university of groningen

University Medical Center Groningen

University of Groningen

The Solvent Mixture Sensitivity of Carbonyl Stretching Frequencies of 2-Pyrrolidinones and Related Compounds

Perjessy, A.; Engberts, Jan; Blandamer, M.J.

Published in:
Default journal

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Perjessy, A., Engberts, J. B. F. N., & Blandamer, M. J. (1995). The Solvent Mixture Sensitivity of Carbonyl Stretching Frequencies of 2-Pyrrolidinones and Related Compounds. Default journal, 29, 89 - 90.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 10-02-2018

THE SOLVENT MIXTURE SENSITIVITY OF CARBONYL STRETCHING FREQUENCIES OF 2-PYRROLIDINONES AND RELATED COMPOUNDS

A. Perjessy, J. B. F. N. Engberts, and M. J. Blandamer

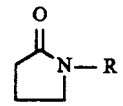
Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH-2, 842 15 Bratislava, Slovakia
Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
Department of Chemistry, The University, Leicester LE1RH, United Kingdom

Received December 10,1994

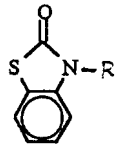
Abstract: The carbonyl stretching frequencies of 1-substituted 2-pyrrolidinones and related compounds were measured in binary mixtures of hexane-$CDCl_3$ and acetonitrile-D_2O and plotted against the mole fraction of the less polar co-solvent The ν(C=O) vs. mole fraction correlations enabled to recognize and assign all species resulting from solvent-solute interactions in binary mixtures. The slopes of the above dependencies for species with angular hydrogen bonds correlate well with the carbonyl group relative basicities and reveal that the solvent sensitivity of species in organic hexane-$CDCl_3$ mixtures remarkably depends on the steric effects of substituents in the vicinity of the C=O group. On the other hand a similar dependence for aqueous acetonitrile-D_2O mixtures indicates that ν(C=O) sensitivity is proportional to the alkyl group effects as expected in Taft substituent constants.

Introduction

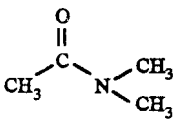
Recentlly[1-3] a significant solvent and solvent mixture sensitivity of the infrared frequencies characterizing the carbonyl stretching vibration of 1-cyclohexyl-2-pyrrolidinone in both aqueous and organic solvent mixtures was used to recognize the solute-solvent interactions. The results suggested that 1-cyclohexyl-2-pyrrolidinone in binary mixtures exists in several different domains, the lifetime of which are much longer than the period over which the C=O stretching frequency is measured. In connection with the above results we decided to investigate the carbonyl stretching frequencies of 1-substituted 2-pyrrolidinones and 3-substituted 2-oxobenzothiazoles in mixtures of hexane-$CDCl_3$ and acetonitrile-D_2O and compare the results with similar data obtained for N,N-dimethyl-acetamides:



R = H	(P)
R = CH_3	(MP)
R = $CH(CH_3)_2$	(IPP)
R = cyclo-C_6H_{13}	(CHP)
R = CH_2CH_2OH	(HEP)



R = H	(OBT)
R = C_8H_{17}	(OOBT)



(DMA)

Experimental

The materials and experimental conditions were similar to those used in[1,2] and will be characterized in more details later.[4,5]

Results and Discussion

Figure 1 represents the dependence of the carbonyl stretching frequencies of 1-cyclohexyl-2-pyrrolidinone (CHP) on the mole fraction of n-hexane in solvents formed by mixing of n-hexane and deuteriotrichloromethane. The absorption band at 1704.4 cm^{-1} in pure hexane belongs to molecules of CHP existing in the free monomeric state (FM). When $CDCl_3$ is added to the solution of CHP in n-hexane the above absorption band is dramatically shifted to the lower frequency region (1685.4-1681.0 cm^{-1}), whereby its position is linearly dependent on the composition of the mixture. Using the recently proposed approach to the stereochemistry of hydrogen bonding[6] the above region can be assigned to the species of CHP bonded via linear hydrogen bonds between the C=O group and $CDCl_3$ molecules (LM). Finally, increasing the concentration of $CDCl_3$ in the mixture the ν(C=O) bands are further shifted to the lower frequencies (1673.1-1664.4 cm^{-1}) creating a new linear dependence upon the mole fraction of n-hexane. The above range evidently belongs to the species of CHP stabilized by classical angular hydrogen bonds with the $CDCl_3$ molecules (AM). The behavior of other studied compounds (2-pyrrolidinones, 2-oxobenzothiazoles and dimethylformamide) is similar to that of CHP, with exceptions described in more details in.[4,5]

