A New Look on the Representation of Electrical Conductivities in Mixed Solvents. The Universal Curves of Limiting Conductances of Electrolytes and the Modified and the Excess Walden Products

Alexander Apelblat*

Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

* *Corresponding author: E-mail: apelblat @bgu.ac.il*

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

Concepts of the modified and the excess Walden products are introduced and discussed when applied together with the ordinary Walden product. The existence of the universal curves of limiting conductances for electrolytes (or for ions) in a given pair of solvents are further examined for a number of mixtures which include ethanol, 2-propanol, 1,1,1,3,3,3-hexafluoro-2-propanol, N,N,-dimethylformamide and 1,4-dioxane with acetone; methanol, 1,4-dioxane, carbon tetrachloride and toluene with acetonitrile; water, methanol and γ-butyrolactane with tetramethylene sulfone; methanol, acetonitrile, toluene, dimethoxymethane and dimethoxyethane with propylene carbonate. Many electrolytes were involved in the evaluation of the universal curves, but the majority are alkali metal halides and tetraalkylammonium salts. These universal curves allow to estimate values of limiting conductances of electrolytes and give an indication about the quality of the performed conductivity measurements. The existence of universal curves of limiting conductances indicates that the properties of electrolytes in pure solvents are, to a great extent, preserved also in the mixture of solvents due to the simple dilution effect. In some cases, for a limited concentration range, it was observed that for a given electrolyte, the limiting conductances are weakly dependent on the type of the second component in the mixture, e.g. in water-rich–alcohol mixtures. A formal mathematical representation of the universal curves (two-adjustable parameter equation) and the limiting conductances (three-adjustable parameter equation) are introduced and for many electrolytes in numerous mixed-solvent systems these parameters are reported.

Keywords: Electrical conductivity, mixed solvents, limiting conductances, various Walden products, universal curves of limiting conductances of electrolytes and ions, formal mathematical representation of limiting conductances in mixed-solvent systems.

1. Introduction

Extensive experimental and theoretical investigations were dedicated to the study of electrical conductivities in the mixed solvent systems[1–13]. Most of them are dealing with conductances of various electrolytes in the water-organic solvent mixtures.[14] Smaller number of electrolytes was considered in binary organic solvents because such studies were often related to the solution of particular technological problems (e.g. high-energy batteries). These studies provided an important source of information about ion-ion and ion-solvent interactions in solutions when the charge transfer is continuously affected by changing conditions, the change of viscosity $\eta(x,T)$ and dielectric constant $D(x,T)$ resulting from the change in composition of the mixture. The mixture composition is usually expressed by the mole fraction of one of solvents x or by the weight fraction of it w.

As a rule, from the experimental data, $\Lambda(c,T)$, by using a suitable conductivity equation, four derived parameters are reported for each electrolyte at given composition x: the limiting conductance $\Lambda^0(x,T)$, the association con-

stant $K_A(x,T)$, the ion-size parameter $a(x,T)$ and the Walden product $\Lambda^0(x,T)\cdot\eta(x,T)$. Thus, in the analysis of electrical conductivities three measurable quantities are involved: the conductances at infinite dilution, the viscosities and the dielectric constants and three model quantities: the association constants, the ion-size parameters and the Walden products. A different behaviour of various electrolytes in mixed solvents is therefore the result of a combine effect which is associated with changes in the physical properties of solvents and with changes in the molecular parameters of ions. Thus, the interpretation of electrical conductances of electrolytes is frequently related to the different nature of ions (small and large ions, structure-making and structure-breaking ions, different charge densities, sizes and polarizabilities of ions, association, hydration and solvation effects, etc.).

Paul Walden[15] observed in 1906 that the product of the molar conductance at infinite dilution $\Lambda^0(T)$ and the viscosity of pure water $\eta(T)$ is nearly independent of temperature, $\Lambda^0(T)\cdot\eta(T) = \text{const}$. From this time, the so-called Walden rule or the Walden product is practically always reported together with determined $\Lambda^0(T)$ values. This is done for two reasons. First, to obtain the limiting conductances at temperatures different than the experimental temperatures, taking into account that temperature dependence of viscosity is easier to determine than $\Lambda^0(T)$. The second reason is that when the product is combined with the Stokes law, it is possible to obtain an indication about the dimensions of ions. The concept of the Walden product was extended also to the mixed solvent systems in the form $\Lambda^0(x,T)\cdot\eta(x,T) = f(x)$, in many cases tacitly assuming without verification that the $f(x)$ function is almost independent of temperature. However, in many cases, the Walden product is only approximately satisfied with regard to the temperature and the derived ionic radii show little correlation with the nature of the electrolyte and solvents, giving sometimes physically unrealistic values. Different modifications of Stokes law[2,12,16–18] or the Eyring theory of absolute reaction rates in the liquid state[19] as applied to systems with mixed solvents were not always successful. Nevertheless, in the examination of electrical conductances there is no doubt that from a practical and also from a theoretical view, the knowledge of the Walden products in pure solvents and in mixed solvents is very important.

Recently[20], the author showed the possibility of adding two more concepts to the analysis and representation of conductivity data, the *modified Walden product* and the *universal curve of limiting conductances of electrolytes*. The modified Walden product is superior when the division of mixtures into concentration regions is desired when an alternative indicator of such division, the maximum of viscosity or the ordinary Walden product are usually less certain. The second concept is associated with the fact that for each solvent mixture, at least in part with regard to its composition, the conductances at infinite dilu-

tion of electrolytes $\Lambda^0(x,T)$ or ions $\lambda^0(x,T)$ can be shifted with a reasonable accuracy to a unique curve. This universal curve gives some indication about the quality of the performed conductivity measurements and gives the possibility of estimating the limiting conductances when the $\Lambda^0(x)$ values are unavailable in the literature.

In this investigation, some new aspects related to the modified Walden products and the universal curves of limiting conductances of electrolytes are discussed. The proposed approach is illustrated by treating a number of new mixed-solvent systems, but also a more complete analysis is presented for a few previously considered mixtures. There is an attempt to give some estimation of the limits of concentration regions and the expected accuracy of $\Lambda^0(x,T)$ values when they are predicted from the universal curves of limiting conductances. Finally, a simple empirical representations of all measurable quantities of the problem, $f(\Lambda^0, \eta, D; x) = 0$ is examined.

2. Walden Products in Mixed Solvents

As pointed earlier, the Walden rule is a simple function, being the product of the viscosity of the pure solvent and the limiting conductance of the electrolyte, $\Lambda^0(T)\cdot\eta(T) = \text{const}$. The Walden product itself is the model quantity introduced because it weakly depends on temperature, contrary to the product components viscosity and limiting conductance. Formally, it was extended to binary mixtures of solvents $\Lambda^0(x,T)\cdot\eta(x,T) = f(x)$ by assuming that for each mole fraction x also its weak temperature dependence is preserved. The Walden product in pure solvents represents a situation when the ion–ion interactions are completely excluded and only the interactions between ions and neighboring solvent molecules are of importance. In binary mixtures, in addition to the ion interaction with two different solvent molecules existing in different proportions, the existence of the solvent–solvent interactions can not be neglected; with, in order to restore the physical situation of the Walden product in pure solvent, the author suggested introducing the modified Walden product which is defined by[20]

$$\Lambda^0(x,T)\eta^{\#}(x,T) = \Lambda^0(x,T)[x\eta_1^0(T) + (1-x)\eta_2^0(T)] \quad (1)$$

where $\eta_1^0(T)$ and $\eta_2^0(T)$ are the viscosities of pure solvents at temperature T. Thus, the actual viscosity of the mixture $\eta(x,T)$ is replaced by the so-called *ideal viscosity* $\eta^{\#}(x,T)$ which represents the sum of the additive contributions from the viscosities of pure solvents. If the viscosity $\eta(x,T)$ indirectly represents the actual solvent-solvent interactions, then the simple dilution effect, i.e. the gradual replacement of solvent molecules in the mixture, is demonstrated by $\eta^{\#}(x,T)$. Depending on the system, $\eta(x,T)$ is a complex function of composition, having concave

downward or concave upward curvatures and sometimes exhibiting a maximum, minimum or both (e.g. maxima in the alcohol with water mixtures[21], a minimum in the ethanol-cyclohexane mixtures[22], both extrema in the methanol with benzene or toluene mixtures[22]). It is supposed that the composition at extreme values of viscosity divides a mixture into two solvent rich regions. On the other hand, the ideal viscosity $\eta^{\#}(x,T)$ is an explicit, linear function of mole fraction x and the difference, $\eta^{E}(x,T) = \eta(x,T) - \eta^{\#}(x,T)$, is called the *excess viscosity*, in analogy with the excess thermodynamic functions. Positive values of $\eta^{E}(x,T)$ are usually associated with attractive interactions between the components of the mixture (structure-making effects) whereas negative values of $\eta^{E}(x,T)$ are attributed to repulsive interactions (structure-breaking effects). Evidently, if the excess viscosity changes sign, dividing the concentration range, $0 \leq x \leq 1$, into two regions, each either dominated by the attraction or by the repulsion forces.

Similarly, the *excess Walden product* can be introduced

$$\Lambda^{0}(x,T)\eta^{E}(x,T) = \Lambda^{0}(x,T)[\eta(x,T) - \eta^{\#}(x,T)]$$
$$= \Lambda^{0}(x,T)[\eta(x,T) - x\eta_{1}^{0}(T) - (1-x)\eta_{2}^{0}(T)] \quad (2)$$

If only dielectric constants of pure components are considered, in the case when one component has a low value of D (say $D < 10$), the limiting conductance as a function of composition is a monotonic function which usually has a concave upward curvature. The same form of the $\Lambda^{0}(x,T)$ curves is also preserved for larger values of dielectric constants but often they have a minimum (e.g. in the mixtures of water with alcohols) and less frequently, the $\Lambda^{0}(x,T)$ curve has a concave downward curvature (e.g.
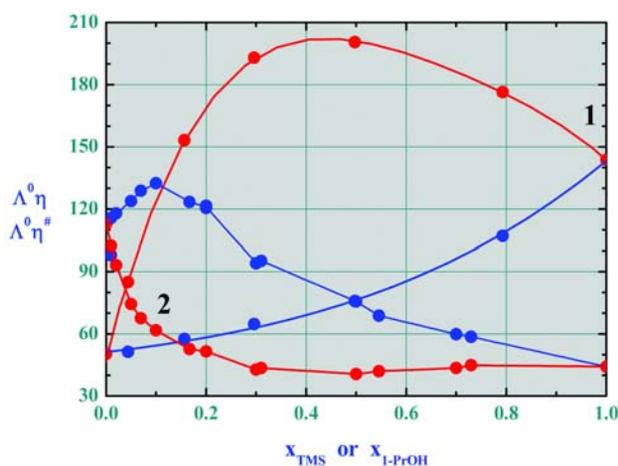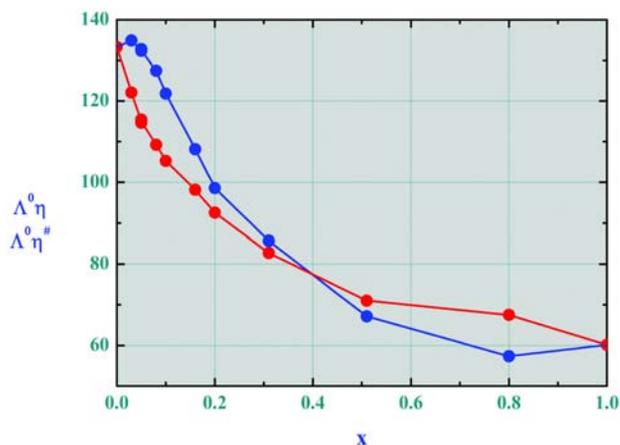

Figure 2. Ordinary Walden products $\Lambda^{0}(x,T) \cdot \eta(x,T)$ (blue line) and modified Walden products $\Lambda^{0}(x,T) \cdot \eta^{\#}(x,T)$ (red line) of potassium chloride as a function of mole fraction x of acetonitrile in the acetonitrile-water mixtures at $T = 298.15$ K.

in the acetotonitrile-methanol[23] or the acetone-ethanol mixtures[24]). As a consequence, it is difficult á priori to predict the form of the products of the limiting conductances and viscosities. The same is true for the magnitude of $\Lambda^{0}(x, T)\eta^{E}(x,T)$. However, the sign of the excess Walden product is known because it is given by the sign of the excess viscosity, $\eta^{E}(x,T)$. Thus, the modified Walden product is larger than the ordinary Walden product if $\eta^{E}(x,T) > 0$ and the modified Walden product is smaller than the ordinary Walden product if $\eta^{E}(x,T) > 0$. If the excess viscosity changes sign, then the excess Walden product also changes sign in the $0 \leq x \leq 1$ concentration interval. The first two cases are illustrated in Figure 1 where over the entire concentration range, in the methanol (MeOH)-tetramethylene sulfone (TMS)[25] mixtures we have Λ^{0}(LiCl; x_{TMS}, $T = 308.15$K) $\cdot$ $\eta^{E}(x_{TMS},T) > 0$ and Λ^{0}(NaCl; x_{1-PrOH}, $T = 298.15$K) $\cdot$ $\eta^{E}(x_{1-PrOH},T) < 0$ in the 1-propanol (1-PrOH)-water mixtures[26,27]. The change of sign of the excess Walden product which occurs in the acetonitrile (AN)-water system[28] is shown in Figure 2.

