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The Determination of Electrolyte Type in an Acetonitrile Medium

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Provided solvolysis and ion association are absent, conductance measurements made at a series of concentrations may be used to distinguish complexes of various ion types by determining the slope (B) of a plot of $\Lambda_o - \Lambda_E$ *against* $c^{1/2}$, *where* Λ_E *is the conductance at concentration c* $equiv \cdot l^{-1}$ *and* Λ_o *is the conductance at infinite dilution. For a 1:1 electrolyte B values typically lie between 300 and 500* $ohm^{-1} \cdot l^{1/2} \cdot equiv^{-1/2}$; *for 2:1 electrolytes B values fall between 600 and 1100* $ohm^{-1} \cdot l^{1/2} \cdot equiv.^{-1/2}$. *B values of about 1300* $ohm^{-1} \cdot l^{1/2} \cdot equiv.^{-1/2}$ *are suggested for 3:1 electrolytes.*

Introduction

The use of conductance measurements in the characterisation of coordination compounds is now a well established technique [1]. It has been observed that conductance measurements at a single concentration do not provide sufficient information to differentiate between compounds of the same empirical formula, but different molecular complexity [2]. Conductance measurements taken over a concentration range in a suitable solvent can be used to unequivocally determine the ion-type of a coordination compound, providing the Onsager law is obeyed over the concentration range studied. Thus, providing relationship (1) is obeyed, a plot of Λ_E *versus* $c^{1/2}$ will be linear with intercept Λ_o; Λ_E = conductance at concentration c $equiv \cdot l^{-1}$, Λ_o = conductance at infinite dilution and B = constant.

$$\Lambda_E = \Lambda_o - Bc^{1/2} \qquad (1)$$

By extrapolation to obtain a value of Λ_o, a plot of $(\Lambda_o - \Lambda_E)$ *versus* $c^{1/2}$ may be produced which will pass through the origin and be of slope B. The magnitude of B is principally determined by the ion-type of the compound and hence for a series of compounds of the same ion-type the values of B will be similar. Some variation does occur because B depends slightly on ion size (*vide infra*) [3].

The usefulness of this experimentally simple technique in the characterisation of coordination compounds is hindered by the lack of suitable reference data on the magnitudes of Λ_o and B in various solvents. Tabulated data is available for studies using water, methanol and nitromethane as the solvent medium [2]. Acetonitrile is a much used organic solvent which satisfies the main criteria for use in conductance studies; it has a high dielectric constant (36.2 at 25 °C), a low viscosity (0.325 $g^1 \cdot s^1$) and low specific conductance (5.9×10^{-8} ohm^{-1} cm^{-1}) [1]. Possible disadvantages in its use are the difficulties encountered if extensive purification is required [4] and possible interpretational difficulties due to dissociation and solvolysis caused by the relatively high coordinating ability of acetonitrile towards some metal ions [5, 6].

The present work is intended to provide reference data on the values of Λ_o and B for coordination compounds of varying ion-type in acetonitrile solution and to assimilate such data as already exists in order to provide an accessible source of reference for comparison purposes. It should be stressed that this work is intended to provide conductance data for the characterisation of ion-types and not to develop or augment the conductance theory of ionic compounds.

Results and Discussion

The scattered data available in the literature have been presented in one of two general forms:

i) By considering the Onsager law in the form (1), the values of Λ_o and B may be obtained directly from a plot of Λ_E *versus* $c^{1/2}$. These values are frequently presented along with the calculated values of B which may be deduced from the limiting law expression using the constants applicable to acetonitrile [7, 8].

ii) From the plot obtained in (*i*) a value of Λ_o is generated which is utilised to produce values of $(\Lambda_o - \Lambda_E)$ [9]. Hence, by considering the Onsager law (1), the value of B may be obtained from a plot of $(\Lambda_o - \Lambda_E)$ *versus* $c^{1/2}$. This method has the

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TABLE I. Λ_o and B Values for 1:41 Electrolytes.

