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## 2. REVIEW

### 2.1. CONDUCTOMETRIC METHOD

Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore ion-ion and ion-solvent interactions can be better studied. Ionic association of electrolytes in solution depends on the mode of solvation of its ions [Das and Hazra, 2002; Guha *et al.*, 2003; Roy *et al.*, 2006] which in turn depends on the nature of the solvent or solvent mixtures. Solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Conductance measurement, besides providing information on the mobility of ionic species in solution, is the most direct and accurate techniques available at present to determine the extent to which ions associate in solution [Debye-Huckel, 1923]. Thus, extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [Das and Saha, 2000; Roy *et al.*, 2008; Chanda and Roy, 2008; Parvatalu and Srivastava, 2003] to examine the nature and magnitude of ion-ion and ion-solvent interactions. Behavior of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity. Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolytic solutions. Because of its relative simplicity and versatility, the measurements of the conductivity of electrolyte solutions which can be carried out to a very high precision, remains an important tool to obtain information about electrolytes in different solvents

[Bianchi *et al.*, 2000]. Conductivity of aqueous system has recently provided valuable information about the influence of the solvent number-density in the low fluid-density regime and its effect on the ion-pairing equilibrium [Gruskiewicz and Wood, 1997; Zimmerman *et al.*, 1997]

## 2.2. ION PAIR AND TRIPLE ION FORMATION IN 2:1 AND 1:1 COMPLEXES

Notwithstanding the non-specific role of water in many non-aqueous solutions, in some cases it may have specific effects due to ion-water interactions which depend on the particular nature of the ions and solvent. Thus the conductance of associated  $\text{AgNO}_3$  and  $(\text{CH}_3)_2\text{TlI}$  in dimethylformamide increase with the water content in contrast to the decrease found for dissociated salts, In methanol and ethanol, the conductance of perchloric acid decreases significantly upon addition of 0.3% water [Goldenberg and Amis, 1962]. This was attributed to the change in the proton transport mechanism.

Yeager and Kratochvil [Yeager and Kratochvil, 1975] have recently reported conductance data for Cu(I), Ag(I) and Tl(I) salts in AN which shows that the salts of the two first cations are essentially dissociated, while Tl(I) salts are associated similarly to KSCN. The  $\Lambda^0$  values indicate that Cu(I) is a very large solvodynamic unit, probably in the form  $\text{Cu}(\text{AN})_4^+$ . The association of  $\text{AgNO}_3$  and  $\text{AgClO}_4$  in AC and Cyclohexanone [Griffiths *et al.*, 1958] can be reasonably accounted for by electrostatic interactions, but  $\text{AgNO}_3$  in benzonitrile and  $\text{AgNO}_3$  and  $\text{MeTl(I)}$  in DMF require too small  $\alpha$  values (1.6, 1.3 and  $1.1\text{\AA}$ ) if association is considered purely electrostatic.

Using conductance method Steekumar, Rajendran and Kalidas had studied ion-solvent interactions of copper (II) Perchlorate in both water-DMSO and water-Pyridine. It was observed that the  $\Lambda_0$  (equivalent conductance) of copper (II) Perchlorate first decrease sharply on addition of pyridine upto 20 wt%, then gradually decreases upto 60 wt% pyridine and

finally it increases. The  $\Lambda_0$  also decreases continuously with the addition of DMSO mixtures. The Walden product of copper (II) perchlorate decreases continuously with the addition of DMSO in water-DMSO mixtures. In case of pyridine, it first decreases sharply with the addition of pyridine and then it increases slightly and subsequently decreases with the addition of pyridine. It may be of interest to point out that strong solvent-solvent interaction resulting in the formation of water-DMSO complexes compete with the ion solvent interactions and presumably give rise to the complex behavior.

Recently, Rajmuhon and Bag [Bag *et al.*, 2009] had studied the conductance and ion association of bis (1-amidino-O-methylurea copper (II) acetate in aqueous medium at 5-40°C using Shedlovsky equation. As evident from experimental values of Stoke's radius of anion ( ${}^{\ominus}\text{CH}_3\text{COO}^{\ominus}$ ) is more or less constant with the variation of temperature. The Stoke's radii for the complex cations increase with temperature which indicates that the cations become more hydrated as the temperature rises. Walden product ( $\Lambda_0\eta_0$ ) of the ions is most nearly constant for those of large size due to their being polyatomic or extensive hydration. The ion association process will occur spontaneously and exothermic in nature which is supported by the positive value of  $\Delta S^0$  and the negative value of  $\Delta H^0$ . Then the variation of  $\Delta G^0$  with temperature reveals that the ion association process is favored at low temperature. Singh, Rajmuhon and Manihar had studied the electrical conductivities and ion pair-formation of bis-1-amidino-O-methylurea-, bis-1-amidino-O-ethylurea-copper (II) halides and nitrates in aqueous solution at 18°, 25° and 35°C. From the values of association constants of these complexes at different temperatures, the thermodynamic functions can be estimated in order to understand the nature of ion-association. The limiting equivalent conductivities ( $\Lambda_0$ ) of the complexes were determined by Onsagar method of extrapolation. The sizes of ion pairs were evaluated from Bjerrum equation, Stokes' law and Dennison-Ramsey theory. The observed

values of association constants ( $K_A$ ) for bis 1-amidino-Omethylurea copper(II) and bis 1 -amidino-O-ethylurea copper(II) chloride, bromide, iodide and nitrate are followed the order:



Using conductivity, Butler, Schiff and Gordon [Butler *et al.*, 1951] found for NaCl solutions in methanol the relative decrease of  $\Lambda$  for 1% of added water varies with the concentration of the salt, extrapolating precisely to the percentage decrease of the fluidity of methanol containing 1% of water when the concentration of salt is zero. Barthel [Barthel *et al.*, 1977] observed the same behavior when water was added to NaOCH<sub>3</sub> in methanol. Similar effects have been found for nitromethane [Unni *et al.*, 1963], dimethylformamide [Prue and Sherrington, 1961], and sulpholane [Fernandez-Prini, 1973] solutions upon addition of water. The observed conductance change can be essentially explained in terms of viscosity change introduced in the media by the addition of water and may be considered of non-specific nature. This justifies the use by some workers of hydrates instead of the anhydrous salts, the first being more readily soluble in some non-aqueous solvents [Dawson *et al.*, 1963]. D'Aprano and Fuoss [D'Aprano and Fuoss, 1963] found a very large increase in the conductance of picric acid dissolved in acetonitrile as water was added ( $\Lambda$  increases ten times for 0.02% of water). Ammonia, which is a likely impurity in acetonitrile, also increases the conductance of picric acid probably due to formation of the ammonium salt which is highly conducting. The abnormal variation of conductance with concentration for transition metal and aluminium salts in N-methylacetamide was attributed to the presence of acetates [Dawson *et al.*, 1962] a common impurity in the solvent.

