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STUDY OF INTERACTIONS OF SUBSTITUTED PYRIDINES WITH 2,3,5-TRIIODOBENZOIC ACID BY MEANS OF GAS CHROMATOGRAPHY

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SUMMARY

A linear free energy relationship for the interactions between substituted pyridines and 2,3,5-triiodobenzoic acid was obtained at different column temperatures. The temperature dependence of the Hammett constant (ϱ) was estimated. The validity of the linear free energy relationship and the proportionality of the calculated enthalpy of adsorption to pK_a values of substituted pyridines is in accordance with the assumption that the specific interactions are predominant in this system.

INTRODUCTION

The validity of the Hammett equation for some chromatographic systems has been established[1,2]. There are sufficient data available on solute–solvent interactions in gas–liquid chromatography for a wide variety of liquid phases[2,3], but fewer on adsorbate–adsorbent interactions[4]. In this work, we used a compound with a well defined structure as the adsorbent and examined the validity of the Hammett equation for the interaction of substituted pyridines with such an adsorbent. 2,3,5-Triiodobenzoic acid was chosen because of its convenient physical properties which made it easy to use in gas chromatography and because it can undergo relatively strong specific interactions with pyridines.

THEORETICAL

The adsorption of a component X on an adsorbent A can be represented by the following expression[5]:

$$X_{(g)} + A \rightleftharpoons XA \qquad (1)$$

where

$X_{(g)}$ = molecule of the component X in the gas phase;
A = adsorbent surface active site;
XA = adsorbate–adsorbent adduct.

The equilibrium constant, K, for this reaction at low concentrations of X can be written as

$$K = \frac{N_{XA}}{N_X} \tag{2}$$

where N_X and N_{XA} are the mole fractions of the component X and of the adduct XA, respectively.

The partition coefficient, K^0, can be defined as the ratio of the adsorbate concentrations in the two phases[6]:

$$K^0 = \frac{C(X)_A}{C(X)_g} \tag{3}$$

where

$C(X)_A$ = concentration of adsorbate X in the adsorbed phase (mole/g);

$C(X)_g$ = concentration of adsorbate X in the non-adsorbed gas phase (mole/ml).

If the total number of moles of adsorbate in the adsorbed phase is n_{XA} and the number of moles of adsorbate in the non-adsorbed phase is n_X, we obtain the following expressions for K and K^0:

$$K = \frac{n_{XA} \cdot n_g}{n_X \cdot n_a} \tag{4}$$

$$K^0 = \frac{n_{XA}}{n_X} \cdot \frac{V_u}{W}$$

where

n_g, n_a = number of moles of carrier gas and of adsorbent, respectively;

W = weight of adsorbent in the column;

V_u = volume of non-adsorbed gaseous phase.

After introducing the adsorbent surface volume, V_a, defined by the following equation:

$$V_a = \frac{n_A}{n_g} \cdot \frac{V_u}{W} \tag{5}$$

we have

$$K^0 = K \cdot V_a \tag{6}$$

The equilibrium constant, K, is related to the standard free energy of adsorption through the following expression:

$$\log K = -\frac{\Delta G^0_A}{2.3\, RT} = \Delta E \tag{7}$$

The definition of the dimensionless adsorption energy, ΔE, equal to $-\Delta G^0_A/2.3\, RT$, is useful[5] and from eqns. 6 and 7 we obtain

$$\log K^0 = \log V_a + \Delta E \tag{8}$$

Let $(K^0)_A$ be the partition coefficient for the unsubstituted pyridine and $(K^0)_B$ the partition coefficient for substituted pyridine. Eqn. 8 can be written for both compounds and we obtain

$$\log (K^0)_A = \log V_a + (\Delta E)_A \tag{9}$$

$$\log (K^0)_B = \log V_a + (\Delta E)_B \tag{10}$$

We can study the linear free energy relationship in the following form:

$$\Delta(\Delta E) = (\Delta E)_B - (\Delta E)_A = \log \frac{(K^0)_B}{(K^0)_A} \tag{11}$$

Introducing the Hammett constants, σ and ϱ, and using the specific retention volume V_g, we can write:

$$\log \frac{(K^0)_B}{(K^0)_A} = \log \frac{V^0_{g\,B}}{V^0_{g\,A}} = \sigma \cdot \varrho \tag{12}$$

We examined this relationship for the adsorption of 3-substituted pyridines on 2,3,5-triiodobenzoic acid.