It is worthwhile to note that the modified Walden product is better suited to indicate the limits between solvent-rich regions than the ordinary Walden product or the viscosity $\eta(x,T)$. In each region, the modified Walden product can be nearly linearly approximated on x or on $1-x$ and the crossing point of these straight lines gives the division into two regions.

For the methanol-sulfolane mixtures, the viscosities and dielectric constants are monotonic functions of concentration ($\partial\eta(x)/\partial x > 0$ and $\partial D(x)/\partial x > 0$). The same can be said for the observed ordinary Walden product of LiCl (Figure 1). Unfortunately, in this system, in addition to LiCl, only $KClO_4$ was investigated[29] at a different temperature $T = 298.15$ K. Taking into account only these two electrolytes, the universal conductivity curve (for these curves see later) can be estimated from the metha-

Figure 1. Ordinary Walden products $\Lambda^{0}(x,T) \cdot \eta(x,T)$ (blue lines) and modified Walden products $\Lambda^{0}(x,T) \cdot \eta^{\#}(x,T)$ (red lines) as a function of mole fraction x. 1. Lithium chloride in the methanol-sulfolane mixtures at $T = 308.15$ K; 2. Sodium chloride in the 1-propanol-water mixtures at 298.15 K.

nol and sulfolane sides and the division between regions $x_{TMS} \sim 0.3$ as predicted by the modified Walden product (Figure 1).

Viscosities in the 1-propanol-water system have a maximum at $x_{1\text{-PrOH}} \sim 0.3$ and dielectric constants monotonically decrease with the mole fraction $x_{1\text{-PrOH}}$. The ordinary Walden product has a maximum at $x_{1\text{-PrOH}} \sim 0.10$ (Figure 1) but as was established previously for this system[20] the water-rich region extends up to $x_{1\text{-PrOH}} \sim 0.30$ when the modified Walden product gives much smaller value of $x_{1\text{-PrOH}} \sim 0.10$.

A complex form of both Walden products in the acetonitrile-water mixtures (Figure 2) results due to the fact that the extreme values of viscosity (a maximum at the water-rich mixture $x_{AN} \sim 0.025$) and the limiting conductances (a minimum at $x_{AN} \sim 0.40$) are far from each other. Following the modified Walden product, the water-rich region is relatively short $x_{AN} < 0.15$.

3. Universal Curves of Limiting Conductances of Electrolytes in Mixed Solvents

Similarly as in water, different electrolytes in a particular mixed-solvent system have different values of the limiting conductances $\Lambda_j^0(x, T)$ where the subscript j denotes a given electrolyte. However, as was shown by the author[20], in the solvent-rich regions, different electrolytes can be shifted with a reasonable accuracy to a unique curve according to

$$\frac{\Lambda_j^0(x, T)}{\Lambda_i^0(x, T)} = \frac{\Lambda_j^0(0, T)}{\Lambda_i^0(0, T)} = \text{const.} \tag{3}$$

or

$$\frac{\Lambda_j^0(x, T)}{\Lambda_i^0(x, T)} = \frac{\Lambda_j^0(1, T)}{\Lambda_i^0(1, T)} = \text{const.} \tag{4}$$

Since the limiting conductances of electrolytes j and i in pure solvents are not equal, i.e. $\Lambda_j^0(0, T) \neq \Lambda_j^0(1, T)$ and $\Lambda_j^0(0, T) \neq \Lambda_j^0(1, T)$, these constants are also not equal. In the case where one solvent has a very low dielectric constant, one of these equations covers almost the entire range of the mixture compositions. Thus, in principle, for a particular mixed-solvent system, it is sufficient to determine the limiting conductances for only one electrolyte because the conductances of other electrolytes can be deduced approximately from eqs. (3) and (4). The choice of this electrolyte which will be called the *standard electrolyte* is arbitrary, but the preferable electrolyte is that which has, over a wide concentration range, many accurate determinations of $\Lambda_j^0(x, T)$.

As was demonstrated by the author,[20] the limiting conductivities of different ions can also be reduced to two equations for cations and two equations for anions, i.e. to equations of the form

$$\frac{\lambda_j^0(x, T)}{\lambda_i^0(x, T)} = \frac{\lambda_j^0(0, T)}{\lambda_i^0(0, T)} = \text{const.} \tag{5}$$

and

$$\frac{\lambda_j^0(x, T)}{\lambda_i^0(x, T)} = \frac{\lambda_j^0(1, T)}{\lambda_i^0(1, T)} = \text{const.} \tag{6}$$

where arbitrarily a *standard cation* and a *standard anion* are chosen for a particular mixture of solvents.

Before discussing the behaviour of different electrolytes in a particular mixed-solvent system, let us consider the case of a particular electrolyte in a number of binary mixtures that consist of one common component and the second component belongs to the same group of solvents. An example of such mixtures, where there is a sufficient amount of experimental data to examine it, are aqueous solutions of low aliphatic alcohols (amphiprotic hydrolytic solvents; for classification of solvents see[13]). It is rather surprising to observe that in the water-rich region, the limiting conductance of a given electrolyte is, to a great extent, independent of the alcohol.

In Figure 3 the limiting conductances of tetrabutylammonium bromide $\Lambda^0(\text{Bu}_4\text{NBr})$ are plotted as a function of the dielectric constant $D(x)$ (dielectric constants are monotonic functions of x) in four different water-aliphatic alcohol mixtures.

As can be observed, in the water-rich region, $D(x) > 68$, $\Lambda^0(\text{Bu}_4\text{NBr})$ forms a common curve for mixtures with methanol[30], ethanol[31], 1-propanol[27] (Bu_4NBr is replaced here by Bu_4NI but the anion contributions of Br^- and I^- are very close) and tert-butanol[32]. Distinction between various alcohols is visible only in the alcohol-rich regions. Other electrolytes behave in a similar way as can be seen in Figure 4 where sodium chloride with EtOH[33], 1-PrOH[27],
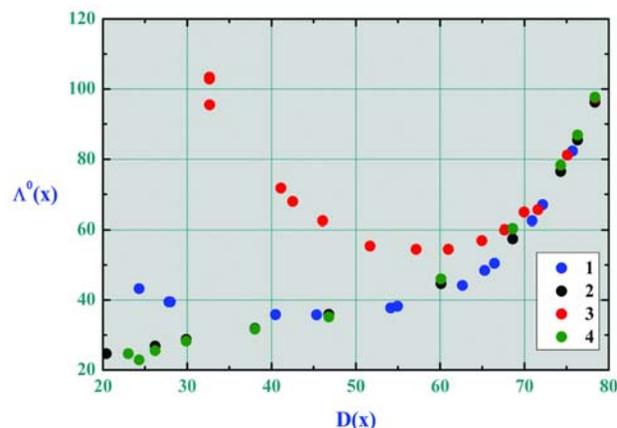

Figure 3. Limiting conductances of tetrabutylammonium bromide $\Lambda^0(x)$ at 298.15 K as a function of dielectric constant $D(x)$ in the aliphatic alcohol-water mixtures. 1 – ethanol; 2 – tert.- butanol ; 3 – methanol and 4 – 1-propanol.

tert.-BuOH[32] and 2-butoxyethanol[34] and potassium chloride with MeOH[35], EtOH[31,36] and tert.-BuOH[32] are plotted in addition to Bu$_4$NBr.

In order to obtain a quantitative indication about the results presented in Figure 4 (i.e. for the water-rich regions), the mean standard deviations were calculated to be
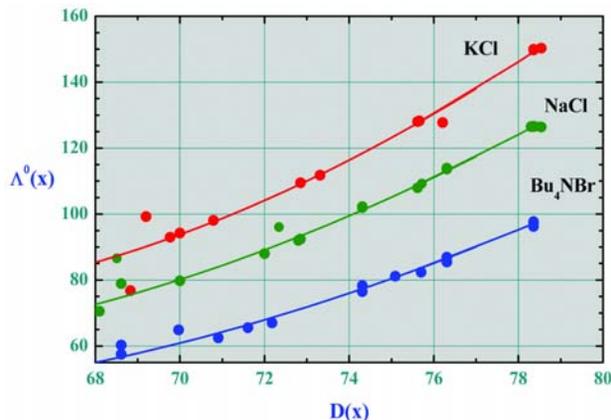

Figure 4. Limiting conductances of sodium chloride, potassium chloride and tetrabutylammonium bromide $\Lambda^0(x)$ at 298.15 K as a function of dielectric constant $D(x)$ in the aliphatic alcohol-water mixtures in the water-rich region. NaCl in the mixtures with ethanol, 1-propanol, tert.- butanol and 2-butoxyethanol. KCl in the mixtures with methanol, ethanol and tert.- butanol. Bu$_4$NBr in the mixtures with methanol, ethanol, 1-propanol and tert.- butanol.

$\sigma(\Lambda^0(NaCl)) = 1.24$ S·cm^2 mol^{-1}, $\sigma(\Lambda^0(KCl)) = 1.18$ S cm^2 mol^{-1} and $\sigma(\Lambda^0(Bu_4NBr)) = 0.81$ S·cm^{2}mol^{-1} (the units of limiting conductances and the Walden products are omitted in the text or in the figures). Considering that the accuracy of $\Lambda^0(x)$ values depends on how accurately the conductivities were determined and how the extrapolation process to infinite dilution was performed, the scattering of points in the alcohol-water mixtures seems to be reasonable. However, whether similar behaviour can be observed in other systems is uncertain and evidently should be examined in the future when more experimental data will be accumulated.

The application of eqs. (3)–(6) to a number of mixed-solvent mixtures with and without water was illustrated in a previous paper[20]. Some new results, mostly associated with binary mixtures having both organic components but also some aqueous mixtures, will be considered here.

4. Limiting Conductances of Electrolytes in Mixed Solvents

4. 1. Limiting Conductances of Electrolytes in Mixtures with Acetone

Contrary to other common organic solvents, (as compared for example with aliphatic alcohols or 1,4-dio-xane with water) studies of the electrical conductances of electrolytes in systems with acetone are rather limited in the literature. In aqueous solutions, measurements were mainly performed in narrow concentration ranges, and the number of investigated electrolytes is small. Non-aqueous mixtures that will be discussed here include ethanol, 2-propanol, 1,1,1,3,3,3,-hexafluoro-2-propanol (HFP), N,N-dimethylformamide (DMF) and 1,4-dioxane (DX).

Acetone is classified as an aprotic protophobic solvent[13] with low viscosity and dielectric constants $\eta = 0.303$ cP and $D = 20.56$ as compared with water $\eta = 0.9803$ cP and $D = 78.36$[13] (1 cP = mPa s). The limiting conductances of electrolytes in pure acetone are therefore higher than those in pure water and $\Lambda^0(x)$ has a minimum (Figure 5). The viscosity $\eta(x)$ has a maximum in the rich in the water region at $x \sim 0.12$ when the dielectric constant $D(x)$ monotonically decreases with the mole fraction of acetone x and $\Lambda^0(x) \cdot \eta^E(x) < 0$.
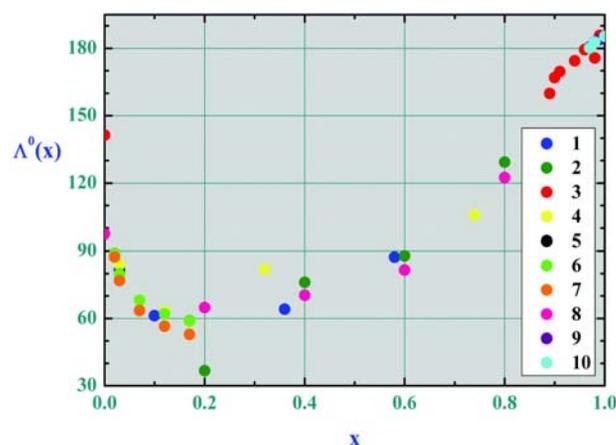

Figure 5. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K (calculated using eqs. 3 and 4) as a function of mole fraction of acetone x in the acetone-water mixtures. 1 – Bu$_4$NBr; 2 – AgCl; 3 – KI; 4 – KCl; 5 – K$_2$S$_2$O$_7$; 6 – (NH$_4$)$_2$S$_2$O$_7$; 7 – Na$_2$S$_2$O$_7$; 8 – AgNO$_3$; 9 – Et$_4$NClO$_4$; 10 – NH$_4$CNS.

