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NATURE OF THE SOLVENT EFFECT IN THE INFRARED SPECTRA OF CARBONYL COMPOUNDS

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A number of papers devoted to the investigation of the effect of solvents on the characteristic frequencies of various bonds has appeared in recent literature.[1-5] In some of these papers the authors[1-3] related the observed frequency shifts due to the solvent to some specific property of the solvent such as the dielectric constant or the refractive index on the assumption of the validity of the Kirkwood-Bauer-Magat theory.[6,7] A new approach to the study of the solvent effect can be seen in the recent communications by Archibald and Pullin[4] and by Bellamy, Hallam, and Williams[5] in which the effect of the solvent was shown to depend both on the properties of the solvent and on the character of the bond concerned.

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[1] L.N.Fuson and M.L.Josien, *J.Phys.Radium* **15**, 652 (1954).

[2] M.L.Josien and L.N.Fuson, *J.Chem.Phys.* **22**, 1169 (1954).

[3] N.S.Bayliss, A.R.H.Cole and L.H.Little, *Australian J.Chem.* **8**, 26 (1955).

[4] L.B.Archibald and A.D.Pullin, *Spectrochim.Acta* **12**, 34 (1958).

[5] L.J.Bellamy, H.E.Hallam and R.L.Williams, *Trans.Faraday Soc.* **54**, 1120 (1958).

[6] J.G.Kirkwood, *J.Chem.Phys.* **2**, 351 (1934).

[7] E.Bauer and M.Magat, *J.Phys.Radium* **9**, 319 (1938).

In the course of our studies of the infrared spectra of some carbonyl compounds the frequencies of the carbonyl stretching vibration of a number of carboxylic acid derivatives, ketones, and aldehydes were measured in a variety of solvents. It was found that the frequency shifts $\Delta\nu_{CO}$, defined as the differences between the frequencies measured in dilute (0.005-M) solutions in n-hexane and in chloroform, are considerably different for different compounds of the class investigated and depend on the polarity of the carbonyl bond. In particular, a linear relationship was established between the frequency shifts, $\Delta\nu_{CO}$, and the values of the carbonyl stretching frequencies, ν_{CO} (measured in n-hexane), for true carboxylic acid derivatives of the type R-CO-X with X = Halogen, $-OR'$, $-NR'R''$. As an example, the plots of $\Delta\nu_{CO}$ vs. ν_{CO} are shown in Fig. 1. for benzoic and acetic acid derivatives for which the following linear relation was found to be obeyed within ± 2 cm^{-1}:

$$\Delta\nu_{CO} = A\ (1 - \alpha\cdot\nu_{CO}) \qquad (1)$$

with A 283.4 cm^{-1}, α $0.5423.10^{-3}$ cm for benzoic acid, and A 380.4 cm^{-1}, α $0.5394.10^{-3}$ cm for acetic acid derivatives. This relation is, however, not valid in the case of ketones and aldehydes.

An analogous behaviour of carboxylic acid derivatives was observed in our previous study of the correlations between the infrared carbonyl stretching frequencies and ultraviolet K-band absorption frequencies.[8] The linear relation between the infrared and ultraviolet frequencies was shown there to be related to a linear relationship between Taft's parameters[9] σ_I and σ_R which can be taken as a measure for the inductive

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[8] O.Exner, M.Horák and J.Plíva, Chem.& Ind. 1174 (1958).

[9] R.W.Taft Jr., J.Amer.Chem.Soc. 79, 1045 (1957).

and mesomeric effects of the substituents X. It was therefore endeavoured to find the relationship between the frequency shifts $\Delta\nu_{CO}$ and the

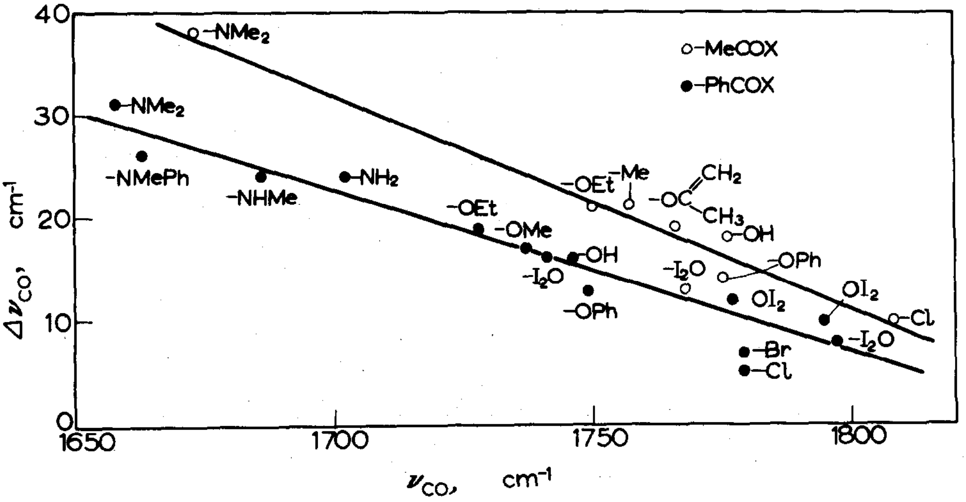

Fig. 1.

Relation between frequency shifts, $\Delta\nu_{CO}$, and carbonyl stretching frequencies, ν_{CO} , for carboxylic acid derivatives, R-CO-X (R = C_6H_5 and R = CH_3).

polar properties of the substituents X as expressed by the σ_I and σ_R constants. Again, a linear relation of the type

$$\Delta\nu_{CO} = \Delta_o(1 + a_I . \sigma_I + a_R . \sigma_R) \qquad (2)$$

was found to be valid not only for the carboxylic acid derivatives for which eq. (I) holds, but in general for aldehydes and ketones as well. The following approximate values of the parameters of eq. (2) were found for the two cases referred to above: the constants a_I -2.1 and a_R -2.9 are approximately equal for both of these cases and the values of the parameters Δ_o 8 cm^{-1} for R = C_6H_5- and Δ_o 11.5 cm^{-1} for R = CH_3- correspond to the frequency shifts observed for the corresponding aldehydes.

The results of this study show that the solvent effect cannot be simply understood if only the overall properties of the solvent are taken into account, and it is necessary to consider both the properties of the solvent and of the solute and their specific interactions. In the particular case investigated in the present work the differences in frequencies found in a nonpolar solvent (hexane) and in a polar solvent (chloroform) are related to the polar properties of the substituents directly attached to the bond the characteristic frequency of which is studied. Thus it is thought that a thorough investigation of this effect might be of interest from the point of view of the study of the polar properties of organic substituents.

It is proposed to publish a more detailed account of our work in the journal "Collection of Czechoslovak Chemical Communications".