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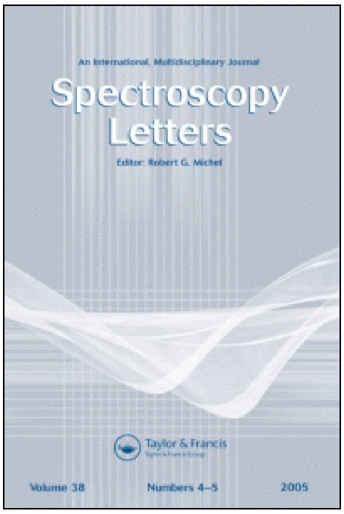

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Infrared Study of the Interaction Between Carbamates and Proton Donors

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INFRARED STUDY OF THE INTERACTION BETWEEN CARBAMATES AND PROTON DONORS

Keywords : Aliphatic carbamates - phenols - hydrogen bonds - thermodynamic data - infrared spectra.

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INTRODUCTION

Owing to its great importance as a structural link in proteins, the NH-CO amide group has been the subject of numerous experimental and theoretical investigations. In contrast, the -NH-COO-carbamate group has been relatively ignored despite its importance in biologically active molecules such as local anaesthetics$^{1-2}$. Up to now, no experimental studies concerning the proton acceptor ability of carbamates have appeared in the literature. It must be pointed out however that ab initio calculations were carried out for the interaction between simple carbamates and model molecules such as N-

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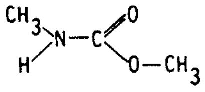
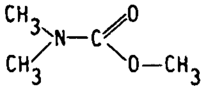
methylacetamide or phenol[3]. In this work, the complexes between N-methyl methyl-carbamate (MMC) and N,N-dimethyl methylcarbamate (DMMC) and model proton donors (phenol derivatives) are studied by IR or FT-IR spectroscopy



MMC



DMMC

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As shown by theoretical[4] and X-ray data[5-6], the carbamates are in a Z conformation, trans for MMC. It is generally accepted that the Z conformers of esters are more stable than the more sterically hindered E conformers[7].

EXPERIMENTAL SECTION

MMC and DMMC have been synthetized from methylchloroformate and the corresponding amine (methylamine or dimethylamine)[8]. The purity of the products has been checked by ^{1}H NMR spectroscopy. The solvents were dried by the standard methods.

The stability constants (K) have been determined from the absorbance of the ν_{OH} stretching vibration of the phenol derivatives at concentrations of phenols ranging from 0.005 to 0.01 M in order to avoid selfassociation. The base was always in excess (0.01 - 0.05 M). The enthalpies of complex formation have been computed from the K values at 298 and 323 K.

The infrared spectra were recorded on the Perkin-Elmer 883 and on the Bruker FT-IR 88 spectrophotometers at a resolution of 2 cm^{-1}.

The integrated molar absorption coefficient A defined as

$$A = 1/cd \int \ln I_0/I \, d\nu \qquad (l mol^{-1} cm^{-2}) \qquad (1)$$

(c = molar concentration, d = cell thickness in cm)

has been computed from the Bruker integration program.

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EXPERIMENTAL RESULTS AND DISCUSSION

a) Thermodynamic Data

The experimental results (K, $-\Delta H$) for the complexes involving MMC and DMMC and some phenol derivatives are given in tables 1 and 2. These tables also report the $\Delta\nu_{OH}$ values defined as the frequency difference (in cm^{-1}) between the absorption maximum of the OH stretch of the free and bonded phenol. The same parameters useful for the comparison of the results have also been measured for some complexes involving N-methylacetamide (NMA) as proton acceptor. These data are collected in table 3.

TABLE 1

Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between MMC and Phenols. Solvent = CCl_4.

Phenol derivative[a]	K^{298K} [b] M^{-1}	K^{323K} [b] M^{-1}	$-\Delta H$ [c] $kJmol^{-1}$	$\Delta\nu_{OH}$[d] cm^{-1}
4-CH_3O phenol (10.21)	23.1	11.6	22.4	222
phenol (9.95)	32.3	15	23.3	227
4-Br phenol (9.34)	60	28.6	24.8	258
3-Br phenol (9.03)	74.2	34.2	25.7	263
3,4-diCl phenol (8.58)	126.5	58.2	26.8	287
3,5-diCl phenol (8.18)	177.9	71.6	27.9	297
3,4,5-triCl phenol (7.75)	280	120	29.1	306

[a] The pK_a of the phenol is indicated in parentheses.
[b] Standard deviation = 5%.
[c] Computed from the K values obtained from the least-mean-square plot of log K vs pK_a.
[d] Error on the maximum = ± 5 cm^{-1}.

