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GAS-LIQUID CHROMATOGRAPHIC STUDIES OF ELECTRON-DONOR-ACCEPTOR SYSTEMS

VI. 2,4,7-TRINITROFLUORENONE AS A COMPLEXING ADDITIVE TO THE STATIONARY PHASE*

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SUMMARY

2,4,7-Trinitrofluorenone has been used as a complexing additive to tritolyl phosphate and polypropylene sebacate as stationary phases for the separation of aromatic amines. Association constants for the interaction of the donor amines with this acceptor have been calculated from the retention data and the variation of these association constants with temperature measured. Comparison of the gas chromatographic association constants with charge-transfer equilibrium constants determined spectroscopically suggest that part of the donor-additive interaction is charge-transfer complex formation. The more polar tritolyl phosphate is the better solvent for both the additive and the amines, thus decreasing donor-additive interactions.

INTRODUCTION

In previous studies we have examined the interactions between electron donor solutes and electron acceptor stationary phases (as bulk liquid) in order to determine the influence of charge-transfer (CT) complexing ability on gas-liquid chromatographic (GLC) retention and have shown that good correlations exist between GLC data and spectrophotometric CT association constants². In particular 2,4,7-trinitrofluorenone was shown to be a good acceptor stationary phase for the study of interactions with anilines, aromatic hydrocarbons and heterocycles³. This particular stationary phase has the advantage of forming 1:1 complexes with aromatic donors⁴ and had earlier been used to separate aromatic compounds⁵. Quantitative comparisons between GLC and spectroscopic data were not possible in the previous work as the

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spectroscopic data were of necessity measured in a solvent. In an attempt to partially overcome this problem we have now measured partition coefficients etc. for anilines using solutions of 2,4,7-trinitrofluorenone in tritolyl phosphate (TTP) or polypropylene sebacate (PPS) as stationary phases.

The use of complexing additives in GLC is not new and this technique has been used by various workers to determine stability constants for silver ion-olefin complexes in ethylene glycol⁶. Using a complexing additive it is possible to measure formation constants and related thermodynamic parameters by the GLC method, the formation constants for 1:1 complexes being given by

$$k = k_0(1 + K_c c_a) \quad (1)$$

where k and k_0 are the partition coefficients of complexed and uncomplexed solute, respectively, K_c the formation constant for the solute-additive complex and c_a is the concentration of the additive. Assuming that partition coefficients can be determined to within 1% and that errors in weighing are trivial, values of K_c ranging from $5 \times 10^{-2} \text{ l. mole}^{-1}$ to $10^6 \text{ l. mole}^{-1}$ should be capable of measurement by GLC, the maximum error (ca. 20%) only entering into the low K_c measurements. It is still necessary to ensure that the values obtained are true values and not special dynamic values but for non-ionic systems comparisons are difficult owing to the lack of data from conventional partitioning methods. LITTLEWOOD AND WILLMOTT⁷ have compared GLC determined values for hydrogen bonding of 1-dodecanol in squalene with NMR values but heats of interaction differ by a factor of 2. LANGER⁸ has obtained agreement in the characterisation of solute-solvent interactions using two different GLC approaches and COOPER *et al.*² obtained self-consistent data for both GLC and spectroscopic studies of CT complex formation. Exact agreement between GLC data and spectroscopic data could not be anticipated as the K_c derived from GLC includes *all* types of solute-solvent interaction and should thus be greater than that measured spectroscopically.

The choice of GLC solvents for 2,4,7-trinitrofluorenone was governed by the low solubility and high complexing ability of this additive. In an attempt to simulate the spectroscopic conditions of COOPER *et al.*², polychlorotrifluoroethylene and fluoro-silicone oil were tried but the acceptor failed to dissolve. Thus the only suitable solvents found were TTP and PPS and these differ only in size and the nature of the polar bond, thus restricting the opportunity to study solvent interaction in these ternary systems.

