

New handy relationship between the conductivity of concentrated nonaqueous electrolyte solutions and the dielectric constant and viscosity of the solvents

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Abstract

For nonaqueous electrolyte solutions, we correlated the equivalent conductance A_0 at infinite dilution and the conductivity maximum κ_{MAX} with only two intrinsic parameters of the pure solvents: the dielectric constant and the viscosity. On the basis of two new handy empirical formulas, predictions of A_0 and κ_{MAX} can now be made for a given salt in any solvent on the basis of only one A_0 or κ_{MAX} measurement in only one solvent. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-energy batteries consist of three major components: electrodes, a generally nonaqueous liquid or solid electrolyte and a separator. For the best performance, electrolytes should have the highest possible ionic conductivity.

The ionic conductivity in nonaqueous solvents is consequently a very important parameter but it is not always well-known or easy to determine, due to the possibility of solvating a great variety of salts in very different solvents. Here, we propose handy empirical relations which make it possible to predict the conductivity, on the basis of the viscosity and dielectric constant of the solvent. The conductivity of nonaqueous electrolyte solutions is interesting not only for these high energy-batteries, but also for many devices such as electrochemical reactors, capacitors, and electrochromic windows [1].

Molar conductivity or equivalent conductance equations of binary symmetrical electrolytes are often given in the form [1,2]

$$A = A_0 + A^{\text{rel}} + A^{\text{el}} \quad (1)$$

where

- A_0 , the limiting conductance of the electrolyte at infinite dilution, is due to the nonperturbed ion movement in the external field at infinite dilution of electrolyte;
- the electrophoric effect A^{el} and the relaxation effect A^{rel} are the conductance diminishing effects.

They can be estimated from different models [1–3].

The most famous equation for unassociated electrolytes came from Fuoss et al. [4,5]

$$A = A_0 - Sc^{1/2} + Ec \ln c + J_1(R)c - J_2(R)c^{3/2} \quad (2)$$

where

- S , E , J_1 , J_2 are of the type $X = X_1A_0 + X_2$;
- X_1 and X_2 are the contributions from the relaxation and electrophoric effect and are functions of the hydrodynamic radius R ;
- c is the salt concentration or the total ionic strength.

There is also a Fuoss–Onsager conductance equation for associated electrolytes

$$A = A_0 - S(c\gamma)^{1/2} + Ec\gamma \log(c\gamma) + (J - FA_0)c\gamma - K_A c\gamma f^2 \quad (2')$$

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where

- γ is the fraction of free ions;
- K_A is the association constant for the equilibrium $M^+ + A^- \leftrightarrow MA$, MA being any species that does not contribute to the conductance of the solution;
- $F\lambda_0 c$ is a corrective term for viscosity changes;
- f is the mean ionic activity coefficient of the dissociated electrolyte.

Other conductance equations have also been proposed, resulting in slight or more consequent improvements. Unfortunately, choosing the equation is not always straightforward. These equations require the knowledge of a multitude of thermodynamic and electrochemical parameters, which are not often available for nonaqueous systems. Moreover, for some solvents (ammonia, methylamine (MA), etc.), thermodynamically stable solutions exist only at high concentrations, at 293 K. It is impossible to synthesize dilute solutions under standard conditions with these solvents and to perform measurements or predict conductance. Consequently, Eq. (2) or (2') cannot be tested.

Recently, we showed [6] that for some amides, as well as propylene carbonate, acetonitrile (AN) and butyrolactone (γ -BL), the maxima of conductivity κ_{MAX} could be computed through the knowledge of the chemical hardness η of the solvent and of the salt.

In this paper, we look for a very simple relationship between κ_{MAX} and intrinsic parameters of the pure solvents, for concentrated nonaqueous liquid electrolyte solutions. We also consider a relationship between the limiting conductance λ_0 at ambient temperature and the same parameters. This study uses our conductivity measurements, as well as data from the literature.

Our measurements used the following salts: $LiPF_6$, $NaPF_6$, KPF_6 , Bu_4NPF_6 , $LiBF_4$, $NaBF_4$, Et_4NBF_4 , $LiSO_3CF_3$ and $LiN(SO_2CF_3)_2$, solvated in ammonia, methylamine, ethylamine (EA), formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMA), γ -BL and AN.

The data from the literature include the conductance values collected by Barthel and Gores [1], Salomon [3], Parsons [7], Janz and Tomkins [8], Jander [9], and Dudley et al. [10].

The explored solvents are thus very different: protic (i.e. water, ammonia, amines, AN) or aprotic (i.e. γ -BL, NMF, DMF, NMP, DMA) with a wide range of dielectric constants (from 6.7 for EA to 187 for NMF) and with different viscosities (from $\nu = 0.14$ cP for ammonia to 2.51 cP for PC).

We will show that simple equations can be used to predict the limiting conductance λ_0 and the maximum of conductivity κ_{MAX} . These equations depend only on the viscosity and on the dielectric constant of the pure solvent. The relation between κ_{MAX} , ε and ν is mainly based on our own results, whereas the relation between λ_0 , ε and ν is only based on the literature data, and supports the first one.

The solvent viscosity ν is the most important conductance-determining factor. The dielectric constant ε rules the dissociation–association of ion aggregates, ion pairs, bilateral (cationic and anionic) triple ions, and ion quadruples.

It will be seen that the proposed relation allows the prediction of λ_0 or of κ_{MAX} for a given salt, in any solvent, from the knowledge of only one λ_0 or κ_{MAX} value of the considered salt in only one solvent.

2. Experimental

The experimental procedures used for synthesis and electrochemical measurements are described elsewhere [6].

The following salts and solvents have been used:

- $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$ (or LiTFSI), $LiSO_3CF_3$ (or LiTrif);
- $NaBF_4$, $NaPF_6$;
- KPF_6 ;
- NEt_4BF_4 ;
- NMF, DMF, DMA, NMP, AN, γ -BL, liquid ammonia (NH_3), MA and EA. Formamide was studied too, but results were not given in this paper because the solutions seemed to decompose.

We synthesized ammoniate, aminate, and amidate liquid electrolytes in a glove box under argon. The solvents and salts were of analytical grade and used as received.

