

# Limiting Conductances of Electrolytes and the Walden Product in Mixed Solvents in a Phenomenological Approach

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The applicability of the Quint–Viallard conductivity equation to the representation of electrical conductivities in mixed solvents is examined. The concept of the modified Walden product is introduced, and the benefits compared with the ordinary Walden product are discussed. The universal curve of limiting conductances for all electrolytes (or for all ions) in a given pair of solvents is introduced and examined in a number of mixtures which include methanol, ethanol, 1-propanol, *tert*-butyl alcohol, 1,4-dioxane, *N,N*-dimethylformamide, sulfolane, tetrahydrofuran, and ethylene carbonate with water. Also examined are nonaqueous mixtures of acetone–ethanol, acetone–1-propanol, dimethyl sulfoxide–propylene carbonate, acetonitrile–methanol, acetonitrile–carbon tetrachloride, and acetonitrile–propylene carbonate. Many electrolytes were involved in the evaluation of the universal curves, but the majority are alkali-metal halides, tetraalkylammonium halides, tetraalkylammonium tetraphenylborides, and potassium xanthates (inorganic and organic acids are treated separately). If in a given mixed solvent system the limiting conductance of electrolyte is unknown, the universal curve permits estimating its value and gives an indication about the quality of 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.

## 1. Introduction

After many years, in which electrical conductance studies concentrated on measurements of aqueous solutions of strong and weak electrolytes, the focus of conductivity measurements has shifted to various mixed-solvent systems. These measurements started mainly in the 1950s, peaked in the late 1960s, and continue to be of interest at present. Extensive experimental and theoretical studies were devoted to the water–organic solvent and binary organic solvents media. The studies yielded important information about ion–ion and ion–solvent interactions under varied conditions. These investigations were closely related with the classical Bjerrum concept of ion association and development of conductivity equations for symmetrical 1:1 electrolytes. Formally, the mathematical problem  $\Lambda = \Lambda(c; \Lambda^0, K_A, a)$  was expressed in terms of different modifications of the Fuoss–Onsager, Pitts, Fernandez–Prini, Justice, or other conductivity equations. It involved determination from the experimental data,  $\Lambda$  vs concentration  $c$ , the limiting conductance of the electrolyte  $\Lambda^0$ , the association constant  $K_A$ , and the ion-size parameter  $a$ . For an exact functional form and analysis of these equations, see, for example, refs 1–6. In the evaluation of  $\Lambda^0$ ,  $K_A$ , and  $a$  parameters, the applied conductivity equations were based on different versions of the interionic attraction theory of charged spheres in a solvent continuum (the so-called primitive model). This continuum is characterized by two macroscopic properties, namely, the dynamic viscosity,  $\eta$ , and the dielectric constant,  $D$ . Evidently, in the case of mixed solvents, the composition, which is usually expressed in weight fractions of the solvent  $w$  or in molar fractions  $x$ , is an additional variable. Since the limiting conductances  $\Lambda^0$  and viscosities  $\eta$  are, to various extents, reflecting the size of the ions in solution, a natural interpretation of conductivities has been formulated

in terms of the Walden and Stokes laws as applied to mixed solvents with and without water.<sup>7–12</sup>

Since 1906 when Paul Walden<sup>13</sup> observed that the product of the molar conductance at infinite dilution  $\Lambda^0(T)$  and viscosity of pure water  $\eta(T)$  is nearly independent of temperature,  $\Lambda^0(T)\eta(T) = \text{constant}$ , the so-called Walden rule or Walden product had a considerable practical importance. The Walden product is used to obtain the limiting conductances because the viscosities of water or other solvents as a function of temperature are supposed to be easier to measure than the corresponding  $\Lambda^0(T)$  values. As often mentioned in the literature, there is no theoretical analysis leading to the Walden product which can be considered as completely satisfactory. In the simplest case Stokes law is involved<sup>7</sup>

$$\Lambda^0(T)\eta(T) = \frac{Fe}{\pi f} \left( \frac{1}{R_+} + \frac{1}{R_-} \right) = \frac{\text{constant}}{R_{12}}$$

$$\frac{1}{R_{12}} = \left( \frac{1}{R_+} + \frac{1}{R_-} \right) \quad (1)$$

where  $R_+$  and  $R_-$  are the cation and anion radii,  $e$  is the charge of an electron,  $F$  is the Faraday constant, and  $f$  denotes the boundary factor which varies between six for perfect stick conditions and four for perfect slip conditions. According to Stokes law, the Walden product for a given ion should be precisely constant in all solvents, provided that the radius of the ion remains unchanged. In many cases, the Walden rule is only approximately satisfied with regard to the temperature  $T$ . Even more crucial, the Stokes radius, as determined from eq 1, sometimes has unrealistic values which show little correlation with the nature of the electrolyte and also vary widely from solvent to solvent for a given electrolyte. Different modifications of the Stokes law introduced to the right-hand side of eq 1 by Zwanzig<sup>14</sup> and Hubbard and Onsager<sup>15,16</sup> or the correlation of  $R_{12}$  with the dielectric constants  $D$  of the solvent by Fuoss<sup>7</sup> were

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only partially successful.<sup>12</sup> In principle, the Eyring theory of absolute reaction rates in the liquid state<sup>17</sup> is capable of correctly expressing the Walden product's functional dependence on the solvent nature and composition. However, in systems with mixed solvents, the number of adjustable parameters is so large that until now it was considered impractical to be used.<sup>18</sup>

The enormous amount of experimental data that exists in the literature is often analyzed in a rather routine procedure. The values of the limiting conductances  $\Lambda^0(x,T)$ , the association constants  $K_A(x,T)$ , and the ion-size parameters  $a(x,T)$  are deduced from the applied conductivity equations using the determined conductivities  $\Lambda = \Lambda(c;x,T)$ , viscosities  $\eta(x,T)$ , and dielectric constants  $D(x,T)$ . These quantities permit calculating the Walden products  $\Lambda^0(x,T)\eta(x,T)$  as a function of the solvent composition and are presented in tabular or graphical form (typical plots are  $\Lambda^0(x,T)\eta(x,T)$  vs  $x$  or  $\Lambda^0(x,T)\eta(x,T)$  vs  $1/R$ ). In many cases, the conductivity measurements are performed only at one temperature, but nevertheless, the Walden products are reported by tacitly assuming that the mutual compensation effect with regard to  $T$  is always expected. The pattern of ionic association in the mixed-solvent systems is frequently illustrated by presenting the plots  $\ln K_A$  vs  $1/D$  (the linearity confirms the Coulombic theory) and  $\ln K_A$  vs  $1/R$ , where  $R$  denotes the reciprocal of either the crystallographic radii of the ions or radii derived from the Walden products.

In this investigation, an alternative form of presentation of conductivity data for mixed solvents is proposed. In this context three topics are considered in detail. The first is whether the Quint–Viallard conductivity equation can be applied to the mixed solvents. The second deals with the new form of the Walden rule. Finally, reduction of the limiting conductances of various electrolytes for specific mixed solvent systems is considered. Evidently, from the voluminous quantity of conductivities which is compiled mostly in the ELDAR data bank,<sup>19</sup> only a tiny fraction is used here to illustrate the proposed procedure. In the literature, many solvents having different molecular properties were investigated (mainly with water), and from an experimental point of view, the systems with the possibility to vary the dielectric constant in a wide interval, i.e., to extend the investigated concentration range, were obviously preferred.

In this work, a number of mixed-solvent systems with water, but also a few nonaqueous mixtures, are considered. Special attention was devoted to two systems: the 1,4-dioxane–water mixtures and the series of aliphatic alcohol–water mixtures. The studies with 1,4-dioxane are characterized by a broad variety of investigated inorganic and organic electrolytes, highly precise conductivity measurements which were performed at many temperatures, and a relatively large concentration range. The same could be said about completely miscible water alcohols, but in this case, the conductance studies cover the entire concentration region because the dielectric constants of pure alcohols are relatively large. Other analyzed systems with water include the following solvents: *N,N*-dimethylformamide (DMF), sulfolane (TMS), tetrahydrofuran (THF), and ethylene carbonate (EC). Analyzed nonaqueous systems include the following: acetone–ethanol (EtOH), acetone–1-propanol (1-PrOH), dimethyl sulfoxide (DMSO)–propylene carbonate (PC), acetonitrile (AN)–methanol (MeOH), acetonitrile–carbon tetrachloride, and acetonitrile–propylene carbonate.

## 2. Results and Discussion

**2.1. Quint–Viallard Conductivity Equation in Mixed Solvents.** As mentioned earlier, analysis of conductivity data for 1:1 symmetrical electrolytes has been performed in the

literature using various conductivity equations. In the initial stage of this investigation it was intended to recalculate these conductances with the help of one equation only. The choice of this equation was influenced by the fact that two new, more general conductivity equations able to reproduce conductivities of symmetrical and unsymmetrical electrolytes or mixtures of them were almost simultaneously proposed in 1978 by Lee and Wheaton<sup>20,21</sup> and Quint and Viallard.<sup>22–24</sup> In the Quint Ph.D. thesis,<sup>25</sup> his and Viallard equation was applied to strong electrolytes and mixtures of them. Rather ironically, the first case when this equation was used for weak electrolytes (oxalic acid in water) is that reported by Lee and Wheaton.<sup>26</sup> Since the present author was many times involved with the Quint–Viallard equation by applying it to various systems of weak electrolytes (for relevant references see ref 27) it was quite natural to examine whether it is possible to extend this equation also to the conductivities in mixed solvents.

Very precise and extensive conductivities of sodium chloride in 1,4-dioxane–water mixtures were performed by Bešter-Rogač et al.<sup>28</sup> and interpreted in the framework of the chemical model of electrolytes<sup>1</sup> to give  $\Lambda^0$ ,  $K_A$ , and distance parameter values. Their experimental conductivities are analyzed once again by the Quint–Viallard conductivity equation in the version applicable for monobasic organic acids<sup>29</sup> (formally, the association or dissociation process can be treated in a similar way,  $K = 1/K_A$ ). Calculations were performed at seven temperatures from 278.15 to 308.15 K in 5 K intervals, but only the conductivities at 298.15 K are reported in Table 1 because at other temperatures the situation is very similar. The determined values of the limiting conductances and association constants are presented in Table 2 when the Walden products will be discussed later. The second case is the conductivities of tetrapentylammonium bromide ( $\text{Pr}_4\text{NBr}$ ) in ethanol–water mixtures measured by Kay and Broadwater<sup>30</sup> at 283.15 and 298.15 K and analyzed using the Fuoss–Onsager conductivity equation.<sup>1</sup> Only recalculated values of  $\Lambda^0$  and  $K_A$  at 298.15 K are reported in Table 2 for this system.