EXPERIMENTAL

Measurements were performed on a Varian 1860 gas chromatograph equipped with a flame ionization detector. Stainless-steel columns, length 1.80 m and I.D. 0.32 cm, were used, loaded with 25% of 2,3,5-triiodobenzoic acid on Embacel, 60–100 mesh. 2,3,5-Triiodobenzoic acid was dissolved in chloroform and the packing was prepared in the usual manner[7]. The exact amount of the adsorbent was determined by the combustion method. The column temperature, measured with an iron–constantan thermocouple, was 120, 130, 140 or 150° and was kept constant to within ±0.2°. The temperatures of the injector block and of the detector were the same as that of the column so as to prevent local overheating of the column. The specific retention volumes were determined from the expression

$$V^0_g\,(\text{ml/g}) = \frac{L \cdot F \cdot 273 \cdot (p_0 - p_{H_2O})}{V \cdot W \cdot T_m \cdot p_0} \cdot \frac{3}{2} \cdot \frac{\left[\left(\frac{p_i}{p_0}\right)^2 - 1\right]}{\left[\left(\frac{p_i}{p_0}\right)^3 - 1\right]} \tag{13}$$

where

L = distance between adsorbate peak maximum and starting point (cm);
F = carrier gas flow-rate (ml/min);
V = recorder chart speed (cm/min);
W = amount of liquid phase (g);
T_m = flow meter temperature (°K);
p_0 = outlet pressure (mm Hg);
p_i = inlet pressure (mm Hg).

The sample sizes were between 0.05 and 0.1 µl. Within this range, we did not find any dependence of the sample retention time on the amount of sample, and well known methods were therefore adopted for the evaluation of the specific retention data[8].

RESULTS

$\Delta(\Delta E)$ values were calculated according to eqn. 12 and are listed in Table I. The correlation of these data with the ordinary Hammett σ values is very good for all temperatures. Figs. 1 and 2 show two examples of the linear relationship between

TABLE I

$\Delta(\Delta E)$ VALUES

Compound	*Temperature (°C)*			
	120	*130*	*140*	*150*
Pyridine	0.00	0.00	0.00	0.00
3-Picoline	0.402	0.435	0.423	0.354
4-Picoline	0.590	0.560	0.539	0.565
3-Chloropyridine	−0.125	−0.111	−0.135	−0.121
3-Ethylpyridine	0.464	0.438	0.420	0.406
3-Bromopyridine	−0.156	−0.141	−0.155	−0.163
3-Fluoropyridine	−0.084	−0.071	−0.085	−0.095

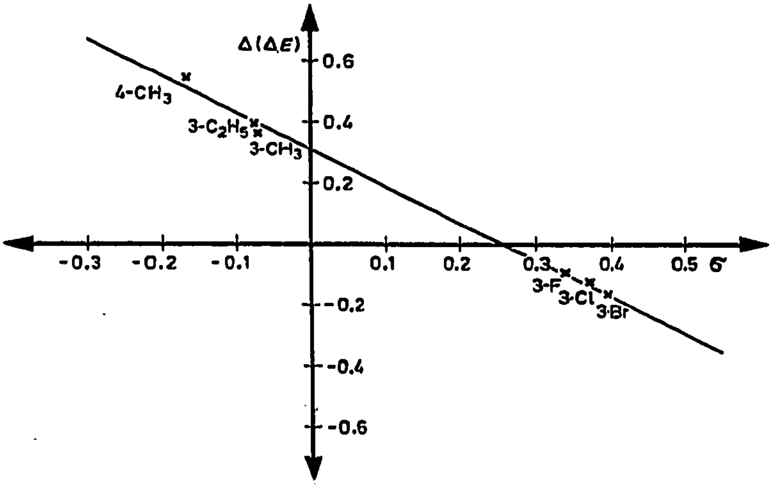

Fig. 1. $\Delta(\Delta E)$ values *versus* σ. Temperature, 150°C; ϱ, −1.22.

