

## Transference number of charge-transfer complexes in solutions : methanol-iodine and ethanol-iodine

S N BHAT\* and RAJEEV DWIVEDI

Chemistry Department, North Eastern Hill University, Shillong 793 003, India

\*All correspondence to be addressed.

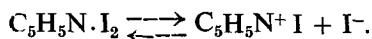
MS received 10 December 1979 ; revised 9 May 1980

**Abstract.** The majority of charge carriers in charge-transfer complexes of methanol-iodine and ethanol-iodine in solutions are anion constituents. The transfer number of cation decreases with the increase in concentration of iodine.

**Keywords.** Transference number ; charge-transfer complex ; methanol-iodine ; ethanol-iodine.

### 1. Introduction

Mulliken (1952) pointed out that a donor-acceptor pair can form either the associative outer complex or dissociative inner complex depending on the distance of approach between the donor and the acceptor and the relative magnitude of the no-bond and dative contributions. The formation of inner complex from outer complex is highly environment-dependent. The increased electrical conductance of iodine in pyridine was explained by Reid and Mulliken (1954) on the basis of an equilibrium involving the outer and inner complexes :



outer complex      inner complex

Recently it has been shown that iodine and its compounds have remarkable property of electrical conduction in polar solvents (Palit 1976; Palit and Ghosh 1979). Examination of the review literature of Rao *et al* (1972) shows that in many donor-iodine acceptor systems, the formation of triiodide ion is often noticed when the medium is highly polar. So if the product is in the ionic form, then the nature of the majority charge carriers in solutions may be estimated by determining the transport number of cation and anion. In view of the non-availability of any information regarding the nature of the charge carriers of the charge-transfer complexes in solutions, we have made an attempt to determine the same for ethanol-iodine and methanol-iodine systems, with particular reference to the concentration effect on transport numbers.

## 2. Materials and methods

Ethanol, methanol and iodine were purified by the standard procedures reported by Riddick and Bunger (1970) and Brandon *et al* (1960). The transport numbers of the ions were determined by Hittorf's apparatus using two platinum electrodes and passing  $\sim 10$  mA current (220 DC Volts) for 3–4 hr. (The apparatus was calibrated for silver nitrate solution.) The temperature of the solution was maintained constant at  $22 \pm 0.1^\circ \text{C}$  using a thermostat. The concentrations of iodine in cathodic and anodic compartments were determined by titrating them with standard sodium thiosulphate solution. The amount of total current passed was determined by using an iodine Coulometer (in series along with Hittorf's apparatus) as described by Washburn and Bates (1912). Each experiment was repeated at least twice and the results were reproducible within the error limit of  $\pm 0.0001$ .

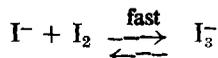
The time dependence of electrical conductance of the solutions at constant temperature ( $22^\circ \text{C}$ ) was measured by using a Philips conductivity bridge. The velocity constant for the transformation of outer charge-transfer complexes into inner complexes was calculated using first order rate constant equation.

## 3. Results and discussion

Tse and Tamres (1977) recently reported that the iodine complexes of ethanol and methanol, in non-polar solvents like cyclohexane, are quite stable; the electrical conductivities of these complexes in cyclohexane are very low ( $\sim 10^{-12}$  Mho) and there are not any appreciable changes in the conductivities with time. When iodine was directly dissolved either in ethanol or in methanol the initial electrical conductivity (higher the concentration, greater is the conductivity) increases with time and reaches a maximum value after about 24 hr. We feel that this is due to the transformation of the initially formed 1 : 1 outer complex into the inner complex followed by the fast reaction of the inner complex with iodine to form triiodide ion :



(R =  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ ) (outer complex) (inner complex)



The kinetics of the transformation of the outer complex to the inner complex was studied by measuring the time dependence of the electrical conductivity of the solution. The reactions are clearly of the first order and the rate constants are  $2.23 \times 10^{-2}$ ,  $3.30 \times 10^{-4}$ ,  $3.73 \times 10^{-2}$ ,  $8.13 \times 10^{-4} \text{ min}^{-1}$  for 0.02 and 0.5 N iodine in methanol and ethanol respectively at  $22^\circ \text{C}$ .

