Energy and Entropy Changes Accompanying the Molecular Association of δ-Valerolactam in Its Carbon Tetrachloride Solution

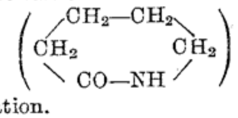
By Masamichi TSUBOI

(Received December 4, 1950)

Introduction

Recently the present writer made measurements of the infra-red absorption intensities of the 3.11 μ and 3.24 μ bands of δ-valerolactam in its carbon tetrachloride solutions at various concentrations and temperatures. The results of these experiments are of interest in connection with the problem concerning the molecular association of cyclic amides, since they show decidedly that δ-valerolactam molecules form on association exclusively ring dimers, the two bands being due to one and the same ring dimer structure. Furthermore, from the data obtained, calculations were made of the changes of energy and entropy accompanying the ring dimer formation. Some details of these experiments and their results are presented in this paper.

Experimental

The samples examined are carbon tetrachloride solutions of δ-valerolactam  purified by vacuum distillation.

As containers of the solutions, specially-made silica glass cells of different lengths (from 0.1 to 10 cm.) were used. (See Fig. 1.) Each cell has windows of plane-parallel silica glass plates (W), set by welding at both ends of its horizontal tube (H), parallel to each other, and an electric heating device is attached to the cell so that its content can be kept at desired temperatures.

The spectrometer with quartz prism here used is the same one which the writer used in his previous work.⁽¹⁾

δ-Valerolactam in carbon tetrachloride solutions exhibits, as reported in a previous paper,⁽¹⁾ three N-H bands, at 2.92 μ (due to free molecule), 3.11 μ (due to associated molecule) and 3.24 μ (also due to associated molecule). In the present experiments, measurements of the absorption intensities of these N-H bands were made with the object of determining the concentrations with respect to the free and associated molecules in the solutions of various concentrations (with respect to δ-valerolactam) at different temperatures.

Unfortunately, accurate absorption intensity measurements of the 2.92 μ band were not possible, owing to the interference of the absorptions in the neighborhood of 2.9 μ by the quartz prism used. Accordingly, measurements were made only of the other two bands at 3.11 μ and 3.24 μ.

Results and Interpretations

(1) From the measurements of transmittance (I/I_0) of the solutions for rays of 3.11 μ and

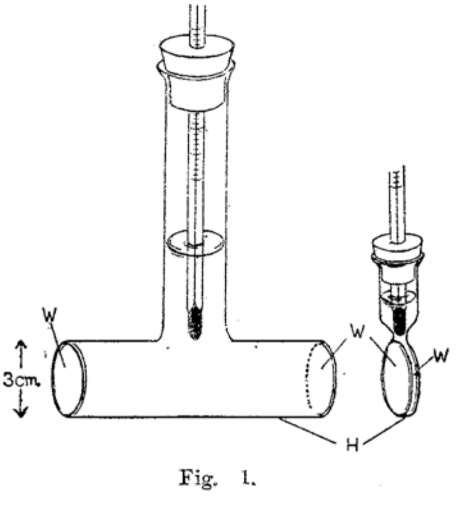


Fig. 1.

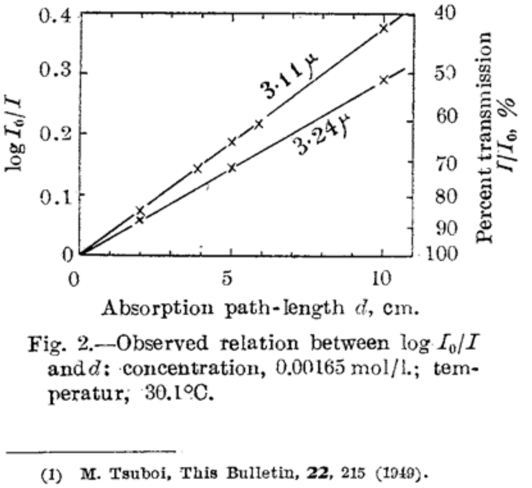


Fig. 2.—Observed relation between log I_0/I and d: concentration, 0.00165 mol/l.; temperatur, 30.1°C.

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(1) M. Tsuboi, This Bulletin, **22**, 215 (1949).

3.24 μ of various path-lengths (d), it was found that the observed relations between I/I_0 and d accord with the Lambert's law, deviations from it due to errors in observation being within a few per cent of $\log I_0/I$. Some examples of the relations obtained are shown in Figs. 2 and 3.

