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## STUDY OF SUBSTITUENT EFFECTS BY MEANS OF GAS CHROMATOGRAPHY IN SOME AROMATIC SYSTEMS

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SUMMARY

Specific retention volumes for a set of aromatic solutes in two systems were measured: substituted phenols and anilines in triphenylmethanol and substituted phenols and anilines in triphenylmethane. All measurements were made at three temperatures and the results were then extrapolated to larger temperature intervals. In this way it was possible to correlate systems with different melting and boiling points.

From the retention data so obtained, some correlations with parameters affecting substituent effect were found. The constants  $\sigma$  and  $\rho$  in the modified Hammett equation were calculated.

The temperature dependence of  $\rho$  was estimated further. A few comments on the analytical applicability of the constant  $\rho$  in these systems are also given.

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## INTRODUCTION

The Hammett equation has been a successful tool in organic chemistry for many years and recently it has become useful in other fields also. The validity of the Hammett equation in the study of solute-solvent interactions was found by means of gas chromatography (GC). Systems with a relatively strong hydrogen bond as the main type of interaction between solute and solvent molecules were studied mostly. In particular, polyester-type stationary phases were examined closely<sup>1,2</sup>.

There are enough data available for these phases but they are important and useful mainly for analytical work. These data enable us to classify stationary phases into groups according to their selectivity. The theoretical interpretation is not easy, mainly because the structure of stationary phases is usually unknown or else it is very complicated.

In our work we tried to use compounds with well defined structures as stationary phases. Such examples are triphenylmethanol and triphenylmethane. Triphenylmethanol is particularly interesting for the study of phenols and anilines. Besides a known structure, it has the following advantages: three phenyl groups on the single

carbon atom enables us to assume the 1:1 formation of a hydrogen-bonded solute-solvent adduct; and because of its relatively high boiling point it is possible to use almost all light aromatic compounds as solutes. Triphenylmethane has similar advantages, so these two compounds were selected for our study.

## THEORY

The Hammett equation was originally written as follows:

$$\log \left( \frac{k_A}{k_B} \right) = \sigma \cdot \rho \quad (1)$$

where  $k_A$  and  $k_B$  are rate or equilibrium constants for reactions A and B, respectively,  $\sigma$  is a parameter dependent only on the substituent and its position, and  $\rho$  is a parameter dependent on the nature of the reaction but not on the substituents<sup>3</sup>.

Eqn. 1 was found to be applicable only to *meta*- and *para*-substituted benzene derivatives but not to *ortho*-substituted derivatives. Many data based on the validity of this equation and similar ones have been given over the past three decades. The equation was quickly extended to *ortho*-substituted derivatives and also to aliphatic compounds, but different constants were defined in these cases<sup>4</sup>.

The Hammett equation is an example of a linear free energy relationship, the general form of which is eqn. 2:

$$\log k_A = m \cdot \log k_B + C \quad (2)$$

It is easy to show that eqn. 2 represents a linear relationship between the standard free energy changes of reactions A and B since:

$$\log K = - \frac{\Delta F^0}{2.303 \cdot RT} \quad (3)$$

and

$$\Delta F_B = m' \Delta F_A + C' \quad (4)$$

In these equations,  $k_A$  and  $k_B$  again represent rate or equilibrium constants,  $\Delta F$  is the standard free energy change,  $m$  is the slope and  $C$  is the intercept in the graph of  $k_A$  vs.  $k_B$ .

For use in GC, it is convenient to modify the Hammett equation. Such a modification given, for instance, by KARGER and co-workers<sup>1,2</sup> first involves the determination of relative volatility as follows:

$$\alpha = \frac{K_x}{K_0} = \frac{t_{Rx} - t_{Ra}}{t_{Ro} - t_{Ra}} \quad (5)$$

which is, in an infinitely dilute solution:

$$\alpha = \frac{\gamma_0 \cdot p_0}{\gamma_x \cdot p_x} \quad (6)$$

where  $p_0$  and  $p_x$  are the saturation vapour pressures at the column temperature of the phenol (or aniline) and the substituted phenol (or aniline), respectively, and  $\gamma_0$  and  $\gamma_x$  are the activity coefficients for this pair of compounds.

Since the activity coefficient ratio reveals the difference between two solutes

regarding solute-solvent interactions, it seems promising to study the Hammett equation in the following form:

$$\log \left( \frac{\gamma_0}{\gamma_x} \right) = \sigma \cdot \rho + b \quad (7)$$

where  $b$  is a constant independent of electronic factors considered in the  $\sigma \cdot \rho$  term.

