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STUDY OF CHARGE TRANSFER COMPLEXATION BY GAS–LIQUID CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

Gas–liquid chromatography (GLC) has been used for many years for the investigation of physico-chemical phenomena. In several cases, such studies have resulted in important advances in our understanding of solution phenomena. One such instance of current wide-spread interest to chemists of many disciplines is the GLC investigation of charge transfer complexation.

In a brief note, Benesi and Hildebrand[1] announced the presence of a newly discovered UV absorption band for a solution of iodine and benzene in 1948. There was evidence of a 1:1 complex between the two components, since the height of the band varied directly with the concentration of either component. One explanation of the phenomenon was to consider benzene as a Lewis base (electron donor), and iodine as a Lewis acid (electron acceptor); the resultant (charge transfer) complex can then be considered a Lewis acid–base adduct, even though only one electron (not an electron pair) is involved.

Since that time, hundreds of papers, many reviews, and at least five books[2–6]

have appeared which discuss charge transfer, and it is not surprising that gas chromatographers have also taken an interest in the subject. As early as 1958, Norman[7] reported the use of 2,4,7-trinitro-9-fluorenone (TNF) as a stationary phase for the separation of the three nitrotoluene isomers. Langer *et al.*[8] investigated di-*n*-alkyl tetrahalophthalates as selective phases for the separation of aromatic hydrocarbons in 1960; baseline resolution of *m*- and *p*-xylene was achieved with di-*n*-propyl tetrachlorophthalate in 90 min at 90°. Cooper and co-workers[9,10] later employed TNF for aromatic hydrocarbons and amines. Several workers have used inorganic salts as complexing agents, including Gil-Av and co-workers[11–15], van de Craats[16], Tenney[17], Bednas and Russell[18], Phillips[19], Muhs and Weiss[20], Banthorpe *et al.*[21], and Gump[22]. Kotsev and Shopov[23] have even studied olefin–liquid crystal complexation by GLC, where *p,p'*-azoxyphenetole in squalane was used as the stationary phase.

Since so many workers have investigated charge transfer complexation, it is somewhat surprising that there remains any disagreement about the nature of the interactions. Yet the authors[24–26] and others[27,28] currently claim that even today, 26 years after Benesi and Hildebrand's initial spectroscopic study of charge transfer behavior, this type of solution phenomenon is still not understood. Therefore, before we can review the study of complexation by GLC, we must first critically examine the nature of these interactions insofar as is possible, bearing in mind that currently accepted views may be substantially incorrect.

2. CHARGE TRANSFER COMPLEXATION: GENERAL CONCEPTS

Mulliken and Person[5] have presented the most recent summary of charge transfer considerations from a molecular orbital approach. If one molecule, D, donates an electron to a second molecule, A, the wave function of the complex, C, can be described as

$$\psi_N(C) = a\psi_0(D,A) + b\psi_1(D^+-A^-) \tag{1}$$

where ψ_N is the total electronic ground-state wave function, ψ_0 is the (no-bond) wave function which describes all the intermolecular interactions except complexation, and ψ_1 is the (dative) wave function of complexation (as if complexation were the only force binding D and A together); a and b are weighting constants. The dative function, ψ_1, is written as a function of D^+ and A^- to indicate that transfer of charge from D to A causes appreciable ionization. If complete ionization does not occur (*i.e.*, if the complex is weakly held together), we represent eqn. 1 by:

$$\psi_N(C) = a\psi_0(D,A) + b\psi_1(D-A) \tag{2}$$

Eqn. 2 will be used here, since only weak complexation will be considered.

As in any electronic description of molecular interactions, we can write the wave function of an excited state

$$\psi_V(C) = -b^*\psi_0(D,A) + a^*\psi_1(D^+-A^-) \tag{3}$$

where $\psi_V(C)$ is the excited-state electronic wave function, and $a^* \approx a \approx 1$ and $b^* \approx b \approx 0$. That is, when we promote (excite) an electron from D to A (by UV radiation for example) we cause appreciable ionization (charge transfer), and (D^+-A^-) is a more appropriate description of the complex than (D–A) or (D,A).

The energy of charge transfer, ΔE_{ct}, is just the difference between the energy levels of the electronic states

$$\Delta E_{ct} = E_V - E_N \tag{4}$$

and is readily found from the wavelength at which a complex absorbs light quanta

$$\Delta E_{ct} = h\nu_{ct} = \frac{hc}{\lambda_{ct}} \tag{5}$$

where ν_{ct} and λ_{ct} are the frequency and wavelength of charge transfer absorption, respectively. Note that ΔE_{ct} is not the energy initially required to form the complex, ΔE_f.

Rose[4] has reviewed the experimental observations of charge transfer phenomena: (1) The relation between charge transfer absorption frequencies and donor ionization potentials is generally (but not always) linear[29–31]. (2) The relation between charge transfer absorption frequencies and acceptor electron affinities is generally (but not always) linear[32]. (3) Donor ionization potentials and charge transfer equilibrium formation constants can sometimes be correlated[32–36]. (4) In weak complexes, dipole–induced dipole interactions account for most of the bonding (*i.e.*, $a \approx 1$, $b \approx 0$); for aromatic donor–acceptor systems, the dipole–induced dipole interactions are mainly electrostatic[37]. (5) There is generally no correlation between donor or acceptor dipole moments and charge transfer interactions[30]; there is a linear relation, however, between the dipole moment of the complex and the energy of charge transfer, and between the complex dipole moment and the donor ionization potential[37].

Several of these observations seem to be contradictory (for example, Nos. 4 and 5). To rationalize the apparent discrepancies, Mulliken and Person[5] have proposed the classification of donors and acceptors given in Table 1. Silver ion–olefin complexes are thus ν–$b\pi$ interactions, aromatic–aromatic complexes are $a\pi$–$b\pi$, and hydrogen bonding is classified as $a\sigma$–n. In the latter case, and in ν–n types (*e.g.*, $H_3N:BCl_3$), an electron pair may be involved, rather than just one electron. This breakdown of types helps to explain most of the above-noted experimental observations, since electrons are being removed from, and transferred into widely different

TABLE I

CLASSIFICATION OF DONORS AND ACCEPTORS[5]

Donors			*Acceptors*		
Electron taken from	*Type*	*Example*	*Electron goes to*	*Type*	*Example*
Non-bonding lone pair	n	$:NR_3$, RO:	Vacant orbital	ν	BCl_3, Ag^+
Bonding π orbital	$b\pi$	benzene, olefins	Anti-bonding σ orbital	$a\sigma$	I_2, R–H
			Anti-bonding π orbital	$a\pi$	TNF, fluoranil

types of molecular orbitals. However, some of the anomalies in the absorption spectra remain; for example, some types of complexes give two prominent charge transfer bands, while others give only one. To help explain these and other phenomena, Mulliken[5] proposed that there were fundamental (and usually sharply divided) degrees of charge transfer, which he called inner (strong, ionic), middle (transition), outer (weak, dative), and contact (random) complexes.

