

CHROM. 7882

CHROMATOGRAPHY OF SUBSTITUTED ANILINES ON 3,5-DINITRO-BENZOYL PAPER

AN EXAMPLE OF ORGANIC CHARGE-TRANSFER CHROMATOGRAPHY

STEPHEN L. SNYDER*

Armed Forces Radiobiology Research Institute, Defense Nuclear Agency, Bethesda, Md. 20014 (U.S.A.)

and

CLARK M. WELCH

Southern Regional Research Center, Agricultural Research Service, USDA, P.O. Box 19687, New Orleans, La. 70179 (U.S.A.)

(First received June 7th, 1974; revised manuscript received August 26th, 1974)

SUMMARY

Simple and substituted anilines are adsorbed by 3,5-dinitrobenzoyl (DNB) paper, a potential polymeric charge-transfer acceptor. The formation of distinct colors observed when DNB paper was contacted with various anilines (donors) is consistent with the hypothesis that charge-transfer interactions play an important role in the binding of these components to DNB paper. The R_F values from organic solvents could be correlated with the Hammett substituent constant (σ), in the case of electron-releasing substituents. Differences in R_F values were sufficient to permit chromatographic separation of some of the substituted anilines, indicating that DNB cellulose is a useful chromatographic medium.

INTRODUCTION

In a recent communication, we reported that a number of aromatic donors were adsorbed by 3,5-dinitrobenzoyl (DNB) cotton cellulose¹. The adsorption was attributed to the formation of discrete charge-transfer complexes between pendant DNB groups as electron acceptors and various mobile phase solutes as donors. A typical example was the complex formed when DNB cotton was contacted with an anisidine solution.

Distinct color change that the DNB cotton underwent when immersed in donor solutions supported charge-transfer complexation as the principal mechanism

* National Research Council Postdoctoral Associate, 1972-1973. Address correspondence to this author.

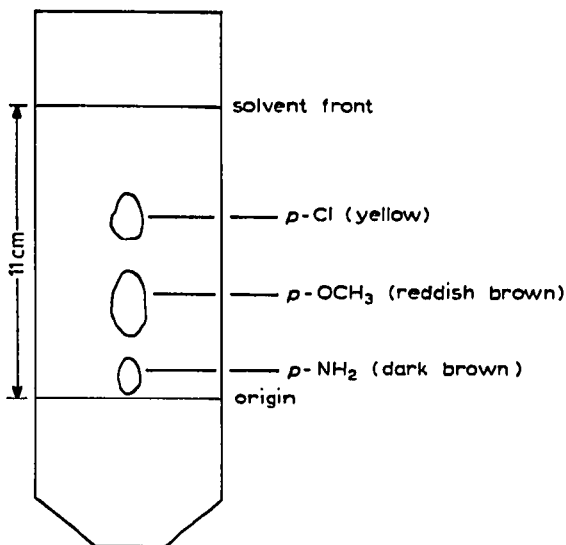


Fig. 1. Typical chromatogram on DNB cellulose paper showing the separation of p -NH₂, p -OCH₃ and p -Cl substituted anilines. The solvent was ethyl acetate-cyclohexane (2:5).

RESULTS AND DISCUSSION

An obvious advantage of using a polymeric acceptor such as DNB cellulose as a chromatographic agent is that in many instances colored complexes are formed. In such cases, the development of a chromatogram can be monitored visually. The color of the spots circumvents the need for a detection reagent and greatly simplifies the task of finding appropriate experimental conditions for separation.

Fig. 1 shows a typical chromatogram. Satisfactory separation of mixtures of substituted anilines could be achieved when the R_F values differed by about 0.2 R_F units.

The R_F values found for the anilines employed in this study are presented in Table I. Inspection of Table I shows that for anilines having electron-releasing sub-

TABLE I
 R_F VALUES FOR SUBSTITUTED ANILINES ON DNB PAPER

Substituent	R_F	Color	σ^*
p -NH ₂	0.05	dark brown	-0.66
p -OH	0.11	brown	-0.37
p -OCH ₃	0.33	reddish brown	-0.27
p -CH ₃	0.64	light brown	-0.17
m -CH ₃	0.68	yellow	-0.07
H	0.57	pale yellow	0.00
p -Cl	0.57	yellow	+0.23
p -SO ₂ NH ₂	0.04	bright yellow	+0.57
p -CN	0.29	yellow	+0.66

* Substituent constant values from ref. 8.

stituents (*m*-CH₃, *p*-CH₃, *p*-OH, *p*-OCH₃, *p*-NH₂) the R_F values decrease as the electron-releasing power of the substituent increases. No such correlation is observed for electron-withdrawing substituents (H, *p*-Cl, *p*-SO₂NH₂, *p*-CN). A decrease in R_F values might be expected for anilines substituted with increasingly electron-releasing groups provided the principal mechanism by which the anilines are adsorbed by the stationary phase used with the DNB paper involves charge-transfer complex formation.

