Conductometric study of charge transfer complexes

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Abstract. A conductometric titration technique has been used for determining the stoichiometry of charge-transfer complexes which ionise in polar media. The systems studied are: Iodine complexes of acetone, methyl ethyl ketone, *iso*-butyl methyl ketone, dimethylsulphoxide triphenyl phosphine, triphenyl arsine, triphenyl stibene, methanol, ethanol and *n*-propanol. The stoichiometry of the above complexes (in highly polar media) were found to be $\approx 2{:}3$ (except in the cases of triphenyl stibene where stoichiometry was $\approx 1{:}4$). The effects of temperature, concentration and dielectric constants (of the media) on conductivities of the complexes have been reported.

Keywords. Conductometry; charge-transfer complexes; iodine complexes.

1. Introduction

The interaction of electron donor, D, with electron acceptor, A, leads to the formation of new molecular species, DA (Mulliken and Person 1969). When the interaction between the donor and acceptor is very strong and the dielectric constant of the medium is high, the complex may dissociate into its ions giving rise to appreciable ionic conductivity. The formation of such inner (charge transfer) complexes can be followed by measuring the changes in the electrical conductivities of the solutions (Reid and Mulliken 1954; Bhat and Rao 1966; Gutmann and Keyzer 1969; Mulliken and Person 1969; Srivastava and Verma 1972; Rao *et al* 1972; Srivastava *et al* 1982).

For determining the equilibrium constant and the other thermodynamic parameters, one must know the stoichiometry of the complex. The usual Job's (1928) continuous variation procedure is of limited application particularly when the outer complex is transformed into an inner complex (due to environmental cooperation), leaving behind only a small amount of neutral unionised complex in solution. Under such circumstances, it is suggested that one may be able to obtain the stoichiometry of the complex in highly polar media by measuring the electrical conductivities of the solutions (Gutmann and Kayzer 1969). Therefore, we have made an attempt to obtain information on the nature of interaction between the donor and acceptor (i.e., the relative strength/stability of the complexes), the stoichiometry of the complex in polar media, the effect of concentration, temperature and dielectric constant of the medium on the electrical conductivities of the complexes in solution. The electron donors chosen for the present studies are: acetone, methyl ethyl ketone, *iso*-butyl methyl

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ketone, dimethyl sulphoxide, triphenyl phosphine, triphenyl arsine, triphenyl stibene, methanol, ethanol, *n*-propanol (all *n*-donors) and iodine was used as an acceptor. Acetonitrile and mixtures of acetonitrile and carbon tetrachloride were used as solvents.

2.   Materials and methods

The electron donors, namely acetone, methyl ethyl ketone, *iso*-butyl methyl ketone, dimethyl sulphoxide, triphenyl phosphine, triphenyl arsine, triphenyl stibene, methanol, ethanol and *n*-propanol, the electron acceptor, iodine, and the solvents-acetonitrile and carbon tetrachloride were purified by standard procedures (Vogel 1978). The refractive indices of the liquid reagents agreed well with the literature data.
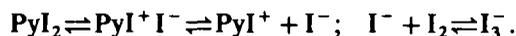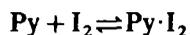
Stock solutions (0·1 M) of the electron donors were prepared in acetonitrile–CCl_4 mixtures of various compositions (for obtaining media of different dielectric constants). The conductivities of the solutions containing different amounts of donors and acceptors (keeping the total concentration constant) were measured using a Philips PR 9500 conductivity bridge at 25, 30, 35 and 40 ($\pm$ 0·1)°C in various dielectric media.

Acetonitrile interacts with iodine and the solution becomes slightly conducting. Therefore, the contribution of the conductivity due to acetonitrile–iodine is deducted from the total conductivity of the complex while reporting the conductivities of the complexes. The stoichiometry of the complex is deduced from the conductivity of the peak of the plot of $\sigma_{complex} - \sigma_{reactants}$ *vs.* concentration of the reactants (Gutmann and Keyzer 1966).