The conductance of Alkali metal (M) halides in methanol, ethanol and propanol of MClO<sub>4</sub> and MNO<sub>3</sub> in methanol [Copley and Hartley, 1930], and of MSCN [Butler *et al.*, 1951] in

propanol were determined before the extension of the conductance theory. Many of the results have been reanalyzed [Prue and Sherrington, 1961; Kay and Evan, 1964] using the conductance equations. For these electrolytic solutions,  $\Lambda^0$  increases with the size of the ions; that is, the solvodynamic units are larger for the smaller ions. In methanol, alkali metal salts are essentially dissociated except the nitrates. Kay and Hawes have measured the conductance of CsCl in methanol and ethanol [Kay and Hawes, 1965]. Analysis of the data in the former solvent using Fuoss and Hsia's equation yields for  $d = 7.00 \text{ \AA}$ ,  $K_A = 20.8 \text{ mol}^{-1}$  corresponding to  $\alpha = 3.6 \text{ \AA}$ . Recent data [Conti and Pistoia, 1968] for  $\text{KClO}_4$  and  $\text{CsClO}_4$  in methanol are at variance with the behavior described above and indicate both salts are associated.  $\text{AgNO}_3$  in methanol [Busby and Griffiths, 1963] and ethanol [Griffiths *et al.*, 1958; Parfitt and Smith, 1963] is more associated than  $\text{MNO}_3$ .  $\text{MPic}$  [Coplan and Fuoss, 1964] and  $\text{MBPh}_4$  [Kunze and Fuoss, 1963] are dissociated in methanol excepty  $\text{M}=\text{K}$ . However,  $\text{KBPh}_4$  can be considered a dissociated electrolyte with  $\alpha = 5.6 \text{ \AA}$ , if Fuoss and Hsia's equation is used to evaluate the data. Lithium and Caesium dinonylnaphthalene-sulphonates [Little and Singleterry, 1964] are probably associated in methanol but definitely so in ethanol and butanol. The association of lithium and ammonium halides in butanol [Venkatesetty and Brown, 1963] in the range  $0\text{-}50^\circ\text{C}$  agrees with Bjerrum's model if  $\alpha = 3.7 \text{ \AA}$ . The Walden product is almost constant in this range of temperatures. Alkali metal salts in alcohols show in general a behavior which may be accounts for by the electrostatic model if the ions are considered solvated. In addition, association is larger for large  $\text{M}^+$  indicating that ion pairs are solvent separated. Interesting exceptions are the MRO bases in ROH [Barthel *et al.*, 1977] ( $\text{R} = \text{Me. or Et.}$ ). For  $\text{R} = \text{Me}$  the salts were considered dissociated but the contact distances increase from  $1.74 \text{ \AA}$  for  $\text{Li}^+$  to  $3.13 \text{ \AA}$  for  $\text{Cs}^+$ . When  $\text{R} = \text{Et}$  the bases are associated and  $K_A$  goes through a minimum at the potassium salt ( $K_A=176$  for  $\text{Li}^+$ , 36 for  $\text{K}^+$ , and 65 for

Cs<sup>+</sup>). Barthel and his groups assumed that large cations form solvent-separated pairs but the small ones polarize the solvent molecules around them such that contact pairs are formed.

This assumption is akin to the hypothesis of localized hydrolysis invoked by Robinson and Harned [Robinson and Harned, 1941] to explain the reversal of the order of activity coefficients of alkali metal hydroxides, fluorides, acetates and formates in water.

The mobilities and association constants of tetraalkylammonium (R<sub>4</sub>N) halides are larger for iodides suggesting solvation of the anions through hydrogen bonds. In general R<sub>4</sub>NI are more associated in ROH than in dipolar aprotic solvents through a minimum for R=Pr. Both these effects shows that the effect is especially marked for bulky cations. Kay, Evans and coworkers [Kay and Evans, 1968; Evan and Broadwater, 1968] have invoked a two step association process similar to the equilibria to explain these results.

The conductance of acids dissolved in alcohols indicates that the proton has excess mobility [Murgulescu *et al.*, 1965; Shedlovsky, 1959; Spivey and Shedlovsky, 1967] due to a proton-jump mechanism of transport. HCL is associated in methanol ( $K_A = 17 \text{ mol}^{-1}$ ) and in ethanol [Bezman and Verhoek, 1967] ( $K_A = 48 \text{ mol}^{-1}$ ). Picric acid is strongly associated in both solvents [DAprano and Fuoss, 1963] ( $K_A = 3960$  and  $5870 \text{ mol}^{-1}$  respectively). The amides and N-monoalkylamides have very large dielectric constants such that no association would be expected for (1:1) salts ( $l = 1.5 \text{ \AA}$  in N-monomethylacetamide (NMA) at  $32^\circ\text{C}$  and  $2.5 \text{ \AA}$  in formamide (F) at  $25^\circ\text{C}$ ). However, a large number of uni-univalent salts show negative deviations from the Onsager limiting law in these solvents and also produce a considerable increase in the viscosity of the solution with increasing concentration. Positive deviations were observed for some uni-univalent salts in acetamide at  $94^\circ\text{C}$ . In F (1:1) salts give small positive deviations [Tewari and Johari, 1963; Dawson *et al.*, 1955] with the exceptions of LiNO<sub>3</sub>, sodium acetate, and Tl<sup>+</sup> salts. Notley and Spiro [Notley and Spiro, 1966] reassessed

