CHARGE—TRANSFER COMPLEXES IN SOLUTION: A CONDUCTOMETRIC STUDY

M. V. Ramanamurti and A. Qayum

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221 005

(Received Sept. 1977; accepted Oct. 1978)

The formation of charge-transfer complexes in the systems benzene-chloranil and anthracene-chloranil in methanol; and p-phenylenediamine–phthalic acid in acetone, methanol and acetonitrile has been studied through conductometric measurements. For all complexes established, the conductivity maxima appear at compositions of simple 1:1 stoichiometry. The linear drop in molecular conductivity of the complex solution on increasing dilution with an inert solvent CCl_4, as also the variation of ΓP, ($\Gamma P - \Gamma O$) and $\alpha \Gamma M_{DA}$ with change in dielectric constant of the medium, are attributed to decrease of ionization or/and triple ion formation with the decrease in dielectric constant of the solvent medium.

The formation of a charge-transfer (CT) complex between an electron acceptor (A) with high electron affinity and an electron donor (D) with low ionization potential can be followed by measuring changes in ionic conductivity caused by the formation and subsequent ionic dissociation of the complex in a solvent of sufficiently high dielectric constant (ϵ)[1]; when a solution of a donor is titrated against a solution of an acceptor (both in the same solvent*) or vice-versa. This, in effect, amounts to a conductivity titration. The plot of measured conductivity (Γ) versus compositions of D and A yields a conductivity peak which determines the stoichiometry of CT-complex [2–7].

The present communication reports results of conductometric studies of the formation of CT-complexes in the systems benzene-chloranil and anthracene-chloranil in methanol; and p-phenylenediamine-phthalic acid in acetone, methanol and acetonitrile.

EXPERIMENTAL

Acetone (BDH, AR), methanol (BDH, AR) and acetonitrile (BDH, LR) were dried and distilled thrice before use. Chloranil and phthalic acid were recrystallized from alcohol and dried in vacuo. Anthracene and p-phenylenediamine were purified by repeated recrystallization from ether. Benzene was distilled twice and the middle cut, at 80°C was collected for use. Standard stock solutions of the donor and the acceptor were prepared in solvents under study.

The conductivity titrations were carried out in a titration vessel at 25°±0.02°C, by adding approximately 1 ml of the acceptor solution to the 15 ml of the donor solution (initially taken in the titration vessel) and vice-versa. After each addition of the titrant, the solution was stirred to attain a suitable steady conductivity value. The change in conductivity was measured with a conductivity bridge (Philips PR 9500/90) using platinized platinum electrodes of known cell constant.

The molar concentrations M_A and M_D of the acceptor and the donor respectively, after each addition of the titrant, were calculated using standard relations [2,6,7]. The molar conductivity coefficient of the complex (ΓM_{DA}) has been calculated using expression (1)

$$\alpha \Gamma M_{DA} = \frac{1}{M_{DA}} \frac{\Gamma P - \Gamma O}{\Gamma O} \quad \ldots (1)$$

where α is a constant incorporating the extent of dissociation of the CT-complex in solution, M_{DA} is the molar concentration of the complex, ΓP is the peak conductivity which is a measure of the total number of ions carrying the current at the stoichiometry of CT-complex and ΓO is the linearly interpolated conductivity value at the concentration ratio corresponding to the peak read off from the base line joining the conductivities of the stock solutions[3,4]. The value of ΓM_{DA} given by eq. (1) is characteristic of a CT-complex and is independent of concentration, temperature and nature of solvent.

RESULTS AND DISCUSSION

The results of the conductivity titrations of CT-complexes studied are shown in Figs. 1–3. The two branches of the curve represent the two titrations, one representing the addition of the donor to the acceptor and the other acceptor to the donor. The conductance data are given in Table 1.

The stoichiometry of a CT-complex formed in solution has been shown to be directly proportional to

*The solvents preferable for such studies are those having low conductivity and high dielectric constant (e.g., acetonitrile, methanol, acetone etc.) because (a) if the conductivity is too high, conductance changes due to complex formation may become obscured and (b) if the dielectric constant is too low, the complex may fail to dissociate.

