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Polymeric Charge-transfer Complexes

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Research results on polymeric donor-acceptor complexes both in the solid state and in solution are summarised. Solid polymeric charge-transfer complexes (crystals, films) are semiconducting materials satisfying the requirements of various branches of science and technology. Study of such complexes in solution reveals several specific features of complex formation in polymer systems and approaches an explanation of the electrophysical characteristics of layers of these complexes in terms of the mechanism of complex formation in solution. A brief account is given of the theory of charge-transfer complexes. Methods for determining and calculating the equilibrium constants of the polymeric complexes are critically examined. A list of 172 references is included.

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I. INTRODUCTION

According to modern ideas charge-transfer complexes are compounds formed by the interaction of two valency-saturated molecules—an electron donor D and an electron acceptor A—the former possessing a filled molecular orbital of quite high energy and a low ionisation potential, while the acceptor has a fairly low vacant molecular orbital and considerable electron affinity[1-7]. The transfer of charge from donor to acceptor forms an intermolecular donor-acceptor bond, probably together with various other types of interaction, including polarisation, dipole-dipole, and also van der Waals forces[8].

The properties and the structure of charge-transfer complexes depend in considerable measure on which donor and acceptor orbitals are involved in forming the intermolecular bond. This principle constituted the basis of Mulliken's classification of these complexes[9], in which he divided all donors into three groups—n, σ, and π— according to a structural criterion. The energetically highest orbital in the first group is a lone pair of n-electrons of a heteroatom (R_2O, R_2S, R_3N, etc.), in the second group the electron pair forming an σ-bond (R-Hal), and in the third group a pair of π-electrons in an unsaturated or an aromatic compound. Acceptors are also divided into three groups—v, σ, and π— containing as lowest molecular orbitals respectively a vacant v-valent orbital of the metal atom (metal halides, certain organometallic compounds), a non-bonding σ-orbital (molecular iodine and bromine, iodine monochloride, etc.), and a system of π-bonds (aromatic and unsaturated compounds containing electron-accepting substituents).

Typical organic acceptors-nitro-derivatives of hydrocarbons, anhydrides and chlorides of di- and poly-carboxylic acids, cyano-derivatives of hydrocarbons, and also quinones and their derivatives—belong mainly to the third group Typical organic donors are present in all three groups in Mulliken's classification.

Combining these types of compounds gives a whole variety of donor-acceptor complexes:

nv ($R_2O \cdot MX_3$)	σv ($RX \cdot MX_3$)	πv ($ArH \cdot MX_3$)
$n\pi$ ($R_2O \cdot ArH$)	$\sigma\sigma$ ($RX \cdot I_2$)	$\pi\sigma$ ($ArH \cdot I_2$)
$n\sigma$ ($R_2O \cdot I_2$)	$\sigma\pi$ ($RX \cdot ArH$)	$\pi\pi$ ($Ar_1H \cdot Ar_2H$) .

At the present time $\pi-\pi$ and $\pi-\sigma$ complexes have been most thoroughly studied, whereas the smallest amount of work has been done on complexes with σ-donors.

Brieglev and Checalla divide charge-transfer complexes into strong and weak[10]: the weaker the donor and acceptor properties of the components, the smaller the gain in energy when they interact, the smaller the fraction of charge transferred, and hence the weaker the complex. The tendency to donor-acceptor interaction increases with decrease in the difference $I_D - E_A$ between the ionisation potential and the electron affinity of the molecules[10]. With very strong donors and acceptors complete transfer of an electron from donor to acceptor is possible in the ground state, with the formation of compounds termed strong complexes or radical-ion salts.

Blyumenfel'd et al. divide charge-transfer complexes into weak and strong on the basis of the decisive role of polar states in the appearance of paramagnetism and current carriers[11]. McConnell's classification of complexes into strong (ionic) and weak (non-ionic) is based on the type of packing of the molecules in crystals[12].

II. THEORY OF CHARGE-TRANSFER COMPLEXES

The most characteristic criterion of the formation of a charge-transfer complex is the appearance of a charge-transfer band, in addition to the absorption bands due to the initial components, in the electronic spectrum. The attempt to explain this band led to the development of several theories of donor-acceptor interaction[14-17], among which Mulliken's quantum-mechanical theory[1,13,18-22], which he developed for weak charge-transfer complexes, is now generally accepted. In this theory the ground state of an equimolecular charge-transfer complex is described by a wave function ψ_N, which can be represented approximately by a linear combination of two functions:

$$\Psi_N = a\Psi_0(D, A) + b\Psi_1(D^+ - A^-) \quad (1)$$

where ψ_0 is the wave function corresponding to the structure of the complex with van der Waals interaction (the wave

function of the non-bonded state), and ψ_1 is the wave function of the dative (bonded) state. With weak complexes $a \gg b$, and with strong complexes $b > a$. The lowest excited state of the complex is described by the wave function ψ_E, also a linear combination of wave functions ψ_1 and ψ_0 corresponding to the ionic and neutral states:

$$\Psi_E = a^*\Psi_1(D^+ - A^-) - b^*\Psi_0(D, A)\,. \qquad (2)$$

For weak complexes $a^* \simeq a$ and $b^* \simeq b$. Transition of the complex from the ground to an excited state is responsible for the appearance of the additional band in its absorption spectrum. The energy of such a transition is

$$E_{chtr} = h\nu_{chtr} = W_E - W_N\,. \qquad (3)$$

Fig. 1 gives a diagram of the energy transitions for weak charge-transfer complexes[30].

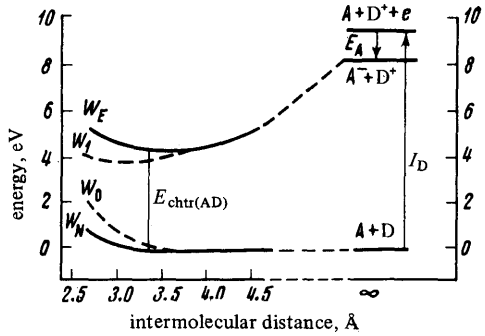


Figure 1. Energy relations of weak charge-transfer complexes between a donor D and an acceptor A, where W_N is the energy corresponding to the ground state of the wave function $\psi_{N(AD)}$ and W_E is the energy corresponding to an excited state of the wave function $\psi_{E(AD)}$, with W_0 and W_1 the corresponding energies in the absence of resonance stabilisation, and $E_{chtr(AD)}$ the energy of the optical intermolecular transition with transfer of charge[22].

