# A Gas Chromatographic Study of the Charge-Transfer Complexes Formed Between 1,3,5-Trinitrobenzene and Aromatic Hydrocarbons

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## Summary

*Gas-liquid chromatography was used for studying the complexing equilibrium at 60 °C between aromatic hydrocarbons and 1,3,5-trinitrobenzene (TNB) dissolved in dinonyl phthalate (DNP). On increasing the molar fraction of TNB in the stationary phase, a significant increase in the activity coefficients at infinite dilution was observed for several non-complexing solutes; said increase cannot be exclusively attributed to variations in the molar volume of the stationary phase. It appears to be evident that the activity coefficient of TNB varies appreciably with its concentration in DNP. A semiempirical method, combining theories for regular and athermal solutions, is applied for calculating the activity coefficient of uncomplexed solute in different stationary phases. The thermodynamic stability constants for the complexes can then be calculated by means of a series of relations that are fulfilled when the molar fraction of the additive tends to zero. Values thus obtained are compared with spectrophotometric data.*

## Introduction

The study of chemical equilibria by means of gas chromatography has been the subject of numerous papers during the last ten years. Since the publication of the paper of *Purnell* in 1967 [1], the majority of the authors have applied his equations to different systems, most of them molecular complexes between a volatile solute (B) and a complexing agent (A) dissolved in an "inert" solvent (S). (For literature data, the reader is referred e.g. to the bibliography in [2]).

The thermodynamic equilibrium constant, K, for the reaction between A and B to give a complex AB within a solvent S, can be written as:

$$K = \frac{X_{AB}}{X_A X_B} \frac{\gamma_{AB}}{\gamma_A \gamma_B} \qquad (1)$$

where $X_i$ represents molar fractions and $\gamma_i$ the activity coefficients (taking pure i as the reference state) of species in equilibrium. The partition coefficient, $K_R$, is defined as the quotient of the total concentration of B in the stationary phase (either complexed or free) and its concentration in the vapour phase in equilibrium. B being the only volatile species, it is easily deduced that:

$$K_R = \frac{RT}{f_B^0 \, v_{A,S}^0 \, \gamma_{B(A,S)}^\infty} \left[ 1 + K \, X_A \frac{\gamma_{A(A,S)} \, \gamma_{B(A,S)}^\infty}{\gamma_{AB(A,S)}^\infty} \right] \qquad (2)$$

where $f_B^0$ is the fugacity of pure B vapour in equilibrium with pure B liquid, and $v_{A,S}^0$ is the molar volume of a mixture of A and S which contains the molar fraction $X_A$ of A. Each activity coefficient is assigned a subindex between parenthesis, indicating the particular solvent; it is assumed that the solute, and consequently the complex, have attained the condition of infinite dilution. The partition coefficient $K_R^0$ for the solute B between pure solvent S and the vapour phase is the particular case of Eq. 2 when $X_A = 0$:

$$K_R^0 = \frac{RT}{f_B^0 \, v_S^0 \, \gamma_{B(S)}^\infty} \qquad (3)$$

where $v_S^0$ is the molar volume of pure S. Combining Eqs. 2 and 3:

$$K_R \, v_{A,S}^0 = K_R^0 \, v_S^0 \, \frac{\gamma_{B(S)}^\infty}{\gamma_{B(A,S)}^\infty} \left[ 1 + K \, X_A \frac{\gamma_{A(A,S)} \, \gamma_{B(A,S)}^\infty}{\gamma_{AB(A,S)}^\infty} \right] (4)$$

By analogy with Eq. 1, it is possible to define another thermodynamic equilibrium constant:

$$K^* = \frac{X_{AB}}{X_A X_B} \frac{\gamma_{AB}^*}{\gamma_A^* \gamma_B^*} \qquad (5)$$

where $\gamma_i^*$ is the activity coefficient of chemical species i when a solution of i at infinite dilution in S is taken as the reference state. In spite of $K^*$ being defined with reference to a given solvent, it is still a thermodynamic constant. Combining Eqs. 4 and 5 and the ratio between the two types of activity coefficients $(\gamma_i/\gamma_i^* = \gamma_i^\infty, [3])$ we can write that

$$K_R \, v_{A,S}^0 = K_R^0 \, v_S^0 \, \frac{\gamma_{B(S)}^\infty}{\gamma_{B(A,S)}^\infty} [1 + K^* \, \gamma_A^* \, X_A] \qquad (6)$$

Eq. 6 is strictly rigurous from a thermodynamic point of view. Impossibility to measure $\gamma_{B(A,S)}^\infty$ and $\gamma_A^*$ experimentally by means of chromatographic methods restricts the application of Eq. 6 in the form given.

In their study of complexing between heterocyclic aromatic compounds and dibutyltetrachlorophthalate dissolved

in squalane, *Eon, Pommier* and *Guiochon* [2] detected two characteristics in the behaviour of the systems which allowed an elegant treatment of the problem. On the one side, mixtures of A and S exhibited a quasiideal behaviour, in the sense that their molar volumes varied linearly with the molar fraction, according to the ratio

$$v_{A,S}^0 = v_S^0 + (v_A^0 - v_S^0) X_A \qquad (7)$$

By applying the well-known simplified Flory-Huggins equation [4] for solute at infinite dilution, and assuming that the molar volume of B in usual chromatographic systems is small as compared to those of A and S, it is possible to write for the athermal contribution to the activity coefficient:

$$\frac{1}{a\gamma_{B(A,S)}^\infty} = \frac{1}{a\gamma_{B(S)}^\infty} + \left[\frac{1}{a\gamma_{B(A)}^\infty} - \frac{1}{a\gamma_{B(S)}^\infty}\right] X_A \qquad (8)$$