Inner (strong) complexes consist of two components which are largely ionized (D^+–A^-), whose spectra show bands for both the donor and acceptor ions (thus two bands per complex), and which may exhibit photoconduction, semiconduction, and paramagnetic properties (*e.g.*, tetramethyl-*p*-phenylenediamine–chloranil). Outer complexes are loosely held together by much weaker (dative) interactions, show the above properties of inner complexes to a much lesser extent (if at all), give only one prominent complex absorption band, and involve minimal transfer of charge in the electronic ground-state. Middle complexes lie between outer and inner complexes in the degree of charge transfer and are not generally distinguishable, since they are transitional electronic and geometrical configurations. Inner and outer complexes are strongly influenced by solvents; for example, tetramethyl-*p*-phenylenediamine–chloranil is an outer complex in cyclohexane, but forms inner complexes in more polar solvents[38], presumably because of ion stabilization by solvation. Finally, contact charge transfer results from random molecular collisions when both donor and acceptor species are present together in appreciable quantities; these interactions explain, for example, the "charge transfer" absorption bands of iodine–heptane and other pairs, which would not be expected to form complexes under normal conditions.

Thus, we can explain the above-noted experimental phenomena in terms of the type and relative strength of charge transfer interactions. For example, the donor and acceptor dipole moments are not related to the energy of charge transfer (*i.e.*, the frequency or wavelength at which the complex absorbs), because ΔE_{ct} depends only on the energy difference between the donor highest occupied molecular orbital and the acceptor lowest unoccupied molecular orbital, not on electrostatic attractive forces. Conversely, the dipole moment of the complex can be related to ΔE_{ct}, since it arises from an already partially transferred electron, and ΔE_{ct} is just the amount of energy needed to complete the process. We therefore find that the larger the complex dipole moment, the lower the energy of charge transfer[37].

The above classifications have not been accepted without criticism. Dewar and Thompson[39] found no correlation between tetracyanoethylene (TCNE)–aromatic hydrocarbon interaction strengths and absorption wavelengths, except that "... the points (with one doubtful exception) all lie in the same quadrant". Hassel and Rømming[40] proved via X-ray crystallography that the I–I axis lies perpendicular to the plane of the benzene ring in benzene–iodine complexes and not parallel to it, as Mulliken's treatment had earlier led him to postulate[33]. Nevertheless, the classification of donors and acceptors on the basis of molecular orbitals explains, for example, why Ag^+ forms complexes while alkali and alkaline earth ions do not. Including hydrogen bonding as merely a specific ($a\sigma$–n) type of charge transfer also allows us to explain the tendency of some donors and acceptors to form weak hydrogen bonds, while others [*e.g.*, pyridine–methyl iodide and $ROH{:}N(C_2H_5)_3$] form very strong ionic bonds[41,42]. The former are of course outer complexes, while the latter are inner complexes. Our rationale, then, for retaining the Mulliken theory of charge transfer is that

it fits most experimental observations, and those that it does not may be explained by our incomplete understanding of solution interactions.

3. SPECTROSCOPIC STUDIES

A. Ionization potentials, electron affinities, and formation constants

We now write the reaction between donor, D, and acceptor, A, to form complex, C, in the generalized form

$$D + A \rightleftharpoons C \tag{6}$$

for which the concentration equilibrium (formation) constant, K_f^c, is given by

$$K_f^c = \frac{[C]}{[D]\,[A]} = K_{eq.}\,\frac{\gamma_D^c \gamma_A^c}{\gamma_C^c} \tag{7}$$

where $K_{eq.}$ is the true thermodynamic equilibrium constant (defined in terms of activities, a_i), and γ_i^c is the concentration activity coefficient of the ith species. As noted earlier, the formation constant should depend at least in part on the ionization potential of the donor, and the electron affinity of the acceptor. [In the case of charge transfer, vertical[43–45] values should be used, since the electronic transitions occur approximately two orders of magnitude faster than nuclear transitions (the Franck–Condon principle). Vertical ionization potentials, I_v^a, and vertical electron affinities, E_v^a, are therefore employed throughout in this discussion; UV–photoelectron spectroscopy (PES) is now used to measure the former[46], while the latter can be inferred from charge transfer data[47].] However, attempts at correlating K_f^c, I_v^a, and E_v^a have generally proved fruitless. Bier[30] found no correlation between log K_f^x (the mole fraction formation constant) and ΔE_{ct} for *sym.*-trinitrobenzene (TNB)–aromatic hydrocarbons. Dewar and Thompson[39] found an approximately linear relation for log $[K_f^c/K_f^c$ (benzene)] *vs.* $[\lambda_{ct}-\lambda_{ct}$ (benzene)] for TCNE–methylbenzene complexes, but no such correlation was found when polycyclic aromatic hydrocarbon donors were used. Emslie *et al.*[48] found curved lines when log K_f^c was plotted *vs.* I_v^a for 26 alkylbenzene donors, and TNB and fluoranil acceptors. Several workers[32,49–57] have plotted the energy or frequency of charge transfer *vs.* the donor ionization potential with varying degrees of success. Plots of the charge transfer frequency[58] or the donor ionization potential[59] *vs.* the Gibbs free energy of formation, ΔG_f^0, however, have been shown to be linear for a variety of aromatic hydrocarbons. Some success has also been achieved with K_f^c (various acceptors) *vs.* K_f^c (TNB) plots[58,59].

In general, it can be said that ΔE_{ct}–K_f–I_v^a–E_v^a relations are tenuous at best, especially when K_f is determined via UV/visible or NMR spectroscopy. Some of the difficulties can undoubtedly be attributed to solvent effects, which are strong enough in some cases to stabilize outer → inner complexation transitions, as we noted earlier. We therefore now examine the solvent dependence of charge transfer behavior via the formation constant, K_f ,at the same time briefly presenting the spectroscopic techniques which have been (and are still being) employed to measure these values.

B. Solvent dependence of spectroscopic K_f values

All of the books[2-6] which have been written about charge transfer cite or fully develop the spectroscopic methods of measuring K_f values. Rose[4], in fact, lists more than twenty different methods which have been used. By far the most important are the UV/visible and NMR techniques, which are briefly summarized below.