Given the very large number of measurements (about 6–10 points for each conductivity versus salt concentration, and more than 18 salts for 11 different solvents) each κ_{MAX} was determined only twice. All measurements were performed at $T = 293$ K and $P = 1$ bar. The viscosity and dielectric constant values used are from the literature [1,8,9].

3. Results

3.1. Experimental considerations regarding the conductivity of concentrated nonaqueous electrolytes

Curves of conductivity versus salt concentration at constant temperature, in our case $T = 293$ K, have a Gaussian-like profile. The maximum κ_{MAX} ranges from 0.6 M ($\kappa_{MAX} = 8$ mS cm^{-1} at 0.6 M for NEt_4BF_4 in NMP) to more than 5 M (in ammonia). They resemble the curves for amides [6]. Figs. 1 and 2 give the curves for ammonia and $MeNH_2$.

Our previous results [6], and the new κ_{MAX} measured values with ammonia and both amines are summarized in Table 1.

New results for $NaSO_3CF_3$ and $Na(SO_2CF_3)_2N$ (prepared in the laboratory from the corresponding lithium salts by cation exchange) are presented in Table 2.

κ_{MAX} varies to a small extent from one solvent to another. These variations have been attributed to variations in chemical hardness of the salt [6]. However, in some solvents,

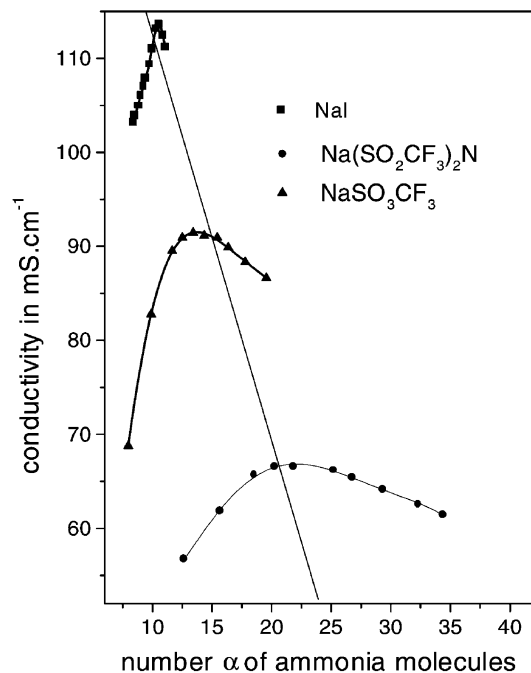


Fig. 1. The conductivity κ of three sodium salts in liquid ammonia vs. the composition α indicated as ammoniate composition (i.e. salt: α NH_3).

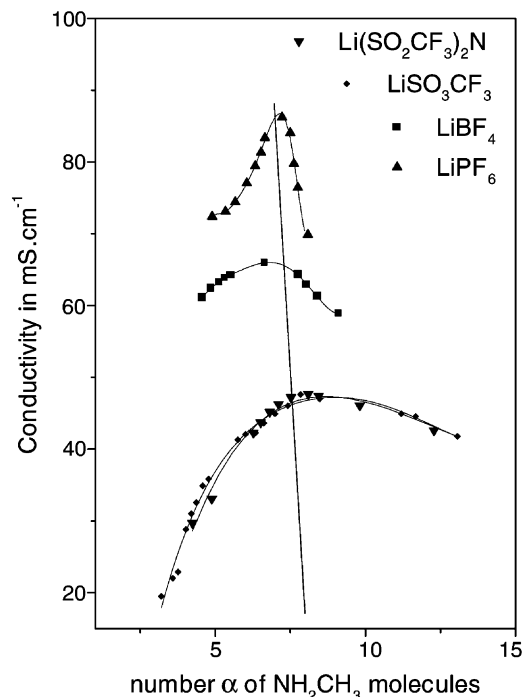


Fig. 2. The conductivity κ of four lithium salts in NH_2CH_3 vs. the composition α indicated as aminate composition (i.e. salt: α CH_2NH_2).

Table 1

Conductivity maxima, κ_{MAX} , (mS cm^{-1}) of nonaqueous electrolytes at 293 K

	NH_3	MA	EA	γ -BL	AN	NMF	DMF	NMP	DMA	PC
LiPF_6	139.5	83.5	24.5	9.3	41.5	15.4	19.4	7.3	12.37	3.5
NaPF_6	108.0	73.5	36.0	9.8	35.3	16.1	22.4	8.5	13.9	2.3
KPF_6	a	a	a	11.0	26.0	15.3	25.2	7.81	11.8	
LiBF_4	62.5	66.0	38.0	6.5	14.8	17.5	20.6	8.3	13.5	4.0
NaBF_4	a	59.0	22.50	–	–	17.0	21.8	8.1	13.25	1.5
Net_4BF_4	a	a	a	18.0	47.2	6.6	24.6	8.0	a	
LiSO_3CF_3	15.3 ^b	47.0	15.5	–	–	12.2	15.0	6.4	10.6	
$\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$	68.0	47.0	22.0	–	–	10.8	14.3	6.2	10.8	

^a The salts are almost insoluble.

^b The electrolyte is very viscous.

electrolyte solutions have a different behavior due to their high viscosity (for example, for $\text{LiSO}_3\text{CF}_3 \cdot 2.9 \text{NH}_3$ whose viscosity is $\nu = 41.8 \text{ cP}$ at 293 K).

Comparison of conductivity curves reveals that for a family of salts in a given solvent, the values of κ_{MAX} lie on a straight line. This has already been observed [6] for solutions in amides, AN and γ -BL. The calculation of the absolute chemical hardness [6] shows that all the considered

Table 2

Conductivity maxima, κ_{MAX} (mS cm^{-1}) at 293 K for NaSO_3CF_3 and $\text{Na}(\text{SO}_2\text{CF}_3)_2\text{N}$ in different solvents

	NH_3	MeNH_2	EtNH_2	DMF
NaSO_3CF_3	92.0	65.5	22.0	16.5
$\text{Na}(\text{SO}_2\text{CF}_3)_2\text{N}$	66.0	67.0	–	–

solvents are hard, and the hardest salt leads to the highest conductivity. SO_3CF_3 and $(\text{SO}_2\text{CF}_3)_2\text{N}$ salts are softer than others and generally yield less conductive solutions. Thus, conductivity depends on the nature of the solvent, as well as on the nature of the salt.