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TABLE 2

Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between DMMC and phenols. Solvent = CCl_4.

Phenol derivative	K^{298K} M^{-1}	K^{323K} M^{-1}	$-\Delta H$ $kJmol^{-1}$	$\Delta\nu_{OH}$ cm^{-1}
4-CH_3O phenol	29	14.8	22.6	239
phenol	36.1	17.2	23.3	247
4-Br phenol	88.4	39.6	24.9	280
3,4-diCl phenol	198	85.6	27	316
3,5-diCl phenol	258	114	28.1	323
3,4,5-triCl phenol	413	166	29.3	335

TABLE 3

Thermodynamic Data and $\Delta\nu_{OH}$ Values for Some Complexes between NMA and Phenols.

Phenol derivative	K^{298K} M^{-1}	K^{323K} M^{-1}	$-\Delta H$ $kJmol^{-1}$	$\Delta\nu_{OH}$ [a] cm^{-1}
4-CH_3O phenol	69	35	21.9	
phenol	96	47	23.1	320
4-Br phenol	210	95	25.7	345
3,4-diCl phenol	560	230	28.9	380

[a] Reference 9.

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One example of a spectrum in the ν_{OH} region is shown in figure 1.

The logarithms of the formation constants are linearly related to the pK_a of the phenols. A least-mean-square treatment yields the following expressions :

For the MMC systems :

$$\log K^{298K} = 5.873 - 0.440\ pK_a \qquad (r=0.9988) \qquad (2)$$

$$\log K^{323K} = 5.200 - 0.404\ pK_a \qquad (r=0.9975) \qquad (3)$$

For the DMMC complexes :

$$\log K^{298K} = 6.344 - 0.477\ pK_a \qquad (r=0.9963) \qquad (4)$$

$$\log K^{323K} = 5.660 - 0.440\ pK_a \qquad (r=0.9958) \qquad (5)$$

As usually found for closely related complexes, greater slopes and intercepts are associated with

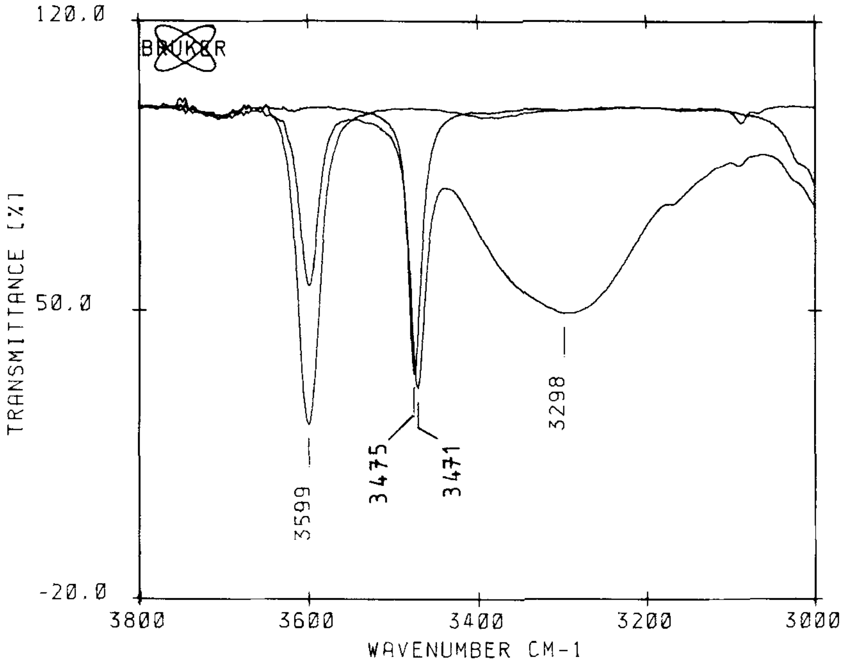

Figure 1

FT-IR spectrum in the ν_{OH} region.