Shifting the limiting conductances of electrolytes (eq. 3 for x < 0.2 and eq. 4 for x > 0.4) and using tetrabutylammonium bromide as the standard electrolyte the universal curve was calculated using the following electrolytes: NH$_4$CNS[38], (NH$_4$)$_2$S$_2$O$_7$[39], Na$_2$S$_2$O$_7$[39], KCl[40], KI[40], K$_2$S$_2$O$_7$[39], AgCl[41], AgNO$_3$[41], Et$_4$NClO$_4$[38] and Bu$_4$NBr[42] (Figure 5). If the ratio of the limiting conductances of Bu$_4$NBr (standard electrolyte) and an electrolyte XY in pure water is denoted by f(Bu$_4$NBr; water) = Λ^0(Bu$_4$NBr)/Λ^0(XY) and that in pure acetone by f(Bu$_4$NBr; acetone) = Λ^0(Bu$_4$NBr)/ Λ^0(XY), then the shift of the limiting conductances in Figure 5 covers a wide range of electrolytes, $0.32 \leq$ f(Bu$_4$NBr; water) ≤ 1.00 and $0.87 \leq$ f (Bu$_4$NBr; acetone) ≤ 2.00. The list includes not only 1:1 but also 1:2 type electrolytes, however $\Lambda^0(x)$ values were always calculated as for the 1:1 electrolytes[39]. Uncertainty associated with the universal curves and ex-

Table 1. Universal Curves of Limiting Conductances of Electrolytes in the Mixed – Solvent Mixtures at 298.15 K as Represented by Equation (7).

System	Λ^0	A	B	$\sigma(\Lambda^0)$
methanol – water, $x < 0.40$	149.74	0.7570	294.18	2.4
ethanol – water, $x < 0.35$	149.74	0.6592	413.88	2.6
1-propanol – water, $x < 0.30$	126.52	0.6145	365.98	2.0
tert-butanol – water, $x < 0.22$	149.74	0.5499	489.84	1.9
1,4-dioxane – water, $x < 0.35$	149.74	0.6798	415.00	1.9
acetone – water, $x < 0.25$	97.46	0.6421	191.52	2.2
acetone – water, $x > 0.45$	185.53	0.6297	514.07	3.0
DMF – water, $x < 0.25$	121.63	0.6952	346.04	2.4
DMF – water, $x > 0.50$	87.10	0.4365	210.04	1.7
TMS – water, $x < 0.50$	96.31	0.7755	286.21	2.4
EC – water, $x < 0.35$	149.74	0.8553	331.15	2.2
THF – water, $x < 0.40$	150.48	0.6149	407.31	2.4
methanol – AN, $x > 0.58$	109.67	0.6224	–225.31	1.6
ethanol – acetone, $x > 0.10$	58.04	0.2851	–527.38	1.5
1-propanol – acetone, $x > 0.05$	20.09	0.1835	–457.19	1.6
2-propanol – acetone, $x > 0.15$	20.63	0.2255	–472.66	1.2
FHP – acetone, $x > 0.20$	20.63	–0.0891	323.43	1.9
acetone – DMF, $x > 0.20$	132.50	0.4495	242.59	2.5
acetonitrile – PC, $x > 0.30$	170.17	0.6792	461.75	1.9
acetonitrile – DX, $x > 0.35$	172.99	0.2525	462.27	2.0
acetonitrile – CCl$_4$, $x > 0.35$	152.27	0.4417	349.01	1.5
acetonitrile – toluene, $x > 0.35$	164.20	0.3259	303.02	1.3

Units of Λ^0, B and $\sigma(\Lambda^0)$ are S·cm^2 mol^{-1}; A is dimensionless.
x is the mole fraction of the first named component of the mixture.

pressed by the mean standard deviations $\sigma(\Lambda^0(x))$ is lower for the water-rich mixtures than for the acetone-rich mixtures (Table 1), but the ratio $\sigma(\Lambda^0(x))/\Lambda^0(Bu_4NBr)$ is practically the same at about 0.017.

    Universal curves in the acetone-aliphatic alcohol mixtures cover practically the entire concentration range $x < 0.95$ (Figure 6). Acetone-ethanol and acetone-1-propanol mixtures behave in a similar way[20]. Here, the repeated universal curve of the acetone-ethanol mixtures is much better documented, in addition to CsClO$_4$[43] (standard electrolyte) and Et$_4$ClO$_4$[43], the mixtures with NaCl[44] and CsCl[44] are added. Two new alcohols are also considered: 2-propanol[45] and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)[45]. What characterizes the acetone-alcohol systems is that they are almost isodielectric mixtures (D(acetone) = 20.56, D(EtOH) = 24.35, D(2-PrOH) = 19.40 and D(HFP) = 16.75 at 298.15 K) but with extreme values, the minima at $x \sim 0.85$ in mixtures with EtOH, the minima at $x \sim 0.40$ in mixtures with 2-PrOH and the maxima at x ~ 0.50 in mixtures with HFP. The viscosity decreases monotonically with increasing mole fraction of acetone x in mixtures (i.e. always $\partial\Lambda^0(x)/\partial x > 0$; η(acetone) = 0.303 cP, η(EtOH) = 1.087 cP, η(2-PrOH) = 2.08 cP and η(HFP) = 1.62 cP) and the modified Walden products are in all cases higher than the corresponding ordinary Walden products. As can be observed in Figure 6, excellent universal curves exist for the acetone mixtures with EtOH (0.97 ≤ f(CsClO$_4$; EtOH) ≤ 1.38), with 2-PrOH and with HFP (LiCl[45], Bu$_4$NCl[45] (standard electrolyte), Bu$_4$NClO$_4$[45],

Bu$_4$NBr[45] and Bu$_4$NI[45]). The ratios of the limiting conductances of electrolytes are: 0.81 ≤ f(Bu$_4$NCl; 2-PrOH) ≤ 1.06 and 0.85 ≤ f(Bu$_4$NCl; HFP) ≤ 1.00.
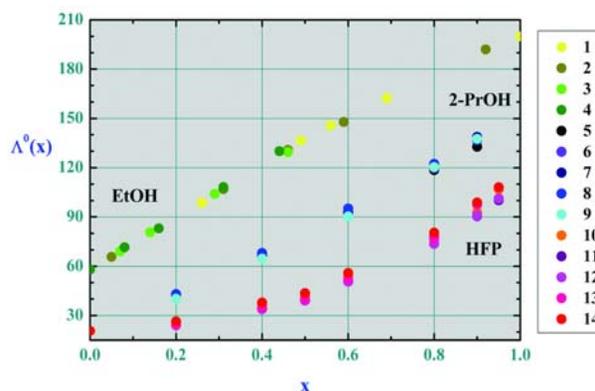
Figure 6. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K (calculated using eq. 3) as a function of mole fraction of acetone x in the acetone-alcohol mixtures. Ethanol: 1 – CsClO$_4$; 2 – Et$_4$NClO$_4$; 3 – CsCl; 4 – NaCl. 2-Propanol: 5 – Bu$_4$NCl; 6 – Bu$_4$NBr; 7 – Bu$_4$NI; 8 – Bu$_4$NClO$_4$; 9 – LiCl. 1,1,1,3,3,3-Hexafluoro-2-Propanol: 10 – Bu$_4$NCl; 11 – Bu$_4$NBr; 12 – Bu$_4$NI; 13 – Bu$_4$NClO$_4$; 14 – LiCl.

    N,N-dimethylformamide (protophilic H-bond donor solvent[13]) has higher viscosity and dielectric constant than acetone (η(DMF) = 0.794 cP[13], D(DMF) = 36.71[13]) and in their mixtures it is observed that $\partial\eta(x)/\partial x < 0$ and $\partial D(x)/\partial x < 0$. The ordinary and the modified Walden pro-

ducts predict that the DMF-rich region extends up to equimolar mixtures of $x^* \sim 0.50$ and contrary to aqueous solutions $\Lambda^0(x) \cdot \eta^E(x) < 0$. The universal curve of the limiting conductances (calculated from the DMF-rich region) of LiI[46], LiClO$_4$[46,47], NaI[46], KI[46], AgClO$_4$[46], Bu$_4$NI[46], Bu$_4$NClO$_4$[46], Bu$_4$NBBu$_4$[46] (tetrabutylammonium tetrabutylborate, standard electrolyte) is plotted in Figure 7 $(0.56 \leq f(Bu_4NBBu_4) \leq 1.00)$. It is evident that the limiting conductances of these electrolytes, if shifted to $\Lambda^0(Bu_4NBBu_4; x < x^*)$, form an unique curve.
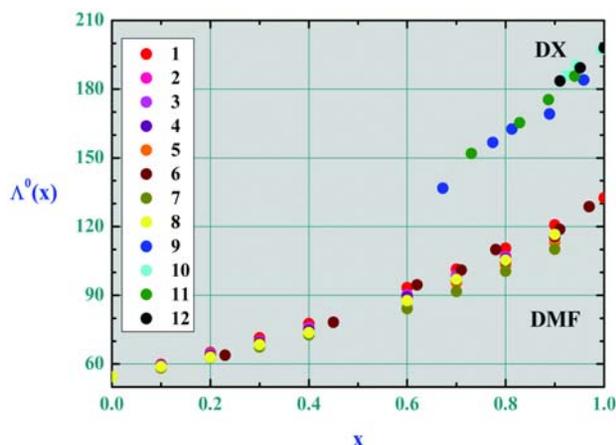

Figure 7. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K (calculated using eq. 3) as a function of mole fraction of acetone x in the acetone-1,4-dioxane and acetone-N,N-dimethylformamide mixtures. N,N-dimethylformamide: 1 – Bu$_4$NBBu$_4$; 2 – Bu$_4$NI; 3 – Bu$_4$NClO$_4$; 4 – KI; 5 – NaI; 6 – LiClO$_4$; 7 – AgClO$_4$; 8 – LiI. 1,4-dioxane: 9 – LiClO$_4$; 10 – LiBr ; 11 – NaClO$_4$; 12 – LiNO$_3$.

For the acetone-DMF system, Gill and Sharma[46] also derived the limiting conductances of ions (without performing transference number measurements) by assuming that $\Lambda^0(Bu_4NBBu_4; x)$ can be sub-divided into two ionic equal parts, i.e. $\lambda^0(Bu_4N^+) = \lambda^0(Bu_4B^-)$. Their values for the limiting conductances of cations $\lambda^0(Me^+; x < x^*)$ where Me$^+$ denotes Li$^+$, Na$^+$, K$^+$, Ag$^+$ and Bu$_4$N$^+$ (standard cation) and for the limiting conductances of anions $\lambda^0(X^-; x < x^*)$ where X$^-$ denotes I$^-$ and ClO$_4^-$ (standard anion) were shifted by using equation 5 and are plotted in Figure 8. As can be observed, the results presented in Figure 7 and 8 are consistent.

The last example of mixtures with acetone is 1,4-dioxane which is classified as a low permittivity electron donor solvent[13] (for aqueous solutions of 1.4-dioxane see[20]). Since its dielectric constant is very low $D(DX) = 2.21$[13], the electrical conductances were investigated only in the acetone-rich region (Figure 7). Similarly to other systems with acetone, we have $\Lambda^0(x) \cdot \eta^E(x) < 0$ ($\eta(DX) = 1.20$ cP[13]). The universal curve of the limiting conductances as constructed from LiBr[48], LiClO$_4$[49](standard electrolyte), LiNO$_3$[50] and NaClO$_4$[51] electrolytes is plotted in Figure 7 $(0.90 \leq f(LiClO_4; acetone) \leq 1.00)$. Once again, equation 3 is very nicely satisfied.
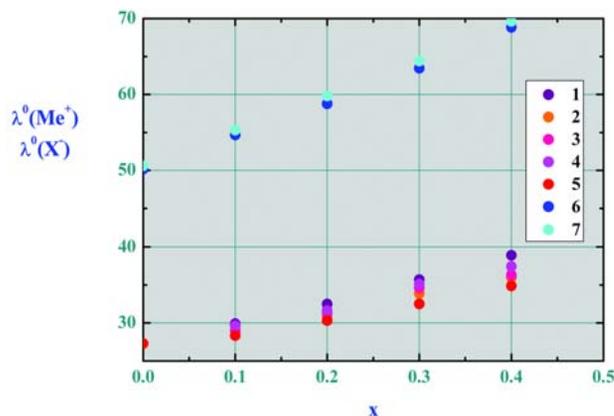

Figure 8. Limiting conductances of cations $\lambda^0(Me^+,x)$ and anions $\lambda^0(X^-,x)$ at 298.15 K (calculated using eq. 5) as a function of mole fraction of acetone x in the acetone-N,N-dimethylformamide mixtures. 1 – Bu$_4$N$^+$; 2 – Li$^+$; 3 – Na$^+$; 4 – K$^+$; 5 – Ag$^+$; 6 – I$^-$; 7 – ClO$_4^-$.

