637. *Solvent Effects in the Infrared Spectra of Carboxylic Acids.*

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For the correlation of the effects of solvents on group frequencies, relative frequency shifts can be replaced by simple frequencies according to the equation $\nu_A = m\nu_B + D$. Unlike other X=O systems, the carbonyl frequencies of carboxylic acids obey this relation only when they are compared with the frequencies of other carboxylic acids. The failure of, *e.g.*, acetophenone to act as a model for the carboxyl group is ascribed to solvent interaction with the hydroxyl group of the acid.

As part of a continuing series of investigations into the factors controlling the position of equilibrium in a number of systems, the effect of solvent has been considered. In general the influence of a solvent can be correlated with its ability to interact with the components of the equilibrating system, and a convenient measure of this is provided by the group frequency shifts induced in the appropriate bands of the infrared spectra.

The classical treatment of the dependence of frequency on solvent considers the effect of bulk dielectric properties on a charged oscillator. In this way Kirkwood[1] and Bauer and Magat[2] were able to relate the frequency shift between the corresponding bands in the spectra of a substance for vapour and solution with the dielectric constant of the solvent:

$$(\nu_{\text{vap}} - \nu_{\text{soln}})/\nu_{\text{vap}} = c(\varepsilon - 1)/(2\varepsilon + 1). \qquad (1)$$

The generally poor correlation with experiment obtained from this expression led to the introduction[3] of refractive index (as n^2) instead of dielectric constant in equation (1), but only Caldow and Thompson's[4] multiple-term expression containing a number of adjustable parameters has given any significant improvement.

An alternative, empirical approach has been developed by Bellamy, Hallam, and Williams.[5] The relative frequency shift of a band for the solution spectrum of a compound A is found to be proportional to that of the corresponding band in the spectrum of a compound B in the same solvent:

$$[(\nu_{\text{vap}} - \nu_{\text{soln}})/\nu_{\text{vap}}]_A = s[(\nu_{\text{vap}} - \nu_{\text{soln}})/\nu_{\text{vap}}]_B. \qquad (2)$$

By this means the effects of macroscopic properties of the solvent are internally compensated and the deviation of the gradient, s, from unity indicates differing microscopic solvent–solute interactions. In general, correlation is good and numerous applications[6] of the treatment have demonstrated its value both in assessing interactions and in establishing band assignments. More widespread use has been precluded in part by the lack of the appropriate vapour frequencies. Occasionally this can be overcome by the use of an alternative, arbitrary standard state, *e.g.*, solution in hexane.[7] A convenient form of equation (2) for this is

$$(\nu_{\text{std}} - \nu_{\text{soln}})_A = m(\nu_{\text{std}} - \nu_{\text{soln}})_B, \qquad (3)$$

in which the gradient, m, is independent of the standard state and is related to the gradient of equation (2) by the expression $m = s(\nu_{A\ \text{vap}}/\nu_{B\ \text{vap}})$. However, by rearranging equation 2), a form even more generally useful can be obtained:

$$\nu_{A\ \text{soln}} = m\nu_{B\ \text{soln}} + D, \qquad (4)$$

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[1] Kirkwood, *J. Chem. Phys.*, 1937, **5**, 14.

[2] Bauer and Magat, *J. Phys. Radium.*, 1938, **9**, 319.

[3] Bayliss, Cole, and Little, *Austral. J. Chem.*, 1955, **8**, 26.

[4] Caldow and Thompson, *Proc. Roy. Soc.*, 1960, *A*, **254**, 1.

[5] Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

[6] *E.g.*, Bellamy and Williams, *Trans. Faraday Soc.*, 1959, **55**, 14; Bellamy and Hallam, *ibid.*, p. 220; Bellamy, Conduit, Pace, and Williams, *ibid.*, p. 1677; Cutmore and Hallam, *ibid.*, 1962, **58**, 40; Bellamy and Rogasch, *J.*, 1960, 2218; Williams, *Ann. Reports*, 1961, **58**, 34.

[7] Morgan, *J.*, 1961, 2151.

where m has the same value as in equation (3) and D $[= (1 - s)\nu_{\mathrm{A\ vap}}]$ is a constant for a given pair of compounds. The simplicity of equation (4) is convenient both for establishing correlations and for obtaining frequencies for states which it is either impossible or undesirable to measure directly.

