CHAPTER V

DISCUSSION AND CONCLUSION

5.1 Conductivities of Thallic Acetate and Thallous Acetate in Acetic Acid.

The graphs of Λ vs. $\sqrt{c}$ (or $\sqrt{I}$) (Figures 3.2 - 3.5, 4.1, 4.4 and 5.1 shown below), show similar trends, that is, they are linear from the beginning until "I" exceeds a certain value, then the conductivity falls off very steeply and finally the nearly constant conductivity with respect to concentration of electrolyte is resulted.

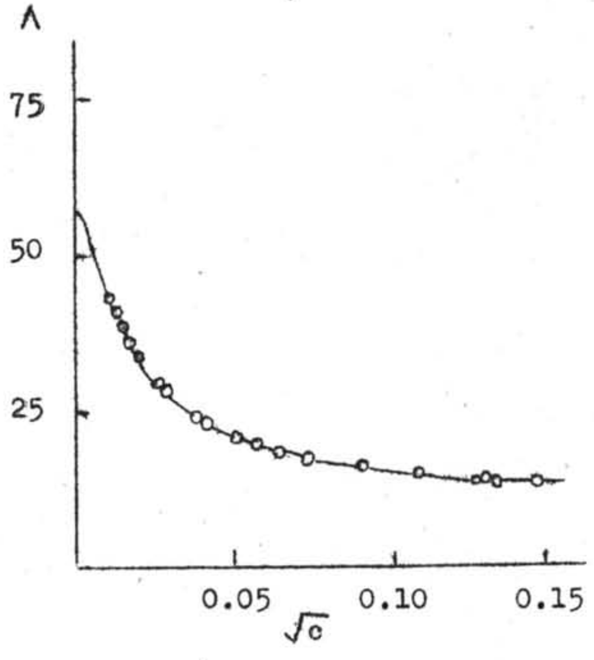


Figure 5.1

Conductivity of Hydrochloric Acid in 82% Dioxane at 25°C $(\varepsilon = 9.53)$(42)

Owen and Waters(42) have attributed this phenomena to the ionic association. In this work, attempt has not been made to estimate the departure of the slope of the phoreogram obtained experimentally from the Onsager slope. Since in doing so one needs to know other quantities such as viscosity, dielectric constant of the system fairly accurately and this is not included in the scope of the present work. Besides we can compare the conductivity of $Tl(OAc)_3$ in glacial acetic acid with that in anhydrous acetic acid, the conductivity of TlOAc in glacial acetic acid with that in anhydrous acetic acid. The conductivities in anhydrous acetic acid in all cases are higher than those in glacial acetic acid (see Tables 3.7.1 vs. 3.7.2, and 3.7.3 vs. 3.7.4). This seems to be in contrast to the fact that glacial acetic acid with small amount of water should have a higher ε than that of anhydrous grade and that the conductance is a function of ε of solvent, it increases uniformly with increasing ε. The explanation can be offered in term of the different extent of association that might occur in the 2 systems. In glacial acetic acid containing a few % of water, should also contain free acetate ions where-as in anhydrous acid, the presence of free ion is negligible {specific conductance = $(4.98 - 5.90) \times 10^{-8}$ mho.cm^{-1} in the former and =$(0.77 - 1.15) \times 10^{-8}$ mho.cm^{-1} in the latter case}. Hence association of thallium salt in glacial acetic acid is very likely to be responsible for the low conductance discussed above. Consequently, the values of "a" and "K" computed from the conductivity data are somewhat different for the two systems. The differences are found to be more pronounced for the "a" and "K" of $Tl(OAc)_3$ than those of TlOAc.