the conductance of salts in F with equation finding an average  $\alpha = 1.8 \text{ \AA}$ . If the conductances are corrected for the increased viscosity of the solution  $\alpha$  becomes  $3.8 \text{ \AA}$ .  $\Lambda^0$  in F increases with the size of the alkali metal and halide ions, while the opposite holds for  $R_4N^+$ . In NMA the conductance of alkali metal halides [Dawson *et al.*, 1955; French and Glover, 1955] varies linearly with  $C^{1/2}$  but the slopes is 5-10% more negative. Even when viscosity corrections were applied to  $\Lambda$  no satisfactory interpretation was found for KCl in NMA [Kortum *et al.*, 1968] and in N-methylpropionamide (NMP) [Hoover, 1964].  $R_4N$  salts in NMA give larger negative deviations than alkali metal halides [Dawson *et al.*, 1958] and there is evidence [Singh *et al.*, 1968] that these salts disrupt the structure of the solvent. A similar behavior was found for 1:1 salts in N-methylformamide (NMF). The suggestion that the continuum model fails in these solvents because ions would depolymerise the solvent chains producing a local region of lower dielectric constant, seems unlikely in view of self-diffusion studies in NMA [Williams *et al.*, 1957], of the increase in viscosity produced by increasing electrolyte concentration, and of the fact that polyvalent salts behave according to the continuum model even if conductances are not corrected for viscosity effects. Alkaline earth halides and perchlorates in NMA [Dawson *et al.*, 1958] show positive deviations which increase from  $Ba^{2+}$  to  $Mg^{2+}$  as expected for solvated ions. Johari and Tewari found bivalent sulphates to dissociate in F [Johari and Tewari, 1965] but having small  $\alpha$  values,  $MgSO_4$  may also be considered slightly associated in F but is completely dissociated in NMF ( $\alpha=3.38\text{\AA}$ ). Copper m-benzenedisulphonate shows positive deviations in NMP [Hoover, 1964]. The conductance of 3:3 salts in F [Johari and Tewari, 1965] is in good agreement with the simple electrostatic model, eg.,  $LaFe(CN)_6$  and  $Co(en)_3Co(CN)_6$  have  $K_A= 243$  and  $605$  respectively, corresponding to  $\alpha = 10.08$  and  $7.0\text{\AA}$ . The values of  $\Lambda^0$  and  $K_A$  indicate that  $La^{3+}$  is a larger species in F than the complex ions  $Co(en)^{3+}$  or  $Co(NH_3)_6^{3+}$ . The behavior found for the conductance of 1:1 electrolytes in these solvents agrees with some evidence of abnormal

equilibrium properties [Held and Criss, 1965; Bonner *et al.*, 1969]. As was in the case for alcohols, it is probable that hydrogen bonded solvents affect the behavior of electrolytes in a way not predicted by the continuum model, this effect being more noticeable with smaller electrostatic interaction between ions.

Conductance measurements of acids in NMA [Dawson *et al.*, 1957] and F [Dawson *et al.*, 1954] indicate that the protons have no excess mobility. Partially substituted ammonium salts show the same behavior as  $R_4N$  salts in NMA [Dawson *et al.*, 1955]. In formic acid (1:1) salts were found to be dissociated [Wehman and Popov, 1968]. HCl is associated ( $K_A=90 \text{ mol}^{-1}$ ) due to the acidic nature of the solvent, and formate and  $H^+$  ions have excess mobility suggesting a proton-jump transport mechanism for these ions. Association of weak bases in acetic acid has been studied by conductance. Brewster, Schmid and Schaap [Brewster *et al.*, 1959] found that the anomalous conductances reported in ethanolamine [Briscoe and Dirkse, 1940] are due to solvent impurities. In this solvent small ions are more solvated as indicated by  $\Lambda^0$ , halides are slightly associated and the nitrates, nitrites and thiocyanates more associated. In ethylene and propylene diamines,  $Br^-$  has a lower conductance than  $I^-$  and  $R_4NI$  are more associated than KI [Fowles and McGregor, 1964]. The difference of  $K_A$  in both solvents can be accounted for by the change in  $\epsilon_r$ .

The large number of conductance measurements for  $R_4N$  salts in dipolar aprotic solvents in dipolar aprotic solvents are in fair agreement with the continuum model, with their association being larger for small R.  $R_4N$  salts are essentially dissociated in nitromethanes (NM) [Coplan and Fuoss, 1964] with the exception of the bromides and chlorides of R= Me and Et. The Stokes radius of  $i\text{-Am}_4\text{NBPh}_4$  is  $8.3\text{\AA}$  in NM [Coetzee *et al.*, 1965], almost the same as in acetonitrile (AN). In nitrobenzene (NB) tetraalkylammonium salts associated [Kay and Evans, 1964] with the association being larger for the smaller cations. They have,

however, more associated than in other dipolar aprotic solvents of similar  $\epsilon_r$  [Boyd, 1961] suggesting NB is a poor solvating medium. Alkenes carbonates are solvents with large dielectric constants. In ethylene carbonate [Kempa and Lee, 1961],  $R_4N$  salts show small negative deviations but the restricted concentration range employed for the conductance measurements does not allow a more detailed analysis of the data. In propylene carbonate (PC) they are dissociated [Fuoss and Hirsch, 1960].

In sulpholane ( $TMSO_2$ ),  $R_4NClO_4$  [Della Monica and Lamanna, 1968] and  $Et_4NI$  are slightly associated ( $K_A=3-6\text{mol}^{-1}$ ) according to the Pitts equation with  $d=5.0\text{\AA}$ . In dimethylsulpholane [Eliassaf *et al.*, 1970],  $PhMe_3NI$  is associated but  $Ph_4AsI$  is not. Recent measurements of conductance of  $R_4N$  salts in dimethylsulphoxide (DMSO) show the salts to be essentially dissociated. Unfortunately the study was restricted to very dilute solutions so that not much weight can be put on the  $\alpha$  values obtained.

