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Theoretical Interpretation of Infrared Spectra of N-Cyclohexyl-2-pyrrolidone in Mixtures of Hexane and $CDCl_3$

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Summary. The infrared spectra of N-cyclohexyl-2-pyrrolidone (*NCP*) in binary mixtures of hexane and $CDCl_3$ 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–$CDCl_3$ solvent mixtures.

Keywords. N-Cyclohexyl-2-pyrrolidone; Solvation in hexane–$CDCl_3$ mixture; AM1 interpretation of infrared spectra.

Theoretische Interpretation von Infrarot-Spektren von N-Cyclohexyl-2-pyrrolidon in Mischungen von Hexan und $CDCl_3$

Zusammenfassung. Es wurden die Infrarot-Spektren von N-Cyclohexyl-2-pyrrolidon (*NCP*) in binären Mischungen von Hexan und $CDCl_3$ im Bereich der C=O Streckschwingung unter Benutzung der semiempirischen AM1-Methode interpretiert. Die Ergebnisse wurden mit denen für N,N-Dimethylacetamid (*DMA*), Cyclohexanon (*CX*) und Propanon (*PR*) verglichen. Es wurde eine gute Korrelation zwischen den Frequenzen der Carbonyl-Streckschwingung und den theoretischen Parametern der freien und solvatisierten Spezies im Gleichgewicht mit den Hexan–$CDCl_3$ Lösungsmittelgemischen gefunden.

Introduction

Nyquist and coworkers [1] reported the ν(C=O) values of N,N-dimethylacetamide (*DMA*) in a mixture of CCl_4 with $CHCl_3$, CH_3NO_2 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 CCl_4–*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 *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 ampiphilic molecule with surfactant properties [3] attracted our attention and we studied its infrared spectra with respect to the solvent sensitivity of ν(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, ν(*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* (ν(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 ν(C=O) values.

Investigating the ν(C=O) values of *NCP* as a function of mole fraction of hexane in $CDCl_3$ [f(C_6H_{14})] reported in [5] we can observe a rapid change passing from the solution in pure C_6H_{14}[ν(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] [ν(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_6H_{14} below 0.92 the frequencies of both ν(C=O) absorption bands shift downward, whereby the intensity of the higher-frequency (monosolvate) band decreases and that of the lower-frequency (disolvate) 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 ν(C=O) value of the lower-frequency one continually decreases until ν(C=O) = $1661.4\,cm^{-1}$, which is the value obtained in the pure $CDCl_3$.

Table 1. Relative basicities and energies of hydrogen bond with phenol

Compound	$\Delta\nu(OH)/cm^{-1}$	$\Delta H/kJ\,mol^{-1}$
PR	205	16.3
CX	220	17.3
DMA	333	24.9
NCP	347	25.8