According to the critical Bjerrum distance,

$$q = \frac{|Z_1 Z_2| e^2}{2 \varepsilon k T}$$

When the dielectric constant of acetic acid, $\varepsilon = 6.21$ is inserted, the above equation gives

$$q = 45.076467 \times 10^{-8}\text{cm for 1:1 electrolyte}$$

$$\text{and } q = 135.229401 \times 10^{-8}\text{cm for 3:1 electrolyte}$$

As has been stated earlier the association will take place if the distance between 2 ions is $a \leq r \leq q$. In the case of $Tl(OAc)_3$ "a" = $(10.46 - 10.88) \times 10^{-8}$cm and $q = 135.23 \times 10^{-8}$cm whereas in the case of TlOAc "a" = $(9.11 - 9.29) \times 10^{-8}$cm and $q = 45.08 \times 10^{-8}$cm. At least qualitatively speaking, the results thus obtained indicate that ion-association indeed occurs quite easily in the solvent of such a low ε as acetic acid

5.2 Solubility Measurement

In the solubility study of electrolyte solution with added sparingly soluble salt whose anion is in common with the solute salt the equilibria of the types below should be considered

$$MX \rightleftharpoons MX\text{ (dissolved ion-pairs)} \rightleftharpoons M^+ + X^-$$

$$\text{and} \quad MX\text{ (ion-pairs)} \rightleftharpoons M^+ + X^-$$

If both salts are negligibly dissociated into free ions (in the solvent of low ε) there should be no appreciable decrease in solubility arising from the familiar common ion effect. The change in solubilities of $Tl(OAc)_3$ and Tl(OAc) in acetic acid with added KOAc and NaOAc (Tables 3.9.1 - 3.9.2 and 3.10.1 - 3.10.2) however indicates that there are additional effects involved in the equilibria processes. These effects may be ion-pair formation, ion-triples formation or higher complexes formation. In the previous chapter, the calculation method for "K" and "a" as developed by Davies was applied to both $Tl(OAc)_3$ and TlOAc solubility data in glacial acetic acid. Only "K'", the stoichiometric equilibrium constant could be obtained. This is due to the fact that in order to obtain "K" the calculated "K'" must be multipliedby $f_{\pm}$, the mean ionic activity coefficient. The problem encountered is that the Debye-Huckel equation or even the modified equation of the similar form is not capable for the evaluation of $f_{\pm}$ in the solvent of very low ε. The Debye-Huckel constant A in the equation below

$$-\log f_{\pm} = \frac{A|Z_1 Z_2|\sqrt{I}}{1 + Ba\sqrt{I}}$$

becomes enormous, about 23 in comparison to 0.5 for water. This will bring $f_{\pm}$ down to an absurdly small value unless "I" is negligibly small. In the solubility studies as presented here "I" cannot be pre-adjusted, since it is largely depending on the extent of the ion-pair formation (see the details of calculations). However, the treatment adopted from Davies shows a good straight line and the amount of ion-pair, and of simple salts could be obtained graphically (Figs. 4.11 - 4.12).

It should be noted here that the sharp decrease of $f_{\pm}$ with increasing c may be caused by the formation of ion-triples of the type

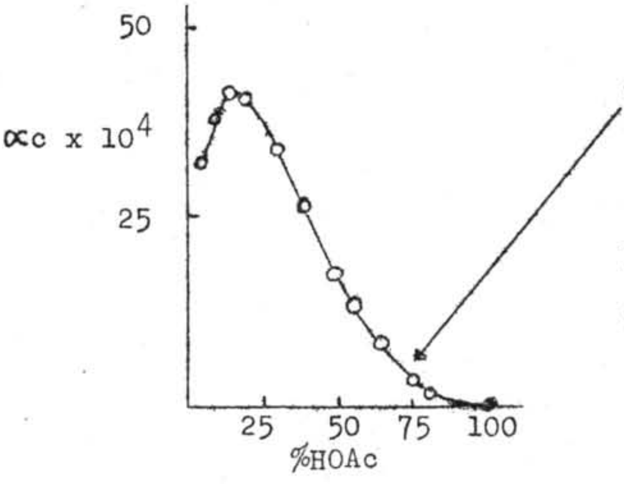
$$A^+ + AB \rightleftharpoons A_2 B^+$$

This is in accord with Creeth's finding(43) from his emf. work on the sulphate of thallium salt that Tl(I) associates with negative ion more strongly than is expected for ion-pair formation.

