Termolecular Complexes of Tetracyanoethylene with Weak Electron Donors

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Summary Association constants and molar absorptivities have been evaluated for 1 : 1 and 1 : 2 complexes of tetracyanoethylene with benzene, toluene, and *p*-xylene in heptane and carbon tetrachloride.

FOSTER and his co-workers[1,2] have presented evidence for both 1 : 1 and 2 : 1 molecular complexes of the strong electron donor, hexamethylbenzene, with several acceptors in carbon tetrachloride solution. They have shown that the presence of 2 : 1 complexes can account, at least in part, for many of the anomalies reported for association constants and related properties of electron donor–acceptor interactions. Confirmation of 2 : 1 complexes in the case of a strong donor raises important questions regarding the universality of higher-order complexes in systems of weak donors and acceptors, their effects on measured and computed properties of the systems, and the extent to which corrections for these higher-order complexes must be applied in order to obtain reliable thermodynamic quantities.

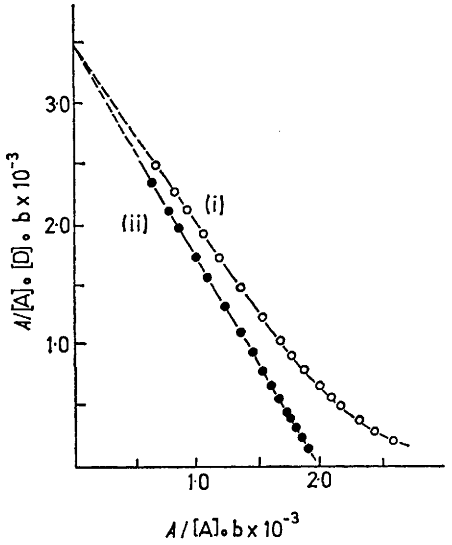

FIGURE. *Scatchard plots for the benzene–TCNE complex in heptane at* 20 °C. *Curve* (i): *experimental data points; curve* (ii): *after correcting for* 2 : 1 *complexes. The final point on each curve represents TCNE dissolved in pure benzene*

We have investigated complexes of tetracyanoethylene (TCNE) with the comparatively weak donors, benzene, toluene, and *p*-xylene in heptane and carbon tetrachloride solutions over a wide donor concentration range. These complexes were studied with a Cary 14 spectrophotometer by use of standard optical absorption methods.

Spectral data were first analysed in terms of the Scatchard[3] equation with the assumption of a simple 1 : 1 donor–acceptor interaction. Results of this treatment for the benzene–TCNE–heptane system are shown in the Figure [curve (i)]. The other mixtures gave analogous Scatchard plots. Such non-linear behaviour was observed by Foster[2] and shown to be consistent with the occurrence of both AD and AD_2 donor(D)–acceptor(A) complexes in which the absorptivity of AD_2 exceeds that of AD. On the basis of this model, 'best values' for association constants (K_{AD} and K_{AD_2}) and molar absorptivities (ϵ_{AD} and ϵ_{AD_2}) were computed by two independent procedures: a computer search method applied to a four-dimensional array covering plausible ranges for each of the variables (see ref. 2 for details), and a gradient search technique described by Bevington.[4] The two approaches yielded very similar results. As a further check, the K and ϵ values were used to compute the concentration and absorbance of AD_2 for each solution. The Scatchard equation was then re-plotted with $[A]' = [A]_0 - [AD_2]$ and $A' = A_{obs} - A_{AD_2}$ in place of the initial acceptor concentration and measured absorbance, respectively.

After correcting for AD_2, straight-line Scatchard plots similar to curve (ii) were obtained for each system. As seen from the Table, K^{corr}_{AD} and ϵ^{corr}_{AD} from the new plots are in excellent agreement with values obtained directly by the computer search techniques. In keeping with the trends reported for strong donor–acceptor interactions, association constants for these AD_2 complexes are 10 to 20 times smaller and their absorptivities about 1·5 times larger than the corresponding values for AD. Both K_{AD} and, to a lesser extent, K_{AD_2} decrease in going from heptane to

Association constants (l mol^{-1}) *and molar absorptivities* (l mol^{-1} cm^{-1}) *at the charge-transfer band maxima for complexes of tetracyanoethylene at* 20 °C

Solvent	$[A]_0$/M	$[D]_0$/M	K_{AD}[a]	ϵ_{AD}[a]	K_{AD}[b]	ϵ_{AD}[b]	K_{AD_2}[b]	ϵ_{AD_2}[b]	K^{corr}_{AD}[c]	ϵ^{corr}_{AD}[c]
Donor benzene										
C_7H_{16}	4×10^{-4}	0·27—11·25	1·49	2320	1·76 ± 0·08	1970	0·12 ± 0·03	3100	1·78 ± 0·08	1980
CCl_4	4×10^{-4}	0·22—11·25	0·90	2520	1·10 ± 0·05	2080	0·08 ± 0·02	3400	1·08 ± 0·05	2110
Donor toluene										
C_7H_{16}	8×10^{-4}	0·10—9·57	3·67	2040	3·98 ± 0·20	1870	0·22 ± 0·04	3020	3·99 ± 0·20	1900
CCl_4	8×10^{-4}	0·20—9·57	1·52	2610	1·88 ± 0·15	2110	0·18 ± 0·04	3150	1·92 ± 0·15	2040
Donor *p*-xylene										
C_7H_{16}	5×10^{-4}	0·07—8·11	8·52	1960	9·38 ± 0·40	1770	0·42 ± 0·08	2650	9·37 ± 0·40	1780
CCl_4	5×10^{-4}	0·07—8·11	3·96	2120	4·63 ± 0·20	1820	0·39 ± 0·08	2670	4·64 ± 0·20	1800

[a] From assumption of a simple 1 : 1 interaction. [b] From computer search procedures. [c] From Scatchard plots corrected for 2 : 1 complexes.

carbon tetrachloride, where solvent–solute interactions compete with the TCNE–donor equilibria.

Recently, the need to consider donor activities in treatments of molecular complex systems has been re-emphasized.[5] Inclusion of donor activity coefficients for these mixtures would lead to increased curvature of the Scatchard plots and require even more extensive corrections for higher order complexes than those given here.

Because of the large number of potential interactions in mixtures of this type it is probable that no single explanation adequately accounts for all the observed anomalies. However, insofar as these systems are representative of weak electron donor—acceptor interactions, the presence of higher-order complexes is indeed a widespread phenomenon. Unless otherwise demonstrated, multiple equilibria should be anticipated and included in the mathematical model to ensure a meaningful thermodynamic treatment. From the Figure it is clear that an uncorrected 1:1 association constant computed even at low donor concentrations, where an apparent straight-line plot normally occurs, still differs from the "true" K_{AD}.

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