

## 7

### Conductimetry in Non-Aqueous Solutions

As described in Section 5.8, the conductivity of electrolyte solutions is a result of the transport of ions. Thus, conductimetry is the most straightforward method for studying the behavior of ions and electrolytes in solutions. The problems of electrolytic conductivity and ionic transport number in non-aqueous solutions have been dealt with in several books [1–7]. However, even now, our knowledge of ionic conductivity is increasing, especially in relation to the role of dynamical solvent properties. In this chapter, fundamental aspects of conductimetry in non-aqueous solutions are outlined.

#### 7.1

##### Dissociation of Electrolytes and Electrolytic Conductivity [1–8]

###### 7.1.1

##### Molar Conductivity of Dilute Solutions of Symmetrical Strong Electrolytes

Molar conductivity,  $A$  ( $S\text{ cm}^2\text{ mol}^{-1}$ ), of the solution of a symmetrical ( $z_+$ ,  $z_-$ ) strong electrolyte is often related to its concentration,  $c$ , by

$$A = A^\infty - (AA^\infty + B)c^{1/2} = A^\infty - Sc^{1/2} \quad (7.1)$$

where  $A^\infty$  is the molar conductivity at infinite dilution,  $A/(\text{mol}^{-1/2}\text{ l}^{-1/2})^{-1/2} = 82.04 \times 10^4 z^3 / (\epsilon_r T)^{3/2}$ ,  $B/(S\text{ cm}^2\text{ mol}^{-3/2}\text{ l}^{-1/2}) = 8.249 z^2 / \{\eta(\epsilon_r T)^{1/2}\}$ , and  $\epsilon_r$  and  $\eta$  are the relative permittivity and the viscosity (P) of the solvent [9].<sup>1)</sup> Equation (7.1) shows the Debye-Hückel-Onsager limiting law (1926) and has the same form as the empirical Kohlrausch law (Section 5.8). It shows that the  $A$  value for a strong

1) For 1:1 electrolytes, the values of  $A$  and  $B$  ( $25^\circ\text{C}$ ) are 0.229 and 60.20 for water, 0.923 and 156.1 for MeOH, 1.83 and 89.7 for EtOH, 1.63 and 32.8 for Ac, 0.716 and 22.9 for AN, and 0.708 and 125.1 for NM. (ii) For ( $z_+$ ,  $z_-$ )-type electrolytes, Onsager derived  $A = A^\infty - (A'A^\infty + B')I^{1/2}$ , where  $A' = 2.80 \times 10^6 |z_+ z_-| q / \{(\epsilon_r T)^{3/2} (1 + q^{1/2})\}$ ,

$B' = 41.25 \times (|z_+| + |z_-|) / \{\eta(\epsilon_r T)^{1/2}\}$ ,  
 $q = \{|z_+ z_-| / (|z_+| + |z_-|)\} \{(\lambda_+^\infty + \lambda_-^\infty) / (|z_+| \lambda_+^\infty + |z_-| \lambda_-^\infty)\}$ , and  $I = (\sum c_i z_i^2) / 2$ . Here,  $\lambda_+^\infty$  and  $\lambda_-^\infty$  are the values for each unit charge of the ions and  $A$  and  $A_0$  are the so-called equivalent conductivities.

electrolyte decreases linearly with the increase in  $c^{1/2}$ , the intercept and slope being  $A^\infty$  and  $-S$  [Onsager slope], respectively.<sup>2)</sup> For 1:1 electrolytes, Eq. (7.1) is accurate up to  $\sim 0.003$  M in water, but this upper limit may be somewhat lower in non-aqueous solvents. From the linear  $A - c^{1/2}$  relation, we can get the value of  $A^\infty$  and can confirm the complete dissociation of the electrolyte. Beyond this concentration range, the experimental  $A$  values are usually higher than the calculated ones. This occurs because Eq. (7.1) is based on the Debye-Hückel limiting law and the effect of ion size (short-range interaction) has not been taken into account.