Evans, Zawoyski and Kay analysed data for  $R_4N$  salts in acetone (AC) [Reynolds and Kraus, 1948; McDowell and Kraus, 1951; Walden *et al.*, 1926] with the Fuoss-Onsager equation. They found  $K_A$  decreases with cation size, and for the anions, association decreases in the order  $Bu_4NBr$  ( $K_A = 264$ )  $> I^-$  (143)  $\cong NO_3^- > ClO_4^-$  (80)  $> Pic^-$  (17). This agrees with the data for methylethylketones [Hughes and White, 1966]. The fact that association of  $Bu_4NClO_4$  [Inami *et al.*, 1961] in AC, benzonitrile, and methylethylketone corresponding to  $\alpha = 4.85\text{\AA}$  for the three solvents, indicates formation of contact ion pairs. Tetraalkylammonium halides in dimethylformamides (DMF) [Sears *et al.*, 1955] have small association constants when the data are evaluated with Shedlovsky's equation. When the data for  $Me_4NPic$  in DMF [Sears *et al.*, 1956] is assessed with Fuoss and Hsia's equation,  $\alpha = 6.0\text{\AA}$

Acetonitrile (AN) is probably the most commonly employed dipolar aprotic solvent medium for studies of electrolytic conductance. Picrates and halides, hexafluorophosphates [Eliassaf

*et al.*, 1970], perchlorates [Springer *et al.*, 1969], nitrates [Berns and Fuoss, 1961] and substituted borates [Brown and Fuoss, 1960] of  $R_4N^+$  cations have been studied conductometrically in AN. Older conductance data for  $R_4N$  salts in AN [Walden and Birr, 1929; Kortum *et al.*, 1955; French and Muggleton, 1957] have been re-evaluated. These results show that the association constants for salts of a given  $R_4N^+$  cation vary with change of anion as in AC, hexafluorophosphates and substituted borates being practically dissociated in AN. No association is found for solutions of  $Am_4N^+$  salts and some  $Bu_4N^+$  salts in AN. The behavior of tetraalkylammonium salts in adiponitrile [Sears *et al.*, 1967] is similar to that in AN.  $Et_4NClO_4$  in valeronitrile [Banewicz *et al.*, 1968] has an association corresponding to  $\alpha = 3.3 \text{ \AA}$  and for  $Bu_4N^+$  in phenylacetonitrile,  $\alpha = 5 \text{ \AA}$  independent of the temperature.

Janz and Dasnyluk [Janz and Danyluk, 1960] have reviewed the conductance data for acids in dipolar aprotic solvents upto 1959. Variations of the conductance of acids with time have been reported for some solvents. The conductances of aged solutions of HBr [Janz and Ahmad, 1964] in benzonitrile and AN and of HCL in the former solvent [Janz and Tomkin, 1973] show the acids are very associated. However, the  $\Lambda^0$  values obtained are much smaller than expected, e.g.,  $\Lambda^0_{HBr} = 11.8$ ,  $\Lambda^0_{HCL} = 1.5$  compared to  $\Lambda^0_{HClO_4} = 51.5 \text{ \Omega}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in benzonitrile. In AC and nitriles,  $HClO_4$  is more associated than  $Bu_4NClO_4$  [Coetzee and McGuire, 1963], the addition of small amounts of water to the acid in AN reduces its association to half of its value due to the efficiency of  $H_2O$  in solvating the ions  $CH_3CNH^+$  and  $ClO_4^-$ . In DMSO, HCL has  $\Lambda^0 = 38.7 \text{ \Omega}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $K_A = 1.15 \times 10^2 \text{ mol}^{-1}$  [Bolzan and Arvia, 1970]. In DMF, HPic is more dissociated than HBr, HCL having an even larger association  $K_A (HCl) = 3.5 \times 10^3$  at  $20^\circ\text{C}$ ) [Thomas and Rochow, 1957]. In AN, HPic is strongly associated [Yeager *et al.*, 1973] suggesting that AN is a poorer solvating medium than DMF and DMSO.

Prue and Sherrington measured the conductance of alkali metal(M) salts in DMF and reassessed existing data for some of these salts in DMSO [Sears *et al.*, 1956], dimethylacetamide (DMA) [Lester *et al.*, 1956], and dimethylpropionamide (DMP) [Wilhoit and Sears, 1956]. Alkali metal salts are dissociated in in these solvents with the exception of nitrates and LiCl in DMF. The sum of the Stokes' radii for alkali metal salts corresponds to large solvodynamic units, e.g., for KI it is 5.3 Å in DMF, 5.6Å in DMP, and 5.1Å in DMSO.  $\text{MClO}_4$  in  $\text{TMSO}_2$  [Della Monica and Lamanna, 1968] and AN [Conti and Pistoia, 1968] are slightly associated while  $\text{MBPh}_4$  in AN are dissociated [Kay and Evans, 1968] except for  $\text{CsBPh}_4$ . For all these electrolytic solutions the mobilities (excepting  $\text{Li}^+$  in  $\text{TMSO}_2$ ) and  $K_A$  increase with the size of  $\text{M}^+$ . However, it has been reported [Della Monica and Lamanna, 1968] that for  $\text{MSCN}$  in  $\text{TMSO}_2$  association is larger for  $\text{M}=\text{Na}$ .

Irregularities occur in the behavior of salts of small  $\text{M}^+$  ions, particularly  $\text{Li}^+$ , in dipolar aprotic solvents [Fernandez-Prini, 1973]. The association of lithium halides in  $\text{TMSO}_2$  and AC [Savedoff, 1966] is 2000 times greater for the  $\text{Cl}^-$  than for  $\text{I}^-$ .  $\text{LiCl}$  is 30 times more associated than  $\text{LiBr}$  in PC. The association constants for these solutions are given where  $\alpha_{\text{Bj}}$  is the constant distance according to Bjerrum's expression for  $K_A$ . Abnormally large  $K_A$  values have been reported also for Li p-toluene-sulphonate in AC, for  $\text{LiClO}_3$  in AN ( $K_A=401$  compared to  $5 \text{ mol}^{-1}$  in methanol) for MPic in AC and NB (the effect being larger in NB which is a poorer electron donor). On the other hand  $\text{NaPic}$  and  $\text{KPic}$  in DMF [Sears *et al.*, 1956] are dissociated ( $\alpha=4.6$  and  $5.0\text{\AA}$ ) according to the Fuoss-Hsia conductance equation. For these picrate solutions, association increases from  $\text{K}^+$  to  $\text{Li}^+$ . The same trend was reported for  $K_A$  of alkali metal salicylates [Hughes and White, 1966] in acetophenone and methylethylketone, opposite to the trend for iodides in these solvents. If Bjerrum's model for ion association is applied, the resulting  $\alpha$  values for the salicylates are in the range 1.4-1.9Å in methylethylketone and 1.5-2.5Å in acetophenone, compared to  $\alpha=3.6-3.9$  and 6.4-7.6Å for