The quantum-mechanical expression for the charge-transfer energy is

$$E_{chtr} = h\nu_{chtr} = \frac{(W_1 - W_0)}{(1 - S_{01}^2)}\left[1 + \frac{4\beta_0\beta_1}{(W_1 - W_0)^2}\right]^{1/2} \qquad (4)$$

where W_1 and W_0 are the energies of the dative and non-bonded structures,

$$S_{01} \equiv \int \Psi_0\Psi_1 d\tau$$

is an overlap integral, and

$$\beta_0 = (H_{01} - S_{01}W_0), \quad \beta_1 = (H_{01} - S_{01}W_1), \quad H_{01} = \int \Psi_0 H \Psi_1 d\tau,$$

where H is the Hamiltonian for the whole system of nuclei and electrons. Mulliken showed that, for interaction to occur between the structures ψ_0 and ψ_1, both S_{01} and H_{01} should differ from zero, which means that, in all cases other than strong spin–orbital coupling, the functions ψ_0 and ψ_1 have the same spin. He confirmed by quantum-mechanical calculations that electron transfer takes place with retention of spin.

Phenomenological examination of the transfer of charge leads to the formula

$$h\nu_{chtr} = I_D - E_A - \frac{e^2}{R_{D^+,A^-}} \qquad (5)$$

where I_D is the ionisation potential of the donor, E_A the electron affinity of the acceptor, and $e^2/R_{D+,A-}$ the Coulombic attraction.

Many empirical equations for the energy of charge transfer in complexes of different donors with a particular acceptor have the general form[23]

$$h\nu_{chtr} = cI_D - e_A \qquad (6)$$

where c and e_A are constants.

Further advances in the theory of charge-transfer complexes entail the description of the energy of complex formation by the method of molecular orbitals[24] and also the application of the free-electron model to these complexes[25].

III. CHARGE-TRANSFER COMPLEXES BASED ON POLYMERS AND THEIR ELECTROPHYSICAL PROPERTIES

Numerous research results on the properties of donors and acceptors, conditions for the preparation of pure charge-transfer complexes, and their structure, stability, and role in organic reactions and biochemical processes have been summarised in monographs[1–5,26]. Special mention need be made only of work during recent years on the use of such complexes as initiators in the polymerisation of monomers exhibiting donor properties, e.g. *N*-vinylcarbazole[27–36] and propylene sulphide methylthi-iran[37].

Special attention has been paid to investigating the semiconductor properties of charge-transfer complexes[38–42]. The complexes exhibit exhanced electrical conductivity[43–46], the activation energy of which (1.5–0 eV) varies linearly with the energy of charge-transfer[45–47]. The theoretical and practical interest in new highly conducting materials has recently stimulated a great development of work on charge-transfer complexes based on polymers. The principle of introducing a polymeric molecule into the complex has been used for example, to prepare a series of chelate compounds, with polymeric phthalocyanine[48], polypyromellitimide[49], and polymeric tetracyanoethylene[50] as ligands. Interest in polymeric complexes is connected with the possibility of improving the conductance by increased intermolecular interaction on complex formation by chain molecules[51] and with use of the film-forming properties of polymers in semiconductor technology.

All the polymeric donors studied can conveniently be classified according to the structure of the repeating unit: (I) polystyrene and its derivatives; (II) polymers with aromatic ring systems in a side-chain; (III) polymers with a heteroatom (usually a nitrogen atom) in a side-chain; and (IV) polymers having a conjugated system in the main chain (Table 1). The acceptors usually studied have been benzoquinone derivatives (chloranil, bromanil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and 7,7,8,8-tetracyanoquinodimethane), 1,3,5-trinitrobenzene, silver perchlorate, molecular bromine and iodine, and tetracyanoethylene.

All the complexes (Table 1) exhibit an exponential temperature dependence of electrical conductivity:

$$\sigma = \sigma_0 \cdot \exp(-\varepsilon/kT) \qquad (7)$$

where ϵ is the activation energy, which has values of 0.8–0 and 1.5–0.01 eV according to Knoesel[52] and Paushkin[53] respectively. The corresponding conductivity ranges are

5×10^{-2}–3×10^{-14} [52] and 10^{-2}–10^{-15} [53] $ohm^{-1}\ cm^{-1}$. Radical-ion salts of tetracyanoquinodimethane possess the highest conductivity[69,74], as also charge-transfer complexes based on polymers having a conjugated system[69,75–79,83]. In most cases a parallelism is observed between the electrical and magnetic properties of charge-transfer complexes having the character of radical-ion salts.

Table 1. Charge-transfer complexes based on polymeric donors.

