

## Interpretation of conductance studies on nonaqueous solutions of unsymmetrical electrolytes

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*Abstract* - The application of the Fuoss-Edelson equation to the conductance of associated 2:1 electrolytes is critically assessed and compared with the conclusions which can be drawn by analysis using the Lee-Wheaton equation which is based on a sounder theory of the conductimetric behaviour of electrolyte solutions.

### INTRODUCTION

Measurements of the conductivity of solutions of electrolytes have been made for nearly a century (ref. 1), and from the earliest times have been one of the most accurate physical measurements made on solutions. Moreover, interest has never been restricted to aqueous solutions and even in 1888 the conductivity of non-aqueous solutions (ref. 2) and mixed electrolytes (ref. 3) was reported. However, throughout this long history most emphasis has been on the conductance of single symmetrical electrolytes for the simple reason that the interpretation of the conductance of a solution containing only two types of ion of equal and opposite charge has been relatively straightforward. A variety of theoretical approaches has been developed to account successfully for the conductance of 1:1 electrolytes in water up to a concentration of about  $0.1 \text{ mol dm}^{-3}$  but to rather lower concentrations for higher charged electrolytes and/or solvents with a lower dielectric constant. These have been extensively reviewed elsewhere (refs. 4,5) and will not be considered further here.

Much less attention, either practical or theoretical, has been paid to the more general problem of unsymmetrical electrolytes (especially associated ones) or to mixtures of electrolytes, although these occur in both natural waters and industrial solutions. This is undoubtedly due to the fact that conductance theory for such systems is far more intractable and the interpretation of the results is far more difficult. Certainly there is a great shortage of reliable, precise conductance data on such systems, particularly in non-aqueous solvents, and this has hindered the testing of such theoretical approaches as have been developed.

It is appropriate to use this opportunity to urge that, in future studies of the conductance of unsymmetrical and mixed electrolytes, a high priority should be given to obtaining data of the highest precision. Too often a broad sweep approach has been adopted in the past, producing results which can at best be used for semi-quantitative interpretations and which are unsuited for analysis by such theoretical equations as have been derived. Probably the most common cause of scatter within a series of experimental results, given that nowadays reasonable temperature control and resistance measurement are fairly straightforward, is the preparation of the measured solutions from a stock solution or solid material. This source of error is particularly prevalent in studies on non-aqueous solutions because expense and the difficulties in purifying the solvent usually mean that small volumes of solution are prepared. Use of a five or six decimal place electronic balance could help to minimize this source of error and it is good experimental practice to use amounts of solvent and solution as large as are feasible. Errors in solvent and salt purity and in absolute temperature control and cell calibration would not cause a scatter in the results for one series of experiments and only become apparent when different runs are compared.

### THE DAVIES APPROACH

One of the earliest attempts to interpret quantitatively the conductance of associated unsymmetrical electrolytes was by Davies (ref. 6) who assumed that an associated 2:1 (or 1:2) electrolyte could be considered as a mixture of the appropriate fractions of strong 2:1 and 1:1 electrolytes whose conductivities were additive but were reduced below their limiting values by an amount equal to the square root of the total ionic strength,  $I$ , multiplied by the relevant Onsager limiting slope,  $S$ . Using the salt  $\text{MX}_2$  as an example, with  $\gamma$  as the fraction of ion pairs  $\text{MX}^+$  formed,

$$\Lambda = (\gamma/2)[\lambda_0(\text{MX}^+) + \lambda_0(\text{X}^-) - S_{1:1}I^{1/2}] + (1-\gamma)[\lambda_0(\frac{1}{2}\text{M}^{2+}) + \lambda_0(\text{X}^-) - S_{2:1}I^{1/2}] \quad (1)$$

with  $I = c(3 - 2\gamma)$

A short series of iterations was necessary to obtain a value of the association constant for the formation of the ion pair,  $K_A$ , once the limiting molar conductivities,  $\lambda_0$ , of the various ions had been fixed. As always, the value of  $\lambda_0$  allocated to the associated species is the one most open to doubt. This approach has been little used in non-aqueous solutions.

### FUOSS-EDELSON EQUATION

Another attempt to tackle the problem quantitatively was by Fuoss and Edelson (ref. 7) and, although this was restricted to the interpretation of the conductance of associated 2:1 salts, it has remained the most frequently used equation to the present day. To simplify the theoretical problems, Fuoss and Edelson made a series of drastic approximations from the original theory by Fuoss and Onsager (ref. 8) and which are outlined in Table 1.