4. 2. Limiting Conductances of Electrolytes in Mixtures with Acetonitrile

The conductivity of many electrolytes in a number of nonaqueous mixtures with acetonitrile (AN) is reported in the literature. Mixtures of acetonitrile (aprotic protophobic solvent; $D(AN) = 35.95$; $\eta(AN) = 0.341$ cP[13]) with methanol, 1,4-dioxane, carbon tetrachloride and toluene are considered here (for those with propylene carbonate see[20] and partly below).

The acetonitrile-methanol (amphiprotic hydroxylic solvent[13]) mixtures are characterized by the strong solvent-solvent interactions considering that methanol is extensively self-associated through H-bonding liquid (for controversial opinions about the structure of acetonitrile see[52]). The dielectric constants of both pure components
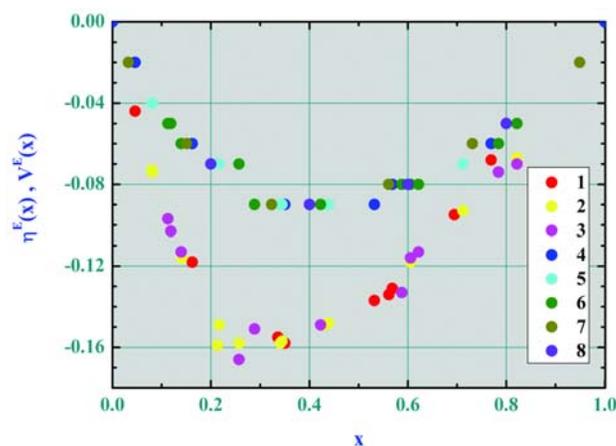

Figure 9. Excess viscosities $\eta^E(x)$ in cP (upper curve) and excess molar volumes $V^E(x)$ in cm^3·mol^{-1} at 298.15 K as a function of mole fraction of acetonitrile x in the acetonitrile – methanol mixtures. Excess molar volumes: 1 – ref. 53; 2 – ref. 54; 3 – ref. 55. Excess viscosities: 4 – ref. 53; 5 – ref. 54; 6 – ref. 55; 7 – ref. 56; 8 – ref. 24;
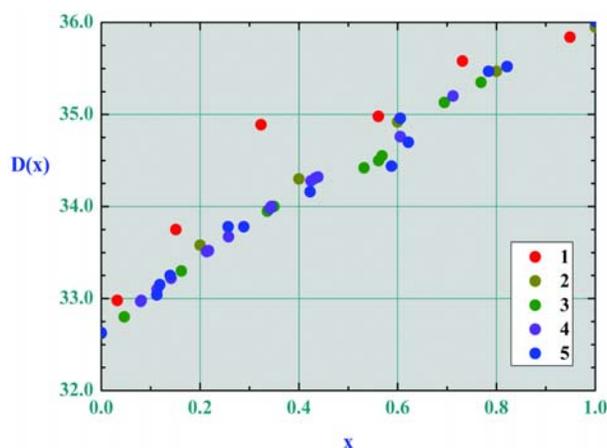
Figure 10. Dielectric constants $D(x)$ at 298.15 K as a function of mole fraction of acetonitrile x in the acetonitrile- methanol mixtures. 1 – ref. 56; 2 – ref. 24; 3 – ref. 53; 4 – ref. 54; 5 – ref. 55.

are close (D(MeOH) = 32.63; η(MeOH) = 0.543 cP[13]). Simultaneously determined with electrical conductivities, viscosities[53–55] and densities[23,24,53–56] allow for the calculation of the excess molar volumes $V^E(x)$ and the excess viscosity $\eta^E(x)$. As can be observed in Figure 9, $V^E(x) < 0$ and $\eta^E(x) < 0$, and the excess properties are asymmetrical functions of x with minima close to the methanol region (the negative values of $\eta^E(x)$ lead also to $\Lambda^0(x) \cdot \eta^E(x) < 0$). The agreement between the dielectric constants in the acetonitrile-methanol mixtures as reported in various investigations is less satisfactory than that for the viscosities (Figure 10, see reported by Gill and Chauhan[56] values).

The conductivities of quaternary ammonium perchlorates and halides were investigated in the acetonitrile–methanol mixtures, Me_4NClO_4, Et_4NClO_4, Bu_4NClO_4, He_4NClO_4 by D'Aprano et al[54]; $KClO_4$ by D'Aprano and Donato[29] and by Conti and Pistoia[53]; $LiClO_4$, $NaClO_4$, KI, $AgNO_3$, $NaBPh_4$, Bu_4NCl, Bu_4NBr, Bu_4NI, Bu_4NClO_4, Bu_4NNO_3, Bu_4NBPh_4 by Gill and Chauchan[56]; Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr, Hex_4NBr, Hep_4NBr, Bu_4NBPh_4 by Das, and Saha[23] and by Das et al[24] whereas Coplan and Fuoss[55] considered triisoamyl-n-butylammonium iodide, picrate and tetraphenyborate (i-Am_3BuNI, i-Am_3BuNPic, i-Am_3BuNBPh$_4$). The acetonitrile-methanol mixtures were already considered by the author[20] but only using the Das group results with Bu_4NBr as the standard electrolyte. In this work, by taking Bu_4NClO_4 as the standard electrolyte, the shifting of the limiting conductances of electrolytes (according to equations 3 and 4, $x^* \sim 0.42$) is performed with a considerably larger number of electrolytes. However, $LiClO_4$, Bu_4NCl and $NaBPh_4$[56] were excluded from further analysis, because their $\Lambda^0(x)$ values are probably inaccurate. The obtained universal curve is plotted in Figure 11 ($0.79 \leq f$ (Bu_4ClO_4; MeOH) ≤ 1.50 and $0.84 \leq f(Bu_4ClO_4$; AN) ≤ 1.38). As can be observed, an excellent universal curve exists in the methanol-rich concentration region. However, the scattering of $\Lambda^0(x)$ values in the acetonitrile-rich region is less satisfactory, especially con-
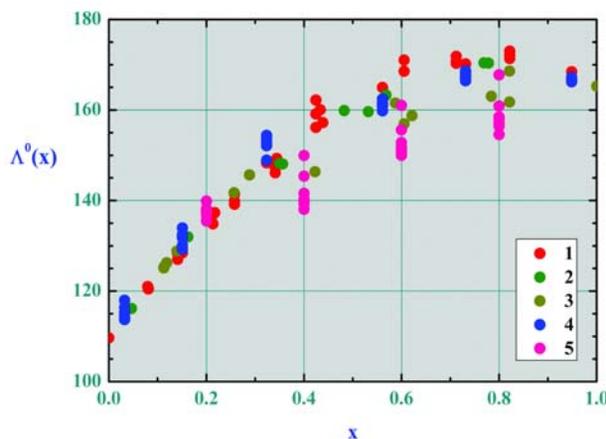

Figure 11. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K (calculated using eqs. 3 and 4) as a function of mole fraction of acetonitrile x in the acetonitrile-methanol mixtures.
1 – Me_4NClO_4, Et_4NClO_4, Bu_4NClO_4, He_4NClO_4 ref. 54; 2 – $KClO_4$ refs. 29 and 53; 3 – i-Am_3BuNI, i-Am_3BuNPic, i-Am_3BuNBPh$_4$ ref. 55; 4 – $NaClO_4$, KI, $AgNO_3$, Bu_4NBr, Bu_4NI, Bu_4NClO_4, Bu_4NNO_3, Bu_4NBPh_4 ref. 56; 5 – Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr, Hex_4NBr, Hep_4NBr, Bu_4NBPh_4 refs. 23 and 24.

sidering the results of the Das group[23,24] which are systematically lower than those obtained by others. Nevertheless, there is no doubt that the shifting procedure produces a unique curve over the entire concentration range of acetonitrile-methanol mixtures.

Electrical conductivities of electrolytes of acetonitrile mixtures with 1,4-dioxane and with carbon tetrachloride (low polarity solvent of high polarizability, D(CCl_4) = 2.23 and η(CCl_4) = 0.905 cP[13]) were only considered in the acetonitrile-rich region where the limiting conductances of $LiClO_4$[49], $NaClO_4$[51], Et_4NClO_4[57], Bu_4NClO_4[58] and
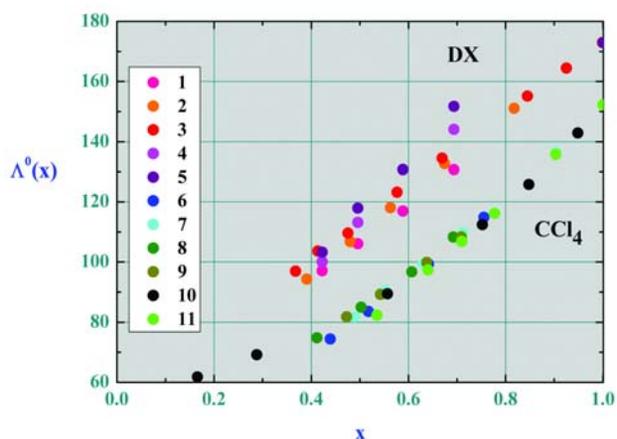

Figure 12. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K (calculated using eq. 4) as a function of mole fraction of acetonitrile x in the acetonitrile-1,4-dioxane and acetonitrile-carbon tetrachloride mixtures.
1.4-dioxane: 1 – $NaClO_4$; 2 – $LiClO_4$; 3 – Bu_4NClO_4; 4 – Bu_4NI; 5 – Et_4NI. carbon tetrachloride: 6 – Me_4NBPh_4; 7 – Et_4NBPh_4; 8 – Pr_4NBPh_4; 9 – Bu_4NBPh_4, ref. 59; 10 – Bu_4NBPh_4, ref. 55; 11 – Bu_4NClO_4.

Bu_4NI[57] were determined in mixtures with 1,4-dioxane and Bu_4NClO_4[58], Me_4NBPh_4[59], Et_4NBPh_4[59], Pr_4NBPh_4[59] and Bu_4NBPh_4[59,60] in mixtures with carbon tetrachloride (in both mixtures $\Lambda^0(x)\cdot\eta^E(x) < 0$; see also[20]). Using $LiClO_4$ and Me_4NBPh_4 as the standard electrolytes, the universal curves were evaluated and are presented in Figure 12 (0.96 ≤ f($LiClO_4$; DX) ≤ 1.06 and 0.92 ≤ f(Me_4NBPh_4; CCl_4) ≤ 1.27). As can be seen, the change of $\Lambda^0(x)$ with mole fraction of acetonitrile x is almost linear, which expresses a simple dilution effect, i.e. the universal curve covers nearly the entire concentration region and that solvent which has the larger dielectric constant is of importance.

The same behaviour of limiting conductances is observed in the acetonitrile-toluene mixtures. Toluene, like carbon tetrachloride, is classified as a low polarity solvent of high polarizability with D(toluene) = 2.38 and η(toluene) = 0.552 cP[13]. Electrolytes in the acetonitrile-toluene mixtures were investigated at three temperatures, 288.15 K, 298.15 K and 308.15 K by Papadopoulos[61] ($NaBPh_4$), Papadopoulos and Ritzoulis[62] (Bu_4NI), Papadopoulos et al[63] (Pr_4NBr) and by Papadopoulos[64] (Pr_4NI, only at 298.15 K). The universal curves of limiting conductances were evaluated for these temperatures choosing Bu_4NI as the standard electrolyte and they are plotted in Figure 13 (0.95 ≤ f(Bu_4NI; T = 298.15 K) ≤ 1.21). Once again, a superb confirmation of the existence of universal curves is observed, this time from conductivities at different temperatures.
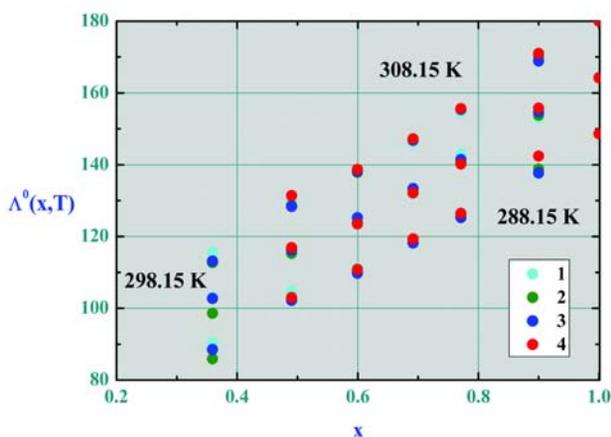
308.15 K) is considered here. Sulfolane is an aprotic protophilic solvent[13] of intermediate dielectric constant and of high viscosity where water belongs to the group of amphiprotic hydroxylic solvents[13] having a high dielectric constant and relatively low viscosity (D(TMS, 298.15 K) = 43.3[13], D(TMS, 308.15 K) = 42.7[65], η(TMS, 298.15 K) = 10.29 cP[13] and η(TMS, 298.15 K) = 9.03 cP[65] where the corresponding values for water are: D(H_2O, 298.15 K) = 78.36[13], D(H_2O, 308.15 K) = 74.64[65], η(H_2O, 298.15 K) = 0.890 cP[13] and η(H_2O, 298.15 K) = 0.791 cP[65]). The excess molar volumes in the sulfolane-water mixtures are negative[65–67] and since $\eta^E(x) < 0$, the modified Walden products are larger than the ordinary Walden products (x^* ~ 0.40 which is also close to the minimum of V^E). From the water-rich region, the universal curves of limiting conductances for the sulfolane-water mixtures were prepared using $LiCl$[65], $NaCl$[68], KCl[72], $NaClO_4$[73] at 308.15 K and $NaCl$[68], KBr[69], KI[69], $KClO_3$[66], $KClO_4$[70], Bu_4NBPh_4[69], Et_4NBr[69], $Bu4NI$[69] at 298.15 K (at this temperature there's also conductivity data for $NaBr$, KI and KNO_3 in very diluted TMS solutions[71]) and they are plotted in Figure 14. KCl (1.00 ≤ f(KCl; T = 308.15 K) ≤ 1.29) and $NaCl$ (0.83 ≤ f($NaCl$; T = 298.15 K) ≤ 3.24) were chosen as the standard electrolytes. What is rather surprising in this system is that the shifting of $\Lambda^0(x)$ by equation 3 is valid for x < 0.9, i.e. considerably far from the x^* value which is expected from the division into concentration regions based on the Walden products. It seems that only water governs the conductivity of electrolytes where sulfolane plays only a

Figure 13. Limiting conductances of electrolytes $\Lambda^0(x)$ at 288.15 K, 298.15 K and 308.15 K (calculated using eq. 4) as a function of mole fraction of acetonitrile x in the acetonitrile-toluene mixtures.
1 – $NaBPh_4$; 2 – Bu_4NI; 3 – Pr_4NI; 4 – Pr_4NBr.