On the other side, the enthalpy of mixing for non-complexing solutes did not change significantly with the composition of the stationary phase. By assuming that dissolution of complexing solutes as uncomplexed species obeys the same law, it is possible to write the following ratio for the thermal contribution to the activity coefficient of B:

$$t\gamma_{B(A,S)}^\infty \cong t\gamma_{B(S)}^\infty \qquad (9)$$

By combining Eqs. 5–9 *Guiochon* et al. arrived to the following expression:

$$K_R\, v_{A,S}^0 = K_R^0\, v_S^0\, [1 + (\psi + K^*) X_A] \qquad (10)$$

·where the function $\psi$ is defined as

$$\psi = \frac{a\gamma_{B(S)}^\infty}{a\gamma_{B(A)}^\infty} - 1 \qquad (11)$$

and, on the basis of the quasiideal behaviour that, from the standpoint of the volumes of their mixture, is exhibited by the mixtures of A and S, it has been assumed that:

$$\frac{\gamma_{A(A,S)}}{\gamma_{A(A,S)}^\infty} = \gamma_{A(A,S)}^* = 1 \qquad (12)$$

Any generalization of Eq. 10 to other systems must be done extremely cautiously. In the first place, the assumption on the basis of no excess volume (Eq. 7) that $\gamma_A^* = 1$, may lead to appreciable errors, particularly when dealing with high values of $X_A$. For a solution to be considered ideal, it must fulfill simultaneously all the requirements of ideality; obviously this is very difficult to be proven for mixtures of A and S on the basis of data of exclusively chromatographic origin. The problem is even more complex in the case of linear volumetric behaviour when A and S are only partially miscible; in these cases it is possible to assign to $v_A^0$ the value of $v_{A,S}^0$ extrapolated to $X_A = 1$, but this value is of dubious physical meaning.

Secondly, the condition described in Eq. 9 should be thoroughly proved; this imposes the study of the behaviour not only of the group A-complexing solutes, but also of

several other structurally similar non-complexing solutes. When $K^* = 0$, Eq. 6 becomes

$$K_R\, v_{A,S}^0 = K_R^0\, v_S^0\, \frac{\gamma_{B(S)}^\infty}{\gamma_{B(A,S)}^\infty} \qquad (13)$$

If the condition described in Eq. 9 is applied, Eq. 13 can be written as

$$\left[\frac{K_R}{K_R^0}\right]_G = \frac{v_S^0}{v_{A,S}^0}\, \frac{a\gamma_{B(S)}^\infty}{a\gamma_{B(A,S)}^\infty} \qquad (14)$$

where subscript G means that *Guiochon's* condition – Eq. 9 – has been applied. A value of $(K_R/K_R^0)_G = 1.025$ has been found by processing *Purnell's* data for each of the systems of methylcyclohexane vs. dipropyltetrachlorophthalate dissolved in squalane [5] and cyclohexane vs. trinitrofluorenone dissolved in dinonyl phthalate [6]. Calculation for the latter had already been made by *Eon* and *Karger* [7] following a somewhat different path; molar volumes of stationary phases from their paper were introduced in our equation. *Purnell* finds $K_R/K_R^0 = 1$ in both cases. Whether or not a difference within the order of 2.5 % for the quotient between two partition coefficients obtained making use of different columns is significant from an experimental point of view, is a matter of discussion. *Cadogan* and *Purnell* themselves [5] give for the partition coefficient of methylcyclohexane a value of 256.5 ± 2, thus implying an experimental variation within 0.8 % around the mean; this range matches that found between partition coefficients in the present paper (see Experimental Section) for a given solute in two columns supposed to be equal. Admitting that the significance of said differences is questionable, they may assume much higher values in other systems, as the one herein studied.

From Eqs. 13 and 14 one can write that

$$\frac{(K_R/K_R^0)_G}{K_R/K_R^0} = \frac{t\gamma_{B(A,S)}^\infty}{t\gamma_{B(S)}^\infty} \qquad (15)$$

In consequence, the difference of 2.5 % between the value calculated assuming the validity of Eq. 9 and the one obtained experimentally, might be attributed to the very simple fact that those systems studied by *Purnell* do not fulfill completely that condition.

In this paper the complexing equilibrium is studied for a series of alkylbenzenes and 1,3,5-trinitrobenzene (TNB) dissolved in dinonyl phthalate (DNP). The choice in favour of DNP was due to its good solvent properties towards TNB which was only scarcely soluble in more inert solvents such as higher paraffins. TNB, by its own, is one of the best-known acceptors, and its capacity to give charge-transfer complexes has been definitely established by other techniques.

## Experimental

### I. Apparatus

The columns were kept at 60.00 ± 0.05 °C by immersion in a modified thermostatic bath Lauda U3. High-purity nitrogen was used as the carrier gas, further purified by

passing through a molecular sieve 5A trap before entering into the column. The flow rate was regulated by means of a Brooks ELF flow controller (Mod. 8743). The inlet pressure was measured with a mercury manometer; the outlet pressure was atmospheric in every case and was read on a barometer at one hour intervals. The carrier gas flow rate was measured at room temperature with a soap-bubble flow meter at the outlet of the detector. The eluates were detected by means of a flame ionization detector model Aerograph 600 D.

## II. Columns and Reagents

Varian Aerograph dinonyl phthalate, $n_D^{25} = 1.48181$, without further purification, was used as the stationary phase diluent. 1,3,5-Trinitrobenzene was prepared according to the procedure of *Desseigne* [8], by oxidation and further decarboxylation of 2,4,6-trinitrotoluene; the final product was obtained by double crystallization from glacial acetic acid, and identity and purity was checked both by IR spectrum and melting point (123.5–123.8 °C).

Solutions used as stationary phases were prepared by careful weighing of their components; seven different stationary phases were used with TNB molar fractions ranging from 0 to 0.273. Solubility tests had shown it would not be possible to reach higher concentrations.

Chromosorb P 60/80 mesh washed with hot concentrated sulfuric and nitric acids was used as the solid support. When preparing the packings, the stationary phase was very carefully weighed and dissolved in chloroform; the support was mixed with this solution and the solvent evaporated under air draft; the packing was finally heated at 80 °C for 2–3 hours. Stationary phase to support ratio was kept around 1:4.

The columns were 60 cm long with an outside diameter of 1/4 inch. The amount of packing in each column was determined by weighing both the columns and the packing before and after filling.