TABLE 1 Assumptions made in the Fuoss-Edelson equation

- |   |
|---|
| (1) The conductance of each ion obeys Onsager's Limiting Law  |
| (2) The Onsager limiting slope is used to correct the conductance of each ion for interionic interactions |
| (3) $\lambda_0(\text{MX}^+) = 0.5\lambda_0(\frac{1}{2}\text{M}^{2+})$                                     |
| (4) Activity coefficients are given by the Debye-Hückel Limiting Law, i.e. $\log y_2 = -4A I^{1/2}$       |
| (5) $I = 3c$ , i.e. it is not corrected for association to $\text{MX}^+$                                  |
| (6) $y_{\text{X}^-} = y_{\text{MX}^+}$  |

After much algebraic manipulation they obtained the deceptively simple expression

$$\Lambda^* = \Lambda_0 - (K_A/\Lambda_0)X \quad (2)$$

$$\text{where } X = 2cy_2\Lambda^*(\Lambda^* - \Lambda_0/2) \quad (3)$$

$$\text{and } \Lambda^* = \Lambda\{[1 - (S_{2:1}/\Lambda_0)(2c)^{1/2} + (\Lambda_0 - \lambda_0)/(2\Lambda)] / [1 + (\Lambda_0 - \lambda_0)/(2\Lambda_0)]\} \quad (4)$$

from which both  $\Lambda_0$  and  $K_A$  can be found by a simple linear least-squares analysis. In eqs. (2) - (4) and Table 1  $\Lambda$  and  $\Lambda_0$  are the molar and the limiting molar conductivity of  $(\frac{1}{2}\text{MX}_2)$ ,  $\lambda_0$  is the limiting molar conductivity of  $\text{X}^-$ ,  $c$  is the molar concentration of  $\text{MX}_2$ ,  $y_2$  is the activity coefficient of  $\text{M}^{2+}$  and  $A$  is the Debye-Hückel constant. As both eq. (3) and (4) include  $\Lambda_0$ , which has to be found from eq. (2), it is necessary to adopt an iterative procedure for the determination of  $K_A$  and  $\Lambda_0$ , using a simple graphical approach to find the starting value of  $\Lambda_0$ .

However, there is no reason why the approximations listed in Table 1 should be valid, except at extremely high dilutions, as they are approximations to the limiting law which is itself known to give an inadequate representation of conductance data in dilute solution. There is some experimental evidence (refs. 9,10) that Fuoss-Edelson plots are in fact not linear but are concave upwards, although this is usually concealed by the experimental scatter in the raw data.

As explained later, it is now possible to fit precise conductance data to a soundly-based theoretical equation. One can then use the fitting parameters so obtained to calculate a "perfect" set of conductance/concentration data with which to test the FE equation and the various modifications which have been suggested. A similar approach for symmetrical electrolytes has recently been published by Fuoss and Jarrett (ref. 11).

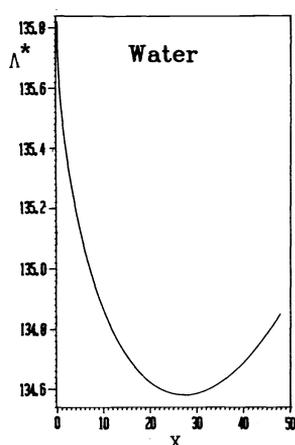
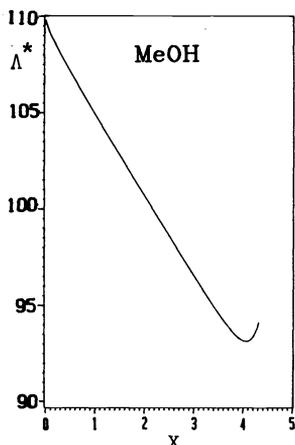
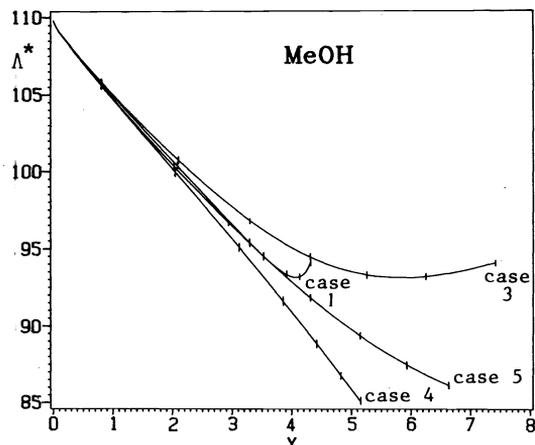
FIG. 1 FE plot for  $\text{CaCl}_2$  in waterFIG. 2 FE plot for  $\text{CaCl}_2$  in methanol