(a) Benesi–Hildebrand[60] equation (UV/visible)

$$\frac{[A]_t b}{A_{ct}} = \frac{1}{\varepsilon_{ct} K_f^c [D]_t} + \frac{1}{\varepsilon_{ct}} \tag{8}$$

where b is the cell pathlength, $[A]_t$ and $[D]_t$ are the total amounts of acceptor and donor initially added to the solution, and A_{ct} and ε_{ct} are the complex absorbance and absorptivity, respectively. ($[D]_t$ is usually maintained in large excess over $[A]_t$ so that the approximation $[D]_t \approx [D]_{eq.}$ can be made). Eqn. 8 is in the form of $Y = mX + b$, so that when the left-hand side is plotted *vs.* $1/[D]_t$ ($[D]_t$ is varied while $[A]_t$ is held constant), a straight line of slope, $1/\varepsilon_{ct} K_f^c$, and intercept, $1/\varepsilon_{ct}$, is obtained.

(b) Scott[61] equation (UV/visible)

$$\frac{[A]_t [D]_t b}{A_{ct}} = \frac{1}{\varepsilon_{ct} K_f^c} + \frac{[D]_t}{\varepsilon_{ct}} \tag{9}$$

Eqn. 9 is obtained from eqn. 8 simply by multiplying the latter by $[D]_t$; it is an important modification, however, since the left-hand side is now plotted *vs.* $[D]_t$, and extrapolation is made to $[D]_t = 0$, not to $[D]_t = \infty$ ($1/[D]_t = 0$). The points at greater dilution are thus given more weight, where, presumably, Beer's law is more closely obeyed.

(c) Foster[62] equation (NMR)

$$\frac{1}{\Delta} = \frac{1}{\Delta_0 K_f^c [D]_t} + \frac{1}{\Delta_0} \tag{10}$$

$$\frac{\Delta}{[D]_t} = -K_f^c \Delta + K_f^c \Delta_0 \tag{11}$$

where Δ_0 is the difference between the chemical shift of pure acceptor and completely complexed acceptor ($\delta_A - \delta_C$), and Δ is the difference between the chemical shift of pure acceptor and acceptor at some value of $[D]_t$ ($\delta_{obs} - \delta_A$; $\delta_A > \delta_{obs} > \delta_C$). Eqns. 10 and 11 are the NMR analogues of eqns. 8 and 9; in the former, the left-hand side is plotted *vs.* $1/[D]_t$, and in the latter, *vs.* Δ.

The solvent dependence of formation constants determined by the above techniques is demonstrated in Table 2. There is an order of magnitude difference for many of the K_f values even with closely related solvents. The table also demonstrates that there is no correlation between UV/visible and NMR, regardless of the solvent used. Nor does it help to argue that mole fraction (K_f^x) or volume fraction (K_f^v) formation constants should be used[65,66] as Purnell and Srivastava have demonstrated[27]:

TABLE 2

SOLVENT DEPENDENCE OF SPECTROSCOPIC FORMATION CONSTANTS

Donor	*Acceptor*	*Solvent*	*Temperature (°C)*	K_f	*Method*	*Reference*
Benzene	Iodine	CCl_4	22	1.72 l/mole	UV	60
		C_7H_{16}	22	1.15 l/mole	UV	60
Mesitylene	Iodine	CCl_4	22	7.2 l/mole	UV	60
		C_7H_{16}	22	5.3 l/mole	UV	60
N,N-Dimethylaniline	TNB	CCl_4	33.5	3.26 kg/mole	NMR	63
			33.5	2.04 l/mole	NMR	63
		$CHCl_3$	33.5	0.726 kg/mole	NMR	63
			33.5	0.455 l/mole	NMR	63
		CH_2Cl_2	33.5	0.399 kg/mole	NMR	63
			33.5	0.250 l/mole	NMR	63
Hexamethylbenzene	TNB	CCl_4	33.5	5.11 kg/mole	NMR	58
		CH_2ClCH_2Cl	33.5	0.59 kg/mole	NMR	58
Hexamethylbenzene	2,5-Dichloro-*p*-benzoquinone	CCl_4	33.5	1.92 kg/mole	NMR	58
		CH_2ClCH_2Cl	33.5	0.62 kg/mole	NMR	58
Hexamethylbenzene	1,4-Dinitrobenzene	CCl_4	33.5	1.01 kg/mole	NMR	58
		CH_2ClCH_2Cl	33.5	0.15 kg/mole	NMR	58
Hexamethylbenzene	Benzoquinone	CCl_4	33.5	0.66 kg/mole	NMR	58
		CH_2ClCH_2Cl	33.5	0.15 kg/mole	NMR	58
Phenanthrene	Pyromellitic dianhydride	$CHCl_3$	25.0	7.0 l/mole	UV	64
		CH_2Cl_2	25.0	2.6 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	0.5 l/mole	UV	64
Durene	Pyromellitic dianhydride	CH_2Cl_2	25.0	1.3 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	0.9 l/mole	UV	64
Naphthalene	Pyromellitic dianhydride	$CHCl_3$	25.0	2.8 l/mole	UV	64
		CH_2Cl_2	25.0	1.3 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	0.7 l/mole	UV	64
Triphenylene	Pyromellitic dianhydride	$CHCl_3$	25.0	16.4 l/mole	UV	64
		CH_2Cl_2	25.0	4.4 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	1.3 l/mole	UV	64
		C_6H_6	25.0	8.7 l/mole	UV	64
Fluoranthene	Pyromellitic dianhydride	$CHCl_3$	25.0	23.8 l/mole	UV	64
		CH_2Cl_2	25.0	7.9 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	1.5 l/mole	UV	64
		C_6H_6	25.0	9.8 l/mole	UV	64
Fluorene	Pyromellitic dianhydride	$CHCl_3$	25.0	2.3 l/mole	UV	64
		CH_2Cl_2	25.0	1.4 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	0.2 l/mole	UV	64

(Continued on p. 54)