Excess enthalpies and entropies of association have been measured for these systems and these indicate that the contribution to the free energy of solution from CT interactions is small though significant. Logarithmic correlations of retention volumes for the two systems studied here indicate the importance of steric effects in these systems and show that the close approach of donor and acceptor, which enhances solubility in the pure acceptor (as stationary phase), is not as important in the solvent-additive systems. The use of a CT complexing additive does result in the improved separation of related donor compounds.

EXPERIMENTAL

The apparatus, measurement technique and column packing have been described^{2,8}. Columns containing up to 0.5 M additive were used.

Materials

Tritolyl phosphate. This was May and Baker "Embaphase" grade and was used without further purification.

Polypropylene sebacate. This was Griffin and George "Chemicals for Gas Chromatography" grade treated as follows. The stationary phase was placed in a sintered glass vessel which was modified so that it could be connected to the nitrogen supply in the chromatography oven. Nitrogen was slowly passed through the material and the oven temperature was raised to 10° above the maximum operating temperature used for the stationary phase. The treatment was maintained until constant weight of the stationary phase was achieved and thus the more volatile lower polyesters had been removed.

2,4,7-Trinitrofluorenone. This was a commercial product, recrystallized twice from glacial acetic acid and dried at 100°, m.p. 175°.

Anilines. These were purified in accordance with the literature, redistilled and collected at their reported boiling points.

RESULTS

Association constants calculated from GLC retention data at three temperatures, together with the derived free energies, enthalpies and entropies of association at 140° for substituted aniline-2,4,7-trinitrofluorenone interactions in TTP and PPS, respectively, are shown in Tables I and II. (Values of the partition coefficients at these temperatures, at varying values of c_a , are not shown here but may be obtained on application to the authors.) According to eqn. 1 a linear relationship is required

TABLE I

ASSOCIATION CONSTANTS, ENTHALPIES, FREE ENERGIES AND ENTROPIES OF COMPLEXATION FOR THE SUBSTITUTED ANILINE-2,4,7-TRINITROFLUORENONE COMPLEXES IN TTP, CALCULATED FROM GLC RETENTION MEASUREMENTS

Donor	$K_c(l \cdot \text{mole}^{-1})$			$-\Delta H^c$ (140°) kcal· mole ⁻¹	$-\Delta G^c$ (140°) kcal· mole ⁻¹	$-\Delta S^c$ (140°) cal·deg ⁻¹ · mole ⁻¹
	150°	140°	130°			
1 N,N-Dimethylaniline	0.34	0.39	0.44	4.37	-0.79	12.5
2 N,N-Diethylaniline	0.17	0.21	0.24	5.84	-1.28	17.2
3 N-Ethyl,N-methylaniline	0.24	0.27	0.33	5.39	-1.07	15.6
4 N,N-Dimethyl- <i>p</i> -toluidine	0.43	0.48	0.54	3.86	-0.60	10.8
5 N,N-Dimethyl- <i>o</i> -toluidine	0.14	0.16	0.19	5.18	-1.50	16.2
6 N,N-Dimethyl-2,4-xylylidine	0.09	0.11	0.13	6.23	-1.81	19.5
7 N,N-Dimethyl-2,6-xylylidine	0.04	0.07	0.10	11.74	-2.93	35.5
8 Aniline	0.30	0.34	0.39	4.45	-0.89	12.9
9 <i>o</i> -Toluidine	0.33	0.36	0.40	3.26	-0.86	10.9
10 <i>m</i> -Toluidine	0.38	0.41	0.45	2.98	-0.73	9.0
11 <i>p</i> -Toluidine	0.40	0.44	0.49	3.44	-0.67	10.1
12 2,4-Nylidine	0.35	0.39	0.45	4.25	-0.77	12.0
13 <i>p</i> -Ethylaniline	0.41	0.44	0.49	3.02	-0.67	8.0
14 N-Methylaniline	0.27	0.31	0.35	4.40	-0.96	13.2
15 N-Ethylaniline	0.22	0.24	0.26	2.83	-1.17	9.7
16 N- <i>n</i> -Propylaniline	0.19	0.21	0.24	3.95	-1.28	12.7
17 N- <i>n</i> -Butylaniline	0.17	0.19	0.21	3.58	-1.36	12.6