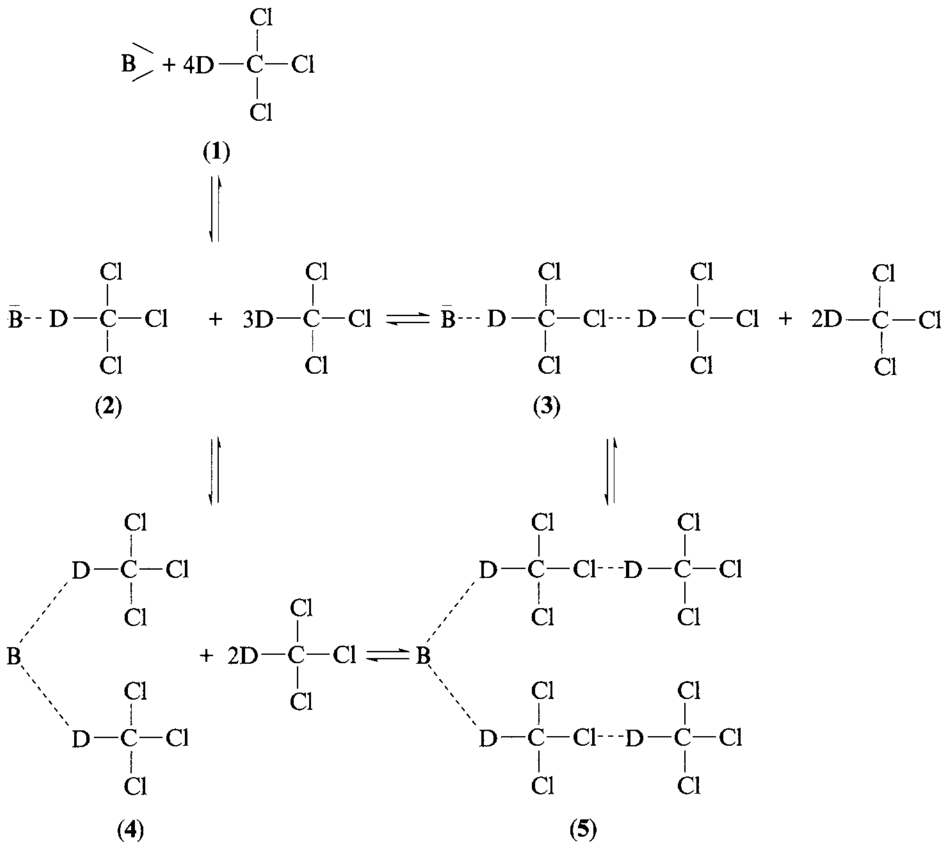
A similar behaviour is observed when investigating the dependence of carbonyl stretching frequencies of *DMA* upon the mole fraction of C_6H_{14} in $CDCl_3$. There are, however, some specific features: In the case of *NCP* the differences between the $\nu(C=O)$ values of mono- and disolvated forms are approximately by $2\,cm^{-1}$ smaller than for *DMA*. On the other hand, the difference between the $\nu(C=O)$ value of free molecules (in C_6H_{14}) and the monosolvated species is for *NCP* by $4.6\,cm^{-1}$ larger than for *DMA*. This means that by a continual addition of $CDCl_3$ the origin of monosolvated form is easier with *NCP* than with *DMA*, whereas the change of monosolvate for disolvate seems to be somewhat more difficult in the case of *NCP* than at *DMA*. The latter is probably caused by the steric effect of the cyclohexyl ring of *NCP* on the carbonyl group.

Before comparing the solvation ability in the series of *PR*, *CX*, *DMA*, and *NCP* we determined experimentally the relative basicities of the compounds on the basis of their interaction with phenol in CCl_4 under the conditions at which the self-association of phenol molecules was excluded. The $\Delta\nu(OH)$ frequency shifts of phenol caused by interaction with carbonyl compounds and the corresponding energies of hydrogen bonds of type $>C=O\cdots H-O-$ calculated using Badger's empirical equation are given in Table 1.

It is evident from the results reported [5] that the linear change of $\nu(C=O)$ values with mole fractions of C_6H_{14} for both the mono- and disolvate of the base B (B = *NCP* or *DMA*) belongs to the secondary solvation effects connected with the self-association of $CDCl_3$ molecules, which can be expressed by the equilibria shown in Scheme 1.

The assignment of carbonyl stretching frequencies to free and solvated species (1)–(5) for investigated carbonyl compounds in Scheme 1 is given in Table 2. The assumed solvation model is in very good agreement with the conclusion [6, 7] that chloroform exhibits a significant tendency of self-association in cyclohexane (comparable with hexane in our case), which is stronger than that in CCl_4, where a competitive association of $CHCl_3$ with CCl_4 molecules takes place, the energy of hydrogen bonding being $\Delta H = 6.3\,kJ\,mol^{-1}$. This conception can serve also as a reasonable explanation for the fact [1] that the $\nu(C=O)$ absorption bands of *DMA* are not splitted in the binary mixtures of CCl_4 and $CHCl_3$.

Comparing the slopes of $\nu(C=O)$ vs. $f(C_6H_{14})$ correlations in Table 3 it can be concluded that the secondary solvation effect of formation of monosolvated species is stronger for *NCP* than for *DMA*. It means that *NCP* as a stronger base supports better the self-association of $CDCl_3$ cosolvent molecules by forming of monosolvate chains, than the less basic *DMA*. A similar behaviour can be observed also by the



Scheme 1

Table 2. Carbonyl stretching frequencies of free and solvated species (compare Scheme 1)

Species	$\nu(C{=}O)/cm^{-1}$			
	PR	*CX*	*DMA*	*NCP*
(1)	1721.2	1723.8	1673.2	1704.4
(2)	–	–	1657.0	1685.4
(3)	–	–	1655.0	1681.0
(4)	–	–	1641.4	1673.1
(5)	1710.2	1704.4	1635.8	1664.4

formation of disolvated species, however, the difference between the effects of two the bases *NCP* and *DMA* is less pronounced.

