# Effect of Solvent Composition on the Molecular Interaction of HCL in 1, 4 Dioxane Mixture Through Conductometry

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**Abstract:** The conductance of HCl solutions of various concentrations in several proportions of 1, 4 dioxane water mixtures is studied. The increase in the observed conductance of these mixtures is individually identified and it is observed that there are specific intermolecular interactions between HCl and 1, 4-dioxane-water mixtures. It is also seen that the specific conductivity of the electrolyte decreases with increasing dioxane content accounting for the possibility of increased molecular interactions, hydrogen bonding and a closer molecular assemblage of the 1, 4 dioxane water mixtures. It is also revealed that the molar conductance decreases with increase in the amount of dioxane which must be due to an increased solvent-solvent interaction and decreased dielectric constant of the dioxane-water medium. The variation in Walden product and degree of dissociation provide useful information on the molecular interaction existing in the system.

**Key words:** Conductivity · Conductometr · Hydrochloric acid · Mixed solvent media · Molecular interactions

## INTRODUCTION

Conductivity is the method used in to test the quality of process water in those applications where ultrapure water is required, such as in the pharmaceutical, microelectronics, waste water treatment, sea water desalination etc [1-3]. As conductance can be measured at low concentrations and reliable values at infinite dilution are readily obtained, it helps in the study of ionic solvation and other related molecular interaction studies [4]. Conductance studies of electrolytes in mixed solvents have received considerable attention in recent years. It is a simple method to study the solvent effects, the nature of ions and the ion-solvent interaction existing in the system, modification in the structure of a solvent due to the presence of an ion and ionic movement in a solution. The study of variation in molar conductance with temperature and solvent composition provides information about ionic mobility, solvent viscosity, hydrogen bonding capability, dielectric constant and its specific interaction with ions [5-7]. Our interest, here is a more detailed interpretation of the observed change of the anomalous proton mobility upon modification of the

structural properties of an amphiprotic solvent either by changing its molecular size and shape or by mixing it with an organic cosolvent. This idea has led to a systematic investigation of the conductance behaviour of hydrogen chloride in this type of solvent medium involving an aprotic solvent. As is known, the 1, 4-dioxane molecule is an apolar (p = 0.45 Dt) and aprotic molecule, but the two oxygen atoms in the ring make it a bifunctional hydrogen-bond acceptor [8, 9].

## MATERIALS AND METHODS

The chemicals used in the present study were of high purity and analytical grade (E.Merck, India). Purification was done by standard procedure [10-12] and the solvent was redistilled before use. A highly precise digital conductivity meter, ModelCDM230 and a conductivity cell were used for conductance measurements. The cell constant of the cell used was $0.92 \text{cm}^{-1}$ with an uncertainty of 0.01%. The instrument was calibrated by using freshly prepared KCl Triply distilled water (specific conductivity of the order of $1 \times 10^{-7} \text{ Scm}^{-1}$) was used throughout this study.

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## RESULTS AND DISCUSSION

**Observed Conductance:** The conductance measurements of 0.1098M, 0.00878, 0.006588M, 0.00549, 0.004392, 0.003294, 0.002196 and 0.001098 M HCl in various proportions of dioxane- water mixtures were studied individually and are represented in Figure 1.

As the concentration of HCl is increased there is a very slight increase in conductance for any given dioxane water composition. This may be due to the fact that the conductance increases with an increase in the mobility of ions. It is also seen that the conductance values observed were very less, when the concentration increases from 0.001 M to 0.1098 M solution. These results indicate that only a minute fraction of the HCl is dissociated into free ions in dioxane -water system which may be due to the presence of non bonding I on pairs present in the oxygen atom of dioxane molecule which are largely aggregated together by coulombic forces. This indicates the presence of specific intermolecular interactions between 1, 4-dioxane and water itself [13]. In addition there is a direct hydrogen bonding between the proton and the free water molecules. This results in lowering the bulk dielectric constant of the solvent medium and the observed conductance decreases with the increase of dioxane content.

**Specific Conductance:** The specific conductance measurements of HCl in various proportions of dioxane-water mixtures were studied individually and are represented in Figure 2. The conductance studies from Figure 4.2 shows that the specific conductance increases with increasing concentration of HCl in dioxane-water medium. The increase in specific conductivity with increasing electrolyte concentrations suggests a multiple series of equilibria involving the formation of triple ions and more highly associated ionic products [14]. As a result contraction of the solvent would be gradually lowered with increasing concentration of HCl, resulting in a net positive volume change per mol of the added HCl.