Following the Debye-Hückel-Onsager theory, several theories were developed, by Pitts (1953) [10]; Fuoss and Onsager (1957) [11]; Fuoss and Hsia (1967) [12]; Justice (1982) [4] and others, taking into account both the long-range and short-range ionic interactions. These theories can generally be expressed by an equation of the Fuoss-Hsia type:

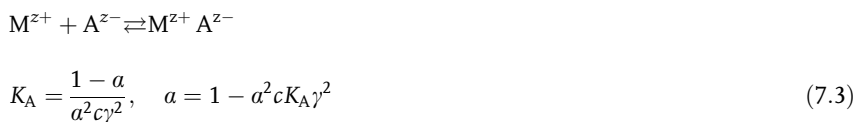
$$A = A^\infty - Sc^{1/2} + E \ln c + J_1 c - J_2 c^{3/2} \quad (7.2)$$

where  $S = (AA^\infty + B)$ . In the Fuoss-Onsager (1957) theory,  $J_2 = 0$ . The coefficients  $S$  and  $E$  are determined by ionic charges and solvent properties, but  $J_1$  and  $J_2$  depend also on the ion parameter,  $a$ . For details, see Refs [1], [4], [5] and [6]. Nowadays the molar conductivity can be measured with high precision (within errors of  $\pm 0.05\%$ ). Here, the above theories can accurately predict the experimental  $A - c^{1/2}$  relations for 1:1 strong electrolytes of up to  $\sim 0.1$  M. Recently, however, the conductivity of electrolyte solutions at higher concentrations have become important in the fields of electrochemical technologies. This will be discussed in Section 7.1.4.

### 7.1.2

#### Molar Conductivity and Association Constants of Symmetrical Weak Electrolytes

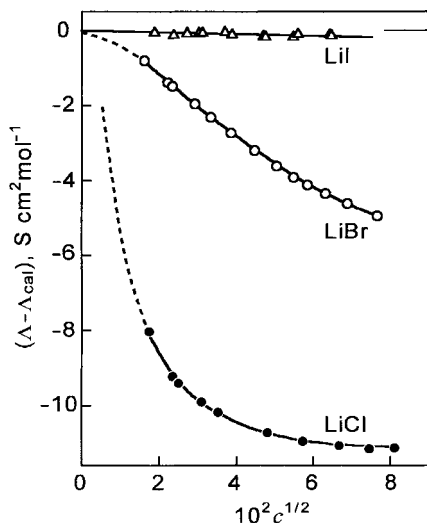
When ion association occurs in the solution of a  $(z, z)$ -type electrolyte, Eq. (7.3) holds:



- 2) Each ion forms in its neighborhood an *ionic atmosphere* that has a slight excess of ions of opposite sign. The ionic atmosphere reduces the ionic mobility in two ways. First, when an ion moves under an applied electric field in the solution, the center of charge of the atmosphere becomes a short distance behind the moving ion, because a finite time ( $\sim 10^{-6}$  s) is necessary to form the atmosphere, and the moving ion is subjected to a retarding force.

This effect is called the *relaxation effect*. Second, in the presence of the ionic atmosphere, a viscous drag is enhanced than in its absence because the atmosphere moves in an opposite direction to the moving ion. This retarding effect is called the *electrophoretic effect*. In Eq. (7.1), the  $AA^\infty$ -term corresponds to the relaxation effect, while the  $B$ -term corresponds to the electrophoretic effect. For details, see textbooks of physical chemistry or electrochemistry.

**Fig. 7.1**  $(\Lambda - \Lambda_{\text{cal}})$  vs  $c^{1/2}$  relations for lithium halide solutions in sulfolane at 30°C, where  $\Lambda$  is the experimental molar conductivity and  $\Lambda_{\text{cal}}$  the molar conductivity calculated from Eq. (7.1) [1a].