Figure 14. Limiting conductances of electrolytes $\Lambda^0(x)$ at 298.15 K and at 308.15 K (calculated using eq. 3) as a function of mole fraction x of sulfolane in the sulfolane-water mixtures.
298.15 K: 1 – $KClO_3$; 2 – $KClO_4$; 3 – $NaCl$; 4 – KI; 5 – KBr; 6 – Bu_4NBPh_4; 7 – $Bu4NI$; 8 – Et_4NBr. 308.15 K: 9 – $NaClO_4$; 10 – KCl; 11 – $LiCl$; 12 – $NaCl$.

4. 3. Limiting Conductances of Electrolytes in Mixtures with Sulfolane

The universal curve of the limiting conductances in the water-sulfolane (tetramethylene sulfone denoted as TMS) mixtures at 303.15 K was already discussed[20]. Conductivity data at two more temperatures (298.15 K and

role of inert diluent. Similarly as reported previously[20] at 303.15 K, at 298.15 K and 308.15 K, the universal curves $\Lambda^0(x)$ are satisfied by a quite different groups of electrolytes, alkali halides, alkali perchlorates and quaternary ammonium salts.

Our knowledge of the conductivities of electrolytes in mixtures of sulfolane with other solvents is very limited (LiCl in mixtures of methanol at 308.15 K[25,74] and KClO$_4$ in mixtures of methanol or acetonitrile at 298.15 K[29]). Nevertheless, it is possible to construct the universal curve of electrolytes for the sulfolane-methanol mixtures because viscosities $\eta(x)$ at these temperatures are known. Using the ordinary Walden product, the values of $\Lambda^0(x, 308.15$ K) of potassium perchlorate were estimated and shifted together with lithium chloride (Figure 15, f(KClO$_4$; T = 308.15 K) = 1.33; $\Lambda^0(x) \cdot \eta^E(x) < 0$). As can be observed, over practically the entire concentration range, a sound universal curve is obtained which can be used to estimate the limiting conductances of other electrolytes in the sulfolane-methanol mixtures.
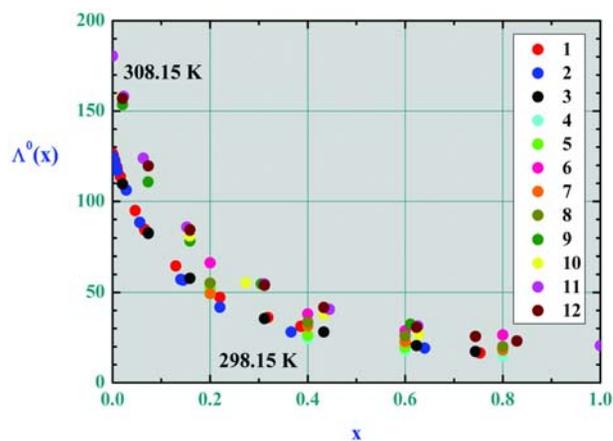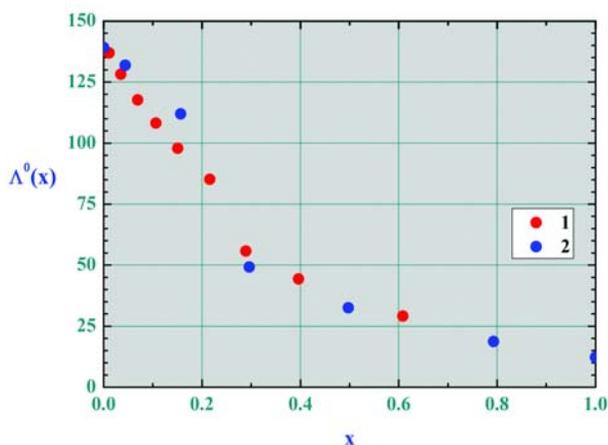

Figure 15. Limiting conductances of electrolytes $\Lambda^0(x)$ at 308.15 K (calculated using eq. 3, see also text) as a function of mole fraction of sulfolane x in the sulfolane-methanol mixtures.
1 – KClO$_4$; 2 – LiCl.

D'Aprano et al[75] investigated electrical conductivities of tetrabutylammonium salts (Bu$_4$NBr, Bu$_4$NClO$_4$, Bu$_4$NNO$_3$, Bu$_4$NBBu$_4$) and picrates (LiPic, NaPic, KPic, RbPic, CsPic, Bu$_4$BPic) in the γ-butyrolactane rich mixtures with sulfolane. γ-Butyrolactane (4-hydroxybutyric acid lactone) is an aprotic protophobic solvent with D(γ-BL) = 39.1 and η(γ-BL, 298.15 K) = 1.732 cP[13], i.e. considerably less viscous liquid than sulfolane but nearly of the same dielectric constant. Their limiting conductances are shifted with potassium picrate (0.84 ≤ f(KPic) ≤ 1.35) chosen as the standard electrolyte . The modified Walden product undoubtedly predicts a division of concentration regions at $x^* \sim 0.45$ where the ordinary Walden product has a nearly constant value ($\Lambda^0(x) \cdot \eta^E(x) < 0$). This is in agreement with the universal curve presented in Figure 16 indicating once more the superiority of the modified Walden product.

Since D'Aprano et al[75] also estimated the limiting conductances of ions (without performing transference
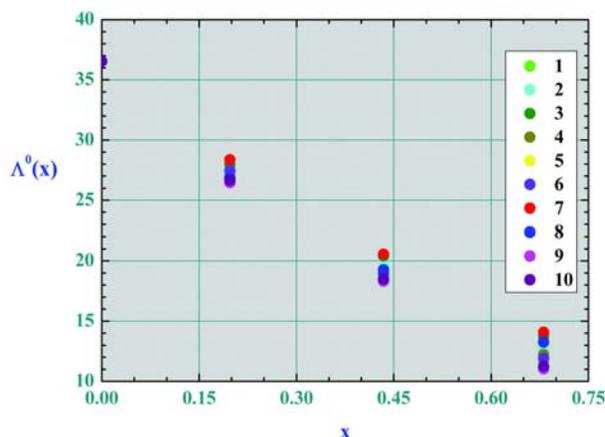

Figure 16. Limiting conductances of electrolytes $\Lambda^0(x)$ at 308.15 K (calculated using eq. 4) as a function of mole fraction of sulfolane x in the sulfolane-methanol mixtures.
1 – Bu$_4$NBBu$_4$; 2 – Bu$_4$NClO$_4$; 3 – Bu$_4$NNO$_3$; 4 – NaPic; 5 – RbPic; 6 – Bu$_4$NPic; 7 – Bu4NBr; 8 – LiPic; 9 – KPic; 10 – CsPic.

number measurements), their values of Li$^+$(standard cation); Na$^+$; K$^+$; Rb$^+$; Cs$^+$; Bu$_4$N$^+$; Br$^-$(standard anion); ClO$_4^-$; Pic$^-$ and Bu$_4$B$^-$ were recalculated by using equation 6 and they are plotted in Figure 17. As can be observed, the universal curves of limiting conductances of electrolytes and of ions in the sulfolane-γ-butyrolactane mixtures (Figures 16 and 17) are consistent.
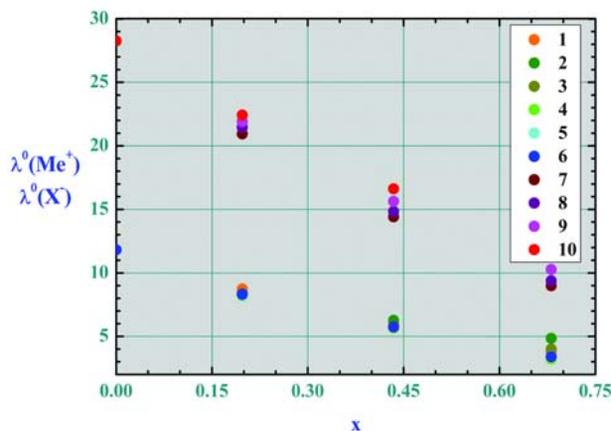
Figure 17. Limiting conductances of cations λ^0(Me$^+$,x) and anions λ^0(X$^-$,x) at 298.15 K (calculated using eq. 6) as a function of mole fraction of sulfolane x in the sulfolane-γ-butyrolactone mixtures.
1 – Bu$_4$N$^+$; 2 – Li$^+$; 3 – Na$^+$; 4 – K$^+$; 5 – Rb$^+$; 6 – Cs$^+$; 7 – Bu$_4$B$^-$; 8 – Pic$^-$; 9 – ClO$_4^-$; 10 – Br$^-$.

4. 4. Limiting Conductances of Electrolytes in Mixtures with Propylene Carbonate

Propylene carbonate (PC) is usually investigated in the context of high-energy lithium batteries being a component of conducting media having at 298.15 K a relatively high dielectric constant D(PC) = 64.95 and viscosity

η(PC) = 2.51 cP[13]. The existence of an excellent universal curve of limiting conductances for LiBr, LiClO4, LiAsF$_6$ (lithium hexafluoroarsenate), Bu$_4$NClO$_4$ and Bu$_4$NBPh$_4$ [76–80] (from PC side) in the acetonitrile-propylene carbonate mixtures was already reported elewhere[20] Since conductivity measurements are mainly limited to lithium salts, the role of propylene carbonate (4-methyl-1,3-dioxolane-2-one; aprotic protophobic solvent[13]) for the same electrolyte but with different solvents is illustrated here (for a similar example of water with various alcohols see earlier). Two cases will be considered LiClO$_4$ and LiBr.

In the case of lithium perchlorate, conductances were determined by Barthel et al[77] in the acetonitrile (AN) – PC mixtures, by Salomon and Plichta[81,82] in the dimethoxymethane (DMM) – PC mixtures and in the dimethoxyethane (DME) – PC mixtures. Moumouzias and Ritzoulis[83] reported limiting conductances in the toluene – PC mixtures and Wawrzyniak and Jasiñski[84] in the methanol – PC mixtures. Thus, using the classification given in the Barthel et al book[13], PC (aprotic protophobic solvent) is mixed with a solvent of similar character (AN), with a low permittivity electron donor solvents (DMM and DME), with a low polarity solvent of high polarizability (toluene) and finally with a amphiprotic hydroxylic solvent (MeOH). Evidently, these solvents differ considerably when their relevant physical properties are compared: D(PC) = 64.95[13]; D(AN) = 35.95[13]; D(DMM) = 2.71[81]; D(DME) = 7.08[13,82,85]; D(toluene) = 2.38[13]; D(MeOH) = 32.63[13] and η(PC) = 2.51 cP[13]; η(AN) = 0.341 cP[13]; η(DMM) = 0.329 cP[81]; η(DME) = 0.41 cP[13,82,85]; η(toluene) = 0.552 cP[13,82]; η(MeOH) = 0.543 cP[13,82]. With the exception of the Wawrzyniak and Jasiñski result for the limiting conductance of lithium perchlorate in pure propylene carbonate Λ^0(LiClO$_4$) = 28.11[84], other reported values are in a good agreement Λ^0(LiClO$_4$) = 26.77[77]; Λ^0(LiClO$_4$) = 26.75[81]; Λ^0(LiClO$_4$) = 26.34[83] and therefore their values of Λ^0(LiClO$_4$;x) in the propylene carbonate-methanol mixtures were multiplied by a constant factor of 0.95 before putting them together with other solvents in Figure 18. As can be observed, if we limit ourselves to the PC-rich mixtures ($x > 0.50$) and if it is assumed that in this concentration region the effect of a co-solvent is secondary then only Λ^0(LiClO$_4$;x) in the propylene carbonate-toluene mixtures are systematically lower than those in other mixtures. At this point, the reason for such behaviour is not clear (there is also an inconsistency between the conductivities of LiClO$_4$[83], Bu$_4$NBPh$_4$[83] and Bu$_4$NClO$_4$[79] if the universal curve is prepared for the propylene-toluene mixtures).