Polymeric donor	Acceptor	Ref.
	Group I	
Polystyrene	tetracyanoethylene	54, 55
Polystyrene	chloranil	54
Polystyrene	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	54
Polystyrene	silver perchlorate	54
Polystyrene	iodine, bromine	56
Poly-*p*-dimethylaminostyrene	chloranil, bromanil	57, 58–60
Poly-*p*-dimethylaminostyrene	7,7,8,8-tetracyanoquinodimethane	61–63
Polyvinyltoluene	iodine, bromine	56
Styrene–α-methylstyrene copolymer	iodine, bromine	56
Styrene–2-vinylnaphthalene copolymer	iodine, bromine	56
Polyvinylmesitylene	tetracyanoethylene, chloranil, dichlorodicyano-*p*-benzoquinone	54
	Group II	
Polyvinylnaphthalene (atactic)	tetracyanoethylene, chloranil	54, 65
Polyvinylnaphthalene (atactic)	dichlorodicyano-*p*-benzoquinone	54
Polyvinylnaphthalene (atactic)	tetracyanoquinodimethane	63
Polyvinylnaphthalene (atactic)	1,3,5-trinitrobenzene	65
Polyvinylnaphthalene (isotactic)	chloranil	54
Polyvinylanthracene	trinitrobenzene, iodine, bromine	66
Polyacenaphthylene	tetracyanoethylene, chloranil	54, 67
Poly-2-vinylnaphthalene	tetracyanoquinodimethane	62
Poly-2-vinylnaphthalene	various	62
	Group III	
Poly-4-vinylpyridine	various	69
Poly-4-vinylpyridine	tetracyanoquinodimethane, antimony pentachloride	70, 64
Poly-4-vinylpyridine	iodine	68
Poly-4-vinylpyridine	chloranil, iodine, tetracyanoquinodimethane	74
Poly-2-vinylpyridine (atactic)		
Poly-2-vinylpyridine (isotactic)	tetracyanoquinodimethane	74, 63
Poly-*N*-vinylcarbazole	tetracyanoquinodimethane	71
Poly-*N*-vinylcarbazole	antimony trichloride, iodine	72
Poly-*N*-vinylcarbazole	iodine	73
Poly-*N*-vinylcarbazole	tetracyanoethylene, chloranil, trinitrobenzene	65
	Group IV	
Polydiphenylamine	tetracyanoethylene, chloranil, iodine	75
Polymeric Schiff bases	iodine, bromine	76
Polyphenylenes	iodine	77
Polyethynylnaphthalene	tetracyanoquinodimethane, iodine	78
Radiation-thermal polyethylene	iodine	81
Polyphenylacetylene	iodine	80
Polyethynylpyridine	tetracyanoquinodimethane	69

Studies have been made not only on the systems listed in Table 1 but also on charge-transfer complexes from polymers obtained by polycondensation, polymers containing ferrocene (with iodine, picric acid, and tetracyanoethylene as acceptors)[82], polyesters of aryliminodiethanols (with tetracyanoethylene, chloranil, and dichlorodicyano-*p*-benzoquinone)[83], and albumen (with chloranil)[84]. Systems have also been examined in which the polymer was an electron acceptor, while a compound of low molecular weight served as donor[85], e.g. complexes of poly-2,4-dinitrostyrene with amines[55]. Stable charge-transfer complexes possessing semiconductor properties have been reported[86] from the copolymerisation of monomers having strongly electron-accepting groups (trinitrostyrene) and electron-donating groups (4-vinylpyridine, *p*-dimethylaminostyrene). Among the most interesting polymers are polyphenylenaminochloranils, which contain both electron-donating and electron-accepting groups in the macromolecular chain[87].

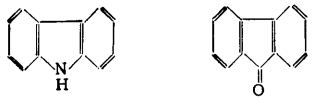
Highly photoconducting systems are of the greatest interest among polymeric semiconductors[88]. Although all insulators and semiconductors are photosensitive, the number of substances suitable for practical use as photosemiconductors is extremely limited. The reason is that many factors governing the photosensitivity of a substance depend on defects in its crystal structure, and only in certain materials and structures is the nature of these defects such that the excited current carriers are sufficiently long lived[88]. Polymers, in particular, are characterised by an immense number of defects in the solid state (regions of differing orientations of crystallites, irregularities in the packing of sheets and strips, etc.). The photosensitivity of many polymers has been studied, including polyconjugated polymers[83], biopolymers[89], polystyrene[90], and polyvinylcarbazole[91]. The mechanism of photoconduction in polymers probably involved as first step excitation of the macromolecule by an absorbed photon, followed by migration of the excited state (exciton) until it encounters a structural or chemical defect, on which a free pair of photocurrent carriers is formed[92].

Polyvinylcarbazole obtained in the presence of a Lewis acid as initiator is more strongly photosensitive than is the thermal polymer[91]. Thus the photosensitivity of the polymer is sensitised by the formation of a charge-transfer complex between the acceptor (the Lewis acid) and the electron donor (the polymer). It has been reported that various chemical compounds sensitise several polymers[91], in particular polyacenaphthylene[93], polyvinylpyridine[74], polystyrene[90], polydiphenylbutadiyne[94], β-iodophenylacetylene[95], and polyvinylcarbazole, which has been the most thoroughly studied during recent years[96–100]. This last polymer possesses thermoplasticity, forms photosensitive, transparent films, and currently finds practical application in electrophotography[91,101–105] (this process consists in producing an electrostatic image in the photosensitive memory layers and then developing it with dyes[106–108]).

A fundamental aspect of the study of the functioning of polymeric charge-transfer complexes under electrographic conditions is to ascertain the mechanisms of complex formation and of photoconduction. Weigle, for example, considers that, on excitation with a light quantum, the complexes inject holes into the valency band of the polymer, whose chains become conducting[109]. Hoegl discusses the mechanism of photoconduction in terms of the types of donor and acceptor[91]. However, the plethora of polymer systems has hitherto prevented the development of a unified view on the mechanism of photoconduction. An important problem is to establish a correlation between the photoconductance and the physicochemical properties of the components of the electrographic layer as well as its structure. Many authors relate the photoconductance to the electronic properties of the acceptor. Thus Meier and Albrecht[110] studied the effect of electron acceptors on the photosensitivity of thin *p*-type merocyanine and phthalocyanine films, and found only a rough correlation between the electron affinity of an acceptor and its ability to sensitise photoconduction. Smith and Weigle[111] tried to correlate spectral photosensitivity with the electron affinity of the acceptor. They conclude in a series of papers that the photosensitivity and the stability of charge-transfer complexes are influenced not so much by the electron affinity as by the spatial dimensions of the components. Thus the complexes of two similar π-systems are more stable than those formed by a donor and an acceptor differing in size[112]. Pyrene forms stronger complexes with tetracyanoquinodimethane than with tetracyanoethylene (K = 78.4 and 29.5 M^{-1}). Hayashi et al. found that the sensitising power of acceptors of the series

—*p*-benzoquinone, 1,4-naphthaquinone, 9,10-anthraquinone—diminishes with increase in their electron affinity[97]. Since these acceptors differ comparatively little in electron affinity (0.5, 0.7, and 0.77 respectively), the size of the π-system is an important factor in their sensitising power. This may be an indication that the stability constant of the complex is a more important parameter in the choice of an effective additive for a given electron-donating photoconductor than is the electron affinity of the acceptor.