We will now look for a simple relation between the conductivity maxima of electrolytic solutions and the dielectric constant ϵ and viscosity ν of the pure solvents.

If we consider for example κ_{MAX} for amide-based electrolytes with LiSO_3CF_3 (see Table 3), we can see that ν plays a more important role than ϵ .

NMF and NMP have nearly the same viscosity, and a large decrease of ϵ has a minor influence: κ_{MAX} is divided by $\cong 2$ whereas ϵ is divided by $\cong 5$.

On the other hand, DMF and DMA have nearly the same dielectric constant, and a weak variation of ν has a large

Table 3

Maxima of conductivities κ_{MAX} of LiSO_3CF_3 in some solvents at 293 K; the dielectric constant ε and the viscosity ν of these solvents are considered at 298 K

	ε	ν (cP)	κ_{MAX} (mS cm ⁻¹) of LiSO_3CF_3 at 293 K
NMF	186.9	1.65	~12
NMP	32.0	1.66	~6
DMF	36.7	0.79	~15
DMA	37.8	0.93	~10

influence: κ_{MAX} increases by 25% when going from DMF to DMA, whereas ν decreases by only 14%.

These remarks are true for all the systems, except for LiBF_4 and LiSO_3CF_3 in ammonia, which have extraordinary viscosity.

To take these observations into account, we tried fitting the data with relations of the type

$$\kappa_{\text{MAX}} \text{ (mS cm}^{-1}\text{)} = K \frac{\sqrt[n]{\varepsilon}}{\nu^x} \quad (3)$$

This relation was fitted with different values for n (2, 3 and 4). For x we chose $x = 1$, as in the Walden and Hilgert [11] product (see later); other values gave aberrant results. The best fit with all our data was obtained for $n = 4$. Consequently,

$$\kappa_{\text{MAX}} = K \frac{\sqrt[4]{\varepsilon}}{\nu} \quad (4)$$

We will see that K is a constant (in mS cm⁻¹) whatever the temperature T .

In fact, $(\kappa_{\text{MAX}} \times \nu)/\varepsilon^{1/4}$ looks like the Walden product [8]. In these conditions, it was tempting to check whether

$(\Lambda_0 \times \nu)/\varepsilon^{1/4}$ or $\Lambda_0/(\sqrt[4]{\varepsilon}/\nu)$ is a constant. In the same way, we exploited the Λ_0 data from the literature [3] for LiClO_4 , $\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$ and LiAsF_6 , in water, AN, PC and methylformate (MF) [3]. $\Lambda_0/(\sqrt[4]{\varepsilon}/\nu)$ gives a constant value, called K'

$$K' = \Lambda_0/(\sqrt[4]{\varepsilon}/\nu) \text{ (with } K' \text{ and } \Lambda_0 \text{ in mS cm}^2\text{)} \quad (5)$$

It should be stressed that K and K' have different meanings. We will see that K' is also independent of the temperature. We will see that for many electrolytes, the term $\Lambda_0/(\sqrt[4]{\varepsilon}/\nu)$ is close to a constant only for $n = 4$. This backs up our statement for the description of the conductivity maximum of salts through relation (4).

Remark. The use of the product, $\kappa(C) \times \nu(C)$, of specific conductivity $\kappa(C)$ and viscosity $\nu(C)$, similar to a Walden product has been proposed by Webber [12], for LiBF_4 , LiCF_3SO_3 , LiTFSI , LiClO_4 , LiAsF_6 , and LiPF_6 , at 1 M concentration in 1:1 PC: DME at 25 °C. From one salt to another, this product is not a constant and ranges from 13.6 to 38.8. This is also true for $K_{\text{MAX}} \times \nu(C_{\text{MAX}})$. Consequently, even if one knows $\nu(C)$ and K_{MAX} for a salt, it is difficult to use the product $K_{\text{MAX}} \times \nu(C_{\text{MAX}})$ for predicting K_{MAX} of any salt.

3.2. Analysis of our data concerning the conductivity of concentrated nonaqueous electrolytes

We computed values of $\sqrt[4]{\varepsilon}/\nu$ for water and 11 non-aqueous solvents, using literature data. See Table 4.

K values computed from relationship (4) on the basis of Tables 1 and 4 are given in Table 5.

Table 4

Computed values of $\sqrt[4]{\varepsilon}/\nu$ at 298 K from ε and ν^a

	H ₂ O	NH ₃	MeNH ₂	EtNH ₂	γ -BL	MF	AN	NMF	DMF	NMP	DMA	PC
ε	78.54	17.5	9.4	6.7	39.10	8.50	35.95	186.90	36.71	32.00	37.80	64.95
ν	0.890	0.135	0.154	0.27	1.73	0.33	0.34	1.65	0.79	1.66	0.93	2.51
$\sqrt[4]{\varepsilon}/\nu$	3.34	15.15	11.4	5.95	1.45	5.17	7.20	2.24	3.12	1.43	2.67	1.14
$\nu/\varepsilon^{1/4}$	0.30	0.066	0.088	0.17	0.69	0.19	0.14	0.45	0.32	0.67	0.37	0.88
$\sqrt[4]{\varepsilon}$	2.98	2.05	1.75	1.61	2.50	1.71	2.45	3.70	2.46	2.38	2.48	2.84

^a The ratio $\nu/\varepsilon^{1/4}$ is computed to point out the difference with ν alone. Notice that $\sqrt[4]{\varepsilon}$ is not a constant.