TABLE II

ASSOCIATION CONSTANTS, ENTHALPIES, FREE ENERGIES AND ENTROPIES OF COMPLEXATION FOR THE SUBSTITUTED ANILINE-2,4,7-TRINITROFLUORENONE COMPLEXES IN PPS, CALCULATED FROM^a GLC RETENTION MEASUREMENTS

Donor	$K_c(l \cdot mole^{-1})$			ΔH^c (140°) kcal· mole ⁻¹	ΔG^c (140°) kcal· mole ⁻¹	ΔS^c (140°) cal·deg ⁻¹ · mole ⁻¹
	150°	140°	130°			
N,N-Dimethylaniline	0.72	0.84	0.96	4.87	-0.14	12.1
N,N-Diethylaniline	0.50	0.62	0.71	5.91	-0.39	15.3
N-Ethyl,N-methylaniline	0.57	0.77	0.80	5.64	-0.21	14.2
N,N-Dimethyl- <i>p</i> -toluidine	0.92	1.16	1.37	6.73	+0.21	15.8
N,N-Dimethyl- <i>o</i> -toluidine	0.32	0.39	0.47	6.51	-0.77	17.6
N,N-Dimethyl-2,4-xylidine	0.29	0.38	0.48	8.53	-0.79	22.6
Aniline	0.68	0.80	0.86	4.49	-0.23	11.4
<i>o</i> -Toluidine	0.74	0.94	1.02	5.38	-0.05	13.1
<i>m</i> -Toluidine	0.76	0.98	1.14	5.76	-0.04	14.0
<i>p</i> -Toluidine	0.78	0.98	1.14	6.41	-0.02	15.5
2,4-Xylidine	0.70	0.84	1.03	6.56	-0.14	16.2
<i>p</i> -Ethylaniline	0.94	1.04	1.25	4.82	+0.03	11.6
N-Methylaniline	0.71	0.81	0.95	5.67	-0.17	14.1

between the partition coefficient of the complexed solute k and c_a and that such relationships are obtained is illustrated by Fig. 1 for the N,N-dimethylaniline data.

The difference in polarity between the two stationary phases used is shown in Table III where data for the "Z-values"^{10,11} are given, together with that for ethanol for

TABLE III

Z VALUES FOR SOLVENTS AT 25°

The concentration of 1-ethyl-4-carbomethoxypyridinium iodide was $2.5 \times 10^{-4} M$ in all solvents.

Solvent	Z value ^a kcal·mole ⁻¹
100% Ethanol	79.8 ^b
TTP	77.8
PPS	70.7

^a See ref. 11.

^b cf. 79.6; ref. 10.

comparison. The greater solubility of the donor molecules in TTP is shown by the retention data plotted in Fig. 2. Comparison of the GLC results with spectroscopically measured association constants for the substituted aniline-2,4,7-trinitrofluorenone systems in dichloromethane² is shown in Fig. 3 where it can be seen that the primary and tertiary amines form two separate, but almost parallel, linear plots. The isokinetic relationships for the two stationary phases are shown in Fig. 4 and good linear relationships are observed. That the contribution from CT interactions to the free energy of solution is small is confirmed by the very small deviations from linearity shown by Fig. 4.