Here,  $c$  is the total concentration of MA,  $K_A$  is the association constant,  $a$  is the degree of dissociation of the ion-pair  $M^{z^+}A^{z^-}$ , and  $\gamma$  is the average activity coefficient of free ions of concentration  $ca$ . Because the ion-pairs do not conduct electricity, the molar conductivity  $\Lambda$  in the presence of ion association is less than in its absence. In Fig. 7.1, the difference between the experimental molar conductivity ( $\Lambda$ ) and the value calculated from Eq. (7.1),  $\Lambda_{\text{cal}}$ , are plotted against  $c^{1/2}$  for lithium halides in sulfolane [1a]. For LiI, the difference between  $\Lambda$  and  $\Lambda_{\text{cal}}$  is small because ion association is not appreciable ( $K_A = 5.6 \text{ mol}^{-1} \text{ l}$ ). For LiBr ( $K_A = 278 \text{ mol}^{-1} \text{ l}$ ) and LiCl ( $K_A = 13860 \text{ mol}^{-1} \text{ l}$ ), however,  $\Lambda$  is much smaller than  $\Lambda_{\text{cal}}$ .

When ion association occurs, the relation  $\Lambda = a\Lambda_f$  holds between the molar conductivity for free ions (concentration  $ca$ ),  $\Lambda_f$ , and that for total electrolyte concentration,  $\Lambda$ . Thus we get Eq. (7.4) from Eq. (7.3):

$$\Lambda = \Lambda_f - \Lambda_f^2 K_A(ac) \quad (7.4)$$

If we use Eq. (7.2) for free ions of concentration  $ac$ , we get

$$\Lambda = \Lambda^\infty - S(ac)^{1/2} + E(ac)\ln(ac) + J_1(ac) - J_2(ac)^{3/2} - \Lambda_f^2 K_A(ac) \quad (7.5)$$

Because the ions in electrolyte solutions are often more or less associated, Eq. (7.5) is useful in analyzing conductivity data. The experimental data for  $\Lambda$  and  $c$  are subjected to computer analysis, by applying the least-squares method, and optimum values of such parameters as  $\Lambda^\infty$ ,  $K_A$  and  $a$  are obtained. Sometimes the ion parameter  $a$  (i.e. the distance of closest approach) is replaced by the Bjerrum's distance  $q$  in Section 2.6. In this case, the parameters obtained from Eq. (7.5) are of two kinds,  $\Lambda^\infty$  and  $K_A$ .

If the ion association is not extensive ( $K_A \leq 20 \text{ mol}^{-1} \text{ l}$ ), the value of  $K_A$  obtained by the computer analysis is greatly affected by the terms  $J_1$  and  $J_2$  used in Eq. (7.5). Then, the value of  $K_A$  does not accurately reflect the extent of ion association.

When ion association is extensive and the concentration of free ions is low, the influence of interactions between free ions can be ignored and the relation  $A = aA^\infty$  is valid. In this case, we get the following Arrhenius-Ostwald relation:

$$\frac{1}{A} = \frac{1}{A^\infty} + \frac{cAK_A}{(A^\infty)^2} \quad (7.6)$$

In this equation, the  $1/A$  vs  $cA$  relation is linear, and we get the approximate values of  $A^\infty$  and  $K_A$  from the intercept and the slope, respectively. The values of  $A^\infty$  and  $K_A$  are often used in starting more precise data analyses by means of Eq. (7.5).

Fuoss and Kraus [13] and Shedlovsky [14] improved Eq. (7.6) by taking the effect of ion-ion interactions on molar conductivities into account. Here, Fuoss and Kraus used the Debye-Hückel-Onsager limiting law [Eq. (7.1)] and Shedlovsky used the following semi-empirical equation:

$$A = aA^\infty - \left( \frac{A}{A^\infty} \right) S(ac)^{1/2}$$

In both cases, Eq. (7.6) is modified to Eq. (7.7) by using  $Z = S(Ac)^{1/2}(A^\infty)^{-3/2}$ :

$$\frac{T_{(Z)}}{A} = \frac{1}{A^\infty} + \frac{K_A}{(A^\infty)^2} \times \frac{c\gamma^2 A}{T_{(Z)}} \quad (7.7)$$