TABLE 2 *(continued)*

Donor	*Acceptor*	*Solvent*	*Temperature (°C)*	K_f	*Method*	*Reference*
Hexamethylbenzene	Pyromellitic dianhydride	$CHCl_3$	25.0	2.2 l/mole	UV	64
		CH_2Cl_2	25.0	1.6 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	1.3 l/mole	UV	64
Chrysene	Pyromellitic dianhydride	$CHCl_3$	25.0	23.3 l/mole	UV	64
		CH_2Cl_2	25.0	14.1 l/mole	UV	64
Benzo[*a*]anthracene	Pyromellitic dianhydride	$CHCl_3$	25.0	10.7 l/mole	UV	64
		CH_2Cl_2	25.0	6.2 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	0.6 l/mole	UV	64
Pyrene	Pyromellitic dianhydride	$CHCl_3$	25.0	18.3 l/mole	UV	64
		CH_2Cl_2	25.0	9.0 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	2.4 l/mole	UV	64
		C_6H_6	25.0	10.6 l/mole	UV	64
Anthracene	Pyromellitic dianhydride	$CHCl_3$	25.0	5.5 l/mole	UV	64
		CH_2Cl_2	25.0	3.7 l/mole	UV	64
		$(CH_3CO)_2O$	25.0	1.1 l/mole	UV	64
		C_6H_6	25.0	3.9 l/mole	UV	64
Perylene	Pyromellitic dianhydride	$CHCl_3$	25.0	57.8 l/mole	UV	64
		CH_2Cl_2	25.0	19.4 l/mole	UV	64
		C_6H_6	25.0	39.0 l/mole	UV	64
		CCl_4	33.5	15.4 kg/mole	NMR	59
Hexamethylbenzene	Fluoranil	$CHCl_3$	33.5	3.9 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	3.6 kg/mole	NMR	59
		CH_2Cl_2	33.5	3.2 kg/mole	NMR	59
Pentamethylbenzene	Fluoranil	CCl_4	33.5	7.9 kg/mole	NMR	59
		$CHCl_3$	33.5	2.0 kg/ml	NMR	59
		CH_2ClCH_2Cl	33.5	1.6 kg/mole	NMR	59
		CH_2Cl_2	33.5	1.8 kg/mole	NMR	59
Durene	Fluoranil	CCl_4	33.5	4.9 kg/mole	NMR	59
		$CHCl_3$	33.5	1.3 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.84 kg/mole	NMR	59
		CH_2Cl_2	33.5	0.85 kg/mole	NMR	59
Mesitylene	Fluoranil	CCl_4	33.5	2.2 kg/mole	NMR	59
		$CHCl_3$	33.5	0.68 kg/mole	NMR	59
p-Xylene	Fluoranil	CCl_4	33.5	1.5 kg/mole	NMR	59
		$CHCl_3$	33.5	0.42 kg/mole	NMR	59
Toluene	Fluoranil	CCl_4	33.5	0.96 kg/mole	NMR	59
		$CHCl_3$	33.5	0.25 kg/mole	NMR	59
Benzene	Fluoranil	CCl_4	33.5	0.70 kg/mole	NMR	59
		$CHCl_3$	33.5	0.16 kg/mole	NMR	59
Hexamethylbenzene	1,4-Dicyano-2,3,5,6-tetrafluorobenzene	CCl_4	33.5	5.2 kg/mole	NMR	59
		$CHCl_3$	33.5	0.92 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.72 kg/mole	NMR	59
		CH_2Cl_2	33.5	0.71 kg/mole	NMR	59

TABLE 2 *(continued)*

Donor	*Acceptor*	*Solvent*	*Temperature (°C)*	K_f	*Method*	*Reference*
Pentamethylbenzene	1,4-Dicyano-2,3,5,6-tetrafluorobenzene	CCl_4	33.5	3.4 kg/mole	NMR	59
		$CHCl_3$	33.5	0.64 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.44 kg/mole	NMR	59
		CH_2Cl_2	33.5	0.48 kg/mole	NMR	59
Durene	1,4-Dicyano-2,3,5,6-tetrafluorobenzene	CCl_4	33.5	2.4 kg/mole	NMR	59
		$CHCl_3$	33.5	0.46 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.26 kg/mole	NMR	59
		CH_2Cl_2	33.5	0.35 kg/mole	NMR	59
Mesitylene	1,4-Dicyano-2,3,5,6-tetrafluorobenzene	CCl_4	33.5	1.5 kg/mole	NMR	59
		$CHCl_3$	33.5	0.29 kg/mole	NMR	59
p-Xylene	1,4-Dicyano-2,3,5,6-tetrafluorobenzene	CCl_4	33.5	1.2 kg/mole	NMR	59
		$CHCl_3$	33.5	0.26 kg/mole	NMR	59
Hexamethylbenzene	TNB	CCl_4	33.5	5.1 kg/mole	NMR	59
		$CHCl_3$	33.5	0.86 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.59 kg/mole	NMR	59
Pentamethylbenzene	TNB	CCl_4	33.5	3.1 kg/mole	NMR	59
		$CHCl_3$	33.5	0.67 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.43 kg/mole	NMR	59
Durene	TNB	CCl_4	33.5	2.1 kg/mole	NMR	59
		$CHCl_3$	33.5	0.49 kg/mole	NMR	59
		CH_2ClCH_2Cl	33.5	0.33 kg/mole	NMR	59

TABLE 3

FORMATION CONSTANTS FOR NAMED AROMATIC HYDROCARBONS WITH TNF AT 40° (REF. 27)

Solvent	*Donor*	K_f *(l/mole)*		K_f		K_f	
		UV	*NMR*	*UV*	*NMR*	*UV*	*NMR*
Di-*n*-butyl succinate	Toluene	0.116	−0.019	−0.045	−0.624	1.087	−0.168
	m-Xylene	0.210	0.072	0.210	0.072	1.670	0.565
	o-Xylene	0.167	0.105	0.241	−0.033	1.357	0.850
Di-*n*-butyl adipate	Toluene	−0.030	−0.010	−0.710	−0.571	−0.272	−0.087
	m-Xylene	0.082	0.096	−0.246	−0.198	0.654	0.769
	o-Xylene	—	—	—	—	—	—
Di-*n*-butyl sebacate	Toluene	−0.008	0.053	−0.730	−0.519	−0.075	0.491
	m-Xylene	0.065	0.041	−0.448	−0.448	0.522	0.333
	o-Xylene	0.145	0.098	−0.180	−0.356	1.177	0.800

their UV and NMR data for K_f^x and K_f^y are shown in Table 3. Many of the values are negative, which is physically meaningless.

Clearly, these are somewhat distressing results, particularly since most of the theory about charge transfer is based on spectroscopic data. The validity of comparisons between other methods and spectroscopic values is also open to serious question. For example, Bertrand and co-workers[67] recently reported the determination of the pyridine/iodine formation constants in cyclohexane and carbon tetrachloride; their results, along with cited spectroscopic values, are shown in Table 4. Although the agreement is good, it may only be fortuitous, given the data in Tables 2 and 3.

TABLE 4

COMPARISON OF CALORIMETRIC K_f^x VALUES FOR PYRIDINE–IODINE WITH SPECTROSCOPIC DATA AT 25°

	K_f^x (l/mole)	
	Calorimetry	*Spectroscopy*
Cyclohexane	124[67]	135[68]
Carbon tetrachloride	103[67]	102[68]
	108[70]	101[69]

4. GAS CHROMATOGRAPHIC STUDIES

A. Classification of experimental methods

Purnell[71] has presented a classification of donor–acceptor–solvent interactions with which the various GLC techniques may be distinguished. These have recently been reviewed by Wellington[72], and so are only briefly considered here; for donor (D) solutes and acceptor (A) stationary phase (S) additives:

Class A. Solute reacts with stationary phase additive to give complexes of the type D_mA_n, where $m, n \geqslant 1$.

Class B. Solute reacts with stationary phase to give complexes of the type S_pD_m, where $m, p \geqslant 1$.

Class C. Solute polymerizes or depolymerizes in solution.

Class D. Additive reacts with stationary phase to give complexes of the type S_pA_n.