the iodides. The formation of contact ion pairs by the salicylates is supported by the distinct decrease in association when 1% of water is added to the solvent. Stabilisation of ion pairs by the solvent dipoles, invoked by Hyne [Hyne, 1963] to explain the behavior of  $\text{Bu}_4\text{NBr}$  in NB, does not explain the anomalies observed for some alkali metal salts in dipolar aprotic solvents. This hypothesis cannot account for the large increase in  $K_A$  when going from LiI to LiCl. Parker has shown that if the ability of dipolar aprotic solvents to solvate cations varies in the order  $\text{DMSO}=\text{DMA}>\text{DMF}>\text{AC}=\text{TMSO}_2>\text{AN}=\text{NM}>\text{benzonitrile}=\text{NB}$ , many properties of electrolytes in these solvents can be explained. This ordering coincides with that found by Drago and co-workers [Drago *et al.*, 1963] for the electron donating power of dipolar aprotic solvents. It is interesting to note that the anomalies in conductance behavior have been encountered most frequently in the solvents having lower cations solvating power.

At low dielectric constant ( $\epsilon_r < 12$ ), electrostatic ionic interactions are very large and often triple ion formation is encountered. The conductance has been observed to pass through a minimum with concentration, indicating the formation of triple ions, for  $\text{R}_4\text{N-p}$ -toluenesulphonated in triaryl phosphides [French and Tomlinson, 1961], for LiCl and bivalent chlorides in tetrahydrofuran (THF) [Strohmeier *et al.*, 1961], and for  $\text{MeEt}_3\text{NI}$  in  $\text{CH}_2\text{Cl}_2$  [Beard and Plesch, 1964]. In *o*-dichlorobenzene (*o*DCB),  $\text{Bu}_4\text{NHPic}$  [Ralph and Gilkerson, 1964] has very low  $\Lambda^0$  probably because it dissociates according to the equilibria. The bromide and iodide in *o*DCB and the picrate in chlorobenzene form triple ions. When only pair formation is observed in these solvents it is usually not necessary to evaluate the data. The simpler Shedlovsky or Fuoss expressions may be employed since the concentration of free ions is very small. However, Treiner and Justice [Treiner and Justice, 1969] have recently used the complete equation with  $d=l$  to evaluate the conductance of  $\text{Bu}_4\text{NClO}_4$  in THF ( $\epsilon_r=7.39$ ) finding the data can be fitted with extreme precision upto  $c = 1.12 \times 10^{-4}$  molar; the value of  $K_A$  corresponds to  $\alpha=4.4\text{\AA}$ . The conductance of  $\text{Bu}_4\text{NPic}$  in

chlorobenzene, mDCB, and oDCB indicates that the association varies according to the values of the dielectric constant. The Bierrum  $\alpha$  values of  $R_4NPic$  in oDCB [Curry and Gilkerson, 1957] are lower than expected. Inami, Bodenseh and Ramsey [Inami *et al.*, 1961] observed that the association of  $Bu_4NClO_4$  in ethylene chloride and 1,2 dichloropropane is smaller than that predicted from their dielectric constants and the association found for this salt in other solvents. They pointed out that spectroscopic and dielectric constant measurements give evidence that, in the presence of an electric field, both solvents (Which are in isomeric equilibria between a gauche (polar) form and trans (non-polar) form show an increase in the amount of polar isomer. They suggested that the microscopic  $\epsilon_r$  is larger in the neighbourhood of the ions than in the pure solvent, thus decreasing the electrostatic interaction between ions.  $MeBu_3NClO_4$  is also less associated in ethylene chloride than in oDCB [Gilkerson and Ezell, 1965] having a similar  $\epsilon_r$ . The addition of triphenylphosphine oxide produces a decrease in  $\Lambda^0$  and  $K_A$ , due to specific solvation of the ions. An association smaller than expected in ethylene chloride has been also reported for other substituted ammonium salts [Accascina *et al.*, 1953; Zwolenik and Fuoss, 1964]. The association and  $\Lambda^0$  values of  $R_4NPic$  in oDCB decrease with the size of the cations. The contact distance of  $Bu_4NBr$  in ethylidene chloride [Bosenseh and Ramsey, 1965] agrees with that found for this salt in other solvents. Evidence for the existence of solvent-separated and contact ion pairs in solutions of alkali metal salts in cyclic ethers has been reported. The conductances of  $MBPh_4$  and  $R_4NBPh_4$  [Carvajal *et al.*, 1965; Bhattacharyya *et al.*, 1965] in THF and dimethoxyethane(DME) indicate that the latter is a better solvating medium. In THF the association of  $MBPh_4$  is similar to that of  $R_4NBPh_4$  except for the caesium salt which is much more associated. Stokes' radii are 4.3 and 2.4Å for  $M=Na$  and  $Cs$  respectively suggesting  $CsBPh_4$  forms contact ionic pairs while the the other  $M^+$  only form solvent-separated pairs. In DME, the Stokes' radii for  $CsBPh_4$  are very similar and the former is only marginally more

associated than NaBPh<sub>4</sub>. The contact distance for solvent-separated pair is large, e.g.,  $\alpha=7.5$  and  $7.3\text{\AA}$  for NaBPh<sub>4</sub> in THF and DME. Spectroscopic and conductance measurements of alkali metal salts of fluorenyl radicals [Ellingsen and Smid, 1969] also indicate that DME is a better solvating medium than THF and that solvent-separated and contact pairs are present in the solutions.