Table 5

Computation of K from the relation (4)

	NH ₃	MeNH ₂	EtNH ₂	γ -BL	AN	NMF	DMF	NMP	DMA	PC
LiPF_6	9.6	7.3	4.0	6.4	5.8	6.9	6.2	5.1	4.6	3.1
NaPF_6	7.4	6.4	6.0	6.8	4.9	7.2	7.2	6.0	5.2	2.0
KPF_6	–	–	–	7.6	3.6	6.8	8.0	5.5	4.5	–
<i>t</i> -Bu ₄ NPF ₆	–	–	–	–	–	3.2	4.0	3.9	3.5	–
LiBF_4	4.3	5.8	7.5	4.5	2.1	7.8	6.6	5.9	5.0	3.5
NaBF_4	–	5.2	4.4	–	–	7.6	7.0	5.7	5.0	1.5
NH_4BF_4	–	12	–	–	–	–	–	7.8	–	–
NEt_4BF_4	–	–	–	12.4	6.6	3.0	7.9	5.6	–	–
LiSO_3CF_3	–	4.1	3.1	–	–	5.5	4.8	4.5	4.0	–
$\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$	4.7	4.1	4.3	–	–	4.8	4.6	4.4	4.0	–

Table 6
Mean value of K for a given salt in all the considered solvents

Salt	LiPF ₆	NaPF ₆	KPF ₆	LiBF ₄	NaBF ₄	LiSO ₃ CF ₃	Li(SO ₂ CF ₃) ₂ N
Mean value of K	5.9	5.9	6.0	5.3	5.2	4.3	4.4

Table 7
Computed values of K'

		H ₂ O	PC	AN	MF	Mean value of K'
LiClO ₄	A_0 (mS cm ²)	105.90	26.75	173.60	157.00	27.5 ± 4
	$K' = A_0/(\sqrt[4]{\epsilon}/\nu)$	31.70	23.67	24.11	30.37	
	$A_0 \times \nu$	94.25	59.41	59.20	51.50	
Li(SO ₂ CF ₃) ₂ N	A_0 (mS cm ²)	70.89	22.76	153.71	131.50	22.0 ± 3
	$K' = A_0/(\sqrt[4]{\epsilon}/\nu)$	21.22	20.14	21.35	25.44	
	$A_0 \times \nu$	63.09	57.13	52.41	43.13	
LiAsF ₆	A_0 (mS cm ²)	95.07	22.53	172.80	168.40	26.2 ± 4
	$K' = A_0/(\sqrt[4]{\epsilon}/\nu)$	28.46	19.94	24.00	32.57	
	$A_0 \times \nu$	84.61	56.55	58.92	55.23	

With a few exceptions (for instance, NEt₄BF₄ in γ -BL), the values of K are of the same order of magnitude for a given salt whatever the solvent (see Table 6).

For instance, if we consider LiPF₆-based electrolytes, we can conclude that whatever the solvent, κ_{MAX} values (in mS cm⁻¹) are given by

$$\kappa_{\text{MAX}} = 5.9 \frac{\sqrt[4]{\epsilon}}{\nu} \quad (4')$$

Relation (4') can be used to predict κ_{MAX} for LiPF₆-based electrolytes, even if K varies up to a factor 1.5 (Table 5), since the conductivity maxima varies by a factor of 10 between methylamine and other solvents such as amines and amides. If the average of all the K values in Table 5 is considered, $K = 5.2$, this accuracy remains better than ±50%. This rivals the accuracy of conductivity measurements, as they vary noticeably from one paper to another, due to, for instance, solvent or salt impurities, or poor conductivity electrodes.

3.3. Experimental considerations regarding the conductance of nonaqueous electrolytes

In order to check relation (5), we also computed values of $\sqrt[4]{\epsilon}/\nu$ for 11 solvents, using literature data. See Table 4.

$K'/(\sqrt[4]{\epsilon}/\nu)$ values for three salts, LiClO₄, Li(SO₂CF₃)₂N, and LiAsF₆, solvated by four different solvents, H₂O, PC, AN, MF, computed from Salomon's data [3] for A_0 , are given in Table 5. They are computed for $x = 1, 2, 3, 4$.

One can see that for $x = 4$, these values range from 20 to 32.7; for $x = 3$ from 14 to 27, for $x = 2$ from 7 to 18.9. The Walden product, $A_0 \times \nu$, varies between 42 and 94. In fact, for each salt, from water to MF the variations of K' are inferior to 20% (see Table 7).

Table 8
Dielectric constant, viscosity and ($\epsilon^{1/4}/\nu$) of water at 0, +25 +100 °C

Temperature (°C)	ϵ	ν	$\epsilon^{1/4}/\nu$
0	88	1.787	1.71
25	78.5	0.890	3.34
100	55	0.282	9.66

The Walden product, $A_0 \times \nu$, is more dispersed for all salts than K' . Water appears as a particular solvent if one considers the Walden product.

For a given salt, variations in K' among the four solvents are small (less than 20%), compared to those of A_0 (from 10 to 400%).

As in the case for κ_{MAX} , A_0 for a given salt can be estimated for any solvent of known viscosity and dielectric constant, on the basis of a measurement in only one solvent.

Table 9
Computed values of $A_0(\epsilon^{1/4}/\nu)$ and $A_0 \times \nu$ (Walden product) for NaCl (Table 9a), NaNO₃ (Table 9b) and LiClO₄ (Table 9c) in water

Temperature (°C)	A_0	$A_0(\epsilon^{1/4}/\nu)$	$A_0 \times \nu$
(a) NaCl			
0	66.9	39.0	119.6
25	126.5	37.8	112.6
100	361.0	37.4	101.7
(b) NaNO ₃			
0	66.5	38.8	118.8
25	123.0	36.8	109.5
100	339.3	35.1	95.6
(c) LiClO ₄			
0	55.0	32.1	92.3
25	104.1	31.1	92.7
100	296.5	30.7	83.6

Table 10
 A_0 , $A_0/(\varepsilon^{1/4}/\nu)$, and $A_0 \times \nu$ for some salts in hydrazine and water at 0 °C and +25 °C

Salts	Hydrazine at +25 °C			Water at +25 °C		
	A_0 (mS cm ²)	$A_0 (\varepsilon^{1/4}/\nu)$ or $(A_0 \times \nu)/\varepsilon^{1/4}$	$A_0 \times \nu$	A_0 (mS cm ²)	$A_0 (\varepsilon^{1/4}/\nu)$ or $(A_0 \times \nu)/\varepsilon^{1/4}$	$A_0 \times \nu$
KCl	130.3	44.0	117	149.8	44.8	133.3
KBr	134.9	45.5	122.1	151.7	45.4	135.0
KI	132.7	44.8	120.1	150.8	45.1	134.2

