An Approach for the Estimation of the Polarity of the β-Cyclodextrin Internal Cavity

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The systematic study and correlation of the spectral shifts suffered by diphenylamine, used as a fluorescent probe, in several solvents, allows the estimation of the β-cyclodextrin internal cavity polarity which is similar to ethanol.

The facility with which cyclodextrins form inclusion compounds with a great variety of organic compounds to modify one or more organic reactions is well known.[1—5] This behaviour is due, essentially, to the specific hydrophobic character of the internal cavity. Consequently, the estimation of the polarity of the cyclodextrin internal cavity is important in that it helps to predict the type of organic compound which may be included in the molecule. The application of this inclusion characteristic in other fields of chemistry such as analytical, kinetic, and organic synthesis has much potential. However, there are great discrepancies between the polarities reported by several authors.[6,7] In this communication we

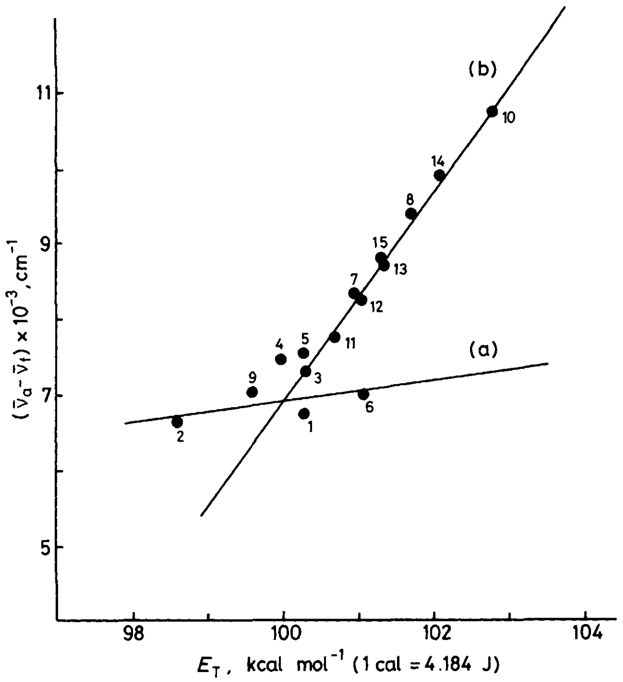

Figure 1. Plot of $\bar{\nu}_a - \bar{\nu}_f$ *vs.* E_T. 1, Dioxane; 2, dioxane–water (80% v/v); 3, ethanol; 4, methanol; 5, dioxane–water (60% v/v); 6, acetonitrile; 7, dioxane–water (40% v/v); 8, dioxane–water (20% v/v); 9, dimethylformamide; 10, water (pH 10.5); 11, ethanol–water (80% v/v); 12, ethanol–water (60% v/v); 13, ethanol–water (40% v/v); 14, ethanol–water (20% v/v); 15, 10^{-2} M β-cyclodextrin aqueous solution.

make a first systematic attempt to evaluate the polarity through the correlation of the spectral shifts shown by the *N,N*-diphenylamine (DPA) fluorescent probe in a selected set of solvents. DPA shows a peculiar spectral behaviour as indicated by the relatively large spectral blue-shift it undergoes in β-cyclodextrin solution. The DPA spectral shifts are sufficiently large to permit their accurate estimation. The inclusion of DPA in β-cyclodextrin effects two changes in its spectral behaviour: a progressive blue-shift in the emission maximum as the β-cyclodextrin concentration increases and a similar enhancement of the fluorescence intensity.