A : MMC (c = 0.011 M)

B : 3,4,5-triCl phenol (c = 0.008 M)

C : 3,4,5-triCl phenol (c = 0.008 M) and MMC (c = 0.010 M). Solvent = CCl_4. d = 0.3 cm.

stronger complexes. As shown by the data of tables 1 and 2, the formation constants of the DMMC-systems are higher than of the MMC complexes and this can be accounted for by the electron donating properties of the CH_3 group. Owing to the experimental error on the enthalpies which are ± 1.5 $kJmol^{-1}$, the difference between the MMC and

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DMMC are not significative. The same remark also holds for the entropy variations which range between -45 and -48 $Jmol^{-1}K^{-1}$ for the two systems.

b) Spectroscopic Characteristics

The $\Delta\nu_{OH}$ values ranging from 220 to 335 cm^{-1} are typical for hydrogen bond complexes of medium strength[10]. They are ordered according to the acidity of the proton donor and show that the DMMC complexes are a little bit stronger than the MMC complexes.

As shown in figure 1, complex formation brings about a strong intensity increase of the ν_{OH} vibration. The values of the integrated molar intensity of the ν_{OH} band (A^c) have been calculated by equation (1) where c, the molar concentration of complexes has been deduced from the K values. The A^c values are indicated in table 4 along with the square root of the intensity enhancement ($\Delta A^{1/2}$). This table also lists the dipole moment derivative taken with respect to the normal coordinate ($\partial\mu/\partial Q$) or to the internuclear distance ($\partial\mu/\partial r_{OH}$) which can be calculated from the expression

$$\frac{\partial\mu}{\partial Q} = \pm\sqrt{\frac{3\,c^2\,A^c\,10^3}{\pi\,N}}$$

$$\frac{\partial\mu}{\partial r_{OH}} = \pm\sqrt{\frac{3\,c^2\,A^c\,\mu_{red}}{\pi\,N}}$$

μ_{red} being the reduced mass of the OH bond.

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TABLE 4

Integrated Molar Intensity of the ν_{OH} Band (A^c), Square Root of the Intensity Enhancement ($\Delta A^{1/2}$) and Dipole Moment Derivatives ($\partial\mu/\partial Q$) and $\partial\mu/\partial r_{OH}$) for Complexes between DMMC and Phenols. Solvent = CCl_4.

Phenol derivative	A^c $l mol^{-1} cm^{-2}$	$\Delta A^{1/2}$ $l^{\frac{1}{2}} mol^{-\frac{1}{2}} cm^{-1}$	$\partial\mu/\partial Q$ $esu.g^{-\frac{1}{2}}$	$\partial\mu/\partial r_{OH}$ $10^{10} esu$
4-CH_3O phenol	87.550	274.4	353.3	4.31
phenol	82.270	266	342.5	4.18
4-Br phenol	106.990	303.3	390.5	4.76
3-Br phenol	100.290	294.3	378.1	4.61
3,4-diCl phenol	112.190	311.1	399.9	4.88
3,5-diCl phenol	111.440	309.2	398.6	4.87
3,4,5-triCl phenol	120.810	319.6	415	5.06

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The dipole moment derivatives do not markedly differ from these computed for the N,N-dimethylacetamide complexes[11,12]. They are ordered according to the strength of the interaction and this is shown in figure 2 where $\partial\mu/\partial r_{OH}$ has been plotted against $\Delta\nu_{OH}$.

The frequency shift of the ν_{OH} stretching vibration to lower wavenumbers, listed in table 5, indicates that complex formation occurs at the oxygen atom of the carbonyl function. One example of a spectrum in the $\nu_{C=O}$ region is reproduced in figure 3. These findings agree with the ab initio calculations of Remko et al.[3] for the 2-methoxycarbamate-phenol complex. The greatest

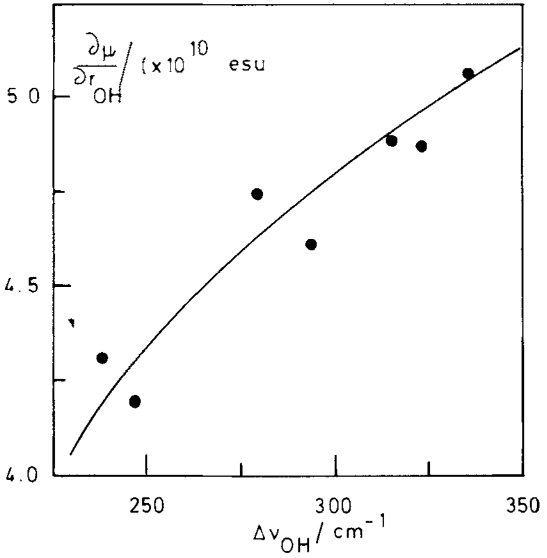

Figure 2

$\partial\mu/\partial r_{OH}$ as a function of $\Delta\nu_{OH}$ (DMMC complexes).