As can be observed (Tables 1 and 2), the Quint–Viallard conductivity equation, in these as well as in many other cases considered by the present author, is capable of representing with high accuracy the  $\Lambda = \Lambda(c;x)$  data. The determined limiting conductances  $\Lambda^0$  are in excellent agreement with those derived by other conductivity equations. Only one serious disagreement exists in the  $\Lambda^0$  value when the last point  $x = 0.6482$  of 1,4-dioxane–water mixtures is considered. It is most likely that experimental difficulties (very small dielectric constant  $D = 6.07$ ) are responsible for the disagreement because the measured  $\Lambda$  values are extremely small (Table 1).

The agreement between determined association constants coming from different conductivity equations is less satisfactory. This can be expected considering that the constant depends on the chosen model. Still all the  $K_A$  values continue to be of the same order of magnitude (Table 2).

Since the main objectives of this work are the limiting conductances and Walden products in mixed solvents and the role of the association constants is rather marginal, in many cases the original values of  $\Lambda^0$  from the literature were preserved (there is no distinction in the notation between them and those calculated using the Quint–Viallard equation).

**2.2. Walden Products in Mixed Solvents.** In the data interpretation it is important to distinguish between the three “measurable” physical quantities,  $\eta(x,T)$ ,  $D(x,T)$ , and evidently  $\Lambda^0(x,T)$  (even though this conductivity value is based on the extrapolation procedure) and the quantities derived from the

**TABLE 1: Experimental and Calculated Molar Conductivities of NaCl in 1,4-Dioxane–Water Mixtures as a Function of Concentration at 298.15 K<sup>a</sup>**

$\tilde{m} \times 10^3$	$\Lambda_{\text{exp}}$	$\Lambda_{\text{calcd}}$	$\tilde{m} \times 10^3$	$\Lambda_{\text{exp}}$	$\Lambda_{\text{calcd}}$	$\tilde{m} \times 10^3$	$\Lambda_{\text{exp}}$	$\Lambda_{\text{calcd}}$
$x$	0.0000			0.0574			0.1104	
0.1778	125.35	125.35	0.3449	85.06	84.73	0.5336	64.33	64.34
0.3359	124.89	124.90	0.5899	84.42	84.30	0.7901	63.95	63.94
0.5696	124.43	124.41	0.7986	84.05	84.01	1.0647	63.60	63.58
0.8645	123.93	123.92	1.0213	83.80	83.74	1.3174	63.32	63.29
1.2066	123.46	123.45	1.3148	83.57	83.42	1.6569	62.94	62.94
1.5043	123.09	123.09	1.7575	83.05	83.02	2.0484	62.55	62.59
1.9518	122.59	122.62	2.2583	82.55	82.62	2.5578	62.13	62.17
2.5391	122.08	122.07	2.9180	82.02	82.16	3.1863	61.74	61.72
$\sigma(\Lambda)$		0.01	3.8427	81.36	81.61	4.1868	61.10	61.08
			5.1898	80.64	80.91	$\sigma(\Lambda)$		0.03
			$\sigma(\Lambda)$		0.19			
$x$	0.2000			0.2979			0.4002	
0.2980	50.73	50.71	0.2523	42.02	41.81	0.2598	32.24	32.01
0.5866	49.91	49.92	0.4325	40.89	40.79	0.5357	29.15	29.19
0.8910	49.26	49.27	0.5861	40.07	40.07	0.8129	27.14	27.28
1.1742	48.79	48.76	0.8237	39.11	39.14	1.1035	25.61	25.79
1.7291	47.91	47.92	1.0572	38.28	38.36	1.4899	24.12	24.26
2.2931	47.18	47.20	1.4256	37.21	37.34	1.9949	22.67	22.75
3.0346	46.36	46.40	1.8951	36.07	36.22	2.6478	21.30	21.29
3.8301	45.65	45.66	2.5085	34.91	35.06	3.4281	20.09	19.97
5.1453	44.65	44.60	3.4092	33.57	33.67	4.5678	18.82	18.55
$\sigma(\Lambda)$		0.08	5.0139	31.81	31.78	$\sigma(\Lambda)$		0.17
			7.6331	29.87	29.57			
			$\sigma(\Lambda)$		0.15			
$x$	0.5009			0.6482				
0.0952	23.84	23.46	0.0515	4.37	4.36			
0.1841	20.03	20.34	0.1035	3.23	3.25			
0.2811	18.05	18.25	0.1579	2.68	2.70			
0.4079	16.21	16.42	0.2248	2.30	2.31			
0.5708	14.66	14.82	0.2907	2.06	2.06			
0.7503	13.49	13.57	0.3723	1.85	1.85			
0.9237	12.64	12.66	0.4867	1.64	1.63			
1.1991	11.67	11.56	0.6443	1.46	1.44			
1.8542	10.13	9.87	0.8964	1.27	1.23			
3.1606	8.56	8.05	1.2275	1.11	1.06			
$\sigma(\Lambda)$		0.28	$\sigma(\Lambda)$		0.02			

<sup>a</sup> Units:  $\tilde{m}$  (molonities = moles of electrolyte per kilogram of solution) mol kg<sup>-1</sup>;  $\Lambda$ , S cm<sup>2</sup> mol<sup>-1</sup>;  $\sigma(\Lambda)$  (standard deviation), S cm<sup>2</sup> mol<sup>-1</sup>;  $x$  is the mole fraction of 1,4-dioxane.

applied model, namely, the association constants  $K_A(x, T)$ , ion-size parameters  $a(x, T)$ , and Walden products or radii  $R_{12}(x, T)$  coming from them. The Walden product is a simple function, being the product of the viscosity of pure solvent or a mixture of solvents and the limiting conductance of the electrolyte. However, the Walden product itself is the model quantity introduced by Walden because it weakly depends on temperature, contrary to the product components viscosity and limiting conductance. Any form of the function is permissible if it provides some particular advantage (another example is  $\Lambda^0 \eta^p = \text{constant}$ ,  $p < 1$ , for details see ref 31). It was also suggested to introduce the normalized Walden product, the ratio  $(\Lambda^0(x, T)\eta(x, T))/(\Lambda^0(0, T)\eta(0, T))$  (see Broadwater and Kay<sup>32</sup>), but it only shifts the actual values of the Walden product.

It is worthwhile to emphasize that the “success” of the Walden product should be attributed to the fact that it represents some kind of limiting law which in the case of pure solvent describes an “ideal” hypothetical situation when the ion–ion interactions are completely excluded and only the interactions between the single ion and neighboring solvent molecules are of importance. If thermodynamic terminology is used, then this situation can be called “ideal” because we have the electrolyte at infinite dilution and pure solvent. However, since the electrical conductance and viscosity are not thermodynamic but dynamic properties, this could be taken only as an analogy.

Evidently, when the continuum is a mixture of two solvents, the situation is quite different. In addition to the single-ion interaction with two kinds of solvent molecules which exist in different proportions in the mixture, the solvent–solvent interactions cannot be neglected. The mixture of solvents starts to be “real”, and therefore, the Walden products in the pure solvent and mixture of solvents are not equivalent.

In mixed solvents, at a given mole fraction  $x$ , the Walden product preserves its basic property with regard to temperature  $T$ , and therefore,  $\Lambda^0(x, T)\eta(x, T) = \text{constant}$ , but the value of this constant depends on  $x$ , i.e.  $\Lambda^0(x, T)\eta(x, T) = f(x)$ . Unfortunately, if the number of experimental points is small, the functional form of  $f(x)$  cannot be predicted. The function  $f(x)$  is an implicit function of  $x$  because its behavior results from the changes in the viscosities and the limiting conductances with  $x$ . The function usually has a maximum in the case of aqueous systems, which divides the mixtures into two regions, the water-rich region and solvent-rich region.

As result of the different functional form of  $\Lambda^0(x)$  (usually decreases with  $x$ ) and  $\eta(x)$  (in aqueous systems often has a maximum), their product  $f(x)$  also has maximum but not at the same composition as the viscosity maximum. For example, in the 1,4-dioxane–water mixtures, the viscosity maximum is at the mole fraction  $x \approx 0.25$  or weight fraction  $w \approx 0.62$  and in the ethanol–water mixtures at  $x \approx 0.25$  or  $w \approx 0.46$  when the

**TABLE 2: Limiting Conductances and Association Constants of NaCl in 1,4-Dioxane–Water Mixtures and Pr<sub>4</sub>NBr in Ethanol–Water Mixtures as a Function of Composition at 298.15 K<sup>a</sup>**

$x^b$	$\Lambda^0(\text{CM})$	$\Lambda^0(\text{QV})$	$K_A(\text{CM})$	$K_A(\text{QV})$
0.0000	126.54	126.55	2.38	2.16
0.0574	86.34	86.35	5.07	3.75
0.1104	66.21	66.16	7.87	4.78
0.2000	52.61	52.53	23.7	17.8
0.2979	45.11	44.66	119	85
0.4002	39.20	38.12	726	543
0.5009	35.21	32.79	7473	5525
0.6482	24.88	18.94	602 600	333 300
$x^c$	$\Lambda^0(\text{FO})$	$\Lambda^0(\text{QV})$	$K_A(\text{FO})$	$K_A(\text{QV})$
0.0000		101.37		
0.0776	57.57	57.56		4.0
0.1311	45.99	46.01		3.7
0.1476	44.07	44.08		4.7
0.2753	38.21	38.18	4 ± 1	6.7
0.5019	38.13	38.08	9 ± 2	13.3
0.7987	41.75	41.61	28 ± 2	42
1.0000	46.88		80 ± 2	

<sup>a</sup> Units:  $\Lambda^0$ , S cm<sup>2</sup> mol<sup>-1</sup>;  $K_A$ , dm<sup>3</sup> mol<sup>-1</sup>;  $x$  is the mole fraction of 1,4-dioxane. <sup>b</sup> For ethanol. <sup>c</sup> CM = chemical model;<sup>1</sup> QV = Quint–Viallard;<sup>25</sup> FO = Fouss–Onsager.<sup>1</sup>

maximum of  $f(x)$  is shifted to a smaller value at  $x \approx 0.06$  and 0.15, respectively. There are always considerable differences between the values of  $x$  and  $w$  because the molar mass of water compared to that of organic solvents is small.

As a model quantity, the combination between viscosity and limiting conductance, can take any functional form. Therefore, an alternative definition of the Walden product is suggested. This new  $f(x)$  is an explicit function of  $x$  and in some way corresponds to that of the Walden products in pure solvents. The change in the form of  $f(x)$  is introduced by replacement of the actual viscosity  $\eta(x, T)$  with  $\eta^\#(x, T) = x\eta_1^0(T) + (1 - x)\eta_2^0(T)$ , which represents the sum of the additive contributions from the viscosities of pure components. If the viscosity  $\eta(x, T)$  indirectly indicates the actual solvent–solvent interactions, then

$\eta^\#(x, T)$  can be associated with the simple dilution effect, i.e., gradual replacement of molecules in the mixture (the solvent molecules of component 1 by the solvent molecules of component 2). The viscosities  $\eta^\#(x, T)$  are linear functions of  $x$ , and the difference  $\eta(x, T) - \eta^\#(x, T)$  is sometimes called the excess viscosity  $\eta^E(x, T)$ . Thus, the modified Walden product is defined by

$$\Lambda^0(x, T) \eta^\#(x, T) = \Lambda^0(x, T)[x\eta_1^0(T) + (1 - x)\eta_2^0(T)] \quad (2)$$

as compared with the ordinary Walden product  $\Lambda^0(x, T)\eta(x, T)$ . In terms of the primitive model of electrolyte solutions, the radius term in eq 1 is replaced by  $1/R_{12} = x/R_1 + (1 - x)/R_2$ , where  $R_1$  and  $R_2$  are the radii of the electrolyte (sum of cation and anion without specification of whether they are solvated or not) in pure solvents.