Wellington[72] has added:

Class E. Solvated donor, D_mS_x, reacts with solvated additive, A_nS_y, to form solvated complexes, $C_{m:n}S_z$, giving up qS solvent molecules in the process.

(a) Class A: Method of Gil-Av and Herling[13]

For 1:1 Class A interactions, solute (donor) solubility in the stationary phase is enhanced by the presence of a complexing (acceptor) additive, so that the distribution coefficient becomes:

$$K_L = \frac{\text{solute concentration in the stationary phase}}{\text{solute concentration in the gas phase}} = \frac{[D]_L^0 + [C]}{[D]_M} \qquad (12)$$

where $[D]^0_L$ is the equilibrium amount of free donor in solution, and $[D]_M$ is the total donor concentration in the gas phase. Multiplying by $[D]^0_L[A]/[D]^0_L[A]$ gives:

$$K_L = \frac{[D]^0_L}{[D]_M} + \frac{[D]^0_L}{[D]_M}\frac{[C]}{[D]^0_L[A]}[A] = K^0_L + K^0_L K^c_f [A] \tag{13}$$

where K^0_L is the solute distribution coefficient in the absence of additive, [A]. ([A] must be present in excess over [C] to ensure that $[A] \approx [A]_{eq.}$).

Eqn. 13 was first presented by Gil-Av and Herling[13] in 1962, and yields formation constants from the slope/intercept quotient of K_L *vs.* [A] plots. The equation was originally employed to study Ag^+–olefin complexation (ethylene glycol stationary phase), but has since been used by many workers for various organic acceptor additives and donor solutes. (Note that the additive need not be the acceptor; the choice of which complex component to dissolve in the liquid phase is in fact purely a matter of convenience, and for donor additives, [A] is replaced by [D] in eqn. 13.) Wellington[72] has summarized the GLC data that have been obtained via eqn. 13, and Purnell[71] and Wellington[72] have commented on its applications and limitations.

(b) Class B: method of Martire and Riedl[73]

There is seemingly no way to get at formation constants when pure complexing agent is used as the stationary phase (Class B). However, Martire and Riedl[73] showed that:

$$K_{eq.} = \left(\frac{1}{\bar{A}\,\gamma_A}\right)\left(\frac{V^A_g\,V^C_g}{V^B_g\,V^D_g} - 1\right) \tag{14}$$

where $K_{eq.}$ is the true thermodynamic equilibrium constant, γ_A and $\bar{A}$ are the activity coefficient and molar volume of the pure (acceptor) complexing phase, V^A_g and V^B_g are the specific retention volumes of an inert (non-complexing) solute on inert and complexing phases, respectively, and V^C_g and V^D_g are the specific retention volumes of a complexing solute on the same stationary phases. The (Raoult's law) activity coefficient, γ_A, is given by[73]

$$\gamma_A = \frac{V^B_g\,MW_C}{V^A_g\,MW_N} \tag{15}$$

where MW_C and MW_N are the molecular weights of the complexing and inert stationary phases, respectively. If the (donor) solute and complex are at infinite dilution, $\gamma^\infty_{D,C} \to 1$ (Henry's law), $K_{eq.}$ is related to K^c_f by

$$K_{eq.} = \frac{[C]}{[D]\,a_A} = K^{c\prime}_f/\bar{A}\,\gamma_A = K^c_f/\gamma_A \tag{16}$$

where a_A is the activity of the neat (acceptor) stationary phase. Liao *et al.*[74] have shown that eqn. 16 is valid when the inert reference phase is identical in all respects to the complexing phase, except that the latter forms complexes while the former does not. While this is a rather stringent requirement of the reference phase, the method

has been used with excellent success to measure charge transfer interactions[74–78], and promises to become a very important technique for the determination of $K_{eq.}$ values. Indeed, eqn. 14 is the only method developed to date by which $K_{eq.}$ can be found.

5. COMPARISON OF METHODS

A. GLC and spectroscopy

The only comparison of GLC and spectroscopic data thus far is that by Purnell and Srivastava[27]. Their GLC concentration formation constant (K_f^c) data for the same solvents and compounds as in Table 3 are now given in Table 5. The values are all positive, but the most remarkable feature of these data is that, even for the same compounds, solvents, and temperature, results by the same workers in the same laboratory suggest that UV and NMR data are not valid. The GLC results, on the other hand, are all positive, decrease with increasing temperature[27], and appear to be physically meaningful.

TABLE 5

GLC[27] FORMATION CONSTANTS FOR NAMED COMPOUNDS WITH TNF AT 40°

Solvent	*Donor*	K_f^c *(l/mole)*
Di-*n*-butyl succinate	Benzene	0.590
	Toluene	0.702
	m-Xylene	0.825
	o-Xylene	0.871
	p-Xylene	0.764
	Ethylbenzene	0.615
Di-*n*-butyl adipate	Benzene	0.481
	Toluene	0.491
	m-Xylene	0.615
	o-Xylene	0.606
	p-Xylene	0.624
	Ethylbenzene	0.448
Di-*n*-butyl sebacate	Benzene	0.353
	Toluene	0.332
	m-Xylene	0.401
	o-Xylene	0.393
	p-Xylene	0.425
	Ethylbenzene	0.355

B. GLC: Class A and Class B

According to eqn. 16, when $\gamma_A = 1$, the equilibrium constant should be identical to the concentration formation constant. That is, the Gil-Av–Herling method (Class A) should give the same results (for the same solutes and complexing solvents) as the Martire–Riedl method (Class B). The only test of this hypothesis (given by eqn. 16) is by Liao *et al.*[74], who used di-*n*-octylmethylamine as the complexing phase, *n*-octadecane as the inert or reference phase, and $CHCl_3$, CH_2Cl_2, and CH_2Br_2 as

the complexing solutes. γ_D was found to be 0.993 ± 0.002 via eqn. 15, in which case $K_{eq.}$ values should be identical to K_f^c values. Their results are given in Table 6, where the agreement is seen to be excellent, indicating that the two GLC methods offer consistent results, further strengthening our contention that GLC data are a valid measure of charge transfer interactions.