Interesting results were obtained by Wagner and Gasner[113], who studied the photosensitivity of polyvinylcarbazole with several acceptors, including nitro-derivatives of fluorenone, an important feature of whose structure (II) is its similarity to that of carbazole (I):



(I) (II)

All the fluorenone derivatives, while differing in electron affinity, fitted on a straight line when the rate constant of the decay of the photocurrent was plotted against electron affinity, whereas points departing from the correlation, and enclosed by the full line in Fig. 2, correspond to acceptors differing in molecular size of the carbazole unit. Thus the photoconductance correlates with the electronic properties of the acceptor only in a homologous series of acceptors with the steric factors of the components taken into account. No correlation is found[114] between the thermodynamic characteristics of charge-transfer complexes of polyvinylcarbazole and of polystyrene with various acceptors and the photoelectric sensitivity under electrographic conditions.

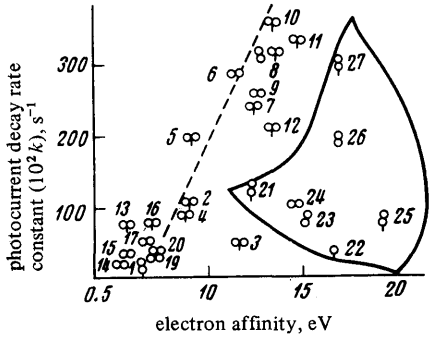


Figure 2. Dependence of photocurrent decay rate constant in charge-transfer complexes of polyvinylcarbazole on electron affinity of a series of acceptors[113]: *1*)–*20*) nitrofluorenone derivatives; *21*) 3,3′,5,5′-tetramethyldiphenoquinone; *22*) *o*-chloranil; *23*) *p*-chloranil; *24*) 2-dicyanomethylenindane-1,3-dione; *25*) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; *26*) tetracyanoethylene; *27*) 7,7,8,8-tetracyanoquinodimethane.

Recently investigators have increasingly arrived at the conclusion that the photosensitivity of a layer should be influenced by its physical macrostructure. Kryszevski, for example, regards all structural defects as traps within a forbidden energy band[115,116]. Electron microscopy has shown the appearance of supermolecular structures of dendritic type in films of charge-transfer complexes based on poly(phenyl methacrylate), poly-(2-naphthyl methacrylate)[117], polyvinylcarbazole, and polystyrene[118]. Such dendritic structures are absent from films of pure polymers. The formation of supermolecular structures is attributed to the increase in chain rigidity of polymeric charge-transfer complexes during complex formation in solution.

IV. PHYSICAL CHEMISTRY OF POLYMERIC CHARGE-TRANSFER COMPLEXES IN SOLUTION

The technology of the production of electrographic layers based on polymeric charge-transfer complexes involves solutions of polymers, so that a study of molecular aspects of the formation of such complexes in solution followed by interpolation of the results into the solid complexes is of great theoretical and practical value. A fair number of publications on the chemistry of polymeric charge-transfer complexes in solution have appeared recently.

In a study of the formation of complexes by poly-2-vinylpyridine and by its styrene copolymer with halide ions in 0.5*N* sulphuric acid Slough[119] noted that both π- and n-charge transfer is possible in heteroaromatic systems, so that they yield stronger complexes than do purely aromatic systems. The intensity of the charge-transfer band at 280–400 nm increased in the sequence—chloride < bromide < iodide—in parallel with the polarisability of the halide ions. The differing force of interaction of ions with a polymer can be used for the production of selectively anion-permeable membranes[120].

Klöpffer and Willicks[121] made a broad spectroscopic investigation of complexes formed by several polymeric donors and by their low-molecular weight analogues with various electron acceptors. Complexes of tetracyanoethylene with poly-10-methyl-3-vinylphenothiazine and with *N*-methylphenothiazine have a double absorption band in the region of 9600 cm^{-1}, which they attribute to splitting of the energy level of the donor in the ground state, so that two ionisation potentials are observed. The complex of poly-*p*-dimethylaminostyrene with tetracyanoquinodimethane exhibits in solution a double band in the range 11 750–13 200 cm^{-1}, which is assigned to the radical-anion of the acceptor. Absorption bands in the range 25 000–23 800 cm^{-1} for the complex formed by the same polymer with tetracyanoethylene indicate the formation of a pentacyanopropanide anion, a conversion product of the radical-ion of tetracyanoethylene. The band in the region of 25 600 cm^{-1} in the spectrum of the complex of this polymer with dichlorodicyano-*p*-benzoquinone is also ascribed to absorption by the radical-anion of the acceptor. The stability of the complexes is not always determined by the difference $I_D - E_A$: thus the ionisation potential of poly-10-methyl-3-vinylphenothiazine (7.0 eV), which forms only a weak complex with tetracyanoethylene, is lower than that of poly-*p*-dimethylaminostyrene (7.2 eV), which gives a strong radical-ion complex with the same acceptor. This is probably due to a difference between the energies of polarisation of individual states.

In a study of radical-ion salts Japanese investigators found[70,74] that tetracyanoquinodimethane (TCQDM) forms with polyvinylpyridines two types of complexes—simple $H^+(TCQDM)_2^-$ and double $BH^+(TCQDM)_2^-$—where B is the radical of the organic base. The absence from the ultraviolet spectra of the absorption band due to the neutral acceptor indicates that the molecule and the radical-anion of the

acceptor form an intermolecular bond in the double complex and add to the same unit in the polymer. The ratio $\epsilon_{\lambda 842}/\epsilon_{\lambda 395}$, where $\epsilon_{\lambda 842}$ and $\epsilon_{\lambda 395}$ are the extinction coefficients of the radical-anion and of the molecule respectively, shows that only every fourth unit of the polymer forms the double complex. When the complexes are kept in the air, $\epsilon_{\lambda 395}$ decreases, while the ratio increases, which corresponds to conversion of the double into the simple complex[70].

