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The Self-Association of ϵ -Caprolactam in Carbon Tetrachloride: A Near-Infrared Spectroscopic Study

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The structure and hydrogen bonding behavior of lactams have attracted the interest of scientists for many years. Lactams have been used as models of the amide group in peptides and the self-association of the *cis*-lactams serves as model for the hydrogen bonding of the bases in nucleic acids. Several spectroscopic studies^{1,2} have shown that the lactams

$\left(\begin{array}{c} \text{C=O} \\ | \\ \text{---} \\ | \\ \text{N=H} \end{array} \right)_n$ are of the *cis* configuration for ring size $n \leq 8$ and of the *trans* configuration for $n > 9$. The $n > 9$ lactams exist in both the *cis* and the *trans* configurations. The associated species are cyclic dimers for lactams having amide group in the *cis* form, while a chain dimers and a small fraction of higher oligomers are involved in the case of *trans* amide group. These studies also indicate that ϵ -caprolactam ($n=7$) having only *cis* configuration exclusively forms cyclic dimers in the concentration ($c \leq 0.15$ M) and temperature range (293 K $\leq T \leq$ 333 K). It is known that at 293 K the model for cyclic dimerization breaks down at concentration distinctly larger than $c=0.2$ M. Despite the attention addressed to self-association constant,³⁻⁷ disagreement between the reported values for the dimerization constant of ϵ -caprolactam still exists. The purpose of present study is to exploit more thoroughly the use of near-IR spectrometry to determine the equilibrium constants and thermodynamic parameters for the dimerization reaction. We have chosen the first overtones of N-H stretching mode for this study. Earlier investigators have observed the absence of a first overtone band corresponding to the hydrogen-bonded inter-amide N-H stretching vibration of cyclic *cis*-lactam dimers in solution.⁵ Thus the concentration dependence of a first overtones of monomeric free N-H stretching mode near 6720 cm^{-1} has been measured in order to find the equilibrium constant for the dimerization. *Ab initio* thermodynamic parameters of dimerization reaction have been calculated and compared with the experimental results.

ϵ -Caprolactam (Aldrich, 99%) was recrystallized and dried under reduced pressure for 24 hours. Carbon tetrachloride (J. T. Baker, HPLC grade) was dried over 3 Å molecular sieves. Densities of CCl_4 solutions were measured by pycnometer at various temperatures and used to calculate the concentration of solution. The samples were prepared in N_2 filled glove box.

The near-IR absorption spectra of ϵ -caprolactam have been obtained with Cary 17DX spectrophotometer, using 10 cm

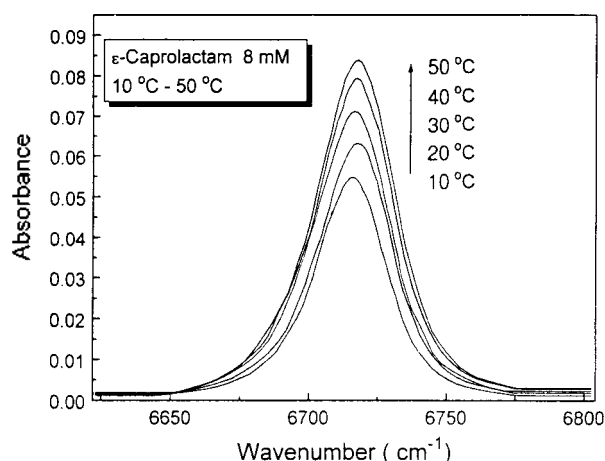


Figure 1. The absorption spectrum of first overtone band $2\nu_{N-H}$ of ϵ -caprolactam (8 mM)/ CCl_4 as a function of temperature.

path length cylindrical quartz cell. The sample and reference cells were placed in the jacketed cell holder connected to a constant temperature bath. The temperature fluctuation during the measurement was less than $0.2\text{ }^\circ\text{C}$.

The near-IR spectrum of ϵ -caprolactam in CCl_4 in the range of $4500\text{--}7000\text{ cm}^{-1}$ is found to be identical with the spectrum reported by Krikorian.⁴ Among the several bands, first overtone band of free N-H stretching vibration ($2\nu_{N-H}$) near 6720 cm^{-1} has a larger molar absorption coefficient compared to the other bands, and is well separated with other overtone or combination bands. The first overtone of hydrogen-bonded dimeric N-H stretching vibration is inactive, which is rationalized based on the differences in symmetry properties between monomeric and dimeric forms.

