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ON THE SPECTRAL BEHAVIOR OF DEUTERIO ANALOGUES OF SOME CARBOXYLIC ACIDS IN HEAVY WATER AND CORRELATION BETWEEN THEIR CARBONYL STRETCHING FREQUENCIES AND THEIR ACIDIC STRENGTHS AT INFINITE DILUTION

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Abstract

Infrared spectra of some deuterio analogues of carboxylic acids in heavy water have been investigated and their spectral behavior in carbonyl stretching frequency region have been interpreted in terms of their structural behavior in aqueous solutions. It has been shown that a linear relationship exists between carbonyl stretching frequency of solvated acids at infinite dilution and their pK_a's.

Introduction

In 1938, Davis and Sutherland noticed that the OH stretching frequency of aliphatic alcohols appears at higher frequencies than that of phenols and both are higher than OH stretching frequencies of carboxylic acids [1]. Since then many investigators have tried to find a systematic relationship between characteristic frequencies of carboxylic acids [$\nu_{(OH)}$ and $\nu_{(C=O)}$] and their acidic strength. Flett reported that although for some substituted benzoic acids there exists a systematic relation between $\nu_{(OH)}$ and their pK_a's, this relation could not be generalized to include all carboxylic acids [2,3]. Goulden [4] and Brooks *et al.* [5] from the investigation of infrared spectra of some carboxylic acids in carbon tetrachloride, acetonitrile and chloroform solutions found that for a given family of carboxylic acids there exists a linear relationship between $\nu_{C=O}$ or ν_{OH} and their pK_a's. Such a linear correlation has also been reported by these authors for ketones, aldehydes and esters of carboxylic acids. Yet Krygowski and Guillene [7], from their re-investigation of the Goulden plot, reported that for precise measurements of OH stretching frequencies the fit between ν_{OH} and pK_a, even for similar compounds, is not good.

In this study, we investigated the dependence of C=O stretching frequencies of some carboxylic acids upon dilution with water. Since D_2O is transparent in 1750-1600 cm^{-1} region we diluted the acids in their deuterated form with D_2O. In order to find out whether the correlation between C=O stretching frequency at infinite dilution is a family dependent correlation or not, we studied the behavior of HCOOD, CH_3COOD, CD_3COOD, C_2H_5COOD, n-C_3H_5COOD and C_6H_5COOD in the carbonyl stretching frequency region.

Keywords: Acidic strengths; Carboxylic acids; Characteristic frequencies; Infrared spectra

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Experimental Section

The samples were dried over molecular sieve 4A, dissolved in DMSO-d_6 and then diluted with D_2O to the desired dilution or directly dissolved in D_2O. The spectra were recorded by a Shimadzu FTIR model 4300A spectrometer using AgCl windows. The resolution of the spectrometer was set at 0.25 cm^{-1} and 50 scans. For the case of formic acid and at a very low concentration of acid, the number of scans was increased to 150, and the smooth program was used to smooth the spectra in the region of interest presented in Figures 1 and 3 to 7.