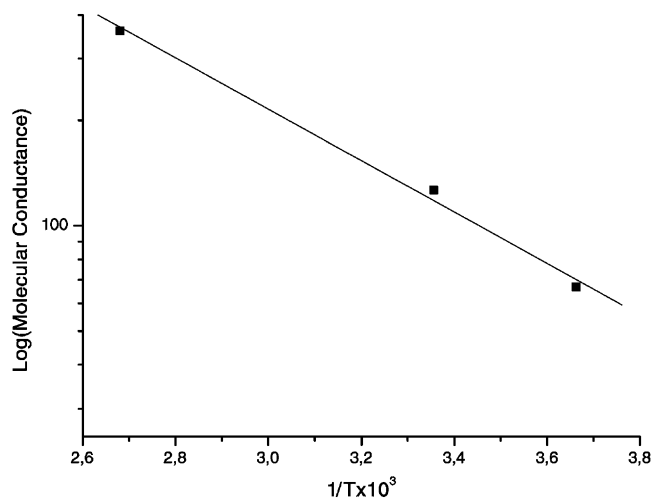


Fig. 3. NaCl in water. Arrhenius plot of A_0 vs. $1/T$. Here, decimal log of the conductance of NaCl, as a function of $1/T$. The slope of the straight line is -0.73 ± 0.05 .

Analysis of literature data concerning the conductivity of concentrated nonaqueous electrolytes.

We tried to see from other literature results whether it is possible to find the same results, i.e. a relation such as (4). We computed the data concerning κ_{MAX} of LiAsF₆ in very different solvents, from [1]. One can see that the best fits of the results are obtained with $\kappa_{\text{MAX}}/(\varepsilon^{1/4}/\nu)$.

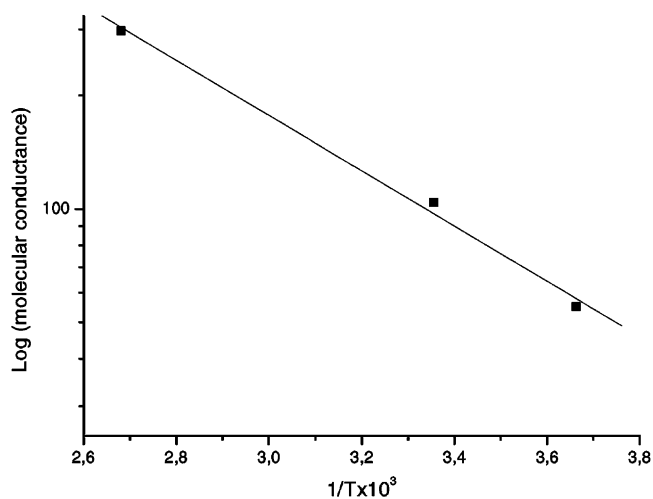
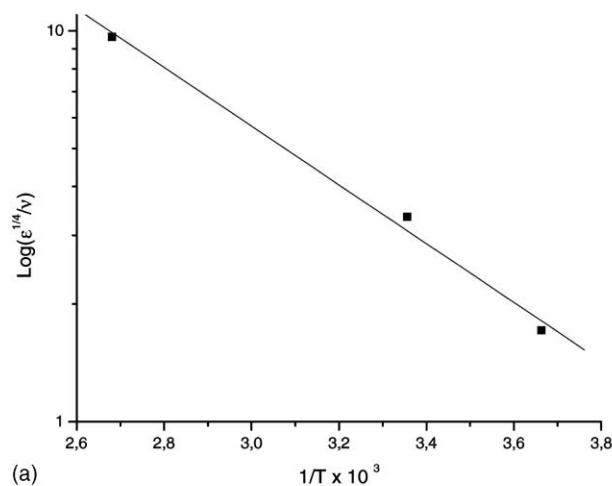


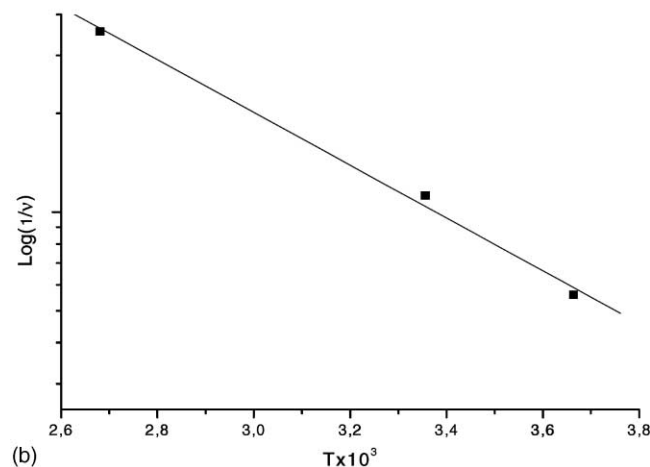
Fig. 4. LiClO₄. Arrhenius plot of A_0 vs. $1/T$. Here, decimal log of the conductance of LiClO₄ in water, as a function of $1/T$. The slope of the straight line is -0.73 ± 0.05 .

3.4. Influence of the temperature

In order to determine the influence of the temperature T on K and K' , we used the data dealing with the variations of A_0 with T for aqueous electrolytes, as water is a solvent for which the results are reliable. The A_0 determinations have been done at 0, 25 and 100 °C. Few A_0 measurements have been performed in nonaqueous solvents. In anhydrous hydrazine, some determinations have been performed at 0 °C and +25 °C.



(a)



(b)

Fig. 5. (a) Pure water. Arrhenius plot of $\varepsilon^{1/4}/\nu$ vs. $1/T$. Here, decimal log of $\varepsilon^{1/4}$ divided by the viscosity ν , as a function of $1/T$. The slope of the straight line is -0.75 ± 0.06 (b) Pure water. Arrhenius plot of $(1/\nu)$ vs. $1/T$. The slope of the straight line is -0.80 ± 0.06 .