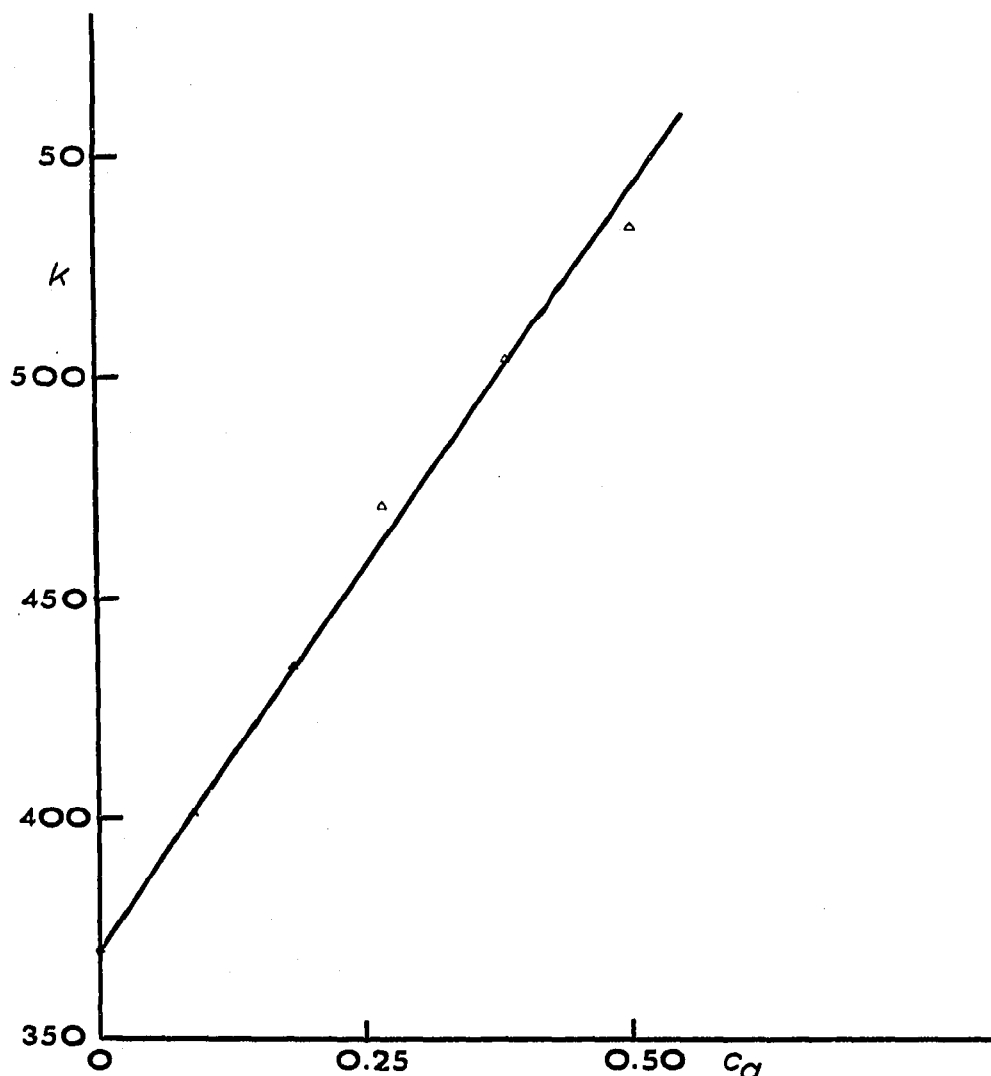


Fig. 1. The variation of the partition coefficient, k , with concentration, c_a , for the N,N-dimethylaniline-2,4,7-trinitrofluorenone system in PPS at 130°.

DISCUSSION

The order of association constants K_c , shown in Tables I and II, follows that expected from considerations of alkyl-substituent effects. Enhancement of association occurs with *para*-substitution but *ortho* groups, which give rise to steric effects in the vicinity of the nitrogen atom, result in a lowering of K_c . The increase in K_c observed spectroscopically, on introduction of a second alkyl group on the nitrogen atom is not pronounced here owing to the convergence of K_c values at the operating temperatures. Free energies of association are positive in both solvents with the exception of *p*-ethyl-aniline and N,N-dimethyl-*p*-toluidine in PPS. These results indicate the stronger interactions between these donors and the complexing additive.

