

## NOTIZEN

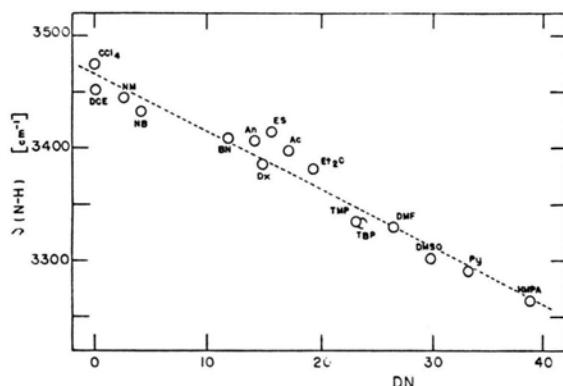
**Solvent Effects on the IR Spectra of N-Methylacetamide**

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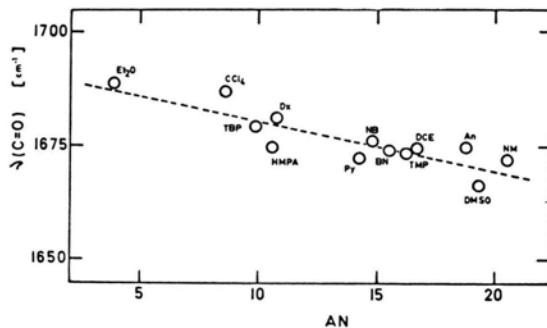
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The solvent effect on the  $\nu(\text{N}-\text{H})$  amide I and amide II IR bands of N-methylacetamide were investigated. The frequency shifts could be related to the solvent donor and acceptor numbers by mean of a two parameters relationship that accounts for the mutual influence between the two interacting sites of the amide.

Although solvent effects on the IR spectra of amides, especially on N-methylacetamide (NMA) because of its relevancy as a biological model, have been frequently studied [1–3], no clear dependence of the observed spectra on properties of solvents has been established. We have reinvestigated the influence of some aprotic solvents on the IR spectra of NMA solutions analysing the solvent shifts of the  $\nu(\text{N}-\text{H})$ , amide I and amide II bands as a function of the donor and acceptor properties of the solvent. As a measure of the Lewis base and acid strength of solvent molecules the donor numbers (DN) [4] and the acceptor numbers (AN) [5] were considered.

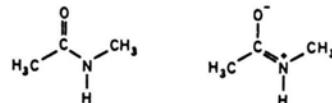
Fig. 1. Relationship between  $\nu(\text{N}-\text{H})$  of N-methylacetamide and the solvent donor numbers.

As expected for this substrate, able to form hydrogen bonds, the shift of the band  $\nu(\text{H}-\text{N})$  towards lower frequencies increases with increasing donor properties of the solvent as shown in Fig. 1.

Fig. 2. Relationship between  $\nu(\text{CO})$  of N-methylacetamide and the solvent acceptor number.

The amide I band corresponding to the stretching frequency  $\nu(\text{CO})$  shows an approximately linear relationship with AN as can be seen in Fig. 2. The assignment of bands appearing in the range of  $\nu(\text{N}-\text{H})$  to an overtone of  $\nu(\text{CO})$  [2] has been in this way corroborated, since this band exhibits the same solvent dependence as  $\nu(\text{CO})$ . The amide II band, that could be observed only in some solvents, is not very sensitive, and slight shifts towards higher frequencies are observed by increasing the solvent donor strength.

In spite of the relatively acceptable correlations observed for the plots in Fig. 1 and 2, it is necessary to consider that both kinds of interactions, through the carbonylic oxygen and through the amidic proton, are mutually influenced because of the electron delocalization in the amidic bond. The relative importance of these two kinds of solute-solvent interactions is fundamentally determined by the contributions of the resonance structures



to the hybrid which describes the actual state of the molecule in a given medium. The mutual influence between the two interacting sites can be established through a two parameter relationship,

$$\nu = c_0 + c_1 \text{DN} + c_2 \text{AN}.$$

Similar expressions have been used to describe solvent effects on the NMR spectrum of thioamide

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Table I. Correlation of the N-H and C=O stretching absorptions in N-methylacetamide with solvent properties.

	$c_1$	$c_2$	$c_0$	R <sup>a</sup>
One parameter Approach	$\nu(\text{N}-\text{H})$	-5.2	-	3464 0.9847
	$\nu(\text{CO})$	-	-1.1	1691 0.8585
Two parameter Approach	$\nu(\text{NH})$	-5.3	-0.6	3473 0.9856
	$\nu(\text{CO})$	-0.2	-1.2	1696 0.9609

<sup>a</sup> Absolute value of the linear or multiple correlation coefficient.

[6] as well as on other physicochemical properties of solutes [7-9]. Table I shows the regression and correlation coefficients corresponding to the one and two parameter approach. It can be clearly seen that the experimental frequencies are better reproduced using the two parameter relationship. This fact clearly shows that the solvent-solute interactions in this amide are extended to the whole molecule, so that in this way the solvent would influence other properties as the rotation about the bond, and the configuration of the amide. Investigations concerning these questions are in progress.

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- [1] E. A. Cutmore and H. E. Hallam, Spectrochim. Acta **25** A, 1767 (1969).
  - [2] M. Rey-Lafon, J. Lascombe, and M. L. Josien, Am. Chim. **8**, 493 (1963).
  - [3] C. N. R. Rao, K. G. Rao, A. Goel, and D. Balasubramanian, J. Chem. Soc. (A) **1971**, 3077.
  - [4] V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett. **2**, 257 (1966).
  - [5] U. Mayer, V. Gutmann, and W. Gerger, Monatsh. Chem. **106**, 1235 (1975).
  - [6] G. González and J. Granijo, Inorg. Chim. Acta **35**, 209 (1979).
  - [7] T. M. Krygowski and W. R. Fowcett, J. Am. Chem. Soc. **97**, 2143 (1975).
  - [8] U. Mayer, Monatsh. Chem. **109**, 775 (1978).
  - [9] C. Reinhart, Solvent effects in organic chemistry, p. 256, Verlag Chemie, Weinheim, New York 1979.