If a 1:1 adduct is formed between solute and solvent molecules, one can use the expression derived by MARTIRE AND RIEDL<sup>5</sup>:

$$V_g = \frac{273 \cdot R(K' \cdot a_D + 1)}{\gamma^* \cdot p_0 \cdot M} \quad (8)$$

where  $\gamma^*$  is the activity coefficient of the uncomplexed solute,  $M$  is the molecular weight of the solvent,  $p_0$  is the saturation vapour pressure of the solute at the column temperature,  $K'$  is the equilibrium constant for the hydrogen-bonded adduct, and  $a_D$  is the solvent activity.

By combining eqns. 6 and 8, taking logarithms and cancelling, we obtain:

$$\log \left( \frac{\gamma_0}{\gamma_x} \right) = \log \left( \frac{\gamma_0^*}{\gamma_x^*} \right) + \log \left( \frac{K_x' \cdot a_D + 1}{K_0' \cdot a_D + 1} \right) \quad (9)$$

If the hydrogen bond is strong enough, then:

$$\log \left( \frac{\gamma_0}{\gamma_x} \right) = \log \left( \frac{\gamma_0^*}{\gamma_x^*} \right) + \sigma \cdot \rho \quad (10)$$

From eqn. 10, it is easy to see that for good correlation between the activity coefficients ratio and the Hammett substituent constants, it is necessary that the term  $K \cdot a_D$  is appreciably greater than unity. Further, it is necessary that the first term on the right-hand side is constant for all solutes. This means that the reference substituent must be inert and must not interact with the solvent itself. Compounds such as hydroxy- and amino-phenols are thus evidently excluded from the validity of eqn. 10.

It is evident that the higher the value of constant  $\rho$ , the stronger is the influence of the solvent on the resolution. The constant  $\rho$  is therefore a direct measure of the solvent selectivity.

We examined this relation for triphenylmethanol and triphenylmethane.

## EXPERIMENTAL

All measurements were performed on a Varian 1860 Gas Chromatograph with a flame-ionization detector. Stainless-steel columns were used, loaded with packing with 25% of liquid phase. The exact amount of liquid phase was determined by a combustion method. Measurements were carried out at 171.5, 184 and 195.6° for triphenylmethanol and at 77, 85 and 98° for triphenylmethane. The true temperature of the column was measured with an accuracy of  $\pm 0.2^\circ$ . A thermocouple (iron-constantan) was introduced into the oven and the temperature was measured with a potentiometer.

The sample sizes were between 0.1 and 0.2  $\mu$ l. Within this limit we did not find any dependence of the sample retention time on the sample amount. Peaks were in all cases symmetrically shaped, so well known methods were adopted for the evaluation

TABLE I

HAMMETT  $\sigma$  VALUES FOR SOME *meta* AND *para* SUBSTITUENTS

Substituent	$\sigma$
3-CH <sub>3</sub>	-0.07
H	0.00
3-Cl	0.37
3-Br	0.38
3-F	0.35
3-I	0.35
3-NO <sub>2</sub>	0.79
4-NO <sub>2</sub>	0.82
3-C <sub>2</sub> H <sub>5</sub>	-0.072
3-CN	0.613
4-CH <sub>3</sub>	0.129
4-F	0.056
4-Cl	0.238
4-Br	0.265
4-I	0.299
4-CN	0.674
4-C <sub>2</sub> H <sub>5</sub>	0.117

of specific retention data. The solutes, being solid at room temperature, were first dissolved in ether. In all cases, column-on injection was employed. The carrier-gas flow-rate was chosen so that the retention times were between 1 and 20 min.

## RESULTS

Activity coefficient ratios were calculated according to eqn. 6. The vapour pressures were determined mainly from graphs of  $\ln P$  versus  $1/T$ . The data for the construction of these graphs were taken from several published sources to minimize the errors. For *meta*- and *para*-substituted derivatives, correlation was found with the ordinary Hammett  $\sigma$  values, but for *ortho*-substituted derivatives the Taft  $\sigma^*$  values were used. Some of these constants are shown in Tables I and II<sup>6,7</sup>.