3.   Results and discussion

3.1   *Iodine complexes of acetone, methyl ethyl ketone, isobutyl methyl ketone and dimethyl sulphoxide*

It is well-known that the electrical conductivity of iodine in pyridine changes with time and has been ascribed to the dissociation of loosely bound donor–acceptor (interaction) product to form N-iodo-pyridinium iodide, an inner (ionic) complex:

$$Py + I_2 \rightleftharpoons Py \cdot I_2$$

$$PyI_2 \rightleftharpoons PyI^+ I^- \rightleftharpoons PyI^+ + I^-; \quad I^- + I_2 \rightleftharpoons I_3^-.$$

(outer complex)   (inner complex)

It is reported that the absorbance of CT bands of iodine complexes decreases with increase in time. Electron donors, namely, acetone, methyl ethyl ketone, *iso*-butyl methyl ketone and dimethyl sulphoxide and iodine were dissolved separately in acetonitrile and the conductivities of "pure solutions" (wherever feasible) and those of "mixed solutions" were measured at constant temperatures. For the sake of brevity, the electrical conductivity data of iodine complexes of acetone, methyl ethyl ketone and dimethyl sulphoxide at one temperature and one concentration are summarised in table 1. It can be seen from table 1 and figure 1 that the electrical conductivity of iodine in acetonitrile (0·01 M) which was initially $1·25 \times 10^{-4}$ mho (the low conductivity

Table 1. The electrical conductivities of iodine complexes of acetone.
Methyl ethyl ketone (Me–Et–ketone), iso-butyl methyl ketone (iso–Bu–Me–ketone), Dimethylsulphoxide (DMSO), triphenyl phosphine ($\Phi_3 P$), triphenyl arsene ($\Phi_3 As$) and triphenyl stibene ($\Phi_3 Sb$) at 25°C.
Solvent: acetonitrile; conc. of iodine solution: 0·01 M; conc. of donor solution: 0·01 M.

Vol. of donor solution (ml)	Vol. of iodine solution (ml)	Conductivity × 10⁴ (mhos)*									
		Acetone– I_2	Me–Et– ketone– I_2	iso–Bu–Me– ketone– I_2	DMSO I_2	$\Phi_3 P$– I_2	$\Phi_3 As$– I_2	$\Phi_3 Sb$– I_2	MeOH– I_2	EtOH– I_2	n-PrOH I_2
0·0	5·0	1·25	1·25	1·25	1·25	1·25	1·25	1·25	1·25	1·25	1·25
0·5	4·5	1·40	1·54	1·75	1·56	4·55	3·57	3·51	1·30	1·41	1·47
1·0	4·0	1·51	1·61	1·81	1·64	7·41	5·88	5·41	1·39	1·49	1·54
1·5	3·5	1·52	1·63	1·83	1·66	9·09	6·67	4·17	1·40	1·51	1·55
2·0	3·0	1·54	1·64	1·85	1·69	11·11	7·14	3·70	1·41	1·54	1·56
2·5	2·5	1·39	1·44	1·64	1·49	9·52	6·45	3·33	1·28	1·39	1·42
3·0	2·0	1·20	1·28	1·43	1·34	8·00	5·88	3·03	1·10	1·19	1·23
3·5	1·5	1·00	1·11	1·20	1·16	5·88	5·00	2·63	0·91	1·00	1·05
4·0	1·0	0·77	0·83	0·95	0·91	4·17	4·00	2·08	0·74	0·80	0·87
4·5	0·5	0·48	0·56	0·64	0·61	2·27	2·13	1·25	0·48	0·51	0·57
5·0	0·0	0·25**	0·30**	0·40**	0·38**	1·00	0·85	0·50	0·25	0·31	0·40