Cyclohexanone (*CX*) and propanone (*PR*) as the simplest cyclic and acyclic ketone-models in C_6H_{14}-$CDCl_3$ binary mixtures show [5] that in both cases no splitting of carbonyl stretching bands was observed in any range of C_6H_{14} mole fractions. That means that in both *CX* and *PR* the mono- and disolvated species

Table 3. Secondary solvation effects: Correlations ν(C=O) vs. mole fraction of C_6H_{14}

Statistical parameter	*NCP*		*DMA*	
	Monosolvate	Disolvate	Monosolvate	Disolvate
ρ^a	14.65 ± 1.50	11.05 ± 0.85	9.16 ± 2.07	9.64 ± 0.61
q^b	1672.4	1664.0	1649.7	1636.2
n^c	6	15	7	14
r^d	0.978	0.962	0.893	0.977
s^e	0.42	0.93	0.71	0.59

[a] Slope

[b] Intercept

[c] Number of points used in correlation

[d] Correlation coefficient

[e] Standard deviation

exist only to a small extent simultaneously in an equilibrium mixture. The initial decrease of ν(C=O) frequency by addition of a small amount of $CDCl_3$ is somewhat larger in the case of *CX* than in *PR*. In both cases there are not clear differences between the spectroscopic behaviour of possible mono- and disolvated species as well as of their secondary solvation effects. It is evident that all discussed effects are a little bit more pronounced in the case of the more basic *CX* than in *PR*.

Using the AM1 semiemperical method with standard parameterization [8] the energies, geometric and electronic structure of *PR*, *CX*, *DMA*, *NCP* and their hydrogen-bonded species (see Scheme 1) were calculated. The results are listed in Table 4.

Table 4. Theoretical parameters[a] for free molecules and solvated species

Species[b]	ΔH^c/kJ mol^{-1}				p(C=O)				$-$q(O)			
	PR	*CX*	*DMA*	*NCP*	*PR*	*CX*	*DMA*	*NCP*	*PR*	*CX*	*DMA*	*NCP*
(1)	–	–	–	–	1.898	1.904	1.748	1.769	0.301	0.298	0.376	0.355
(2)	11.2	11.8	14.3	13.3	1.879	1.884	1.722	1.743	0.324	0.321	0.406	0.381
(3)	10.9	11.3	13.3	14.0	1.877	1.880	1.719	1.739	0.325	0.329	0.408	0.387
(4)	13.4	10.6	12.4	11.2	1.861	1.865	1.697	1.718	0.343	0.341	0.425	0.405
(5)	10.1	10.2	11.5	10.9	1.857	1.862	1.691	1.706	0.349	0.346	0.431	0.410

[a] In the case of two sterioisomeric species connected with hydrogen bonding of $CDCl_3$ molecules to the carbonyl group only small differences were obtained, and therefore their arithmetic means are listed

[b] For numbering see Scheme 1

[c] The energy of hydrogen bond between the carbonyl group and $CDCl_3$ molecules was calculated as the difference between the total energy of hydrogen-bonded species and the sum of energies of non-bonded species