In a spectrophotometric study of complexes of poly-*p*-dimethylaminostyrene with chloranil Knoesel[58] observed that in freshly prepared solutions the charge-transfer bands for complexes of this polymer and of its low-molecular analogue coincide, but after some time the band due to the polymeric complex shifts to the red range. This was explained by compaction of the packing of the acceptor between donor groups of the polymer, a phenomenon on which the authors termed "the polymer effect". The displacement of the charge-transfer band of this polymer with chloranil and also with dichlorodicyano-*p*-benzoquinone was confirmed by Klöpffer[121].

Hallensleben isolated[122] and studied[123] complexes of poly-4-vinylpyridine with tetracyanoethylene in solution in methanol and in chlorinated hydrocarbons. The variation in the ultraviolet spectra of the complexes correlated with the time variation of the viscosity. At low polymer concentrations the viscosity tended to constant values, and at high concentrations passed through a maximum. The extinction coefficients of solutions of the complex increased to a constant value. The experimental results were explained by conformational changes in the macromolecular chain on interaction with the acceptor.

Zwick's spectrophotometric study of complexes of polyvinyl alcohol with iodine in the presence of boric acid is distinguished by its elegance and completeness[124]. He showed that the position of the principal absorption maximum of the complex in the range 580–700 nm depends on the relative concentrations of iodine ions, boric acid, and polymer, as well as on the temperature, which is all evidence of the complexity of the process. In the presence of boric acid the polyvinyl alcohol molecule emerges from the coiled conformation and forms helices, which associate and finally crystallise, during which process the channels within the helices of the polymer molecule fill with polyiodide chains and become longer and more regular, all these changes being accompanied by a characteristic blue coloration. A limiting intensity of colour is reached when one iodine molecule is associated with 24 monomer units (two turns of the helix) in the polyvinyl alcohol macromolecule.

The thermodynamics of complex formation in polymer systems was not considered in the work discussed above, although the thermodynamic properties of the lower-molecular-weight charge-transfer complexes have been studied very carefully[1–6]. The most important thermodynamic characteristic of complex compounds in general and of macromolecular compounds in particular is the equilibrium (instability, stability) constant, which is a measure of the free energy of complex formation, although the reliability of this parameter is disputed in several cases (Ref. 5, p.383).

Equilibrium constants of polymeric charge-transfer complexes (formed by iodine with polystyrene and with rubber) were first determined by Evans by the Benesi-Hildebrand method[126], earlier used for low-molecular-weight complexes. According to Evans equilibrium constants and extinction coefficients have the same values for polymers as for model compounds (ethylbenzene, propylbenzene, *cis*- and *trans*-butenes) owing to the isolation of the electron-donor groups in the polymer and the absence of additional steric hindrance in the polymer complexes.

Kryszewski[127] obtained different equilibrium constants for complexes of polymers and of their low-molecular analogues with silver perchlorate. The equilibrium constants for charge-tranfer complexes of atactic and isotactic polystyrene and poly-α-methylstyrene with iodine are respectively 0.14, 0.18, and 0.26 M^{-1}; those for toluene, benzene, styrene, and ethylbenzene agree well with Evan's results[126] and are respectively 0.16, 0.14, 0.15, and 0.17 M^{-1}. It is assumed that complexes of various configurations are formed in solution, the least symmetrical of which is unstable. Therefore complexes based on low-molecular analogues and atactic polystyrene possess the lowest equilibrium constants. In conformity with the theory of contact charge-transfer[128] lower intensities of absorption correspond to higher stability constants:

$$K_{\text{pst,atact}} < K_{\text{pst,isotact}} < K_{\text{pamst}} \cong \epsilon_{\text{pst,atact}} > \epsilon_{\text{pst,isotact}} > \epsilon_{\text{pamst}} .$$

It was shown spectrophotometrically that charge-transfer complexes of *p*-benzoquinone with nitrogen-containing monomers, such as poly-2- and 4-vinylpyridines, poly-2-methyl-5-vinylpyridine, and poly-*NN*-dimethylmethacrylamide, are more stable than the corresponding complexes of their model compounds[120]. However, Markova[69] found from kinetic data that the equilibrium constant for the complex of poly-4-vinylpyridine with tetracyanoethylene is rather smaller than that for 4-ethylpyridine (0.5 and 0.6 M^{-1}). Rembaum et al. studied the charge-transfer complexes of *N*-ethylcarbazole and poly-*N*-vinylcarbazole with tetracyanoethylene in dichloromethane (K = 5.83 and 1.3 M^{-1}), and attributed the lower equilibrium constant for the polymeric complex to steric hindrance in the polymer chain[130]. A similar explanation is given for the complexes of polystyrene and polyvinylcarbazole with quinonoid acceptors, which have smaller equilibrium constants than those of the complexes of model analogues—ethylbenzene, cumene, *N*-isopropylcarbazole[131].

Smets et al. studied complexes formed by polyvinylcarbazole, poly-2-vinylnaphthalene, poly-2-naphthylmethylene, and their simple analogues with several organic acceptors[65]. The equilibrium constants were always smaller for the polymeric complexes than for the model compounds. This relation was preserved even when the constants were determined by nuclear magnetic resonance[132].

An original approach to polymeric donor-acceptor complexes was adopted by Braun and Sterzel[133], who studied the formation of donor-acceptor complexes of a styrene-*p*-dimethylaminostyrene copolymer with chloranil and with dichlorodicyano-*p*-benzoquinone, and found the equilibrium constants calculated by the Benesi–Hildebrand method to be functions of the copolymer composition, the highest values being observed for the complex of the copolymer containing 80 mole % of *p*-dimethylaminostyrene (Fig. 3). From these results it was concluded that the thermodynamic parameters (equilibrium constant $\overline{K}$ and free energy of formation of the complex ΔG) are significantly affected by solvation of donor, acceptor, and complex. On complex formation the mobility of the polymer chain diminishes, the entropy decreases, and hence the absolute value of ΔG increases. The equilibrium constants for the complexes with dichlorodicyano-*p*-benzoquinone exceed those for the chloranil complexes by factors of 10^4–10^5, which is attributed to the difference in electron affinity between these acceptors (1.95 and 1.37 eV respectively).