Before discussing the properties of the modified Walden product, the most important question is whether it continues to be a nearly independent function of temperature. Once again, the conductivity data is examined for the NaCl–1,4-dioxane–water system<sup>28</sup> in the 278.15–308.15 K temperature range (1,4-dioxane will be denoted as DX). Values of the ordinary and modified Walden products based on the experimentally determined  $\Lambda^0(x, T)$  and  $\eta(x, T)$  and the calculated viscosities  $\eta^\#(x, T)$  are presented in Table 3. The viscosity of pure 1,4-dioxane is 1.197 cP, and that of pure water is 0.8903 cP.<sup>1</sup> As can be observed, both Walden products have a similar very weak dependence on  $T$  (less than 3.5% over the investigated temperature range).

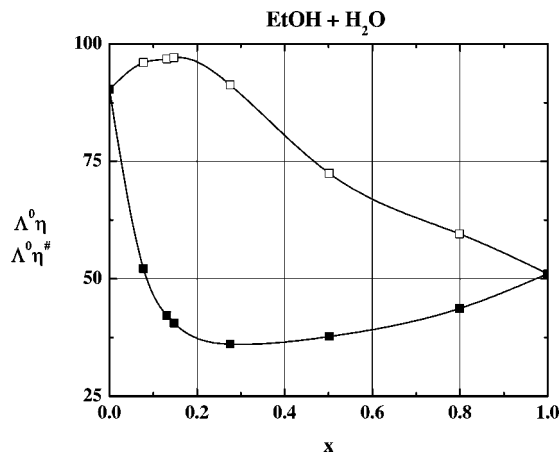
As can be expected, both Walden products behave differently (Figures 1 and 2). The modified Walden product also has two distinct concentration regions, the water-rich region and the ethanol-rich region in the Pr<sub>4</sub>NBr–ethanol–water system or the water-rich region and the 1,4-dioxane-rich region in the NaCl–1,4-dioxane–water system. However, the boundaries of these regions are shifted to much larger values of  $x$ . In each region the modified Walden product depends nearly linearly on  $x$  or on  $1 - x$ , and both straight lines near the boundary gradually change the curvature of the curve to meet. Therefore, interpolation between experimental values of  $\Lambda^0(x, T)$  or extrapolation

**TABLE 3: Walden Products  $\Lambda^0\eta$  and Modified Walden Products  $\Lambda^0\eta^\#$  of NaCl in 1,4-Dioxane–Water Mixtures as a Function of Mole Fraction  $x^a$** 

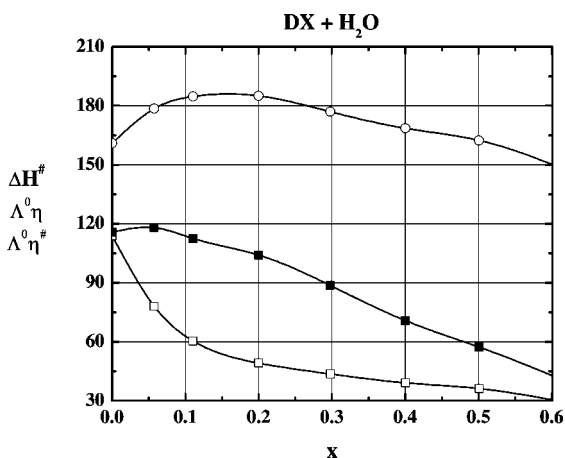
$x/T$	$\Lambda^0\eta$							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	$(\Lambda^0\eta)_{\text{av.}}$
0.0000	118.06	116.47	115.06	113.80	112.66	111.61	122.64	115.76 ± 3.75
0.0574	121.93	120.37	119.15	117.69	116.52	115.33	115.48	118.06 ± 2.52
0.1104	115.96	114.81	113.61	112.67	111.55	109.41	110.16	112.60 ± 2.40
0.2000	106.68	105.89	105.03	103.93	103.39	102.56	101.62	104.16 ± 1.81
0.2979	90.43	90.05	89.23	88.57	88.00	87.39	86.74	88.64 ± 1.36
0.4002	71.71	71.46	71.19	70.80	70.53	70.13	69.74	70.79 ± 0.71
0.5009	57.23	57.33	57.36	57.42	57.45	57.43	57.40	57.38 ± 0.08
0.6482	35.07	35.86	35.60	36.13	35.34	35.13	34.82	35.42 ± 0.47
$x/T$	$\Lambda^0\eta^\#$							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	$(\Lambda^0\eta^\#)_{\text{av.}}$
0.0000	118.06	116.47	115.06	113.80	112.66	111.61	110.64	114.04 ± 2.66
0.0574	76.87	77.20	77.56	77.97	78.38	78.77	79.11	77.98 ± 0.82
0.1104	58.30	58.97	59.69	60.44	61.17	61.88	62.55	60.43 ± 1.55
0.2000	46.87	47.61	48.41	49.22	50.05	50.83	51.59	49.23 ± 1.71
0.2979	41.75	42.42	42.95	43.59	44.26	44.91	45.53	43.63 ± 1.36
0.4002	37.76	38.20	38.69	39.18	39.68	40.17	40.62	39.18 ± 1.04
0.5009	35.09	35.45	35.84	36.28	36.72	37.16	37.58	36.30 ± 0.91
0.6482	26.39	27.06	26.98	27.52	27.07	27.08	27.00	27.01 ± 0.33

<sup>a</sup> Units:  $\Lambda^0\eta$  and  $\Lambda^0\eta^\#$ , S cm<sup>2</sup> mol<sup>-1</sup>, cP 10<sup>2</sup>.





**Figure 1.** Ordinary Walden products  $\Lambda^0(x)\eta(x)$  and modified Walden products  $\Lambda^0(x,T)\eta^\#(x,T) = \Lambda^0(x,T)[x\eta_1^0(T) + (1-x)\eta_2^0(T)]$  of  $\text{Pr}_4\text{NBr}$  as a function of mole fraction  $x$  of ethanol in ethanol–water mixtures.  $\Lambda^0(x)\eta(x)$ : (□) ref 30; (■)  $\Lambda^0(x)\eta^\#(x)$ , this work.



**Figure 2.** Ordinary Walden products  $\Lambda^0(x)\eta(x)$ , modified Walden products  $\Lambda^0(x,T)\eta^\#(x,T) = \Lambda^0(x,T)[x\eta_1^0(T) + (1-x)\eta_2^0(T)]$ , and enthalpies of activation  $\Delta H^\#(x) \cdot 10$  in  $\text{kJ mol}^{-1}$  of NaCl as a function of mole fraction  $x$  of 1,4-dioxane in 1,4-dioxane–water mixtures: (■)  $\Lambda^0(x)\eta(x)$ , ref 28; (□)  $\Lambda^0(x)\eta^\#(x)$ , this work; (○)  $\Delta H^\#(x) \cdot 10$ , this work.

to  $x = 1$ , when  $\Lambda^0(1,T)$  is unknown, is much easier than for the ordinary Walden product.

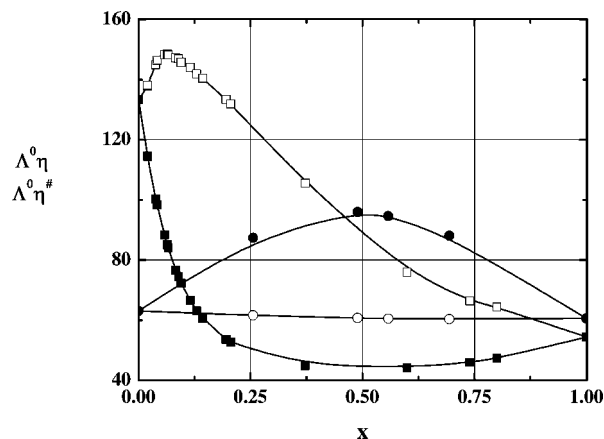
In Figures 1 and 2 the behavior of the Walden products can be characterized as “normal” (i.e.,  $\Lambda^0(x)\eta^E(x) > 0$ ), but there are also systems with  $\Lambda^0(x,T)\eta^E(x,T) < 0$  (in Figure 3 both cases are compared), and they will be considered later.

At first glance, the accuracy of the modified Walden products depends only on the accuracy of the determined  $\Lambda^0(x,T)$  values. However, they indirectly depend also on the accuracy of  $\eta(x,T)$  because  $\Lambda^0(x,T)$  are derived from conductivity equations which include these viscosities.

The temperature dependence of the limiting conductances can also be examined in the framework of the Eyring theory<sup>33</sup> (the transition-state theory of electrical conductance)

$$\ln[\Lambda^0(x,T)] + \frac{2}{3} \ln[d(x,T)] = -\frac{\Delta H^\#(x)}{RT} + \text{const.} \quad (3)$$

where  $\Delta H^\#(x)$  is the enthalpy of activation of the charge transport and  $d(x,T)$  is the density of the solvent. Values of  $\Delta H^\#(x)$  together with  $\Lambda^0(x,T)\eta(x,T)$  and  $\Lambda^0(x,T)\eta^\#(x,T)$  for the NaCl–1,4-dioxane–water system<sup>28</sup> are presented in Figure 2. The maximum value of  $\Delta H^\#(x)$  appears at the mole fraction of



**Figure 3.** Ordinary Walden products  $\Lambda^0(x)\eta(x)$  and modified Walden products  $\Lambda^0(x,T)\eta^\#(x,T) = \Lambda^0(x,T)[x\eta_1^0(T) + (1-x)\eta_2^0(T)]$  of KCl in ethanol–water mixtures (curves with □ and ■) and  $\text{CsClO}_4$  in acetone–ethanol mixtures (curves with ○ and ●).

1,4-dioxane which is nearly the same as the end of the water-rich region, as predicted by the modified Walden product. On the other hand, the corresponding value of  $x$  based on the ordinary Walden product is far from the actual maximum of  $\Delta H^\#(x)$  (Figure 2). Thus, the consistency between  $\Delta H^\#(x)$  and  $\Lambda^0(x,T)\eta^\#(x,T)$  functions, if division into two concentration regions is considered, is not surprising.