**Molar Conductance:** Figure 3 shows the molar conductivities of HCl as a function of the square root concentration at 303 K. From the figure it is revealed that the molar conductance decreases with increase in the amount of dioxane which must be due to an increased solvent-solvent interaction and decreased dielectric constant of the dioxane-water medium. Due to the hindrance in the movement of the ions, the ionic velocity is decreased. In other words the bulkier and low dielectric constant dioxane enters into the solvated or hydrated

ions and replaces certain water molecules from either the primary or secondary hydration sheath of the ion, leading to decrease in conductance. The minimum conductance value was observed at 80% dioxane. Moreover, as can be seen, the two oxygen atoms in the 1, 4-dioxane molecule have a distinct influence on the magnitude of the water content corresponding to the minimum value of the limiting molar conductance of hydrogen chloride.

**Walden Product:** The Limiting molar conductance and theWalden product values are shown in Table 1. From Table 1 it is observed that the Walden product increases when the dioxane composition was increased upto 20%. However at higher proportions of dioxane the Walden product was found to decrease. The increase of the Walden product indicates weak solvation of ions. The cluster of water molecules has a lower abiity to donate a hydrogen atom to the solvation of ions. This may reduce the ability of hydrophobic ions to promote the structure in the water rich region resulting in excess mobility, which in turn results in an increase in the Walden product values to attain a maximum [15]. On further addition of aprotic components the self associated structure of water molecules gradually breaks down due to preferential solvation and specific solute- solvent interactions.

**Degree of Dissociation:** Figure 4 shows the degree of dissociation of HCl as a function of the molar concentration at 303 K. From the figure it is seen that when the concentration of both HCl and dioxane increases, the degree of dissociation decreases. This observation confirms the controlling influence of the higher proton affinity of water with respect to the amphiprotic cosolvent on the proton transfer process by decreasing the dielectric constant of the medium and also by increasing the viscosity. Literature studies prove the fact that the addition of dioxane into the HCl binary system worsens the stabilization of the charged particles formed and thereby lowers the dissociation [16]. The values observed in the present work are in perfect agreement with the literature values.

**Dissociation Constant:** Figure 5 represents the plot between the dissociation constant of HCl in dioxane-water as a function of the different molar concentration at 303 K. In mixed solvent systems decrease in hydration of ions also leads to decrease in values of $K_d$ [17]. The variation in values of $K_d$ with dioxane composition is primarily due to change in dielectric constant and the changes in the ionic environment, surrounding the ionic species.
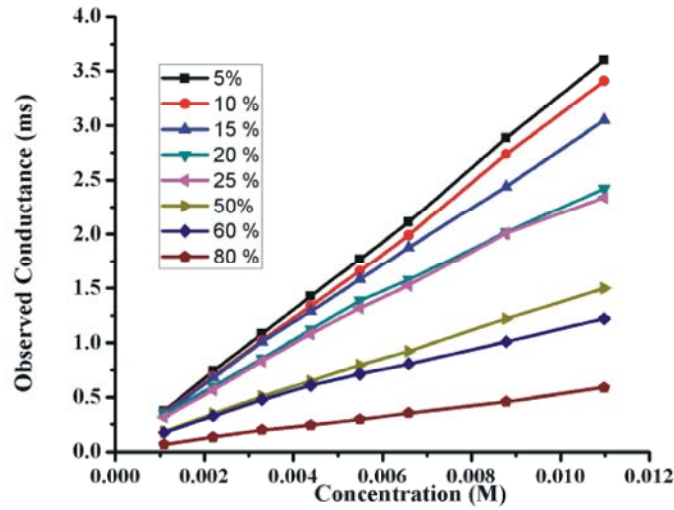
Fig. 1: The observed conductance of HCl in dioxane-water as a function of the different molar concentration at 303 K
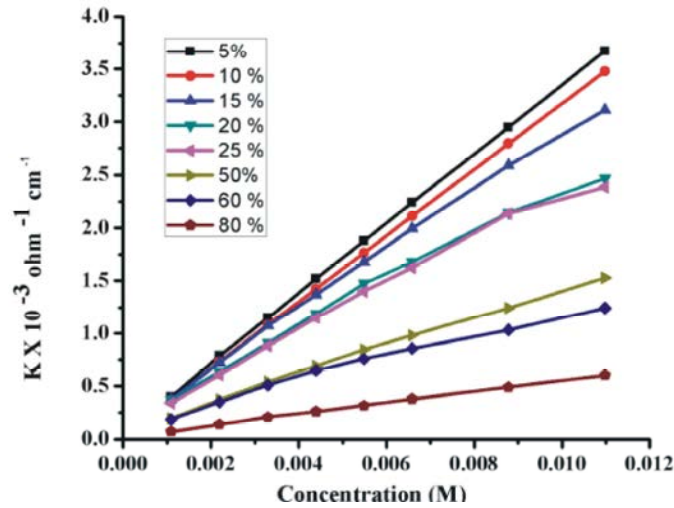