For water the values of ε and ν are available at 0, 25 and 100 °C [13] (see Table 8). One can see that $\varepsilon^{1/4}/\nu$ varies from 1.714 at 0 °C up to 9.664 at 100 °C, an increase by a factor of 5.6, while ν decreases from 1.787 down 0.2818, a decrease by a factor of 6.4.

We chose the Λ_0 values of NaCl, NaNO₃, and LiClO₄ [7] (see Table 76, p. 81–82) as examples (see Table 9a–c).

One can see that $\Lambda_0/(\varepsilon^{1/4}/\nu)$ decreases slightly from 0 °C to 100 °C and is roughly a constant for every salt. The Walden product decreases faster than K' . This allows us to conclude that K' is independent of the temperature. The term $\varepsilon^{1/4}/\nu$ is sufficient to describe the influence of temperature. We assume that K , as K' , is independent of the temperature.

Another interesting case is anhydrous hydrazine. Its physical properties as functions of T are available and reliable [14].

The conductances Λ_0 , of different salts [11] (see Table 3, p. 203) in hydrazine and in water at +25 °C are collected in Table 10.

For each salt, the Walden product, $\Lambda_0 \times \nu$, is different in hydrazine and in water. The $(\Lambda_0 \times \nu)/\varepsilon^{1/4}$ term is generally roughly the same in hydrazine and in water. For water, and from Table 9a and c, one can plot $\log(\Lambda_0) = f(1/T)$ for NaCl or LiClO₄ for example (Arrhenius plots) and $\log(\varepsilon^{1/4}/\nu) = f(1/T)$. The same kind of variation and the same slope (activation energy) are found. See Figs. 3–5a. Fig. 5b shows the variation of $\log(1/\nu) = f(1/T)$: the corresponding straight line has a slope that is rather different from those in Figs. 3–5a.

4. Discussion

Until now, no “handy” relation has been proposed for the conductivity of very concentrated nonaqueous electrolyte solutions. Some authors [12] have shown that for a given salt in any solvent (even for solvents with a low dielectric constant) the Fuoss–Hsia conductivity equation [13]) can be extended to fit the conductance curve at almost any low concentration ($c < 0.1$ M) for solvents having a low dielectric permittivity. But, this equation requires the knowledge of K_A (the equilibrium constant of ion pairing) and K_T (the equilibrium constant of bilateral triple ion formation) for the considered salt, conductivity measurements at very low concentrations, and the determination of κ_{MAX} by derivation of the conductivity equation. Consequently, such a relation is difficult to use with new solvents and new salts to predict κ_{MAX} with good accuracy. Another possibility is the Casteel–Amis equation [7], (see Table 76, p. 81–82); although it is simpler, it requires the determination of four parameters and is difficult to apply for predicting κ_{MAX} in any solvent.

Different solvent parameters have been considered in order to take into account the role of the solvent [1], ([7], see Table 76, p. 81–82), but curiously no attempt was made to consider only the intrinsic parameters of the pure solvent alone.

We submit that both Λ_0 (at high dilution) and κ_{MAX} (at high concentration, i.e. 1–2 M) seem to be correlated to the viscosity and the dielectric constant by the same constant $\sqrt[4]{\varepsilon}/\nu$. It should, therefore, be possible to factor out this expression from the general equations for conductance or conductivity.

Although ion aggregate formation (ion pairs, triple ions, quadruple ions, etc.) was not taken into account in our formula, we have been able to find simple relations for κ_{MAX} and Λ_0 on terms of the two most important parameters of the pure solvent: its dielectric constant and its viscosity. In both relations, these parameters intervene as the factor $\sqrt[4]{\varepsilon}/\nu$. That conductivity is inversely proportional to viscosity is generally accepted [1,2]. The role of the dielectric constant to the power of 1/4, which appears from our study of a wide range of systems, is intriguing and warrants further study into its fundamental origin.

The theoretical basis [15] of Walden’s rule is Stokes’ law (which holds only for a restricted range of conditions).

The equivalent conductivity of an electrolyte is the sum of the equivalent conductivities of its ions

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \quad (6)$$

A theoretical consideration of the relation between λ_0 , ν_0 , r_i , and ε was proposed by Zwanzig [16]

$$\lambda_0 \times \nu_0 = \frac{zeF}{A_V \pi r + R_D [(ze)(\varepsilon_0 - \varepsilon_\infty)\tau/r^3(\varepsilon_0 + 1)\nu]} \quad (7)$$

Here τ is the dielectric relaxation time, ε_0 and ε_∞ the dielectric permittivities at 0 and infinite frequencies. A_V and R_D are the constants related to the forces of viscous inhibition and dielectric relaxation.

The relation (7) is not handy to use. Therefore, we proposed to check our empirical constant $\nu_0/\varepsilon^{1/4}$ for κ_{MAX} and for Λ_0 .

The dielectric constant ε should play a role, as shown by the relation (8), deduced from (7)

$$\lambda_0 \nu_0 = \frac{ae_0(r\varepsilon_0 + 1)\nu_0}{b(\varepsilon_0(r\varepsilon_0 + 1) + c(\varepsilon_0 - \varepsilon_\infty)\tau)} \quad (8)$$

where a , b , c are constants.

Obviously, relation (8) and our empirical relations (4) and (5) have a different dependence on ε .

It must be emphasized that the calculated values of $(\Lambda_0 \times \nu)/\varepsilon^{1/4}$ are less dispersed than the values of the classical Walden product. This is intriguing. If one could find a true constant or a good approximation to a constant, this should help to predict accurate values of κ_{MAX} , as well as Λ_0 , in pure solvents or in mixtures of solvents.

The fact that the Walden product is more dispersed than $\Lambda_0/(\sqrt[4]{\varepsilon}/\nu)$ is confirmed from our computations based on data collected by Parsons [7], and presented Table 11.