In the next example lithium bromide is considered in the PC – AN[76], PC – MeOH[84] and PC – DME[85] mixtures (Λ^0(LiBr) = 27.15[76]; Λ^0(LiBr) = 27.80[84]; Λ^0(LiBr) = 27.15[85]). The limiting conductances Λ^0(LiBr;x) are plotted in Figure 19 together with two more salts which have similar limiting conductances in pure propylene carbonate (LiAsF$_6$ in the PC – AN mixtures, Λ^0(LiAsF$_6$) = 24.93[78] and Bu$_4$NClO$_4$ in the PC – toluene mixtures,

Figure 18. Limiting conductances of lithium perchlorate Λ^0(x) at 298.15 K as a function of mole fraction of propylene carbonate *x* in the propylene carbonate-solvent mixtures.
1 – acetonitrile; 2 – dimethoxyethane; 3 – dimethoxymethane; 4 – toluene; 5 – methanol;

Λ^0(Bu$_4$NClO$_4$) = 28.06[79]). Once again for $x > 0.50$, the existence of a common curve Λ^0(LiBr;x) is observed which indicates that in the propylene carbonate rich mixtures, the limiting conductivities very weakly depend on the type of the second component in the mixture and even on the type of the dissolved electrolyte.
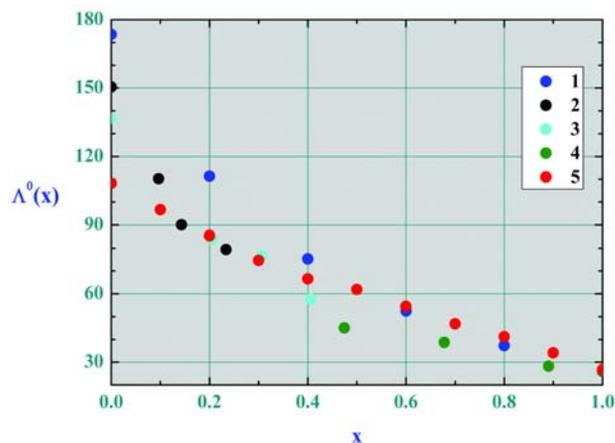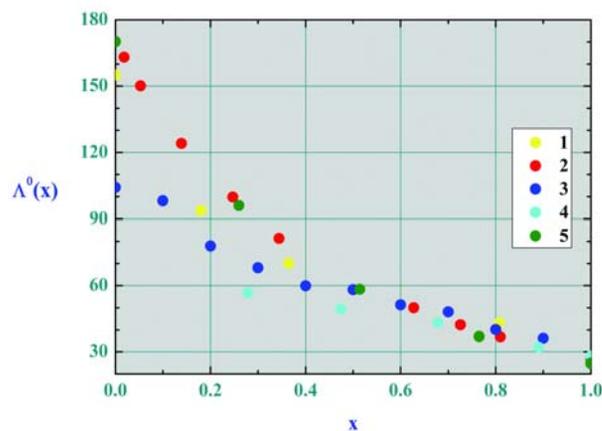

Figure 19. Limiting conductances of lithium bromide Λ^0(x) at 298.15 K as a function of mole fraction of propylene carbonate *x* in the propylene-solvent mixtures.
3 – methanol; 1 – dimethoxyethane; 2 – acetonitrile; 3 – methanol; 4 – toluene (Bu$_4$NClO$_4$, see text); 5 – acetonitrile (LiAsF$_6$, see text).

5. Formal Representation of Limiting Conductances of Electrolytes in Mixed Solvents

The limiting conductances of electrolytes in mixed-solvent systems Λ^0(x,T) as a function of composition (or the Walden products Λ^0(x,T)·η(x,T) = f(x)) are usually reported only in tabular form. It seems worthwhile to present them

also by using formal mathematical expressions which will be convenient in further calculations and allow, if necessary, to obtain the intermediate values of $\Lambda^0(x,T)$. Since at present-day there is no theoretical guiding about the form of such expressions, any empirical equation which is able to represent accurately the data can be chosen. However, the preferable equation should be simple and with a small number of adjustable parameters which are easy to evaluate. The simplest case is evidently the polynomials of various orders of x but they have two disadvantages. Usually to obtain a desired accuracy, a large number of terms is required and because $0 < x < 1$, the absolute value coefficients increase considerably when passing from one to the next coefficient. If a two-parameter fitting of the universal curve in mixed solvents is desired at a given temperature T (limiting conductances of the standard electrolyte XY in the corresponding concentration regions, e.g. for $0 \leq x < x^*$) then the following equation is proposed

$$\Lambda_{XY}^0(x,T) = \Lambda_{XY}^0(0,T) - Bx^A(1 - x^A)$$
$$0 \leq x < x^* \tag{7}$$

This equation was found to be very suitable to represent with a reasonable accuracy the universal curves of electrolytes. Selected A, B and x values are reported where $x = x^*$ is the mole fraction of the first named component of the mixture in Table 1. In calculations, conductivity data was taken from the previous paper[20] and from the systems considered here. The mean standard deviations $\sigma(\Lambda^0(x,T))$ which characterize the scattering of the limiting conductances in the investigated mixtures are also reported in Table 1. The values of $\sigma(\Lambda^0(x,T))$ represent the combined effect of the accuracy of derived limiting conductances for different electrolytes, of the suitability of the applied equation 7 and, most importantly, of the correctness of the assumption that the universal curves exist.

On the other hand, when the limiting conductances of a *particular electrolyte* $\Lambda^0(x,T)$ over entire concentration range $0 \leq x \leq 1$ are required (or for a limited range of compositions, $x > 0$, for example when measurements are limited by a low value of dielectric constant, see 1,4-dioxane – water mixtures), the knowledge of the viscosities $\eta(x,T)$ and the dielectric constants $D(x,T)$ allows for only measurable physical quantities to be involved in the representation of $\Lambda^0(x,T)$. From the functional dependence $f(\Lambda^0, \eta, D; x) = 0$, the composition x can be excluded and therefore given only indirectly. Following a frequently applied engineering practice (see for example[37]), these physical quantities are raised to various powers and expressed as the modified product of them

$$\Lambda^0(x,T) = C \frac{D(x,T)^\beta}{\eta(x,T)^\alpha} \tag{8}$$

i.e. the fit of $\Lambda^0(x,T)$ is a three-adjustable parameter (α, β and C) equation which for the ordinary Walden product

takes the form

$$\Lambda^0(x,T)\eta(x,T) = CD(x,T)^\beta \eta(x,T)^{1-\alpha} \tag{9}$$

It was found that eq. (8) represents reasonably well experimental results and the evaluation of parameters is easy because the logarithmic form of it is linear (the multivariate least-square method was applied to obtain these parameters whereas larger weight factors were introduced in the case of pure solvents). Values of α, β, C and $\sigma(\Lambda^0(x,T))$ for a number of electrolytes in mixed-solvent systems with and without water are reported in Table 2. In order to limit the number of them, only these mixtures which were repeatedly investigated in the literature are considered. Once again it should be stressed that $\sigma(\Lambda^0(x,T))$ depends on the accuracy of the determined $\Lambda^0(x,T)$, $\eta(x,T)$ and $D(x,T)$ values and the capability of equation 8 to represent conductivity data of electrolytes in different solvent-mixed systems (the ratio $\sigma(\Lambda^0(x))/\Lambda^0$ for all reported in Table 2 mixtures is less than 0.02).

Formally, it follows that in a given mixed-solvent system, equation (8) leads to the universal curve for electrolytes (eqs. (3) and (4)). However this will happen only

Table 2. Limiting Conductances of Electrolytes in the Mixed – Solvent Mixtures at 298.15 K as Represented by Equation (8).

Electrolyte	α	β	C	$\sigma(\Lambda^0)$
methanol – water				
LiCl	0.8161	0.7270	4.414	0.8
LiBr	0.7942	0.7874	3.435	1.3
NaBr	0.7547	0.7077	5.429	1.2
NaI	0.7703	0.6206	7.775	0.5
$NaNO_3$	0.7431	0.5835	8.781	0.2
KNO_3	0.7408	0.7037	6.186	0.3
CsCl	0.8042	0.7876	4.465	0.4
Et_4NPic	0.7872	–0.1838	128.02	0.3
$NaBPh_4$	0.6585	0.1682	31.209	0.6
Et_4NCl	0.8389	0.4534	13.715	1.2
Et_4NBr	0.8414	0.4166	16.298	0.7
Et_4NI	0.8366	0.3402	22.462	0.6
Et_4NClO_4	0.8148	0.1457	48.011	0.5
ethanol – water				
LiCl	0.6026	0.8061	3.182	1.0
LiBr	0.7258	0.7668	3.782	0.6
$LiNO_3$	0.6673	0.8150	5.202	0.8
NaCl	0.7093	0.8281	3.351	1.0
$NaNO_3$	0.6700	0.8818	5.004	0.9
KCl	0.6974	0.6910	3.759	1.4
KBr	0.6887	0.8751	3.005	0.8
$KClO_4$	0.7163	0.6815	6.397	1.1
KNO_3	0.6651	0.7146	3.923	1.2
CsCl	0.6636	0.8109	3.114	0.5
Me_4NBr	0.7488	0.5796	8.970	0.2
Et_4NBr	0.7662	0.4946	11.668	0.3
Pr_4NBr	0.7639	0.5241	9.410	0.4
Bu_4NBr	0.7535	0.5535	7.945	0.6

1-propanol – water			
NaCl	0.4700	0.9861	1.618	1.2
NaBr	0.5233	0.9750	1.716	1.5
NaI	0.5566	0.8808	2.535	1.8
$NaClO_4$	0.5394	0.7467	4.220	1.6
$NaBPh_4$	0.7024	0.4968	7.371	0.7
Bu_4NI	0.6047	0.6495	5.236	1.3

tert.-butanol – water			
LiBr, $x < 0.15$	0.7635	0.2819	31.313	0.7
$LiClO_4$, $x < 0.89$	0.6222	0.5814	7.739	1.4
NaBr, $x < 0.20$	0.6514	0.5442	11.085	0.6
$NaClO_4$, $x < 0.59$	0.6773	0.5262	10.995	0.8
KCl, $x < 0.20$	0.6170	0.6648	7.687	1.0
KBr, $x < 0.50$	0.5365	0.9166	2.602	1.5
$KClO_4$, $x < 0.50$	0.6627	0.6140	8.942	0.6
Me_4NBr, $x < 0.20$	0.7040	0.4529	15.693	0.8
Me_4NI, $x < 0.20$	0.7314	0.3688	22.321	0.6
Bu_4NBr, $x < 0.70$	0.6542	0.5862	6.969	1.0

1,4-dioxane – water			
HCl, $x < 0.48$	0.2823	0.9582	6.313	1.5
LiF, $x < 0.17$	0.6614	0.3799	16.627	0.1
LiCl, $x < 0.43$	0.6741	0.3864	19.707	0.2
$LiClO_3$, $x < 0.54$	0.5887	0.3504	20.725	0.8
$LiClO_4$, $x < 0.45$	0.8802	0.2038	39.333	0.4
NaF, $x < 0.26$	0.5929	0.4463	14.066	0.1
NaCl, $x < 0.50$	0.5613	0.4804	14.547	0.9
NaBr, x < 0.43	0.6627	0.4003	20.751	0.5
$NaClO_4$, $x < 0.48$	0.8118	0.2710	32.608	1.1
$NaBrO_3$, $x < 0.20$	0.6480	0.3109	25.285	0.2
$NaNO_3$, $x < 0.44$	0.5646	0.4163	18.481	1.2
KCl, $x < 0.44$	0.6368	0.5007	15.651	0.5
KBr, $x < 0.15$	0.6549	0.5078	15.332	0.3
$KClO_3$, $x < 0.43$	0.6199	0.4323	19.476	1.5
$KClO_4$, $x < 0.48$	0.8177	0.3420	28.712	0.9
KNO_3, $x < 0.40$	0.7220	0.3719	26.303	0.5
RbCl, $x < 0.46$	0.6502	0.4993	16.121	0.4
RbBr, $x < 0.44$	0.6398	0.5009	16.191	0.9
RbI, $x < 0.41$	0.7681	0.4049	24.067	0.4
$RbClO_4$, $x < 0.38$	0.8899	0.2956	35.808	0.2
CsCl, $x < 0.54$	0.5903	0.5358	13.775	0.9
CsBr, $x < 0.52$	0.6636	0.4739	18.131	1.0
CsI, $x < 0.43$	0.7510	0.4216	22.396	0.9
Bu_4NBr, $x < 0.09$	0.9050	0.0960	57.745	0.3
Bu_4NI, $x < 0.18$	1.0358	0.0680	63.458	0.2
Et_4NClO_4, $x < 0.43$	0.9139	0.1485	46.574	0.9
Bu_4NClO_4, $x < 0.43$	1.0496	0.0565	59.952	0.6
Me_4NPic, $x < 0.33$	–0.0914	1.0398	0.8171	0.4