FIG. 3 FE plots obtained from various assumptions

TABLE 2 Fitting parameters for  $\text{CaCl}_2$  solutions from the LW equation.

	$\frac{K_A}{\text{dm}^3 \text{ mol}^{-1}}$	$\lambda_0(\frac{1}{2}\text{Ca}^{2+})$	$\lambda_0(\text{Cl}^-)$	$\lambda_0(\text{CaCl}^+)$	$\frac{R}{\text{pm}}$	$\frac{\text{viscosity}}{\text{poise}}$	dielectric constant
water	5.5	59.47	76.35	47.58	440	0.008903	78.30
methanol	450.0	57.45	52.35	45.96	550	0.005445	32.62

This has been done for  $\text{CaCl}_2$  in water and methanol at 298 K, using the parameters listed in Table 2 which were obtained using the Lee-Wheaton equation (ref. 12). The standard FE plots obtained are shown in Figs. 1 and 2 for water and methanol respectively. The actual points marked represent values of  $\Lambda^*$  and  $X$  calculated for values of  $\sqrt{\text{concentration}}$  increasing by  $0.01 (\text{mol dm}^{-3})^{1/2}$  the maximum concentration plotted being  $5.0 \times 10^{-3}$  for each solvent. It must be emphasized that these plots are obtained from perfect data and that most of the curvature, particularly at lower concentrations, would be masked by an experimental scatter of 0.1% in the results. Hence the repeated emphasis on the need for results of the highest precision if reliable information is to be deduced from them. It is also possible that the curvature at higher concentrations in methanol is spurious because the original fitting parameters were obtained over a smaller concentration range. As the plots in Figs. 1 and 2 are curved it is obvious that the values of  $K_A$  and  $\Lambda_0$  obtained from them will depend on the concentration range used.

Several simple modifications to the basic FE equation are possible. The basic FE equation includes the Debye-Hückel Limiting Law expression for the activity coefficient of the divalent metal ion,  $y_2$ . Particularly in methanol solutions, this factor becomes quite significant (e.g.  $y_2 = 0.20$  when  $c = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ) and Doe et al. (ref. 13) have suggested that a factor  $(1 + \kappa R)$  should be included in the denominator of the equation for  $\log y_2$ .  $R$  represents the closest distance of approach of free ions. Ions closer than  $R$  are considered to be associated. More recently it has been suggested (ref. 14) that the same factor should be included in the denominator of the  $(2c)^{1/2}$  term in eq. (4) for  $\Lambda^*$ . If these changes are being made it would seem logical also to allow during the iteration for the effect on  $\kappa$  of changes in the ionic strength of the solution due to association. This turns out to have a dramatic effect on the plots. These changes are summarized below and the resultant FE plots are shown in Fig. 3. Values of  $\Lambda_0$  and  $K_A$  obtained from linear least-squares analyses over various concentration ranges for the various cases are given in Table 3.

- Case 1 Basic FE equation, most dilute point  $1 \times 10^{-4} \text{ mol dm}^{-3}$
- Case 2 Basic FE equation, most dilute point  $1 \times 10^{-3} \text{ mol dm}^{-3}$
- Case 3  $(1 + \kappa R)$  in  $\log y_2$ , Doe (ref. 13)
- Case 4  $(1 + \kappa R)$  in both  $\log y$  and eq. (4), Doe (ref. 14)
- Case 5 As Case 4 but correcting ionic strength for association
- Case 6 As Case 1, but with model  $K_A = 1000 \text{ dm}^3 \text{ mol}^{-1}$ , methanol only