In solutions at room temperature, the DPA fluorescence spectra is red-shifted as solvent polarity increases. A plot of $\bar{\nu}_a - \bar{\nu}_f$ in cm^{-1} (absorption and fluorescence maxima in each solvent) *vs.* transition energy E_T (kcal/mol) = 2.859×10^{-3} $\bar{\nu}_a$ (in cm^{-1}), and *vs.* the *Z* index of Kosower,[8] indicates the correlation between the solvent polarity characteristics and spectral shifts (Figures 1 and 2, respectively). Both figures show two distinct linear correlation profiles which imply two different solvent cage interactions of the electronic excited singlet state (S_1^*). One corresponds to solvents with aprotic character and no hydrogen bonding capacity (line a), the other is associated with protic solvents (line b). The slope value of line b indicates a highly polar charge transfer emission and the sign indicates the π–π* nature of the electronic transfer. It should be noted that in protic solvents, in addition to the polar effects, there may be a significant contribution from hydrogen bonding to $\bar{\nu}_a - \bar{\nu}_f$.

The most interesting observation in Figures 1 and 2 is the location of the point corresponding to 10^{-2} M aqueous β-cyclodextrin solution (point 15). This is situated on line b in both figures, and by means of linear correlation analysis from Figure 2, a *Z* index value of 88 may be determined, which implies that β-cyclodextrin has an internal cavity polarity similar to ethanol. This agrees well with Turro's conclusions following his studies of intramolecular exciplex emission in aqueous β-cyclodextrin solutions.[7] On the other hand, the results obtained in our study contradict those of Hamai who assigns a β-cyclodextrin internal cavity polarity similar to dioxane[6] which, in turn, suggests that the interaction between the guest molecule and the surrounding β-cyclodextrin may occur in the proximity of the primary hydroxy groups of the β-cyclodextrin. Additional support to this hypothesis is given by the fact that similar conclusions are reached by Turro who used a different fluorescent probe.[7] Current studies in our laboratory using an *N*-arylaminonaphthalene sulphonate series of fluorescent probes appear to confirm the results discussed in this paper.

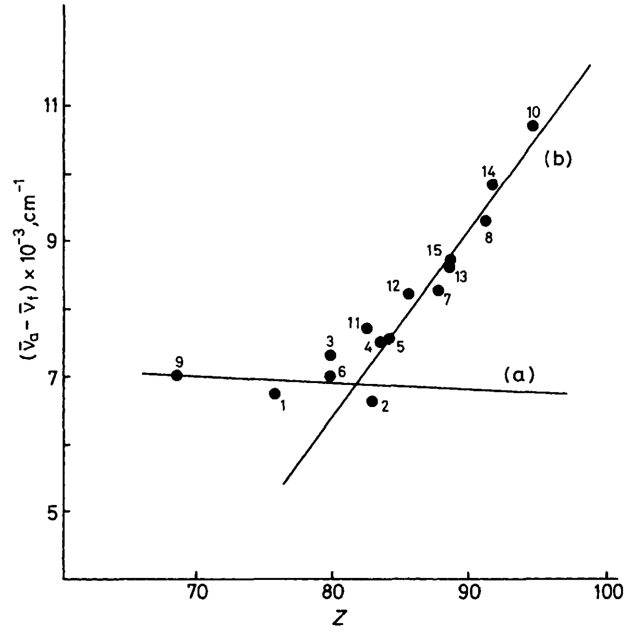

Figure 2. Plot of $\bar{\nu}_a - \bar{\nu}_f$ *vs.* *Z* values. Numbers as in Figure 1.

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References

1 M. L. Bender and M. Komiyama, in 'Cyclodextrin Chemistry,' Springer-Verlag, Berlin, 1978.
2 W. Saenger, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 344.
3 J. Emert, D. Kodal, and R. Catena, *J. Chem. Soc., Chem. Commun.*, 1981, 758.
4 K. Kano, I. Takenoshita, and T. Ogawa, *Chem. Lett.*, 1982, 321.
5 Y. Hul, J. R. Wiukle, and D. G. Whitten, *J. Phys. Chem.*, 1983, **87**, 23.
6 S. Hamai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2721.
7 G. S. Cox, N. J. Turro, N. C. Yang, and M. J. Chen, *J. Am. Chem. Soc.*, 1984, **106**, 422.
8 E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253.