**2.3. Limiting Conductances of Electrolytes in Mixed Solvents.** As in pure water, different electrolytes in a particular mixed-solvent system have different values of limiting conductances  $\Lambda_j^0(x,T)$ , where the subscript  $j$  denotes a given electrolyte. The question is whether from knowledge of the limiting conductances of one electrolyte it is possible to predict the limiting conductances of another electrolyte. The answer to this question is positive, at least in part, especially when the water-rich region (as defined by the modified Walden product) is taken into account. If the limiting conductances of electrolytes  $j$  and  $i$  in pure water are denoted as  $\Lambda_j^0(0,T)$  and  $\Lambda_i^0(0,T)$ , then the limiting conductances of these electrolytes at mole fraction  $x$  and a particular temperature  $T$  are given with very reasonable accuracy by

$$\frac{\Lambda_j^0(x,T)}{\Lambda_i^0(x,T)} = \frac{\Lambda_j^0(0,T)}{\Lambda_i^0(0,T)} = \text{constant} \quad (4)$$

Since the ratio of the limiting conductances in water is known for practically all electrolytes (its value for various  $T$  can be determined from the Walden products) then, in principle, it follows from eq 4 that for a particular mixed-solvent system it is sufficient to determine the limiting conductances for only one electrolyte because for other electrolytes they can be estimated from eq 4. This electrolyte will be called the *standard electrolyte*. Thus, after the standard electrolyte is chosen, the reduction of the limiting conductances of various electrolytes to one curve can be performed using eq 4. The choice of the standard electrolyte is arbitrary, but the case when many accurate determinations of  $\Lambda_i^0(x,T)$  are available over a wide concentration range is evidently preferable. In this work, when possible, KCl was used as the standard electrolyte.

The possibility to reduce all electrolytes to one “universal curve” suggests that their behavior in pure water continues to be preserved in proportion which depends only on the added organic solvent and that simple dilution is the most important effect. Since hydrogen ions have different mechanism of charge transfer than other ions, they will be discussed separately later.

The possible extension of eq 4 to both concentration regions or introduction of an analogous expression for the solvent-rich region yielding

$$\frac{\Lambda_j^0(x, T)}{\Lambda_i^0(x, T)} = \frac{\Lambda_j^0(1, T)}{\Lambda_i^0(1, T)} = \text{constant} \quad (5)$$

was usually found to be less successful. At this moment, it is not clear whether this results from insufficient accuracy of the determined limiting conductances or a different mechanism of charge transfer in pure solvents or solvent-rich regions.

In the next subsections a number of water–solvent and nonaqueous mixtures are considered to illustrate the applicability of eq 4. Most of the recalculated  $\Lambda_j^0(x, T)$  are based on the original values from the literature (the Quint–Viallard conductivity equation was only used when the measured conductivities were taken directly from ELDAR data bank<sup>19</sup>), and only in few cases is their accuracy reported there. Some systems were repeatedly investigated, and the observed scattering gives some estimation about the accuracy of the performed conductivity measurements.

**2.3.1. Limiting Conductances of Electrolytes in 1,4-Dioxane–Water Mixtures.** The conductivities of many electrolytes in 1,4-dioxane–water mixtures were measured mainly by Fuoss, Accascina, Kay, and Justice and their co-workers. 1,4-Dioxane is classified as a low-permittivity electron-donor solvent;<sup>1</sup> its dielectric constant is very low, only  $D = 2.21$  as compared with water  $D = 78.35$  at 298.15 K.<sup>1</sup> The limiting conductances of 15 electrolytes at 298.15 K (KCl,<sup>3,34–36</sup> LiF,<sup>37</sup> LiCl,<sup>38,39</sup> LiClO<sub>3</sub>,<sup>40</sup> LiClO<sub>4</sub>,<sup>3,41</sup> NaCl,<sup>28,34,42,43</sup> NaNO<sub>3</sub>,<sup>44</sup> KBr,<sup>36</sup> RbCl,<sup>45</sup> RbBr,<sup>46</sup> RbI,<sup>47</sup> CsCl,<sup>48–50</sup> CsBr,<sup>51</sup> CsI,<sup>52</sup> Bu<sub>4</sub>NBr<sup>36</sup>) were recalculated using eq 4 and are plotted in Figure 4. If the ratio of the limiting conductances of KCl (standard electrolyte) and the electrolyte XY in water is denoted by  $f(\text{KCl}) = \Lambda^0(\text{KCl})/\Lambda^0(\text{XY})$ , then the shift of the limiting conductances in Figure 4 covers a wide range of electrolytes,  $0.96 \leq f(\text{KCl}) \leq 1.59$ .

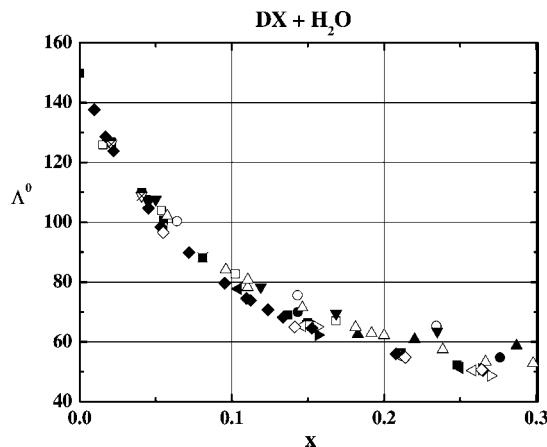
The water-rich region (based on the modified Walden product of KCl or the maximum of viscosity) stretches up to  $x \approx 0.20$  ( $w \approx 0.55$ ), but it is evident that the applicability of eq 4 can be extended even up to  $x \approx 0.35$  ( $w \approx 0.72$ ). As expected, the scattering of the recalculated  $\Lambda^0(x)$  values from the common curve is more and more significant when the amount of 1,4-dioxane in the mixture increases.

It is of interest to see whether the limiting conductivities of different ions can be reduced to one equation for cations and one equation for anions, i.e., to equations having a similar form as eq 4

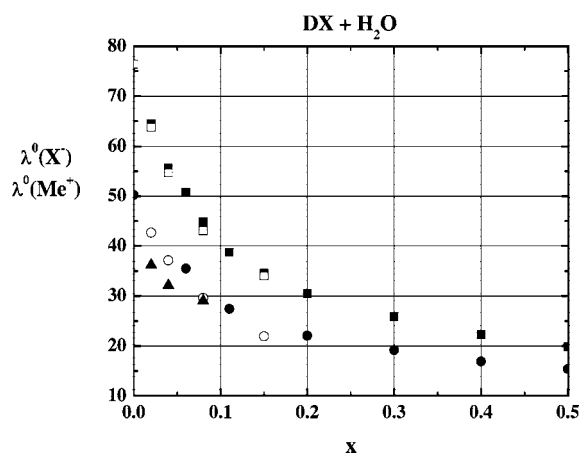
$$\frac{\lambda_j^0(x, T)}{\lambda_i^0(x, T)} = \frac{\lambda_j^0(0, T)}{\lambda_i^0(0, T)} = \text{constant} \quad (6)$$

Since the transference number measurements are rarely performed in mixed solvents, eq 6 can be illustrated by only few ions for which data is available. In 1,4-dioxane–water mixtures,<sup>28,36</sup> the standard cation was chosen to be Na<sup>+</sup> and the other cations are K<sup>+</sup> and Bu<sub>4</sub>N<sup>+</sup>, and the standard anion was chosen to be Cl<sup>−</sup> and the other anion is Br<sup>−</sup>. The results are presented in Figure 5. It can be observed that eq 6 is very nicely satisfied by the anions Cl<sup>−</sup> and Br<sup>−</sup>, but Bu<sub>4</sub>N<sup>+</sup> has slightly lower values than predicted by the curve for cations.

**2.3.2. Limiting Conductances of Electrolytes in Aliphatic Alcohol–Water Mixtures.** The second group of investigated systems includes series of alkanol–water mixtures (amphiprotic hydroxylic solvents<sup>1</sup>) which are characterized by relatively large dielectric constants and great possibility to form a highly



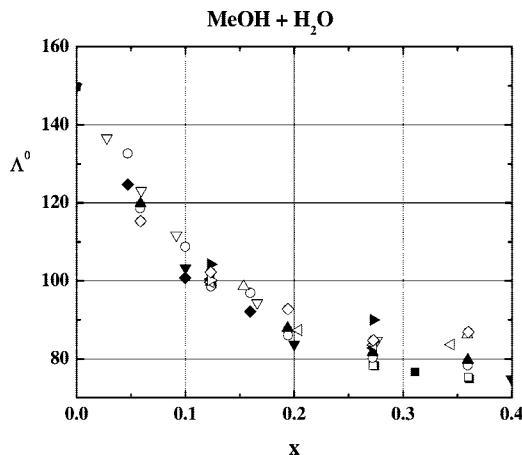
**Figure 4.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of 1,4-dioxane in 1,4-dioxane–water mixtures: (■) KCl; (□) LiF; (●) LiCl; (○) LiClO<sub>3</sub>; (▲) LiClO<sub>4</sub>; (△) NaCl; (▼) NaNO<sub>3</sub>; (▽) KBr; (◀) RbCl; (▶) RbBr; (◆) RbI; (◇) CsCl; (◻) CsBr; (◻) CsI; (×) Bu<sub>4</sub>NBr.



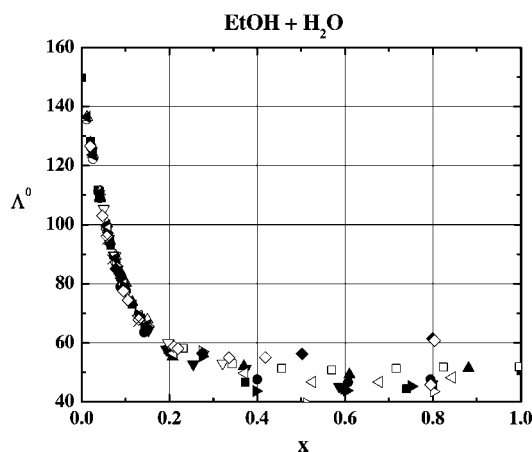
**Figure 5.** Ionic limiting conductances  $\lambda^0(x)$  at 298.15 K (calculated using eq 6) as a function of mole fraction  $x$  of 1,4-dioxane in 1,4-dioxane–water mixtures: (■) Cl<sup>−</sup>; (□) Br<sup>−</sup>; (●) Na<sup>+</sup>; (○) K<sup>+</sup>; (▲) Bu<sub>4</sub>N<sup>+</sup>.

complex hydrogen-bonded structure in the liquid state. The first considered alcohol is methanol ( $D = 32.63$ ;<sup>1</sup>  $\eta_{\text{max}}$  at  $x \approx 0.29$  or  $w \approx 0.43$ ). The water-rich region based on the modified Walden product of KCl extends up to  $x \approx 0.40$  or  $w \approx 0.54$ . The limiting conductances of 14 electrolytes at 298.15 K, mainly of alkali halides and quaternary ethyl- and butylammonium halides (KCl,<sup>53</sup> LiCl,<sup>54</sup> LiBr,<sup>54</sup> NaBr,<sup>55,56</sup> NaI,<sup>55</sup> NaClO<sub>3</sub>,<sup>57</sup> CsCl,<sup>58</sup> KClO<sub>3</sub>,<sup>57</sup> Et<sub>4</sub>NCl,<sup>59</sup> Et<sub>4</sub>NBr,<sup>59,60</sup> Et<sub>4</sub>NClO<sub>4</sub>,<sup>59</sup> Et<sub>4</sub>NI,<sup>59</sup> Bu<sub>4</sub>NBr,<sup>56</sup> AgOAc<sup>61</sup> (silver acetate)), were shifted according to eq 4 to the KCl curve, and they are plotted in Figure 6 ( $0.99 \leq f(\text{KCl}) \leq 1.51$ ). As can be seen, taking in account the variety of the involved small alkali-metal ions and large organic ions, the reliability of eq 4 seems satisfactory. The scattering of the  $\Lambda^0(x)$  values appears to be more evident near the transition from the water-rich region to the methanol-rich region.