From the data obtained, graphs of logarithms of activity coefficient ratios versus  $\sigma$  or  $\sigma^*$  were constructed. From these graphs,  $\rho$  was determined by the least-squares

TABLE II

TAFT  $\sigma^*$  CONSTANTS FOR SOME *ortho* SUBSTITUTENTS

Substituent	$\sigma^*$
CH <sub>3</sub>	0.000
H	0.490
C <sub>2</sub> H <sub>5</sub>	-0.100
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	-0.115
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	-0.130
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	-0.190
CH <sub>3</sub> COO	1.650
CCl <sub>3</sub>	2.650
C <sub>6</sub> H <sub>5</sub>	0.600

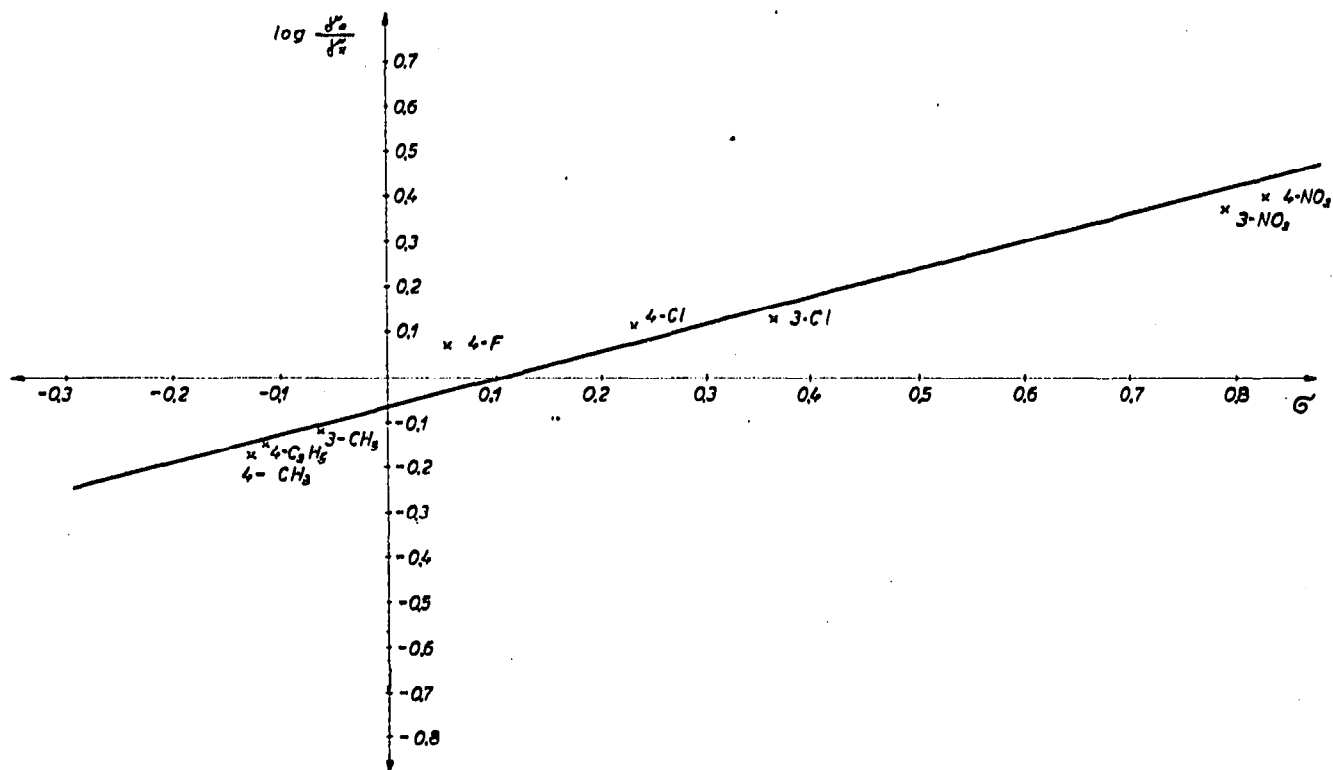


Fig. 1. Graph of  $\log \left( \frac{\gamma_0}{\gamma_x} \right)$  vs.  $\sigma$  for *meta*- and *para*-substituted phenols in triphenylmethanol. Temperature = 171.5°;  $\rho = 0.625$ ;  $b = -0.07$ .