The equilibrium for the dimer formation and the equilibrium constant K are following;



$$K = \frac{[M_2]}{[M]^2} \quad (2)$$

The molar concentration of ϵ -caprolactam is defined as C_T . $C_T = [M] + 2[M_2]$. Since $[M_2] = K \cdot [M]^2$, C_T is

$$C_T = [M] + 2K[M]^2 \quad (3)$$

The $[M]$ is proportional to the integrated absorbance (A_M) of overtone band by Beer's law, $[M] = A_M / (b \cdot \epsilon_M)$ where b is cell path length and ϵ_M is integrated molar absorption coefficient. Using Beer's law, eq. (3) becomes

$$\frac{C_T b}{A_M} = \frac{1}{\epsilon_M} + \frac{2K}{\epsilon_M} \cdot \frac{A_M}{b} \quad (4)$$

From the plot of $C_T b / A_M$ vs. A_M / b , ϵ_M and K is obtained directly from the intercept and the slope of fitted straight line.

The spectrum of ϵ -caprolactam has been measured in the concentration range of $0.4\text{ mM--}8.0\text{ mM}$ and in the temperature range of $10\text{ }^\circ\text{C--}50\text{ }^\circ\text{C}$, where ϵ -caprolactam exclusively forms cyclic dimers. Figure 1 shows the absorption spectrum of $2\nu_{N-H}$ bands as a function of temperature, indicating that the concentration of ϵ -caprolactam monomer increases as the temperature increases. The integrated absorbance A_M has been obtained by integrating the area of $2\nu_{N-H}$ band. The values of ϵ_M and K at various temperatures are listed in Table 1. The average value of ϵ_M is 73.9 ± 0.4 and K at 298 K is $160 \pm 8\text{ M}^{-1}$. The ΔH° and ΔS° for the dimerization can be obtained from van't Hoff equation, $-d(\ln K)/d(1/T) = \Delta H^\circ / (R)$. The plot of $R \ln K$ vs. $1/T$ yields $-\Delta H^\circ = 28.6 \pm 1.5\text{ kJ mol}^{-1}$ and $-\Delta S^\circ = 53.9 \pm 2.0\text{ J K}^{-1}\text{ mol}^{-1}$.

For ϵ -caprolactam in CCl_4 solution, the values of K and ΔH° have been found by other workers. Using near-IR technique, Josefiak and Schneider³ determined the dimerization equilibrium constant K (293 K) and ΔH° to be 90 M^{-1} and $-30 \pm 1.5\text{ kJ mol}^{-1}$, respectively, and Krikorian⁴ reported the K as 120 M^{-1} at 294 K . Lord and Porro⁵ found the equilibrium constant at 299 K and the reaction enthalpy to have value 106 M^{-1} and $22.8 \pm 0.8\text{ kJ mol}^{-1}$, respectively, by analyzing the N-H stretching IR absorption band of monomeric and dimeric forms. Using IR technique, Affstrung *et al.*⁶ measured the equilibrium constant $K = 168\text{ M}^{-1}$ at 298 K and the reaction enthalpy $\Delta H = -23\text{ kJ mol}^{-1}$, while Hopmann⁷ reported $K = 60\text{ M}^{-1}$ at 298 K and $\Delta H = -26.3\text{ kJ mol}^{-1}$. Among these reported values, our equilibrium constant $K = 160 \pm 8$ at 298 K and reaction enthalpy $\Delta H = -28.6 \pm 1.5\text{ kJ mol}^{-1}$ are very consistent with the result of Affstrung *et al.*

We have performed *ab initio* MO calculations to have some understanding about qualitative picture of the dimerization reaction. Geometry optimizations were carried out for monomeric and dimeric forms at the RHF level using STO-3G basis sets which usually lead to quite good structural parameters. Constraints of C_s and C_{2h} symmetries were imposed on monomer and dimer, respectively. In order to consider the solvent effects, Onsager reaction field theory based on self-consistent reaction field (SCRF) method has been used. The solute is modeled as occupying a spherical cavity of radius in a continuous medium with a dielectric constant.

Table 1. The integrated absorption coefficient ϵ_M of the overtone band $2\nu_{N-H}$ and the thermodynamic parameters for the dimerization of ϵ -caprolactam

	283 K	288 K	293 K	298 K	303 K	308 K	313 K	318 K
ϵ_M	74.6	73.5	74.1	74.1	73.5	74.1	73.5	74.1
$^a K$	312	234	197	160	122	109	85	73
ΔG (kJ mol^{-1})	-13.5	-13.1	-12.9	-12.6	-12.1	-12.0	-11.6	-11.3
$-\Delta H$ (kJ mol^{-1})				28.6 \pm 1.5				
$-\Delta S$ ($\text{J mol}^{-1}\text{K}^{-1}$)				53.9 \pm 2.0				

^a $\pm 5\%$ experimental error

Table 2. Calculated energies and entropies of ϵ -caprolactam monomer and dimer in CCl_4 at 298 K

Molecules	E_e (hartree) ^a	E_{therm}^{298} (hartree) ^b	S^{298} (J/mol K)
Monomer	-358.4426083	0.2054575	334.915
Dimer	-716.9021656	0.4158267	516.665