For TlOAc, the additional problem to what have been discussed for $Tl(OAc)_3$ is that TlOAc is far from being a sparingly soluble salt in acetic acid and hence the method of Davies could not be applied for the determination of K and "a". Attempts however have been made to study the effect of acidity and dielectric constant on the solubility of TlOAc. The effects of which will be discussed in the following section.

5.3 Effects of Dielectric Constant of the Solvent, Size and Charge of Ions on Solubility

Solubilities of $Tl(OAc)_3$ and TlOAc increase with decreasing per cent of acid (increasing of per cent of water). This cen be attributed to two effects namely the effect of increasing acetate ion concentration and the effect of increasing ϵ of the solvent mixture. In the range of the working acid concentration used in this work, the two effects were operating side by side. It is premature at present to decide which is the predominating effect on the solubilities of the salts since the working concentration of acid does not permit the discussion. If, however, the similar experiments would be carried out at the other range of the acid concentration i.e., at the left side of the maximum of the curve shown in Fig. 5.2,



Working acid concentration of this work

Figure 5.2

Plot of $[OAc^-] = \alpha c$ of acetic acid as a function of % HOAc$^{(35)}$.

The increase in αc then will automatically decrease the value of the ϵ of the solvent mixture. Hence the direction of the change in the solubility will serve as a guide for the development of a satisfactory proof to the influence of one or the other effect mentioned above. This kind of investigation should be of interest for future work of this project.

When the solvent mixture was changed to KOAc in glacial acetic acid and NaOAc in glacial acetic acid, the situation is somewhat different. In this case ϵ of the solvent mixture is approximately the same throughout and can be assigned to the value of that of pure acetic acid i.e., 6.21. The difference in solubilities of $Tl(OAc)_3$ in KOAc-HOAc mixture and in NaOAc-HOAc mixture is therefore not governed by ϵ but may be due to the different in the competition of OAc^- for association to the ion of the solute and of the solvent itself. The size and the charge of cation concerned will be topics of discussion. Tl^{3+} is **smaller** in size than K^+ but is equally small when compare with Na^+. If association is responsible for the solubility of Tl^{3+} in such mixtures, the two factors, i.e., size and charge will work in an opposite direction. It was found in some systems such as in the case of solution of tetraalkyl ammonium picrate in organic solvent that the large anion displays a surprising tendency to associate with large cations. Hence in the case of Tl^{3+} and K^+, acetate ion may associate to K^+ better than Tl^{3+} as far as the size of the cation is concerned whereas the extent of association of Tl^{3+} and Na^+ by acetate ion may be more or less of the same degree. However, ionic charge also plays an important deciding factor on association. A better solubility of Tl^{3+} in KOAc - HOAc mixture than $NaOAc \cdot 3H_2O$ - HOAc mixture may be due to the multicharge on Tl^{3+} which facilitate the association regardless of the size effect.

In the case of TlOAc, it is not possible to say much about the solubility of this salt in any system chosen for study. It is partly due to the fact that TlOAc exhibits a large solubility in the solvent mixtures under investigation so much so that the existing ionic association theories are not applicable. Again if ionic association is thought to cause the solubility equilibria to shift more to the right what have been found by the former workers can then be used to explain the excessive solubility of TlOAc in the presence of acetate ion. Tl(I) has a marked tendency to form complex and this is in contrast with Rb of almost identical radius. It is likely that in an unsymmetrical electric field the 6s electron pair moves to a 6 sp orbital leaving a vacant 6 sp orbital on the opposite side of the cation for an ion-coordination. Results from the present work lead to the conclusion that solubilities are quite specific in nature and must depend on quite specific interaction between solute and solvent.