As every solute tested was 99+ %, purity not being a determing factor in this kind of study, they were used as such, without further purification. Following solutes were studied: cyclohexane (cyclo-$C_6$), methylcyclohexane (Mcyclo-$C_6$), n-hexane (n-$C_6$), n-heptane (n-$C_7$), isooctane (2,2,4-TMC$_5$), benzene ($\phi$H), toluene ($\phi$CH$_3$), ethylbenzene ($\phi C_2 H_5$), isopropylbenzene ($\phi i C_3 H_7$), o-xylene (o–X), m-xylene (m–X) and p-xylene (p–X).

## III. Procedure

Solutes were injected in the vapour form with help of 10- and 50-$\mu$l Hamilton syringes; sample size was the least compatible with a favourable signal-to-noise ratio, this resulting in a sample in the order of $10^{-2}$ $\mu$ moles. Symmetric peaks were obtained for every solute.

A small amount of methane was injected with the solute in every case; the adjusted retention times were measured on the recorder chart with a ruler divided to 1/60 inch, between the methane peak and the maximum of the so-

lute peak. Neither the excellent symmetry of the peaks nor the retention times were affected by a 50-fold increase in the sample size.

Carrier gas flow rates employed ranged between 30 and 100 ml/min. Each column was operated at least at three different flow rates, and no appreciable variation in the retention volumes was detected. Partition coefficients given for each solute are the average of not less than eight independent injections distributed in at least two different flow rates. For $X_A = 0$ and $X_A = 0.234$ duplicate columns were assembled; partition coefficients determined with each pair differed in less than 0.8 %.

## Results

### I. Molar Volumes of the Stationary Phases

The molar volume of a mixture of density $d_{A,S}$ is defined by

$$v_{A,S}^0 = \frac{X_A M_A + X_S M_S}{d_{A,S}} \tag{16}$$

where $X_A$, $X_S$, and $M_A$, $M_S$ stand for the molar fractions and molecular weights of the components. Density at 60 °C for each of the seven stationary phases was determined with a picnometer. From the analysis of the values obtained it was found that the density is a linear function of the molarity of TNB and not of the molar fraction, as the plots of $d_{A,S}$ vs. $X_A$ are concave towards the density axis. On the contrary, and as it could be predicted on the basis of the relationship between molarity and molar fraction, molar volumes are a linear function of the molar fraction, but not of TNB molarity. A least-squares analysis of said behaviours resulted in the following equations:

$$d_{A,S} = 0.9412 + 0.0869 \, C_A \qquad s_{yx} = 0.00013$$
$$v_{A,S}^0 = 444.77 - 310.70 \, X_A \qquad s_{yx} = 0.054$$

$s_{yx}$ being the standard error of the estimate of y on the respective x.

### II. Partition Coefficients and Activity Coefficients

Net retention volumes, $V_N$, were calculated from the following equation (see e.g. [9]):

$$V_N = j \, t_R' \, F_o \frac{T_c}{T_a} \left(1 - \frac{p_w}{p_o}\right) \tag{16a}$$

where j is the compressibility correction factor, $t_R'$ the adjusted retention time of the solute, $F_o$ the carrier gas flow rate measured at column outlet pressure and ambient temperature, $p_o$ the ambient pressure, $p_w$ the partial pressure of water at $T_a$ temperature, and $T_a$ and $T_c$ are the ambient and column temperatures respectively (both in °K).

From $V_N$ values the retention volumes $V_N^0$ for the condition $p_i = p_o = 0$ were calculated using the equation of *Cruickshank, Windsor*, and *Young* [10]:

$$\ln \frac{V_N^0}{V_N} = -\beta p_o J_3^4 \tag{17}$$

**Table I.** Partition Coefficients, $K_R$, at 60 °C

| Solute | $X_A$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.000 | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| cyclo-$C_6$ | 140.4 | 137.6 | 134.3 | 131.7 | 128.8 | 125.9 | 123.2 |
| Myclo-$C_6$ | 244.5 | 238.8 | 232.0 | 228.3 | 222.7 | 216.2 | 210.6 |
| n-$C_6$ | 75.26 | 73.22 | 70.99 | 70.21 | 67.39 | 66.22 | 64.37 |
| n-$C_7$ | 185.7 | 180.4 | 173.2 | 167.0 | 164.6 | 159.8 | 154.3 |
| 2,2,4-$TMC_5$ | 164.5 | 160.5 | 155.4 | 152.7 | 148.2 | 143.3 | 140.7 |
| $\emptyset H$ | 221.7 | 221.9 | 222.1 | 224.1 | 225.7 | 227.8 | 230.1 |
| $\emptyset CH_3$ | 579.5 | 581.8 | 585.8 | 590.9 | 598.9 | 604.9 | 616.0 |
| $\emptyset C_2 H_5$ | 1297 | 1298 | 1298 | 1303 | 1307 | 1316 | 1339 |
| $\emptyset iC_3 H_7$ | 2161 | 2155 | 2149 | 2141 | 2143 | 2125 | 2154 |
| o-X | 1846 | 1871 | 1907 | 1938 | 1986 | 2018 | 2082 |
| m-X | 1489 | 1507 | 1532 | 1551 | 1585 | 1605 | 1655 |
| p-X | 1435 | 1452 | 1479 | 1502 | 1540 | 1569 | 1614 |

**Table II.** Corrected Solute Activity Coefficients ($\gamma^{\infty}_{B(A,S)}$) at 60 °C

| Solute | $X_A$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.000 | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| cyclo-$C_6$ | 0.881 | 0.931 | 0.995 | 1.042 | 1.109 | 1.174 | 1.241 |
| Myclo-$C_6$ | 0.962 | 1.021 | 1.096 | 1.144 | 1.220 | 1.302 | 1.381 |
| n-$C_6$ | 1.131 | 1.187 | 1.295 | 1.345 | 1.459 | 1.537 | 1.633 |
| n-$C_7$ | 1.224 | 1.306 | 1.417 | 1.484 | 1.596 | 1.701 | 1.819 |
| 2,2,4-$TMC_5$ | 1.360 | 1.449 | 1.556 | 1.626 | 1.745 | 1.868 | 1.966 |
| $\emptyset H$ | 0.552 | 0.579 | 0.612 | 0.634 | 0.670 | 0.703 | 0.736 |
| $\emptyset CH_3$ | 0.588 | 0.613 | 0.645 | 0.666 | 0.699 | 0.730 | 0.761 |
| $\emptyset C_2 H_5$ | 0.654 | 0.682 | 0.717 | 0.740 | 0.770 | 0.811 | 0.846 |
| $\emptyset iC_3 H_7$ | 0.717 | 0.747 | 0.789 | 0.810 | 0.850 | 0.887 | 0.925 |
| o-X | 0.624 | 0.648 | 0.680 | 0.700 | 0.746 | 0.764 | 0.795 |
| m-X | 0.640 | 0.665 | 0.698 | 0.719 | 0.754 | 0.785 | 0.817 |
| p-X | 0.638 | 0.663 | 0.695 | 0.716 | 0.750 | 0.781 | 0.812 |