^athe electronic energy. ^bthe thermal energy

The solute charge distribution is represented by a single-center multipolar expansion truncated at the dipolar term. Thus, the solute-solvent interaction is treated as only the dipole-dipole interaction between the solute and the continuum. All calculation have been performed using Gaussian 92 series of program.⁸ The electronic energy (E_e), and thermal energy (E_{therm}^{298}) and entropy (S_{298}) at 298 K of monomer and dimer are given in Table 2. The reaction enthalpy is obtained by the equation $\Delta H = \Delta E + \Delta(PV)$, where $\Delta E = \Delta E_e + \Delta E_{\text{therm}}$ (ΔE_e and ΔE_{therm} are the electronic energy and the thermal energy changes, respectively). Since the values of $\Delta(PV)$ is negligible in solution, $\Delta H = \Delta E = \Delta E_e + \Delta E_{\text{therm}}$. For the dimerization, ΔE_e is $E_e(\text{dimer}) - 2 E_e(\text{monomer})$ and ΔE_{therm} is $E_{\text{therm}}(\text{dimer}) - 2 E_{\text{therm}}(\text{monomer})$. ΔE_e and ΔE_{therm} at 298 K ($\Delta E_{\text{therm}}^{298}$) are -0.0169397 hartree ($-44.47 \text{ kJ mol}^{-1}$) and 0.0049117 hartree ($12.89 \text{ kJ mol}^{-1}$), respectively. Using these values, the reaction enthalpy ΔH^{298} is calculated to be $-31.58 \text{ kJ mol}^{-1}$, showing fairly good agreement with experimental value. The entropy change ΔS at 298 K is also calculated to be $-153.17 \text{ J mol}^{-1} \text{ K}^{-1}$.

In summary, the association of ϵ -caprolactam in CCl_4 solution has been investigated using near IR spectroscopy. The integrated molar absorption coefficient of the overtone band $2\nu_{\text{NH}}$ of ϵ -caprolactam monomer has been determined to be 73.9 ± 0.4 . The thermodynamic parameters for the dimerization are determined to be $K = 160 \pm 8 \text{ M}^{-1}$ (298 K), $\Delta H^\circ = -28.6 \pm 1.5 \text{ kJ mol}^{-1}$, and $\Delta S^\circ = -53.9 \pm 2.0 \text{ J K}^{-1} \text{ mol}^{-1}$. The *ab initio* calculations have been performed to obtain ΔH and ΔS at 298 K, which are -31.58 kJ/mol and $-153.17 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

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Synthesis of Bisspiromacrocylic Ionophores Tailor-Made for Lithium Ion

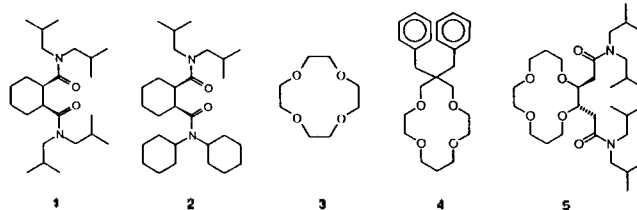
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Ion-selective electrodes (ISEs) and ion-selective field effect transistors (ISFETs) are being developed for the continuous measuring cations in body fluids.¹ Many natural ionophores, for example valinomycin for potassium ion,² monencin for sodium ion,³ nonactin for ammonium ion⁴ and calcimycin for calcium ion,⁵ selectively interact with the specific ion. Numerous synthetic diamide ionophores also display high selectivity to alkali metal ions and alkaline earth metal ions, such as N,N,N',N'-tetracyclohexyl-3-oxapentanediamide for calcium ion,⁶ N,N'-diheptyl-N,N'-dimethyl-1,4-butanediamide for magnesium ion,⁷ N,N,N',N'-tetracyclohexyl-1,2-phenylenedioxydiacetamide for sodium ion,⁸ and several synthetic lithium ionophores. Ionophores with high selectivity of lithium ion over sodium ion in blood and with stability for long time usage are currently required.⁹

Analyzing some known lithium ionophores such as N,N,N',N'-tetraisobutyl-*cis*-cyclohexane-1,2-dicarboxamide **1**,¹⁰ N,N-dicyclohexyl-N',N'-diisobutyl-*cis*-cyclohexane-1,2-dicarboxamide **2**,¹¹ 12-Crown-4 **3**,¹² 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetradecane **4**¹³ and 14-crown-4 derivatives **5**,¹⁴ we modeled



principles to design new types of lithium ionophores playing for the high selectivity toward to lithium ion over interfering ions in blood: (1) As binding sites four or five oxygen atoms in amide functionality play important role to interact with hard and small lithium ion based on 'hard and soft acid-base' principle.¹⁵ Furthermore the binding sites spherically arrange to interact with spherical lithium ion to form stable and selective complexes based on preorganization theory. In case of four binding sites tetrahedral arrangement will be favored. (2) Cyclic hosts interact with ions more strongly than acyclic their counterparts based on preorganization and size selectivity of host-guest chemistry. (3) Selectivity of ionophores in membrane in ISEs and ISFETs also depends