N,N-dimethylformamide – water			
NH_4NO_3	0.8508	0.6839	6.722	2.8
$LiNO_3$	0.9804	0.5527	8.860	1.6
$NaNO_3$	0.8474	0.5967	8.266	2.7
$NaClO_4$	0.9205	0.6074	7.451	0.4
$NaBPh_4$	0.7935	0.4324	9.699	0.4
KNO3	0.8423	0.7944	4.144	2.1
KSCN	0.9212	0.7294	5.228	1.1
KPic	0.8300	0.6790	4.891	0.4
$i-Am_3BuNI$	0.9888	0.4475	12.115	0.8

tetrahydrofuran – water			
HCl, $x < 0.78$	0.4762	1.1323	2.897	3.1
$NaClO_4$, $x < 0.37$	0.9468	0.3414	23.896	0.7
KCl, $x < 0.58$	0.7915	0.7260	5.776	1.8
KI, $x < 0.48$	0.7473	0.6855	6.944	1.6
$KClO_4$, $x < 0.58$	0.8864	0.5186	13.244	1.3
CsCl, $x < 0.74$	0.9519	0.7161	6.044	2.2
CsBr, $x < 0.70$	0.7445	0.7098	6.463	1.9
$CsNO_3$, $x < 0.37$	0.6595	0.6920	6.562	0.5

tetramethylene sulfone – water, 303.15 K			
NaBr	0.8641	0.4855	14.226	1.4
NaI	0.9715	0.4755	14.302	2.8
$NaBPh_4$	0.9615	0.4675	8.330	2.2
Bu_4NCl	0.7270	0.5454	8.351	2.3
Bu_4NBr	0.8150	0.5444	8.451	1.5
Bu_4NI	0.8950	0.5560	7.711	2.5
Bu_4NClO_4	0.9555	0.4195	12.441	2.4
$i-Am_3BuNI$	0.9215	0.4575	11.872	3.3

methanol – acetonitrile			
$NaClO_4$	0.8682	0.3666	19.115	0.8
KI	0.9561	0.2880	23.732	0.7
$KClO_4$	0.8818	0.1847	37.863	0.7
$AgNO_3$	1.0738	–0.1583	106.62	0.4
Et_4NBr	0.6527	1.6995	0.2087	1.2
Pr_4NBr	0.6367	2.2975	0.02298	1.4
Bu_4NBr	0.5920	2.6279	6.9993e-3	1.2
Pen_4NBr	0.6063	2.6506	6.1276e-3	1.4
Hep_4NBr	0.5522	3.0273	1.5916e-3	1.1
Hex_4NBr	0.6201	2.7020	4.8588e-3	1.4
Bu_4NI	0.9021	0.5487	8.7030	0.3
Me_4NClO_4	0.9675	–0.9319	1997.1	0.4
$Et4NClO_4$	0.9013	–0.4859	413.07	0.5
Bu_4NClO_4	0.9380	–0.1905	120.55	0.7
Hex_4NClO_4	0.9472	–0.2120	120.43	0.3
Bu_4NNO_3	0.9034	0.3960	15.330	0.9
Bu_4NBPh_4	0.8920	0.5238	7.060	0.5
$i-Am_3BuNI$	0.7435	1.4164	0.4550	0.5
$i-Am_3BuNPic$	0.7682	1.3214	0.5251	0.5
$i-Am_3BuNBPh_4$	0.8972	0.5199	6.943	0.1

methanol – 1,4-dioxane, $x > 0.61$			
LiBr	2.5992	–0.2568	48.283	0.5
$NaClO_4$	5.7108	–0.6260	31.699	0.7
KNO_3	–1.5139	0.6304	31.764	0.4
RbCl	2.5296	–0.0141	24.362	0.8
RbBr	0.5782	0.1944	40.362	0.3
$RbNO_3$	–0.2579	0.3847	35.619	0.8
CsCl	0.3034	0.2356	41.464	0.5
$CsNO_3$	0.1752	0.3014	38.988	0.6
Et_4NBr	–0.3193	0.3580	42.195	1.2

acetonitrile – propylene carbonate			
LiBr	0.7896	–0.4181	322.16	0.3
$LiClO_4$	0.8343	–0.3267	225.79	0.1
$LiAsF_6$	0.8902	–0.2390	153.58	0.3
Bu_4NBPh_4	0.9971	0.0895	29.999	0.2

acetonitrile – 1,4-dioxane				
LiClO$_4$, $x > 0.38$	0.0277	0.6300	17.573	0.2
NaClO$_4$, $x > 0.38$	1.0530	0.0144	55.852	0.9
Bu$_4$NClO$_4$, $x > 0.36$	–0.2993	0.7743	14.096	0.6
Bu$_4$NI, $x > 0.45$	–5.1329	3.8976	0.0332	1.5

acetonitrile – carbon tetrachloride				
Bu$_4$NClO$_4$, $x > 0.53$	0.0035	0.6232	17.628	0.8
Me$_4$NBPh$_4$, $x > 0.43$	0.0139	0.5832	18.553	0.1
Et$_4$NBPh$_4$, $x > 0.48$	0.3390	0.3972	23.948	0.6
Pr$_4$NBPh$_4$, $x > 0.40$	0.2536	0.4265	21.249	0.3
Bu$_4$NBPh$_4$, $x > 0.15$	1.2968	–0.0912	41.616	0.3

acetonitrile – toluene				
Pr$_4$Br, $x > 0.48$	0.1038	0.2832	55.562	0.9
Pr$_4$NI, $x > 0.34$	0.1405	0.2807	54.542	0.5
Bu$_4$NI, $x > 0.34$	0.0350	0.3245	49.572	1.0
NaBPh$_4$, $x > 0.48$	0.0971	0.2873	43.610	0.6

acetone – ethanol				
NaCl	1.7816	4.3818	4.1394e-5	1.0
CsCl	1.7817	4.5967	2.1441e-5	1.4
CsClO$_4$	0.9967	0.2263	30.629	0.1
Et$_4$NClO$_4$	1.0962	0.8583	4.2695	0.6

acetone – N,N-dimethylformamide				
LiI	–0.0454	–1.5991	25945	1.6
LiClO$_4$	0.3806	–0.8471	1539.0	1.0
NaI	0.4509	–0.6991	941.06	1.3
KI	0.7640	–0.2009	145.03	0.6
AgClO$_4$	0.3909	–0.7134	1068.7	0.6
Bu$_4$NI	0.9644	0.1131	41.421	0.4
Bu$_4$NClO$_4$	1.0486	0.2662	23.392	0.5
Bu$_4$NBBu$_4$	1.2629	0.5466	5.6316	0.3

acetone – 1-propanol				
LiCl	1.2311	3.5070	1.1620e-3	1.1
Bu$_4$NCl	1.1246	2.1208	0.07497	1.5
Bu$_4$NBr	1.1135	2.3335	0.04240	1.7
Bu$_4$NI	1.0810	1.6912	0.3089	1.3
Bu$_4$NClO$_4$	1.0069	0.2883	22.272	1.2

acetone – 2-propanol				
LiCl	1.1080	2.7387	0.01307	1.5
Bu$_4$NCl	1.0500	1.6227	0.3627	1.1
Bu$_4$NBr	1.0563	1.6723	0.3278	1.3
Bu$_4$NI	1.0370	1.2621	1.1666	0.9
Bu$_4$NClO$_4$	0.9959	0.3576	18.185	0.4

tetramethylene sulfone – γ-butyrolactane, $x < 0.68$				
LiPic	0.9755	0.5338	6.854	0.9
NaPic	0.8316	0.4855	8.154	0.7
KPic	1.0120	0.4950	9.984	0.4
CsPic	0.8498	0.5465	7.798	0.8
RbPic	0.8984	0.5635	7.305	0.5
Bu$_4$NPic	0.8921	–0.2909	150.86	0.1
Bu$_4$NBr	0.8518	0.5050	10.056	0.6
BU$_4$NClO$_4$	0.8448	–0.0220	71.006	0.1

Bu$_4$NNO$_3$	0.7950	1.1321	0.9645	0.3
Bu$_4$NBBu$_4$	0.9585	1.5742	0.1274	0.1

propylene carbonate – dimethoxymethane				
LiClO$_4$	0.5308	–0.1730	90.044	1.1
LiAsF$_6$	0.7534	–0.0815	63.664	0.6
Bu$_4$NClO$_4$	0.6008	–0.1075	77.015	0.5
Bu$_4$NBPh$_4$	0.7926	–0.0569	45.325	1.0

propylene carbonate – 1,2-dimethoxyethane				
LiBr, $x < 0.81$	0.1091	–0.5586	417.44	0.3
LiClO$_4$	0.2437	–0.6068	411.53	1.2
LiAsF$_6$, $x < 0.24$	0.4446	–0.3076	168.93	0.1
Bu$_4$NCl	–0.2347	–0.9080	987.55	0.7
Bu$_4$NClO$_4$	0.3926	–0.3653	184.69	0.5
Bu$_4$NBBu$_4$	0.5002	–0.4666	190.60	0.5

α and β are dimensionless; C is in   S cm^{2}mol^{-1} cP^{-1} and $\sigma(\Lambda^0)$ in
S·cm^2·mol^{-1}.
x is the mole fraction of the first named component of the mixture.

if the parameters α and β will be the same for any pair of electrolytes because then $\Lambda_j^0(x,T)/\Lambda_i^0(x,T) = C_j C_i = $ const. ($\eta(x,T)$ and $D(x,T)$ are the same for all electrolytes). Unfortunately, such situation is rarely observed, because α and β have different values for electrolytes (Table 2).

6. Conclusions and Remarks

Considering its importance, the ordinary Walden product, $\Lambda^0(x,T)·\eta(x,T)$, (even when unverified for a number of temperatures) is routinely discussed in the analysis of conductivity experiments of electrolytes in mixed solvents. Previously[20] and here, it is suggested to use it together with the modified Walden product, $\Lambda^0(x,T)\eta^\#(x,T)$, and the excess Walden product $\Lambda^0(x,T)\eta^E(x,T)$. Both these Walden products are often superior when the division of mixtures into concentration regions is desired. An alternative indicator of such division, the maximum of viscosity or the ordinary Walden product are less adequate tools. The sign and magnitude of the excess viscosity $\eta^E(x,T)$ which is included in the excess Walden product, is of significance because usually it is associated with the type of interactions between solvents in the mixture.

For the first time, it is proposed to correlate, by a formal mathematical expression, the universal curves of limiting conductances as a function of mole fraction x and the limiting conductances $\Lambda^0(x,T)$ as a function of measurable physical properties of the mixture $\eta(x,T)$ and $D(x,T)$. This will provide a convenient additional tool when behavior of electrolytes in various mixed solvent systems is quantitatively compared.

Here and earlier[20], the existence of universal curves of limiting conductances was satisfactorily verified for many mixed solvent systems with various types of electrolytes or ions and there is no doubt that they can serve to

estimate the unknown values of $\Lambda^0(x,T)$ and to give some indication about the quality of the performed conductivity measurements. This is of importance because from the analysis of conductivity data it is clear that the results reported in the literature have unequal value if the accuracy is taken into account. This is evident when viscosities or dielectric constants from different investigations are compared. It is not clear why nitrates are usually a less suitable choice to be the standard electrolyte than for example metal halides or tetraalkylammonium salts. It is also rather surprising that the water-acetonitrile mixtures, the universal curves are very short as compared with other hydrogen-bonded systems. It seems that the water-acetonitrile system needs to be reexamined and much better documented by performing new measurements. Many electrolytes were already investigated in this system but more accurate and systematic measurements are necessary to supplement those which often were limited to narrow concentration regions. The same situation exists for a number of aqueous and organic systems with nitrates.

There is not enough experimental conductivity data to examine in a detail the general behaviour of electrolytes in mixtures including one solvent together with the series of solvents which have similar structure. Two examples presented here, aqueous solutions of low aliphatic alcohols and propylene carbonate with different-type solvents, indicate that in the limited concentration regions, $\Lambda^0(x,T)$ depend very weakly on the type of the second component in the mixture and even on the type of the dissolved electrolyte. At this point, it is not clear to what extent such behaviour is of a general character. Nevertheless, these two examples support the hypothesis that influence of the mixture properties on the mobility of electrolytes is less important than the differences associated with the structure of pure solvents and the mechanism of charge transfer of various ions in them. To the great extent, this fact can be interpreted as a simple dilution effect.