TABLE 3 Parameters determined from FE plots under various conditions

	$10^4 \times (\text{conc range})$ mol dm <sup>-3</sup>	H <sub>2</sub> O		MeOH	
		$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$
		S cm <sup>2</sup> mol <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>	S cm <sup>2</sup> mol <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>
Model values		135.82	5.5	109.80	450
	1.0 → 3.2	135.55	12.0	109.21	466
	1.0 → 7.8	135.46	8.3	109.14	459
Case 1	1.0 → 14.4	135.36	5.9	109.07	454
	1.0 → 23.0	135.26	4.1	108.91	444
	1.0 → 33.6	135.16	2.7	108.59	425
	10.0 → 16.0	134.97	2.4	108.17	418
Case 2	10.0 → 36.0	134.67	0.2	104.89	304
	10.0 → 64.0	134.35	-1.5	97.06	70
	1.0 → 3.2	135.55	11.9	109.02	434
Case 3	1.0 → 14.4	135.36	5.7	108.03	361
	1.0 → 33.6	135.15	2.5	106.00	260
	1.0 → 3.2	135.55	15.6	109.26	496
Case 4	1.0 → 14.4	135.38	10.0	109.30	499
	1.0 → 33.6	135.21	7.3	109.50	510
	1.0 → 3.2	135.55	15.6	109.12	475
Case 5	1.0 → 14.4	135.38	10.0	108.53	430
	1.0 → 33.6	135.21	7.2	107.65	385
	1.0 → 3.2	-	-	109.10	912
Case 6	1.0 → 14.4	-	-	108.55	859
	1.0 → 33.6	-	-	107.10	750

As can be seen from Table 3, the effect on the derived parameters of the assumptions made, the concentration range covered and particularly the lowest concentration used are dramatic for both solvents. Of course, it is the most important points, those at the lowest concentrations, that are most likely to suffer from the largest experimental error. For all cases in methanol every calculation underestimates the true value for  $\Lambda_0$  by a significant amount due to the concave nature of the real plot, particularly when the larger concentration ranges are used. However, only the basic FE equation gives values of  $K_A$  which are roughly constant for different concentration ranges analysed and which agree with the model value supplied. Case 5, which intuitively might be expected to give the best results, is by far the worst. Similar results are observed for the aqueous system, but here the agreement of  $K_A$  is worse due to the more pronounced curvature of the original plots. The errors become worse if the model association constant is larger, as shown for Case 6.

In conclusion, it can be said that the basic FE equation does appear to give a reasonable fit in certain cases, but the proposed changes do not yield a significant improvement. Moreover, given the availability of the LW equation and powerful computers there is not much to be said in favour of using the FE equation in the future, except in the analysis of poor quality data.

### QUINT-VIALLARD EQUATION

Two conductance equations have been developed to account for the totally general case of the conductance of solutions containing many ions in dilute solution. One, by Quint and Viillard (ref. 15), has been presented in an expanded form, similar to that used for single symmetrical electrolytes, in which the conductivity of each ion is given by the expression

$$\lambda_j = \lambda_{0j} - S_j I^{1/2} + E_j I \ln I + J_{1j} I - J_{2j} I^{3/2} \quad (5)$$

where the coefficients  $S_j$ ,  $E_j$ ,  $J_{1j}$  and  $J_{2j}$  are specific to a particular ion in a given mixture and depend on the values of  $\lambda_0$  of the other ions as well as solvent properties, fundamental constants and the closest distance of approach of free ions,  $R$ . Of course, one might expect a different value of  $R$  for each pair-wise combination of ions, but there does not seem to be much lost by treating  $R$  as a single adjustable parameter for the whole system whereas much is gained by so doing. Unfortunately, so far the equation does not seem to have been tested very rigorously, although Lee and Wheaton (ref. 16) claimed to have shown that an earlier version (ref. 17) gave a satisfactory fit of data for the alkaline earth chlorides (ref. 18) in methanol.

