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# SOLVENT EFFECTS ON NMR SPECTRA OF 8-HYDROXYQUINOLINE DILUTION COEFFICIENTS

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The dilution coefficients $(\Delta\delta/\Delta c)_{solv.}$ are introduced from the dilution shifts of PMR spectra of 8-hydroxyquinoline in various solvents, and correlations between these values are examined. There are good correlations between the dilution coefficients of every pair of H-2, H-3, H-4, H-6, H-7, but not between the dilution coefficients of H-5 and the other protons.

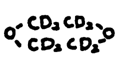
The PMR spectra of 8-hydroxyquinoline have been investigated.(1) The resonance lines of each ring proton of this compound in various solvents indicate the specific dilution shifts; low field shifts of H-2, H-3, H-4, H-6, H-7, and high field shifts of H-5 and OH in most solvents. The tendency of these low or high field shifts with dilution regardless of the nature of solvents suggests a chemical association formed between solute molecules (self-collision complex).(2)

On the other hand, the magnitude of the dilution shifts are all considerably affected by the nature of solvents. This suggests that solvent effects are characterized by the slopes of the dilution curves. Then, the dilution coefficients $(\Delta\delta/\Delta c)_{solv.}$ of each ring proton corresponding to the various solvents are defined from the slopes of the dilution curves, Where $\delta$ is the proton chemical shift and c is concentration. Measurements are all made on solutions ranging in concentrations from ca. 1 M to ca. 19 M. Since the applied concentration ranges are relatively high, not only the solute-solvent but also solute-solute interactions play an important part. The values of $(\Delta\delta/\Delta c)_{solv.}$ can be roughly regarded as constant within the experimental concentrations, for most dilution shifts bear nearly linear relationships between shift and concentration ( See reference 2, Fig. 1,2,3 and 4 ). And also, the linear relationships are well confirmed by the least squars method. By examining the correlations between the dilution coefficients of the ring protons, the solvent effects to each ring proton are discussed in detail.

The experimental and sample preparation precedures are the same as those used in our previous paper.(1) The experimental errors of the dilution coefficients are all within ca. 5 %.

The dilution coefficients of the ring protons in various solvents are summarized in Table 1. These dilution coefficients indicate the different values with the nature of solvents. The values of the dilution coefficients of H-3 are $(\Delta\delta/\Delta c)_{CS_2} < (\Delta\delta/\Delta c)_{CCl_4} < (\Delta\delta/\Delta c)_{CDCl_3} < (\Delta\delta/\Delta c)_{CD_3CN} < (\Delta\delta/\Delta c)_{(CD_3)_2CO} < (\Delta\delta/\Delta c)_{C_4D_8O_2} < (\Delta\delta/\Delta c)_{C_5D_5N} < (\Delta\delta/\Delta c)_{DMSO}$ .
A similar trend is found for the dilution coefficients of the other ring protons

Table 1. Dilution coefficients $(\Delta\delta/\Delta c)_{solv.}$ of each proton in various solvents (Hz/M)

| SOLVENT | DILUTION COEFFICIENT $(\Delta\delta/\Delta C)_{solv.}$ of | | | | | | |
|---|---|---|---|---|---|---|---|
| | H-2 | H-3 | H-4 | H-5 | H-6 | H-7 | OH |
| $CS_2$ | -0.48 | -1.03 | -0.88 | 0.39 | -0.37 | -0.54 | 6.13 |
| $CCl_4$ | -0.22 | -0.89 | -0.83 | 0.16 | -0.27 | -0.50 | 4.32 |
| $CDCl_3$ | -0.19 | -0.61 | -0.61 | 0.06 | -0.37 | -0.65 | 2.76 |
| $CD_3CN$ | -0.22 | -0.47 | -0.71 | 0.44 | -0.08 | -0.35 | 4.36 |
| $(CD_3)_2CO$ | 0.0 | -0.38 | -0.36 | 0.32 | -0.07 | -0.22 | 1.84 |
|  | -0.07 | -0.36 | -0.35 | 0.43 | -0.01 | -0.10 | 1.13 |
|  | -0.17 | -0.25 | -0.34 | — | — | — | -1.14 |
| DMSO | 0.30 | 0.05 | 0.08 | 0.67 | 0.28 | 0.21 | 0.81 |

except for H-5,OH. The above relation seems to be roughly parallel to the strength of the solute-solvent interactions ( solvent effects ).