During the electrolysis, the solvated anions namely  $\text{I}_3^-$  and  $\text{I}^-$  migrate towards the anode, and the solvated cation,  $(\text{ROHI})^+$ , moves towards the cathode. At the anode, (mainly) triiodide and iodide ions become iodine molecules and thus the concentration of iodine increases. At the same time, the cation,  $(\text{ROHI})^+$

moves towards the cathode. We noticed a decrease in the concentration of iodine in the cathode compartment. This may be due to the migration of  $[I_3^-]$  and  $I^-$  towards the anode [while  $(ROHI)^+$  moves towards the cathode during the same interval of time] resulting in a net loss of iodine in the cathode compartment. Thus, the concentration of iodine in the anode compartment increases whereas that in the cathode compartment decreases. The transport numbers of anion constituents and cations are given in table 1. It is evident from the results that the transport number of anion constituents is larger than that of cation; it indicates that the anion constituents are the majority charge carriers in these solutions. It has been mentioned earlier that the triiodide ion formation is faster than the formation of iodide ion. So the anion constituent is mainly  $I_3^-$ . (Our attempt to determine the concentration of  $I^-$  spectroscopically in the solution was not successful as methanol and ethanol have high absorption in the region of 226 nm. At present, we are not in a position to separate the contributions of  $I^-$  and  $I_3^-$  from the total value of transference number of anion constituents.

It is clear from the data that the transport number of cation ( $t_+$ ) decreases with the increase in concentration of the iodine solution. This observation goes in parallel with the literature data compiled by Fried *et al* (1977) for potassium ion where the change (decrease) in transport number is 0.0003 over a twenty-fold change (increase) in the concentration of potassium ion. It is interesting to note that the change in the transport number with concentration, over the concentration range of 0.02 N to 0.5 N, decreases with the increase in concentration; the change being more in iodine-methanol than in iodine-ethanol system. The transport number of  $(CH_3OHI)^+$  is considerably higher than that of  $(C_2H_5OHI)^+$ . This can be visualised in terms of the lesser number of solvent molecules associated with  $(CH_3OHI)^+$  [due to the weaker interaction between  $(CH_3OHI)^+$  and solvent compared to  $(C_2H_5OHI)^+$  and solvent]; so the solvated smaller ion  $(CH_3OHI)^+$  moves faster compared to the solvated bigger ion  $(C_2H_5OHI)^+$ . There is no change in the transport numbers whether the electrolysis is carried out before the steady value of conductivity is reached or afterwards; this indicates that transference number is independent of the fact that the ions are generated continuously or are produced in one step.

Thus iodine which is supposed to be non-conductor (in non-polar solvents) conducts current in polar solvent (like methanol and ethanol) and anion constituents are the majority charge carriers.

Table 1. Transport number of cation and anion of  $(I_2 + MeOH)$  and  $(I_2 + EtOH)$  at 22°C.

Conc.	$I_2 + \text{Methanol}$		$I_2 + \text{Ethanol}$	
	$t_+$	$t_-$	$t_+$	$t_-$
0.02 N	0.432	0.568	0.332	0.668
0.05 N	0.421	0.579	0.323	0.677
0.20 N	0.410	0.590	0.315	0.685
0.50 N	0.400	0.600	0.309	0.691

**Acknowledgement**

The authors are thankful to Prof. O P Malhotra, Chemistry Department, Banaras Hindu University, for providing the facilities, to Prof. H Junjappa, Chemistry Department, for the encouragement and to the University Grants Commission, New Delhi, for financial support.

**References**

- Brandon S M, Tamres M and Searles Jr. S 1960 *J. Am. Chem. Soc.* **82** 2129  
Fried V, Hammett H F and Blukis U 1977 *Physical chemistry* (New York: Macmillan Co.)  
Mulliken R S 1952 *J. Phys. Chem.* **56** 801  
Palit S R 1976 *J. Indian Chem. Soc.* **53** 1238  
Palit S R and Ghosh S 1979 Annual Convention of Chemists, Abstracts, Phy-1  
Rao C N R, Bhat S N and Dwivedi P C 1972 *Appl. Spectrosc. Rev.* **5** 1  
Reid C and Mulliken R S 1954 *J. Am. Chem. Soc.* **76** 3869  
Riddick J A and Bunger W B 1970 *Techniques of chemistry II. Organic solvents* (New York : Wiley Interscience)  
Tse H and Tamres M 1977 *J. Phys. Chem.* **81** 1367, 1376  
Washburn E W and Bates S J 1912 *J. Am. Chem. Soc.* **34** 1341