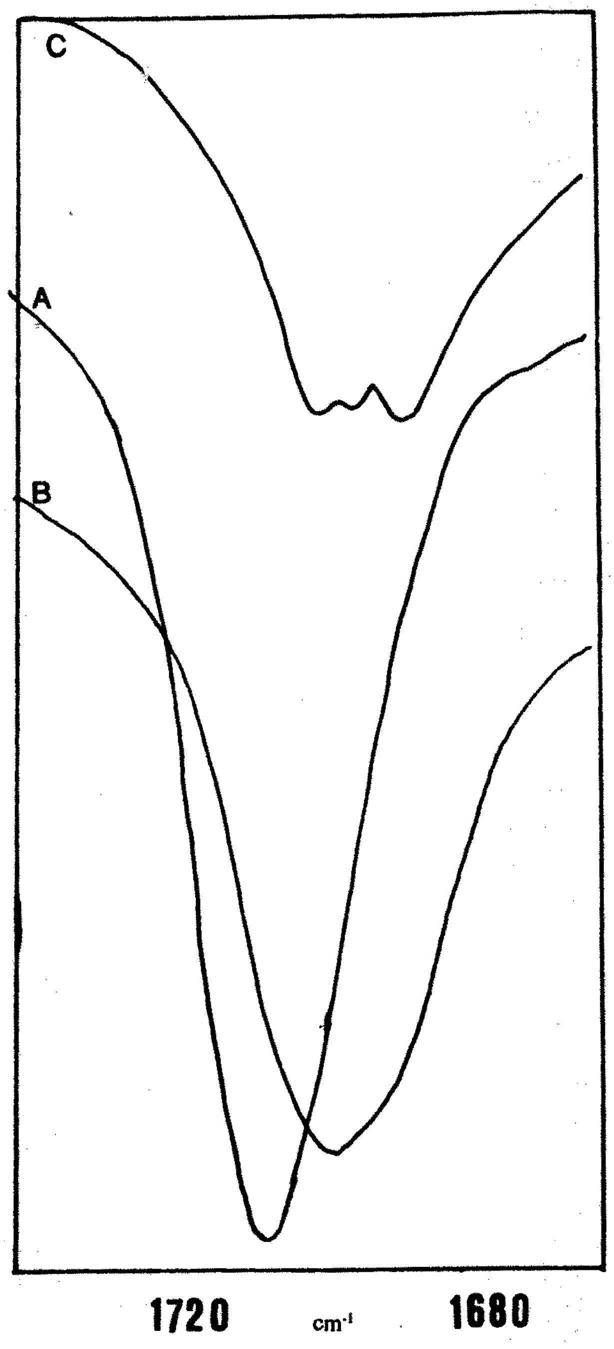

Figure 1. Representative spectra of C_6H_5COOD/DMSO(-d_6)-D_2O system. (A) n D_2O/n DMSO= 0, (B) n D_2O/n DMSO= 1 and (C) n D_2O/n DMSO= 7

Results and Discussion

Our interpretation of carbonyl stretching frequencies of carboxylic acids in aqueous solutions is based on their structural behavior in aqueous solutions. It is well known that characteristic group frequencies depend on the immediate environments of the group concerned [7-16]. On the other hand, pK_a's are obtained from the measurement of pK_a's in aqueous solutions at low concentration and extrapolation to infinite dilution.

In aqueous solutions, with the exception of formic acid, carboxylic acids form open dimers solvated with water [18-22]. Scheraga *et al.* have shown that increased stability of carboxylic acid dimers could be attributed to the formation of a pairs wise hydrophobic bond between the carboxylic acid side chains, i.e. alkyl-alkyl or benzyl-benzyl interaction [21]. Dimerization constants for formation of open dimer in aqueous solutions for benzoic, n-butyric and propionic acid are 0.75, .36 and .23 in comparison with dimerization constants of .16 and 0.4 for acetic acid and formic acid, respectively [22]. The stability of open dimer increases by dilution and the dimerization constants for deuterio analogues are higher [23]. On the other hand, Fischer *et al.* have shown that

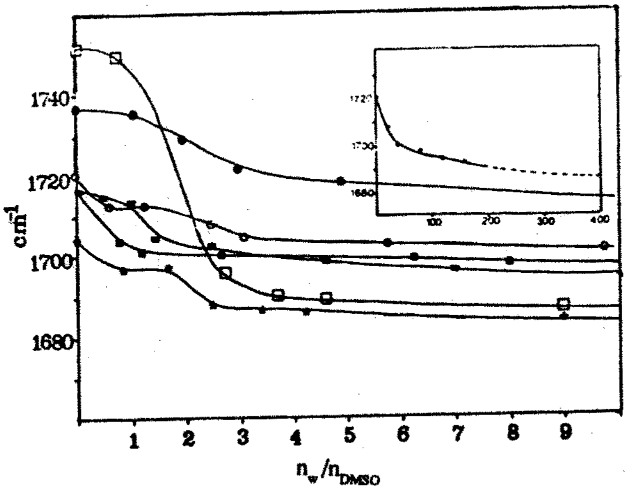

Figure 2. Change in C=O stretching frequencies of acid/DMSO systems upon dilution with D_2O
(a-*) benzoic acid (b- ■) propionic acid
(c-○) butyric acid (d-■) acetic acid (-d_4)
(e-□) acetic acid (f-●) formic acid

spectrum of water changes under the influence of solutes such as aliphatic amines and carboxylic acids [24] and Kitano *et al.* [23] in their Raman spectroscopic studies of deuterio analogues of carboxylic in D_2O solutions (90-100 wt%) observed remarkable changes in carbonyl stretching, COD bending and C-C stretching mode. Therefore, it seems reasonable in an investigation of this kind to look for the correlation between $\nu_{C\dot{=}O}$, or ν_{OH} stretching frequencies of solvated open dimer in aqueous solutions and their pK_a's at infinite solutions.