The values of ΔG^e for TTP as solvent are more positive than those for PPS, indicating a less favourable interaction between donor and acceptor in this solvent. Although the same order of K_c values is obtained in both solvents the absolute values

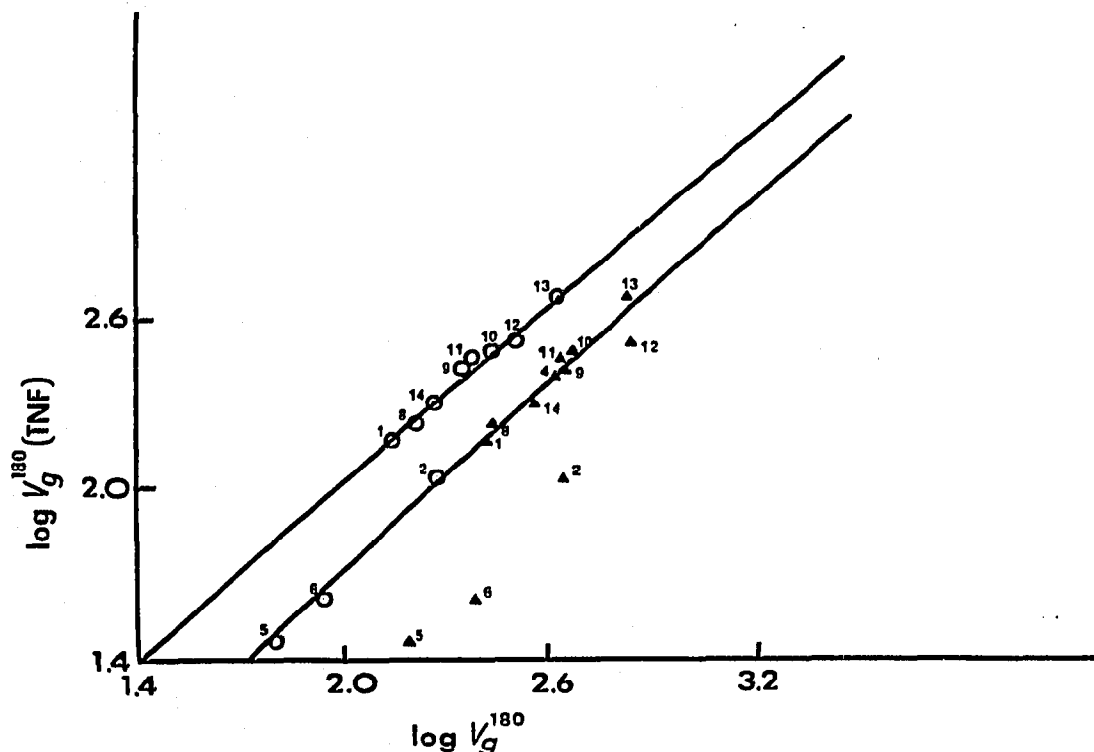


Fig. 2. The variation of $\log V_g^{180}$ for the substituted aniline-2,4,7-trinitrofluorenone² with $\log V_g^{180}$ for the substituted aniline-2,4,7-trinitrofluorenone-TTP and 2,4,7-trinitrofluorenone-PPS systems (extrapolated data). Numbering as in Table I: ○, PPS system; ▲, TTP system.

are smaller in TTP by a factor of 2 to 3. Further, partition coefficients for N,N-dimethylaniline in TTP and PPS are 274.5 and 196.5, respectively, showing that TTP is a better solvent for the donors used. Considerations of solvent properties indicate that this is to be expected and that donor-acceptor interactions will be less favourable in TTP. Thus the dipole moments of alkyl phosphates suggest that $\mu(\text{P}=\text{O})$ is approximately 3.3 D whereas $\mu(\text{C}=\text{O})$ is 2.0 D and the solubility of polar molecules should be enhanced in the phosphate. DE MAINE¹² has suggested that a well defined liquid lattice of solvent molecules can be formed by systems in which cohesive forces are strong and that acceptor molecules can fit into cavities formed by this lattice. The liquid lattice penetration complex should be stronger between the acceptor and the more polar TTP and differences in relative K_c values shown by the two stationary phases should be measures of the abilities of the donor molecules to penetrate this liquid-lattice complex and undergo CT interaction with the acceptor. In addition DE MAINE¹² postulated that aggregates of solvent molecules with the acceptor may themselves be held together by CT forces and such stabilisation is also more probable between 2,4,7-trinitrofluorenone and the aromatic rings of TTP. Both geometric and electronic considerations would disfavour CT interactions between PPS and the acceptor. PURNELL¹³ has also shown recently the importance of structural similarities between solute and solvent in studies of dichlorobenzene-tetrachloroterephthalate ester interactions. Although CT interactions may play a small role in GLC systems, as compared to "normal" solution forces, the additive technique for measuring associa-