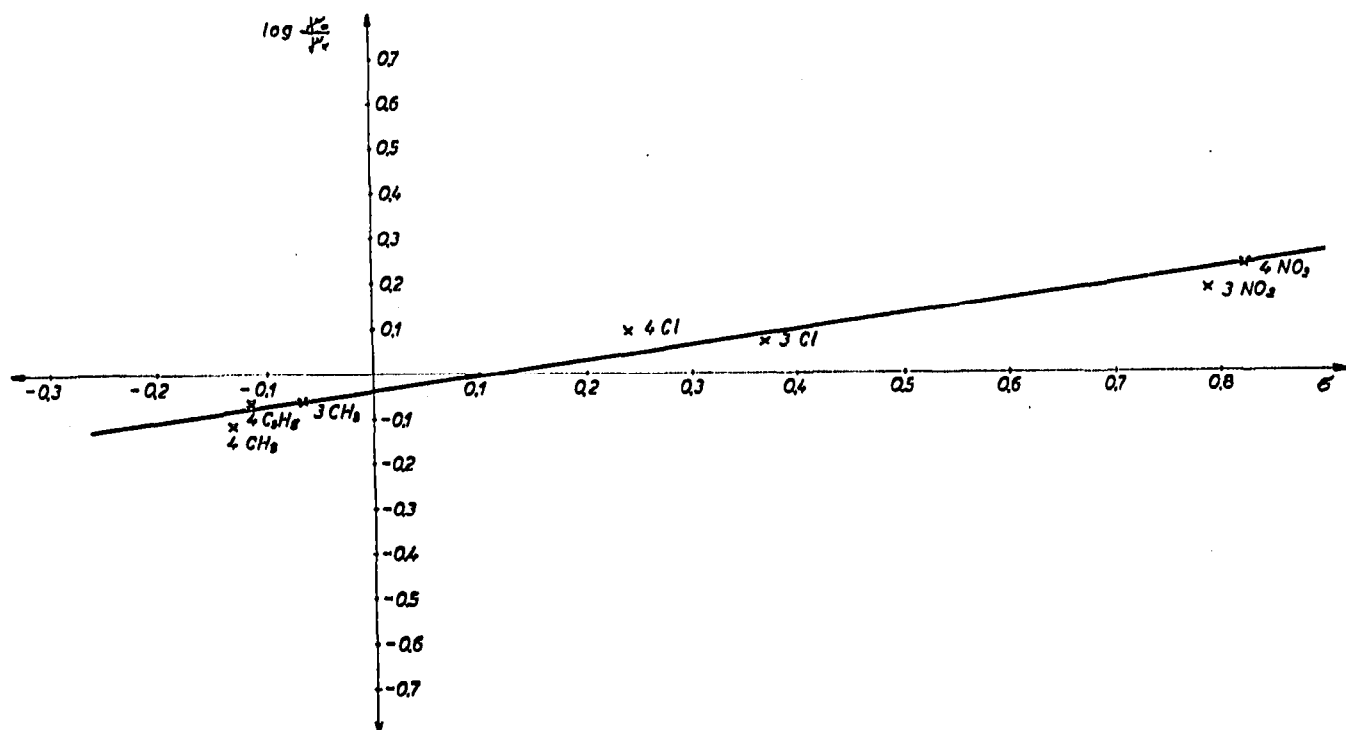


Fig. 2. Graph of  $\log \left( \frac{\gamma_0}{\gamma_x} \right)$  vs.  $\sigma$  for *meta*- and *para*-substituted anilines in triphenylmethanol. Temperature = 171.5°;  $\rho = 0.339$ ;  $b = -0.04$ .

method. In the case of triphenylmethanol, relatively good correlation was obtained. For triphenylmethane, there was a poorer correlation and high scattering.

At this stage, our intention was only to determine  $\rho$  for these two phases for various types of solutes, and to find the dependence of  $\rho$  on temperature. Before the temperature dependence of  $\rho$  is examined, let us discuss briefly the results for particular groups of solutes.

#### *Meta- and para-substituted phenols*

Eight substituted phenols were chromatographed, and the results are presented in Fig. 1 for the temperature 171.5°. The constant  $\rho$  in this case was found to be 0.625. For triphenylmethane and the same set of solutes it was found by extrapolation that the constant  $\rho$  at the same temperature would be 0.22.