We start by examining the benzoic acid (-d_1)/ DMSO (-d_6) -D_2O system. The IR spectrum of benzoic acid in DMSO(-d_6) shows a medium and relatively sharp band at 1705 cm^{-1} (Figure 1).

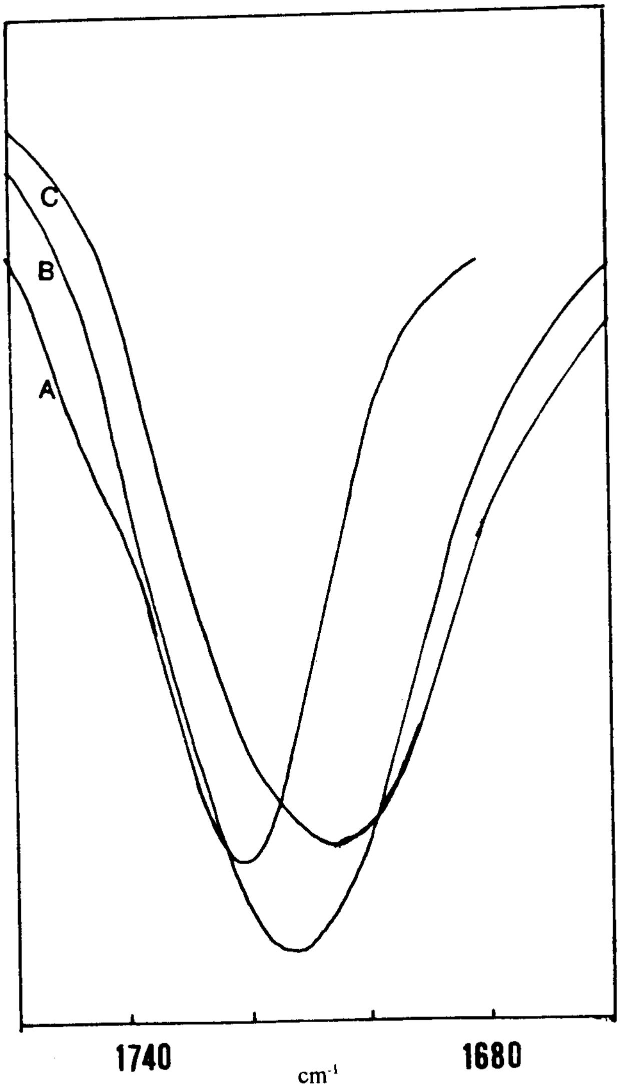

Figure 3. Representative spectra of propionic (-d_1)/DMSO(-d_6)-D_2O system. (A) n D_2O/DMSO= 0, (B)n D_2O/n DNSO= 0.6 and (C) n D_2O/n DMSO= 3.1

Odinokov *et al.* [25] in their investigation of infrared spectrum of DMSO-benzoic acid system in CCl_4 solution assigned the band at 1712 cm^{-1} to DMSO-benzoic acid adduct. When D_2O is added to this system, this band becomes broader and shifts to 1696 cm^{-1}. Upon further dilution, this broad band splits into three bands and the band at the lower frequency side shifts further down and its intensity increases by dilution. We assign this band to the stretching frequency of the terminal carbonyl of open dimer solvated with D_2O.

Figure 2(a) shows the change in carbonyl stretching frequency of benzoic acid-DMSO solution by dilution with D_2O. This figure has a characteristic shape which shows that at $n_{water}/n_{DMSO} \approx 2.2$, the immediate environment of carbonyl group has changed from DMSO to water. Extrapolation of this portion gives the value of 1683 cm^{-1} for stretching frequency of the terminal group of the open dimer at infinite dilution. This result is in agreement with the results of Nyquist *et al.* [16] which show that the carbonyl stretching frequencies of ketones occur at lower frequencies in dimethyl sulfoxide solutions than in carbon tetrachloride and occur in intermediate frequencies depending upon the mole percent ratio of $(CH_3)_2SO/CCl_4$.