Conductance and NMR measurements agree in suggesting that THF solvates the sodium ion specially [Hammonds *et al.*, 1969]. The conductance of NaAlBu<sub>4</sub> in cyclohexane increases abruptly upon the addition of THF to the solution until the ratio salt/THF is 1. This is due to a decrease in association because Na<sup>+</sup>THF<sup>-</sup> is formed. As the concentration of THF increases,  $\Lambda$  decreases slightly up to a value of  $\frac{1}{4}$  for the ratio salt/THF due to formation of Na(THF)<sub>4</sub><sup>+</sup>. From this point onwards,  $\Lambda$  increases according to the variation of  $\epsilon_r$  of the solvent mixture. No evidence of solvation was found when benzene or toluene was added to NaAlBu<sub>4</sub> in cyclohexane [Hammonds *et al.*, 1969]. For NaAlEt<sub>4</sub> in toluene,  $\Lambda$  increases upon addition of diethylether (Et<sub>2</sub>O) until NaEt<sub>2</sub>O<sup>+</sup> is formed [Davies, 1963].

### 2.3. SOLVENT MIXTURES

In binary mixtures of MeOH, AN and NM having an almost constant  $\epsilon_r$ , *i*-Am<sub>3</sub>BuN<sup>+</sup> [Coplan and Fuoss, 1964] salts are dissociated; but the variation of the Walden product with solvent composition suggests specific ion-solvent interactions. D'Aprano and Fuoss [D'Aprano and Fuoss, 1963] observed specific effects on the conductance of the Pic<sup>-</sup>, Br<sup>-</sup> and BPh<sub>4</sub><sup>-</sup> of Bu<sub>4</sub>N<sup>+</sup> in isodielectric mixtures of dioxin with water, MeOH, AN and *p*-nitroaniline(PNA).  $K_A$  and the Walden products of the salts are reduced when PNA is present in the solvent mixture, the effect being largest for Br<sup>-</sup> and least for BPh<sub>4</sub><sup>-</sup>, due to anion-PNA interactions which are stronger for the bromide. HPic would interact with anions even more strongly than PNA

[D'Aprano and Fuoss, 1963]. These interactions seem to depend not on the dipole moment of the added substance but primarily on the facility with which it hydrogen bonds to the anions [Treiner and Justice, 1969].

In MeOH-AN mixtures, CsClO<sub>4</sub> and KClO<sub>4</sub> [Conti and Pistoia, 1968] become fully dissociated when the medium has 60% of AN, inspite of the small and monotonous change in  $\epsilon_r$  with solvent composition. For Bu<sub>4</sub>NBr in binary mixtures of NB, EtOH and MeOH with CCl<sub>4</sub> [Sadek and Fuoss, 1959], association is somewhat larger than predicted by the electrostatic model. The excess association decreases in the order NB>EtOH>MeOH which agrees with the solvating power of these solvents. In NB-MeOH mixtures with practically constant  $\epsilon_r$ , anomalies are observed in the association of Bu<sub>4</sub>NBr [Kay and Evans, 1964; Hyne, 1963]. Specific interactions have been reported between Ag<sup>+</sup> in AC and cycloalkenes [Griffiths *et al.*, 1958], and for the same ion in MeOH when nitroalkanes are added [Busby and Griffiths, 1963]. The association constants of Me<sub>4</sub>NNO<sub>3</sub> and Bu<sub>4</sub>NNO<sub>3</sub> in AN-CCl<sub>4</sub> [Coetzee *et al.*, 1965], vary according to the predictions of the electrostatic model with contact distances of 4.01 and 5.41Å respectively. In AN-dioxan and MeOH-dioxan mixtures, LiClO<sub>3</sub> has  $\alpha=3.70$  and 5.04Å compared to 6.8Å in the water-dioxan mixture, showing that contact pairs are favored in dipolar aprotic solvents and solvent-separated pairs in the protic solvents. Agreement with the electrostatic model has been reported [Treiner and Justice, 1969] for the association of Bu<sub>4</sub>NClO<sub>4</sub> and Bu<sub>4</sub>NBr in THF with less than 15% of water ( $\alpha=4.4$  and 4.9Å respectively), for CsCl and KCl in EtOH-H<sub>2</sub>O, for Bu<sub>4</sub>NBPh<sub>4</sub> [Kay and Hawes, 1965] ( $\alpha=7$ Å) in NB-CCl<sub>4</sub> and in AC-CCL<sub>4</sub> [Berns and Fuoss, 1960; Accascina and Petrucci, 1959]. Alkali metal halides in mixtures of NMA-DMF [Dawson and Wharton, 1960] provide no evidence of specific interactions. Et<sub>4</sub>NPic in MeOH-EtOH does not show the anomalies encountered in ROH-H<sub>2</sub>O mixtures.

## 2.4. EFFECTS OF PRESSURE ON THE ELECTROLYTIC CONDUCTANCE

Measurements of conductance at different pressures and temperatures may be used to test the predictions of the continuum model, especially as regards association, and to study the mechanism of the ionic transport.

Skinner and Fuoss measured the conductance of *i*-Am<sub>4</sub>NPic in diethylether and benzene upto  $5 \times 10^6 \text{ Nm}^{-2}$ . Ion pairs and triplets are present because  $\epsilon_r$  is small. Since  $\epsilon_r$  increases with pressure, the variation of  $\Lambda$  may be expected to depend on the ratio of both associated species. If pairs dominate  $\Lambda$  will increase with pressure. On the other hand, if triple ions predominate,  $\Lambda$  decreases, the actual variation depending on whether the concentration of the solution is smaller or bigger than that corresponding to the minimum conductance. According to the predictions,  $\Lambda$  is found to increase in benzene and to decrease in diethylether where  $\alpha = 4.9\text{\AA}$  for the ion pairs. This behavior was also encountered for Bu<sub>4</sub>NPic in where the variation of  $\Lambda$  with pressure depends on the concentration of the solution. The effect of pressure on the conductance of salts and HBr in MeOH has been studied. The mobility of H<sup>+</sup> decreases less with pressure than that of the other ions. For HPic solutions in MeOH,  $\Lambda$  increases with the pressure because the enhanced dissociation of the acid dominates the variation of mobilities. In MeOH, Bu<sub>4</sub>NBPh<sub>4</sub> has Walden product constant upto  $5 \times 10^6 \text{ Nm}^{-2}$ , NaBr shows an increase in the Walden product with pressure, and the R<sub>4</sub>N bromides are intermediate cases. Variations of K<sub>A</sub> values with pressure were also observed to depend on the particular salt.