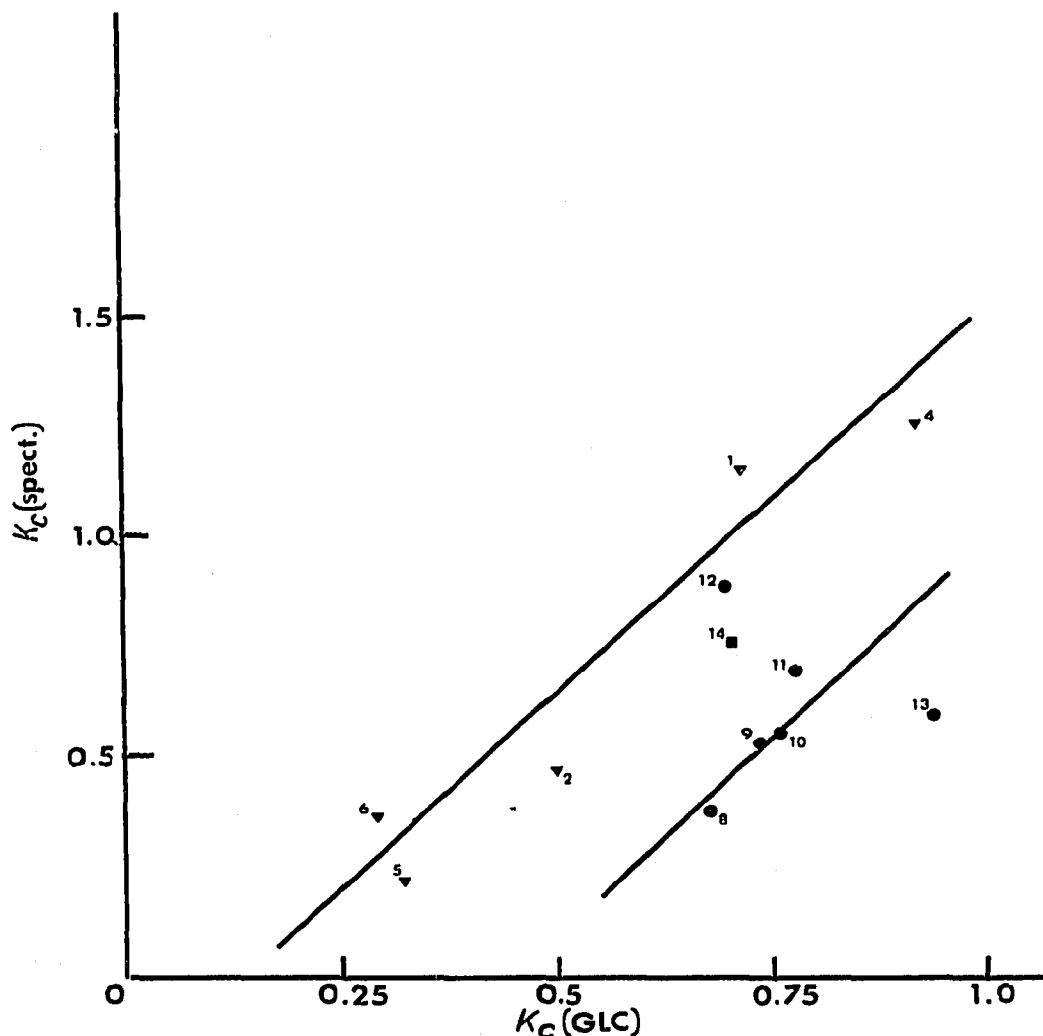


Fig. 3. The variation of the charge-transfer association constant for the substituted aniline-2,4,7-trinitrofluorenone system, K_c , measured spectroscopically at 4° in dichloromethane², with K_c values obtained by GLC for the 2,4,7-trinitrofluorenone-PPS system at 150° . Numbering as in Table I: ●, primary amines; ■, secondary amines, ▼, tertiary amines.