In other conductivity measurements involving alcohols, ethanol was a very popular solvent in mixtures with water ( $D = 24.35$ ;<sup>1</sup>  $\eta_{\text{max}}$  at  $x \approx 0.24$  or  $w \approx 0.45$ ). The water-rich region based on the modified Walden product of KCl is slightly lower than that predicted by the viscosity maximum,  $x \approx 0.20$  or  $w \approx 0.39$ . Among the many investigations dealing with various electrolytes in ethanol–water mixtures, that of Kay and Broadwater<sup>30</sup> holds a special place. The results of calculations using



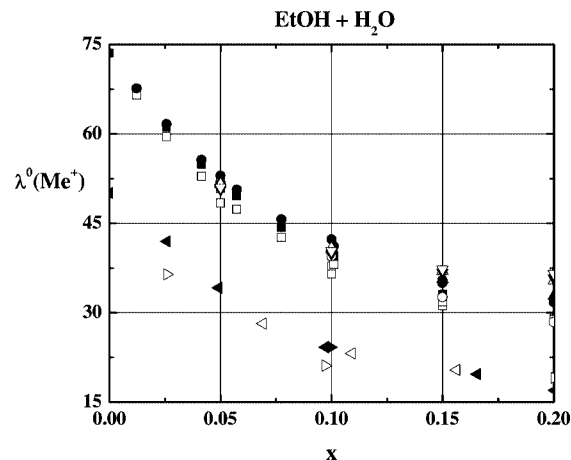
**Figure 6.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of methanol in the methanol–water mixtures: (■) KCl; (□) LiCl; (●) LiBr; (○) NaBr; (▲) NaI; (△) NaClO<sub>3</sub>; (▼) CsCl; (▽) KClO<sub>3</sub>; (left and right-pointing open and filled triangles) Et<sub>4</sub>NCl; Et<sub>4</sub>NBr; Et<sub>4</sub>NClO<sub>4</sub>; Et<sub>4</sub>NI; (□) Bu<sub>4</sub>NBr; (□) AgOAc.



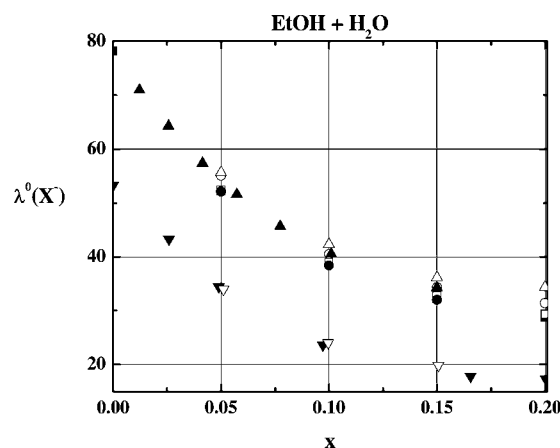
**Figure 7.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of ethanol in ethanol–water mixtures: (■) KCl; (□) LiCl; (●) LiBr; (○) LiNO<sub>3</sub>; (▲) NaCl; (△) NaNO<sub>3</sub>; (▼) KBr; (▽) KClO<sub>4</sub>; (left and right-pointing open and filled triangles) KNO<sub>3</sub>; CsCl; Me<sub>4</sub>NBr; Et<sub>4</sub>NBr; (□) Pr<sub>4</sub>NBr; (□) Bu<sub>4</sub>NB; (×) Bu<sub>4</sub>NI.

eq 4 for 15 electrolytes at 298.15 K (KCl,<sup>30,62</sup> LiCl,<sup>63</sup> LiBr,<sup>30</sup> LiNO<sub>3</sub>,<sup>64</sup> NaCl,<sup>65</sup> NaNO<sub>3</sub>,<sup>64</sup> KBr,<sup>30</sup> KClO<sub>4</sub>,<sup>30</sup> KNO<sub>3</sub>,<sup>64</sup> CsCl,<sup>30,66</sup> Me<sub>4</sub>NBr,<sup>30</sup> Et<sub>4</sub>NBr,<sup>30</sup> Pr<sub>4</sub>NBr,<sup>30</sup> Bu<sub>4</sub>NBr,<sup>30</sup> Bu<sub>4</sub>NI<sup>30</sup>) are presented in Figure 7 ( $0.99 \leq f(\text{KCl}) \leq 1.55$ ). As can be observed, there is an excellent verification of the proposed universal equation for the water-rich region and the equation is valid up to  $x \approx 0.35$  or  $w \approx 0.58$ . Reduction of  $\Lambda^0(x)$  for different electrolytes to the KCl curve from the ethanol-rich region ( $x > 0.35$ ) can be performed using eq 5. Since the ratio of the limiting conductances of electrolytes in pure ethanol is known,<sup>1</sup> it is possible to evaluate  $\Lambda^0(x)$  in the ethanol-rich region (i.e., for  $x > 0.35$ ). As can be seen in Figure 7, the agreement with eq 5 (i.e., on the ethanol-rich region) is reasonable but much less satisfactory than using eq 4.

The ionic limiting conductances in the ethanol–water mixtures are relatively better known than in other systems. They were reported by Kay and Broadwater<sup>30</sup> (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Me<sub>4</sub>N<sup>+</sup>, Et<sub>4</sub>N<sup>+</sup>, Pr<sub>4</sub>N<sup>+</sup>, Bu<sub>4</sub>N<sup>+</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, and ClO<sub>4</sub><sup>−</sup> at  $T = 298.15$  K and Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Bu<sub>4</sub>N<sup>+</sup>, Cl<sup>−</sup>, and Br<sup>−</sup> at  $T = 283.15$  K) and at  $T = 298.15$  K by Sanchez et al.<sup>66</sup> (the values of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NO<sub>3</sub><sup>−</sup> were extrapolated from the Estes and



**Figure 8.** Cation limiting conductances  $\lambda^0(\text{Me}^+;x)$  (calculated using eq 6) as a function of mole fraction  $x$  of ethanol in ethanol–water mixtures.  $T = 298.15$  K: (■) K<sup>+</sup>; (□) Li<sup>+</sup>; (●) Na<sup>+</sup>; (○) Cs<sup>+</sup>; (▲) Me<sub>4</sub>N<sup>+</sup>; (△) Et<sub>4</sub>N<sup>+</sup>; (▼) Pr<sub>4</sub>N<sup>+</sup>; (▽) Bu<sub>4</sub>N<sup>+</sup>.  $T = 283.15$  K: (left and right-pointing open and filled triangles) K<sup>+</sup>; Na<sup>+</sup>; Cs<sup>+</sup>; Bu<sub>4</sub>N<sup>+</sup>.

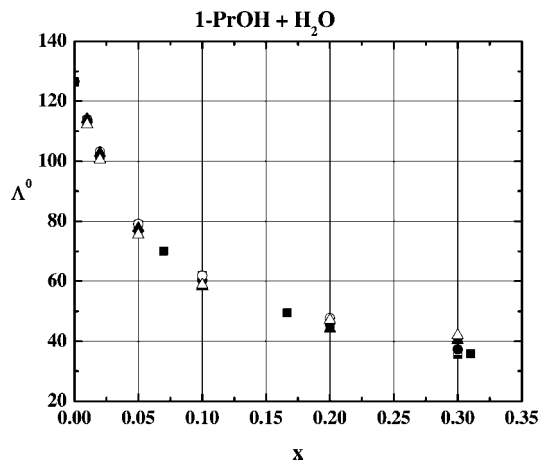


**Figure 9.** Anion limiting conductances  $\lambda^0(\text{X}^-)$  (calculated using eq 6) as a function of mole fraction  $x$  of ethanol in ethanol–water mixtures.  $T = 298.15$  K: (■) Br<sup>−</sup>; (□) Cl<sup>−</sup>; (●) I<sup>−</sup>; (○) ClO<sub>4</sub><sup>−</sup>; (▲) NO<sub>3</sub><sup>−</sup>; (△) Pic<sup>−</sup>.  $T = 283.15$  K: (▼) Br<sup>−</sup>; (▽) Cl<sup>−</sup>.

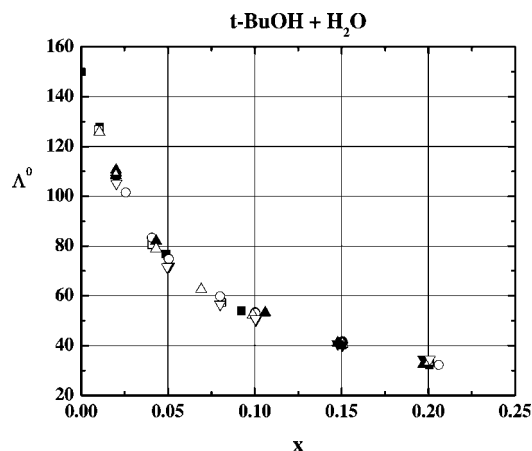
Grandoso<sup>67</sup> transference numbers) and by Kortüm<sup>68</sup> (Li<sup>+</sup>, Pic<sup>−</sup>, lithium picrate). The recalculated values of the ionic limiting conductances for these ions (eq 6) are plotted in Figures 8 and 9. The standard cation chosen was K<sup>+</sup>, and the standard anion chosen was Br<sup>−</sup>. At both temperatures the results confirm the possibility to obtain, with reasonable accuracy, the universal curves for the cations and anions in the water-rich region.