In the case of Fuoss-Kraus,

$$T_{(Z)} \equiv F_{(Z)} = 1 - Z(1 - Z(1 - \dots)^{-1/2})^{-1/2}$$

and in the case of Shedlovsky,

$$\frac{1}{T_{(Z)}} \equiv S_{(Z)} = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} + \dots$$

Values of  $F_{(Z)}$  and  $S_{(Z)}$  are listed in the literature [15, 16]. From Eq. (7.7), the  $T_{(Z)}/A$  vs  $c\gamma^2 A/T_{(Z)}$  relation is linear, with an intercept of  $1/A^\infty$  and a slope of  $K_A/(A^\infty)^2$ , from which we can obtain the values of  $A^\infty$  and  $K_A$ . These  $A^\infty$  and  $K_A$  values are also used in data analyses by Eq. (7.5). The values of  $K_A$  obtainable by Eqs (7.6) and (7.7) range from  $10^3$  to  $10^7 \text{ mol}^{-1} \text{ l}$ .

If  $K_A \geq 10^7 \text{ mol}^{-1} \text{ l}$ , the slope of the linear relation is too large to obtain reliable  $A^\infty$  (or  $K_A$ ) values. In these cases, we obtain the value of  $A^\infty$  separately, either by use of Walden's rule or from the known values of ionic molar conductivities ( $\lambda_i^\infty$ ), and use it to obtain  $K_A$ .

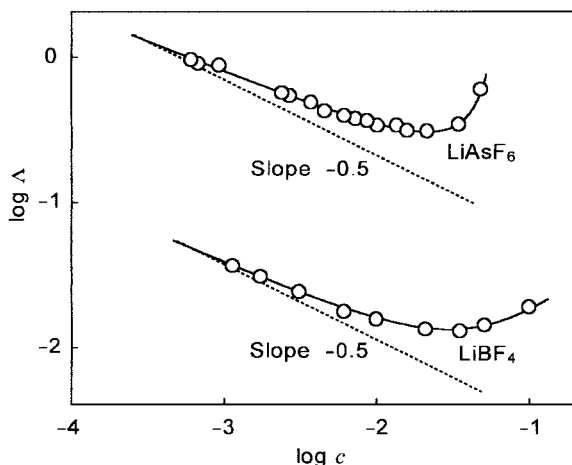
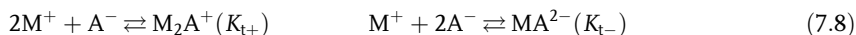


Fig. 7.2 Molar conductivities of  $\text{LiBF}_4$  and  $\text{LiAsF}_6$  solutions in 2-methyltetrahydrofuran at  $25^\circ\text{C}$  [17].

### 7.1.3

#### Molar Conductivity and the Formation of Triple Ions

In solvents of low permittivity ( $\epsilon_r \leq 10$ ), most ions are associated as in Eq. (7.3), even at dilute electrolyte concentrations. Moreover, with increasing electrolyte concentrations, triple ions are formed, as in Eq. (7.8), and sometimes even quadrupoles (or dimers), as in Eq. (7.9):



Ion pairs do not conduct electricity, but triple ions ( $\text{M}_2\text{A}^+$  and  $\text{MA}_2^-$ ) are conductive. Thus, the formation of triple ions is detected by conductimetric measurement. Figure 7.2 shows the  $\log \Lambda$ - $\log c$  relations for  $\text{LiAsF}_6$  and  $\text{LiBF}_6$  in 2-methyltetrahydrofuran (2-MeTHF) [17]. After passing a minimum, the value of  $\log \Lambda$  increases again with  $\log c$ , showing that a triple ion formation occurred in the solution.