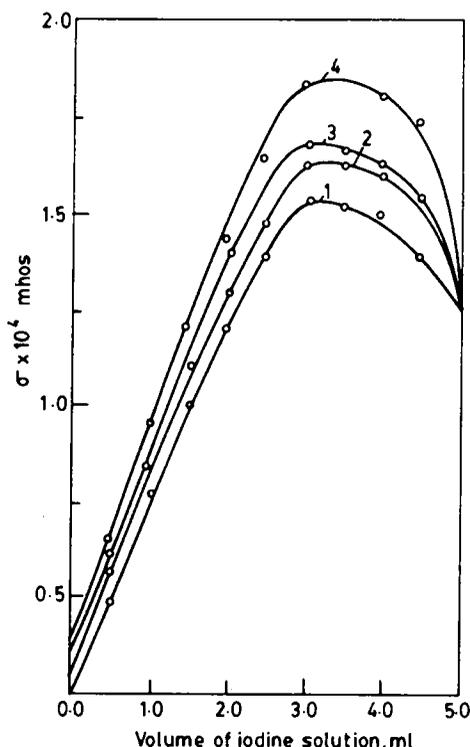*Error limit: ±0·01; **Extrapolated values.

Figure 1. Variation of electrical conductivity of ketones/DMSO–I_2 systems (isomolar) at 25°C. Concentration of donor as well as iodine = 0·01 M.

Solvent: acetonenitrile–(1) acetone–I_2; (2) methyl ethyl ketone–I_2; (3) DMSO–I_2; (4) *iso*-butyl methyl ketone I_2.

is due to few I^-/I_3^- formed) has increased with the addition of acetone (0·01 M, keeping the total volume/concentration constant, i.e., 5 ml of 0·01 M) and reached a maximum value of $1·54 \times 10^{-4}$ mho and then started decreasing with further addition of acetone. Here it can be noted that the conductivities of the mixed solutions (which are lower) are relatively higher compared to that of iodine in pure solvent. The decidedly nonlinear plot in an isomolar series indicates that the reactants 'interact' with each other. A peak becomes evident at a stoichiometry of $\approx 2:3$ (D:A). (It must be noted here that due to nonlinear behaviour the conductivity peaks occur slightly off the stoichiometry.) When iodine was titrated against ketones, the conductivity reached a maximum value at a stoichiometry of 2:3 and then it remained constant. These results go in parallel with those obtained from refractometric studies (Singh and Bhat 1978) and the literature values of Gutmann and co-workers (Gutmann and Keyzer 1966) obtained by conductivity measurements.

In order to understand the effect of media on the electrical conductivities of solutions, the media dielectric constants were changed by mixing appropriate amounts of acetonitrile with CCl_4. As the dielectric constant of the medium is increased from 15 to 36·7, the electrical conductivity is increased (table 2) due to the increase in the number of charge carriers as well as due to the increase in the mobilities of the charge carriers. The results are in accordance with our earlier findings where it has been

Table 2. Effect of dielectric constant on the electrical conductivity of acetone–iodine System at 25°C.
Solvent: acetonitrile + carbon tetrachloride; Conc. of iodine solution: 0·01 M; Conc. of Acetone solution: 0·01 M.

Volume of acetone solution (ml)	Volume of iodine solution (ml)	Conductivity × 10^4 (mhos)*			
		$\varepsilon = 36\cdot7$	$\varepsilon = 30$	$\varepsilon = 25$	$\varepsilon = 15$
0·0	5·0	1·25	0·52	0·24	Resistance of
0·5	4·5	1·40	0·63	0·29	the solution
1·0	4·0	1·51	0·69	0·30	was too high
1·5	3·5	1·52	0·70	0·31	($> 10^6$ ohm)
2·0	3·0	1·54	0·71	0·31	
2·5	2·5	1·39	0·65	0·28	
3·0	2·0	1·20	0·59	0·26	
3·5	1·5	1·00	0·53	0·23	
4·0	1·0	0·77	0·42	0·18	
4·5	0·5	0·48	0·33	0·14	
5·0	0·0	0·25**	0·20**	0·09**	

*Error limit: ±0·01; **Extrapolated values

shown that the rate of electron transfer in 'electron donor acceptor' complexes is enhanced by solvent polarity (Bhat and Rao 1966). A general trend of decrease in electrical conductivity with decrease in the dielectric constant of the media has been observed in all the cases we have studied.