tion in these systems attempts to maintain these "normal" forces of solution constant and thus observe the variations in CT contributions.

Bond dipole moments are macroscopic measurements of solvent polarity and a polarity scale dependent upon microscopic solvent behaviour might be more appropriate to GLC data and CT interactions. The Z -values of KOSOWER¹⁰ are particularly pertinent to CT interactions and the relevant data for TTP and PPS are shown in Table III. On this scale also TTP is the more polar solvent even though relative Z -values do not necessarily correspond to other measurements of polarity for the more common solvents. All considerations of solvent interaction, polarity etc. suggest that competition for the donor occurs in the 2,4,7-trinitrofluorenone-TTP system.

A further indication of the greater solubility of the donors in TTP is given in Fig. 2 where $\log V_{\theta}^{180}$ for the 2,4,7-trinitrofluorenone system is plotted against $\log V_{\theta}^{180}$ for the additive systems. CT interaction should give rise to enhanced retention

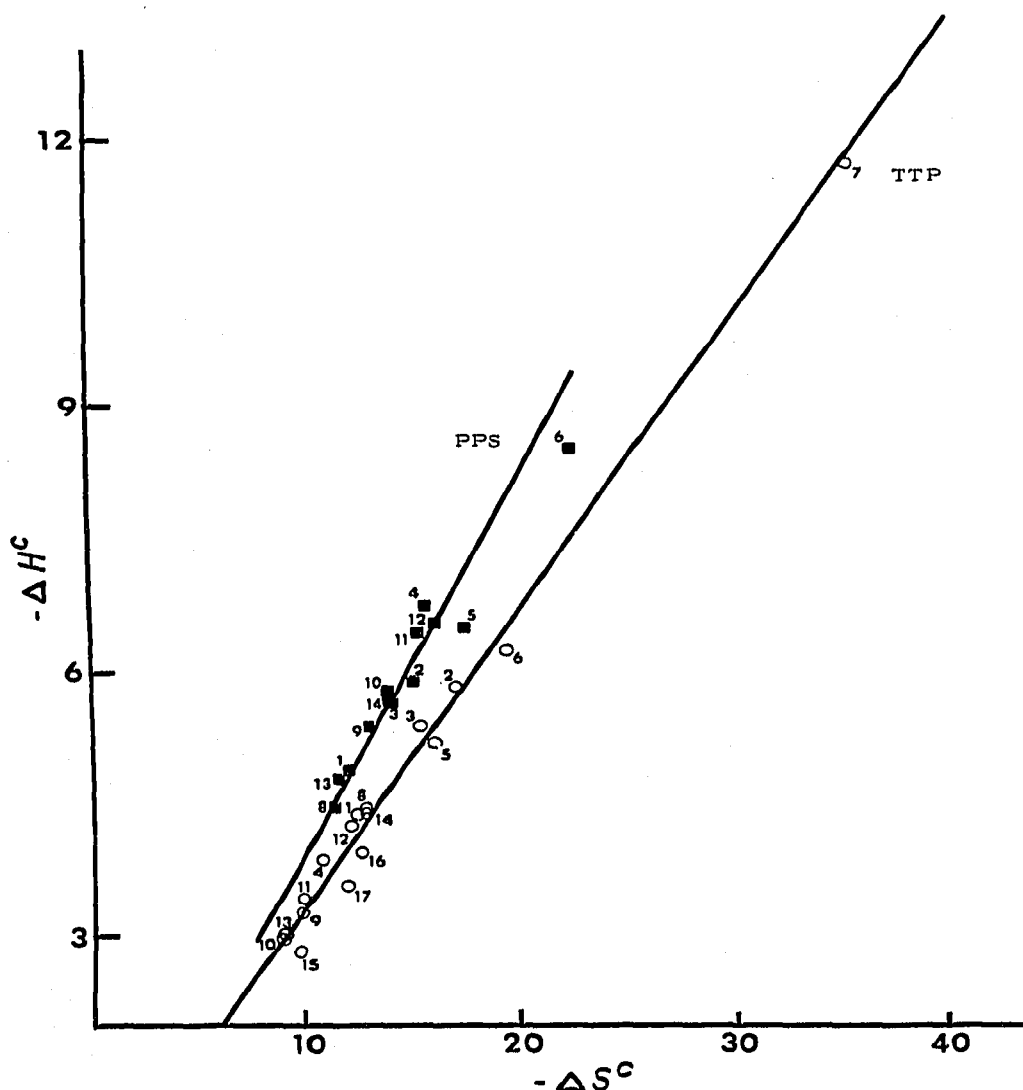


Fig. 4. Isokinetic relationships for the TTP and PPS systems. Values taken from Tables I and II; numbering as in Table I.

and for alkyl-substituted anilines this should increase as the number of alkyl groups, provided that steric factors are unimportant. Steric factors, however, are extremely important in these systems and donors having substituents around the N atom show greater solubility and stronger interaction with the binary stationary phase than with pure 2,4,7-trinitrofluorenone as stationary phase². This implies that the requirement of close approach of donor and acceptor to allow CT interaction is less easily satisfied in the additive-solvent system and supports DE MAINE'S suggestions of solvent aggregation around the acceptor additive¹². The deviation from linearity of the more bulky groups is more marked in TTP as solvent than in PPS, in accord with the entropy and enthalpy variations. These departures from linearity are measures of the depression of solubility produced by steric factors in the pure 2,4,7-trinitrofluorenone stationary phase, where CT forces form a significant contribution to the process of solution.