TABLE 6

COMPARISON[74] OF $K_{eq.}$ AND K_f^c WHEN $\gamma'_D = 1$

Solute	K_f^c *(l/mole) (eqn. 13)*	$K_{eq.}$ *(eqn. 14)*
$CHCl_3$	0.405 ± 0.019	0.403 ± 0.006
CH_2Cl_2	0.179 ± 0.014	0.187 ± 0.004
CH_2Br_2	0.222 ± 0.004	0.219 ± 0.004

6. RATIONALIZATION OF THE DIFFERENCE BETWEEN GLC AND SPECTROSCOPIC DATA: SOLVATION

We now explore possible explanations for the discrepancy between GLC and spectroscopic values. In both UV and NMR studies, donors, acceptors, and complexes exist in solution as solvated species such that interactions must occur through shells of solvent molecules surrounding each component. For strong (inner) complexes, some solvent molecules may be removed so that donor and acceptor are in direct contact; for weak (outer) complexes, this may or may not be true. We assume, for now, that for 1:1 complexes, the following reactions occur in solution:

$$A + S_n \leftrightharpoons AS_n \tag{17}$$

$$D + S_m \leftrightharpoons DS_m \tag{18}$$

$$AS_n + DS_m \leftrightharpoons CS_p + qS \tag{19}$$

Thus, formation of a complex is an interaction between solvated A and D which gives solvated C plus q solvent molecules which have been cast off (or added, in which case q is negative) such that: $n + m = p + q$. Carter *et al.*[79] and others[80–82] have pointed out that solvent effects must be considered whenever weak interactions are measured spectroscopically, but few workers have taken notice of this fact. Yet the work of Carter *et al.*[79] offers a very straightforward method of determining the extent of solvation, as well as solvent-independent formation constants. We therefore now examine the technique of Carter *et al.* in an attempt to explain the differences between spectroscopic and GLC data.

The formation constant, K_f^c, is now defined in terms of eqn. 19

$$K_f^c = \frac{[CS_p]\,(X_s)^q}{[AS_n]\,[DS_m]} \tag{20}$$

where X_s is the free solvent mole fraction, given by

$$X_s \cong \frac{[S]_{free}}{[S]_t + [D]_t + [A]_t} \tag{21}$$

$[S]_{free}$ is the concentration of free solvent at equilibrium, and $[S]_t$ is the total solvent concentration. X_s rather than [S] is used in eqn. 20 so that the formation constant will retain units of 1/mole, and can therefore be compared to the Benesi–Hildebrand equation. When $[D]_t \gg [A]_t$, $[D]_t = [D]_{eq.}$, and

$$\frac{[A_t]b}{A_{ct}} = \frac{(X_s)^q}{\varepsilon_{ct}K_f^c[D]_t} + \frac{1}{\varepsilon_{ct}} \tag{23}$$

The only difference between eqn. 23 and the original Benesi–Hildebrand relation, eqn. 8, is the appearance of $(X_s)^q$ in the numerator of the first term on the right-hand side. Eqn. 8 failed to include solvent effects, which is a serious omission: if we assume that eqns. 17–19 are reasonable (*i.e.*, if a compound dissolves in a solvent it becomes solvated by that solvent), then according to eqn. 19 as more donor is added to a solution containing an acceptor, complex CS_p is formed and qS amount of solvent is released, thus diluting what we had assumed was a constant $[A]_t$. The freshly added donor also takes up some amount of solvent to form DS_m, further compounding the problem. Let us represent $[S]_0$ as the free solvent concentration when $[D]_t = 0$ but after $[A]_t$ has been added to the solution. Assuming that the change in the total solution volume is negligible when $[D]_t$ is added

$$[S]_{free} = [S]_0 - [D]_t\left(\frac{\bar{V}_D}{\bar{V}_S}\right) \tag{24}$$

where $\bar{V}_D$ and $\bar{V}_S$ are the donor and solvent molar volumes, whose ratio we conveniently represent by λ

$$[S]_{free} = [S]_0 - \lambda[D]_t \tag{25}$$

Eqn. 25 merely says that the total amount of solvent in the solution remains constant

$$\bar{V}_S[S]_{free} + \bar{V}_D[D]_t = \bar{V}_S[S]_0 \tag{26}$$

(Note that $[S]_0 > [S]_{free}$.) $[S]_{free}$ is now given by

$$\begin{aligned}[S]_{free} &= [S]_t - n[A]_t - m[D]_t + q[C] \\ &= [S]_0 - \lambda[D]_t - m[D]_t - n[A]_t + q[C] \\ &= [S]_0 - (m + \lambda)[D]_t - n[A]_t + q[C]\end{aligned} \tag{27}$$

Substituting eqn. 27 into eqn. 21 yields

$$\begin{aligned}X_s &= \frac{[S]_0 - (m + \lambda)[D]_t - n[A]_t + q[C]}{[S]_t + [D]_t + [A]_t} \\ &= \frac{[S]_0 - (m + \lambda)[D]_t}{[S]_0 + (1 - \lambda)[D]_t}\end{aligned} \tag{28}$$

since $n[A]_t \ll [D]_t < [S]_0 \approx [S]_t$. Eqn. 23 now becomes

$$\frac{[A]_t b}{A_{ct}} = \frac{1}{\varepsilon_{ct}K_f^c[D]_t}\left[\frac{1 - (m + \lambda)[D]_t/[S]_0}{1 + (1 - \lambda)[D]_t/[S]_0}\right]^q + \frac{1}{\varepsilon_{ct}} \tag{29}$$

Since $[S]_0 \gg [D]_t$, and neglecting higher terms

$$\frac{[A]_t b}{A_{ct}} = \frac{1}{\varepsilon_{ct} K_f^c [D]_t} [1 - q(m + \lambda)([D]_t/[S]_0)][1 - q(1 - \lambda)([D]_t/[S]_0)] + \frac{1}{\varepsilon_{ct}}$$

$$= \frac{1}{\varepsilon_{ct} K_f^c [D]_t} + \frac{1}{\varepsilon_{ct}} \left[1 - \frac{q(m + 1)}{K_f^c [S]_0}\right] \quad (30)$$

The formation constants of eqns. 8 and 30 are related by

$$K_f^c \text{ (eqn. 8)} = K_f^c \text{ (eqn. 30)} - \frac{q(m + 1)}{[S]_0} \quad (31)$$

and

$$\varepsilon_{ct} \text{ (eqn. 8)} = \varepsilon_{ct} \text{ (eqn. 30)} \frac{K_f^c \text{ (eqn. 30)}}{K_f^c \text{ (eqn. 8)}} \quad (32)$$

K_f^c and ε_{ct} (eqn. 8) are thus underestimated and overestimated, respectively, and the Benesi–Hildebrand equation will only be approximately correct when

$$K_f^c \gg q(m + 1)/[S]_0 \quad (33)$$

i.e., when complexation is strong. For the cases of weak or contact charge transfer

$$K_f^c < \frac{q(m + 1)}{[S]_0} \quad (34)$$

may be true, and the Benesi–Hildebrand equation will fail badly.