In conductimetric studies of triple ion formation, it is often assumed that  $\text{M}_2\text{A}^+$  and  $\text{MA}_2^-$  have the same formation constants ( $K_t = K_{t+} = K_{t-}$ ) and the same molar conductivities at infinite dilutions ( $\lambda_t^\infty = \lambda_{t+}^\infty = \lambda_{t-}^\infty$ ). If we denote by  $a$  and  $a_t$  the mole fractions of ( $\text{M}^+$ ,  $\text{A}^-$ ) and ( $\text{M}_2\text{A}^+$ ,  $\text{MA}_2^-$ ), respectively, against the total electrolyte concentration,  $c$ , and assume that the concentrations of the ionic species are negligibly small compared to  $c$ , we get the relation  $\Lambda = a\Lambda^\infty + a_t \lambda_t^\infty$  and, therefore, Eq. (7.10):

$$\Lambda c^{1/2} = K_A^{-1/2} \Lambda^\infty + K_t K_A^{-1/2} c \lambda_t^\infty \quad (7.10)$$

Tab. 7.1 Ion-pair and triple-ion formation constants ( $K_A$  and  $K_t$ ) at 25 °C<sup>1)</sup>

Solvent	$\epsilon_r$	Electrolyte	$K_A/M^{-1}$	$K_t/M^{-2}$
1,2-Dimethoxyethane	7.08	LiAsF <sub>6</sub>	$0.071 \times 10^6$	176
		LiBF <sub>4</sub>	$24.0 \times 10^6$	30.8
Methyl acetate	6.76	LiClO <sub>4</sub>	$77.8 \times 10^6$	38
Tetrahydrofuran (THF)	7.58	LiClO <sub>4</sub>	$48.4 \times 10^6$	153
2-Me-THF	6.97	LiClO <sub>4</sub>	$182 \times 10^6$	33

1) From Ref. [18b].

From Eq. (7.10), if we plot the value of  $\Lambda c^{1/2}$  against  $c$ , we get a linear relation of slope equal to  $K_t K_A^{-1/2} \lambda_t^\infty$  and intercept equal to  $K_A^{-1/2} \Lambda^\infty$ . If we get the value of  $\Lambda^\infty$  from Walden's rule and assume that  $\lambda_t^\infty = \Lambda^\infty/3$  or  $2\Lambda^\infty/3$  ( $\lambda_t^\infty$  cannot be determined experimentally), we can obtain the values of  $K_A$  and  $K_t$  [18]. The values of  $K_A$  and  $K_t$  in Table 7.1 were obtained in low permittivity solvents. The cationic and anionic triple ions can remain stable in low permittivity solvents, because triple ions are large in size and are not easily associated (Section 2.6). Thus, some electrolytes are highly soluble in low permittivity solvents and they show conductivities comparable to or higher than solutions in high permittivity solvents. For example, the solution of 2 M LiAsF<sub>6</sub> in methyl acetate ( $\epsilon_r=6.76$ ,  $\eta$  (viscosity) = 0.37 cP) has higher conductivity than 1 M LiClO<sub>4</sub> in PC ( $\epsilon_r=64.9$ ,  $\eta=2.53$  cP).

As mentioned in Section 2.6, triple ion formation is not limited to low permittivity solvents. It also occurs in high permittivity solvents, if they are of very weak acidity and basicity: for example,  $K_t$  for the formation of Li<sub>2</sub>Cl<sup>-</sup> and LiCl<sub>2</sub><sup>-</sup> in AN has been determined by polarography to be  $\sim 10^5$  M<sup>-2</sup> [19]. Li<sup>+</sup> and Cl<sup>-</sup> in AN are only weakly solvated and tend to be stabilized by forming triple ions. For conductimetric studies of triple ion formation in dipolar protophobic aprotic solvents, see Ref. [20].