The conductivity of any solution depends on the number of charge carriers, the charge on the charge carriers and on the mobilities of the charge carriers. In the present case (i.e., the transformation of the outer complex into an inner complex) the number of charge carriers depends on the concentration of the complex (assuming the charge on the ion to be one) and on the media. As the concentrations of the donors as well as of acceptors are increased from 0·005 M to 0·02 M the electrical conductivities (at the peak) increase from $0\cdot95 \times 10^{-4}$ mhos to $3\cdot23 \times 10^{-4}$ mhos at 25°C. This increase in conductivity with the increase in concentration of the donor/acceptor is probably due to an increase in number of charge carriers (arising due to the dissociation of more neutral/ion pair complexes into ions). When the temperature of the solution is increased, the number of charge carriers decreases and the mobilities of the charge carriers are affected. In the present case (i.e., in transformation of the outer complex to an inner complex) when the temperature of the system is increased, the equilibrium constant for the formation of complex is decreased, i.e., the amount of complex formed will be less and hence the number of ions formed (from the complex) will also be less (Shedbalkar and Bhat 1983). However, the mobility of the charge carriers increases with temperature (assuming that the solvation number and hence the size of the solvated ions do not change wih temperature). The increase or decrease of conductivity of the solution depends upon which factor will be more predominant. In iodine complexes, we have observed an increase in conductance with increase in temperature (table 3). So, we feel that the increase in conductivities with the increase in temperatures is due to the increase in mobilities of the ions.

Table 3. Effect of temperature on the electrical conductivities of acetone–iodine system.
Conc. of iodine solution = 0·01 M; conc. of acetone solution = 0·01 M.

Volume of acetone solution (ml)	Volume of iodine solution (ml)	Conductivity $\times 10^4$ (mho)*			
		25°C	30°C	35°C	40°C
0·0	5·0	1·25	1·33	1·54	1·72
0·5	4·5	1·40	1·47	1·70	1·85
1·0	4·0	1·51	1·58	1·79	1·96
1·5	3·5	1·52	1·61	1·80	1·98
2·0	3·0	1·54	1·64	1·82	2·00
2·5	2·5	1·39	1·49	1·61	1·79
3·0	2·0	1·20	1·35	1·47	1·59
3·5	1·5	1·00	1·18	1·26	1·31
4·0	1·0	0·77	0·87	0·91	1·00
4·5	0·5	0·48	0·59	0·65	0·69
5·0	0·0	0·25**	0·35**	0·39**	0·43**

*Error limit: $\pm$ 0·01; **Extrapolated values.

The electrical conductivities of iso-molar solutions of methyl ethyl ketone, *iso*-butyl methylketone, dimethyl sulphoxide–iodine complexes in different dielectric media of different concentrations were determined, at different temperatures (25, 30, 35 and 40°C). It can be seen from table 1 and figure 1 that methyl ethyl ketone, *iso*-butyl methyl ketone and dimethyl sulphoxide also form 2:3 complexes with iodine in acetonitrile. The electrical conductivities of these (0·01 M) complexes are $1·64 \times 10^{-4}$, $1·85 \times 10^{-4}$ and $1·69 \times 10^{-4}$ mho respectively. The equilibrium constants and the other thermodynamic parameters show that the stabilities of the complexes vary in the order DMSO-$I_2 > $ *iso*-butyl methyl ketone-$I_2 > $ methyl ethyl ketone-$I_2 > $ acetone-I_2 in cyclohexane (Drago *et al* 1963). As the equilibrium constants and the other thermodynamic data available in the literature are under different experimental conditions (i.e., the nature and dielectric constants of the medium are different), it is not possible to compare the trends of the conductivities with those of available thermodynamic parameters.

Dimethyl sulphoxide forms an outer complex with iodine and, under favourable conditions, the outer complex formed is transformed into an inner complex (Bhat and Rao 1966). It is expected that the non-bonding electron of sulphur/oxygen will be taking part in the formation of the complex. It is reported in the literature that in DMSO-I_2 and acetone-I_2 complex the shift in v_{C-S} is higher ($\sim 30–60\,cm^{-1}$) than that of $v_{C=O}$ ($15–50\,cm^{-1}$) which go in parallel with the conductivity data (Augdahl and Klaeboe 1964).