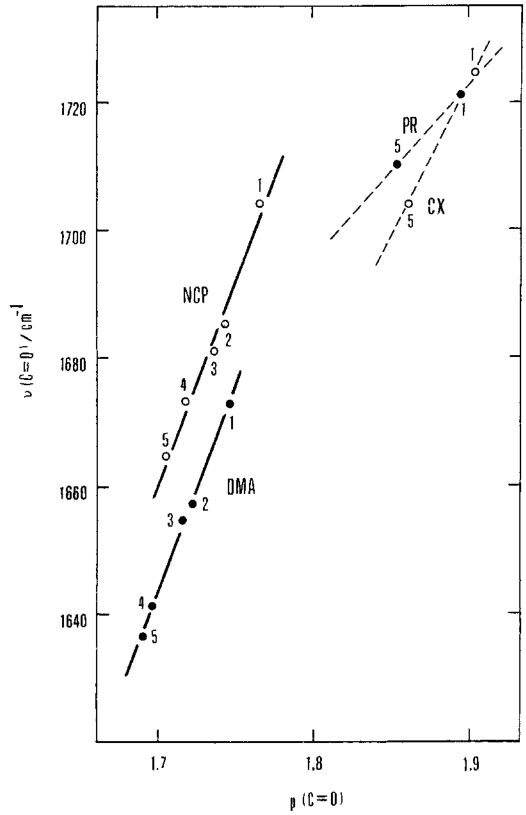


Fig. 1. Dependence of carbonyl stretching frequencies of free molecules and solvated species on the C=O bond order

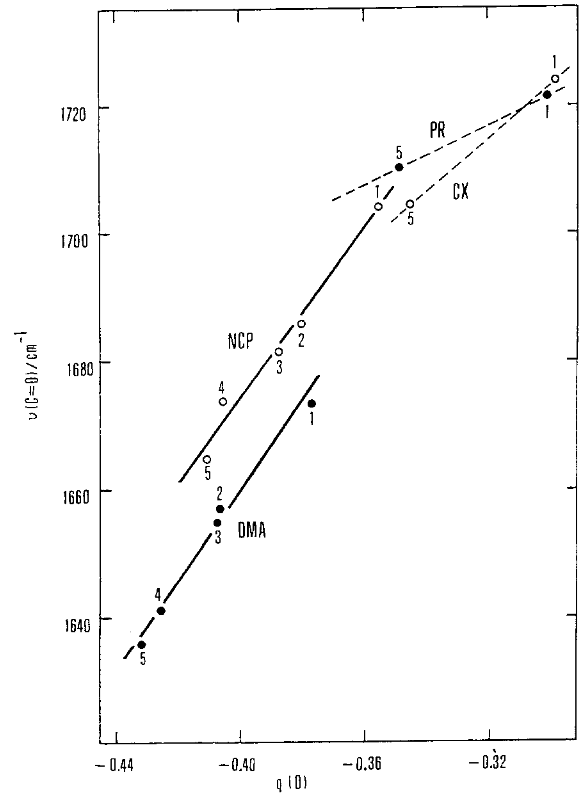


Fig. 2. Dependence of carbonyl stretching frequencies of free molecules and solvated species on the oxygen charge density

The carbonyl stretching frequencies of free and all solvated species for *NCP* and *DMA* (cf. Table 2) provide excellent linear correlations with calculated C=O bond orders, p(C=O) as well as with oxygen atom charge densities, q(O) (cf. Table 4), which is illustrated in Figs. 1 and 2. In the figures also the tendencies of similar correlations for *PR* and *CX* are shown for comparison. The straight lines of ν(C=O) vs. p(C=O) and ν(C=O) vs. q(O) correlations are for both *NCP* and *DMA* nearly parallel and their slopes are larger than in the case of *PR* and *CX*, which suggests a higher sensibility of the C=O group to the solvation effects. The above correlations confirm that the assigment of the ν(C=O) values in Table 2 is correct and that the solvation process takes place according to Scheme 1.

It is evident from Table 4 that the calculated values of hydrogen bond energies, ΔH in most species containing two hydrogen-bonded $CDCl_3$ molecules decrease in comparison with systems including only one $CDCl_3$ molecule. The difference between the ΔH values observed in equilibria (2)$\rightleftharpoons$(4) and (3)$\rightleftharpoons$(5) are generally somewhat higher as in the case of equilibria (2)$\rightleftharpoons$(3) and (4)$\rightleftharpoons$(5). It is evident for equilibria (2)$\rightleftharpoons$(4) and (3)$\rightleftharpoons$(5) that the change in the hydrogen bond energy is more pronounced for *NCP* molecules than for other compared bases i.e. *DMA*, *CX*, and *PR*. This is most probably caused by the steric effect of the cyclohexyl ring, which partially hinders the $CDCl_3$ molecule to approach the second lone electron pair of the C=O group.

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