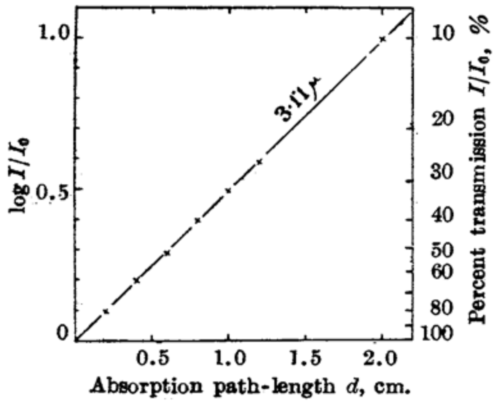


Fig. 3.—Observed relation between $\log I_0/I$ and d: concentration, 0.00997 mol/l; temperature, 30.1°C.

Based on the relations stated above, the value of $\frac{1}{d}\log\frac{I_0}{I}$ (denoted hereafter as x) for each solution is conveniently used in this paper to represent the absorption intensity of each band, for this value is independent of the path-length and is proportional to the concentration of the associated molecules to which the absorption band is assigned.

(2) In Table 1 are given the results of exploratory observations made as to how the values of x of the solutions for the 3.11 μ and 3.24 μ rays vary with the temperatures (t) and concentrations (c) with respect to δ-valerolactam. A notable fact seen in the table is that, while the values of both x for the 3.11 μ ray ($x_{3\cdot 11\mu}$) and x for the 3.24 μ ray ($x_{3\cdot 24\mu}$) vary with t and c, the ratios $x_{3\cdot 11\mu}/x_{3\cdot 24\mu}$ for any given t and c remain constant. This fact indicates that the two bands are due to one and the same kind of associated molecule and that the determination of one of the x's is sufficient for determination of the concentration of that molecule.

Table 1

Temp. °C.	Concn. mol/l.	x obsd. for the 3.11 μ ray	x obsd. for the 3.24 μ ray	$\frac{x_{3\cdot 24\mu}}{x_{3\cdot 11\mu}}$
30.1	0.03338	1.98	1.60	0.81
30.1	0.00997	0.498	0.395	0.79
30.1	0.00507	0.202	0.154	0.76
60.7	0.00487	0.100	0.077	0.77
30.1	0.00399	0.148	0.116	0.79
30.1	0.00165	0.0377	0.0291	0.77

(3) In the third column of Table 2 are given the values of x for the 3.11 μ ray, as observed with the solutions of various concentrations (with respect to δ-valerolactam) and temperatures. It is to be shown below that these results can be explained on the assumption, in accordance with the indication given in (2), that there is only one kind of associated molecule in the solutions, *i.e.*, $(C_5H_9NO)_2$, to which the 3.11 μ band is attributable, and that this dimer coexists with monomer C_5H_9NO in equilibrium, $2C_5H_9NO \rightleftarrows (C_5H_9NO)_2$.

Table 2

Temp. °C.	Concn. mol/l.	x for 3.11 μ ray (obsd.)	x for 3.11 μ ray (calcd.)
30.1	0.03338	1.98	2.01
	0.02158	1.24	1.22
	0.01362	0.700	0.709
	0.01320	0.682	0.681
	0.00997	0.498	0.483
	0.00905	0.441	0.429
	0.00757	0.355	0.343
	0.00555	0.231	0.220
	0.00507	0.202	0.203
	0.00399	0.148	0.147
	0.00296	0.0922	0.0975
	0.00165	0.0377	0.0415
45.3	0.01295	0.528	0.538
	0.00497	0.147	0.143
60.7	0.03204	1.47	1.42
	0.01270	0.381	0.392
	0.00487	0.100	0.097
	0.00159	0.0129	0.0143