LEE-WHEATON EQUATION

The other equation, derived by Lee and Wheaton themselves (ref. 12), has been tested extensively (ref. 10) in both aqueous and non-aqueous systems and seems to provide a satisfactory explanation of the conductimetric behaviour of a variety of systems. However, as we shall see, even the LW equation is not without its problems in application and a complete theoretical exposition is still awaited. Unlike Quint and Viillard (ref. 15), Lee and Wheaton (ref. 12) did not expand and truncate the exponential integrals in their equation but retained them explicitly in terms up to order 3 in  $\kappa R$ . They obtained an equation of the form

$$\lambda(j) = \lambda_0(j) \left\{ 1 + z_j \sum_{p=2}^s \chi_j^p \sum_{v=1}^s t_v \kappa^v [A_v^p(t)(\beta\kappa) + B_v^p(t)(\beta\kappa)^2 + C_v^p(t)(\beta\kappa)^3] \right\} - \frac{|z_j|(\kappa\tau)}{2(1+t)} \{ 1 + V_j^{(1)}(t)(\beta\kappa) + V_j^{(2)}(t)(\beta\kappa)^2 + \Pi_j^{(5)}t/6 \} \quad (6)$$

with  $\Lambda_{\text{equiv}} = \sum_{j=1}^s (|z_j| m_j \lambda_j / c) \quad (7)$

where  $s$  is the number of charged species,  $z_j$  and  $t_j$  are the charge and transference number of species  $j$ ,  $\beta = e^2/DkT$ ,  $\kappa^2 = (4\pi/DkT) \sum_{j=1}^s n_j e_j^2$  and is proportional to the ionic strength,  $t = \kappa R$  and  $\tau = Fe/6\pi\eta$ ,  $m_j$  is the molar free ion concentration of species  $j$ ,  $c$  is the equivalent stoichiometric concentration of the electrolyte and all other terms are defined in the original papers (ref. 12).

One of the problems that has beset all theoretical approaches to the conductivity of complex solutions is the symmetry factor,  $q$ . This is equal to  $\frac{1}{2}$  for a symmetrical electrolyte but for a system of  $s$  ions there are  $s-1$  such factors  $q_p$ ,  $p = 2, s$ , given by

$$q_p = \frac{\sum_{i=1}^s \bar{\omega}_i t_i \omega_i}{(\omega_i^2 - \alpha_p^2)} \quad (8)$$

where  $\omega_i$  is the mobility of the  $s$  <sup>th</sup> ion and  $t_i$  its limiting transference number defined by  $t_i = n_i e_i^2 \omega_i / \sum_{i=1}^s n_i e_i^2 \omega_i$ . The values of  $\alpha_p$  are the solutions of the equation

$$\alpha_p \sum_{i=1}^s t_i / (\omega_i^2 - \alpha_p^2) = 0 \quad (9)$$

When  $s = 3$ ,  $\alpha_2$  and  $\alpha_3$  are simply the roots of a quadratic equation, but when  $s > 3$  the values of  $\alpha_p$  must be found by an iterative procedure once the ions have been sorted into a sequence of increasing mobility. A plot of the function in eq. (9) divided by  $\alpha_p$  against  $\alpha_p^2$  is shown in Fig. 4 for the case of 1.0 mM  $\text{CaCl}_2$  in methanol. The solutions for  $\alpha_p^2$  are where the function crosses the horizontal axis, leading to  $\alpha_2 = 2.59 \times 10^8$  and  $\alpha_3 = 3.03 \times 10^8$  and  $q_2$  and  $q_3 = 0.477$  and  $0.437$  respectively.

Even as complex an expression as the LW equation is necessarily only an approximation and the higher terms  $C_v^{(2)}$  and  $V_j^{(2)}$  are not complete. Consequently Wheaton (refs. 12,18) has suggested that they may be omitted. As can be seen from Figs. 5 and 6, calculated for the model cases used earlier to test the FE equation, the effect of including these terms is dramatic, especially in a solvent like methanol. It has been shown (ref. 10) that in low dielectric constant solvents such as methanol it is necessary to omit both terms to obtain a satisfactory fit with sensible parameters (see later) whereas with solvents like water and DMSO it is helpful to include the  $V_j^{(2)}$  term.

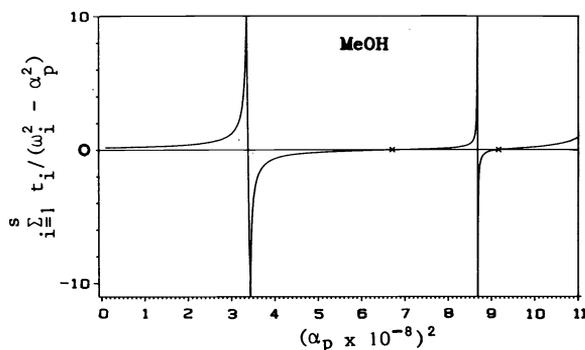


Fig. 4 Plot for the graphical determination of  $\alpha_p$  values for  $\text{CaCl}_2$  in methanol.