Activity coefficients for each of the solutes in DNP and for alkanes and cycloalkanes in every stationary phase were determined in the usual form (see Results). Activity coefficients for aromatic solutes in stationary phases containing TNB were determined by a semiempirical method described in the Discussion. Dotted line in Table II indicates this difference in the origin of reported values.

where

$$J_3^4 = \frac{3}{4} \frac{(p_i/p_o)^4 - 1}{(p_i/p_o)^3 - 1} \tag{17a}$$

$$\beta = \frac{2\,B_{BG} - v_B^{\infty}}{RT} \tag{17b}$$

and $p_i$ and $p_o$ are the inlet and outlet pressures of the carrier gas.

The molar volume of the solute at infinite dilution, $v_B^{\infty}$, was assimilated in our calculations to $v_B^0$, the molar volume in the pure state. $B_{BG}$ is the second virial (cross-term) coefficient for the interactions solute (B)-carrier gas (G), and was calculated from the corresponding states equation of *McGlashan* and *Potter* [11], using the critical constants compiled by *Kudchadker, Alani* and *Zwolinski* [12]; it was assumed that $n_G = 1$, and the actual number of car-

bon atoms in the molecule of the solute was taken as $n_B$. Under our experimental conditions, correction is almost constant and around 2 %.

Partition coefficients at zero pressure, $K_R$, were calculated from $K_R = V_N^0/V_L$, where $V_L$ is the volume of stationary phase contained in the column; their values have been collected in Table I.

Activity coefficients at zero pressure and infinite dilution, $\gamma_B^{\infty}$, of every solute in DNP, and of non-complexing solutes in each one of the stationary phases were calculated using the equation deduced by *Everett* [13]:

$$\ln \gamma^{\infty}_{B(A,S)} = \ln \frac{RT}{K_R\, v_{A,S}^0\, p_B^0} - \frac{(B_{BB} - v_B^0)}{RT} p_B^0 \tag{18}$$

where $v_{A,S}^0$ and $v_B^0$ keep the already assigned meaning, and $p_B^0$ is the vapour pressure of the pure solute at the experi-

mental temperature; properties of the pure solutes were taken from the compilation of *Dreisbach* [14]. $B_{BB}$ is the second virial coefficient for the pure solute vapour, and was calculated in a similar way as $B_{BG}$. Table II include $\gamma_B^\infty$ values thus determined. Activity coefficients of complexable solutes in columns containing complexing additive, are also given in this table; said coefficients were calculated by a semiempirical procedure described in the last section of this paper.

Table III collects the scarce data of activity coefficients in DNP at 60 °C which can be found in the literature; they have been taken from [10], and static data are therein attributed to *Ashworth* and *Everett* [15]. Unfortunately, other studies with this stationary phase reported in the literature were conducted at a single temperature, thus excluding the possibility of interpolating to 60 °C.

On the basis of the coincidence attained by *Ashworth* and *Everett* by static methods for activity coefficients of hydrocarbons in bulk DNP and in DNP spread on Celite, it was considered superfluous to check experimentally the non-adsorption on the gas-liquid or liquid-solid interphase.

Table III. Comparison of Corrected Activity Coefficients with Published Values in DNP at 60 °C

| Solute | This Paper | Reference [10] (GLC) | Reference [15] (static) |
|---|---|---|---|
| n-C$_6$ | 1.131 | 1.144 | 1.131 |
| ØH | 0.552 | 0.547 | 0.554 |

## Discussion

Figure 1 clearly shows an increase of the activity coefficients of non-complexing solutes with the concentration
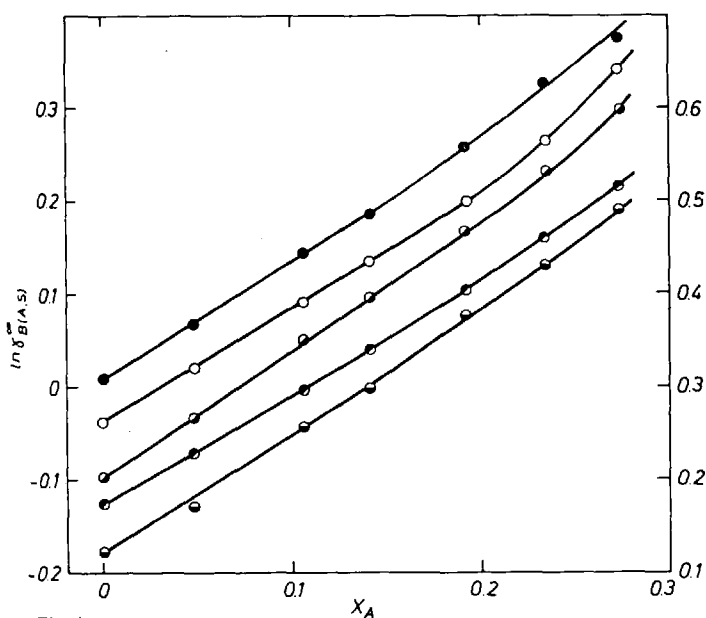


Fig. 1

● Natural logarithm of the infinitely dilute solute activity coeffient vs. additive mole fraction.