The spectra of solutions of carboxylic acids illustrate this. Carboxylic acids can exist in the vapour state and in condensed phases in both monomeric and dimeric forms. In many solvents the two forms are in equilibrium and the infrared spectra of these solutions show bands which can be assigned to either monomer or dimer: the carbonyl region of the spectra contains two such bands. The higher-frequency band is solvent-dependent both in frequency and in intensity; its extinction coefficient increases on dilution and this band is consequently assigned to the stretching frequency of the free carbonyl group. Plots of the frequency of this band, for acids dissolved in a variety of solvents, against that of similar solutions of benzoic acid (chosen arbitrarily as a convenient standard) give good straight lines (Fig. 1); the gradients of some of these are recorded in the Table.

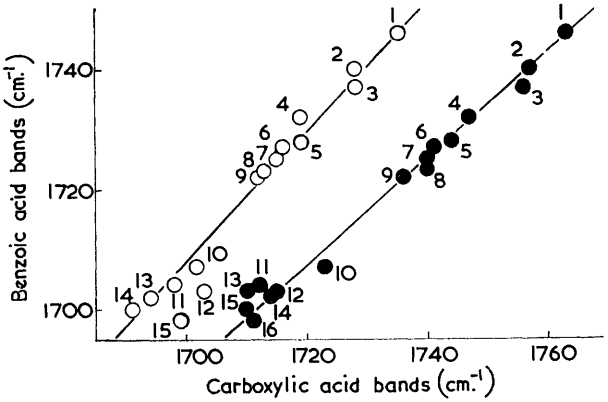

FIG. 1. Correlation of free-carbonyl stretching frequencies for solutions of carboxylic acids with those of benzoic acid.

● γ-Phenylbutyric acid. ○ Cinnamic acid.

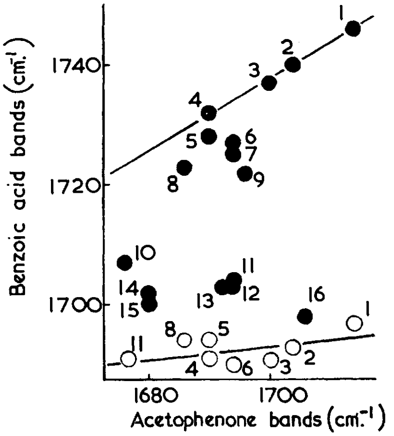

FIG. 2. Frequency of carbonyl bands for solutions of benzoic acid plotted against carbonyl frequency of solutions of acetophenone.

● Non-associated carbonyl band. ○ Associated carbonyl band.

Key to solvents for Figs. 1 and 2. 1, Hexane. 2, Carbon tetrachloride. 3, Carbon disulphide. 4, Methylene chloride. 5, Nitromethane. 6, Anisole. 7, Acetonitrile. 8, Chloroform. 9, Dioxan. 10, Pyrrole. 11, Pyridine. 12, *NN*-Diethylaniline. 13, *NN*-Dimethylaniline. 14, Dimethyl sulphoxide. 15, Propan-2-ol. 16, Triethylamine.

Solvent effects on the free-carbonyl band of carboxylic acids.

	Frequency (cm.$^{-1}$)					
Acid	Carbon tetrachloride	Dioxan	Dimethyl sulphoxide	Vapour [a]	Gradient [b] m	s
Acetic	1768	1752	1715	1792	0·83	0·82
Benzoic	1740	1722	1702	1760	1·0	1·0
Phenylacetic	1760	1737	—	1779	0·96	0·95
β-Phenylpropionic	1756	1735	1715	1778	0·95	0·94
γ-Phenylbutyric	1757	1736	1714	1779	0·90	0·89
Cinnamic	1728	1712	1694	1748	1·06	1·07

[a] Estimated by extrapolation, except for acetic acid. [b] Benzoic acid taken as standard.

Since the spectrum of acetic acid vapour is readily accessible, it is possible by extrapolation to estimate the positions of the free carbonyl stretching bands for less volatile acids as vapours. The recorded values[8] of the free-carbonyl stretching frequency for acetic acid vapour range from 1770 to 1800 cm.$^{-1}$ with a median value close to 1790 cm.$^{-1}$; under our experimental conditions the band was located at 1792 cm.$^{-1}$, and this value has been used for the subsequent correlations. In this way a value of 1760 cm.$^{-1}$ is obtained for benzoic acid, in satisfactory agreement with the frequency of 1757 cm.$^{-1}$ reported[9] for benzoic acid vapour at 170°. Estimated vapour frequencies for other acids are given in the Table together with values of the gradient, *s*, computed from them.

