Theoretical Interpretation of Infrared Spectra of N-Cyclohexyl-2-pyrrolidone in Mixtures of Hexane and CDCl₃

D. Loos¹, A. Perjéssy¹,* and J. B. F. N. Engberts²

¹ Institute of Chemistry, Department of Organic Chemistry, Comenius University, SK-84215 Bratislava, Slovakia
² Department of Organic and Molecular Inorganic Chemistry, University of Groningen, NL-9747 AG Groningen, The Netherlands

Summary. The infrared spectra of N-cyclohexyl-2-pyrrolidone (NCP) in binary mixtures of hexane and CDCl₃ were interpreted theoretically in the region of C=O stretching vibrations using the AM1 semiempirical method. The results were compared with those obtained for N,N-dimethylacetamide (DMA), cyclohexanone (CX) and propanone (PR). Good correlations were found between the carbonyl stretching frequencies and the theoretical parameters of free and solvated species in equilibria with hexane–CDCl₃ solvent mixtures.

Keywords. N-Cyclohexyl-2-pyrrolidone; Solvation in hexane–CDCl₃ mixture; AM1 interpretation of infrared spectra.

Introduction

Nyquist and coworkers [1] reported the ν(C=O) values of N,N-dimethylacetamide (DMA) in a mixture of CCl₄ with CHCl₃, CH₃NO₂ and DMSO for different compositions of solvent couples. However, they have not described the splitting of the carbonyl band resulting from the solvent–solute interaction. They found that in CCl₄–DMSO mixtures the ν(C=O) values change with the composition of the mixture as the basicity of the carbonyl compound increases. Eaton and Symons [2]
devoted a detailed spectroscopic study to the solvation of \textit{DMA} in mixed and pure solvents, however, the properties of \textit{DMA} in non-aqueous mixtures have not been investigated.

\textit{N-cyclohexyl-2-pyrrolidone (NCP)} as a typical small amphiphilic molecule with surfactant properties\cite{3} attracted our attention and we studied its infrared spectra with respect to the solvent sensitivity of $v(C=O)$ in binary aqueous mixtures\cite{4}. Recently we reported the infrared spectra of \textit{NCP} in non-aqueous mixtures of hexane and CDCl$_3$ in the region of C=O stretching frequencies and compared the results with those obtained for \textit{DMA}, cyclohexanone (\textit{CX}) and propanone (\textit{PR})\cite{5}. When CDCl$_3$ is added to a solution of \textit{NCP} in hexane, $v(C=O)$ shifts to lower frequencies but over a range of mixture composition two bands are observed for the carbonyl group in \textit{NCP}. The origin of these bands was explained in terms of two types of hydrogen bonding in mono- and disolvated species and this should serve as a good model-example for substrate bonding to enzyme systems\cite{5}.

The main goal of the present work was therefore to interpret theoretically the infrared spectral data of \textit{NCP} in hexane–CDCl$_3$ mixture reported previously\cite{5} using AM1 quantum chemical method and to compare the results with those for \textit{DMA}, \textit{CX} and \textit{PR}.

\section*{Results and Discussion}

\textit{NCP} as a typical five-membered lactone due to the small-ring strain effect exhibit in non-polar aprotic solvent (hexane) the carbonyl stretching band at 1704.4 cm$^{-1}$, which is by 31.2 cm$^{-1}$ higher compared to simplest acyclic model: \textit{DMA} ($v(C=O) = 1673.2$ cm$^{-1}$). This is the reason that the basicity, electron-releasing and hydrogen-bonding properties of both compounds cannot be compared directly by $v(C=O)$ values.

Investigating the $v(C=O)$ values of \textit{NCP} as a function of mole fraction of hexane in CDCl$_3$[$f(C_6H_{14})$] reported in\cite{5} we can observe a rapid change passing from the solution in pure C$_6$H$_{14}$[$v(C=O) = 1704.4$ cm$^{-1}$][$f(C_6H_{14}) = 1.00$] to the mixture with the addition of a small amount of CDCl$_3$ [$f(C_6H_{14}) = 0.92$] [$v(C=O) = 1685.4$ cm$^{-1}$], the difference being $\Delta v = 19.0$ cm$^{-1}$. Increasing gradually the portion of CDCl$_3$, two absorption bands appeared in the region of carbonyl stretching vibrations. The higher frequency band in the region of 1681.0–1685.4 cm$^{-1}$ belongs to a hydrogen bonded C=O group with one CDCl$_3$ molecule, or one linear chain of self-associated molecules, which can be simply treated as a monosolvated species. The lower frequency one in the region of 1664.4–1673.1 cm$^{-1}$ is connected with the existence of disolvated molecules i.e. possessing a C=O group with a hydrogen bond towards two molecules of CDCl$_3$ or two linear chains of self-associated CDCl$_3$ molecules. Decreasing the mole fraction of C$_6$H$_{14}$ below 0.92 the frequencies of both $v(C=O)$ absorption bands shift downward, whereby the intensity of the higher-frequency (monosolvate) band decreases and that of the lower-frequency (dissolvate) one increases. It is evident from the above results that in the region of mole fractions $f(C_6H_{14}) = 0.92$–0.59 both the mono- and disolvated species exist together in range of equilibrium mixtures. At the value of mole fraction $f(C_6H_{14}) = 0.53$ the higher-frequency band disappears and the $v(C=O)$ value of the lower-frequency one continually decreases until $v(C=O) = 1661.4$ cm$^{-1}$, which is the value obtained in the pure CDCl$_3$. 