Iwatsuki and Arai[134] used complexes of the same copolymer with several acceptors (chloranil, trinitrotoluene, iodine, maleic anhydride) to elucidate the "polymer effect".

They observed a bathochromic shift in the charge-transfer band maximum and an increase in the equilibrium constant with lengthening of the continuous sequence of *p*-dimethylaminostyrene units and increase in their mole fraction in the copolymer (Fig. 4). The bathochromic shift was attributed to a fall in the ionisation potential *I* of the polymeric donor resulting from $\pi-\pi$ interaction of the dimethylaniline groups with the phenyl rings. The two-stage character of the variation in equilibrium constant was ascribed to the contribution by the energy of Brownian movement of the polymer chain of the donor to the total free energy of complex formation.

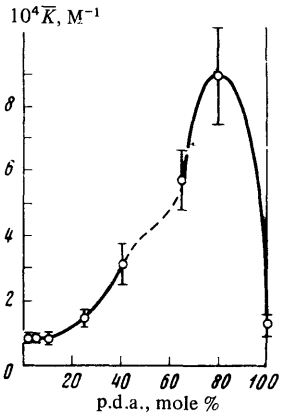


Figure 3. Dependence of equilibrium constant $\bar{K}$ on *p*-dimethylaminostyrene (p.d.a.) content of its styrene copolymer with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as acceptor and cyclohexanone as solvent[133].

The influence of conformational changes in the macromolecular chains on complex formation has been examined[114,135]. Complexes formed by polystyrene, poly-α-methylstyrene, and polyvinylcarbazole of various molecular weights with several quinonoid acceptors and with tetracyanoethylene showed that the temperature dependence of the equilibrium constant depends on the molecular weight of the polymeric donor. With polymers of comparatively low molecular weight (e.g. polyvinylcarbazole having $\bar{M}_n$ = 1000) the equilibrium constants of the complexes decrease with rise in temperature, as with simple charge-transfer complexes. Complexes of polymers of intermediate molecular weight (polyvinylcarbazole with $\bar{M}_n$ = 30 000) the constants vary very little with temperature. Charge-transfer complexes of polymers of high molecular weight (polyvinylcarbazole with $\bar{M}_n$ = 460 000, polystyrene with $\bar{M}_n$ = 10 000–860 000) have equilibrium constants which increase with rise in temperature (Fig. 5). The occurrence of conformational transitions in polystyrene, polyvinylcarbazole, and their charge-transfer complexes in solution is confirmed by the temperature dependence of the dielectric loss angle. For the temperature variation of the conformation of polymers and the effect of these conformational transitions on complex formation these workers conclude that the van't Hoff method for calculating change in enthalpy during complex formation is incorrect when high molecular weights characterise one or both components. Methods ensuring isothermal experimental conditions, e.g. microcalorimetry in solution, must be used to determine the enthalpies of such processes.

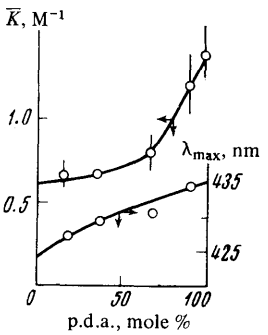


Figure 4. Dependence of $\bar{K}$ and λ_{max} of charge-transfer complex of styrene–*p*-dimethylaminostyrene copolymer with maleic anhydride on composition of copolymer in benzene as solvent[134].

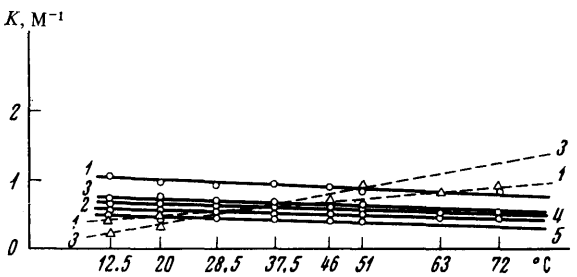


Figure 5. Temperature dependence of equilibrium constants in dichloroethane of charge-transfer complexes of polyvinylcarbazole varying in molecular weight M_n: –o–) 30 000; –Δ–) 460 000 with several acceptors: *1*) tetracyanoethylene; *2*) 7,7,8,8-tetracyanoquinodimethane; *3*) chloranil; *4*) bromanil; *5*) fluoranil[135].

Kinetic investigations of polymeric charge-transfer complexes have begun recently. Boudevska and Neitchev[137] used the "stopped flow" spectrometric method to study the kinetics of complex formation by tetracyanoethylene with polyvinylcarbazole, poly(naphthyl methacrylate), and the corresponding simple analogues in chloroform solution. All the complexes showed high rate constants ($\sim 10^4$ + M^{-1} s^{-1}), which were independent of the molecular weight of the donor. The rate constants of complex formation by tetracyanoethylene with polyvinylcarbazole and with *N*-ethylcarbazole were somewhat higher than with poly(naphthyl methacrylate) and naphthyl methacrylate, from which it was concluded that the rate of complex formation depended on the electron-donating power of the complexing unit.

The reversibility of the equilibrium of polymeric donor-acceptor complexes can be utilised for the chromatographic separation of complicated mixtures of chemical compounds, in particular to separate nitrated polystyrene[125].

Table 2.