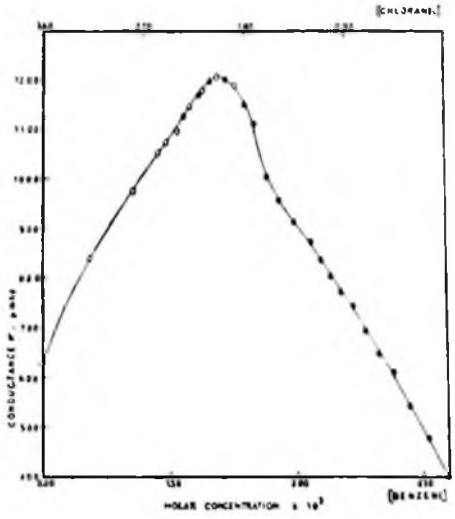


Fig. 1. Plots of conductance versus concentration of benzene/chloranil in methanol (open points, addition of benzene solution ; shaded points additon of chloranil solution).

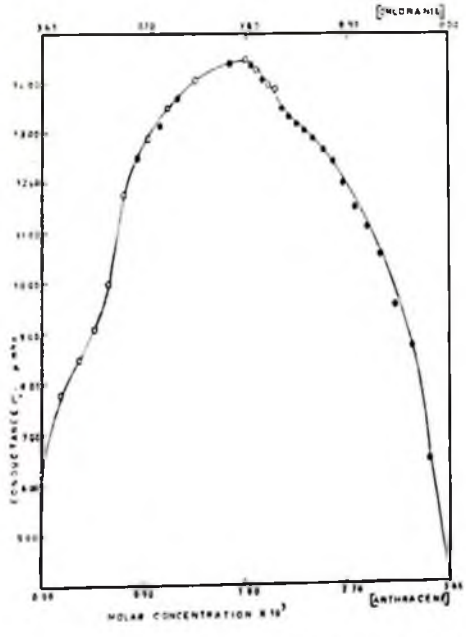


Fig. 2. Plots of conductance versus concentration of anthracene/chloranil in methanol (open points, addition of anthracene solution; shaded points, addition of chloranil solution).

the position of the conductivity maximum obtained in the conductometric titration curve[2,3]. The stoichiometry of benzene : chloranil and anthracene : chloranil

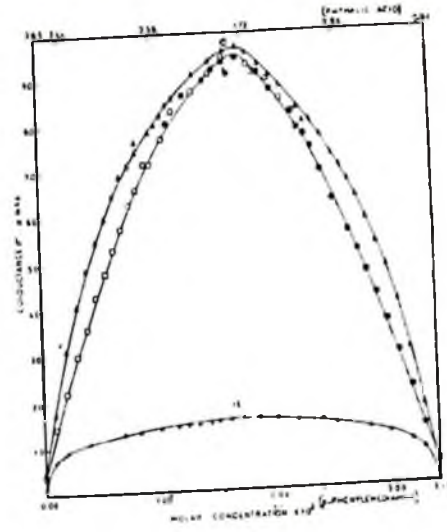


Fig. 3. Plots of conductance versus concentration of p-phenylene-diamine/phthalic acid in (a) acetone, (b) methanol and (c) acetonitrile (open points, addition of the diamine solution ; shaded points, addition of phthalic acid solution).

complexes in methanol (cf. Figs. 1&2) : and p-phenylene-diamine : phthalic acid complex (cf. Fig. 3) in acetone, methanol and acetonitrile is 1 : 1, as revealed from the conductivity peak obtained during the conductometric titrations. A well defined conductivity maximum for p-phenylenediamine : phthalic acid complex appeared in methanol and acetonitrile (cf. Fig. 3). In acetone, however, the conductivity titration curve has no sharp maximum. This is attributable to the low ϵ of the solvent which suppresses ionization of the complex. The complexing between p-phenylene-diamine and phthalic acid is achieved through a localized orbital on the nitrogen atom whereas the formation of benzene : chloranil and anthracene : chloranil complexes is attributable to complexing through delocalized π-orbital[7].

The increase in the value of $^{\tau}P$, ($^{\tau}P—^{\tau}O$) and $\alpha^{\tau}M_{DA}$, for p-phenylenediamine : phthalic acid complex, with the increase in ϵ of the solvent medium (cf. Table 1) e.g., acetonitrile ($\epsilon=36.0$)> methanol ($\epsilon=31.2$)> acetone ($\epsilon=20.7$) indicates the extent of increase in the ionization, and hence the enhanced probability of formation of CT-complex in solution with the increase in ϵ of the solvent medium. Value of $\alpha^{\tau}M_{DA}$ for the three complexes established

TABLE: 1. **Complex stoichiometry and conductance data of CT-complexes in different solvents**