Since n-butyric acid and propionic acid form a relatively strong open dimer in aqueous solutions, it is expected that the spectral behavior of these acids should be somehow similar to that of benzoic acid. Neat spectrum of propionic acid (-d_1) shows a strong band at 1718 cm^{-1} with a shoulder at 1745 cm^{-1}. The shoulder is absent in the infrared spectrum of propionic acid in DMSO(d_6) solution ($x_{acid} = 0.095$) and the band at 1722 cm^{-1} is relatively sharp. We assign the shoulder band to carbonyl stretching of monomer in equilibrium with the cyclic dimer and the band at 1722 cm^{-1} (1718 cm^{-1} in neat solution) to anti-symmetric stretching of carbonyl group. The 1714 cm^{-1} band in neat spectrum of n-butyric acid (1716 cm^{-1} in DMSO solution) and the shoulder band at 1745 cm^{-1} are similarly assigned. When D_2O is added to the neat acids, the shoulder disappears and the broad band becomes broader and shifts to the lower frequency side of the broad band in the spectrum of both acids in acid/D_2O and acid/DMSO-D_2O solutions. The intensity of the shoulder increases by dilution but it does not resolve (see Figures 3 and 4). We assign the lower unresolved band to carbonyl stretching of terminal group in the open dimer solvated by water and the upper band to the inner carbonyl stretching. Extrapolation of the former to infinite solution gives the value of 1690 cm^{-1} for propionic (-d) acid and 1695 cm^{-1} for n-butyric (-d) acid.

The plot of change in carbonyl stretching frequency with dilution for propionic and n-butyric acids has a similar shape to that of benzoic acids {2(b) and 2(c)} but it shows that the immediate environment of the carbonyl group changes at much lower values of $n_{water}/n_{DMSO}=2$ and 1.2 for propionic and n-butyric acids, respectively.

Kitano *et al.* have studied the Raman spectrum of acetic, propionic and n-butyric acids in aqueous solutions in the 1m to 18m concentration range [26]. By using a computer resolving technique they were able to show that monomer, open and cyclic dimers and polymer species exist in aqueous solutions. They also showed that equilibrium constants between these species depend on the concentration of the acid. We will not try to interpret the infrared spectral behavior of acetic solutions strictly in terms of these structures, rather we will simply follow the change of carbonyl stretching frequency upon dilution with tentative assignments of the bands whenever possible.

Neat spectrum of CD_3COOD shows a strong band at 1708 cm^{-1} with a shoulder at 1736 cm^{-1}. When D_2O is added the shoulder disappears and the 1708 cm^{-1} band becomes broader and, in more diluted solutions, a shoulder appears at the lower side of the strong band. Infrared spectrum of CD_3COOD/DMSO(-d_6) in this region shows a doublet with equal intensity at 1717 cm^{-1} and 1708 cm^{-1}. On dilution, the former disappears and the latter becomes broader and shifts to lower frequency. By further dilution it becomes relatively sharp (Fig. 5). Extrapolation of this band gives the value of 1691 cm^{-1} for carbonyl stretching

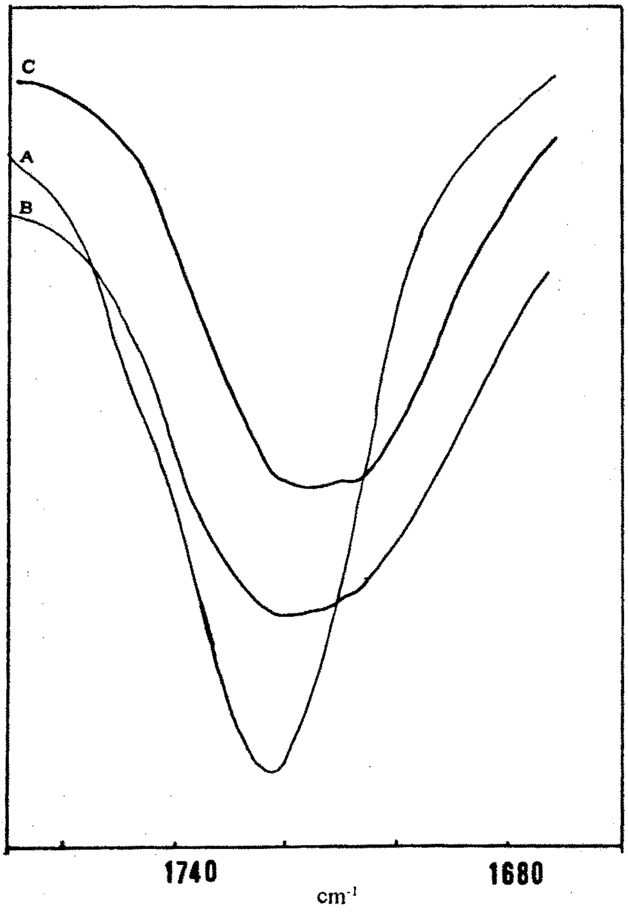

Figure 4. Representative spectra of butuyric (-d$_1$)/DMSO(-d$_6$)-D$_2$O system. (A) n D$_2$O/DMSO= 0, (B) n D$_2$O/n DNSO= 1.7 and (C) n D$_2$O/n DMSO= 3.4