TABLE 5

$\Delta\nu_{C=O}$ Values for the Complexes between MMC and DMMC and Phenols. Solvent = CCl_4.

Phenol derivative	$\Delta\nu_{C=O}$(MMC)[a] cm^{-1}	$\Delta\nu_{C=O}$(DMMC)[b] cm^{-1}
4-CH_3O phenol	17	16
phenol	19	19
4-Br phenol	21	21
3-Br phenol	22	22
3,4-diCl phenol	23	23
3,5-diCl phenol	23	23
3,4,5-triCl phenol	25	24

[a] The $\nu_{C=O}$ vibrations of free MMC and DMMC are observed at 1735 and 1711 cm^{-1} respectively. The spectra have been recorded in extended scale and the error on $\Delta\nu_{C=O}$ is ±1 cm^{-1}.

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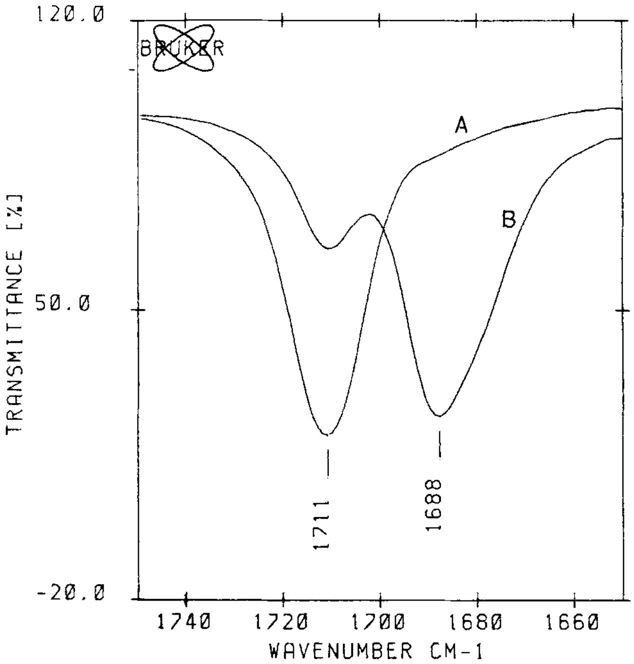

Figure 3

FT-IR spectrum in the $\nu_{C=O}$ region.

A : DMMC (c = 0.0065 M)

B : DMMC (c = 0.0065 M) and 3,4-diCl phenol (c = 0.023 M)

interaction energy (22 kJmol^{-1}) is found for the hydrogen bond formed between the OH group and the carbonyl oxygen atom. This value agrees very well with the experimental value of 23 kJmol^{-1} found in this work. The calculated energy for the hydrogen bond formed between the NH function of the carbamate and the oxygen atom of phenol acting as proton acceptor is lower (16.3 kJmol^{-1}). This structure is not detected in the infrared spectrum.

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Indeed, only a small shift of 4 cm^{-1} to lower frequency (figure 1) is observed and this shift can be attributed to a secondary perturbation brought about by the formation of the C=O...HO hydrogen bond. Formation of a NH...O bond should broaden and shift the ν_{NH} band by about 100 cm^{-1}. For the interaction between N-phenylurethane and di-n-propylether which can be considered as a stronger base than phenol, the ν_{NH} band is shifted by 150 cm^{-1} [13].