Complex D : A	Solvent	Complex stoichio-metry	Conductance (μmho)		$\alpha^{\urcorner}M_{DA}$
			$^{\urcorner}P$	($^{\urcorner}P$—$^{\urcorner}O$)	
Benzene : CHL	methanol	1 : 1	12.05	6.76	623
Anthracene : CHL	methanol	1 : 1	14.46	9.23	1009
p-PDA : Phthalic acid	acetone	1 : 1	15.50	14.60	9202
p-PDA : Phthalic acid	methanol	1 : 1	95.00	90.60	11690
p-PDA : Phthalic acid	acetonitrile	1 : 1	96.50	93.00	15070

CHL = Chloranil, p-PDA = p-phenylenediamine

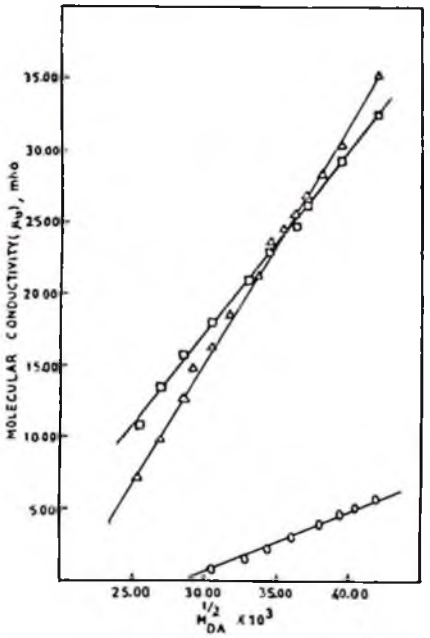


Fig. 4. Plots of molecular conductivity (μ_v) versus $M_{DA}^{1/2}$ of p-phenylenediamine : phthalic acid complex in acetone (O—O—O), methanol (□—□—□) and acetonitrile (△—△—△); upon dilution wiih CCl_4.

in the solvent methanol varies as (p-PDA : phthalic acid) > (anthracene : CHL) > (benzene : CHL) indicating the ease of formation of these complexes in the same order in solvent methanol.

The molecular conductivety (μ_v) of the complex solution of p-phenylenediamine : phthalic acid complex at the complexing ratio, drops linearly on increasing dilution with an inert solvent CCl_4 (cf. Fig. 4) i.e., confirming the validity of $\mu_v = A + BM_{DA}^{1/2}$ where A and B are constants and M_{DA} is the molar concentration of the complex. The positive slope in the plot of μ_v vs $M_{DA}^{1/2}$ as well as the variation of $^{\urcorner}P$, ($^{\urcorner}P$—$^{\urcorner}O$) and $\alpha^{\urcorner}M_{DA}$ with change in ϵ of the solvent medium are attributable to decrease of ionization or/ and triple ion formation with the decrease in ϵ of the solvent medium.

REFERENCES

1. R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London and New York, 1969.
2. F. Gutmaun and H. Keyzer., Electrochim. Acta, 11 (1966) 555.
3. F. Gutmaun and H. Keyzer, ibid., 11 (1966) 1163.
4. F. Gutmaun and H. Keyzer, ibid., 12 (1967) 255.
5. R. D. Srivastava and P.C. Varma, ibid., 17 (1972) 2129.
6. M.V. Ramanamurti and A. Qayum, Ind. J. Chem., 12 (1974) 1308.
7. M. V. Ramanamurti and A Qayum, Trans. SAEST, 11 (1976) 503.

FASHION MOVES AHEAD ON T. C. C. PRODUCTS

T. C. C.'s products, Rayon grade Caustic Soda, Chlorine, Sodium Hydrosulphite, and Iron-free Sodium Sulphide comparable in quality to imported stuff play fundamental roles in the manufacture of multivarious everyday articles essential for sophisticated life—Soap, Textiles, Rayon Silk, Perfumes, Depilatory Preparations, Leather and Leather Products, Paper, Engraving, Lithography etc.

In short T.C.C. Products lie at the core of very many articles essential for the average man as well as to the jet set.

PIONEERING AND PACE SETTING HAS BEEN THE ROLE OF T. C. C. IN THE FIELD OF BASIC CHEMICALS.

The Travancore-Cochin Chemicals Limited

UDYOGAMANDAL-683 501.
KERALA STATE

T. N. G. S. T. No. 75673
C. S. T. No. 2260

Phone : 431088

●●

VASU CHEMICAL INDUSTRIES

Manufacturers & Suppliers of :

Wax Crayons, Sodium Hypochlorite, Bleaching Solution and Alumina Hydrate

Plot No. 26, Guindy Industrial Estate (North)
Ekkaduthangal, Madras-97