It can be seen that  $\rho$  for triphenylmethane is much lower than for triphenylmethanol. This corresponds to the fact that  $\rho$  measures the effect of the solvent on resolution, which is greater in the case of triphenylmethanol because the hydrogen bonding between solute and solvent molecules is much stronger than in the case of triphenylmethane. Nevertheless,  $\rho$  for triphenylmethanol is not so high that triphenylmethanol could not be recommended for use as the stationary phase for general analytical work. Almost all commercial polyester and other types of phases have much higher  $\rho$  values, usually about unity. But since our primary task is not to study the analytical aspects of resolution, we decided to use well defined phases that can serve as basic points for further studies. It is important to notice that in the case of triphenylmethanol the Hammett equation holds relatively well at quite high temperatures, where the term  $K \cdot a_D$  for the formation of the hydrogen-bonded adduct is

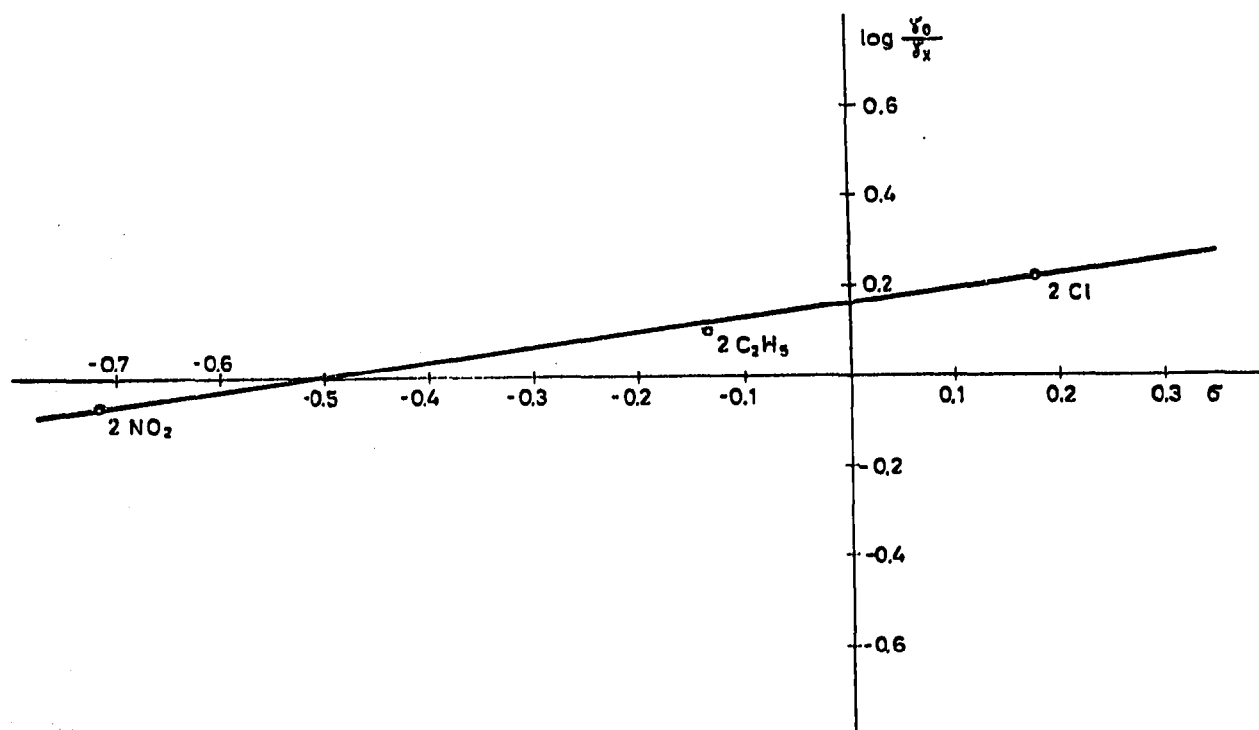


Fig. 3. Graph of  $\log \left( \frac{y_0}{y_x} \right)$  vs.  $\sigma$  for *ortho*-substituted phenols in triphenylmethanol. Temperature 171.5°;  $\rho = 0.32$ .

not as close to unity as it is in the case with electron-rich stationary phases. A similar situation exists with substituted anilines where  $\rho$  under the same conditions is 0.339 for triphenylmethanol (Fig. 2).