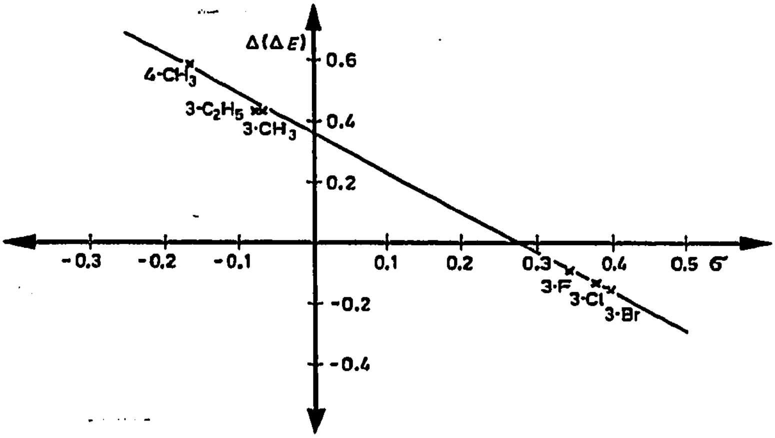

Fig. 2. $\Delta(\Delta E)$ values *versus* σ. Temperature, 120 °C; ϱ, −1.29.

TABLE II

HAMMETT σ CONSTANTS

Group	σ
$3\text{-}CH_3$	-0.07
$4\text{-}CH_3$	-0.17
$3\text{-}C_2H_5$	-0.072
3-Cl	0.373
3-Br	0.391
3-F	0.337

TABLE III

HAMMETT ϱ VALUES

Temperature (°C)	ϱ
120	-1.29
130	-1.26
140	-1.24
150	-1.22

the $\Delta(\Delta E)$ values and the Hammett σ constants. The σ values used in this work are collected in Table II.

Least-squares analysis of the results, performed on a Wang 100 calculator, yielded constant ϱ values for all temperatures. The results are shown in Table III. The constant ϱ is negative in all instances, reflecting the stronger interaction of pyridines substituted with electron-donating groups (methyl and ethyl) compared with derivatives with electron-withdrawing groups (halogens), as expected. The validity of the linear free energy relationship in our work shows that the predominant part of the adsorbate–adsorbent interactions could be attributed to specific interactions.

The absolute value of the constant ϱ measures the effect of the adsorbent on the relative adsorption of the substituted pyridines and reveals indirectly the strength

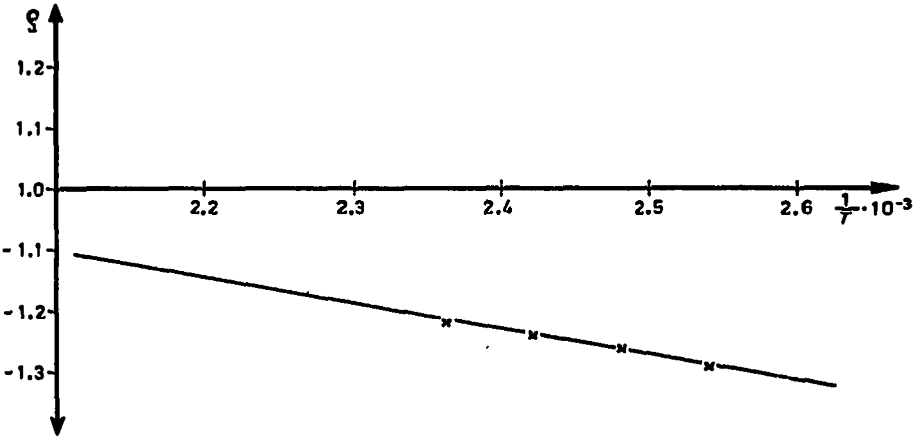

Fig. 3. ϱ *versus* $1/T$.

