variables are defined by

$$\boldsymbol{T} = TK/\beta_{20} \tag{14}$$

$$\boldsymbol{\theta} = \theta K/\beta_{20} \tag{15}$$

and

$$\boldsymbol{b} = bK \tag{16}$$

Equations (12)—(16) may be combined to yield

$$\boldsymbol{T} = \boldsymbol{b}(2 - \boldsymbol{b})/(1 - \boldsymbol{b})^2 \tag{17}$$

and

$$\boldsymbol{\theta} = \boldsymbol{b}/(1 - \boldsymbol{b}) \tag{18}$$

for a system in which $\boldsymbol{b} < 1$ and Q is very large. The normalised curves are calculated by using eqns. (17) and (18). The values of the parameters β_{20} and K are found by solving eqns. (16) and (14) or (15) in the position of best fit (see Fig. 3). The limits of errors of these parameters are found from the permissible displacements of the experimental functions log T (log b) and log θ (log b) over the normalised curves parallel to the co-ordinate axes. In this way, we find

$$\log \beta_{20} = 2{\cdot}37 \pm 0{\cdot}03$$

and

$$\log K = 2{\cdot}88 \pm 0{\cdot}01$$

Lassettre's method.[6] The only other two-parameter model in the literature was suggested by Lassettre [6] in 1937. For a system $B(S)$, which conforms to the linear equation

$$(B - S)/S^2 = (C_B B/S) + C_S$$

(where the parameters C_B and C_S denote a functional dependence of B/S upon B and S respectively), it may be shown that

$$\beta_{q0} = \frac{\prod_{m=0}^{m=q-2} [qC_B + (q - m)C_S]}{q!} \tag{19}$$

Our data $B(S)$ may be represented by the linear equation

$$(B - S)/S^2 = (470B/S) - 170 \tag{20}$$

Stability constants have been calculated by substituting the parameters of eqn. (20) into eqn. (19).

DISCUSSION

Values of the first few self-association constants of the linear oligomers of imidazole, calculated by the various methods, are collected together in Table 2. Actual values of the equilibrium constants presumably lie within the ranges delineated by the various methods, which have given results in substantial agreement.

The percentage distribution of imidazole between the various oligomers has been calculated as a function of the total imidazole concentration B by using the constants obtained by curve fitting and eqn. (3). These data are shown in Fig. 4. Subject to the assumptions of the model, values of β_{q0} may be considered to be significant provided that the corresponding values of qB_q/B are significantly greater than zero. Hence, we find that significant concentrations of all oligomers up to the dodecamer ($q = 12$) are present in saturated solutions. Possibly, this fact explains the low solubility of imidazole ($\sim 5 \times 10^{-3}$M) compared with that pyrazole ($>$M) in carbon tetrachloride at 18°.

Dimeric and trimeric pyrazole are less stable thermodynamically than the dimers and trimers of imidazole, in spite of the fact that the former are cyclic and the latter linear. In the imidazole system, the equilibrium constant for the association of monomer with monomer is smaller than the equilibrium constant for the association of monomer with

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[6] Lassettre, *J. Amer. Chem. Soc.*, 1937, **59**, 1383.

any larger oligomer (*i.e.*, $\beta_{20} < K$). This is to be expected both on the grounds of Saroléa-Mathot's statistical treatment[7] concerning the entropy term and from electrostatic considerations[8] concerning the enthalpy term. According to the statistical treatment,[7] the ratio K/β_{20} equals the number of equivalent orientations of the monomer in the solvent. The present value of ~ 3 is approximately equal to values reported elsewhere[5] for 2-n-butylbenzimidazole and some amides in benzene solution.

TABLE 2. *Self-association constants for the imidazole system obtained by various methods.*

	Eqn. (7)	Eqn. (8)	Eqns. (15) & (16)	Eqns. (19) & (20)
$\log \beta_{20}$	$2{\cdot}45 \pm 0{\cdot}03$	$2{\cdot}38 \pm 0{\cdot}02$	$2{\cdot}37 \pm 0{\cdot}03$	$2{\cdot}48 \pm 0{\cdot}04$
$\log \beta_{30}$		$5{\cdot}23 \pm 0{\cdot}03$	$5{\cdot}25 \pm 0{\cdot}04$	$5{\cdot}20 \pm 0{\cdot}04$
$\log \beta_{40}$		$\sim 8{\cdot}00$	$8{\cdot}13 \pm 0{\cdot}05$	$8{\cdot}02 \pm 0{\cdot}05$
$\log \beta_{50}$			$11{\cdot}01 \pm 0{\cdot}06$	$10{\cdot}89 \pm 0{\cdot}05$
$\log \beta_{60}$			$13{\cdot}89 \pm 0{\cdot}07$	$13{\cdot}78 \pm 0{\cdot}05$
$\log \beta_{q0}$			$2{\cdot}37 + (q - 2)2{\cdot}88$	Cf. eqn. (19)

Within the experimental precision, the free N–H groups in both the pyrazole and imidazole systems have been found to absorb at an identical frequency (3485 ± 10 cm.$^{-1}$) and with identical apparent molar extinction coefficients $\varepsilon_1 = 222 \pm 4$. These facts lend some support to our assumption in eqn. (2) that the various oligomers of imidazole have equal extinction coefficients. It is noteworthy that the bonded N–H regions from 3400 to 2000 cm.$^{-1}$, each with six peaks, are remarkably similar for both the pyrazole and the imidazole system. However, the self-association of imidazole in carbon tetrachloride is far more extensive than that of pyrazole. The latter only forms cyclic dimers and trimers, whereas imidazole (like 2-n-butylbenzimidazole in benzene[5,9]) forms a large number of linear oligomers. A comparison of Figs. 1 and 4 suggests that the peak at 3125 cm.$^{-1}$ may tentatively be assigned to the bonded N–H absorption of the dimer, and the remainder of the band to the bonded N–H absorptions of all larger oligomers, B_q ($q > 2$), which will be expected to have similar spectra.

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[7] Saroléa-Mathot, *Trans. Faraday Soc.*, 1953, **49**, 8.
[8] Coggeshall, *J. Chem. Phys.*, 1950, **18**, 978.
[9] White and Kilpatrick, *J. Phys. Chem.*, 1955, **59**, 1044.