On the other hand, the relationships between the dilution coefficients are all graphically examined ( as is partly shown in Fig. 1 ) and are all ascertained by the estimations of the correlation coefficients ( Table 2 ). Consequently, it is found good correlations between the dilution coefficients of every pair of H-2, H-3, H-4, H-6 and H-7 relative to the other correlations. Especially, there are better correlations between the dilution coefficients of H-3 and H-4, H-6 and H-7. And also, it is found good correlations between the dilution coefficients of H-3 and H-6, H-4 and H-7 except for a point of chloroform.
In this way, the good correlations suggest that not only solute-solute interaction but also solute-solvent interaction ( solvent effect ) to these protons are similar in mechanism regardless the nature of solvents. However, it is found no correlations between the dilution coefficients of H-5 and H-2, H-3, H-4 except for H-6, H-7. This suggests that the solvent effect to H-5 may be somewhat similar in mechanism to that to H-6, H-7, but differs from that to H-2, H-3, H-4. This is for a specific contribution other than the factors affecting the other ring protons. According to the investigation on the origins of the dilution shifts, the dilution shifts of the ring protons are successfully accounted for by assuming the specific steric arrangement formed between the solute molecules.2) Then, the unusual dilution shifts of H-5 are well-accounted for by the influence of the magmetic anisotropy of the nitrogen atom of another solute molecules in the complex. No correlations between the dilution coefficients of H-5 and

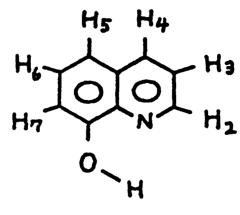


Table 2. Correlation coefficients (r) between the dilution coefficients of each proton

| | (r) | | (r) | | (r) |
|---|---|---|---|---|---|
| H-2 - H3 | 0.875 | H3 - H5 | 0.630 | H4 - OH | -0.813 |
| H4 | 0.918 | H6 | 0.918 | H5 - H6 | 0.827 |
| H5 | 0.523 | H7 | 0.872 | H7 | 0.850 |
| H6 | 0.888 | OH | -0.828 | OH | -0.319 |
| H7 | 0.863 | H4 - H5 | 0.628 | H6 - H7 | 0.980 |
| OH | -0.646 | H6 | 0.889 | OH | -0.734 |
| H3 - H4 | 0.944 | H7 | 0.901 | H7 - OH | -0.739 |

the other ring protons can be ascribed to the contribution arising from the nitrogen atom.

The remaining problem is the correlations between the dilution coefficients of OH and the ring protons. The correlations are not so good as the correlations between the dilution coefficients of the ring protons. This suggests that not only the solvent effect to OH differs from that to the ring protons in mechanism, but also the origin of the dilution shifts of OH essentially differs from that of the ring protons. More noticeable is the inverse correlations which are found between the dilution coefficients of OH and the other ring pro-