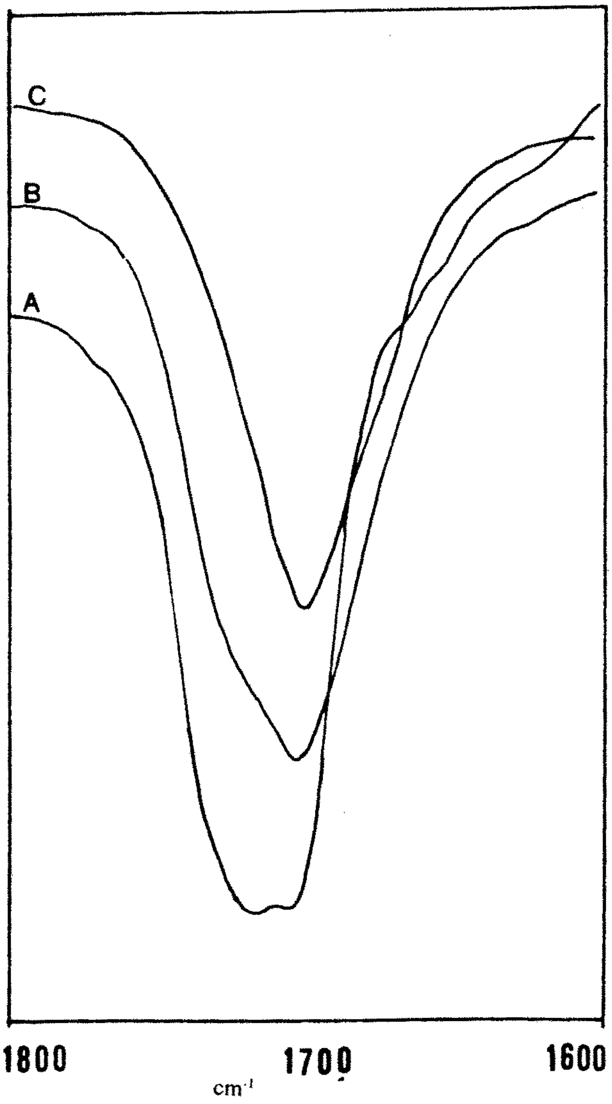

Figure 5. Representative spectra of CD$_3$COOD/DMSO(-d$_6$)-D$_2$O system. (A) n D$_2$O/DMSO= 0, (B) n D$_2$O/n DNSO= 3 and (C) n D$_2$O/n DMSO= 5

frequency of the solvated terminal group of open dimer at infinite dilution (Fig. 2-d).

The behavior of CH_3COOD/D_2O solutions is similar to CD_3COOD/D_2O solutions, but spectra of CH_3COOD/DMSO (-d_6)-D_2O solutions are rather different. In the spectrum of undiluted solutions, a relatively sharp band appears at 1716 cm^{-1} with two shoulders at 1737 cm^{-1} and 1752 cm^{-1}. The former disappears upon dilution with D_2O, but the latter moves to 1758 cm^{-1} due to less overlap of the strong band and then disappears in diluted solutions because of the change in environment at $n_w/n_{DMSO}=2.2$. In dilute solutions, two broad bands appear where, after band contour resolution, the center of the two are located at 1713 and 1689 cm^{-1} (Fig. 6). Extrapolation of the latter gives the value of 1688 cm^{-1} for the carbonyl stretching frequency of the solvated terminal groups (Fig. 2-e).

We assign the 1716 cm^{-1} band in neat and DMSO solutions of CH_3COOD and the corresponding band at 1708 cm^{-1} in neat CD_3COOD and in CD_3COOD/DMSO solutions to unsymmetrical carbonyl stretch in cyclic dimer and the 1717 cm^{-1} band in the spectrum of the latter to acid-DMSO adduct. The corresponding band in CH_3COOD/DMSO)-d_6) spectrum probably is the band at 1737 cm^{-1}, but the band at 1752 cm^{-1} is also a good candidate. The 1758 cm^{-1} band in the neat spectrum of CH_3COOD and the corresponding band at 1736 cm^{-1} in neat CD_3COOD are assigned to carbonyl stretching frequency of the monomer in equilibrium with the cyclic dimer. Kitano *et al.* [23] have attributed the Raman band at 1768-1792 cm^{-1} to monomer and the band at 1713 cm^{-1} to hydrogen bonded monomer species.