Fig. 2: The specific conductance of HCl in dioxane-water as a function of the different molar concentration at 303 K
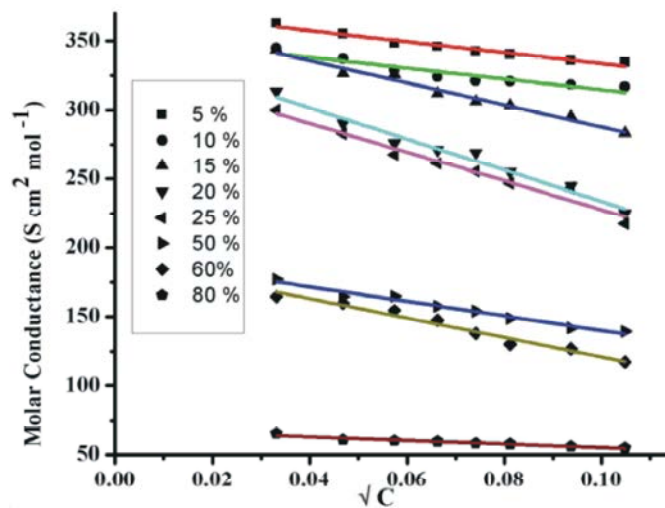


Fig. 3: The Molar conductance of HCl in dioxane-water as a function of the different molar concentration at 303 K
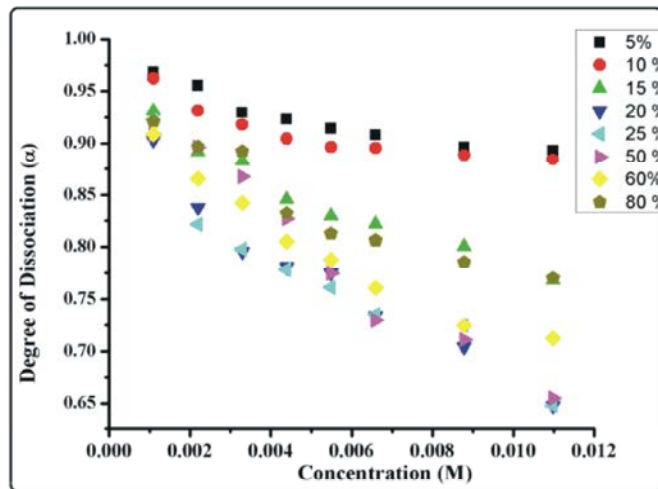
Fig. 4: The degree of dissociation of HCl in dioxane-water as a function of the different molar concentration at 303 K
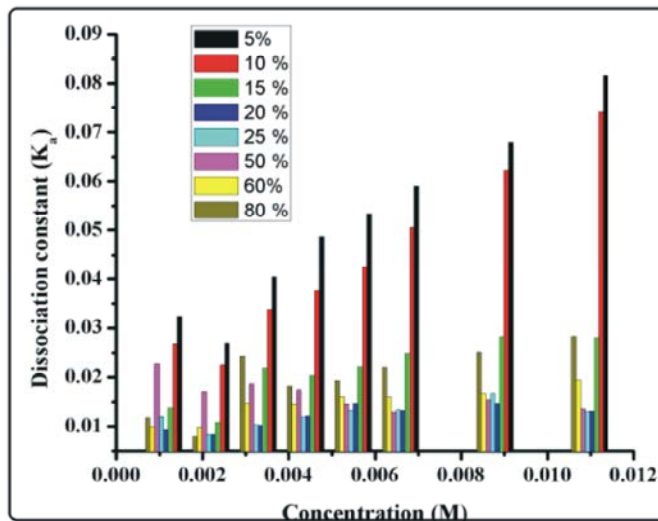


Fig. 5: The dissociation constant of HCl in dioxane-water as a function of the different molar concentration at 303 K

Table 1: Limiting molar conductance and Walden Product of HCl dioxane-water as a function of the different molar concentration at 303 K

| Conc of dioxane (%) | Limiting molar conductance | Walden Product |
|---|---|---|
| 5 | 373.16 | 408.19 |
| 10 | 353.6 | 438.37 |
| 15 | 367.6 | 462.43 |
| 20 | 346.7 | 480.38 |
| 25 | 331.98 | 475.12 |
| 50 | 192.5 | 352.71 |
| 60 | 191.01 | 361.44 |
| 80 | 67.5 | 139.06 |

## CONCLUSION

As is well known, when a cosolvent like dioxane is added to an electrolyte solution we observe a modification of the macroscopic properties of the solvent system along with a change in the transport properties of the solute. In fact, the dioxane can either produce structural changes in the solvent system or perturb the electric field of the ions, owing to the large number of different interactive situations involved. These results, therefore, should yield further information on the proton conductance behavior resulting from possible structural modifications of the amphiprotic medium. Since the solvent has a low dielectric constant and has little tendency to stabilize individual ions through solvation the extent of dissociation of the solute into free, or conducting, ions is quite small. The results of conductivity measurements thus provide detailed information on the ion-ion and the ion-solvent interactions existing in the system.

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