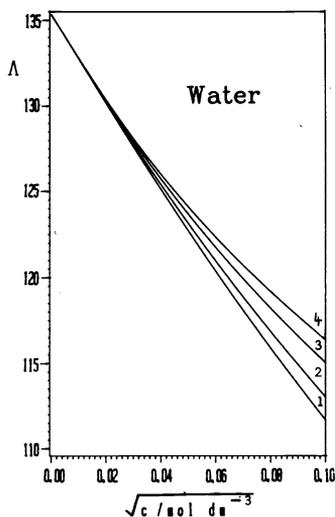


Fig. 5

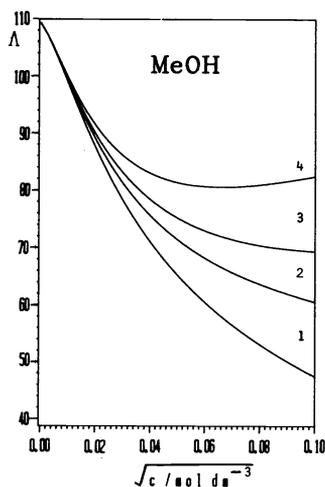
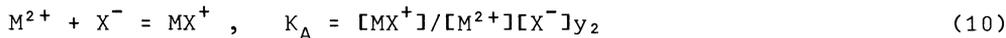


Fig. 6

- 1  $C_V^P$  and  $V_j^{(2)}$  omitted
- 2  $C_V^P$  only included
- 3  $V_j^{(2)}$  only included
- 4  $C_V^P$  and  $V_j^{(2)}$  both included

Figs. 5 and 6 Effect of including higher terms in the LW equation for  $\text{CaCl}_2$  in water (ref. 19) and methanol (ref. 20)

The simplest case to which the LW equation can be applied is that of a 2:1 salt which associates according to the scheme



In such a system five variables must be fixed before the conductance of the solution can be calculated; these being the limiting molar conductivities of the three ions, the value of  $K_A$  and a value for  $R$ . Of these,  $\lambda_0(\text{X}^-)$  can be obtained from conductance and transference measurements on solutions of a single symmetrical electrolyte, but the remaining four are too many to be determined by a fitting routine from the experimental data, three independent parameters being the most that can be extracted from the best data. The present author has found it useful (ref. 10) to express  $\lambda_0(\text{MX}^+)$  as a fixed ratio of  $\lambda_0(\frac{1}{2}\text{M}^{2+})$  and to calculate pairs of values of  $\lambda_0(\frac{1}{2}\text{M}^{2+})$  and  $K_A$  which fit the data at selected values of  $R$  and the conductivity ratio,  $\lambda_0(\text{MX}^+)/\lambda_0(\frac{1}{2}\text{M}^{2+})$ , expressing the results in a series of grids. Values of  $y_2$  are calculated from the extended Debye-Hückel equation with  $(1 + \kappa R)$  in the denominator. This has been reported elsewhere (ref. 10) for  $\text{CaCl}_2$  in methanol and is shown in Table 4 for the results for  $\text{MgCl}_2$  at 298 K reported by the same authors (ref. 20).

The criteria for the best fit are a minimum in the standard deviation of  $\Lambda_{\text{obs}} - \Lambda_{\text{calc}}$  values plus the absence of any obvious trend in the values of these differences. Table 4 shows that several sets of parameters give an equally good fit, but for a given value of the conductivity ratio the value of  $R$  obtained for  $\text{MgCl}_2$  is greater than that found for  $\text{CaCl}_2$ . This may indicate some extra solvation of the  $\text{Mg}^{2+}$  ion, but the values of  $\lambda_0(\frac{1}{2}\text{M}^{2+})$  are very similar for the two ions and the difference may just be due to some very small systematic error in one of the sets of data. However, the values of  $\lambda_0(\frac{1}{2}\text{M}^{2+})$  and  $K_A$  which give the best fit are almost independent of the exact pair of values of  $R$  and the conductivity ratio. This gives one confidence in the reliability of these values, particularly when comparing the values obtained for a series of salts analysed under similar conditions. For many systems a reasonable fit is obtained with the conductivity ratio equal to 0.8 and in the absence of other information it is recommended that this value should be used (ref. 10).