Donor	Donor concn., M	Acceptor	Acceptor concn., M	K_{eq}, M^{-1}	ε_{max}	$\delta_0 - \delta_{AD}$ n.m.r.	Solvent	Ref.
N-Ethylcarbazole	$4.0\cdot10^{-2}$—$9.6\cdot10^{-2}$	tetracyanoethylene	$2.0\cdot10^{-3}$	5.85 20°	1090			130
Polyvinylcarbazole	$3.1\cdot10^{-2}$—$6.2\cdot10^{-2}$	tetracyanoethylene	$8.0\cdot10^{-3}$	1.3	1060		dichloromethane	
N-Ethylcarbazole	$3.0\cdot10^{-2}$—$2.4\cdot10^{-1}$	tetracyanoquinodimethane	$1.0\cdot10^{-3}$	2.87	2770			
Polyvinylcarbazole	$3.0\cdot10^{-2}$—$1.2\cdot10^{-1}$	tetracyanoquinodimethane	$2.0\cdot10^{-3}$	1.19	1310			
N-Ethylcarbazole		tetracyanoethylene		10.8 25°	1460			
Polyvinylcarbazole		tetracyanoethylene		2.9	1245			
N-Ethylcarbazole		trinitrobenzene		2.75		1.821	chloroform	65
Polyvinylcarbazole		trinitrobenzene		1.5 25°				
N-Ethylcarbazole	$0.26\cdot10^{-2}$—$1.0\cdot10^{-2}$	tetracyanoethylene		94.1	500		chloroform	136
Polyvinylcarbazole	$0.39\cdot10^{-2}$—$1.0\cdot10^{-2}$	tetracyanoethylene		261.0	80			
N-Ethylcarbazole	$3.0\cdot10^{-2}$—$7.0\cdot10^{-2}$	tetracyanoethylene	$3.0\cdot10^{-3}$	5.25 20°	927			
Polyvinylcarbazole (30 000)	$3.0\cdot10^{-2}$—$1.2\cdot10^{-1}$	tetracyanoethylene	$5.0\cdot10^{-3}$	0.94	1250		dichloroethane	135
Polyvinylcarbazole (460 000)	$9.0\cdot10^{-2}$—$2.0\cdot10^{-1}$	tetracyanoethylene	$1.0\cdot10^{-1}$	0.15 20°	1820			
NN-Dimethyl-*p*-toluidine*		chloranil		1.75	1490		benzene	134
Poly-*p*-dimethylaminostyrene		chloranil		4.38	610		benzene	
Poly-*p*-dimethylaminostyrene	$2.0\cdot10^{-2}$	chloranil	$2.0\cdot10^{-2}$	2.77	785			
Poly-*p*-dimethylaminostyrene		dichlorodicyano-*p*-benzoquinone	$2.5\cdot10^{-4}$	$3.89\cdot10^{4}$	5700		benzene	133

* Model compound of poly-*p*-dimethylaminostyrene.

Thus the main lines of research on polymeric charge-transfer complexes have been connected with applied problems of semiconductor technology and electrography, with the physical chemistry of the formation and behaviour of the complexes in solution. Microcalorimetry and nuclear magnetic resonance, ultraviolet, visible, and infrared spectroscopy have been used to study the polymeric complexes[138]. Thermodynamic parameters calculated by the van't Hoff method and obtained for the same polymeric complexes in different laboratories do not agree (Table 2). Since macromolecules in solution may undergo complicated conformational transformations depending on the temperature and influencing the thermodynamics of complex formation, all thermodynamic characteristics of such processes will be functions of temperature, so that the van't Hoff method for determining enthalpies cannot be accepted as valid. Microcalorimetric methods must be used, enabling heats of formation to be determined under isothermal conditions. The main problem—the relation between the equilibrium constants of the polymeric complexes and those of their low-molecular analogues—is not always definitely solved. It is quite likely that such a state of quantitative data on polymeric charge-transfer complexes is due to a series of inaccuracies in the generally accepted methods for determining equilibrium constants. We shall therefore examine briefly the general principles of the calculation of equilibrium constants for complex formation in solution.

V. GENERAL PRINCIPLES OF THE CALCULATION FROM SPECTROPHOTOMETRIC DATA OF THE EQUILIBRIUM CONSTANTS OF CHARGE-TRANSFER COMPLEXES

In the investigation of charge-transfer complexes in solution, where they may undergo dissociation, the observed parameters characterise not the individual complex but an equilibrium mixture with the starting materials. Several monographs have been published on methods for the investigation of equilibrium mixtures[5,139–141]. When only one equilibrium

$$q[D] + p[A] \rightleftarrows [D]_q[A]_p \qquad (8)$$

is established, the problem of the simultaneous determination of physicochemical parameters and equilibrium constants has been solved for the simplest and most frequent case of unit coefficients $p = q = 1$.

On the assumption of unit activity coefficients of all species present in solution, the equilibrium constant expressed in molar concentrations is

$$K = \frac{[AD]}{[D][A]} \cdot \qquad (9)$$

The material balance of the system is represented by the relations

$$[A]_0 = [A] + [AD] , \qquad (10)$$

$$[D]_0 = [D] + [AD] , \qquad (11)$$

where $[A]_0$ and $[D]_0$ are the initial concentrations of the components A and D. If the optical density D is additive, we have

$$D = \varepsilon_{AD}[AD] + \varepsilon_A[A] + \varepsilon_D[D] + \varepsilon_S . \qquad (12)$$

Equations (9)–(12) contain five unknowns—[A], [D], [AD], ϵ_{AD} and K_{AD}—for the spectrophotometric case. Only simultaneous solution of equations for two experimental points obtained under different concentration conditions will enable ϵ_{AD} and K_{AD} to be determined. Owing to the cumbersome form of the equation obtained, various approximations are used depending on the stability of the complex.

For weak complexes Eqns. (9) and (12) reduce to a single equation containing the two unknowns ϵ_{AD} and K_{AD}. The coefficients ϵ_A and ϵ_D are determined experimentally, and then simplifying functions concerning the experimental conditions are introduced to bring this equation to a form which can be solved graphically. The simplifying condition in the deduction of the Benesi–Hildebrand equation

$$\frac{[A]_0}{D} = \frac{1}{K_{AD}\cdot\varepsilon_\lambda^{AD}}\cdot\frac{1}{[D]_0} + \frac{1}{\varepsilon_\lambda^{AD}} \qquad (13)$$

is that $[D]_0 \gg [A]_0$. This method[142] requires extrapolation to concentrated solutions. Scott[143] suggests the preferable variant

$$\frac{[D]_0[A]_0}{D} = \frac{[D]_0}{\varepsilon_\lambda^{AD}} + \frac{1}{K_{AD}\cdot\varepsilon_\lambda^{AD}} \qquad (14)$$

which entails extrapolation to dilute solutions for the estimation of ϵ_{λ}^{AD} and K_{AD}. Several modifications of Eqn. (13) are available depending on specific experimental conditions[143–147].