Carter *et al.*[79] tested the validity of eqn. 30 by plotting ε_{ct} *vs.* K_f^c for methylbenzenes–iodine, TNB, and chloranil, each in CCl_4 solvent, for which $[S]_0$ is given by density/molecular weight = 10.3 moles/l. (Recall that $[S]_0 > [D]_t \gg [A]_t$.) If Beer's law is correct, and if K_f^c is measured at a wavelength at which only charge transfer interactions cause absorption, then

$$\text{as } K_f^c \to 0, \ \varepsilon_{ct} \to 0 \quad (35)$$

Carter *et al.* found that this was obeyed for each set of methylbenzenes/acceptor data only at discrete values, namely, $q(m + 1) = 9$ (iodine), 30 (TNB), and 6 (chloranil). The largest change is for TNB, and we therefore assume that it is the most solvated, while chloranil is the least solvated. Further evidence of the validity of eqn. 30 was found when the gas-phase data of Lang and Strong[83] for benzene–iodine were compared to the liquid-phase data in CCl_4. Assuming $q(m + 1) = 9$, $\varepsilon_{ct}^{liquid}$ was found to be 2400, whereas ε_{ct}^{gas} was 1700; $\varepsilon_{ct}^{corr.\ 8}$ was 17,000 when solvation effects were not considered.

Clearly, solvent effects are responsible for most of the anomalies in Table 2, but may be removed by the treatment of Carter *et al.*; it is remarkable, in fact, that many more investigations have not been in this direction. Assuming discrete solvation shells surrounding the donor, acceptor, and complex moieties, one can also rationalize differences between UV and NMR data. In the former, electronic transitions form inner complexes which may have different geometrical configurations (and

most certainly have different electronic configurations) than the ground state. The accuracy of UV K_f^c values therefore depends implicitly on how closely related the solvated electronic ground state is to the solvated electronic excited state. In the NMR technique, chemical shifts depend on solvent shielding effects, which can be appreciably different even for closely related solvents[6]. Thus, the UV and NMR techniques are at variance simply because solvent effects are manifested differently in each; that is, even the same solvent will affect electronic transitions differently than it will chemical shifts, because two fundamentally different properties are being measured.

We now consider GLC data. Eqn. 13 allows the determination of all solution effects except the change in X_s; as in eqn. 23, varying [A] will alter $[S]_{free}$, so that K_L^0 will not be a true constant. Meen[84] and Wellington[72] are thus far the only workers who have considered the application of the argument of Carter *et al.* to GLC. For an acceptor additive and donor solutes

$$K_L = K_L^0 \left[1 + \frac{K_f^c [AS_n]}{(X_s)^q}\right]$$

$$= K_L^0 \left\{1 + K_f^c [A]_t \left[1 - \frac{[A]_t q(n+1)}{[S]_t}\right]\right\} \tag{36}$$

where $(X_s)^q$ is approximately given by

$$(X_s)^q \approx 1 + \left[\frac{[A]_t\, q(n+1)}{[S]_t}\right] \tag{37}$$

analogous to eqns. 21 and 28. Note that the term $q(n+1)$ and not $q(m+1)$ is used here, since in GLC the acceptor is in large excess over the donor, not *vice versa* as in spectroscopy. If $[A]_t \ll [S]_t$, eqn. 36 reduces to eqn. 13, the Gil-Av–Herling relation, which will usually be the case if less than 0.2 *M* solutions of A in S are employed. "Best" values of $q(n+1)$ should be available from spectroscopic data via the method of Carter *et al.*[79], so that eqns. 30 and 36 should now yield identical K_f^c values, regardless of the solvent or method. Purnell[85] has very recently applied these considerations to NMR equations as well, and does indeed find that GLC and spectroscopic data are identical when solvent effects are taken into account. This is the most exciting development yet in the study of charge transfer complexation, and will clearly be applied much more so in the future than in the past; workers in the field will finally have a means whereby formation constant data from many different techniques can be compared on a common basis, and we anticipate great strides in solution theory in the very near future as a result.

7. DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES VIA GLC COMPLEXATION STUDIES

A. Vertical ionization potentials and electron affinities

If true charge transfer forces are operative, we would expect the formation

constant to be a function of the donor vertical ionization potential, as we noted earlier

$$K_f^c = F(I_v^d) \tag{38}$$

To establish that this is the case, we have examined several types of donors on different complexing phases[24–26]. The results are encouraging: the lower the ionization potential, the larger the formation constant. Data by Meen *et al.*[86] also indicate that K_f^c is a function of I_v^d. This variation has in fact been used in a very recent publication[25] to determine vertical ionization potentials: the GLC K_f^c data of butadienes with known[87–92] I_v^d values were plotted as K_f^c *vs.* I_v^d at three temperatures. The lines were curved, and so a non-linear least-squares treatment[93,94] was necessary to fit the data. The approximate equation constants were:

$$45°: K_f^c = -9.075 \times 10^{-3}(I_v^d)^2 + 0.750 \tag{39}$$

$$50°: K_f^c = -9.237 \times 10^{-3}(I_v^d)^2 + 0.750 \tag{40}$$

$$55°: K_f^c = -9.445 \times 10^{-3}(I_v^d)^2 + 0.750 \tag{41}$$

where TNF in di-*n*-butyl phthalate (DNBP) was used as the stationary phase. To ensure that eqns. 39–41 were good approximations, the known ionization potentials were back-calculated from the respective formation constants at each temperature; the known and averaged values agreed to 1.02% at worst, and generally much better than that. To ascertain the accuracy of the GLC-determined I_v^d values, we have collaborated with Heilbronner and Bieri[95] in obtaining PES data for the dienes whose ionization potentials were previously unknown; the results are presented in Table 7, where the difference between the GLC and PES values for each compound, δ, is also given. The first four compounds agree to within $\pm$ 0.10 eV, a remarkable feat since the GLC instrument we used was by no means a precision device, and many of the formation constants bordered on the experimental error of K_f^c (determined to be

TABLE 7

COMPARISON OF PES AND GLC I_v^d VALUES[25,95]

Diene	I_v^d *(eV)*		
	PES	*GLC*	δ *(eV)*
cis-1,3-Pentadiene	8.61 (*trans*)	8.65	0.04
2-Ethyl-1,3-butadiene	8.79	8.76	0.03
2-Methyl-1,3-pentadiene	—	8.53	—
3-Methyl-1,3-pentadiene	8.40	8.51	0.11
4-Methyl-1,3-pentadiene	8.45	8.49	0.04
1,3-Hexadiene	8.53	8.70	0.17
1,3-Heptadiene	8.51	8.75	0.24
1-Methoxy-1,3-butadiene	8.26	7.98	0.28
5-Methyl-1,3-hexadiene	8.47	8.81	0.34
2,4-Dimethyl-1,3-pentadiene	9.31	8.85	0.46
2,4-Heptadiene	8.14	8.71	0.57

± 0.010 l/mole). The remaining compounds disagree by increasing amounts, the worst case being 2,4-heptadiene. We have attributed these δ values to steric hindrance to charge transfer, and will discuss them shortly. Meanwhile, where no anomalous (*e.g.*, steric) effects occur, GLC can be used to determine vertical ionization potentials to ± 0.1 eV (PES data are usually accurate to ± 0.02–0.03 eV).