In adsorption chromatography the fundamental expression relating R_F to the strength with which a particular solute is bound by the stationary phase, as reflected in the association constant K , is⁵

$$R_F = \frac{1}{1 + \alpha K} \quad (1)$$

In this expression α is the ratio of the quantities of stationary and mobile phase donor and is constant at any point behind the solvent front. Eqn. 1 indicates that those donors that interact strongly with the adsorbent, and therefore have large K values, will have correspondingly low R_F values. Foster and Morris⁶ have shown that the formation constants for the trinitrobenzene charge-transfer complexes of a series of benzenes substituted with electron-releasing groups could be correlated by means of the Hammett equation⁷, while those benzene derivatives with electron-withdrawing groups could not be correlated. The Hammett equation is:

$$\log K = \sigma \rho + \text{constant} \quad (2)$$

The symbol σ is the substituent constant and is a measure of the electron-releasing or withdrawing power of the substituent; ρ is the experimentally determined reaction constant and is a measure of the sensitivity of K to a change of substituent. Combining eqn. 2 with eqn. 1 in logarithmic form, and assuming $\alpha K \gg 1$, a Hammett relationship is obtained which predicts a linear dependence of $-\log R_F$ on the substituent constant (σ):

$$-\log R_F = \sigma \rho + \text{constant} \quad (3)$$

Fig. 2 shows a Hammett plot of the R_F values determined for anilines substituted with electron-releasing groups. No linear dependence of $-\log R_F$ versus σ was found when the substituents were electron-withdrawing. From a least-squares treatment of the data in Fig. 2, a ρ value of -2.0 was calculated. The simple correlation coefficient between σ and $\log R_F$ was -0.955 , which, in spite of the small number of observations, is significant at the 95% level. The correlation of R_F values with eqn. 3 found for anilines with electron-releasing substituents is consistent with the hypothesis that charge-transfer interaction plays an important role in the binding of these compounds to the stationary phase. Apparently, the breakdown in the Hammett correlation when anilines substituted with electron-withdrawing groups were used results from the diminished importance of charge-transfer interactions as compared with other forces involved in adsorption (such as dipole-dipole interactions).

The chromatography of anilines on DNB paper might be viewed as a type of

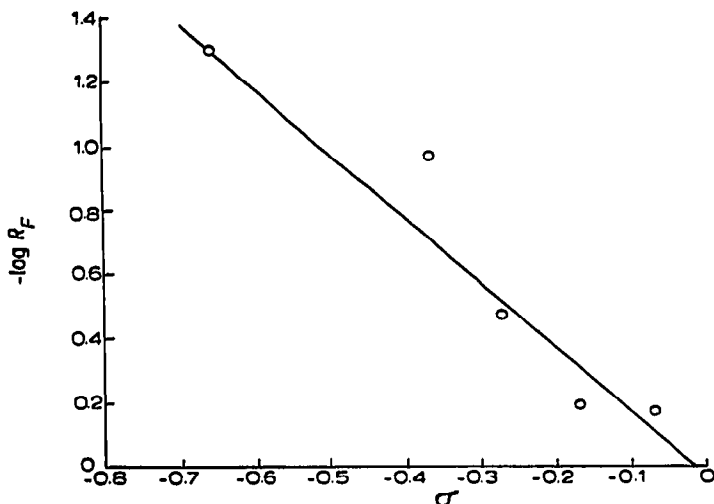


Fig. 2. Hammett-type plot showing the relationship between $-\log R_F$ and σ .

small molecule "affinity" chromatography since a specific complex is formed on the stationary phase between an immobilized acceptor and a mobile phase donor. We believe that the application of the principle of charge-transfer chromatography on celluloses modified with various donor or acceptor groups may be useful for the separation of a wide variety of chemical and biochemical substances.

REFERENCES

- 1 S. L. Snyder and C. M. Welch, *J. Polym. Sci. Polym. Lett. Ed.*, 11 (1973) 695.
- 2 R. G. Harvey and M. Halonen, *J. Chromatogr.*, 25 (1966) 294.
- 3 N. P. Buu-Hoi and P. Jacquignon, *Experientia*, 13 (1957) 375.
- 4 J. T. Ayres and C. K. Mann, *Anal. Chem.*, 36 (1964) 2185.
- 5 L. R. Snyder, *Advan. Chromatogr.*, 4 (1967) 7.
- 6 R. Foster and J. W. Morris, in R. Foster (Editor), *Organic Charge-Transfer Complexes*, Academic Press, London, New York, 1969, p. 197.
- 7 L. P. Hammett, *Chem. Rev.*, 17 (1935) 125.
- 8 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23 (1958) 420.