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

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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 v(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 v(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 DMA in mixed and pure solvents, however, the properties of DMA in non-aqueous mixtures have not been investigated.

N-cyclohexyl-2-pyrrolidone (NCP) as a typical small amphilic molecule with surfactant properties [3] attracted our attention and we studied its infrared spectra with respect to the solvent sensitivity of $\nu$(C=O) in binary aqueous mixtures [4]. Recently we reported the infrared spectra of 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 DMA, cyclohexanone (CX) and propanone (PR) [5]. When CDCl$_3$ is added to a solution of NCP in hexane, $\nu$(C=O) shifts to lower frequencies but over a range of mixture composition two bands are observed for the carbonyl group in 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 [5].

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

**Results and Discussion**

*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: DMA ($\nu$(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 $\nu$(C=O) values.

Investigating the $\nu$(C=O) values of NCP as a function of mole fraction of hexane in CDCl$_3$ [f(C$_6$H$_{14}$)] reported in [5] we can observe a rapid change passing from the solution in pure C$_6$H$_{14}$($\nu$(C=O) = 1704.4 cm$^{-1}$) [f(C$_6$H$_{14}$) = 1.00] to the mixture with the addition of a small amount of CDCl$_3$ [f(C$_6$H$_{14}$) = 0.92] ($\nu$(C=O) = 1685.4 cm$^{-1}$), the difference being $\Delta\nu$ = 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 $\nu$(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$_6$H$_{14}$) = 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$_6$H$_{14}$) = 0.53 the higher-frequency band disappears and the $\nu$(C=O) value of the lower-frequency one continually decreases until $\nu$(C=O) = 1661.4 cm$^{-1}$, which is the value obtained in the pure CDCl$_3$. 