Right scale, alkanes (●, n-C$_6$; ◑, n-C$_7$; ●, 2,2,4-TMC$_5$)
Left scale, cycloalkanes (◉, cyclo-C$_6$; ○, Mcyclo-C$_6$).

of the additive. Such a behaviour might be interpreted through the equation:

$$\ln \frac{\gamma_{B(A,S)}^\infty}{\gamma_{B(S)}^\infty} = k_1 \, X_A + k_2 \, X_A^2 \tag{19}$$

which is a linear relationship assuming low values of $X_A$. The athermal contributions to the activity coefficients, $a\gamma_{B(A,S)}^\infty$, were calculated for these solutes making use of the simplified Flory-Huggins equation [4]:

$$a\gamma_{B(A,S)}^\infty = \frac{v_B^0}{v_{A,S}^0} \exp. \left(1 - \frac{v_B^0}{v_{A,S}^0}\right) \tag{20}$$

Subsequently, the thermal activity coefficients, $t\gamma_{B(A,S)}^\infty$, were calculated:

$$\gamma_{B(A,S)}^\infty = a\gamma_{B(A,S)}^\infty \, t\gamma_{B(A,S)}^\infty$$

Values of $t\gamma_{B(A,S)}^\infty$ are listed in Table IV; a logarithmic variation of these coefficients with the molar fraction of TNB can be observed. The variation is important enough as to undoubtedly prove the inapplicability of the approximation given in Eq. 9 to these systems.

We shall assume that the variation of the activity coefficient of uncomplexed aromatic solute with the additive concentration can be described by a relation similar to that found for alkanes and cycloalkanes. Then, by combining Eqs. 6 and 19 it is possible to define a parameter Z:

$$Z = \frac{K_R \, v_{A,S}^0}{K_R^0 \, v_S^0} = (1 + K^* \gamma_A^* \, X_A) \exp. (- k_1 \, X_A - k_2 \, X_A^2) \tag{21}$$

By expanding the exponential in a power series and multiplying as indicated, we obtain:

$$Z = 1 + [K^* \gamma_A^* - k_1] X_A + [\tfrac{1}{2} k_1^2 - k_2 - K^* \gamma_A^* k_1] X_A^2 +$$

$$+ [K^* \gamma_A^* (\tfrac{1}{2} k_1^2 - k_2) + k_1 k_2 - \tfrac{1}{6} k_1^3] X_A^3 + \ldots \ldots \tag{22}$$

In a first attempt to calculate $K^*$, $\gamma_A^*$ was assumed to remain constant, and the experimental values of Z were fitted using the method of least squares to equations of the form

$$Z = 1 + b_1 \, X_A + b_2 \, X_A^2 + b_3 \, X_A^3 \tag{23}$$

using a IBM 360/60 computer. Good fits were obtained, with correlation coefficients better than 0.998. Figure 2 illustrates graphically some representative cases of these equations, the points corresponding to experimental values. It is evident that the curves qualitatively fit with relations of the type described in Eq. 21.

In principle, the coefficients $b_i$ in Eq. 23 might be identified with the expression in brackets in Eq. 22, then state a system of equations and solve it for $K^* \gamma_A^*$, $k_1$, and $k_2$. Such attempts, however, gave incoherent results, including negative values of $K^* \gamma_A^*$ for a few solutes.

It was also tried to represent the ratio of activity coefficients which appears in Eq. 6 by a third degree polynomial, expand the product and assimilate the coefficients of $X_A$ thus obtained to those in the polynomial of Eq. 23 (and

**Table IV.** Thermal Activity Coefficients ($t\gamma^{\infty}_{B(A,S)}$) of Alkane and Cycloalkane Solutes at 60 °C

| Solute | $X_A$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.000 | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| cyclo-$C_6$ | 1.637 | 1.687 | 1.747 | 1.795 | 1.856 | 1.919 | 1.982 |
| Mcyclo-$C_6$ | 1.594 | 1.650 | 1.721 | 1.764 | 1.833 | 1.912 | 1.986 |
| n-$C_6$ | 1.825 | 1.893 | 1.984 | 2.024 | 2.139 | 2.204 | 2.295 |
| n-$C_7$ | 1.834 | 1.916 | 2.022 | 2.082 | 2.184 | 2.282 | 2.395 |
| 2,2,4-$TMC_5$ | 1.896 | 1.972 | 2.071 | 2.132 | 2.237 | 2.349 | 2.430 |
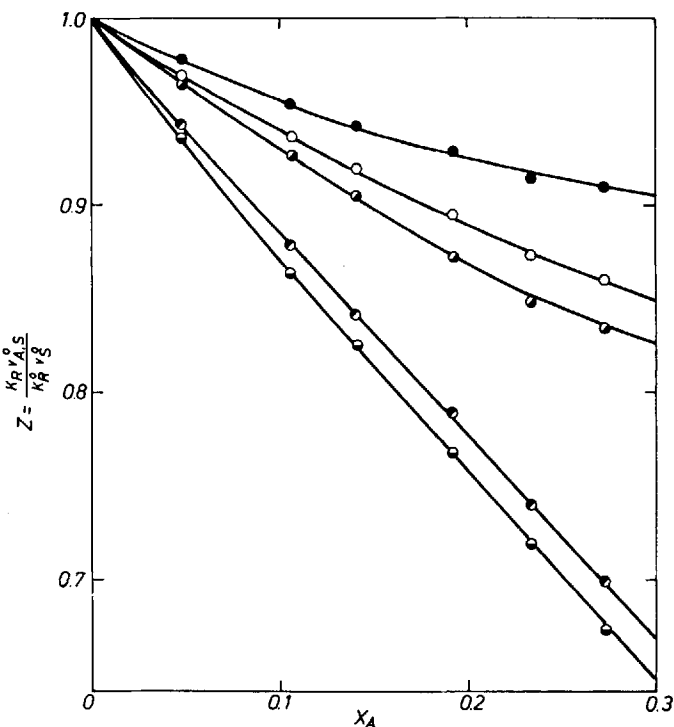


**Fig. 2**

● Z vs. $X_A$ for several representative solutes.
(●, p-X; ○, $\emptyset CH_3$; ◑, $\emptyset C_2 H_5$; ◉, Mcyclo-$C_6$; ◓, n-$C_7$)

even with one of fourth degree), but this approach also failed.