All approximate methods yield[148] an overall equilibrium constant K relating to all the isomeric equimolecular complexes, including contact complexes, together with an average extinction coefficient.

$$K_{AD} = \Sigma K_i \ , \qquad \varepsilon_{\lambda}^{AD} = \Sigma K_i \varepsilon_{\lambda i} / K \ . \tag{15}$$

The concept of contact complexes or contact charge transfer was introduced by Orgel and Mulliken[148] to explain the discrepancy arising in the relation between equilibrium constants and extinction coefficients. Mulliken had remarked[19] that increase in the equilibrium constant should be accompanied by an increase in the quantum-mechanical dipole moment and in the oscillator strength of the transition in the transfer of charge. A corresponding strengthening of the charge-transfer band may be expected[149]. However, the calculated equilibrium constants and extinction coefficients for weak complexes show the opposite relation[150]. Orgel and Mulliken suggested that the exchange of electrons occurring in the absorption of light could occur not only between donors and acceptors combined in a complex but also on the random collision of the free donors and acceptors. The weaker the complex the more significant the contribution of contact charge transfer to the total absorption by the complex. When the whole of the absorption characteristic of donor–acceptor interaction results from contact charge transfer, the Benesi–Hildebrand method yields $K = 0$ and $\epsilon = \infty$. Thus the chief defects of approximate graphical methods of calculation for weak systems are due to the "conspiracy of errors effect", when the total experimental inaccuracies distort the true values of K and ϵ[151–155].

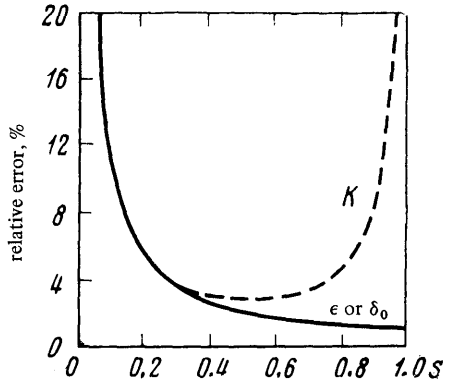


Figure 6. Dependence of relative error on concentration ratio S of components[162].

The literature on weak charge-transfer complexes has recently been overflowing with critical investigations of two-parameter equations used to determine equilibrium constants and extinction coefficients[156–163], in which various criteria of reliability were suggested for determining equilibrium constants of weak complexes. Person, for example, stated[161] that the most accurate values are obtained when the concentration of the donor lies in the range (0.1 to 9)K^{-1}. At donor concentrations below $0.1K^{-1}$ graphical solution of Eqns. (13) and (14) will give negative values. Derenleau[162] analysed theoretically the minimum error as a function of the concentration ratio S of the components, and showed that the most reliable values of K and ϵ are formed in the range $S = 0.2–0.8$ (Fig. 6). This diagram shows also that the relative errors for experiments conducted within the range $S = 0.01–0.1$ will correspondingly vary by 100–101%, and attempts to obtain accurate values of K and ϵ by a graphical method are meaningless.

Further, as shown above, the deduction of the Benesi–Hildebrand equation assumes the presence of only one equilibrium, but the linearity of Eqn. (13) by no means implies the absence of a complicated equilibrium[164,165]. This simplification may lead to inadequacy of the suggested reaction mechanism and of the equation describing the reaction.

VI. USE OF ELECTRONIC COMPUTERS TO CALCULATE COMPLEX-FORMATION EQUILIBRIA IN POLYMER SYSTEMS

A method of trial and error entailing use of an electronic computer has recently been suggested, in contrast to approximate methods for estimating equilibrium constants and extinction coefficients. A graphical variant is Drago's method[166], in which arbitrary component concentrations are chosen and appropriate equilibrium constants are calculated for each series of experiments, after which graphs are plotted of equilibrium constant against extinction coefficient. In the ideal case the lines representing all series of experiments should intersect in a single point, which gives the true values of K and ϵ. However, such a procedure is extremely laborious.

The method of trial and error using a computer[167–172] has several advantages over approximate methods: a solution can be found for complexes other than equimolecular, approximation becomes unnecessary, and the restriction to the extremal conditions $[D]_0 \gg [A]_0$ is removed. For example, Conrow[168] finds the concentration of the complex from initial calculation of the equilibrium constant. This concentration is then used to find the most suitable value of the extinction coefficient ϵ^{AD} in Eqn. (12). The required equilibrium constant K and extinction coefficient ϵ are found by calculating the absorption at every experimental point and accumulating the sums of the squares of differences between calculated and experimental values. The computation is terminated when the change in the difference

$$F_{min} = \sum_{i=1}^{N} (D_{calc.} - D_{exp.})^2 \tag{16}$$

becomes arbitrarily small. The non-linear methods described for calculating equilibrium parameters have hitherto been applied to systems of low molecular weight[167–172]. The complexity of the equilibrium of polymer systems due to the possible presence of several complexes and the irreproducibility of published data make resort to electronic computers necessary.

The method of minimisation of the function for polymer systems has hitherto been applied only to solutions of complexes of poly(phenyl methacrylate), poly(naphthyl methacrylate), polyvinylcarbazole, and their model analogues

with tetracyanoethylene[136]. Equimolar initial concentrations of the components were taken, and the reaction was thus regarded as a simple one-stage formation of an equimolecular complex. However, the values obtained[136] for the equilibrium constants were hundredfold the usual values, which is inconsistent with our ideas on weak complexes. Furthermore, the relations between equilibrium constants for polymeric and low-molecular complexes were opposite to those found by Rembaum[130] and by Smets[65].

The survey of methods for investigating charge-transfer complexes in solution reveals the complexity of the study of equilibrium complex formation in polymer systems, where the usual phenomena for the simple complexes (contact charge transfer) are accompanied by the specific behaviour of chain molecules (variation in configuration of the macromolecule, mobility of the chain, etc.).

The study of complex formation between polymeric donors and low-molecular acceptors obviously requires further deepening of research using the latest achievements of physicochemical methods and of calculations by means of electronic computers.

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