structure can only be carried out, however, when single crystals are provided.

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Studies on Sulfinic Acids

V.* Correlation of the IR-Frequencies of the Sulfur-Oxygen Bonds in Substituted Aromatic Sulfinates and Sulfonates with Hammett Substituent Constants

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This communication forms part of a series which has hitherto been mainly concerned with the reactivity and conjugation of the ionic aromatic sulfinate group, using the linear free energy relationship approach.[1] Good correlations with the Hammett equation were obtained.

In 1948 Flett suggested that if a relationship could be established between IR-frequencies and reaction rates, it would be possible to use IR-frequencies to gain the same kind of information as is obtained from the correlation of reaction rates with substituent constants and illustrated this with some series of substituted aromatic compounds.[2] Since then interest in the linear relationships between non reactivity data and substituent constants has grown, and IR-frequencies have attracted much attention from this point of view.

The Hammett equation and it's modifications have been applied to various group

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frequencies as well as to intensities with good results,[3,4] and Rao and Venkataraghavan have evaluated the correlations of IR group frequencies and intensities in organic molecules with substituent constants, statistically.[5]

The correlations mentioned were obtained with, for instance, various aromatic carbonyl groups, aromatic isothiocyanates, nitrobenzenes, benzonitriles, phenols and anilines. In connection with the work reported in part III of this series,[6] the SO-frequencies of the aromatic sodium sulfinates under study were therefore recorded in order to investigate whether similar correlations could be demonstrated with these compounds. In aqueous solution, fairly good correlations with the Hammett equation were obtained for the frequencies assigned to the SO symmetric and SO asymmetric stretching vibrations. There was, however, at that time insufficient material to confirm the assignments or interpret the results. Since then ex-
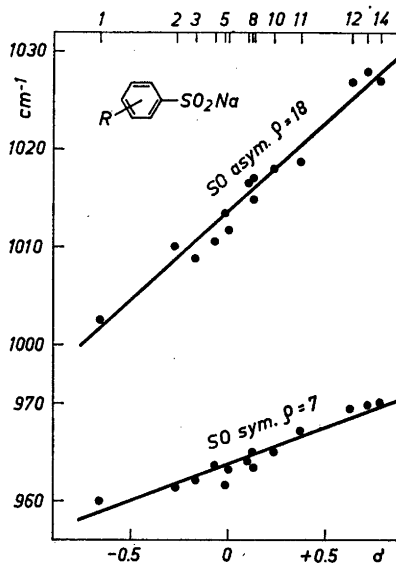

Fig. 1. Asymmetric and symmetric SO-stretching vibrations for substituted aromatic sodium sulfinates in 15 % aqueous solution. Substituents: 1, *p*-NH₂; 2, *p*-CH₃O; 3, *p*-CH₃; 4, *m*-CH₃; 5, *p*-CH₃CONH; 6, none; 7, *m*-COO⁻; 8, *m*-CH₃O; 9, *p*-COO⁻; 10, *p*-Cl; 11, *m*-Cl; 12, *p*-CN; 13, *m*-NO₂; 14, *p*-NO₂. Substituent constants from Jaffé.[11]
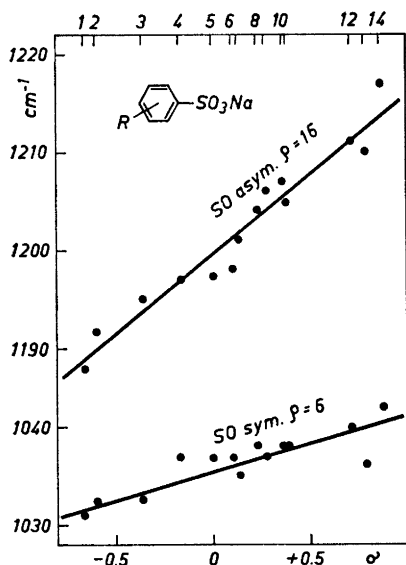
Fig. 2. Asymmetric and symmetric SO-stretching vibrations for substituted aromatic sodium sulfonates in 12 % aqueous solution. Substituents: 1, p-$(CH_3)_2N$; 2, p-NH_2; 3, p-OH; 4, p-CH_3; 5, none; 6, m-COO^-; 7, p-COO^-; 8, p-Cl; 9, p-COOH; 10, m-COOH; 11, p-SO_3^-; 12, p-CN; 13, m-NO_2; 14, p-NO_2. Substituent constants from Jaffé.[11]

tensive studies on the correlation of SO-frequencies with substituent constants in various substituted aromatic series of related compounds have appeared especially from Italian and Japanese laboratories.[7-9] This material has confirmed the assignments originally made for the aromatic sodium sulfinates and

provides a very interesting basis for discussion of the results. It has therefore been deemed of interest to report the correlations obtained for the aromatic sulfinates. For comparison, the SO-frequencies for a series of substituted aromatic sodium sulfonates in aqueous solution have also been included in this work, and nearly as good correlations as for the sulfinates were obtained with the Hammett equation.

Fig. 1 shows the correlations obtained for the sulfinates and Fig. 2 those for the sulfonates. The asymmetric vibration is the more sensitive to substituent effects in both cases. The spectra in the regions of the SO-vibrations will be reported in detail and the results will be fully discussed in a future paper.[10]

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