Brummer and Hills derived relations between the activation parameters and the variations of conductance with temperature and pressure according to an activated transport mechanism. They have emphasized the importance of the isochoric activation energy in characterizing the energetic of activated transport. Barreira and Hills found that for R<sub>4</sub>NPic in NB, E<sub>v</sub> is similar for all R and also to the isochoric activation energy for viscous flow of the pure solvent. The

activation volume is also practically the same for all the salts. If the rate determining step in ionic transport is displacement of solvent molecules in the neighbourhood of the ions, the different ionic mobilities are due to the fact that the effective movement of the ions caused by the solvent displacement depends on their size.

Similar behavior was found for salts in MeOH and in NB. In DMF at various pressures the conductance of picrates shows that only for large cations is activation volume independent of cationic size. The variation of conductance with temperature and pressure for  $R_4NI$  in AC [Adams, 1967] show activation volume for transport is almost independent of ionic size. It is found to be similar for conductance of dilute solutions, solvent self-diffusion and viscosity for a number of solvents. There is evidence that ions are not followed by their solvation sheaths when they move. From these studies it is suggested that the free volume of the solvent is an important parameter in determining the mobility of ions.

## **2.5. SPECTROPHOTOMERIC/SPECTROSCOPIC METHOD**

Infrared Spectroscopy has been a widely used tool for the study of organic solvent systems for many years and the techniques involved can be learned from many good monographs [Luthian, 1969; Alpert *et al.*, 1970; Davies, 1963; Bauman, 1962; Colthup *et al.*, 1964]. Raman spectroscopy has also been employed to provide significant information about the constitution and physical properties of the systems. Infrared and Raman are complementary forms of spectroscopy. Both provide information about the vibrational and rotational modes of motion of polyatomic molecules and crystals. The absorption of infrared radiation occurs when the dipole moment changes during a vibration. The frequency of the absorbed radiation is directly relatable to the frequency of the vibration. This change may occur when no dipole moment change occurs, as during a symmetric stretching vibration of a homonuclear diatomic molecule. Many non-aqueous solvents possess a rich vibrational spectrum of their own. This presents the spectroscopic with severe problem. Although, for

electrochemical reasons, it may wish to study a particular solute in a particular solvent, the interference resulting from overlap of bands of the solvent with those generated by the solute, or species such as ion pairs or solvates formed after dissolution, may make the interpretation impossible. In addition to the normal modes of vibration, combinations, and overtones, many organic liquids generate low frequency Raman lines (30-85  $\text{cm}^{-1}$  region) [Blatz, 1967; Waldstein and Blatz, 1967]. The low frequency lines shift and intensity changes occur on addition of a solute such as  $\text{AgNO}_3$  or  $\text{Zn}(\text{NO}_3)_2$ . Such modes are also found in the far infrared spectra of polar solvents and have been attributed to dipole-dipole complexes or clusters [Jakobsen and Brasch, 1964; Bulkin, 1969]

In 1965, Edgell and co-workers [Edgell and Watts, 1965] reported an infrared band, from solutions of alkali metal salts of  $\text{Co}(\text{CO})_4^-$  dissolved in tetrahydrofuran (THF), which was assigned to the cation vibrating in a solvent cage. French and Wood also studied salts of  $\text{BPh}_4^-$ . The value of  $175 \text{ cm}^{-1}$  which they report for  $\text{NaBPh}_4$  in THF has not been reproduced and  $194$  to  $198 \text{ cm}^{-1}$  appears to be a better value. Because the frequency was insensitive to solvent for  $\text{NaBPh}_4$  in Py, D, Pip and THF they ascribed the band to contact ion pairs. The change of extinction coefficient with solvent, cation and concentration, and the isotopic shift were also reported while possible ion-pair potential functions were considered.

Electrolyte chemists turn to non-aqueous solvents to explore the effect of a changing, and usually low, dielectric constant on the degree of ion pair formation and to observe differences attributed to a changed solvation sphere, specific solvation or changed solvent structure. The stretching vibration of an ion pair  $\text{M}^+ - \text{A}^-$  may be detectable by infrared spectroscopy. If  $\text{A}^-$  is a polyatomic anion, however, new lines characteristic of a 'bound' species may be detected. Janz and co-workers have observed that the stretching mode of nitrate ion can be resolved into two Raman active components at  $1041$  and  $1036 \text{ cm}^{-1}$  for  $\text{AgNO}_3\text{-CH}_3\text{CN}$ . Because the lines are very intense it has been possible to follow the intensity

ratio down to 0.034M. Good agreement was obtained between the degree of ion-pair formation measured by and that obtained from conductance using the Wishaw-Stokes equation.

In order to elucidate the mechanism of extraction of nitrates by tri-n-butyl phosphate (TBP) several authors have examined the infrared frequencies of metal nitrates in TBP [Ferraro, 1959; Katzin, 1962]. The magnitude of the separation of a component lines in the region of  $1380\text{ cm}^{-1}$  was considered to be a measure of the dis-symmetry induced in the nitrate group. The presence of a diagnostic metal-nitrate Raman vibration provides the strongest evidence for covalence in such an interaction [Irish, 1971]. The splitting in tri-n-octyl phosphine oxide (TOPO) in  $\text{CCl}_4$  and tri-octyl amine nitrate was inferred, the metal being the principal factor controlling the magnitude of the separation; the influence of the medium is small [Verstegen, 1964]. Infrared bands of inorganic nitrates in acetone have also been tabulated [Nortwitz and Chasan, 1969].