of the adsorbate–adsorbent interactions. The strength decreases with temperature and the corresponding behaviour of ϱ is evident from Fig. 3. The absolute value of ϱ decreases with temperature. Least-squares analysis of this relationship yields the following equation:

$$\varrho = -0.31 - 383.8\,(1/T) \tag{14}$$

The correlation coefficient in this instance is found to be 0.997. After we had checked the validity of the linear free energy relationship in our experimental system, we tried to calculate ΔE values from eqn. 8. The adsorbent surface volume, V_a, must be evaluated first. If we substitute W/M_A for n_A and $n_g\,RT/\bar{p}$ for V_a, which is correct at low sample concentrations, we obtain from eqn. 5 the expression

$$V_a = \frac{RT}{\bar{p}\cdot M_A} \tag{15}$$

where

$\bar{p}$ = average pressure in the column;
M_A = molecular weight of the adsorbent.

Using V_a values from eqn. 15 and the experimental retention data, we obtain ΔE values from eqn. 8. The results are listed in Table IV. These values are equal to log K. From the plot of log K *versus* $1/T$, the $-\Delta H$ values for the adsorbent–adsorbate interaction given in Table V were found. The $-\Delta H$ values are the sum of all interaction forces, specific and non-specific. Because of the validity of the Hammett equation for this system, and keeping in mind that 2,3,5-triiodobenzoic acid has a small specific surface compared with those of some commercially used adsorbents (Al_2O_3, SiO_2), we

TABLE IV

ΔE VALUES

Compound	*Temperature (°C)*			
	120	*130*	*140*	*150*
Pyridine	2.60	2.54	2.51	2.42
3-Picoline	3.00	2.97	2.93	2.79
4-Picoline	3.19	3.10	3.05	3.01
3-Chloropyridine	2.48	2.43	2.37	2.32
3-Bromopyridine	2.45	2.39	2.35	2.28
3-Fluoropyridine	2.52	2.46	2.44	2.36

TABLE V

$-\Delta H$ VALUES

Compound	*$-\Delta H$ (kcal/mole)*	*pK_a*
Pyridine	4.22	4.59
3-Picoline	4.89	4.70
4-Picoline	4.36	
3-Ethylpyridine	4.71	4.70
3-Chloropyridine	3.97	3.46
3-Bromopyridine	4.04	
3-Fluoropyridine	3.67	3.50

can assume that the $-\Delta H$ values obtained consist of a large contribution of specific interactions and a relatively small contribution of non-specific interactions. It may be noted from Table V that the $-\Delta H$ values are proportional to the pK_a values, which is in accordance with the above assumption. The pK_a values were taken from the work of Bryson[9].

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REFERENCES

1 R. B. Sleight, *Chromatographia*, 6 (1973) 3.
2 B. L. Karger, Y. Elmehrik and R. L. Ster, *Anal. Chem.*, 40 (1968) 1227.
3 B. L. Karger, Y. Elmehrik and W. Andrade, *J. Chromatogr. Sci.*, 7 (1969) 209.
4 L. R. Snyder, *J. Chromatogr.*, 17 (1965) 73.
5 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
6 J. H. Purnell, in A. B. Littlewood (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 3.
7 D. E. Martire, *J. Phys. Chem.*, 72 (1966) 3478.
8 D. H. James and C. S. G. Phillips, *J. Chem. Soc.*, (1953) 1600.
9 A. Bryson, *J. Amer. Chem. Soc.*, 82 (1960) 4871.