	Λ_o	B	Method of calculation	Reference
Non-complex compounds				
Me_4NBr	197.3	641	i	10
Et_4NBr	185.5	413	*i*	10
$^nPr_4NBr$	170.9	404	*i*	10
$^nBu_4NBr$	162.8	391	*i*	10
Am_4NBr	156.7	405	*i*	10
Me_4NI	198.8	542	*i*	10
Et_4NI	186.7	411	*i*	10
$^nPr_4NI$	173.2	377	*i*	10
$^nBu_4NI$	164.8	409	*i*	10
Am_4NI	158.3	596	*i*	10
Me_4NI	201.5	700	*ii*	This work
Et_4NI	191.0	680	*ii*	This work
$^nPr_4NI$	183.0	599	*ii*	This work
$^nBu_4NBr^a$	96.7	202	*i*	8
$(^nBu_4N)(ClO_4)$	165.1	353	*i*	8
$(^nBu_4N)(BPh_4)$	119.7	319	*i*	8
$(Am_4N)(ClO_4)$	160.6	349	*i*	8
$(Am_4N)(BPh_4)$	115.0	316	*i*	8
$(Am_4N)(BAm_4)$	114.5	315	*i*	8
$NaBPh_4$	151.0	485	*ii*	This work
NaI	195.0	584	*ii*	This work
Complexes of type (A^+) $[ML_n]^-$				
$(Pr_4N)[TlCl_3Br]$	165	*ca.* 500^b	*ii*	11
$(Pr_4N)[TlCl_4(bipy)]$	185	*ca.* 750^b	*ii*	11
$(Et_4N)[TlCl_4]$	190	*ca.* 750^b	*ii*	11
$(Et_4N)[Ni\{S_2C_2(CN)_2\}_2]$	169	340	*i*	12
$(Ph_4As)[Cu\{S_2C_2(CF_3)_2\}_2]$	145	390	*i*	12
$(Bu_4N)[Ni\{S_2C_2Ph_2\}_2]$	145	450	*i*	12
$(Bu\ N)[Co\{S_2C_2Ph_2\}_2]$	142	460	*i*	12
Complexes of type $[ML_n]^+$ (X^-)				
$[Cu(MeCN)_4](BF_4)$	140	^{c}	*i*	13
$[Cu(MeCN)_4](ClO_4)$	136	^{c}	*i*	13
$[Cu(MeCN)_4](NO_3)$	131	^{c}	*i*	13
$[Pd(Ph_2PCH_2CH_2PPh_2)(PPh_3)Cl](ClO_4)$	131	363	*ii*	This work
$[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_3)Cl](ClO_4)$	135	357	*ii*	This work
$[Pd(Ph_2PCH_2CH_2AsPh_2)(PPh_3)Cl](ClO_4)$	131	360	*ii*	This work
$[Pt(Ph_2PCH_2CH_2AsPh_2)(PPh_3)Cl](ClO_4)$	132	376	*ii*	This work

[a] Values of Λ_o and B appear inexplicably low for this compound; probably unsuitable for use as a reference standard. [b] Estimated from Fig. 1 in reference 11. [c] Plots in the Figure in reference 13 show deviations from linearity so that B values could not be determined.

advantage that the plot is fixed at the origin and so one point is free from experimental error.

In the present work the experimental B values were obtained by method (*ii*), where reference is made to the results of other workers a note is made of which treatment was applied. In the selection of compounds for this study, the following criteria were considered:

TABLE II. Λ_o and B Values for 2:1 Electrolytes.