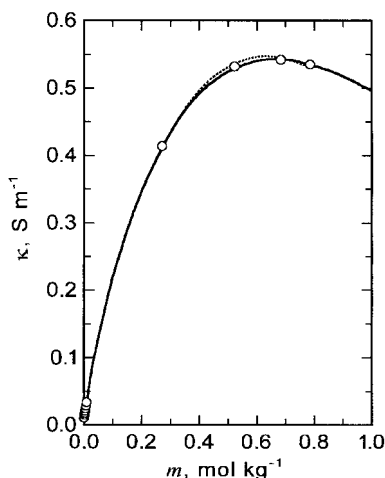
The problem of triple ion formation has been studied in detail, because it is related to lithium battery technologies [18]. In some cases, however, the occurrence of the minimum in the  $\log \Lambda - \log c$  curve, as observed in Fig. 7.2, is not attributed to triple-ion formation but is explained by ion-pair formation only. The increase in  $\log \Lambda$  at high electrolyte concentrations is attributed either to the increase in the distance of closest approach of ions, the increase in the solution permittivity, or the decrease in the activity coefficient of the ion-pairs. Although there is still some controversy, it seems certain that triple ions are actually formed in many cases.

#### 7.1.4

#### Conductivity of Solutions of Symmetrical Strong Electrolytes at Moderate to High Concentrations

Here we consider the conductivity of strong electrolyte solutions at moderate to high concentrations in polar non-aqueous solvents. The conductivity of such solutions has been studied extensively, because of their importance in applied fields.

Fig. 7.3 Conductivity ( $\kappa$ ) vs concentration ( $m$ ) relation for  $\text{LiClO}_4/\text{PC}$  ( $25^\circ\text{C}$ ). ( $\circ$ ) experimental data; (—) Casteel-Amis equation; (.....) MSA [24 b].



If the conductivity of an electrolyte in a polar solvent is measured up to high concentrations, the conductivity-concentration relation usually shows a maximum as in Fig. 7.3. Such a relationship is explained by the competition between the increase in the number of charge carriers and the decrease in ionic mobilities, mainly due to the strengthening of ion-ion interactions. Various empirical equations have been reported to express such a relation. The Casteel-Amis equation [21] for the relation between  $\kappa$  and the molal concentration  $m$  is

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^a \exp\left[b(m - \mu)^2 - \frac{a}{\mu}(m - \mu)\right]$$

where  $\kappa_{\max}$  is the maximum value of conductivity,  $\mu$  is the concentration at which  $\kappa_{\max}$  is obtained, and  $a$  and  $b$  are empirical parameters having no physical meanings. The values of  $\kappa_{\max}$  and  $\mu$  have been listed in Table 1.4 of Ref. [6b].  $\kappa_{\max}$  and  $\mu$  are mainly determined by solvent viscosity and ionic radii; thus,  $\kappa_{\max}$  and  $\mu$  shift to higher values with increasing temperature at constant solvent compositions, and shift to lower values with increasing viscosity of the solvents at constant temperature.

Recently, Chagnes et al. [22] treated the molar conductivity of  $\text{LiClO}_4$  in  $\gamma$ -butyrolactone ( $\gamma$ -BL) on the basis of the quasi-lattice theory. They showed that the molar conductivity can be expressed in the form  $\Lambda = (\Lambda^\infty)' - k'c^{1/3}$  and confirmed it experimentally for 0.2 to 2 M  $\text{LiClO}_4$  in  $\gamma$ -BL. They also showed, using 0.2 to 2 M  $\text{LiClO}_4$  in  $\gamma$ -BL, that the relation  $\kappa = \Lambda c = (\Lambda^\infty)'c - k'c^{4/3}$  was valid and that  $\kappa_{\max}$  appeared at  $c_{\max} = [3(\Lambda^\infty)'/4k']^3$  where  $d\kappa/dc=0$ .

The concept of mean spherical approximation (MSA, <sup>3</sup>) in Chapter 2) has also been used to reproduce the conductivity data of electrolytes of fairly high concentration [23]. The MSA method applies to both associated and non-associated electrolytes and can give the values of association constant,  $K_A$ . Although not described here,

以上内容仅为本文档的试下载部分，为可阅读页数的一半内容。如要下载或阅读全文，请访问：<https://d.book118.com/957112144044006114>