Solvation of  $\text{Zn}^{2+}$  by acetonitrile in the system  $\text{ZnCl}_2\text{-CH}_3\text{CN-H}_2\text{O}$  was inferred from Raman spectral studies by Evans and Lo [Evans and Lo, 1965]. Bands characteristic of two distinct forms of  $\text{CH}_3\text{CN}$ , in equilibrium, were observed. The complex involved zinc-containing species and was not influenced greatly by the nature and number of other ligands attached to zinc. It was shown that the complex formation caused an increase in the C-N stretching force constant. Raman spectra of  $\text{ZnCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{LiCl}$  and  $\text{HCl}$  in methanol have been investigated [Kecki, 1962]. A set of equilibria involving  $\text{ZnCl}_2\text{L}_4$ ,  $\text{ZcCl}_4\text{L}_2^{2-}$  and a possible  $(\text{ZnCl}_2)_{2n}$  polymer were invoked for  $\text{ZnCl}_2$ , somewhat as in aqueous solution [Irish *et al.*, 1968] although no attempt was made to measure species concentrations. Similar complex ions were proposed for mercuric chloride and evidence for ion pairs was discovered in methanol solutions of  $\text{LiCl}$  and  $\text{CaCl}_2$ . The vibrational spectrum of zinc chloride in triphosphate (TBP) diluted with benzene, acetone or pyridine has also been studied. Bands at

345  $\text{cm}^{-1}$  and 305  $\text{cm}^{-1}$  were attributed to a  $\text{ZnCl}_2$  species of symmetry (bent molecule) when TBP:  $\text{ZnCl}_2$  ratio is less than 2:1.[Coates and Ridley, 1964]

Silver thiocyanate-pyridine solutions have been investigated with infrared spectroscopy [Larsson and Mieziš, 1968]. The intensities of the C-N stretching vibration of free  $\text{SCN}^-$  (2059  $\text{cm}^{-1}$ ) and S-bonded mononuclear complexes (2089  $\text{cm}^{-1}$ ) were measured for various compositions. Stability constants were obtained by the graphical method of Fronaeus [Fronaeus, 1963] for the species  $\text{AgSCN}$ ,  $\text{Ag}(\text{SCN})_2$ ,  $\text{Ag}(\text{SCN})_3$ . Minc, Kecki and Kryzwicki [Minc *et al.*, 1963] had also noted that  $\text{LiCl}$  and  $\text{LiClO}_4$  affect the molar intensity in opposite ways. Explanations in terms of ion pairs were advanced. A correlation between molar intensity of  $\nu$  (C-O) and cation electric-field intensity is discussed in terms of bond polarity [Kurowski and Minc, 1963]. A new line at 1112  $\text{cm}^{-1}$  has been tentatively assigned to a  $\text{LiCl}$  complex in methanol [Hester and Plane, 1967]. Bufalini and Stern [Bufalini and Stern, 1959] have reported on the effect of a number of electrolytes on the infrared spectra of some hydrogen bonded compounds (methanol, 1-butanol, t-butanol, N-methylacetamide) when both are dissolved in dilute benzene solution. They noted that the absorption maximum of methanol associated to the electrolyte decreased with increasing anion radius,  $\text{ClO}_4^- < \text{NO}_3^- < \text{Br}^- < \text{Cl}^-$ . Picrate produced no shifted peak. Lund [Lund, 1958] reported a similar correlation with apparent molar volume of the anions, for a series of tetrabutylammonium salts in chloroform containing 0.10 M p-cresol; for the same series the apparent integrated intensity increased when the apparent molar volume decreased. Minc *et al.*, [Minc *et al.*, 1963] in a more extensive Raman study of perchlorates in acetone, show that the cation affects the line positions and integrated molar intensities in the order  $\text{Na}^+ < \text{Li}^+ < \text{Ba}^{2+}$ . The perchlorate ion spectrum was most perturbed for  $\text{LiClO}_4$ . Perchlorate ion and hexane were both found to cause destruction of the the dipole structure of acetone. The acetone-cation interaction is considered to be a similar to hydrogen bond formation, causing the C=O bond to weaken and

the C-C-C angle to decrease. The larger size of  $\text{Ba}^{2+}$  is partly responsible for greater effects on the lines of acetone, whereas formation of  $\text{Li}^+\text{-ClO}_4^-$  ion pairs could cause the pronounced changes of the perchlorate spectrum and reduce the  $\text{Li}^+$ -acetone interaction. Changes in the infrared spectra of acetonitrile caused by dissolved  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{NaI}$  or  $\text{LiI}$  were studied by Perelygin [Perelygin, 1962]. Perchlorate ion had no effect on the absorption bands. The blue shift of the  $\text{C}\equiv\text{N}$  vibration and C-C vibration and the increase of intensity of the  $\text{CH}_3$  band were attributed to binding to cations. Evidence that  $\text{I}^-$  binds to the  $\text{CH}_3$  group was also presented. Kecki [Kecki, 1970] has reported that the C-C and  $\text{C}\equiv\text{N}$  infrared stretching bands of acetonitrile are split into two components on addition of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Na}^+$ . One band is at the position of the pure solvent. The second, at higher frequencies, is attributed to acetonitrile solvating the cations; the shift is larger for the transition metal ions.

Vibrational spectra of many inorganic crystalline compounds, in which molecules of interest to the non-aqueous solution chemist are bonded to metal ions, have been tabulated by Adams [Adams, 1967] and Nakamoto [Nakamoto, 1970]. Frequencies of similar species in solution will be displaced from those of the solids because of the change of state, but the latter provide guidance for the assignment of the former. The intensities of polarized Raman bands of binary mixtures of many solvents have been studied over a wide concentration range by Fini and his groups [Fini *et al.*, 1968]. The scattering coefficient increases, in most cases linearly, with the refractive index of the mixture and is in good agreement with a theoretical formula, derived from Onsager's theory of dielectric polarization [Mirone, 1966].

Spectroscopic methods have been employed extensively to study ion-pairing phenomena and often have advantages over other techniques, especially for the study of very complicated equilibria. They have provided valuable information about the binding sites of multidentate ligands and on the kinetics and structures of many species in solution. IR-

Spectrometry is a powerful tool for investigating fast equilibria between free ions and associated species in non-aqueous solution [Irish *et al.*, 1963]. IR spectroscopy resembles Raman spectroscopy in that it provides information on the vibrational and rotational energy levels of a species, but it differs from the latter techniques in that it is based on studying the light transmitted through a medium after absorption and not that scattering by light [Das, 2008]. In most cases internal vibration of the polyatomic anions are used as probes of cation-anion interactions [Debye and Huckel, 1923]. The technique of Raman and IR spectroscopy are generally considered complementary in the gas and solid phases because some of the species under study may reveal themselves in only one of the techniques. Nevertheless, it must be stressed that Raman scattering is not affected by an aqueous medium, whereas the strong absorption in the infrared shown by water proves to be a troublesome interfering factor in the study of aqueous solution by the IR method.