	Λ_o	B	Method calculation	Reference
Complexes of type $(A^+)_2[ML_n]^{2-}$				
$(Et_4N)_2[Re(CO)_3(NCS)_3]$	181	599	*i*	14
$(Bu_4N)_2[Co\{S_2C_2(CN)_2\}_2]$	188	740	*i*	12
$(Bu_4N)_2[Ni\{S_2C_2(CN)_2\}_2]$	190	790	*i*	12
$(Bu_4N)_2[Cu\{S_2C_2(CN)_2\}_2]$	187	740	*i*	12
Complexes of type $[ML_n]^{2+}(X^-)_2$				
$[Pd(Ph_2PCH_2CH_2PPh_2)_2](ClO_4)_2$	190	936	*ii*	This work
$[Pt(Ph_2PCH_2CH_2PPh_2)_2](ClO_4)_2$	183	958	*ii*	This work
$[Pt(Ph_2PCH_2CH_2AsPh_2)_2](ClO_4)_2$	170	1099	*ii*	This work
$[Pd(MeS\{CH_2\}_3SMe)_2](ClO_4)_2$	206	1004	*ii*	This work
$[Pt(MeS\{CH_2\}_3SMe)_2](ClO_4)_2$	214	1007	*ii*	This work
$[Pd(MeS\{o\text{-}C_6H_4\}SMe)_2](ClO_4)_2$	205	999	*ii*	This work
$[Pd(\{CH_2\}_3\{S(CH_2)_3SMe\}_2)](ClO_4)_2$	206	1049	*ii*	This work
$[Pt(\{CH_2\}_3\{S(CH_2)_3SMe\}_2)](ClO_4)_2$	192	900	*ii*	This work
$[Pd(\{CH_2\}_3\{S(o\text{-}C_6H_4)SMe\}_2)](ClO_4)_2$	205	963	*ii*	This work

(*a*) The compounds should be sufficiently soluble in acetonitrile to allow conductance measurements to be made over a suitable concentration range (10^{-2}–10^{-6} equiv·l^{-1}).

(*b*) Complexed metal ions should be inert to solvolysis to prevent the formation of new compounds, of a different ion-type, in solution.

(*c*) Anions should be classically non-coordinating.

(*d*) The ligand donor set should be varied to facilitate the comparison of unknowns.

1. 1:1 Electrolytes

The currently available Λ_o and B values for 1:1 electrolytes are given in Table 1.

Non-complex compounds.

For tetraalkylammonium ions the Λ_o value is inversely dependent on the size of the cation, a consequence of the lower mobility of the larger cations which emphasises the need to choose standards of comparable size to the ion under study. Λ_o values fall between 114.5 ohm^{-1}·l$^{1/2}$ for the very bulky $(Am_4N^+)(BAm_4^-)$ and about 200 ohm^{-1}·l$^{1/2}$ for tetramethylammonium halides. B values are also inversely dependent on ion size ranging from 315 ohm^{-1}·l$^{1/2}$·equiv.$^{1/2}$ for $(Am_4N^+)(BAm_4^-)$ to 700 ohm^{-1}·l$^{1/2}$·equiv.$^{1/2}$ for the tetramethylammonium halides.

Complex compounds of the type $(A^+)[ML_n^-]$.

Conductance data of tetraalkylammonium salts of complex anions in acetonitrile solution shows reasonable correlation with the results described above. Thus, Λ_o values lie in the range 142 to 190 ohm^{-1}·l$^{1/2}$ and B values lie in the range 340 to 750 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$.

Complex compounds of the type $[ML_n]^+(X^-)$

For complexes of the type $[ML_n]^+(X^-)$ so far reported Λ_o values lie in the rather narrow range of 131 to 140 ohm^{-1}·l$^{1/2}$ and B values in the similarly narrow range of 357 to 376 ohm^{-1}·l·$^{1/2}$·equiv.$^{1/2}$.

Summary for 1:1 electrolytes

The overall situation for 1:1 electrolytes shows that the extreme range for Λ_o is very large (*ca.* 115–200) but that typical values of 130–160 ohm^{-1}·l$^{1/2}$ may be expected. The range of B values used to characterise 1:1 electrolytes is also very large, but without considering anomalously low or high results, a range of 300–500 covers most coordination compounds, with a typical value of B being *ca.* 370 ohm^{-1}·l$^{1/2}$·equiv.$^{1/2}$.