3.2 *Iodine complexes of Triphenyl phosphine, Triphenyl arsine and Triphenyl stibene*

The conductometric titrations of iodine solutions against solutions of triphenyl phosphine, triphenyl arsine and triphenyl stibene were carried out at different concentrations (0·02, 0·01 and 0·005 M) in acetonitrile and acetonitrile–carbon tetrachloride mixtures (dielectric constants of 36·7, 30, 25 and 15) and at different

temperatures (25, 30, 35 and 40°C). For the sake of brevity the conductance data at one temperature (25°C) and one concentration (0·01 M) are reported in table 1. Triphenyl phosphine-iodine and triphenyl arsene-I_2 systems have conductance maxima at $\approx 2:3$ stoichiometry whereas triphenylstibene-I_2 has a conductance maximum at $\approx 1:4$ stoichiometry.

At 25°C, the electrical conductivities (at the maxima) of $\Phi_3 P-I_2$, $\Phi_3 As-I_2$ and $\Phi_3 Sb-I_2$ complexes were $11·11 \times 10^{-4}$, $7·14 \times 10^{-4}$ and $5·41 \times 10^{-4}$ mhos respectively (concentration, 0·01 M), i.e., the electrical conductivities vary in the order $\Phi_3 P-I_2 > \Phi_3 \cdot As-I_2 > \Phi_3 Sb-I_2$. The stabilities (i.e., enthalpies) of these complexes vary in the reverse order, i.e., $\Phi_3 P-I_2 < \Phi_3 As-I_2 < \Phi_3 Sb-I_2$ (Bhaskar *et al* 1966). These data show that as expected, the electrical conductivities of the complexes decrease with the increase in stabilities of the complexes.

In the case of the Φ_3 As-iodine system, it was observed that as the dielectric constant of the medium was varied from 36·7 to 15 the stoichiometry of the complex varied from 2:3 to 1:4. Similar observations were made in our laboratory in the case of pyridine iodine and picolines-iodine, i.e., as the polarity of the medium is decreased, the amount of iodine in the complex has increased. Similar trends were noted by Sahai *et al* (1981) for triphenyl phosphine-iodine (but their values could not be reproduced in our laboratory). This unexpected observation (of high iodine content in Φ_3 As-Iodine) can not be explained with the existing model.

3.3 *Iodine complexes of methanol, ethanol and n-propanol*

The conductance measurements of iodine complexes of methanol, ethanol and *n*-propanol of different concentrations (0·02, 0·01 and 0·005 M) were carried out at different temperatures (25, 30, 35 and 40°C) and in different dielectric media (36·7, 30, 25 and 15). Conductance data at one temperature and one concentration are included in table 1. All these complexes have the conductance maximum at 2:3 stoichiometry. The electrical conductivities of the solutions, as in other cases, increase ($1·11 \times 10^{-4}$ to $3·51 \times 10^{-4}$ mhos at 25°C) with increase in concentration (0·005 M to 0·02 M), temperature and dielectric constant of the media. Here it should be noted that as the temperature of the system increases the interaction between alcohol molecules (i.e., hydrogen bonding polymers) decrease, which in turn affect the alcohol–iodine complex concentration (Tse and Tamres 1977. The decrease in electrical conductivity of iodine-alcohols with the decrease in dielectric constants must be due to the decrease in the mobility of the charge carriers as well as due to the formation of lesser number of "free" ions (in low dielectric media). The stability of these complexes vary in the order n-PrOH-$I_2 > $ EtOH-$I_2 > $ MeOH-I_2, but the electrical conductivities of these complexes are nearly the same.

From these observations, we feel that conductometric titration (where the outer complex is transformed into an inner complex which is assisted by environmental cooperation) method can be used to determine the stoichiometry of the complex formed in polar media. However, if more than one type of complex is formed, or if the interaction between solute and solvent is considerable, then one has to be cautious in establishing the stoichiometry of the complex by this method. Moreover, if interaction between the molecules is weak, or if the permitivity of the medium is low, then this conductivity method will be of little help in determining the stoichiometry of the complexes in solutions.

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