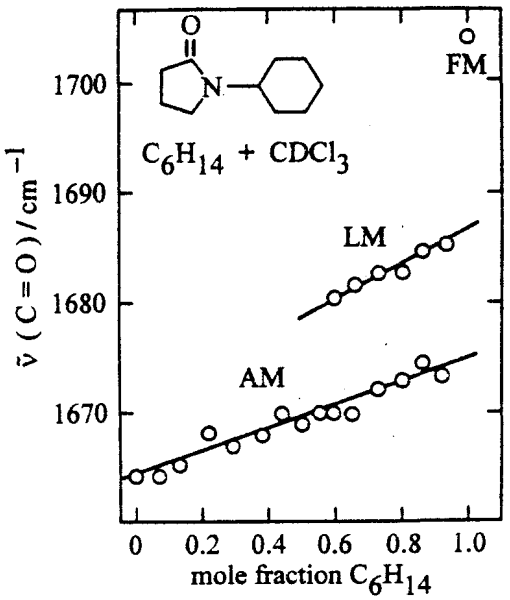


Figure 1. Dependence of carbonyl stretching frequencies for 1-cyclohexyl-2-pyrrolidinone (CHP) on the mole fraction of hexane formed by mixing of hexane and $CDCl_3$.

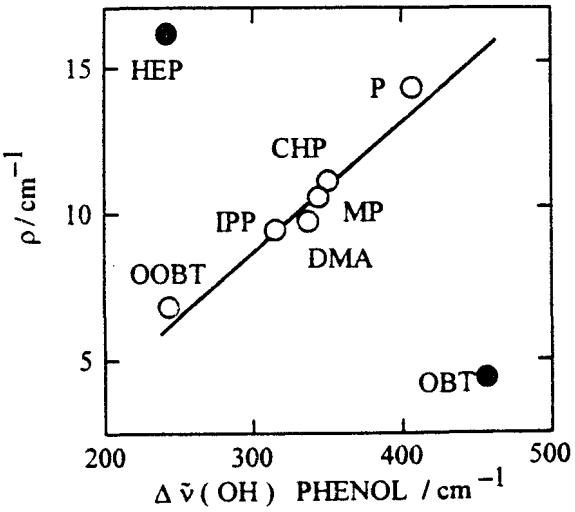


Figure 2. Correlation between the slopes ρ of ν(C=O) vs. mole fraction (C_6H_{14}) dependences in hexane-$CDCl_3$ mixtures and relative basicities (Δν(OH)) for 1-substituted 2-pyrrolidinones and related compounds.

The most remarkable common feature of all studied compounds in both organic and aqueous binary solvent mixtures is a statistically significant correlation between the carbonyl stretching frequencies of species forming angular hydrogen bonds (AM) with the more polar co-solvent and the composition of the solvent mixture. The ρ values of the above dependencies can be plotted against the relative basicities of studied compounds as it is illustrated in Figure 2 and Figure 3.

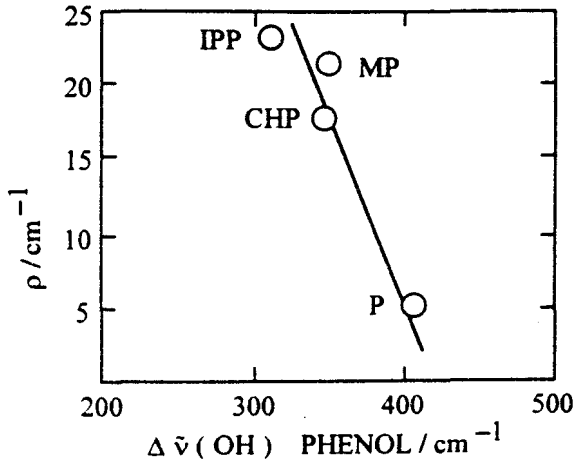


Figure 3. Correlation between the slopes ρ of ν(C=O) vs. mole fraction (CH_3CN) dependences in CH_3CN-D_2O mixtures and relative basicities (Δν(OH) for 1-substituted 2-pyrrolidinones.

It follows from the comparison of the above figures that the solvent sensitivity of the AM species of the above substances in organic mixtures of hexane-$CDCl_3$ depends on the steric effects of substituents in the vicinity of the C=O group. On the other hand, for aqueous CH_3CN-D_2O mixtures the above solvent sensitivity is proportional to the electron-donating effects of the substituents attached to the nitrogen atom. The above distinct behavior of solvent/solute interactions in organic and aqueous mixtures can be easily explained as the difference in the size of small D_2O and bulky $CDCl_3$ molecules interacting with sterically hindered C=O group.

Acknowledgment. Financial support for this work by European Community, Brussels, Belgium (collaborative research grant ERB-CIPA-CT-9-0409) is gratefully acknowledged.

References

1. J. B. F. N. Engberts, A. Perjéssy, M. J. Blandamer, G. Eaton, *J. Chem. Soc. Faraday Trans.*, **88**, 2493 (1992).
2. J. B. F. N. Engberts, A. Perjéssy, M. J. Blandamer, *J. Chem. Soc. Faraday Trans.*, **89**, 4199 (1993).
3. D. Loos, A. Perjéssy, J. B. F. N. Engberts, *Monatsh. Chem.*, **125**, 293 (1994).
4. J. B. F. N. Engberts, A. Perjéssy, in press.
5. J. B. F.N. Engberts, A. Perjéssy, in press.
6. C. Laurence, M. Berthelot, M. Helbert, *Spectrochim. Acta*, **A41**, 883 (1985).