Furthermore, for a given salt in water, the dispersion of the Walden product as a function of T is larger than that of $\Lambda_0/(\sqrt[4]{\varepsilon}/\nu)$. This confirms the interest of our term $\sqrt[4]{\varepsilon}/\nu$. As

Table 11

Comparison between $(A_0 \times v)/\varepsilon^{1/4}$ or $A_0/(\sqrt[4]{\varepsilon}/v)$ and the Walden product $A_0 \times v$

Salt	Solvent	Conductance A_0 (mS cm ²)	$A_0/(\sqrt[4]{\varepsilon}/v)$ or $(A_0 \times v)/\varepsilon^{1/4}$	Walden product ($A_0 \times v$)
NaI	Methanol	107.8	24.6	58.7
NaI	Ethanol	46	22.3	49.6
NaI	Acetone	161	22.9	48.9
KI	Methanol	113.3	25.7	61.8
KI	AN	181.4	25.2	61.7
KI	Ethanol	46.5	22.6	50.1
KI	Acetone	181.4	25.9	55.1
NaSCN	Methanol	106.9	24.43	58.3

Table 12

Computed values of $\kappa_{\text{MAX}}/(\varepsilon^{1/4}/v)$ for LiAsF₆ in MF, DMSO, PC and NMP, with different x values

Solvent	ε	v	κ_{MAX}	$\kappa_{\text{MAX}} (\varepsilon/v)$	$\kappa_{\text{MAX}} (\varepsilon^{1/2}/v)$	$\kappa_{\text{MAX}} (\varepsilon^{1/3}/v)$	$\kappa_{\text{MAX}} (\varepsilon^{1/4}/v)$ or $(\kappa_{\text{MAX}} \times v)/\varepsilon^{1/4}$	$(\kappa_{\text{MAX}} \times v)$ Walden product
MF	8.5	0.328	31	1.2	3.5	5.0	6.0	10.2
DMSO	46.5	2	10	0.43	2.9	5.5	7.6	20
PC	65	2.51	5.6	0.22	1.7	3.5	5.0	14
NMP	32	1.66	11.2	0.6	3.3	5.9	7.9	18.3

a matter of fact, this term is very different from $1/v$. Even if ε is small, i.e. in the case of THF and MF, the difference is discernible. See Table 4.

It is possible to use our relation (4), $\kappa_{\text{MAX}} = K(\sqrt[4]{\varepsilon}/v)$, with $K \cong 5.5$ (mS cm⁻¹), a mean value which can be computed from Tables 5 and 12, for all values, to predict the conductivity of a salt in any solvent.

This is shown in Table 13. We compared our values computed from (4) with $K = 5.5$ (mS cm⁻¹), with the experimental values taken in reference [1], (see Table 1.4, p. 35).

Except for LiBF₄ in THF and for LiSO₃CF₃ or LiCO₂CF₃ in PC, there is a good agreement between the experimental values and those computed.

Another computation was done in the case of the Ziegler complexes which are very conductive in toluene, despite its low dielectric constant. The experimental κ_{MAX} is equal to 25 mS cm⁻¹ [1] (see Table 1.14, p. 96) at +100 °C.

Using our relation, $\kappa_{\text{MAX}} = K(\sqrt[4]{\varepsilon}/v)$ with $K = 5.5$, $\varepsilon \sim 2$ and $v = 0.3$ (deduced by extrapolation from the data [17]), we found $\kappa_{\text{MAX}} = 5.5(\sqrt[4]{2}/0.30) = 21.8$ mS cm⁻¹. This value is very close to the experimental one. Notice that this relation does not work with aqueous electrolytes. In water, κ_{MAX} values are very high.

As shown in Table 10, for water and for hydrazine, Walden products as well as $A_0/(\sqrt[4]{\varepsilon}/v)$ values are higher [8] than in all other solvents, see Table 11. This is likely due to the large absolute chemical hardness η of water and hydrazine. The difference between η_{solvent} and η_{salt} seems to be responsible [8] for the differences of $A_0/(\sqrt[4]{\varepsilon}/v)$ for a given salt from a solvent to another, and particularly from water to an organic solvent. This will be analyzed in a forthcoming paper.

Consequently, for organic solvents such as those listed in Table 11, $A_0/(\sqrt[4]{\varepsilon}/v)$ or $(A_0 \times v)/\varepsilon^{1/4} \cong 23$ mS cm². For

Table 13

Comparison between experimental κ_{MAX} and computed values from our relation

Salt	Solvent	Experimental κ_{MAX}^a (mS cm ⁻¹)	Computed values from $\kappa_{\text{MAX}} = 5.5(\sqrt[4]{\varepsilon}/v)$ (mS cm ⁻¹)
LiClO ₄	γ -BL	11	8
LiClO ₄	DMF	22.2	17.2
LiClO ₄	DMSO	10	7.2
LiClO ₄	NMP	11.2	7.9
LiClO ₄	MF	32	29
LiClO ₄	MF	30	29
LiClO ₄	EF	16	25
LiAsF ₆	THF	16.5	28.4
LiAlCl ₄	THF	16	28.4
LiAlCl ₄	NM	25	22
LiSO ₃ CF ₃	PC	2	6.3
LiCO ₂ CF ₃	PC	0.6	6.3
LiBF ₄	THF	4.2	28.4

^a From [1], Table 1.4, p. 35.

the conductivity maximum, except in water, the relation $\kappa_{\text{MAX}} = 5.5(\sqrt[4]{\varepsilon}/\nu)$ mS cm⁻¹ seems general, even for ammoniates liquid at room temperature (MX·xNH₃). We did not find any exception, even for organic solvent mixtures, as shown later.

4.1. What about mixtures of solvents?

We tried to predict κ_{MAX} for mixtures of solvents through a simplifying assumption: the dielectric constant and the viscosity vary linearly with the composition in weight or in volume. This is not strictly true, as we will see later, but it gives a good prediction of κ_{MAX} . We chose the paper of Gores and Barthel [18] to illustrate one computation. They studied the PC/DME mixtures with LiClO₄ as electrolyte: $\kappa_{\text{MAX}} \cong 15$ mS cm⁻¹ for 34.5% of PC in weight, at +25 °C.