Table 5 reports the $\Delta\nu_{C=O}$ values for the MMC and DMMC complexes. Generally, the $\Delta\nu_{C=O}$ values for carbonyl acceptors split into lines when plotted against $\Delta\nu_{OH}$ (or $-\Delta H$) for the common proton donor[14-15]. This has been extensively discussed in a recent work[16]. MMC and DMMC are closely related carbonyl acceptors and as shown in figure 4, $-\Delta H$ vs $\Delta\nu_{C=O}$ gives a single relation. Interestingly, the correlation is not obviously linear, even in this limited $-\Delta H$ domain. This has been discussed in a recent theoretical work for the interaction between $H_2C=O$ with H_2O and various cations[17]. The slope of the $-\Delta H$ vs $\Delta\nu_{C=O}$ line is such that each $kcal.mol^{-1}$ in $-\Delta H$ is associated with a decrease of the $\nu_{C=O}$ frequency of 2 cm^{-1}. The experimental results depicted in figure 4 show that a difference of 1 $kcal.mol^{-1}$ in $-\Delta H$ corresponds to a decrease of the $\nu_{C=O}$ frequency of about 3.5 cm^{-1}. This is not unexpected owing to the stronger electron donor properties of the substituents of MMC and DMMC as

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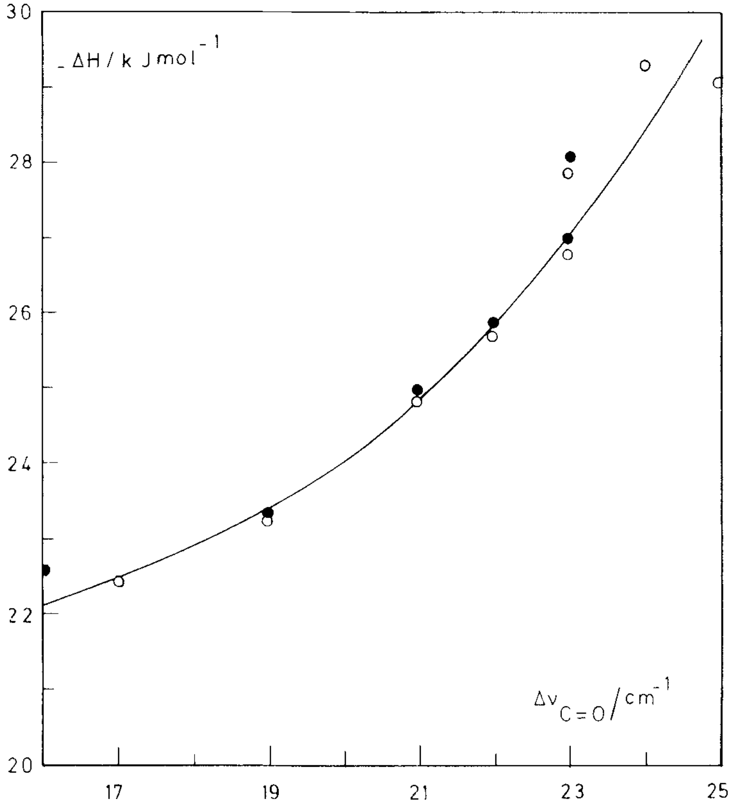

Figure 4
$-\Delta H$ versus $\Delta\nu_{C=O}$ for complexes involving phenols and
○ : MMC, ● : DMMC

compared with H_2CO[15]. The non-linearity of the $-\Delta H$ vs $\Delta\nu_{C=O}$ correlation has been accounted for by some mixing of the $\nu_{C=O}$ vibration with other modes[17]. It must be pointed out however, that the experimental values of the energies contain all the terms (electrostatic, repulsion, polarisation and charge transfer) contributing to the

TABLE 6

K^{298K}, $\Sigma\sigma_I$ and $\Sigma\sigma_R^+$ for some carbonyl bases complexed with phenol.

Base	K^{298K}	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$
DMA	130	0.02	-2.11
NMA	96	0.04	-1.81
DMMC	36	0.31	-2.48
MMC	32	0.33	-2.28
MeAc	7.5	0.21	-1.09
Ac	11	-0.08	-0.50

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total energy. The $\Delta\nu_{C=O}$ values are related to the increase of the polarity of the C=O bond and depend mainly on the dispersion and charge transfer contribution. This may also contribute to the deviation to the linearity.

c. Comparison with Other Closely Related Systems

Table 6 allows to compare the experimental value of the formation constant of N,N-dimethylacetamide (DMA)[18], NMA, MMC, DMMC, methylacetate (MeAc)[19] and acetone (Ac)[15] with phenol as reference acid. This table also indicates the sum of the inductive ($\Sigma\sigma_I$) and resonance ($\Sigma\sigma_R^+$) substitution constants[20].