In our opinion, there are two different reasons for this results. One of them is the error inherent to coefficients $b_i$. Even though the number of experimental data for each solute is not scarce for this kind of studies, probably a much larger number might be required to assign physical meaning to the coefficients. Specially, $b_3$ may be appreciably modified without worsening the correlation too much. Nevertheless, it is necessary to resort at least to a third degree polynomial to represent data adequately; in addition, the resolution of the systems of equations needs three numerical coefficients once Eq. 19 is adopted as a relationship between the activity coefficients, and four numerical coefficients if a third degree polynomial is adopted.

The second reason is that the assumption that the activity coefficient of the additive remains constant and equal to unity, may be too far from reality; $\gamma^*_A$ can be very sensitive to concentration variations, particularly within the

rather broad range of molar fractions considered. Nevertheless, the activity coefficient of the additive will hopefully be a continuous function (even though unpredictable) of its molar fraction; in that case, its variation would add to that expressed in Eq. 22 and there would be no apparent reason why Z could not be adequately interpreted by a third degree polynomial.

When the additive concentration in the stationary phase approaches zero, a series of conditions are fulfilled which allow to estimate the value of $K^*$. These conditions are:

1) $\gamma^*_A \rightarrow 1$, from the definition of the reference state for activity coefficients $\gamma^*_i$.

2) according to Eqs. 22 and 23 and the previous condition,

$$\left[\frac{dZ}{dX_A}\right]_{X_A = 0} = K^* - k_1 = b_1 \qquad (24)$$

3) from Eq. 19 it follows that

$$\left[\frac{d\ln(\gamma^{\infty}_{B(A,S)}/\gamma^{\infty}_{B(S)})}{dX_A}\right]_{X_A = 0} = k_1 \qquad (25)$$

Finally, by combining Eqs. 24 and 25, it is possible to calculate $K^*$; this imposes the knowledge of the variation of the activity coefficients of uncomplexed aromatic solute with the concentration of the additive.

Trying to solve this problem a semiempirical approach was devised which shall be explained here. The treatment of regular solutions by *Hildebrand* and *Scatchard* [16], gives the following expression for the thermal contribution to the activity coefficient of the solute at infinite dilution:

$$\ln t\gamma^{\infty}_{B(A,S)} = \frac{v^0_B}{RT}(\delta_{A,S} - \delta_B)^2 \qquad (26)$$

where $\delta_i$ is the solubility parameter of component i. Solubility parameters of the solutes can be found in Tables V and VI, and have been calculated according to *Tewari, Martire* and *Sheridan* [17], using the values compiled by *Dreisbach* [14] for the physical properties of the pure solutes.

From the values in Table IV and using molar volumes and solubility parameters of alkanes and cycloalkanes, it is possible to calculate values for the solubility parameters of different mixtures of DNP and TNB used as stationary phases, by applying Eq. 26. On examining Table V, an appreciable dispersion becomes apparent in the values obtained for the solubility parameter of a given stationary phase when evaluated on the light of data pertaining to different solutes.

Table V. Calculated Solubility Parameters of the Stationary Phases, $\delta_{A,S}$, at 60 °C

| Solute | $v_B^0$ | $\delta_B$ | $X_A$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 0.000 | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| cyclo-$C_6$ | 113.7 | 7.833 | 9.527 | 9.578 | 9.635 | 9.678 | 9.730 | 9.781 | 9.829 |
| Mcyclo-$C_6$ | 133.4 | 7.493 | 9.014 | 9.070 | 9.134 | 9.171 | 9.227 | 9.286 | 9.338 |
| n-$C_6$ | 138.4 | 6.955 | 8.651 | 8.702 | 8.765 | 8.791 | 8.862 | 8.899 | 8.948 |
| n-$C_7$ | 154.6 | 7.075 | 8.687 | 8.743 | 8.811 | 8.847 | 8.904 | 8.955 | 9.013 |
| 2,2,4-$TMC_5$ | 173.4 | 6.551 | 8.113 | 8.162 | 8.218 | 8.251 | 8.304 | 8.356 | 8.392 |
| $\overline{(\delta_{AS}/\delta_S)}$ | | (a) | 1.000 | 1.006 | 1.013 | 1.017 | 1.024 | 1.029 | 1.035 |
| Coefficient of variation | | | – | 0.05 % | 0.10 % | 0.09 % | 0.12 % | 0.14 % | 0.18 % |

(a) Average value of the ratio $\delta_{AS}/\delta_S$ for the five solutes in a given stationary phase.

Molar volumes, $v_B^0$, as $cm^3/mole$

Solubility parameters, $\delta$, as $\sqrt{(cal/cm^3)}$


Table VI. Calculated Activity Coefficients of Alkanes and Cycloalkanes at 60 °C

| Solute | $X_A$ | | | | | |
|---|---|---|---|---|---|---|
| | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| cyclo-$C_6$ | 0.935 | 1.005 | 1.049 | 1.125 | 1.195 | 1.267 |
| Mcyclo-$C_6$ | 1.020 | 1.094 | 1.140 | 1.220 | 1.294 | 1.370 |
| n-$C_6$ | 1.185 | 1.294 | 1.352 | 1.451 | 1.544 | 1.638 |
| n-$C_7$ | 1.302 | 1.404 | 1.469 | 1.579 | 1.682 | 1.788 |
| 2,2,4-$TMC_5$ | 1.449 | 1.557 | 1.627 | 1.746 | 1.858 | 1.972 |