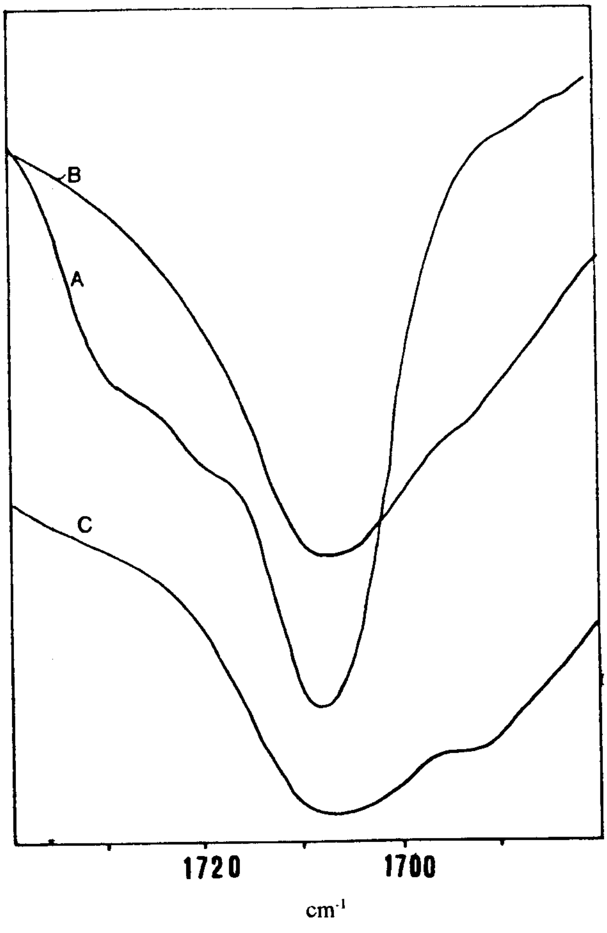

Figure 6. Representative spectra of CH_3COOD/DMSO(-d_6)-D_2O system. (A) n D_2O/DMSO= 0, (B) n D_2O/n DNSO= 1.18 and n D_2O/n DMSO= 3.67

Because of the strong hydrogen bonding between two molecular entities of formic acid and the formation of a cyclic dimer in solid, liquid, vapor and in solution, formic acid has been the subject of many experimental and theoretical studies [27]. Unlike other carboxylic acids, formic acid does not form open dimer in aqueous solutions and therefore the spectral behavior of formic acid should be interpreted in terms of cyclic dimer and solvated monomer equilibrium. Infrared spectrum of neat formic acid in carbonyl stretching frequency shows a broad and a very strong band centered at 1722 cm^{-1}. By dilution, the broad band becomes relatively sharper and an unresolved doublet appears at higher dilution with an apparent shift to lower frequencies (Fig. 7). In acid-DMSO solution a resolved doublet appears at 1708 cm^{-1} and 1737 cm^{-1} where the former is assigned to unsymmetric carbonyl stretch in the cyclic dimer and the latter to formic acid-DMSO adduct. Upon dilution with the D_2O, the latter band persists with no apparent shift in the frequency being observed, indicating that the adduct is very strong, but the former gradually shifts to lower frequencies and its relative intensity decreases. At high dilution, a shoulder appears at the lower frequency side of the band at 1708 cm^{-1} which now has moved to 1704 cm^{-1}. At high dilution, the intensity of both bands decreases and the latter moves to lower frequencies around 1696 cm^{-1}. The bands are very weak and accumulation of 150 scans were necessary to differentiate between the noise and the signal. Extrapolation of this portion to infinite dilution gives the value of 1675 ±5 cm^{-1} (see the inserted section in Fig. 2-f). Although the assignment of this value to carbonyl stretching frequency of solvated HCOOD might seem unreasonable, but in view of the large difference between symmetric and un-symmetric carbonyl stretching frequency in formic acid dimer (1754 - 1670 = 84 cm^{-1}), the origin of which has been discussed by Dybal, Cheam and Krim [28], it is not very