5.4 Concluding Remarks

The values of "K" and "a" (see Tables 4.3, 4.6, 4.8, 4.10) seem to be acceptable. Griswood and collaborators(44) have measured conductivity of a number of univalent salts and got ion-pairs dissociation constant of the order of 10^{-7}. Such small values of the constant strongly suggested that the explanation of the neutral salt effect describes here cannot be given in terms of long range interionic effects. Since the extent of ionic association depends upon the potential energy of an ion-pair (or more complex aggregate), and this in turn depends upon how else the charges on the ions may be brought together, ionic size is a very important factor in determining the individuality of dissociation constants. Here, the Bjerrum's model was used in the computation of "a" and K. It should be stressed that this is the simplest model among other electrostatic models. The theory of Fuoss and Onsager(15) was also considered but in presenting their theory of the conductance of free ions they were careful to point out that it is applicable only to dilute solution below a concentration where the value κa is less than 0.2, which is, unfortunately not the operating range of concentration of this work. It is realised that for weak electrolyte $\Psi(r)$ in the original Debye-Huckel equation is a much more complicated function of than that postulated by Bjerrum's theory. On the other hand, we may expect this theory to hold in media of low ε for electrolytes which have sufficiently large "a" value. Seward and Hamlet(45) have shown by solubility measurement of univalent salts in glacial acetic acid that "a" is equal to .

8.5 - 9.5 A$^{\circ}$, which is comparable to what is obtained in this work.

The present work has achieved its goal in a way that the simplest electrostatic model of Bjerrum has been applied to the conductivity data of salts in the solvent of low ϵ resulted in the reasonable value of K and "a". Both conductivity and solubility work indicate that there are ion-association taking place in the system of TlOAc and $Tl(OAc)_3$ in acetic acid. The discrepancy between such values obtained by two different experimental methods, namely conductivity and solubility measurements should not be of any surprise since it is well known from the previous work that "a" is an operational concept which has a definite value only for specific conditions of measurement and calculation and that in many cases this size is a description of the influence of the ion on it's environment. Factors such as size, charge, dipole moment and symmetry would all be expected to affect the ion-solvent interaction and therefore, the ionic conductance and ion pair formation. Solubility measurement in organic solvent of low ϵ have not, in general, led to agreement with theory except in a qualitative way in particular when the determination of $f_{\pm}$ of the electrolyte in the system under-study is not possible. The $f_{\pm}$ values should be obtained by other methods such as isopiestic method to enable the thermodynamic equilibrium constant "K" and hence "a" to be calculated, in such systems that are far from working limit of the Debye-Huckel law.

Appendix I

Cell Constant Determination

For cells E and F which have small cell constant values, the intercomparison method depends on that for the same solution, the specific conductance must be equal.

$$(L)_{\text{cell C}} = (L)_{\text{cell E}}$$

$$\left(\frac{1}{R_{\text{corr}}} \times \text{cell constant}\right)_{\text{cell C}} = \left(\frac{1}{R_{\text{corr}}} \times \text{cell constant}\right)_{\text{cell E}}$$

$$(\text{cell constant})_E = \frac{\left(\frac{1}{R_{\text{corr}}}\right)_C (\text{cell constant})_C}{\left(\frac{1}{R_{\text{corr}}}\right)_E}$$

The method of reference (30) uses the following relations

$$\frac{1}{R_{\text{solution}}} - \frac{1}{R_{\text{solvent}}} = \frac{1}{R_{\text{solute}}} = \frac{1}{R_{\text{corr}}}$$

$$L_{\text{corr}} = 0.14992\,c - 94.67 \times 10^{-3} c^{3/2}$$

$$\text{and} \quad L_{\text{corr}} = \left(\frac{1}{R_{\text{corr}}}\right) \times (\text{cell constant})$$

where c is in equi/l

In the same way, the method of reference (31) uses the relation that

$$\Lambda = 149.93 - 94.65\sqrt{c} + 58.74\, c \log c + 198.4\, c$$

Both of them are valid at very dilute solution.