On the assumption as stated above, the monomer $\rightleftarrows$ dimer equilibrium constant K now at issue must be expressed as

$$K=\frac{x/\kappa}{(c-2x/\kappa)^2},$$

where κ is the molecular absorption coefficient for the 3.11 μ ray and c the concentration with respect to δ-valerolactam. While, the observed relations between c and x seen from Table 2 accord well with the relations obtained from the above equation, if appropriate values are given to K and κ. Thus, the values of x observed at 30.1° (given in the third column of Table 2) show close agreement with those calculated by putting $K=206$, $\kappa=158$ in the equation (given in the fourth column), differences between them being less than several per cent of the values of x, with one exception.(2) The values of x observed at 60.7° also agree well with those calculated from the equation by putting $K=45$, $\kappa=159$. Furthermore, it is to be noticed that the values of κ given above for 30.1° and for 60.7° are practically equal to each other. This is just as it should be, since in the temperature range now in concern the molecular absorption coefficient for the ray of 3000 cm.$^{-1}$ or thereabout in frequency must be independent of temperatures.(3)

The value of K at 45.3° is 90, as calculated from the observed values of x and the assumed value of κ (=159).

In Table 3 the values of K for three different temperatures are given, with, in parallel column, the values of free energy change (ΔF) on association, which were calculated from the corresponding values of K (by the formula $\Delta F = -RT \ln K$). When the logarithms of these values of K are plotted against $1/T$, the points obtained fall on a single straight line (as shown in Fig. 4) From the inclination and the intercept of this straight line, the values of energy change (ΔE) and the entropy change (ΔS) accompanying the dimer formation in the solution are obtained as $\Delta E = -10.3 \pm 1.0$ kcal./mol and $\Delta S = -23.5 \pm 2.5$ E. U. The ΔE value here obtained is about twice as much as the value known for ordinary single hydrogen bond.

Table 3

Temperature, °C.	K	ΔF, kcal./mol	ΔS, E. U.	ΔE, kcal./mol
30.1	206	−3.21		
45.3	90	−2.84	−23.5	−10.3
60.7	45	−2.52		

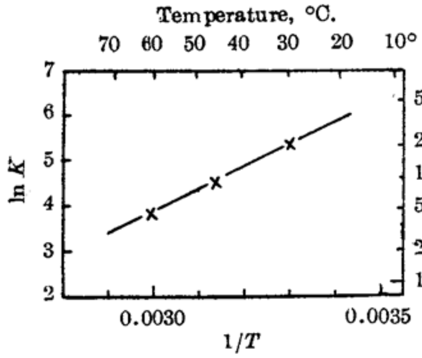
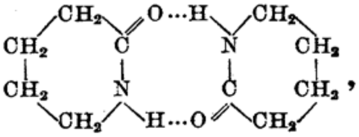


Fig. 4.

All the facts stated above, in combination, show decisively that δ-valerolactam molecules form on association only one type of dimer—the ring dimer with the inter-monomer double hydrogen bonds of the structure:



and that both of the two N-H association bands (at 3.11 μ and 3.24 μ) are attributable to this single structure.

The conclusion reached here does not agree with the view advanced by some previous writers, as Darmon and Sutherland,(4) who tend to attribute the two N-H association bands exhibited by cyclic amides to two different types of associated molecules.

Appendix.—In Fig. 5 is shown graphically the relation between association degree of δ-valerolactam molecules and the concentration and temperature of the solution, as obtained from the values of ΔE and ΔS.

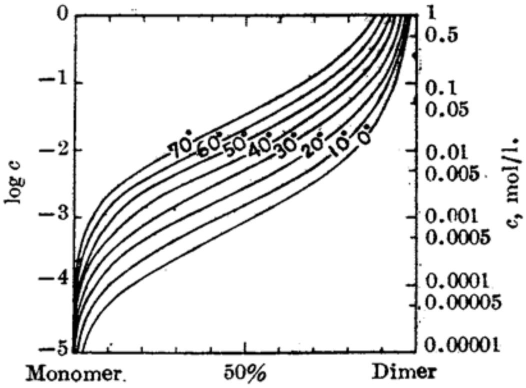


Fig. 5.

The writer wishes to express his sincere thanks to Professor San-ichiro Mizushima and Dr. Takehiko Shimanouchi for their kind guidance throughout this work. The cost of this research has been partly defrayed from Grant in Aid for Scientific Research from the Ministry of Eduction.

Chemical Institute, Faculty of Science,
the University of Tokyo, Tokyo

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(2) In the exceptional case where $c=0.00165$ mol/l., the difference between the calculated and observed values of x is about 10% of it. This is probably attributable to the error in determining such a small concentration.

(3) R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry", 1927, p. 175.

(4) S. E. Darmon and G. B. B. M. Sutherland, *Nature*, **164**, 440 (1949).