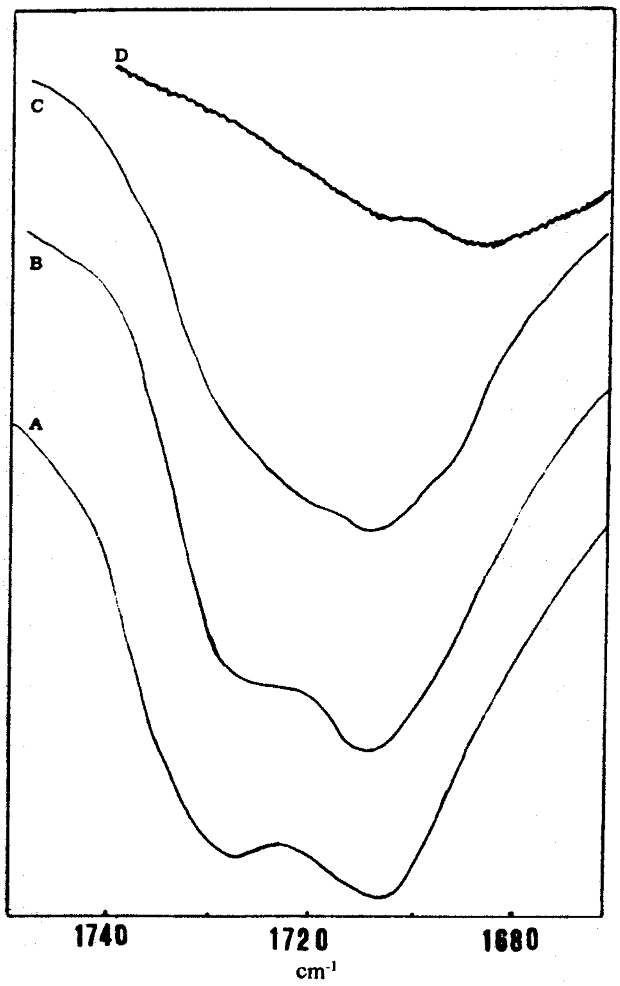

Figure 7. Representative spectra of HCOOD/DMSO(-d$_6$)-D$_2$O system. (A) n D$_2$O/DMSO= 0, (B) n D$_2$O/n DNSO= 2, n D$_2$O/n DMSO= 4 and (D) n D$_2$O/n DMSO= 80

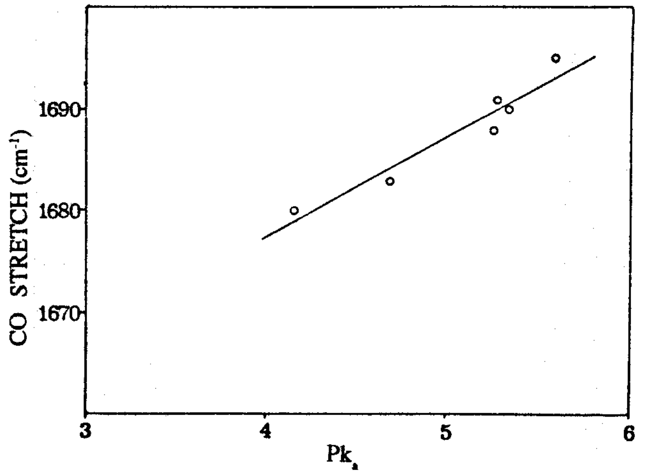

Figure 8. Plot of C=0 stretching frequency of D$_2$O solvated of some carboxylic acids verses their pk$_a$

Table 1. Carbonyl stretching frequencies of some solvated carboxylic acids at infitite dilution and their corresponding pk$_a$'s

Acid	CO stretching (cm^{-1})	pk$_a$'s
HCOOD	4.15	1680
CH_3COOD	5.26	1688
CD_3COOD	5.28	1691
C_2H_5COOD	5.38	1690
n-C_3H_7COOD	5.59	1695
C_6H_5COOD	4.69	1683

unrealistic.

Carbonyl stretching frequencies of solvated acid at infinite solutions and the corresponding pK_a's are given in Table 1. pK_a's for benzoic acid $(-d_1)$, acetic acid $(-d_1)$ and formic acid are taken from references 29, 30 and 31, respectively. The pK_a's for propionic $(-d_1)$ and n-butyric $(-d_1)$ are estimated from the plot of $pk_a(-d)$'s versus $pK_a(H)$'s for compounds given in tables 7-3 of reference 32. The plot of carbonyl stretching frequencies in aqueous solutions at infinite dilution versus pK_a's (Fig. 7) is a straight line within the error involved in estimating pK_a for propionic $(-d_1)$ and n-butyric $(-d_1)$ and the assumption that the extrapolated value for formic acid lies in the right region.