When the spectroscopic values for K_c , obtained by COOPER *et al.*² for the aniline-2,4,7-trinitrofluorenone complexes in dichloromethane, are plotted against the GLC values in PPS, two separate linear relationships are obtained as can be seen from Fig. 3. These results may be interpreted as indicating an additional interaction between the primary amines and the additive due to either hydrogen bonding or dipole-dipole interactions². The GLC determined K_c values are much greater than the spectroscopic values and, even though extrapolation over such a wide temperature range is very inaccurate, large differences exist if the two sets of results are compared at the same temperature. These differences do not arise from surface adsorption effects⁹ and the similar complexing order observed spectroscopically and by GLC does imply a similarity of interaction, *i.e.* CT.

The variations of excess enthalpy with excess entropy for the two systems studied are shown in Fig. 4. Small deviations from linearity occur for tertiary amine values in PPS as solvent, the entropy of mixing becoming increasingly unfavourable as the size of the alkyl group increases. Linearity of the isokinetic relationship is evident for primary amines in PPS, the CT interactions being superimposed upon other association mechanisms. Where steric effects are large (and unfavourable) CT effects are weak and deviations from the linear relationship occur. In TTP as solvent there is virtually no deviation from linearity, reinforcing our suggestions of only very weak CT interaction between 2,4,7-trinitrofluorenone and the donor amines. Within the donor series more negative heats of association tend to be compensated by more negative entropy terms, resulting in a levelling effect on ΔG^e . Large solute molecules have more negative partial molar entropies as would be expected.

Attempts to measure CT interactions by spectroscopic methods using TTP as solvent were only marginally successful¹. The values for K_c obtained were very low and no allowance made for the acceptor-solvent complex was made in these studies. A similar trend to that in dichloromethane² was observed for the few compounds studied and we are continuing work in this area. GLC results to date do confirm the improved separation obtained when using complexing additives and confirm that this improvement is a result of CT interaction.

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