1-Propanol ( $D = 20.34$ ;  $\eta_{\text{max}}$  at  $x \approx 0.31$  or  $w \approx 0.60$ ) was investigated by Goffredi and Shedlovsky<sup>69</sup> in the case of NaCl. The Bald group<sup>70</sup> determined limiting conductances of NaCl, NaBr, NaI, NaClO<sub>4</sub>, NaBPh<sub>4</sub> (sodium tetraphenylboride), and Bu<sub>4</sub>NI. The standard electrolyte chosen in the 1-propanol–water mixtures was NaCl, and the universal limiting curve is plotted in Figure 10 ( $0.98 \leq f(\text{NaCl}) \leq 1.81$ ). As can be seen, the shifting of  $\Lambda^0(x)$  for these electrolytes according to eq 4 produces a very nice universal curve.

*tert*-Butyl alcohol (2-methyl-2-propanol)–water mixtures were extensively and very accurately investigated by Kay and Broadwater<sup>32</sup> in the water-rich region ( $x < 0.20$ ). Eight electrolytes, KCl, LiBr, NaBr, KBr, CsCl, Me<sub>4</sub>NBr, Me<sub>4</sub>NI, and Bu<sub>4</sub>NBr, were considered and their limiting conductances  $\Lambda^0(x)$  recalculated to give the KCl curve. Once again, the excellent verification of eq 4 can be observed in Figure 11 ( $0.99 \leq f(\text{KCl}) \leq 1.54$ ).



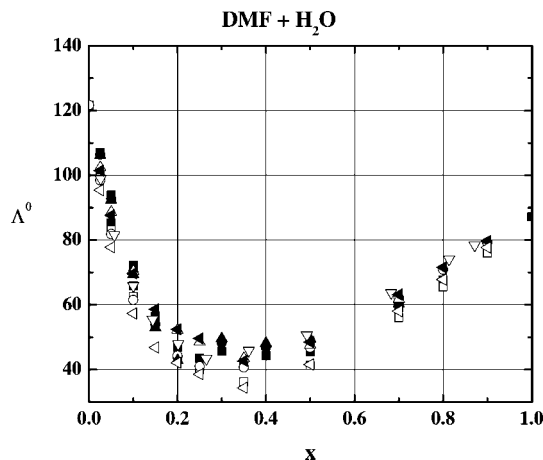
**Figure 10.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of 1-propanol in 1-propanol–water mixtures: (■) NaCl; (□) NaBr; (●) NaI; (○) NaClO<sub>4</sub>; (▲) NaBPh<sub>4</sub>; (Δ) Bu<sub>4</sub>NI.



**Figure 11.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of *tert*-butyl alcohol in *tert*-butyl alcohol–water mixtures: (■) KCl; (□) LiBr; (●) NaBr; (○) KBr; (▲) CsCl; (Δ) Me<sub>4</sub>NBr; (▼) Me<sub>4</sub>NI; (▽) Bu<sub>4</sub>NBr.

**2.3.3. Limiting Conductances of Electrolytes in *N,N*-Dimethylformamide–Water, Sulfolane–Water, Ethylene Carbonate–Water, and Tetrahydrofuran–Water Mixtures.** The third group of systems with water analyzed here includes two aprotic protophilic solvents, *N,N*-dimethylformamide (DMF) and sulfolane (TMS, tetramethylene sulfone), one aprotic protophobic solvent (ethylene carbonate (EC)), and a low-permittivity electron-donor solvent (tetrahydrofuran (THF)) (for classification of solvents and their general characteristics, see ref 1).

The conductivities of nitrates (NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>) in the binary mixtures of DMF (dielectric constant  $D = 36.71$ ) with water were investigated by Bahadur and Ramanamurti.<sup>71</sup> A much larger number of electrolytes was considered by the Bald group<sup>72,73</sup> (LiNO<sub>3</sub>, NaNO<sub>3</sub>, NaClO<sub>4</sub>, KSCN, PrONa (sodium propionate), KPic (potassium picrate), NaBPh<sub>4</sub>, i-Am<sub>3</sub>BuNI (triisomylbutylammonium iodide)). In the case of sodium nitrate,  $\Lambda^0(x)$  values differ significantly between the two investigations. On the basis of the modified Walden product of NaNO<sub>3</sub><sup>73</sup> and the maximum of the viscosity, the water-rich region extends up to  $x \approx 0.25$  or  $w \approx 0.575$ . The universal curve of these electrolytes was prepared from the water-rich and the DMF-rich regions (eqs 4 and 5) and plotted in Figure 12 ( $0.84 \leq f(\text{NaNO}_3) \leq 1.74$ ). There is no doubt that this



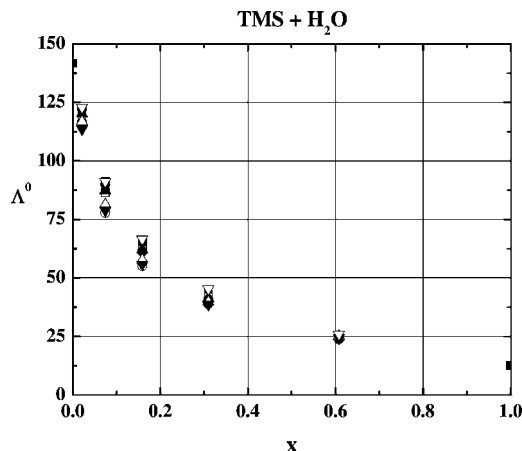
**Figure 12.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eqs 4 and 5) as a function of mole fraction  $x$  of *N,N*-dimethylformamide in *N,N*-dimethylformamide–water mixtures: (■) NaNO<sub>3</sub>; (□) LiNO<sub>3</sub>; (●) NH<sub>4</sub>NO<sub>3</sub>; (○) NaClO<sub>4</sub>; (▲) KNO<sub>3</sub>; (Δ) KSCN; (▼) PrONa; (▽) KPic; (left and right-pointing filled and open triangles) NaBPh<sub>4</sub>; i-Am<sub>3</sub>BuNI.

universal curve exists also in the DMF–water mixtures. However, contrary to other systems, the scattering of the limiting conductances is more evident. It is not clear whether this results from the accuracy of the performed experiments or from the applied extrapolation procedures to obtain  $\Lambda^0(x)$ .

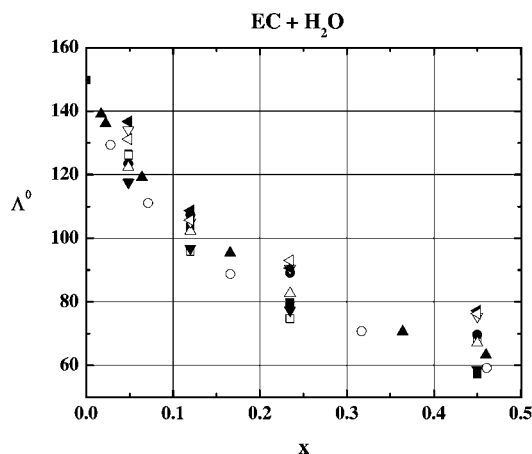
The physical properties of the TMS–water mixtures differ considerably from those in previously considered systems. When the dielectric constants of the mixture at 303.15 K monotonically decrease from  $D = 76.77$  for pure water to  $D = 43.33$  for pure sulfolane, the viscosity  $\eta(x)$  has no maximum as a function of composition and there is a substantial difference in the viscosities of the pure components ( $\eta(x = 0) = 0.80$  cP and  $\eta(x = 1.0) = 10.3$  cP<sup>74</sup>). The limiting conductances  $\Lambda^0(x)$  decrease as a function of  $x$ . As a consequence, contrary to the previously analyzed systems for which it was always observed that  $\Lambda^0(x,T)[\eta(x,T) - \eta^{\#}(x,T)] = \Lambda^0(x,T)\eta^E(x,T) > 0$ , for the TMS–H<sub>2</sub>O mixtures we have  $\Lambda^0(x,T)[\eta(x,T) - \eta^{\#}(x,T)] = \Lambda^0(x,T)\eta^E(x,T) < 0$ , i.e., values of the ordinary Walden products are lower than those of the modified Walden products for any composition of  $x$  (other similar examples will be discussed later). The ordinary Walden product divides the TMS–water mixtures into the water-rich and TMS-rich regions at  $x \approx 0.16$  or  $w \approx 0.56$ , while the modified Walden product indicates a far different value at  $x \approx 0.50$  or  $w \approx 0.87$ . Conductivity measurements made by Petrella et al.<sup>74,75</sup> with the following electrolytes NaBr, NaI, Bu<sub>4</sub>NCl, Bu<sub>4</sub>NClO<sub>4</sub>, Bu<sub>4</sub>NBr, Bu<sub>4</sub>NI, i-Am<sub>3</sub>BuNI, and NaBPh<sub>4</sub> shifted to the NaBr curve by eq 4 are plotted in Figure 13 ( $1.00 \leq f(\text{NaBr}) \leq 1.82$ ). As can be observed, the sound universal curve can be derived for the TMS–water mixtures over practically the entire concentration range.

Ethylene carbonate at 298.15 K has a higher dielectric constant than water,  $D = 90.3$ ,<sup>1</sup> and is more than twice as viscous as water,  $\eta = 1.85$  cP<sup>76</sup> ( $D(x)$  and  $\eta(x)$  monotonically increase with  $x$ ). In terms of the mole fraction  $x$ , the determined limiting conductances of KCl, AgClO<sub>4</sub>, NaI, KI, KClO<sub>3</sub>, KClO<sub>4</sub>, KNO<sub>3</sub>, Me<sub>4</sub>NCl, Et<sub>4</sub>NBr, and Bu<sub>4</sub>NI are reported<sup>55,76,77</sup> up to  $x \approx 0.50$  or  $w \approx 0.80$  and also for pure EC. The behavior of the Walden products can be characterized as “normal” (i.e.,  $\Lambda^0(x)\eta^E(x) > 0$ ), and the boundary between the two regions which is not sharp is at  $x \approx 0.15$  or  $w \approx 0.465$ . Taking KCl as the standard electrolyte, the limiting conductances of the above-mentioned electrolytes are plotted in Figure 14 ( $1.00 \leq f(\text{KCl})$





**Figure 13.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eqs 4 and 5) as a function of mole fraction  $x$  of sulfolane in sulfolane–water mixtures: (■) NaBr; (□) NaI; (●) Bu<sub>4</sub>NCl; (○) Bu<sub>4</sub>NClO<sub>4</sub>; (▲) Bu<sub>4</sub>NBr; (△) Bu<sub>4</sub>NI; (▼) i-Am<sub>3</sub>BuNI; (▽) NaBPh<sub>4</sub>.