For this composition [1] (see Fig. 2, p. 944), $\nu \cong 0.6$. The dielectric constant being unknown, we admitted that it varies linearly with the composition in weight from pure DME to pure PC. Consequently, since $\varepsilon = 7.07$ for pure DME, and $\varepsilon = 65$ for pure PC, we find $\varepsilon = 25.5$ for the mixture (35% in weight). From relation (5), with $K_0 = 5.5$ mS cm⁻¹, one finds

$$\kappa_{\text{MAX}} = 5.5 \frac{\sqrt[4]{25.5}}{0.6} \cong 20 \text{ mS cm}^{-1}$$

The experimental value is 15 mS cm⁻¹. Referred to this last value, the accuracy of the prediction is 33%. Notice that if one computes the viscosity value by interpolation, for 35% in weight of PC, one finds $\nu \cong 1$ ($\nu = 0.4$ for pure DME and $\nu = 2.5$ for pure PC). Such a value leads to $\kappa_{\text{MAX}} \cong 11$ mS cm⁻¹ (or an accuracy of 26%, referred to the experimental value). Other data have been also analyzed: EC–DMC mixtures, 2:1 [19,20] with LiPF₆ at +25 °C, and EC–PC mixtures, 1:1 [21] with LiClO₄. The predictions from (5) are reliable as well ($\pm 20\%$).

5. Conclusion

The conductivity of different salts was studied in various nonaqueous solvents, aprotic or protic, with a low or high dielectric constant, and high or low viscosity. From our results and those found in the literature, the main factors ruling the conductivity (as well as the conductance) are shown to be the viscosity ν and, to a lesser extent, the dielectric constant ε of the pure solvent. Empirical relations were proposed for the conductance A_0 and the conductivity maximum κ_{MAX} in terms of only ν and ε

$$\kappa_{\text{MAX}} = K \frac{\sqrt[4]{\varepsilon}}{\nu} \quad (4)$$

$$K' = A_0 / \frac{\sqrt[4]{\varepsilon}}{\nu} \quad (5)$$

These equations allow one to predict A_0 as well as κ_{MAX} . For K , a mean value of 5.5 mS cm⁻¹ is adequate to predict κ_{MAX}

in many nonaqueous solvent, even in solvent mixtures, at any temperature. The influence of temperature is only due to changes in ε and ν .

The variation of A_0 or κ_{MAX} upon dissolution of a given salt in any nonaqueous solvent can be calculated from the conductance or “conductivity versus concentration” curve of this salt in only one solvent, through the knowledge of a unique, easy to determine constant K or K' .

The values of $A_0/(\sqrt[4]{\varepsilon}/\nu)$ are less dispersed than those of the Walden product ($A_0 \times \nu$). This ratio $A_0/(\sqrt[4]{\varepsilon}/\nu)$ is independent of the temperature and equal to a constant (23 mS cm²) for solvents other than water and hydrazine. For a given salt in water, and in anhydrous hydrazine, another inorganic solvent which is as hard as water (in term of HSAB), a higher constant is found. This role of ε for A_0 is surprising since conductances are determined at very high dilution, at concentrations where no ionic association takes place. The knowledge of a A_0 value, at one temperature, allows the knowledge of A_0 at any temperature T , through the computation of $\sqrt[4]{\varepsilon}/\nu$ at T .

These relations give good predictions of the variation of A_0 and κ_{MAX} from one solvent to another, provided that the salt is sufficiently soluble. They were verified for many nonaqueous solvents (and their mixtures), protic as well as aprotic, which have wide electrochemical windows and can be used for energy storage, a field where the knowledge of A_0 or κ_{MAX} is very useful for the development of lithium batteries, (super)capacitors, and electrochromic devices.

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References

- [1] J. Barthel and H.-J. Gores, in: G. Mamantov and A. I. Popov (Ed.), Chemistry of Nonaqueous Solutions, VCH, New York, pp. 55–56, 1994.
- [2] P. Turq, J. Barthel, M. Chemla, in: Transport, Relaxation and Kinetic Processes in Electrolyte Solutions, Springer Verlag, Berlin Heidelberg, 1992.
- [3] M. Salomon, J. Solution Chem. 22 (1993) 715.
- [4] R.M. Fuoss, L. Onsager, J. Phys. Chem. 61 (1957) 668.
- [5] R.M. Fuoss, L. Onsager, J.F. Skinner, J. Phys. Chem. 69 (1965) 2581.
- [6] G. Herlem, J. Solution Chem. 28 (1999) 223.
- [7] R. Parsons, in: Handbook of Electrochemical Constants, Butterworths Scientific Publications, London, 1959.
- [8] G. J. Janz, R.P.T. Tomkins, in: Nonaqueous Electrolytes Handbook, Academic Press, New York, 1985.
- [9] J. Jander, in: Anorganische und allgemeine Chemie in fl ssigen Ammoniak, Friedr., Viewig & Sohn, Braunschweig, 1966.

- [10] J.T. Dudley, D.P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M.W. Juzkow, B. Denis, P. Juric, P. Aghakian, J.R. Dahn, *J. Power Sources* 35 (1991) 59.
- [11] P. Walden, H. Hilgert, *Z. physikal. Chem, A* 165 (1933) 241, and references therein.
- [12] A. Webber, *J. Electrochem. Soc.* 2586 (1991) 2586.
- [13] from *Handbook of Chemistry and Physics*, 68th Ed., CRC Press Inc., FL, p. E56.
- [14] L.F. Audrieth, B.A. Ogg, in: *The Chemistry of Hydrazine*, from Table 6 p. 61, and Table 7, p. 63, J. Wiley, New York, 1951.
- [15] R. M. Fuoss, F. Accascina, in: *Electrolytic Conductance*, Interscience Publishers Inc., New York, 1959, p. 59–61, (see Walden's rule in Chapter III).
- [16] R. Zwanzig, *J. Chem. Soc.* 52 (1970) 3625–3628.
- [17] *Handbook of Chemistry and Physics*, 68th Edition, 1987, CRC Ed., Boca Raton, FL, USA.
- [18] H.-J. Gores, J. Barthel, *J. Solution Chem.* 9 (1980) 939.
- [19] D. Guyomard, J.-M. Tarascon, *J. Electrochem. Soc.* 140 (1993) 3071.
- [20] J.-M. Tarascon, D. Guyomard, *Solid State Ionics* 69 (1994) 293.
- [21] H.P. Chen, J.W. Fergus, B.Z. Jang, *J. Electrochem. Soc.* 147 (2000) 399.