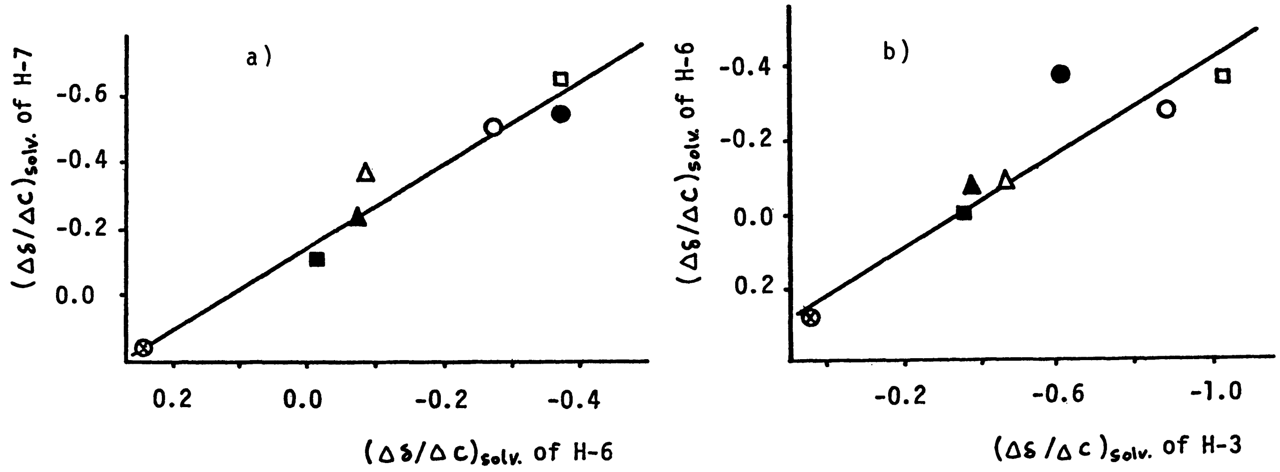


Fig. 1. Relationships between the dilution coefficients of a) H-6 and H-7 b) H-3 and H-6, □ – $CS_2$, ○ – $CCl_4$, △ – $CD_3CN$, ▲ – $(CD_3)_2CO$, ● – $CDCl_3$, ■ – $C_4D_8O_2$, ◑ – $C_5D_5N$, ⊗ – DMSO.

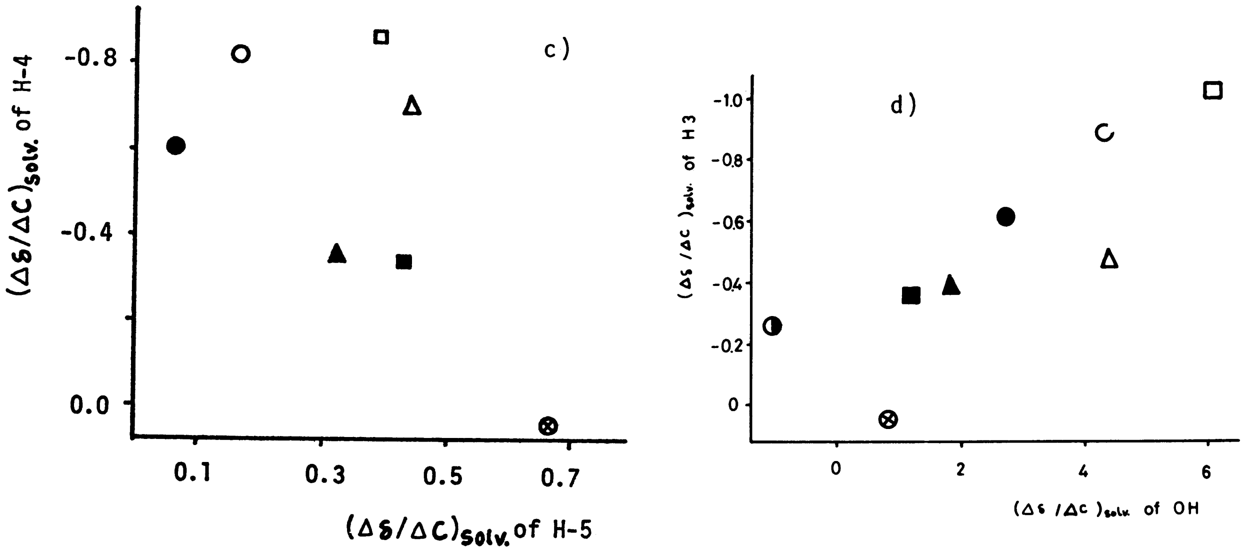


Fig. 1. Relationships between the dilution coefficients of c) H-4 and H-5 d) H-3 and OH.

tons. This is consistent with the view that the origin of the dilution shifts of the ring protons arises chiefly from the solute-solute interaction, and that of OH mainly comes from the intermolecular hydrogen bond respectively.

In this way, the consideration on the correlation between the dilution coefficients is one of useful method to discuss the solvent effects on each ring proton around a molecule. And the result can be presents not only the informations on the mechanism of the intermolecular interaction occured in this system but also one of evidence supporting a self-collision complex which will be discussed in forthcoming paper.

## References and Notes

1) S.Katayama, Y.Akahori, and H.Mori, Chem. Pharm. Bull., 21, 2622 (1973).

2) S.Katayama and Y.Akahori, Submitted to Bull. Chem. Soc. Japan.

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