7. Acknowledgments

8. References

1. R. M. Fuoss, F. Accascina, Electrolytic Conductance. Interscience Publishers, Inc., New York, **1959**.
2. R. M. Fuoss, *Proc. Nat. Acad. Sci.* **1959**, *45*, 807–813.
3. R. M. Fuoss, *The Conductance of Symmetrical Electrolytes.* In Chemical Physics of Ionic Solutions. B. E.Conway, R. G. Barradas, (Eds.) J. Wiley and Sons, New York, **1966** pp. 463–485.
4. F. Accascina, S. Schiavo, *Ion-Pair Formation and Conductance Behavior in Solvents of Low Dielectric Constant.* In Chemical Physics of Ionic Solutions. B. E. Conway, R. G. Barradas, (Eds.) J. Wiley and Sons, New York, **1966** pp. 515–520.
5. J. Barthel, *Angew. Chem.* **1968**, *7*, 260–277.
6. R. L. Kay, G. P. Cunningham, D. Fennell, *The Effect of Solvent Structure on Ionic Mobilities in Aqueous Solvent Mixtures.* In Hydrogen-Bonded Solvent Systems. A. K. Covington, P. Jones, (Eds.) Taylor and Francis Ltd. London, **1968** pp. 249–260.

7. J. Padova, *Ionic Solvation in Nonaqueous and Mixed Solutions*. In Modern Aspects of Electrochemistry, No.7. B. E. Conway, J.O'M. Bockris, Butterworths, London, **1972** pp.1-82.

8. R. L. Kay, *IonicTransport in Water and Mixed Aqueous Solvents*. In Water A Comprehensive Treatise. Vol. 3. F. Franks (Ed.) Plenum Press New York, **1973** pp. 173–209.

9. Fuoss, R. M. *J. Solution Chem.* **1978,** *7*, 771–782.

10. J. Barthel, R. Wachter, H. J. Gores, *Temperature Dependence of Conductance of Electrolytes in Nonaqueous Solutions*. In Modern Aspects of Electrochemistry, No.13. B. E. Conway, J. O'M. Bockris, Plenum Press, New York, **1979** pp.1–79.

11. J. C. Justice, *Conductance of Electrolyte Solutions*. In Comprehensive Treatise of Electrochemistry, Vol. 5. Conway, B. E.; Bockris, J. O'M.; Yeager, E., (Eds.) Plenum Press, New York, **1983** pp.223–337.

12. R. L. Kay, *Pure Appl. Chem.* **1991,** *63*, 1393–1399.

13. J. M. G. Barthel, H. Krienke, W. Kunz, Physical Chemistry of Electrolyte Solutions – Modern Aspects. Springer, Darmstadt, **1998**.

14. J. Barthel, J.; ELDAR: Electrolyte Data Base Regensburg, Dechema, Frankfurt, **1991**.

15. **P.** Walden, *Z. Physik. Chem.* **1906,** *55*, 207, 246.

16. R. Zwanzig, *J. Chem. Phys.* **1970,** *52*, 3625–3628.

17. J. Hubbard, L. Onsager, *J. Chem. Phys.* **1977,** *67*, 4850–4857.

18. J. B. Hubbard, *J. Chem. Phys.* **1978,** *68*, 1649–1664.

19. S. Glasstone, K. J. Laidler, H. Eyring, The Theory of Rate Processes. McGraw-Hill Book Company, New York, **1941**.

20. A. Apelblat, *J. Phys. Chem. B* **2008,** *112*, 7032–7044.

21. R. Macías-Salinas, F. García-Sánchez, G. Eliosa-Jiménez, *Fluid Phase Equilibria* **2003,** *210*, 319–344.

22. L. Qunfang, H. Yu-Chun, *Fluid Phase Equilibria* **1999,** *154*, 153–163.

23. B. Das, N. Saha, *J. Chem. Eng. Data* **2000,** *45*, 2–5.

24. B. Das, N. Saha, D. K. Hazra, *J. Chem. Eng. Data* **2000,** *45*, 353–357.

25. G. Petrella, A. Sacco, M. Castagnolo, *Adv. Chem. Series* **1979,** *171*, 77–98.

26. M. Goffredi, T. Shedlovsky, *J. Phys. Chem.*, **1967,** *71*, 2176–2181.

27. A. Wypych-Stasiewicz, A. Szejgis, A. Chmielewska, A. Bald, *J. Mol. Liq.* **2007,** *130*, 34–37.

28. G. Petrella, M. Castagnolo, A. Sacco, M. Petrella, *J. Solution Chem.,* **1980,** *9*, 331–339.

29. A. D'Aprano, I. D. Donato, *J. Chem. Soc., Faraday Trans.* I **1973,** *69*, 1685–1693.

30. A. Chatterjee, B. Das, *J. Chem. Eng. Data* **2006,** *51*, 1352–1355.

31. R. L. Kay, T. L. Broadwater, *J. Solution Chem.* **1976,** *5*, 57–76.

32. R. L. Kay, T. L. Broadwater, *J. Phys. Chem.*, **1970,** *74*, 3802–3812.

33. A. Arevalo, A. Vivo, M.A. Esteso, M. L. Llorente, *Ann. Quim.* **1977,** *73*, 195–199.

34. H. Piekarski, M. Tkaczyk, A. Bald, A. Szejgis, *J. Mol. Liq.* **1997,** *73/74,* 209–221.

35. N. G. Foster, E. S. Amis, *Z. Physik. Chem. NF* **1955**, *3*, 365–381.

36. M. Ueno, K. Ito, N. Tsuchihashi, K. Shimizu, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1175–1180.

37. A. Apelblat, P. S. Fialho, C.A. Nieto de Castro, *Fluid Phase Equilibria* **2005,** *227*, 215–223.

38. O. L. Hughes, H. Hartley, *Phil. Mag.* **1933**, *15*, 610–637.

39. U. N. Dash, M. R. Patnik, *Fluid Phase Equilibria* **1999**, *157*, 159–168.

40. G. J. Janz, R. P. T. Tomkins, Nonaqueous Electrolytes Handbook. Vol.1. Academic Press, New York, 1**972**.

41. D. S. Gill, B. Arora, K. C. Pathak, I. M. Joshi, M. S. Bakshi *JCS Faraday Trans*. I, **992**, *88* 57–60.

42. S. Schiavo, B. Scrosati, *Z. Physik. Chem. NF* **1976**, *102*, 9–24.

43. G. Pistoia, G. Pecci, *J. Phys. Chem.*, **1970**, *74*, 1450–1454.

44. G. Pistoia, *Ric. Sci.* **1968**, *38*, 1250–1256.

45. D. F. Evans, M. I. McElroy, *J. Solution Chem.* **1975,** *4*, 413–430.

46. D. S. Gill, A. N. Sharma, *J. Chem. Soc., Faraday Trans.* I **1982,** *78*, 465–474.

47. M. S. K. Niazi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2165–2170.

48. G. Pistoia, M. Polcaro, S. Schiavo, *Ric. Sci.* **1967**, *37*, 227–233.

49. F. Accascina, G. Pistoia, S. Schiavo, *Ric. Sci.* **1966**, *36*, 560–566.

50. G. Pistoia, M. Polcaro, S. Schiavo, *Ric. Sci.* **1967**, *37*, 300–308.

51. G. Pistoia, M. Polcaro, S. Schiavo, *Ric. Sci.* **1967**, *37*, 309–314.

52. K. Jerie, A. Baranowski, S. Koziol, J. Glinski, A. Burakowski, *Chem. Physics* **2005**, *309*, 277–282.

53. F. Conti, G. Pistoia, *J. Chem. Phys.* **1968,** *72*, 2245–2248.

54. A. D'Aprano, M. Goffredi, R. Triolo, *J. Chem. Soc., Faraday Trans.* I **1976**, *72*, 72–84.

55. M. Coplan, R. Fuoss, *J. Chem. Phys.* **1964**, *68*, 1181–1185.

56. D. S. Gill, M. S. Chauhan, *Z. Physik. Chem. NF* **1984**, *140*, 139–148.

57. D. Singh, I. P. Aggarwal, *Acad. Chim. Sci. Hung*. 1972, 73, 325–333.

58. M. Goffredi, R. Triolo, *J. Chem. Soc., Faraday Trans.* I **1972,** *68*, 2324–2331.

59. D. S. Berns, R. M. Fuoss, *J. Am. Chem. Soc.* **1960,** *82*, 5585–5588.

60. F. Accascina, S. Petrucci, R. M. Fuoss, *J. Am. Chem. Soc.*. **1959**, *81*, 1301–1305.

61. N. Papadopoulos, *Can. J. Chem.* **1986**, *67*, 1624–1627.

62. N. Papadopoulos, G. Ritzoulis, *J. Solution Chem.* **1987,** *16*, 31–37.

63. N. Papadopoulos, G. Ritzoulis, D. Jannakoudakis, *Ann. Chim, Soc. Chim. Ital.* **1986**, *76*, 307–314.

64. N. Papadopoulos, *Electrochim. Acta* **1986**, *31*, 181–183.

65. G. Petrella, M. Castagnolo, A. Sacco, L. Lasalandra, Z. Naturfors., A: *Phys. Sci.* **1972**, *27*, 1345–1349.

66. A. D'Aprano, D. Donato, *Gazz. Chim. Ital.* **1977**, *102*, 923–928.

67. Y. X. Yu, J. G. Liu, G. H. Gao, *J. Chem. Eng. Data* **2000,** *45*, 570–574.

68. M. Castagnolo, L. Jannelli, G. Petrella, A. Sacco, Z. Naturfors., A: *Phys. Sci.* **1971,** *26*, 755–759.

69. A. K. Srivastava, A. R. Desai, *J. Chem. Eng. Data* **1992,** *37*, 322–327.

70. A. D'Aprano, I. D. Donato, R. Palombo, *J. Phys. Chem..* **1972,** *76*, 2923–2925.

71. A. D'Aprano, A. Capalbi, M. Battistini, *J. Electroanal. Chem.* **1993,** *353*, 121–130.

72. A. Sacco, G. Petrella, M. Castagnolo, Z. Naturfors., A: *Phys. Sci.* **1971,** *26*, 1306–1308.

73. G. Petrella, M. Castagnolo, A. Sacco, Z. Naturfors., A: *Phys. Sci.* **1975,** *30*, 533–536.

74. G. Petrella, M. Castagnolo, Z. Naturfors., A: *Phys. Sci.* **1973,** *2*, 1149– 1151.

75. A. D'Aprano, D. I. Donato, A. Carrubba, *J. Solution Chem.* **1983,** *12*, 209–213.

76. J. Barthel, R. Neueder, P. Rawytsch, H. Roch, *J. Electroanal. Chem.* **1999**, *471*, 78–87.

77. J. Barthel, R. Neueder, M. Poxleitner, J. Seitz-Beywl, L. Werblan, *J. Electroanal. Chem.* **1993**, *344*, 249–267.

78. A. Bałkowska, A. Kowalska, W. Góral, L. Werblan, *J. Electroanal. Chem.* **1993**, *354*, 11–23.

79. G. Moumouzias, G. Ritzoulis, *J. Solution Chem.* **1996**, *25*, 1271–1280.

80. G. Moumouzias, G. Ritzoulis, *J. Chem. Eng. Data* **1996**, *41*, 326–330.

81. M. Salomon, E. J. Plichta, *Electrochim. Acta*, **1983**, *28*, 1681–1686.

82. M. Salomon, E. J. Plichta, *Electrochim. Acta*, **1985**, *30*, 113–119.

83. G. Moumouzias, G. Ritzoulis, *Ber. Bunsenges. Phys. Chem.* **1998**, *102*, 786–791.

84. G. Wawrzyniak, T. Jasiñski, *Polish J. Chem.* **1985**, *58*, 1181–1187.

85. H. Roch, Dissertation, Regensburg, **1991**.

Povzetek

Delo obravnava vpeljavo modificiranega in presežnega Waldenovega produkta, primerjavo z običajnim Waldenovim produktom ter podaja splošno odvisnost molske ter ionske električne prevodnosti pri neskončnem razredčenju različnih elektrolitov v številnih mešanicah topil: etanol, 2-propanol, 1,1,1,3,3,3-heksafluoro-2-propanol, N,N,-dimetilformamid, 1,4-dioksan + aceton; metanol, 1,4-dioksan, CCl_4, toluen + acetonitril; voda, metanol, γ-butirolakton + tetrametilen sulfon; metanol, acetonitril, toluen, dimetoksimetan, dimetoksietan + propilen karbonat. Dobljena odvisnost omogoča oceno električne prevodnosti pri neskončnem razredčenju, preverja zanesljivost izvedenih meritev električne prevodnosti ter kaže na dejstvo, da se lastnosti elektrolitov v čistih topilih večinoma ohranijo tudi v mešanicah. Izkaže se, da je splošno odvisnost molske oz. ionske električne prevodnosti pri neskončnem razredčenju možno zapisati z enostavnimi matematičnimi izrazi.