TABLE 4 Fit of  $\text{MgCl}_2$  in methanol (ref.20) with the LW equation with  $C_V^P$  and  $V_j^{(2)}$  terms omitted

	standard deviation grid				$K_A$ grid				$\lambda_0(\frac{1}{2}\text{Mg}^{2+})$ grid			
ratio	0.70	0.80	0.90	1.0	0.70	0.80	0.90	1.0	0.70	0.80	0.90	1.0
R/pm												
600	0.06	0.05	0.03	<u>0.01</u>	256	279	307	<u>342</u>	56.3	56.4	56.5	<u>56.6</u>
700	0.05	0.03	<u>0.01</u>	0.03	274	299	<u>330</u>	367	56.4	56.5	<u>56.6</u>	56.7
800	0.04	0.02	0.02	-	289	317	349	-	56.5	56.6	56.7	-
900	0.03	<u>0.01</u>	0.02	-	302	<u>331</u>	365	-	56.5	<u>56.6</u>	56.7	-

TABLE 5 Examples of fit of data for  $\text{MgCl}_2$  in methanol (ref. 20) with the LW equation using different assumptions about the terms included.

Assumptions	R/pm	ratio	$K_A$	$\lambda_O(\frac{1}{2}\text{Mg}^{2+})$	st.dev.
$C_V^D$ and $V_j^{(2)}$ omitted (see Table 4)	900	0.80	331	56.6	0.01
$C_V^D$ only included	$\left\{ \begin{array}{l} 2000 \\ 1200 \\ 770 \end{array} \right.$	0.80	434	56.7	0.01
		0.60	354	56.7	0.01
		0.15	265	56.6	0.02
$V_j^{(2)}$ only included	$\left\{ \begin{array}{l} 2500 \\ 1500 \\ 1000 \end{array} \right.$	0.80	417	56.7	0.01
		0.60	389	56.7	0.01
		0.15	299	56.6	0.01
$C_V^D$ and $V_j^{(2)}$ included	$\left\{ \begin{array}{l} 2300 \\ 1600 \\ 1150 \end{array} \right.$	0.80	472	56.7	0.01
		0.60	415	56.8	0.01
		0.15	330	56.8	0.02
$K_2$ included via eq.(11) (with $K_2 = 17.5 \text{ dm}^3 \text{ mol}^{-1}$ )	600	1.15	376	56.6	0.01

A small value for the standard deviation can also be obtained by forcing a fit when  $C_V^D$  and/or  $V_j^{(2)}$  are included but the values of the other parameters obtained are unrealistic (i.e. very high values of R at sensible conductivity ratios or very small ratios at reasonable values of R). Moreover, in sharp contrast with the situation when both terms are omitted, the values of  $K_A$  giving the best fit change a great deal. The values of  $\lambda_O(\frac{1}{2}\text{Mg}^{2+})$  all agree within  $\pm 0.2\%$ , so this is not helpful in judging the goodness of fit. These results are summarized in Table 5.

It is interesting to look at the effect of varying each of the four adjustable parameters in turn to see the effect of each on the calculated values of the conductivity. This is shown in Figs. 7 and 8 where the differences between the standard conductivities calculated from the parameters given in Table 2 and the conductivities calculated after the appropriate change in one parameter has been made are plotted for  $\text{CaCl}_2$  in water and methanol at 298 K. The effects of changing R, the conductivity ratio and  $K_A$  all tend to zero as  $c \rightarrow 0$ , whereas the effect of changing  $\lambda_O(\frac{1}{2}\text{Mg}^{2+})$  is a maximum at this point. This, and the fact that the plots for the first three changes are differently shaped, explains why it is possible to extract three independent parameters from a good set of experimental data. The effect of changing the conductivity ratio in methanol is greater because the larger value of  $K_A$  means the concentration of the ion pair is much higher. The differences between the curves increase as the concentration increases. Consequently, one should always aim to analyse data over as wide a concentration range as is consistent with the approximations made in the derivation of the theory. However, this latter point is more difficult to judge for the complex equations used for unsymmetrical and mixed electrolytes.