#### *Ortho-substituted phenols*

Results are presented in Fig. 3 for *ortho*-substituted phenols. A correlation with the Taft  $\sigma^*$  constant clearly exists. The results in Fig. 3 refer to triphenylmetha-

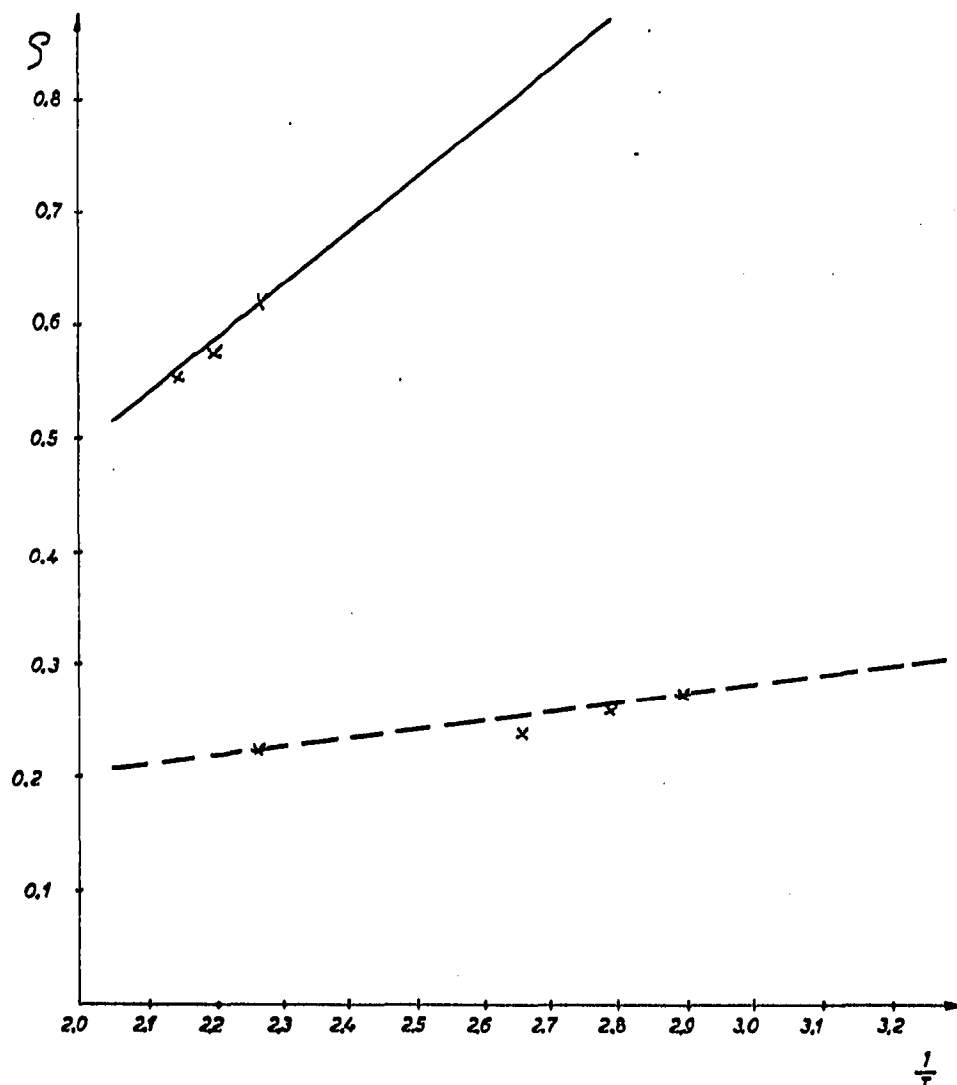


Fig. 4. Graphs of  $\rho$  vs.  $\frac{1}{T}$  for *ortho*- and *meta*-substituted phenols in triphenylmethanol (—) and in triphenylmethane (---).

not. In the case of triphenylmethane, under the same conditions the constant is 0.256. It can be seen that the difference is smaller than in the case of *meta*- and *para*-substituted phenols, but because of the small number of solutes this result is not of great value. Other *ortho*-substituted phenols were excluded from our work because of the lack of vapour pressure data.

## CONCLUSIONS

In conclusion, we can say that in all the systems measured the Hammett equation can be used. Only the temperature dependence of  $\rho$  remains to be examined. In Fig. 4 there is an example of plots of  $\rho$  versus  $1/T$ . Straight lines were found in all cases, but the temperature dependence of  $\rho$  is appreciably greater for triphenylmethanol than for triphenylmethane, and this is indicated in Fig. 4 also.

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