The logarithms of the stability constants can be expressed by the dual expression

$$\log K^{298K} = 0.41 - 2.22\ \Sigma\sigma_I - 0.80\ \Sigma\sigma_R^+$$

which reproduces the experimental values with a correlation coefficient of 0.981. Similar correlations have been calculated for the $\Delta\nu_{OH}$ values of carbonyl complexes[15]. In this case the ρ_1/ρ_R ratio is about 1.7.

The $-\Delta H$ vs $\Delta\nu_{OH}$ correlation for complexes involving phenols and a common proton acceptor (DMA[18], NMA, MMC, DMC, Ac[15] and MeAc[19,21] (figure 5) can be written :

for DMA[18] and NMA complexes :

$$-\Delta H = -8.02 + 0.096\ \Delta\nu_{OH} \quad (r = 0.966)$$

for MMC and DMMC complexes :

$$-\Delta H = 8.89 + 0.061\ \Delta\nu_{OH} \quad (r = 0.934)$$

for Ac complexes :

$$-\Delta H = -1.65 + 0.083\ \Delta\nu_{OH} \quad (r = 0.985)$$

for MeAc complexes :

$$-\Delta H = -28.4 + 0.28\ \Delta\nu_{OH} \quad (r = 0.967)$$

These correlations show that the two carbamates studied in this work are situated between the aliphatic amides and the aliphatic esters. For the methylacetate complexes the $\Delta\nu_{OH}$ value for a given $-\Delta H$ value is obviously lower than for the other carbonyl systems. This can be accounted for, at least qualitatively, by the fact that the lone pair of electrons of the carbonyl

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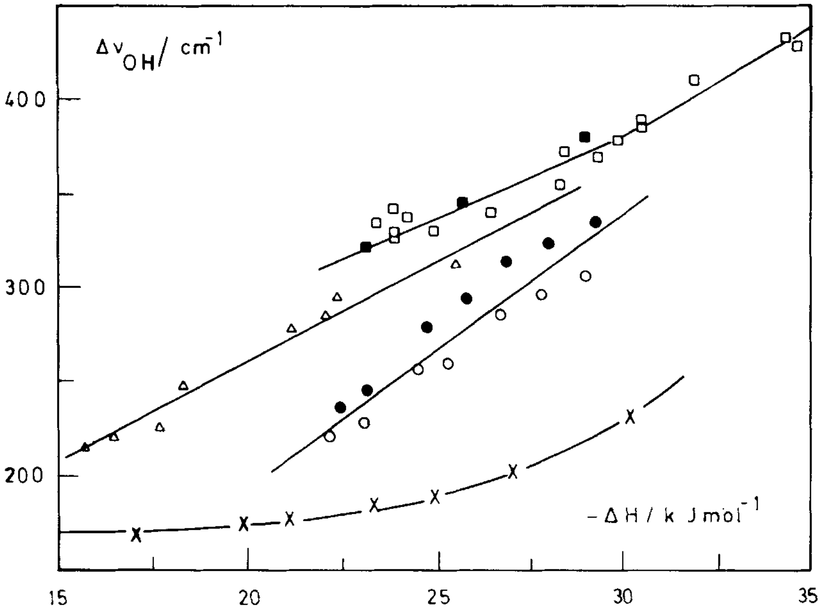

Figure 5

$-\Delta H$ vs $\Delta\nu_{OH}$ for hydrogen bond complexes involving phenol derivatives and ☐ : DMA, ■ : NMA, △ : Ac, O : MMC, ● : DMMC, X : MeAc.

group in the cis-position with respect to the methoxy group is markedly more involved in hydrogen bonding than the trans pair. Moreover, as shown by dipolar studies[22] and ab initio calculations[23], the angle formed between the C=O direction and the direction of the hydrogen bond is not 60 but takes values between 40 and 48°. As a consequence, the overlapping between the σ_{OH}^* and the free lone pair will not be optimal and this effect can have a greater influence on the $\Delta\nu_{OH}$ than on the $-\Delta H$

values. Further, for the NMA.H_2O complex, quantum mechanical calculations have shown that the water molecule is in trans position with respect to the C-N bond and that the angle between the C=O group and the hydrogen bond is about 60°[24] allowing an optimal overlapping between the O sp^2 and σ_{OH} orbitals. There are no experimental or theoretical data on the geometry of carbamate complexes. The optimized geometry of protonated MMC indicates that the angle between the C=O and the OH^+ bonds is 58°[25]. This angle can be slightly different in the neutral complexes.

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