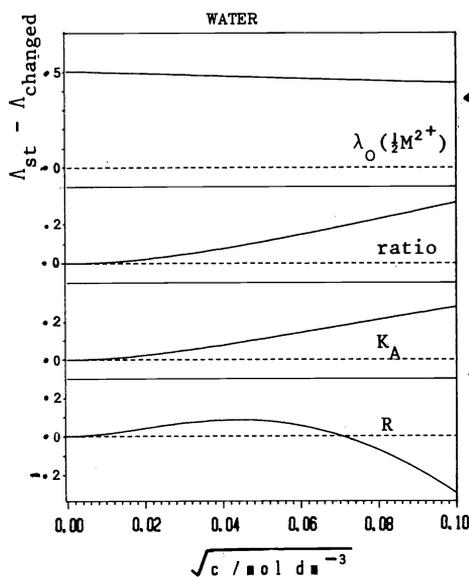
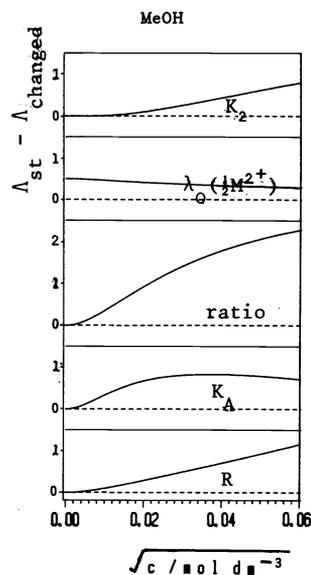


Fig. 7 LW parameter changes for water

model	
R/pm change	440 → 340
$K_A$	5.5 → 6.0
ratio change	0.8 → 0.6
$\lambda_O(\frac{1}{2}\text{M}^{2+})$	
change	59.47 → 58.97
$K_2$ change	-

Fig. 8 LW parameter changes for methanol

	550 → 450
	450 → 500
	0.8 → 0.6
	57.45 → 56.95
	0 → eq.(11)



If the value of  $K_A$  is large it is possible that further association may take place, leading to the formation of dissolved but undissociated  $MX_2$  for which a second association constant exists given by the expression  $K_2 = [MX_2] / [MX^+][X^-]y_1^2$ . Indeed, in solutions of transition metal halides further association to anionic complexes may take place, for example, when nickel bromide is dissolved in dimethyl sulphoxide (ref. 21) anionic complexes such as  $NiBr_3^-$  and  $NiBr_4^{2-}$  are formed even at low concentrations. Any attempt to analyse conductance data for such a system would require the introduction of additional association constants and ionic conductivities leading to an excess of parameters which must be adjusted. One possible approach is to analyse data at low concentrations where higher complexes are not formed and then to use the parameters so obtained to fit the data at higher concentrations in terms of the additional association constants.

If only association via  $K_2$  to  $MX_2$  takes place, it has suggested (ref.22) that the introduction of an additional adjustable parameter,  $K_2$ , can be avoided by using Fuoss' equation for the association constant between two ionic species (ref. 24). When the resultant expressions for  $K_A$  and  $K_2$  are combined, the expression

$$K_2 = K_A / \exp(e^2 / 4\pi\epsilon_0\epsilon_r kTR) \quad (11)$$

is obtained in which  $K_2$  is expressed solely in terms of fundamental constants and existing parameters. This approach is sometimes useful, but can also lead to strange results. For example, the last line of Table 5 shows that with the data for  $MgCl_2$  in methanol (ref. 20) a fit can only be obtained when  $K_2$  is introduced via eq.11 by setting the conductivity ratio greater than unity - which is contrary to all other experience. However, this approach is quite satisfactory for a system such as  $Sr(NO_3)_2$  in methanol (ref.10) which is more strongly associated with  $K_A = 5490 \text{ dm}^3 \text{ mol}^{-1}$  and  $K_2 = 375 \text{ dm}^3 \text{ mol}^{-1}$  at  $R = 640 \text{ pm}$  and the conductivity ratio = 0.68.

Finally, one word of caution should be added. Every system discussed to far has involved some kind of mixed electrolyte system in a single solvent. Very little work has been done on mixed electrolytes in mixed solvents, but recently Perie, Perie and Chemla (ref.23) have shown that preferential solvation of the ions in such mixed solvent systems can lead to effects that cannot be predicted by present theories of conductance. Consequently, it seems much safer at the present moment to deal with one major problem at a time and to restrict studies on mixed electrolyte systems to a single solvent.

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