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Note

Adsorption of monosubstituted phenols on Sephadex G-15

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Haglund¹ determined the distribution coefficients, K_d , of benzene, nine monosubstituted benzenes and the corresponding 3- and 4-substituted phenols, for the distribution of these solutes over Sephadex G-15 beads and an external aqueous solution. From the data on benzene and the monosubstituted benzenes he calculated the contribution of the substituents CH_3 , OH , OCH_3 , CHO , COCH_3 , F , Cl , Br and I to $\log K_d$. Further, he calculated the difference, Δ , between the experimental values of $\log K_d$ of the 3- and 4-substituted phenols and the sum of the contributions of the phenolic moiety and the substituent. If Δ represents the contribution to $\log K_d$ of the interaction between the substituent and the adsorption centre in the phenolic moiety, the values of Δ should be linearly related to the values of the Hammett substituent constant, σ . The regression equation

$$\Delta = 0.180 \sigma + 0.013 \quad (1)$$

appeared to hold with a standard deviation of only 0.005. Haglund concluded: "the correlation is good, and this suggests the same mechanism of adsorption to the gel for all the investigated monosubstituted phenols, although no definite conclusion about the mechanism itself can be drawn as yet".

Although I agree with Haglund's first two statements, I think that the last is too pessimistic, and that more can be said about the adsorption mechanism on the basis of his data.

It is improbable that the adsorption is due to a hydrogen bond between the phenolic OH group and an ether bridge in the Sephadex, as suggested by some workers^{2,3}. Firstly, the contribution of the OH group to $\log K_d$ is rather small. It is of the same magnitude as the contribution of the CH_3 group, and replacement of the acidic H atom by the apolar CH_3 group, yielding the OCH_3 substituent, causes only a small decrease in the group contribution. (see Table I). Secondly, the data for 3- and 4-hydroxyphenol are in perfect agreement with eqn. 1. However, these compounds contain two equivalent phenolic OH groups, so the chance of formation of a hydrogen bond by these compounds is twice that for the other monosubstituted phenols. Hence, if adsorption were due to hydrogen bonding of a phenolic OH group, a statistical correction of $-\log 2 = -0.3$ should be applied to the values of $\log K_d$ of the hydroxyphenols before they can be compared with the data on the other monosubstituted phenols. However, this correction would destroy the good correlation of the values of Δ with those of σ .

TABLE I

DISTRIBUTION COEFFICIENTS AND GROUP CONTRIBUTIONS FOR BENZENE AND SOME MONOSUBSTITUTED BENZENE DERIVATIVES¹

Compound	Log K_d	Group	Group contribution
Benzene	0.48	Φ	0.48
Toluene	0.60	CH_3	0.12
Phenol	0.61	OH	0.13
Anisole	0.58	OCH_3	0.10

When the adsorption centre in the phenolic moiety is not the OH group, it must be the phenyl ring, acting as a electron donor towards the OH groups of the Sephadex. This assumption is in agreement with the large value of log K_d of benzene, compared with the contribution to log K_d of the OH group (see Table I). The good correlation of the values of Δ for 3-substituted phenols with the values of σ for *meta*-substituents, and of the values of Δ for 4-substituted phenols with the values of σ for *para*-substituents, can be explained as follows. The interaction of the substituents with the phenyl ring is incorporated in the values of their group contributions to log K_d . Hence, the values of Δ represent only the interaction of the substituents with the phenolic OH group, although the phenyl ring is the adsorption centre. In relation to the OH group, the substituents are in *meta*- and *para*-positions, respectively.

In the substituted phenols, the substituents disperse their electron-donating or -withdrawing action over the OH group and the phenyl ring. Hence, their influence on the electron density in the phenyl ring will be smaller than in the substituted benzenes. The same holds for their influence on the strength of hydrogen bonding with the phenyl ring. Electron-donating substituents will increase it more with substituted benzenes than with substituted phenols, while electron-withdrawing substituents will decrease it more with substituted benzenes than with substituted phenols. Hence, Δ values of electron-donating substituents will be negative and those of electron-withdrawing substituents positive, or, in other words, ρ will be positive, as is actually observed ($\rho = 0.180$).

REFERENCES

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