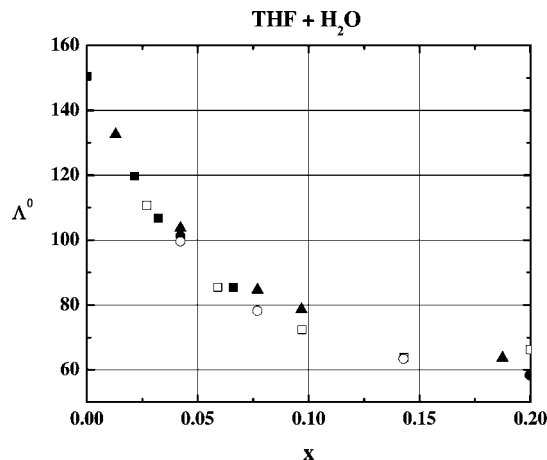


**Figure 14.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of ethylene carbonate in the ethylene carbonate–water mixtures: (■) KCl; (□) AgClO<sub>4</sub>; (●) NaI; (○) KI; (▲) KClO<sub>3</sub>; (△) KClO<sub>4</sub>; (▼) KNO<sub>3</sub>; (▽) Me<sub>4</sub>NCl; (left and right-pointing filled and open triangles) Et<sub>4</sub>NBr; Bu<sub>4</sub>NI.

$\leq 1.55$ ). These shifted  $\Lambda^0(x)$  values were calculated using eq 4 up to  $x = 0.5$ , i.e., far from the estimated end of the water-rich region. As can be observed, the organic electrolytes deviate more from the universal curve than the inorganic electrolytes, but the overall agreement continues to be quite reasonable also for the EC–water system.

Tetrahydrofuran has a low dielectric constant at 298.15 K,  $D = 7.4$ .<sup>1</sup> Its viscosity is nearly one-half that of water,  $\eta = 0.46$  cP,<sup>1</sup> and  $\eta(x)$  has a maximum at  $x \approx 0.20$  or  $w \approx 0.50$ . Precise conductance measurements of KI,<sup>78</sup> NaClO<sub>4</sub>,<sup>79</sup> KCl,<sup>80</sup> KClO<sub>4</sub>,<sup>80</sup> CsNO<sub>3</sub>,<sup>81</sup> CsCl,<sup>46,51</sup> and CsBr<sup>82</sup> were performed in THF–water mixtures. According to the modified Walden product, the water-rich region is similar to that predicted by the maximum of the viscosity while the ordinary Walden product gives a much smaller value of  $x$ . The universal curve for these electrolytes, with potassium iodide as the standard electrolyte, is presented in Figure 15 ( $0.97 \leq f(\text{KI}) \leq 1.27$ ). Excellent results based on eq 4 are observed, once more confirming that the applied shifting procedure of the limiting conductances  $\Lambda^0(x)$  is a very reasonable procedure.

#### 2.4. Limiting Conductances of Electrolytes in Nonaqueous

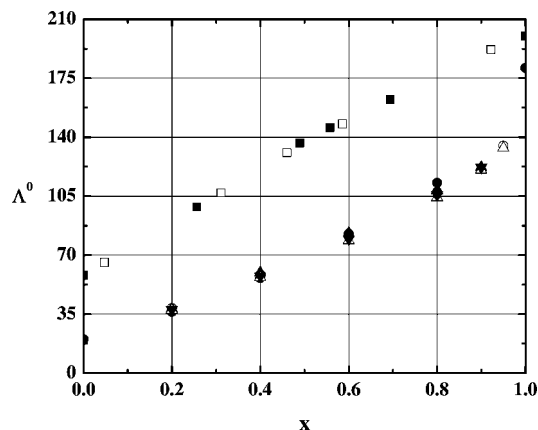


**Figure 15.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of tetrahydrofuran in tetrahydrofuran–water mixtures: (■) KI; (□) NaClO<sub>4</sub>; (●) KCl; (○) KClO<sub>4</sub>; (▲) CsNO<sub>3</sub>; (△) CsCl; (▼) CsBr.

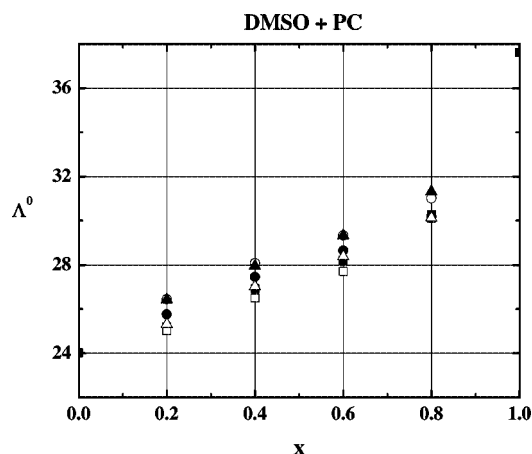
**Mixed Solvents.** There are a very large number of investigations where electrical conductivities were determined in binary mixtures of organic solvents. However, contrary to mixtures with water, it is difficult to find the same system with many different electrolytes because conductivity measurements were often performed with specific electrolytes in technical applications. Thus, analysis will be restricted to few electrolytes only. The selection of organic mixtures presented here is not only limited but also accidental. Nevertheless, it will illustrate the discussed representation of conductivities in nonaqueous mixed solvents.

The first two systems are mixtures of the aprotic protophobic (acetone) with amphiprotic hydroxylic solvent (aliphatic alcohol). What characterizes the acetone–ethanol and acetone–1-propanol mixtures is that they are almost isodielectric mixtures over the entire concentration range ( $D(\text{acetone}) = 20.56$ ,  $D(\text{EtOH}) = 24.35$ , and  $D(1\text{-PrOH}) = 20.45$  at 298.15 K<sup>1</sup>), viscosities monotonically increase as a function of the acetone fraction  $x$  ( $\eta(\text{acetone}) = 0.303$  cP,  $\eta(\text{EtOH}) = 1.087$  cP, and  $\eta(1\text{-PrOH}) = 1.97$  cP<sup>1</sup>), and  $\Lambda^0(x)$  are nearly linear functions of  $x$ . In the CsClO<sub>4</sub>–acetone–ethanol and LiCl–acetone–1-propanol systems (these electrolytes are chosen as the standard electrolytes) the values of the ordinary Walden products are lower than those of the modified Walden products (Figure 3). The limiting conductances of CsClO<sub>4</sub> and Et<sub>4</sub>NClO<sub>4</sub> determined by Pistola and Pecci<sup>83</sup> were shifted from the ethanol-rich region using eq 4, and with the exception of pure acetone both electrolytes form the same curve (Figure 16,  $f(\text{CsClO}_4) = 0.97$ ). The same situation is observed in the case of LiCl, Bu<sub>4</sub>NCl, Bu<sub>4</sub>NClO<sub>4</sub>, Bu<sub>4</sub>NBr, and Bu<sub>4</sub>NI investigated by Evans et al.<sup>84</sup> in acetone–1-propanol mixtures (Figure 16,  $0.74 \leq f(\text{LiCl}) \leq 1.00$ ).

The third example are mixtures of dimethyl sulfoxide (DMSO) and propylene carbonate (PC = 4-methyl-1,3-dioxolane-2-one). This is the mixture of the aprotic protophilic and aprotic protophobic solvents.<sup>1</sup> In the system, the dielectric constants decrease as the mole fraction  $x$  of DMSO increases ( $D(\text{DMSO}) = 47.0$  and  $D(\text{PC}) = 64.95$ ), where the viscosities have a very flat minimum ( $\eta(\text{DMSO}) = 1.99$  cP,  $\eta(\text{PC}) = 2.51$  cP<sup>1</sup>). For DMSO–PC mixtures, Srivastava and Shankar<sup>85</sup> determined the conductivities of a number of potassium alkyl xanthates (salts of xanthic acids ROC(S)SH are used in the removal of metallic mercury from contaminated industrial land sites), namely, KMeX, KEtX, KPrX (potassium 2-propyl



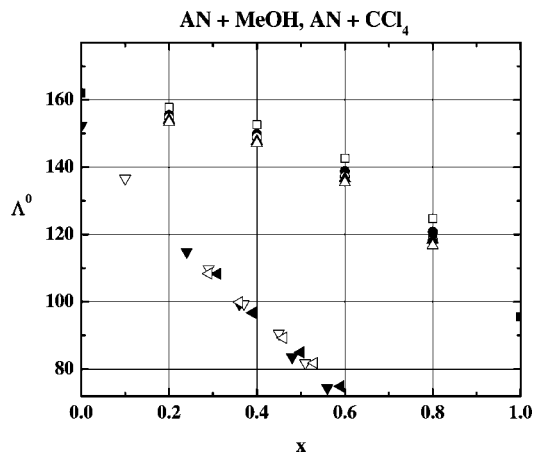
**Figure 16.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of acetone. Acetone–ethanol mixtures: (■)  $\text{CsClO}_4$ ; (□)  $\text{Et}_4\text{NClO}_4$ . Acetone–1-propanol mixtures: (●)  $\text{LiCl}$ ; (○)  $\text{Bu}_4\text{NCl}$ ; (▲)  $\text{Bu}_4\text{NClO}_4$ ; (△)  $\text{Bu}_4\text{NBr}$ ; (▼)  $\text{Bu}_4\text{NI}$ .



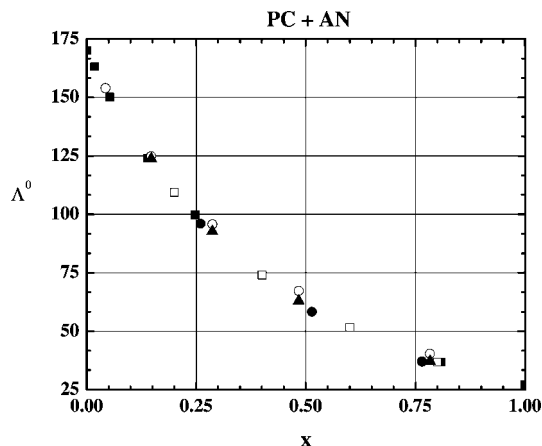
**Figure 17.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of dimethyl sulfoxide in dimethyl sulfoxide–propylene carbonate mixtures: (■)  $\text{KPrX}$ ; (□)  $\text{KMeX}$ ; (●)  $\text{KEtX}$ ; (○)  $\text{KBuX}$ ; (▲)  $\text{KMeBuX}$ ; (△)  $\text{KClO}_4$ .

xanthate),  $\text{KBuX}$ ,  $\text{KMeBuX}$  (potassium 3-methyl-1-butyl xanthate), and  $\text{KClO}_4$ . In all cases the modified Walden product is lower than the ordinary Walden product (similarly as in Figure 3), and the shifted limiting conductances are plotted in Figure 17 using  $\text{KPrX}$  as the standard electrolyte in pure PC ( $0.81 \leq f(\text{KPrX}) \leq 1.09$ ). As can be seen from Figure 17, there is a very reasonable agreement with the predictions coming from eq 4.