Table VII. Calculated Thermal Activity Coefficients, $t\gamma_{B(A,S)}^\infty$, of Alkylbenzenes at 60 °C

| Solute | $v_B^0$ | $\delta_B$ | Pure DNP | | $X_A$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $t\gamma_{B(S)}^\infty$ | $\delta_S$ | 0.048 | 0.106 | 0.141 | 0.192 | 0.234 | 0.273 |
| $\emptyset H$ | 93.5 | 8.737 | 1.193 | 9.854 | 1.216 | 1.245 | 1.263 | 1.294 | 1.322 | 1.352 |
| $\emptyset CH_3$ | 111.2 | 8.525 | 1.112 | 9.320 | 1.130 | 1.151 | 1.165 | 1.189 | 1.211 | 1.234 |
| $\emptyset C_2H_5$ | 127.8 | 8.405 | 1.117 | 9.162 | 1.136 | 1.160 | 1.175 | 1.201 | 1.225 | 1.250 |
| $\emptyset iC_3H_7$ | 145.0 | 8.172 | 1.122 | 8.896 | 1.142 | 1.167 | 1.183 | 1.211 | 1.237 | 1.264 |
| o-X | 125.5 | 8.625 | 1.079 | 9.257 | 1.094 | 1.113 | 1.125 | 1.147 | 1.167 | 1.188 |
| m-X | 127.9 | 8.458 | 1.091 | 9.128 | 1.107 | 1.128 | 1.141 | 1.164 | 1.185 | 1.208 |
| p-X | 128.5 | 8.405 | 1.084 | 9.050 | 1.100 | 1.120 | 1.132 | 1.154 | 1.174 | 1.196 |

Molar volumes, $v_B^0$, as $cm^3/mole$

Solubility parameters, $\delta$,

as $\sqrt{(cal/cm^3)}$

This result is not surprising on account of previous findings. *Cadogan* and *Purnell* [5], through an analysis similar to the one described in the preceding paragraph, obtained for squalane in its mixtures with aromatics, values of $\delta_S$ between 9.44 and 10.32 with a mean of 9.65 ± 0.2. These values are between 1 and 2 units higher than the expected value, 8.1, on the basis of information dealing with other paraffins. Unfortunately, values or data of DNP are not known as to make possible the certain and independent calculation of its solubility parameter. *Frostling* [18] has compiled evaporation enthalpies for a series of phthalic acid esters; there is a wide variation among values attributed by different authors to the same ester, but in a first ap-

proach an evaporation enthalpy between 22 and 26 kcal/mole could be attributed to DNP, this corresponding to a solubility parameter between 7.0 and 7.7 at 60 °C. As it can be seen, our values are also between 1 and 2 units higher, their means being 8.80 ± 0.46 against saturated hydrocarbons, and 9.24 ± 0.25 against aromatics, at a 95 % confidence level.

Another divergence from regular solutions theory lies in obtaining different values of $\delta$ for a given stationary phase, when it is calculated from data corresponding to different solutes. *Martire* [19] found a very satisfactory agreement between experimental data and calculated results when instead of using the molar volume of the solute, $v_B^0$, he

used a volume $v_B^*$ obtained by adjustment of data. Even more, $v_B^*$ showed to be a constant fraction $\epsilon$ of $v_B^0$ when the solute was studied in a series of nonpolar or slightly polar stationary phases; attempts to assign to $\epsilon$ a theoretical meaning were unsuccessful. In case such a correction for the molar volumes of the solutes were necessary in our systems, and assuming with Martire constant values of $v_B^*$ in different stationary phases, the quotients $\delta_{A,S}/\delta_S$ for these should be independent of the solute for which they are calculated. The one-before-last line in Table V gives the average value of $\delta_{A,S}/\delta_S$ for each column and in the last line, respective variation coefficients appear.

With the average values $(\overline{\delta_{A,S}/\delta_S})$ corresponding to each stationary phase, and with the value of the solubility parameter obtained for pure DNP as referred to each solute, it is possible to calculate a "practical" value or $\delta_{A,S}$ for each solute-stationary phase pair. Then, by using Eq. 26 thermal activity coefficients can be recalculated for each of the alkanes and cycloalkanes in every stationary phase. After carrying out such a calculation, it is found that the process results in activity coefficients practically identical with the original ones (see Table VI).

Assuming that all the interactions derived from the aromaticity of aromatic solutes are contained in the complexation term, the interactions of uncomplexed aromatic solute with the stationary phase must be described in the same terms as for alkanes and cycloalkanes. Then, the thermal activity coefficients for uncomplexed solutes might be calculated as indicated in the preceding paragraph. Table VII gives the results of this calculation, together with the solubility parameters and the molar volumes used in each case. By combining these results with the athermal contributions (as calculated by Eq. 29), it is possible to obtain the activity coefficient of the uncomplexed aromatic solute in each of the stationary phases. Values thus originated have been collected in Table II, together with the experimental activity coefficients of the saturated hydrocarbons. Plots of $\ln \gamma_{B(A,S)}^{\infty}$ vs $X_A$ for aromatics are entirely similar to those in Figure 1, and, consequently, have not been reproduced.

Table VIII compiles values of $k_1$ and $b_1$ and those of $K^*$ deduced with them for each aromatic hydrocarbon. Substitution of hydrogen by a methyl group would induce an increase in the complex stability, but the substitution by longer chains would derive in a stability value lower than for benzene. This trend does not agree with expectation on the basis of respective ionization potential values; similar behaviours are shown by many systems for two reasons.

First, in the basic state, the "dative" structure corresponds to a fraction (at times small) of the total binding energy; orientation, induction and London forces may be responsible for a high percentage of the total binding energy. From this standpoint, the ease with which a donor may release an electron (as it is measured by the ionization potentials) may happen to be of secondary importance for the complex stability.

Second, even though a higher electronic density might be expected at the nucleus as a consequence of longer sub-

Table VIII. Summary of Results

| Solute | $-b_1$ [a] | $k_1$ [b] | $K^*$ |
|---|---|---|---|
| $\emptyset H$ | 0.772 | 0.971 | 0.199 |
| $\emptyset CH_3$ | 0.660 | 0.870 | 0.210 |
| $\emptyset C_2H_5$ | 0.677 | 0.865 | 0.188 |
| $\emptyset iC_3H_7$ | 0.695 | 0.854 | 0.159 |
| o-X | 0.420 | 0.811 | 0.391 |
| m-X | 0.428 | 0.825 | 0.397 |
| p-X | 0.468 | 0.813 | 0.345 |

(a) Coefficient of the first degree term in Eq. 23; see also Eq. 24

(b) Limiting value of the slope of the graph of $\ln \gamma_{B(A,S)}^{\infty}$ vs. $X_A$, when $X_A \to 0$ (see Eq. 25)

stituent chains, its volume can create considerable steric hindrance. When dealing with systems as ours, this might be consistent with a complex configuration where both the donor and acceptor molecules try to accomodate with their planes parallel to each other.