Conclusion

Based on the results of this work, one can tentatively conclude that acidic strength is related to carbonyl stretching frequency and at infinite dilution this relation is not family dependent. In order to come to more definite conclusions however, further experimental work of this sort is necessary.

References

1. Davies, M. M. and Sutherland, G. B. B. M. *J. Chem. Phys.*, **6**, 755, (1938).
2. Flett, M. St. C. *Trans. Faraday Soc.*, **44**, 767, (1948).
3. Flett, M. St. C. *J. Chem. Soc.*, 962, (1951).
4. Goulden, J. S. D. *Spectrochimica Acta*, **6**, 129, (1954).
5. Brooks, C. J. W., Eglinton, E. and Morman, J. F. *J. Chem. Soc.*, 106, (1961).
6. Allerhand, A. and Von R. Schleyer, P. *J. Am. Chem. Soc.*, **85**, 371, (1938).
7. Krygowski, M. T. and Guillene, J. *J. Chem. Soc. Perkin Tran.*, **2**, (5), 531, (1982).
8. Kirk Wood, J. G., West, W. and Edwards, R. T. *J. Chem. Phys.*, **8**, 14, (1937).
9. Allerhand, A. and Schleyer, P. Von R. *J. Am. Chem. Soc.*, **75**, 871, (1963).
10. Cordy, N. and Stanford, S. C. *J. Chem. Phys.*, **9**, 204, (1946).

11. Hallam, H. E. and Ray, T. C. *Nature*, **189**, 915, (1961).
12. Bauer, E. and Magatm, M. *J. Phys. Radiation*, **9**, 319, (1938).
13. Corish, P. G. and Davison, W. H. T. *J. Chem. Soc.*, 6005, (1955).
14. Fraenkel, G., Belford, R. and Yankwich, P. E. *J. Amer. Chem. Soc.*, **76**, 15, (1954).
15. Nyquist, R. A. *Appl. Spectrosc.*, **45**, 92, (1991), and related references.
16. Nyquist, R. A., Chrzan, V. and Houck, J. *Ibid.*, **43**, 981, (1989).
17. Davis and Hetzer. *J. Res. Nat. Bur. Stand.*, **60**, 569, (1958).
18. Nash, G. R. and Monk, C. B. *J. Chem. Soc.*, 4276, (1957).
19. Suzuki, K., Taniguchi, Y. and Watanab, T. *J. Phys. Chem.*, **77**, 1918, (1973).
20. Cartwright, D. R. and Monk, C. B. *J. Chem. Soc.*, 2500, (1955).
21. Schrier, E. E., Pottle, M. and Scheraga, H. A. *J. Amer. Chem. Soc.*, **86**, 344, (1964).
22. Katchalsky, A., Eisenberg, H. and Lifson, S. *Ibid.*, **73**, 5889, (1951).
23. Tanaka, N., Kitano, H. and Ise, N. *J. Phys. Chem.*, **95**, 1503, (1991).
24. Fischer, W. B., Bertie, J. E., Amhed, M. K. and Eysel, H. H. *Proc. SPIE-INT. Soc. Opt.*, 1575, (1992).
25. Odinokov, S. E., Maximov, O. B. and Dzizenko, A. K. *Spectrochim Acta*, **25A** 131, (1969).
26. Tanaka, N., Kitano, H. and Ise, N. *J. Phys. Chem.*, **94**, 6290, (1990).
27. See for example: Chang, V. T., Yamaguchi, Y., Miller, W. H. and Schaefer, H. E. *J. Amer. Chem. Soc.*, **109**, 7247, (1987).
28. Dybal, J., Cheam, T. C. and Krim, S. *J. Mol. Struct.*, **159**, 183, (1987).
29. Lowe, B. M. and Smith, D. G. *J. Chem. Soc. Faraday Trans. I*, **75**, 389, (1975).
30. Lamer, V. K. and Chittum, J. P. *J. Amer. Chem. Soc.*, **58**, 1542, (1936).
31. Laughton, P. M. and Robertson, R. E. *Solute-solvent interaction*. (ed. S. F. Coetzee and C. D. Ritcie), Marcel Dekker, London p. 409, (1965).
32. *Ibid.*,