The final three examples include acetonitrile ( $D(\text{AN}) = 35.95$  and  $\eta(\text{AN}) = 0.341 \text{ cP}^1$ ), which is the aprotic protophobic solvent.<sup>1</sup> Das et al.<sup>86,87</sup> measured electrical conductances in methanol–acetonitrile mixtures for the series of tetraalkylammonium bromides,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{Pen}_4\text{NBr}$ ,  $\text{Hex}_4\text{NBr}$ , and  $\text{Hep}_4\text{NBr}$ . The dielectric constants or viscosities of the components do not differ by much ( $D(\text{MeOH}) = 32.63$  and  $\eta(\text{MeOH}) = 0.543 \text{ cP}^1$ ), and all mixtures are characterized by  $\Lambda^0(x,T)\eta^E(x,T) < 0$ . Choosing  $\text{Bu}_4\text{NBr}$  as the standard electrolyte, the shifting of electrolytes in the  $\text{MeOH}$ – $\text{AN}$  system to the universal curve is presented in Figure 18 ( $0.87 \leq f(\text{Bu}_4\text{NBr}) \leq 1.10$ ) and a fair scattering of experimental points is observed. Berns and Fuoss<sup>88</sup> investigated the conductances of tetraalkylammonium tetraphenylborides ( $\text{Me}_4\text{NBPh}_4$ ,  $\text{Et}_4\text{NBPh}_4$ ,  $\text{Pr}_4\text{NBPh}_4$ , and  $\text{Bu}_4\text{NBPh}_4$ ) in acetonitrile–carbon



**Figure 18.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of acetonitrile. Acetonitrile–methanol mixtures: (■)  $\text{Bu}_4\text{NBr}$ ; (□)  $\text{Et}_4\text{NBr}$ ; (●)  $\text{Pr}_4\text{NBr}$ ; (○)  $\text{Pen}_4\text{NBr}$ ; (▲)  $\text{Hex}_4\text{NBr}$ ; (△)  $\text{Hep}_4\text{NBr}$ . Acetonitrile–carbon tetrachloride mixtures: (▼)  $\text{Me}_4\text{NBPh}_4$ ; (▽)  $\text{Et}_4\text{NBPh}_4$ ; (left and right-pointing filled and open triangles)  $\text{Pr}_4\text{NBPh}_4$ ;  $\text{Bu}_4\text{NBPh}_4$ .

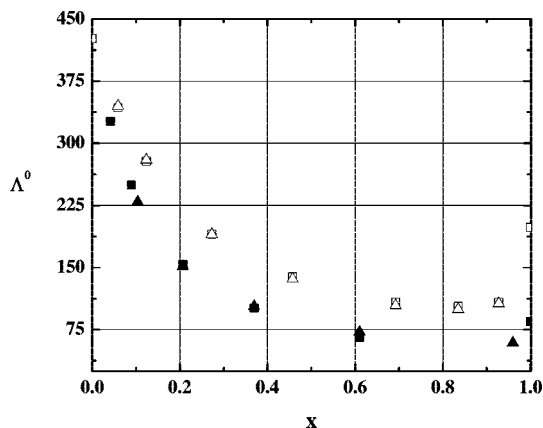


**Figure 19.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of propylene carbonate in propylene carbonate–acetonitrile mixtures: (■)  $\text{LiBr}$ ; (□)  $\text{LiClO}_4$ ; (●)  $\text{LiAsF}_6$ ; (○)  $\text{Bu}_4\text{NClO}_4$ ; (▲)  $\text{Bu}_4\text{NBPh}_4$ .

tetrachloride mixtures. The dielectric constant of  $\text{CCl}_4$  is very small ( $D = 2.23$  and  $\eta = 0.905^1$ ), and therefore, measurements were only performed for the  $x < 0.59$  or  $w < 0.843$  concentration region. Similarly to other investigated systems with acetonitrile,  $\Lambda^0(x,T)\eta^E(x,T)$  is negative. The unique curve of the limiting conductances of tetraalkylammonium tetraphenylborides is formed when they are shifted by eq 4 (Figure 18,  $1.00 \leq f(\text{Me}_4\text{NBPh}_4) \leq 1.27$ ).

Four very precise determinations of conductivities were performed in acetonitrile–propylene carbonate mixtures. Barthel et al.<sup>89,90</sup> considered  $\text{LiBr}$  and  $\text{LiClO}_4$ , Bałkowska et al.<sup>91</sup> investigated  $\text{LiAsF}_6$ , and Moumouzias and Ritzoulis<sup>92,93</sup> investigated  $\text{Bu}_4\text{NClO}_4$  and  $\text{Bu}_4\text{NBPh}_4$ . Dielectric constants and viscosities of PC and AN differ significantly ( $D(\text{PC}) = 64.95$  and  $\eta(\text{PC}) = 2.51 \text{ cP}^1$ ), and in mixtures these properties have no extreme value. Lithium bromide was chosen as the standard electrolyte in pure PC, and the result of the shifting is presented in Figure 19 ( $0.98 \leq f(\text{LiBr}) \leq 1.42$ ). Once again, the excellent prediction of the universal  $\Lambda^0(x)$  curve from eq 4 is observed.

**2.5. Limiting Conductances of Acids in Mixed Solvents.** It is well known that the limiting ionic conductances of  $\text{H}^+$  and  $\text{OH}^-$  ions in aqueous solutions are significantly larger than those of other inorganic or organic ions owing to a special proton-



**Figure 20.** Limiting conductances of electrolytes  $\Lambda^0(x)$  at 298.15 K (calculated using eq 4) as a function of mole fraction  $x$  of alcohol. Methanol–water mixtures: (□) HCl; (△) CH<sub>3</sub>COOH. Ethanol–water mixtures: (■) HCl; (▲) HClO<sub>4</sub>.

transfer mechanism.<sup>94</sup> Due to “excess” conductivity, acids or bases normally cannot be placed together with other electrolytes on the same universal curve unless one of the acids is chosen as the standard electrolyte. Only two examples are presented here to illustrate the behavior of acids, HCl and CH<sub>3</sub>COOH in methanol mixtures<sup>95</sup> and HCl<sup>96</sup> and HClO<sub>4</sub><sup>97</sup> in ethanol–water mixtures. Hydrochloric acid is chosen in both cases as the standard electrolyte. Results of using eq 4 for the methanol–water and ethanol–water mixtures are plotted in Figure 20. Each universal curve covers practically the entire concentration region, and there is no doubt that  $\Lambda^0(x)$  values for acids can be accurately estimated helped by the fact that the  $f$  factors do not differ significantly because the contributions coming from the hydrogen ion to the molecular conductivity  $\Lambda^0(x)$  are predominant.

### 3. Conclusions and Remarks

Extrapolation procedures to obtain the limiting conductances of electrolytes in mixed solvents  $\Lambda^0(x)$  are shown in this work to be less influenced by the choice of conductivity equations than by the evaluation of the association constants  $K_A$ . It was found that the Quint–Vialard conductivity equation, which was used here for the first time for mixed solvents, is able to very accurately represent the conductivities of electrolytes.

There is no doubt, from a practical as well as a theoretical view, that knowledge of the Walden products of pure solvents and those of mixed solvents is very important. In this work, the modified Walden product is introduced which is easy to evaluate because the viscosities of pure solvents are always known. The modified Walden product is in many cases superior when the division of mixtures into concentration regions is desired. An alternative indicator of such division, the maximum of viscosity or ordinary Walden product, is a less adequate tool. In addition, the modified Walden product could also give a fair estimate of the limiting conductances in pure solvents when the dielectric constants have a very low value.

It is rather surprising to find that there is no simple relationship between  $\Lambda^0(x)$  and the dielectric constants of mixtures ( $D(x)$  are introduced only through the applied conductivity equations). However, it was observed that in many cases the simple quotient  $\Lambda^0(x)\eta(x)/D(x) = f(x)$  is initially a linear function of the mole fraction  $x$ , and these straight lines have similar slopes for different electrolytes. This means that they can be shifted (e.g., in 1,4-dioxane–water mixtures), but usually these linear regions are smaller than the water-rich

regions (e.g., in alcohol–water mixtures). It seems that the possibility of the existence of a simple function that includes all measurable quantities of the problem,  $f(\Lambda^0, \eta, D; x) = 0$ , should be examined in the future in greater detail.

The modified Walden products and universal conductivity curves, introduced in this work, should be treated as an additional tool which will help to estimate unknown  $\Lambda^0(x)$  values and obtain some indication about the quality of the performed conductivity measurements. Since this is the first attempt to present the universal curves for each solvent mixture, it seems too early to express them by specific mathematical functions (e.g., polynomials) to give the limits of concentration regions and the expected accuracy of  $\Lambda^0(x)$  values. The statistical analysis of conductivity data combined with more experience with the applied procedure (e.g., with the correct choice of the standard electrolyte) will certainly take place in future analysis of mixed-solvent systems. It is worthwhile to note that for a given pair of solvents the existence of a universal curve of limiting conductances  $\Lambda^0(x)$  is equivalent to the existence of a universal Walden product curve because the viscosities of the mixture  $\eta(x)$  are evidently known.

There was no intention in this work to replace existing literature representation of electrical conductivities in mixed solvents by an alternative procedure but only to provide additional means in the analysis. However, if it is accepted that the universal curve of electrolytes exists for each solvent mixture or for a part of it (even if it is treated only as a fair approximation) then this fact cannot be excluded from the interpretation of the electrolytes behavior. The possibility to shift various electrolytes to one universal curve of limiting conductances (or to one universal Walden product) has an important consequence that should be taken into account. The interpretation of conductivities in mixed solvents as a function of composition is usually attributed to changes in ion–solvent interactions, structural effects (hydrogen-bonded structures, existence of dipoles), nature of involved ions (small and large ions, structure-making and structure-breaking ions, charge densities, sizes and polarizabilities of ions, association of ions), physical properties of solvents (dielectric constants and viscosities), hydration and solvation effects, and other molecular parameters. Since for a given mixed-solvent system the importance of the above-mentioned parameters varies between different electrolytes, a dissimilar behavior of electrolytes (or individual ions) is expected and has a reasonable explanation if these differences in properties are taken into account.<sup>1,8–12,98–102</sup>

However, as observed in so many systems considered in this investigation, the existence of universal curves of  $\Lambda^0(x)$  which include electrolytes having different properties (e.g., structure-breaking and structure-making electrolytes) is rather surprising and therefore requires some interpretation. Probably, the most plausible explanation is that the influence of the mixture properties on the mobility of electrolytes is only of secondary importance. The predominant effect is associated with the differences in properties between various ions in pure solvents. These properties continue to be preserved in the mixtures (i.e., ions in the mixtures are to a great extent surrounded only by molecules of pure solvent, and the original mechanism of charge transfer is preserved), and the observed change in conductivities is related to a proportional change in composition when the second solvent is added. At first glance, this simple dilution effect is more evident in nonaqueous mixtures, where the universal curves (from the region of the solvent that has the larger dielectric constant) cover nearly the entire concentration region as is illustrated in Figures 16–20. However, the same is



also observable for mixtures with water and to a lesser extent for water-rich regions (expressed in terms of mole fractions), resulting apparently from the small molecular mass of water. Thus, the ends of the water-rich regions are already highly concentrated solutions of the second component. In summary, the phenomenological treatment of electrical conductivities proposed here is expected to add more elements involved in the analysis and understanding of the behavior of electrolytes in mixed solvents.

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