Within the xylenes, the ortho- and meta- isomers give almost identical values of $K^*$, while the para- isomer exhibits a lower value. This behaviour, already detected by *Foster* et al. [20a], is again opposed to the trend in the ionization potentials (8.58 eV for the ortho- and meta- isomers, against 8.48 eV for the para- isomer).

In spite of abundant references on the stability of charge-transfer complexes, there are usually large discrepancies among different authors. These discrepancies are even more important for visible and UV spectroscopic studies, where equilibrium constants may become very sensitive to changes in the wavelength used [21]. Present status seems to attribute to NMR measurements the most reliable data
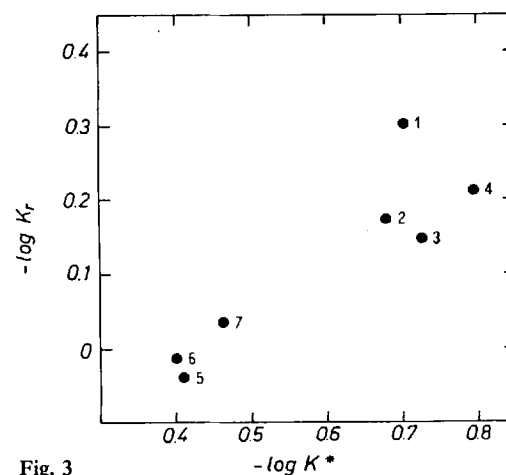


Fig. 3     $-\log K^*$

● Log $K^*$ (this paper) vs. log $K_r$ (ref. [20a]). In the reference, the stability constants are expressed in terms of kg solution per mole ($K_r$)
(1) $\emptyset H$; (2) $\emptyset CH_3$; (3) $\emptyset C_2H_5$; (4) $\emptyset iC_3H_7$; (5) o-X; (6) m-X; (7) p-X.

Originals

among spectroscopic techniques [20b]. On this basis, we have compared our results with those obtained by *Foster* et al. [20a], using NMR spectroscopy on solutions in carbon tetrachloride at 33.5 °C. Figure 3 shows an acceptable correlation between both series of data, even more taking into account the great experimental differences, both with regard to solvent and to working temperature. The largest discrepancy corresponds to benzene, this perhaps been related to its high vapour pressure at 60 °C.

Both merits and disadvantages of gas chromatography for studying chemical equilibria have been discussed many times. As a primary conclusion of this paper it might be confirmed that very cautious judgement should precede any attemp to apply any scheme to a given system, or any approach developed for another system. In principle, plots of Z vs. $X_A$ may be very helpful in this sense to detect and ascertain the kind of behaviour in which a concrete system fits. Further, the precaution of injecting not only one but several non-complexing solutes as close and similar as possible to the complexing solutes, should be never overlooked or omitted.

### List of Symbols

| | |
|---|---|
| A | complexing agent, additive |
| B | volatile solute |
| AB | 1:1 charge transfer complex between A and B |
| $B_{BB}$ | second virial coefficient for the pure solute vapour |
| $B_{BG}$ | second virial coefficient for the solute — carrier gas interactions |
| $b_1, b_2, b_3$ | the three coefficients for the representation of Z by a third degree polynomial |
| $d_{A,S}$ | density of the mixture of A and S |
| DNP | dinonyl phthalate |
| $f_B^0$ | fugicity of pure B vapour in equilibrium with pure B liquid |
| $F_a$ | carrier gas flow rate measured at ambient temperature and outlet pressure |
| G | carrier gas |
| j | compressibility correction factor |

$$j = \frac{3}{2} \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}$$

| | |
|---|---|
| $J_3^4$ | defined in Eq. 17a |
| K | thermodynamic equilibrium constant for the association between A and B to give a complex AB, using the pure substances as reference state for the chemical potentials |
| $K^*$ | thermodynamic equilibrium constant for the association between A and B to give a complex AB, using the infinitely diluted solution of each chemical species in solvent S as the reference state for the chemical potentials |

| | |
|---|---|
| $K_R$ | partition coefficient of the solute, i.e. the ratio of its total concentration (under either complexed or uncomplexed forms) in the liquid phase to the concentration in the gas phase |
| $K_R^0$ | partition coefficient of the solute between the pure inert solvent S and the gas phase |
| $k_1$ | limiting value of the slope of the graph of ln $\tilde{\gamma}_{B(A,S)}$ vs. $X_A$ when the latter approaches zero |
| $K_r$ | stability constant, kg of solution per mole |
| $M_i$ | molecular weight of the species i |
| $n_B$ | effective number of carbon atoms in the molecule of solute (considered equal to the actual number of carbon atoms) |
| $n_G$ | effective number of atoms in the molecule of carrier gas (taken as one) |
| $p_i$ | inlet pressure |
| $p_o$ | outlet pressure |
| $p_w$ | partial pressure of water at ambient temperature |
| S | solvent |
| s | standard error |
| $T_a$ | ambient temperature (°K) |
| $T_c$ | column temperature (°K) |
| TNB | 1,3,5-trinitrobenzene |
| $V_L$ | total volume of the stationary phase contained in the column |
| $V_N$ | net retention volume defined in Eq. 16a |
| $V_N^0$ | the value of $V_N$ corresponding to the condition $p_i = p_o = 0$ |
| $v_i^0$ | molar volume of the species i |
| $v_B^\infty$ | partial molar volume of the solute at infinite dilution |
| $X_i$ | molar fraction of the species i |
| Z | defined in Eq. 21 |
| $\beta$ | defined in Eq. 17b |
| $\delta_i$ | solubility parameter of the species i |
| $\gamma_{i(j)}$ | activity coefficient of the species i in the solvent j; reference state: pure i |
| $a\gamma_{i(j)}$, $t\gamma_{i(j)}^0$ | athermal and thermal contributions to the activity coefficient of the species i at infinite dilution in the solvent j |
| $\gamma_{i(j)}^*$ | activity coefficient of the species i in the solvent j; reference state: infinitely diluted solution of i in j |

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