Charge transfer forces should also be proportional to the acceptor electron affinity

$$K_f^c = F(E_v^a) \tag{42}$$

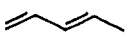
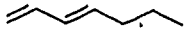
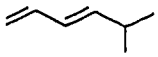
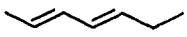
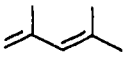
No study has appeared which uses eqn. 42, but our K_f^c data[25] for aromatic hydrocarbons and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in DNBP are two to three times as large as those by Meen *et al.*[86], even if normalized to the same K_L^0 values. DDQ has an electron affinity of 1.95 eV, compared to 1.00 eV for TNF[47], and so the results are entirely as expected. The relation could perhaps be improved if solvation were taken into account (recall that TNB and chloranil differed by $\Delta[q(m+1)] = 24$ solvation molecules); we are now examining closely related classes of acceptors, for example, the pyridazinediones, for which no E_v^a data exist[96,97], but which could in principle be found via GLC, analogous to our procedure for I_v^d values.

B. Substituent effects and steric hindrance to charge transfer

The values of Table 7 are now presented in a different manner, in Table 8. For the first four compounds, as the substituent on the end of the butadiene skeleton be-

TABLE 8

EFFECTS OF STERIC HINDRANCE ON CHARGE TRANSFER

Donor	δ *(eV)*
	0.04
	0.17
	0.24
	0.34
	0.57
	0.46
	0.03

comes larger, the difference between PES and GLC I_v^d values increases. Since K_f^c is proportional to $(I_v^d)^{-1}$, we note that if steric hindrance (or other factors) causes a decrease in K_f^c, I_v^d will be increased by a similar amount, resulting in δ values larger than 0.1 eV (the experimental error of the GLC method). The δ values then become a measure of steric hindrance to charge transfer. Bulky end-groups clearly appear to hinder (planar) complex formation with TNF, but a large δ value is also found for 2,4-dimethyl-1,3-pentadiene. This compound is known to be twisted about the central single bond[98] and is thus partially deconjugated, which results in a higher ionization potential than expected. Conversely, 2-ethyl-1,3-butadiene does not appear to be sterically hindered, which is most surprising. Although further work is needed to verify this result, we are forced to postulate that charge transfer in butadiene–TNF complexes is an end–on interaction, rather than planar–planar, as has historically been assumed. We are therefore now investigating 2-alkyl-1,3-pentadienes to confirm this finding.

In another recent paper[26], we attempted to measure out-of-plane deformation angles for a series of β-ionones via the Class B technique of Martire and Riedl. Aromatic hydrocarbons were first examined with di-*n*-butyl tetrachlorophthalate, and $K_f^{c\prime}$ (eqn. 16) was shown to vary inversely as I_v^d, as expected. Next, a series of substituted aromatic amines was investigated, and out-of-plane substituents at the nitrogen[99] were shown to profoundly affect charge transfer behavior. Finally, out-of-plane twisting for the β-ionone series was measured by NMR[100,101], but could not be correlated to GLC $K_f^{c\prime}$ values because the angles were too severe ($\approx 30°$). An upper limit of the GLC method was thus established to be approximately 10°–15°. Work is now under way with the compounds described by Forbes *et al.*[98] to further clarify the usefulness of GLC for the determination of out-of-plane deformation angles.

8. FUTURE AREAS OF INVESTIGATION

Several approaches to the question of charge transfer now become apparent. The method of Martire and Riedl[73] offers great promise for the evaluation of thermodynamic equilibrium constants. A modified Gil-Av and Herling equation which includes solvent effects (eqn. 30) also appears to be an extremely useful approach which will enable results from different experimental methods to be compared. Eon and Guiochon[28] and Martire[102] have very recently presented a theoretical treatment of this problem, and Purnell *et al.*[85] have been able to show that GLC and spectroscopic data do indeed yield identical results when solvation effects (determined via the method of Carter *et al.*[79]) are taken into account. Liao and Martire[77] have begun to investigate (hydrogen bonding) complexation in the light of acid–base theory[103], and we[25,26] have shown that many molecular properties can also be deduced from GLC charge transfer data, including ionization potentials, electron affinities, steric factors, out-of-plane deformations, and so forth.

Finally, several new approaches await investigation. The question of end–on *vs.* planar intermolecular interaction looms as a most important study, since the very nature of charge transfer may thereby be elucidated. Another study that would be most interesting is the illumination of a glass capillary GLC column during the elution of complex-forming donors. Suppose, for example, that the liquid phase was DDQ

in DNBP, and benzene, toluene, and the three xylenes were being chromatographed. $\lambda_{max.}$ for aromatic hydrocarbons–DDQ differs by over 200 nm in some cases[56,104], being 427 nm for benzene and 450 nm for toluene ($CHCl_3$ solvent[56]). Suppose that we now irradiate the glass GC column at 420 nm, well away from the toluene and xylene maxima, but close enough to benzene to produce an outer → inner complex transition. Benzene should then be strongly retained, while the other solutes will elute unaffected by the illumination. If this does not occur, then charge transfer theory as we know it is incorrect, and the entire subject would require complete re-evaluation. If benzene is strongly retarded, the difference, ΔK_L, between "dark" and "illuminated" distribution coefficients should be a good measure of the strength (hence ε_{ct}) of charge transfer interactions, which could easily be verified by UV studies. Conversely, it may be possible to obtain ε_{ct} values at infinite dilution via GLC, which can only be done indirectly (by extrapolation to [D] = 0; Beer's law) in UV. Illumination may also be used as an added dimension for difficult separations. Meen *et al.*[86] have evaluated the use of complexing agents in analytical GC applications, and we[25] have shown that even DDQ in high concentrations will not be of much use in adding to column selectivity. The ability to cause inner complex transitions by UV/visible irradiation, however, may considerably brighten the outlook on this approach. Lastly, while we have limited the discussion here to GLC, there is every reason to expect that high-performance liquid–liquid chromatography will prove equally as useful[105]. Gil-Av *et al.*[106] have already begun complexation studies by high-performance liquid–liquid chromatography, and it has been suggested[107] that solvation effects could greatly improve separations when complex-forming stationary phases are used in this technique. In short, the study of charge transfer is currently in a high state of flux, and offers every promise of being one of the most rewarding physicochemical topics yet investigated by gas (and liquid) chromatographers.

9. SUMMARY

The study of charge transfer complexation by gas–liquid chromatography (GLC) is presented. The GLC results differ significantly from spectroscopic data, and it is argued that the chromatographic technique seems to be valid, whereas other methods are at best questionable. Very recent data by the authors also indicate that much more information is available from GLC studies than had previously been recognized, such as the determination of vertical ionization potentials, vertical electron affinities, molecular substituent and out-of-plane deformation effects, and steric hindrance to charge transfer.

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