The extinction coefficient of the lower-frequency band in the carbonyl region of the spectra of carboxylic acids decreases on dilution, and this band is consequently assigned to the stretching frequency of the associated carbonyl group. In frequency it is largely independent of solvent and so no useful graphical correlation can be made. However, it may be noted that when they are plotted on the same axes the frequencies of the associated carbonyl groups lie close to the lines defined by the free carbonyl groups.

In establishing correlations for X=O stretching frequencies it has become conventional to use the carbonyl band of acetophenone for the reference frequency; in this way a wide variety of X=O groups have given linear plots.[6] When the carbonyl frequencies of carboxylic acids are plotted against those of acetophenone an approximately linear relationship is shown only by the largely solvent-independent frequency of the associated carboxyl group. A similar plot of the frequencies of the non-associated carbonyl band is linear only in the least polar solvents; in the more polar solvents the distribution of points appears to be almost random (Fig. 2). It is clear that the interaction of carboxylic acids with many solvents differs significantly from that of ketones. The extent of the interaction is indicated by the magnitude of the frequency shift: when the solvents are listed in order of the displacements induced in the free carbonyl stretching frequency of a carboxylic acid it is found that this order corresponds closely to the order of their displacement of X–H frequencies.[5] Thus the N–H frequency of pyrrole provides a better model for the solvent-dependence of the carbonyl frequency of a carboxylic acid than does acetophenone. Conversely, the frequency of the free hydroxyl group in solutions of carboxylic acids behaves typically and gives a linear plot against the N–H frequency[5] of the corresponding solutions of pyrrole. Solvent interactions of this kind can be recognised as arising from hydrogen-bonding, and such donor–acceptor interactions will reduce the electronegativity of an X–H group. In a carboxylic acid this will be accompanied by greater mesomeric release by the hydroxyl group and consequently by a reduction in the carbonyl stretching frequency through a mechanism not available to acetophenone.

The relative intensity of the associated and non-associated carbonyl bands follows a sequence related to that of the frequency shifts. Thus the proportion of non-associated carbonyl groups increases from solution in hexane (apparent extinction coefficient, ε_{app}, for benzoic acid, 50) to solution in dioxan (ε_{app} 320) when the associated carbonyl band has become vanishingly weak and remains so in the more basic solvents. Accordingly, it is noteworthy that in the most basic solvents the frequency of what must be the non-associated carbonyl group[10] is not readily distinguishable from that of the associated carbonyl group in less basic solvents. The competition between solvent and carboxylic acid to form a hydrogen bond with the hydroxyl group enables the environment and consequently the polarisation of the majority of the carboxyl groups to be largely independent of solvent under normal conditions of temperature and concentration. Conversely, it is reasonable to surmise that, in the least basic solvents when hydroxyl–solvent interaction is small, the solvent–solute interaction of acetophenone and

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[8] *E.g.*, Gillette and Daniels, *J. Amer. Chem. Soc.*, 1936, **58**, 1139; Herman and Hofstadter, *J. Chem. Phys.*, 1938, **6**, 534; Hartwell, Richards, and Thompson, *J.*, 1948, 1436; Pierson, Fletcher, and Ganitz, *Analyt. Chem.*, 1956, **28**, 1218; Wilmshurst, *J. Chem. Phys.*, 1956, **25**, 1171.

[9] Mecke, D.M.S. Collection of Infrared Spectra, Butterworths, London.

[10] Innes, *J.*, 1901, 261; Flett, *J.*, 1951, 962; Lassettre, *Chem. Rev.*, 1937, **20**, 259.

associated carboxyl groups will be similar. In accordance with this, the gradient of the non-linear section of a plot of $\nu_{C=O}$ values for benzoic acid against those for acetophenone (Fig. 2) measured directly ($m = 0{\cdot}89$) is in satisfactory agreement with that computed (0·91) from the gradients of plots of $\nu_{C=O}$ values for benzoic acid against those for acetic acid, and of acetic acid *vs.* acetophenone (linear section).

Experimental.—Solvents were of spectroscopic grade, where available, or were purified by conventional means. Acids were purified by distillation and recrystallisation until they showed satisfactory m. p. Spectra were recorded on a Perkin-Elmer 21 spectrophotometer equipped with rock-salt optics, and matched cells of nominal thicknesses 1·0 and 0·1 mm.

One of us (A. J. C.) thanks Glaxo Ltd. for a maintenance grant.

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[*Received, January* 10*th*, **1963**.]