2. 2:1 Electrolytes

Complexes of type $(A^+)_2[ML_n]^{2-}$

Only a few 2:1 electrolytes of the type $(A^+)_2$-$[ML_n]^{2-}$ have been studied (Table II). The reported Λ_o values (181–190 ohm^{-1}·l$^{1/2}$) are similar to those of 1:1 electrolytes. However the B values (599–790 ohm^{-1}·l$^{1/2}$) allow their clear distinction from 1:1 electrolytes.

Complexes of type $[ML_n]^{2+}(X^-)_2$.

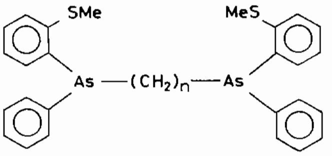
Data from our studies of 2:1 electrolytes of Group V and VI ligands (Table II) show that these electrolytes are readily distinguished from 1:1 electrolytes by the magnitude of the B value (mean = 990 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$). A variation in Λ_o caused by varying the ligand set is apparent; complexes of Group V ligands have values of Λ_o in the range 170–190 ohm^{-1}·l$^{1/2}$ (mean = 181) whereas complexes of Group VI ligands show substantially larger values (mean = 205).

Summary for 2:1 electrolytes

The situation for 2:1 electrolytes generally shows considerable variation in the magnitude of Λ_o, but values of B in the range 600–1100 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$ appear to be typical thus clearly differentiating them from 1:1 electrolytes (300–500).

3. 3:1 and 4:1 Electrolytes

The data for higher electrolyte types (3:1, 4:1 *etc.*) is less clear cut and in our hands the standard electrolytes of these types, such as $[CoL_3]Cl_3$ (L = ethylenediamine, tetraethylethylenediamine), $[CoL_6]Cl_3$ (L = py, NH_3), $K_4[Fe(CN)_6]$ *etc.*, were insufficiently soluble to permit measurements over a suitable concentration range. Some data for palladium(II) complexes of the potentially tetradentate ligands C_2 and C_3, I, $\{[PdC][ClO_4]_2\}_n$ gave B values of 1250–1310 ohm^{-1}·l$^{1/2}$·equiv.$^{1/2}$ and a 3:1 electrolyte nature is possible for these rather unusual species [15]. The complex $[{}^nBu_4N]_3[Re_2(CO)_2\text{-}NCS)_{10}]$ has also been formulated as a 3:1 electrolyte with a B value of 1320 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$ [16].



I C_2, n = 2
C_3, n = 3

Conclusions

Conductance studies in acetonitrile provide reliable data for the classification of ion-types of coordination compounds, provided solvolysis and ion association are not encountered. The values of Λ_o are related to ionic size and ligand donor set and so reference to the B value is necessary for classification. 1:1 electrolytes (range 300–500 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$), 2:1 electrolytes (600–1100 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$) and 3:1 electrolytes (*ca.* 1300 ohm^{-1}·l$^{1/2}$·equiv.$^{-1/2}$) may be distinguished by their B values. No data on higher electrolytes is available.

Experimental

The salts Me_4NI, Et_4NI, ${}^nPr_4NI$, $NaBPh_4$ and NaI are commercially available and were used as supplied after drying finely ground samples *in vacuo.* The platinum(II) and palladium(II) phosphine [17] and thioether [18, 19] complexes were prepared and characterised as previously described. Acetonitrile (spectrograde) was dried as previously described [17] and measurements corrected for its inherent conductivity. Conductance measurements were made on a Universal Wayne-Kerr bridge equipped with a glass cell contained platinised electrodes, calibrated with standard potassium chloride solution. Results were analysed by the method of least squares and plots considered linear when the linear regression exceeded 0.99.

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